

SCIENCE & COOKING

A COMPANION TO THE HARVARD COURSE



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HARVARD
UNIVERSITY

TABLE OF CONTENTS

[Introduction](#)

[Acknowledgments](#)

Chapter 1: [Food Components](#)

Chapter 2: [Energy, Temperature and Heat](#)

Chapter 3: [Phase Transitions](#)

[Chocolate](#)

Chapter 4: [Elasticity](#)

Chapter 5: [Diffusion, Gelation and Spherification](#)

Chapter 6: [Heat Transfer](#)

Chapter 7: [Viscosity and Polymers](#)

Chapter 8: [Emulsions and Foams](#)

Chapter 9: [Baking](#)

Chapter 10: [Enzymatic Reactions and Fermentation](#)

INTRODUCTION

This book is based on, and meant to serve as a companion to, the Harvard course Science and Cooking: from Haute Cuisine to Soft Matter Science. It should also be a useful resource for other courses and initiatives aiming to teach physics and chemistry through food and cooking.

In 2008 Ferran Adrià, chef of the famed restaurant, El Bulli, and known for his unique and highly innovative approach to cooking, came to give a talk at Harvard University. The interest in the talk was tremendous — with more than a thousand people trying to get in. This occurred around the same time that Harvard was remodeling its general education requirements for undergraduates, the purpose of which are to “connect in an explicit way what students learn at Harvard to life beyond Harvard”. Food and cooking is, of course, a part of everyone’s every day life, both while in college and beyond. What we do in the kitchen is strongly rooted in science. Moreover, when cutting edge chefs create novel dishes, they too exploit basic scientific principles.

From this confluence of events and ideas, Science and Cooking was born. The first on campus course was launched in 2010, a collaboration between Harvard and Ferran Adrià’s El Bulli Foundation. Every week features a scientific theme, illustrated by visiting, world-renowned chefs explaining the remarkable creations from their kitchens, and explained in scientific terms by the course staff. The course also featured a lab, where recipes such as molten chocolate cake or aioli were used to explain the scientific principles of heat transfer or emulsions.

This approach to physics and chemistry education appeared to resonate with and motivate a broad audience — more than 700 students tried to get into the course the first year it was offered, and the accompanying weekly lecture to the public continued to draw large crowds with lines forming hours ahead.

The interest led us, in 2013, to embark on the adventure of creating an online class available to a wider, international audience on EdX. We both wanted to share the material that was developed in the Harvard course with

a wider audience, and also hoped that developing the material would allow us to improve the on-campus college course in a number of ways. One of the challenges of the course had always been that there was often far more science in the chefs' creations than could possibly be addressed and explained in the limited time we had in class. In addition, like any course covering novel material, there was no textbook available that explained the science we covered in depth. The online course allowed us to address both of these concerns. By creating video materials of both basic and advanced topics, the curriculum could be modeled to students with varying science preparation. Similarly, the creation of the online videos could play the role of an online textbook.

This Companion is a direct product of the online course creation process. As part of it, we developed graphics and short videos illustrating key concepts. Additionally, in the process of producing subtitles, we generated word for word transcripts of all videos. In this Companion, the transcripts have been used as a rough draft for each chapter, which have then been heavily edited and augmented with the graphics and short videos. Thus, the order and content of the chapters and sub-chapters closely follow how the concepts would ordinarily be explained in an on-campus lecture or online video. The book contains the scientific information only, whereas in the complete course, the science is interspersed with culinary segments by the visiting chefs. It is our hope that this book is a helpful supplement to students taking the course, either on campus or online.

ACKNOWLEDGMENTS

The list of people who have, in a multitude of ways, contributed to what ultimately led to the production of this work is very long.

We would like to thank everyone who was involved in the early development of the college class: most importantly our partner Ferran Adrià, and his foundation, run by Pere Castells, who freely shared their wisdom, knowledge, and excitement about the subject; José Andrés, whose energy for the course seemed unbounded, and has dedicated much time to its development. The first year we co-taught the course with two postdoctoral fellows, Amy Rowat and Otger Campas, both of whom were indispensable. The head teaching fellow during the first year of the course, Naveen Sinha, was as sleep deprived as the rest of us; and we were also assisted by the tireless and amazing Christina Andújar with all things organizational, as well as the demo guru Daniel Rosenberg.

Stephanie Kenen of the General Education office at Harvard encouraged us from the very beginning, and gave us important critical feedback at exactly the right times, with tremendous grace. We also thank Anne Marie Calareso, Kristina Barrett, and Karen Galvez from the General Education office.

We are deeply grateful to the visiting chefs and culinary experts who have taken time out of their busy schedules to come and talk to us and the students over the last five years. First, a special thank you to Harold McGee whose infinite knowledge continues to inspire us, and whose yearly opening lecture and treatise *On Food and Cooking* are in every way integral to the course. Further, we extend thanks to Grant Achatz, Jody Adams, Ferran Adrià, José Andrés, Dave Arnold, Dan Barber, Jack Bishop, Martin Breslin, Pere Castells, David Chang, Joanne Chang, Dominique Crenn, Wylie Dufresne, Carles Gaig, Daniel Humm, Nandu Jubany, Mark Ladner, Harold McGee, Ramon Morató, Nathan Myhrvold, Pere Planagumà, Fina Puigdevall, Joan and Jordi Roca, Enric Rovira, Carme Ruscalleda, Raul Balam Ruscalleda, Ted Russin, Dan Souza, Carles Tejedor, Christina Tosi, Bill Yosses.

The production of the online course was a whirlwind adventure that we feel

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CHAPTER 1

Food Components

TABLE OF CONTENTS: 1

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1.1 The Components of Food

1.1.1 Fats

1.1.2 Carbohydrates

1.1.3 Proteins

1.2 A Glass of Water

1.2.1 How Many Molecules Are There?

1.2.3 The Definition of a Molarity

1.3 Chocolate Chip Cookies – Drawing a Molecular Picture

1.3.1 Baking Soda

1.3.2 Salt and Sugar

1.3.3 Ovalbumin and Vanillin

1.3.4 Butter and Starch

1.4 Molecular Weight

1.4.1 The Origins of Molecular Weight

1.4.2 Calculating Molecular Weight

1.5 Lemonade – Acidity and pH

1.5.1 The Definition of Acidity

1.5.2 The Definition of pH

1.5.3 The pH of lemonade – measured and predicted

1.6 Why Use Equations

1.6.1 Equations are Tools

1.6.2 Equations have Predictive Power

CHAPTER 1

1.1 The Components of Food

If we want to think scientifically about cooking, we have to start by thinking a little bit about what food is made of. After all, it is the constituents of food that will be the major players in this adventure that we are about to launch ourselves on.

To find the constituents of food, you can go and examine any food label in your pantry and see what it says the food is made of. What you will see is that there tends to be three major components listed (Fig. 1.1). There are fats. There are carbohydrates. And there are proteins. You are undoubtedly already familiar with each of these components. For example, if you are interested in calorie content and calorie consumption, you probably know something about the relative roles these components play in human health. But from the point of view of cooking, the different properties of proteins, fats, and carbohydrates are interesting and important for a whole range of different reasons. What we want to do now is describe each of them to you in a some detail, both as an introduction to what we are going to be studying in this class, and also to start thinking about the role different food components play in how cooking works.

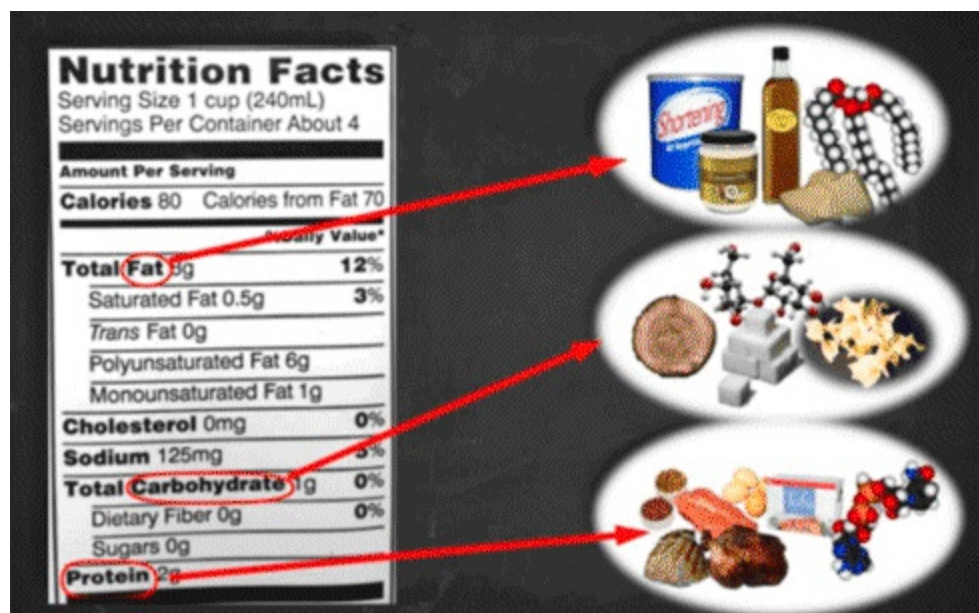


Figure 1.1 The amounts of the three major food components, fats, carbohydrates, and proteins, can be found on all typical nutrition facts labels.

Let's start with the very basic fact, which is that all of us, and all of our food, are made of molecules. We are biological entities. The foods we eat are

also biological entities—they tend to come from plants or animals. All biological entities are made of molecules, and molecules, in turn, are made of atoms (Fig. 1.2). Carbon dioxide, for example, which is a simple molecule, is made of carbon and oxygen. Water is made of hydrogen and oxygen, and so on. The molecules of cooking, namely fats, proteins, and carbohydrates, are much larger and more complex than simple molecules. Interestingly, all three food molecules also agglomerate and form even more complex structures and networks. It's these networks that make up food, and us too, for that matter. In the next three sections we will learn more about the properties of all three classes of major food molecules.

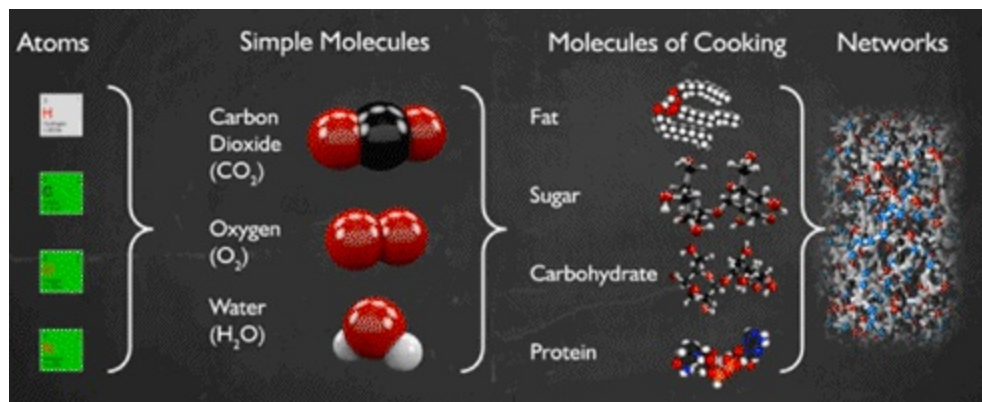


Figure 1.2 The components important for cooking are made of molecules, which in turn are made of atoms. Carbon dioxide, oxygen, and water, are examples of simple molecules, whereas fats, carbohydrates, and proteins are complex molecules. The latter assemble to form complex networks that ultimately make up, not only food, but all biological objects.

1.1.1 Fats

Fats appear in cooking in many shapes and forms. You may encounter them on a daily basis, in the form of butter, olive oil, coconut oil, cocoa butter, shortening, or corn oil (Fig. 1.3). They are very different than the two other major food components.



Figure 1.3 Examples of fats commonly used in the kitchen: Olive oil, coconut oil, cocoa butter, and shortening.

As a way to start thinking about fats, let's focus on two of its most interesting properties. The first property is that at room temperature fats can either be in liquid or in solid form. Olive oil, for example, is liquid at room temperature. Coconut oil, on the other hand, is a white solid. We will talk about the physics of this as we go further in this course, but this is one of the unusual features that fats have.

The second property of fats is that they do not dissolve in water. This is also something that you have probably experienced, perhaps when making a salad dressing with vinegar and oil. Since vinegar is primarily composed of water, it is typically quite difficult to get it to mix with the oil. Even if you vigorously shake the dressing bottle, the two liquids may initially mix, but only briefly. If you leave the bottle sitting, the two liquids will eventually separate with the oil on top and the water on the bottom. It turns out that the role of mustard in salad dressings is to help keep the vinegar and oil mixed for longer; we will study the scientific reasons for this in more detail later on in the course.

1.1.2 Carbohydrates

We usually eat carbohydrates either as simple sugars or as long chains of sugars. Starch is an example of the latter, it is a long chain of individual sugar molecules stuck together. Fructose, is an example of a simple sugar molecule, a monosaccharide. It is the molecule that makes fruit taste sweet. Sucrose, the scientific name for regular white table sugar, is also a simple sugar, although it is actually a disaccharide, i.e. composed of two sugar molecules, a fructose and glucose molecule (Fig. 1.4).

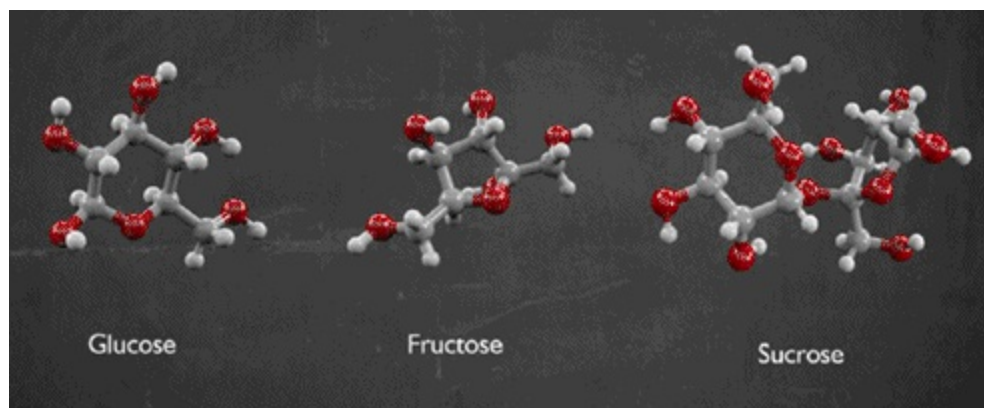


Figure 1.4 The molecular structure of glucose, fructose and sucrose. Sucrose is composed of one glucose and one fructose molecule. Carbon atoms are shown in grey, oxygen atoms in red, and hydrogen atoms in white.

Sugars have their own interesting properties. One of them is that they are very hard substances. If you try to crush a solid piece of sugar, you will find that it is quite hard to do. If you compare rock candy, for example, either to your skin or to jello or something similar, it is very hard by comparison. This hardness, as we will discover, is a property of the molecules that make it up.

Another interesting property of sugar is that it dissolves very well in water. Consider for example how much sugar there was in that glass of soda you drank last week. You will probably find that there was quite a bit. In fact, it turns out that the amount of sugar that you can dissolve in one pound of water at room temperature is twice as much, two pounds! If you don't believe this, then stop reading, go into your kitchen and do the following experiment: Fill one measuring cup with about a cup of water. Then fill another measuring cup with a cup of sugar. Pour the sugar into the water, and stir. You will find that all of the sugar dissolves. Then pour another cup of sugar into the sugar water mixture, and stir again. You may have to stir

and wait for a while, but eventually you will see that the sugar dissolves. The solubility limit of sugar in water is one of the remarkable properties of sugars.

Next to simple sugars, the other main type of carbohydrate is starches. Starches are polymers. This means that they are made up of long chains of simple sugar molecules, in this context we usually refer to each molecule as a monomer. Amylose is an example of a starch that is a polymer of glucose monomers. It is just a long chain of glucose molecules linked together. Another starch is amylopectin, which is the same as amylose, except instead of being a linear polymer, it is branched (Fig. 1.5). You can imagine that you can build lots of different conformations of sugar polymers just by varying which monomers you use and their branching.

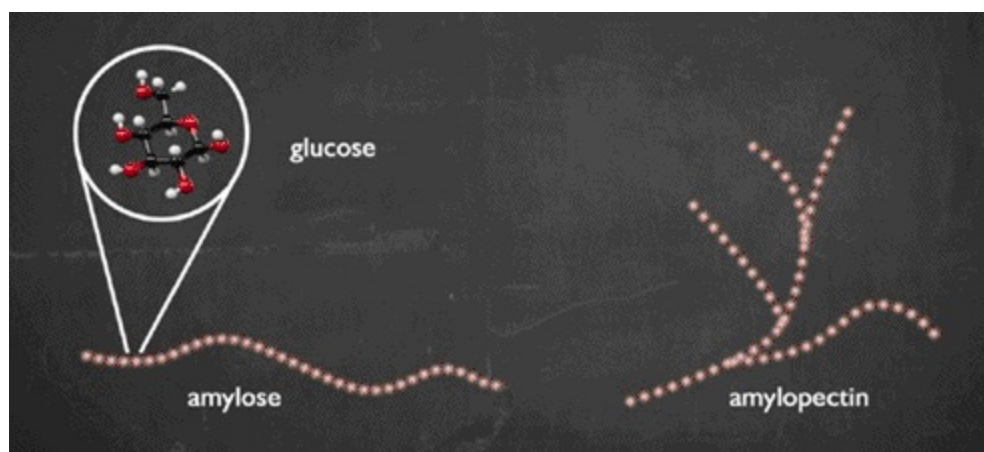


Figure 1.5 Amylose and amylopectin are examples of starches. Both are polymers that are built of glucose monomers, the only difference between them being the structure: amylose is linear and amylopectin is branched.

Many of the chefs in this course will introduce you to molecules that may be new to you. These are molecules that are commonly used in cooking to achieve certain effects, perhaps to stabilize emulsions or create gels. Many of these turn out to be carbohydrates. Ferran Adria, for example, is a great fan of agar-agar, which is a carbohydrate that is extracted from seaweed. Other examples are pectin, guar gum, methylcellulose, gellan, and xanthan gum. Although their names might sound peculiar, these are naturally occurring carbohydrates in the same way that flour consists of naturally occurring carbohydrates. Just as flour is made by grinding wheat seeds, these molecules are usually extracted from other plants or animals. For example, pectin is extracted from fruits, guar gum comes from a type of bean, and gellan and xanthan gum come from microbes. These are just

some examples of the vast number of different molecules that are made by organisms on our planet that we can, and do, use as part of our foods. Throughout this course, we will encounter examples of the remarkable things that can be made when you enlarge the set of molecules that are at your disposal in the kitchen.

1.1.3 Proteins

The third major food component is protein. Proteins occur in many of the things you eat, usually in many different varieties. For example, one of the proteins in steak, hemoglobin, which contributes to the red color of raw meat. Milk contains a protein called casein, and eggs, as we already mentioned, contains ovalbumin and ovotransferrin among many others (Fig. 1.6).

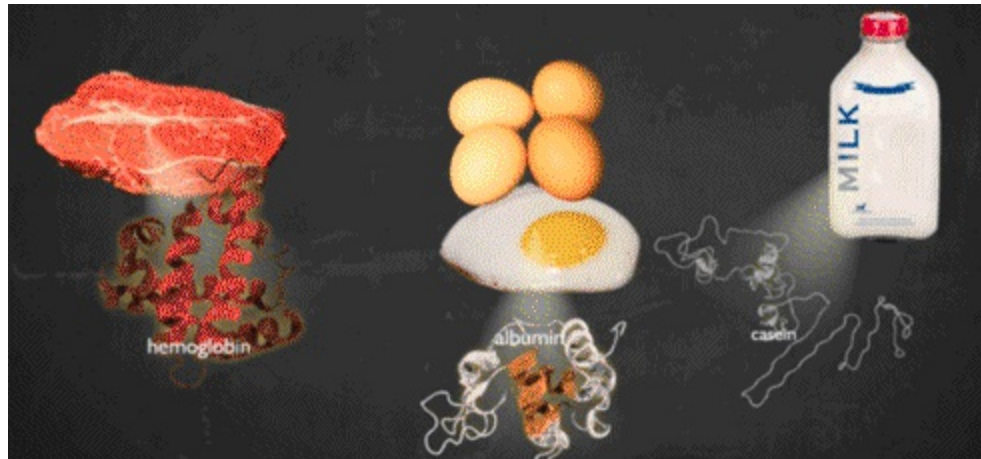


Figure 1.6 Hemoglobin, albumin, and casein, are some examples of proteins in common foods. The picture shows how each protein is folded into a characteristic three-dimensional structure, also referred to as a conformation.

Proteins have their own interesting properties, which are distinct from those of fats or carbohydrates. Similar to carbohydrates, proteins are polymers (Fig. 1.7). In this case though, the monomers are amino acids, and since there is a larger variety of amino acids than sugars to choose from, 20 to be precise, there is a greater variability in the kinds of proteins you can make just by varying the order of the amino acids. The 20 amino acids that are the building blocks of life all have different physical properties. Some of them dissolve in water, whereas some of them don't. Some have an electric charge, others don't. As we go through this class, we will see how the different amino acids give rise to the transformations that occur in proteins when we cook them.

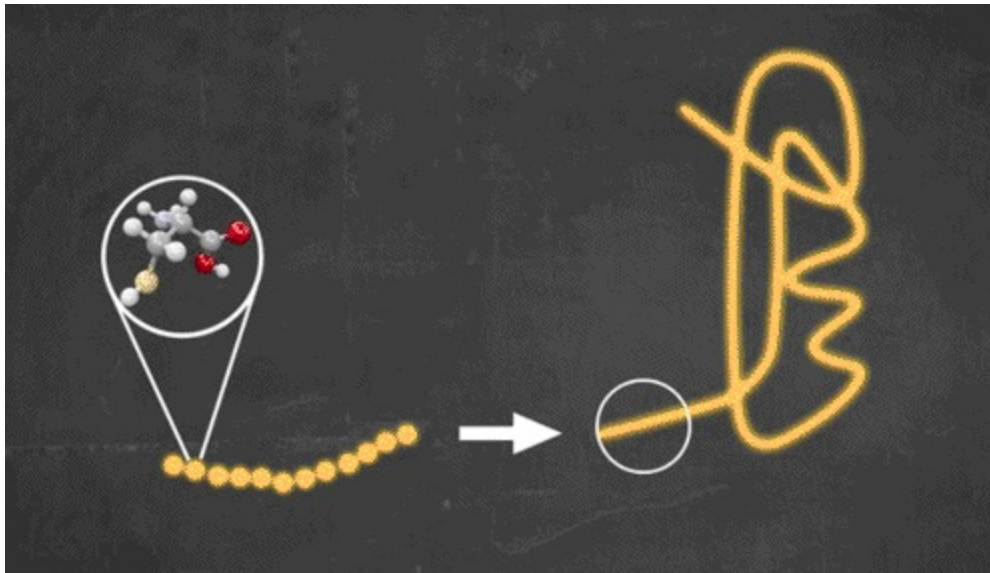


Figure 1.7 Proteins are polymers of amino acids. The long amino acid chains fold into characteristic conformations, whose shapes and functions are ultimately determined by the sequence of amino acids.

Similar to carbohydrates, proteins dissolve in water. But a protein water solution differs from a sugar water solution in how it behaves when heated. Why is this important? It's important because many foods are essentially just this—proteins dissolved in water. An egg, for example, primarily consists of water which has various proteins dissolved in it. Even if you heat the egg by a relatively small amount, say 100°C , or even 50°C , the proteins will change conformation. Proteins are active molecules. They don't keep the same shape as you cook them. Initially, they tend to be in a state in which the long polymer strand is tightly folded into a carefully arranged structure (Fig. 1.8). When heated, the long strand unfolds, and parts of the polymer get in proximity with other random parts on the same or other polymers. As a result, random bonds form. When this happens, we say that the protein coagulates. It forms a gelatinous mass. This process, the changing of a protein from a compact shape to a big, gelatinous mass of many proteins interacting, is at the heart of cooking an egg. It is also at the heart of making Jell-O and many of the other food transformations that we will see in this class.

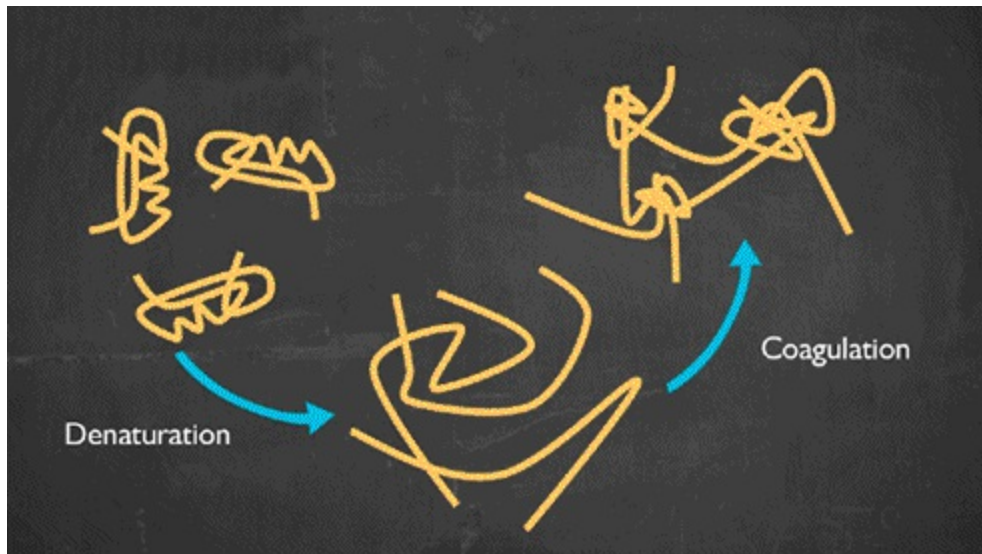


Figure 1.8 Application of heat causes proteins to unfold (denature). Once unfolded, the long polymers tend to coagulate into new random structures. On a macroscopic level, this changes the texture of the food or substance.

1.2 A Glass of Water

1.2.1 How Many Molecules Are There?

When most of us cook, we use measuring devices, be it measuring spoons or measuring cups, and we measure various amounts of ingredients, mix them all together, follow any other instructions in the recipe, and out comes the final food. For example, in making Nestle Tollhouse chocolate chip cookies, which is Michael Brenner's favorite recipe, you are supposed to combine $2\frac{1}{4}$ cups of flour with a teaspoon of baking soda, add some butter, brown and white sugar, a few other ingredients, mix it all together, and out comes chocolate chip cookies (Fig. 1.10).

Recipes like the chocolate chip cookie recipe tend to be the standard way to describe cooking. But the point of this class is to ask how it is that recipes like this work. Why is it that if you follow the protocol given in this recipe, you end up with Nestle Tollhouse chocolate chip cookies? What is it about the ingredients that gives rise to the properties of the cookies? Why is it that when you bake the cookies for longer than 9-11 min, the cookies get browner? Why is it that if you forget to add baking soda, they don't come out quite right? Why does the recipe call for a mixture of brown sugar and white sugar? These are the types of questions that we would like to answer and understand in scientific terms.

Hopefully by now, you agree that a good place to start looking scientifically at a recipe like this one is to understand the molecules that make it up. If we apply what we have learned already, we see that the flour in the recipe is contributing carbohydrates in the form of starch, which in turn is made up of sugars; the white and brown sugar are contributing sucrose, which we know is another form of carbohydrate; the butter, of course, is contributing fats; the eggs and the flour contribute protein, and so on. If we wanted to dig deeper into this recipe, a reasonable next question to ask would be, how do these different molecules contribute to the final cookie? That is, what does its interior look like on a molecular level? Imagine that you wanted to draw a view of the molecular structure of the inside of a chocolate chip cookie. You would have strands of starch, molecules of salt and sugar, larger fat molecules and so on. All the ingredients would be dispersed in

some way, ultimately resulting in the wonderful taste and texture of a Nestle Toll House chocolate chip cookie. Now, the picture would look very different if there were many more long starch molecules than little sugar molecules, rather than the other way around. In other words, knowing the relative amounts of molecules would inform the picture you drew and help you understand what's going on.

What if we could rewrite the recipe in such a way that instead of listing the ingredients the usual way, we would have a list of how many molecules of each substance the recipe is calling for. This is what we will try to figure out next. The process, as you will see, contains some approximations in some places, but it should give you a sense for how to start thinking molecularly.

How would you figure out how many molecules there are of something? In general, you would either have to know the mass or the volume of the molecule in question, and then compare it to the total mass or volume of the food. We are going to use both methods below and see how they compare.

Let's start by using the first approach, the one where we focus on the mass, and let's use it on what is arguably one of the most important substances for understanding food and cooking, namely water. How many water molecules are there in a glass of water? Imagine a glass containing 250 ml of water, a quarter of a liter (Fig. 1.9).

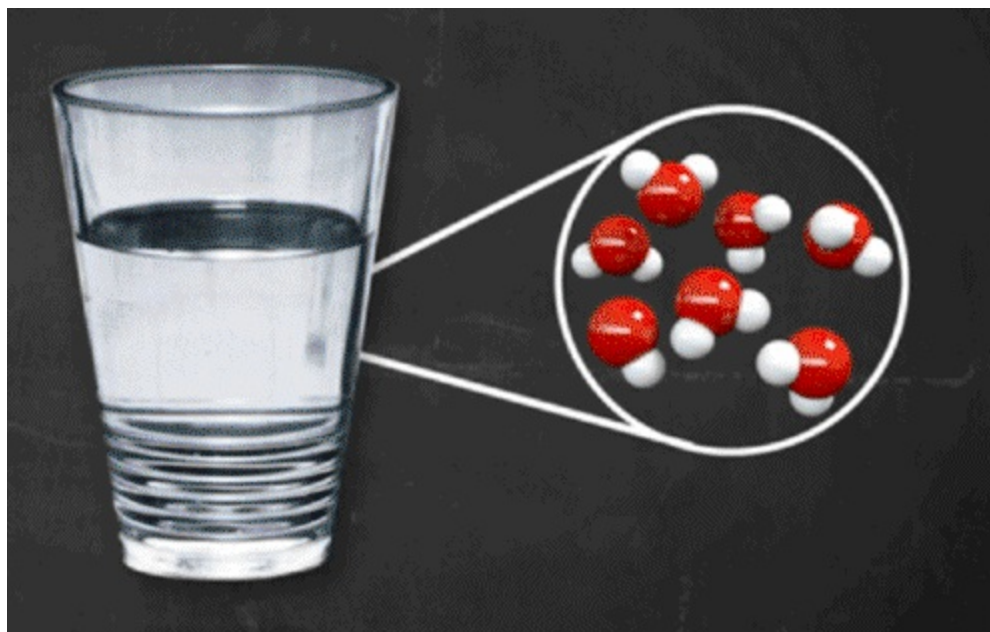


Figure 1.9 A glass of water is composed of an incredibly large number of individual water molecules.

Since the density of water is 1 g/ml, we can find that its mass is 250 g. A water molecule, scientists have determined, weighs $3 \cdot 10^{-23}$ grams, a very small number. So the number of water molecules in the glass is:

$$\frac{(250 \text{ ml}) \cdot (1 \text{ g/ml})}{(3 \cdot 10^{-23} \text{ g/molecule})} = 8.3 \cdot 10^{24} \text{ molecules}$$

This is a huge number, 8 with 24 zeros after it. Science is filled with big numbers, and since they are so common, and also often complicated to say, scientists have agreed upon several commonly accepted units for big numbers like these. In the case of molecules, scientists have decided, for various reasons, that the standard unit is supposed to be the same as the number of atoms of carbon that are present in 12g of the substance carbon-12. This number is $6.022 \cdot 10^{23}$. It is often referred to as Avogadro's number, but when used as a unit it is referred to as a mole. We will discuss its origins in more detail later on in this chapter, but for now, here is the definition:

$$1 \text{ mole} = 6.022 \cdot 10^{23} \text{ molecules or atoms}$$

This is a big moment, because this is the first "equation of the week" in this class. Every week of this course, or chapter of this book, has a mathematical equation that in some way summarizes one of the main ideas of the week, and expresses it in quantitative terms. In the Harvard College class, we have over the years adopted a tradition, which is that whenever the equation of each week is presented, the students, as well as the professors, clap. The reason for this tradition is two-fold. First, it is to show our appreciation and affection for the equation, because many people don't have as much affection for equations as we do. And second it is to emphasize the importance of the equation in expressing the idea of the week. In the current context, the idea of this chapter is that one can think about food in scientific terms, and one of the most basic realizations in this quest is that food is made of molecules. Perhaps the simplest question that you can ask yourself about the molecular structure of food is just how many molecules there are, and this equation helps us answer that question.

A second way to estimate how many molecules of water there are in a glass

of water is to focus on the volume instead of the mass. This way is less precise, but it still captures the ideas at work. Since it is difficult to physically measure the volume of a water molecule, we would have to start by estimating the size. Let's say, just for the sake of argument, that a water molecule is a cube with each side being 3 Ångströms. This seems like a reasonable estimate given that atoms have a size on the scale of Ångströms, i.e. 10^{-10} m, and water, H_2O , has three atoms. Since the glass of water contained a volume of 250 ml, which is the same as 250 cm^3 , we can calculate the number of molecules by dividing the total volume by the volume of a molecule:

$$\frac{250 \text{ cm}^3}{(3 \cdot 10^{-8} \text{ cm})^3} = 9.3 \cdot 10^{24} \text{ molecules}$$

As you can see, despite the approximations we used, the number from our first approach, $8.3 \cdot 10^{24}$, is very similar to what we get with this approach. This confirms that the estimate for the size of a water molecule, i.e. as being a cube with sides of 3Å, is probably not that far off.

1.2.3 The Definition of a Molarity

So we now know the number of molecules in a glass of water, and we can take a first stab at using the equation of the week by asking how many moles this corresponds to. To figure this out, all we have to do is divide the number of molecules, $8.3 \cdot 10^{24}$, by Avogadro's number:

$$\frac{8.3 \cdot 10^{24} \text{ molecules}}{6.022 \cdot 10^{23} \text{ molecules/mol}} = 13.8 \text{ mol}$$

In other words, a glass of water contains 13.8 moles of molecules. So the next time you buy a liter of water, a liter being four times this amount, what you are really buying is $13.8 \cdot 4$, i.e. 55 moles of water. This unit, the number of moles there are in a liter of a liquid, is another important unit for this class. When discussing liquids, we often want to know how concentrated they are, and so we speak of them in terms of how many moles in a liter they contain. The unit has a special name, molarity (M), i.e. the molarity of water is 55 M. We will discuss the significance of this in the context of pH later on in this chapter.

1.3 Chocolate Chip Cookies – Drawing a Molecular Picture

Now that we have learned how to count the number of molecules in a glass of water, let's figure out how many molecules there are in the various ingredients of Michael's favorite recipe, the Nestle Toll House chocolate chip cookies (Fig. 1.10). This is a way to get a flavor for what this molecular way of looking at food can tell us about a recipe.



Original NESTLE® TOLL HOUSE®
Chocolate Chip Cookies

Ingredients

- 2 1/4 cups all-purpose flour
- 1 teaspoon baking soda
- 1 teaspoon salt
- 1 cup (2 sticks) butter, softened
- 3/4 cup granulated sugar
- 3/4 cup packed brown sugar
- 1 teaspoon vanilla extract
- 2 large eggs
- 2 cups (12-oz. pkg.) NESTLE® TOLL HOUSE® Semi-Sweet Chocolate Morsels
- 1 cup chopped nuts

Directions

PREHEAT oven to 375° F.

COMBINE flour, baking soda and salt in small bowl. Beat butter, granulated sugar, brown sugar and vanilla extract in large mixer bowl until creamy. Add eggs, one at a time, beating well after each addition. Gradually beat in flour mixture. Stir in morsels and nuts. Drop by rounded tablespoon onto ungreased baking sheets.

Bake 9-11 minutes

Figure 1.10 Recipe for Nestle Toll House chocolate chip cookies

1.3.1 Baking Soda

Let's start with baking soda. The role of baking soda, as you may already know, is to puff up the cookies and make them rise. It works by having every molecule of baking soda produce a molecule of carbon dioxide gas. We will learn about this in more detail later on in the semester, but as you can tell based on this description alone, the number of baking soda molecules is going to be very important for how much gas we end up with, and by extension, how much the cookies rise. The recipe tells us that we need a teaspoon of this ingredient, and we can look up that a teaspoon of baking soda typically weighs about 5 grams. The exact mass will vary depending on how fluffy or compact it is on your spoon, which is the reason that you should always weigh your ingredients when baking, but this is another discussion, and 5 grams is a good approximation for our purposes. The weight of baking soda is 84 grams/mol. In other words, 1 mole, i.e. $6.022 \cdot 10^{23}$ molecules, weigh 84 grams. You can find this number either online, or by calculating it from its molecular formula, we will cover how to do the latter in the next section. Based on this information, we can compute how many moles of baking soda we are adding to the cookies by dividing the weight of a teaspoon with the molecular weight:

$$\frac{5 \text{ g}}{84 \text{ g/mol}} = 0.06 \text{ mol}$$

Unless you have a very well-developed sense for how much a mole is, the fact that we are adding 0.06 moles of baking soda may not tell you very much. The molecular number is much more impressive:

$$(0.06 \text{ mol}) \cdot (6.022 \cdot 10^{23} \text{ molecules/mol}) = 3.6 \cdot 10^{22} \text{ molecules}$$

In other words, when making this recipe you are adding about 10^{22} molecules of baking soda, and consequently you are releasing about the same number of molecules of carbon dioxide gas. We will come back to the importance of this later.

1.3.2 Salt and Sugar

Michael confesses to sometimes leaving out salt altogether when baking cookies, because there is so little of it anyway, only a teaspoon. How many salt molecules is he leaving out when doing this? The molecular weight of sodium chloride, which is the scientific name for salt, is 58 grams/mol, and a teaspoon of it weighs about 10.6 grams. So using the same reasoning as above, we find that the number of salt molecules in the recipe is:

$$\left(\frac{10.6 \text{ g}}{58 \text{ g/mol}} \right) \cdot (6.022 \cdot 10^{23} \text{ molecules/mol}) = 1.1 \cdot 10^{23} \text{ molecules}$$

Interestingly, there are actually more salt molecules in the recipe than there are molecules of baking soda. The reason this seems surprising, of course, is that salt is a much smaller molecule.

Next, what about sugar? Granulated sugar is made of sucrose, which has a molecular weight of 342 grams/mol. It's much heavier than salt by about six times. The amount of sugar we are adding is $\frac{3}{4}$ cups, which weighs about 151 grams. So the number of sucrose molecules is:

$$\left(\frac{151 \text{ g}}{342 \text{ g/mol}} \right) \cdot (6.022 \cdot 10^{23} \text{ molecules/mol}) = 2.6 \cdot 10^{23} \text{ molecules}$$

Notice how the number of sugar molecules is not all that different from the number of salt molecules, $2.6 \cdot 10^{23}$ versus $1.1 \cdot 10^{23}$ molecules. This may seem surprising. We typically think of cookies as having a sweet taste rather than salty, and so you would think that there is much more sugar than salt. It turns out that there is only about twice as many molecules! Of course the brown sugar in the recipe also contributes to the sweetness. Using a similar calculation as above, we find that the number of sucrose molecules contributed from the brown sugar is $2.4 \cdot 10^{23}$. So all in all there are about five times as many sucrose molecules as salt molecules.

1.3.3 Ovalbumin and Vanillin

We can do similar conversions for the other ingredients. What about protein? Many of the ingredients in the recipe contribute protein in various forms. Let's focus on the eggs. One egg contains about four grams of protein, we can read this off any food label. So with the two eggs in the recipe we have a total of about 8 grams. Eggs are complicated and have lots of different protein types in them, so we will need to simplify this dramatically and assume that all of it is made up of ovalbumin, which is one of the main protein components. One ovalbumin protein, i.e. the entire chain of amino acids, weighs about $7 \cdot 10^{-23}$ grams. So the number of ovalbumin molecules is:

$$\left(\frac{8 \text{ g}}{7 \cdot 10^{-23} \text{ g/molecule}} \right) = 1.1 \cdot 10^{23} \text{ molecules}$$

As you can see, even though the protein chains and the salt molecules are widely different in size, the number of molecules is actually not so different.

Moving on, the recipe also calls for one teaspoon of vanilla extract, which corresponds to about 4 grams. The main ingredient of vanilla extract is a flavor molecule which tastes of vanilla—it's been given the creative name vanillin. Vanillin has a molecular weight of 151 grams/mol. So the number of vanillin molecules in the vanilla extract is:

$$\left(\frac{4 \text{ g}}{151 \text{ g/mol}} \right) \cdot (6.022 \cdot 10^{23} \text{ molecules/mol}) = 1.6 \cdot 10^{22} \text{ molecules}$$

Again, the number of vanillin molecules is not so much smaller than that of the other ingredients. In fact, almost all of the different molecules in this recipe are within a factor of ten of each other, the only exceptions being the fat from butter and the starch from flour as we will see below.

1.3.4 Butter and Starch

If we assume that all of the fat molecules in butter are butyric acid, we find that there are $1.6 \cdot 10^{24}$ molecules of this molecule. This is the largest number on the list. Similarly, there are only about $6 \cdot 10^{20}$ starch molecules, which is the smallest number. This, naturally, can be explained by the starch molecules being such long molecules.

So we now have a list of ingredients for the Nestle Toll House chocolate chip cookies expressed in molecules. It raises many questions that we encourage you to think about. Why are the different ratios what they are? How do these molecules interact with each other? How do they get together to build the architecture of the perfect Nestle Toll House chocolate chip cookie? We will explore the answers to these questions throughout the rest of this course.

1.4 Molecular Weight

1.4.1 The Origins of Molecular Weight

Based on what we learned so far, the critical number in figuring out how many molecules there are of an ingredient is the weight in grams/mol. In fact, it was the differences in this number that gave rise to the number of molecules in the recipe being so similar. Now we want to delve a little bit more deeply into where these numbers come from, and again, the answer has to do with the molecular structure.

Recall that we defined a mole to be 12 grams of the element carbon-12. Carbon-12 is an isotope of carbon, which means that it has within it six protons and six neutrons. Protons and neutrons, along with electrons, are some of the elementary constituents of matter, they are the ingredients, so to speak, that make up atoms.

Protons and neutrons have about the same weight, whereas electrons are so much lighter that we usually just neglect their mass. The weight of a proton or a neutron is a fundamental unit of nature, and is given by either of two different units: One is called an atomic mass unit (amu). And the other is called a Dalton (Da). They are equal to each other, so an atomic mass unit is equal to a Dalton, is equal to the mass of a proton or a neutron. Expressed in a more familiar unit, either quantity is equal to $1.66 \cdot 10^{-27}$ kilograms, which of course, is an incredibly small number.

With six neutrons and six protons, carbon-12 has 12 atomic mass units, i.e. it weighs $12 \cdot (1.66 \cdot 10^{-27}) = 2.0 \cdot 10^{-26}$ kg. Knowing this, how many molecules are there in 12 grams of carbon-12? We can use the same method we used for the glass of water and divide the total weight by the weight of a single molecule:

$$\left(\frac{12 \text{ g}}{2.0 \cdot 10^{-26} \text{ kg/molecule}} \right) = 6.02 \cdot 10^{23} \text{ molecules}$$

You should recognize that this, of course, is Avogadro's number. And since Avogadro's number is the same as a mole, and since we defined a mole to

be the number of molecules in 12 grams of carbon-12, this is exactly the number we would expect from this calculation.

1.4.2 Calculating Molecular Weight

Having covered the molecular reasons for why substances have the weights they do, how can we find out what the weights of different substances are? Again, we look at the molecular structure. Water is given by the molecular formula H_2O . H is a hydrogen atom, and there are two of these. Each hydrogen atom consists of a single proton. O is an oxygen atom. It consists of eight protons and eight neutrons, and thus weighs 16 amu. So the molecular weight of an H_2O molecule is 18 amu. Conveniently, one amu is also equal to 1 g/mol, so the molecular weight of water is 18 g/mol.

Let's look at a few more cooking materials. White sugar is given by the chemical formula $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. It consists of 12 carbons, 22 hydrogens, and 11 oxygens. We already know that a carbon atom weighs 12 amu. And from the example above, we know that a hydrogen atom is 1 amu and an oxygen atom 16 amu. The total number of atomic mass units of all carbons is therefore 144 amu ($12 \cdot 12$), of all oxygens 176 amu ($11 \cdot 16$), and of all of the hydrogens 22 amu ($1 \cdot 22$). If we add all of these up we get 342 amu total, or 342 g/mol ($144 + 176 + 22$). In other words, there are 342 protons and neutrons present in a molecule of sucrose, i.e. the reason it is so heavy is because there are so many protons and neutrons per molecule.

As one final example let's look at baking soda. The chemical name of baking soda is sodium bicarbonate, and it has the chemical formula NaHCO_3 . One atom of sodium (Na) has a molecular weight of 23 amu. The other weights we know from before, so the molecular weight of baking soda adds up to be:

$$23 \text{ amu} + 1 \text{ amu} + 12 \text{ amu} + (3 \cdot 16 \text{ amu}) = 84 \text{ amu} = 84 \text{ g/mol}$$

Given what we have just covered, you should be equipped to figure out the molecular weight of just about any ingredient in a recipe. You just have to find out what the chemical name and the chemical formula for the ingredient is—a quick search on the internet will tell you this. And then you have to know the molecular weight of each of the pieces in the chemical formula—internet works for this too, or you can turn to a periodic table. Once you have this information, you can calculate the molecular weight, and even go on to find the number of molecules of each ingredient in your

favorite recipe.

1.5 Lemonade – Acidity and pH

So far we have studied the molecular composition of two things: Nestle Toll House chocolate chip cookies and water; the latter being perhaps one of the most essential substances of food. In this section we will discuss what turns out to be the perfect complement to our chocolate chip cookies: lemonade. Appropriately, the main ingredient of lemonade is water. Only a small number of ingredients need to be added to turn water into lemonade, so this will build well on what we have already learned.

Figure 1.11 shows a recipe for lemonade. It's very simple, just add six lemons, five cups of sugar, and some water to a pitcher, stir, and serve over ice. As simple as it is though, this recipe is already a great illustration of a number of scientific concepts that show up in cooking all the time. One is the various physical ideas involved in mixing ice with water. Another is the solution of sugar in water. These are complicated enough that we will leave them for more thorough discussions in Chapter 2 and 4 respectively. Yet another concept, is the notion of acidity. This will be the focus of this section.

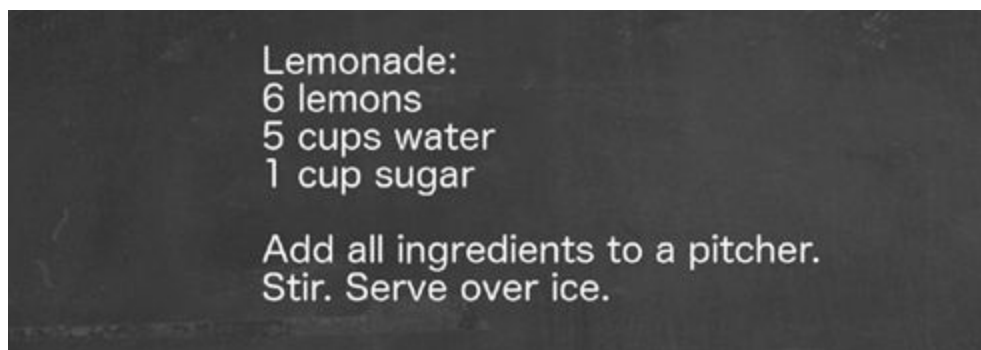


Figure 1.11 Recipe for lemonade

Imagine biting into a lemon, and even just the thought may make your face scrunch. Few foods are as closely associated with sourness as lemons are. The sourness is, in this case, due to an acid, and it turns out that this is generally the case with sour tasting foods. In the case of lemons, the acid is citric acid. Apples contain malic acid, among many others, and there is a whole host of other common organic acids occurring in foods; tartaric acid, benzoic acid, ascorbic acid, and so on. Citric acid is a weak acid, as opposed to other, stronger acids you may have heard of such as sulfuric acid, which is used in car batteries. The other organic acids found in foods are also

weak acids.

1.5.1 The Definition of Acidity

What exactly is an acid? By definition, an acid is a molecule that can release a hydrogen ion, i.e. a proton. Depending on how easily the proton is released, we refer to the acid either as strong or weak, a weak acid is a more reluctant proton donor than a strong acid. Citric acid, for example, does not give up its proton as easily as sulfuric acid. Video 1.1 shows a simplified scenario of citric acid donating a proton to a water molecule.

The opposite of acids are bases. These are molecules that are extremely reluctant to give up protons, in fact they very easily take up protons from other molecules. If a liquid is neither acidic nor basic, it is referred to as neutral. Water is a neutral solution. It is as likely to release a proton as it is to take up a proton.

So when we add lemons to the lemonade recipe, the citric acid in the lemon juice releases a hydrogen, and since hydrogens generally don't float around on their own, what really happens is that one of the many, many water molecules in the solution picks it up. As a result the water molecule is converted from being an H_2O molecule to being an H_3O^+ molecule, also referred to as a hydronium ion. The more hydronium ions present in the solution, the more acidic it is.

Sorry, it appears your system either does not support video playback or cannot play the MP4 format provided. However, you can view the video by clicking on this link:

[01_foodcomps_slide_58.mov](#)

Video 1.1 Animation of a citric acid molecule giving up a hydrogen ion, H^+ , to a water molecule. As a result the citric acid acquires a negative charge and the water molecule is transformed to a hydronium ion, H_3O^+ .

1.5.2 The Definition of pH

Even regular water without any lemon juice added has a small number of hydronium ions floating around, 10^{-7} moles per liter to be more specific. We just learned that a liter of water has 55 moles of water molecules in it, so by comparison this is a tiny number. Since 10^{-7} is even somewhat unwieldy to say, scientists have invented a mathematical formula that expresses the same idea more succinctly. The formula says that pH equals the logarithm of how many moles per liter of hydrogen ions there are in the solution. The square brackets around H^+ , indicate that the hydrogen ions are given as a concentration, with the unit being M, or moles/liter. It is written like this:

$$pH = -\log [H^+]$$

If we use this formula for water, already knowing that the number of hydrogen ions is 10^{-7} , we find that the pH of water is:

$$pH = -\log [10^{-7}] = 7$$

The number 7 shouldn't surprise you. The fact that a neutral solution has a pH of 7 is probably something that many of you are familiar with, and if not, this is a good reminder.

1.5.3 The pH of lemonade – measured and predicted

If in doubt about the pH of water, or anything else for that matter, you can test it by using a pH strip. You can find pH strips online and in many hardware stores, and you just use them by dipping them into the substance you are interested in, and comparing the resulting color change to the pH chart on the package. They are fun to have around the house and, as you will see later on in the course, they may even be helpful when cooking. We used pH strips to measure the pH of a store bought lemonade, which turned out to be just above 2. This is quite acidic on the pH scale, which generally covers pHs between 1-14. The pH of lemons, by contrast, was a little more acidic than lemonade. If we rearrange the equation above, we can solve for the molarity of H^+ ions:

$$\text{pH} = -\log [\text{H}^+]$$

$$[\text{H}^+] = 10^{-\text{pH}}$$

$$[\text{H}^+] = 10^{-2} = 0.01 \text{ mol/L}$$

So, the concentration of H^+ in lemonade is 0.01 mol/L. This is a lot higher than that of water, which had 10^{-7} mol/L. It's a difference of five orders of magnitude. And in fact, this is an important feature of pH in general. If you compare pH 4 to pH 5, there is a tenfold difference in hydrogen ion concentration. Comparing pH 3 to pH 5, there is a hundredfold difference, and so on (Fig. 1.12).

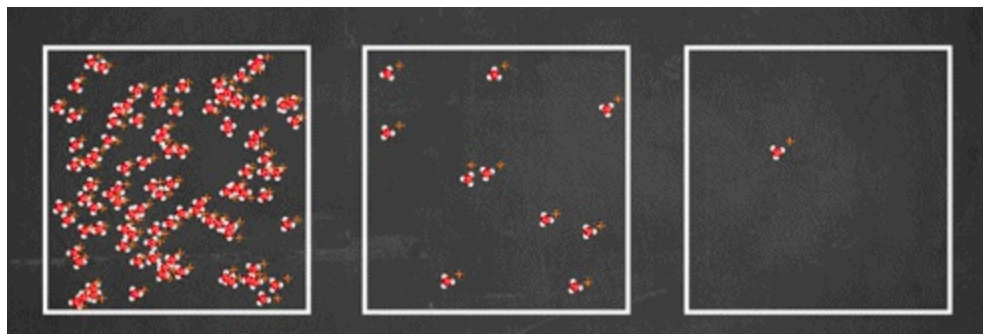


Figure 1.12 Each one-unit pH increment corresponds to a tenfold difference in the concentration of hydrogen ions. For example, a solution with pH 3 has ten times more hydrogen ions than a solution with pH 4. The concept is illustrated above: from left to right the squares contain 100, 10, and 1 hydronium ions, indicating that the pH would increase with one unit from left to right, i.e. the corresponding pH values could be pH 3, pH 4, and pH 5.

Imagine that we make lemonade according to the recipe in Fig 1.11. Is there a way to figure out what the final pH will be without measuring it with a pH strip? It turns out we can calculate it based on what we have just learned. About three tablespoons of lemon juice can usually be squeezed from a lemon, so with six lemons, we have 270 ml, or 0.27 liters, of lemon juice. The pH of lemon juice is 2. We also know that five cups of water corresponds to 1.2 liters of water. Hence, if we calculate how many hydrogen ions are contributed in total from the lemon juice and the water, and then divide by the total volume of liquid, we will arrive at the hydrogen concentration of the final solution:

$$\frac{(0.27 \text{ L}) \cdot (10^{-2} \text{ mol/L}) + (1.2 \text{ L}) \cdot (10^{-7} \text{ mol/L})}{(1.2 \text{ L} + 0.27 \text{ L})} = 0.0018 \text{ mol/L}$$

According to the pH equation, this corresponds to a pH of 2.7 according to the calculation below:

$$\text{pH} = -\log [\text{H}^+] = -\log [0.0018] = 2.7$$

So next time you make lemonade, you can simply give the recipe as: mix lemon juice and water to a pH of 2.7, add sugar to taste, stir, and serve over ice!

Figure 1.13 shows a chart with several common foods and household items. They range from lemon juice at pH 2, orange juice at pH 3, water at pH 7, baking soda at pH 9, etc. Given what we have just told you, you can now fill in the chart with the pH of other foods in your home and calculate their proton concentrations. What you will probably find in your explorations, is that foods with lower pH tend to taste more sour. This is because acidity is closely related to what we experience as a sour taste. Taste is something that scientists are still learning a lot about though, and it is important to note that our taste buds do not detect the hydrogen ions. They detect the molecule as a whole. So a stronger acid doesn't necessarily taste more sour than a weaker acid. The sourness of something is only an indication of how acidic something is, of how low the pH is, but it is not directly correlated.

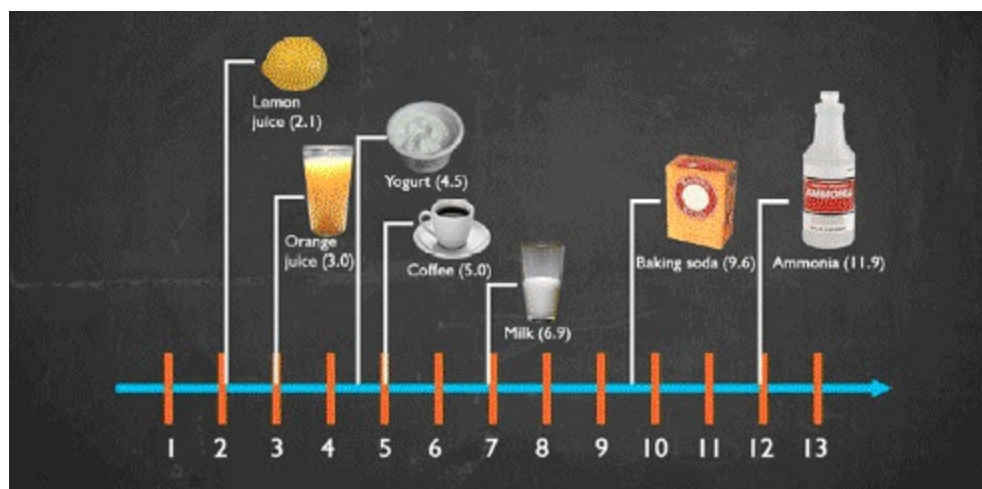


Figure 1.13 pH values of some common foods and household items

As you will see throughout this course, acids play a role in many aspects of cooking, not just in regard to taste. Ceviche, for example, is made by marinating fish in lemon juice; the acidity causes the proteins to denature, which essentially cooks the fish. In recipes for ricotta cheese, it is the addition of vinegar, an acid, which causes the curdling of the cheese to happen. Reactions between acids and bases are also important for baking, both in causing rising of doughs and batters, but also in contributing to Maillard and other browning reactions.

1.6 Why Use Equations

1.6.1 Equations are Tools

One of the things that we are doing in this class that you may find unusual is that we are associating the various ideas in cooking with mathematical equations. Before we delve into the rest of the course, let's take a moment to think about why. What is the value of being quantitative? Why do scientists approach things in this way?

Figure 1.14 shows the ten equations that you will encounter working through this course. Since there is one for each week, or chapter, of the course, we generally refer to each of them as the "equation of the week". We have already covered the first one stating that one mole is $6.022 \cdot 10^{23}$ molecules. Next chapter covers the equation $Q = mc_p \Delta T$, Chapter 3 covers $U = Ck_B T$, and so on.

$$1 \text{ mole} = 6.022 \cdot 10^{23}$$
$$Q = mc_p \Delta T$$
$$U = Ck_B T$$
$$E = \frac{F / A}{\Delta L / L_0} \quad E = \frac{U}{l^3}$$
$$t = \frac{L^2}{4D}$$
$$T(t) = (T_{\text{initial}} - T_{\text{external}}) e^{(-t/\tau)} + T_{\text{external}} \quad L = \sqrt{4Dt}$$
$$\eta = E \times \tau$$
$$E = \frac{\sigma}{R} (\phi - \phi_c) \quad \phi > \phi_c$$
$$\text{NaHCO}_3 + \text{AcidH} \rightarrow \text{AcidNa} + \text{H}_2\text{O} + \text{CO}_2$$
$$N(t) = N_0 e^{kT}$$

Figure 1.14 Each week of the course, or chapter of this book, has an equation associated with it: the

Equation of the Week.

You can think of all of these equations, and we certainly do, as tools. Equations in general are just tools that help us do and understand things in which there are no equations at all. For example, accompanying Chapter 6 is a lab where you cook molten chocolate cake. It's delicious. Looking at it scientifically though, one can ask many questions: Why do you cook it for the time you do? What is the role of each of the ingredients? As we try to figure out the answers to these questions, we come up with various theories. The problem is that often there are competing qualitative theories. What one really would like to do when doing science, is to come up with ways of deciding which of the many possible qualitative explanations are correct. And this, in fact, is the reason we make an effort to be quantitative. It's not because we care about quantification as such. It's because what we really want to do is to be qualitative. And it turns out that the best way to investigate a qualitative explanation is often to test it quantitatively, and then use that framework to make the explanation better.

One example that we have already seen, is the Nestle Toll House chocolate chip cookie recipe, where we converted many of the ingredients to numbers of molecules using the equation of the week. Why was this useful? Recall that the reason we did this was because knowing how many molecules there were of each ingredient helped us understand what the cookie looked like on a molecular level, and this in turn helps us understand how each ingredient is contributing to the overall texture and taste of the cookie. This is the sense in which the equation of the week, which counts the number of molecules, is really a fundamental qualitative idea as well as a quantitative one.

Looking ahead slightly, the equation for Chapter 5 expresses the relationship between the length and time in what we call a diffusion process. This is something that will actually be relevant for two weeks of the course. We will talk about it in the context of spherification, the culinary invention pioneered by Ferran Adria, as well as in the context of heat transfer. In terms of spherification, which works by immersing a spoonful of food into an alginate bath, thus causing a thin shell around the food, the big question is: how long should you leave the food in the alginate for the shell to get the correct thickness? To figure this out it's helpful to understand how the process works on a molecular level, which is that calcium ions move into

the alginate and bond with it. Next the question becomes, how do the calcium ions move into the alginate in the first place? And whichever quantitative model we invent needs to take this into consideration.

1.6.2 Equations have Predictive Power

There is another important reason for being quantitative, besides that it helps you to be qualitative, which is that when you are quantitative, you can predict things. If a concept is expressed in a well formulated equation, you could use it, for example, to predict how long it would take to bake a molten chocolate cake, or to spherify a food, or any other of a number of things, without even having tried it. If you are used to cooking lasagna in a certain size pan, but find that at your friend's place there is only a much smaller pan available, then, as long as you have access to an equation that predicts how quickly thermal energy moves into food, you can predict how long you should cook lasagna to the perfect temperature with the smaller pan just as nicely as with the big pan. You can also estimate how much heat it takes to cook an egg. You can figure out how many strawberries to put into your milkshake for it to flow and have the texture you want. You can estimate how cold to make your Jell-O for it to feel exactly the right way in your mouth, and so on and so forth. If you understand how to think quantitatively, many aspects of cooking become clear. Moreover, you can start to understand the connections between things that seem very disparate on the surface. For example, we will discover that the process of spherification is, in a very fundamental way, similar to the process of heat transfer. Similarly, by weighing a cup of flour several times and discovering that the weights always differ, we will also uncover a fundamental principle at work in the seemingly very different context of making whipped cream.

All in all, since the essence of what we are trying to do in this course is to explain why foods behave the way they do when we cook them, quantitative models have to be a part of our mission.

CHAPTER 2

Energy, Temperature and Heat

TABLE OF CONTENTS: 2

2.1 What is Cooking?

[2.1.1 A Definition](#)

[2.1.2 Phase Diagrams](#)

[2.1.3 Looking Ahead](#)

2.2 Cooking with Heat

[2.2.1 Energy Density of Fuels](#)

[2.2.2 The Power of Ovens](#)

[2.2.3 What is Heat?](#)

2.3 The Equation of the Week

2.4 Applications of the Equation of the Week

[2.4.1 Boiling a Cup of Water](#)

[2.4.2 Heating a Cup of Oil](#)

[2.4.3 Heating an Oven](#)

[2.4.4 Cooking an Egg](#)

2.5 Molecular Origins of Specific Heat

2.6 Specific Heat

[2.6.1 Burning a Hamburger](#)

[2.6.2 What is a Calorie?](#)

[2.6.3 Bomb Calorimeter: A Precise Way to Measure Calorie Content](#)

[2.6.4 The 4-4-9 Rule](#)

2.7 Molecular Origins of the 4-4-9 Rule

[2.7.1 Digesting Sugar - The Chemical Reaction](#)

[2.7.2 The Calorie Content of Sugar -Breaking and Forming Bonds](#)

2.8 Latent Heat

[2.8.1 Adding Heat at a Phase Transition](#)

[2.8.2 The Equation for Latent Heat](#)

[2.8.3 Steam Burns: Latent Heat of Evaporation](#)

[2.8.4 Ice Water: Latent Heat of Fusion](#)

[2.8.5 Summary](#)

CHAPTER 2

2.1 What is Cooking?

2.1.1 A Definition

We asked Dave Arnold, chef and owner of the bar Booker and Dax in New York City, to propose a drink with which we could toast the beginning of this class. He responded by preparing a version of Campari and Soda, a classic cocktail traditionally consisting of Campari, soda water, and lime. Dave Arnold's version, however, replaces the lime with a pinch of lactic and tartaric acid, and, rather than relying on the carbonation of the soda water, he carbonates the final drink as a whole in order to achieve the perfect amount of fizz on your tongue.

With this recipe in mind, let's toast the beginning of the class and get to work!

Let's start by asking, what is cooking? This is, after all, a course that is supposed to combine science and cooking. A good way to find out what something like cooking is, is to go and look it up in the Oxford English Dictionary, the source of knowledge of all things. In the Oxford English Dictionary, it states that cooking is:

"To make food fit for eating by due application of heat, as by boiling, baking, roasting, broiling, etc"

This is actually a rather narrow definition. And throughout the course of this class, you will see that cooking is much richer than this. Indeed, you even saw that from our very first recipe. The Campari and Soda had no application of heat in it whatsoever. But nonetheless, it was a process in which you took raw ingredients, which individually were not very delicious, and combined them into a single drink that we can assure you is really quite delicious. And that is, after all, cooking.

But as scientists, when we want to analyze this and try to understand what the transformations are that occur when we cook, what we like to do is to make things quantitative. We do this not just because we want to torture people who listen to us but because, as you will see in this course, when we start to make ideas quantitative then we'll start better to understand qualitatively what is happening as we do things. You will see this as we

move on.

2.1.2 Phase Diagrams

To start this process, let's recast the definition from the Oxford English Dictionary as a plot, or a phase diagram. We can start out with an arrow, where the arrow represents the increase of temperature (fig 2.1).

On the left side, the temperature is low, and on the right side, the temperature is high. The Oxford English Dictionary said that food is cooked when it's heated, so that must mean it goes above some critical temperature. We can therefore draw a line on our temperature arrow, and we can say that on the left side of the line the food is uncooked, and on right side of the line, the food is cooked.

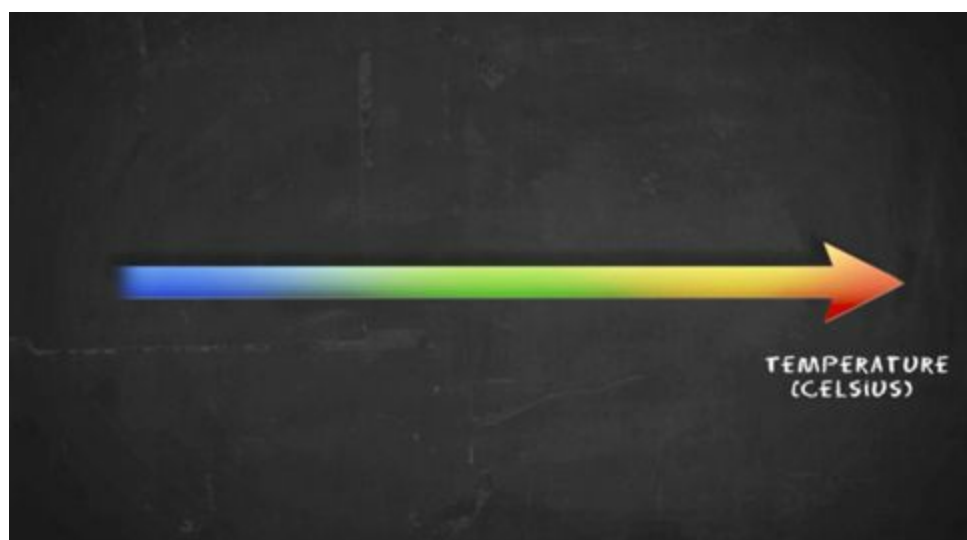


Figure 2.1 A temperature arrow with low temperatures on the left and high temperatures on the right. Food will "cook" at some critical temperature along this axis.

As an example, we can take perhaps one of the simplest foods to cook, the egg (fig. 2.2). An uncooked egg is on the left side of the diagram. And we know that when we cook an egg by applying heat to it, it changes conformation. It goes from being a liquid egg inside its shell to being a solid, either scrambled eggs or hard-boiled eggs or however you like them. This is the transformation that occurs. So the cooked egg is on the right side of the phase diagram.

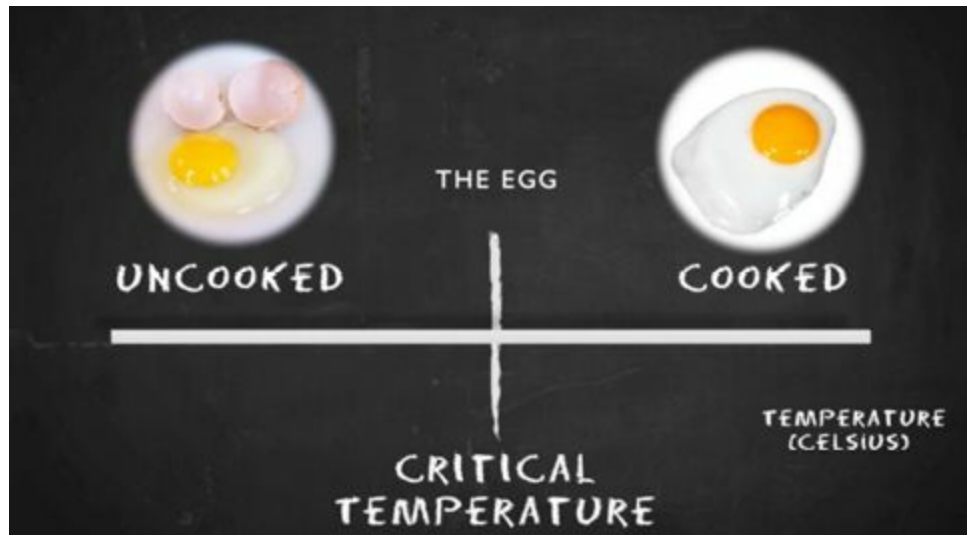


Figure 2.2 Phase diagram of an egg. The temperature arrow has been turned into a straight horizontal line and the critical temperature is marked with a vertical line. The egg is uncooked on the left side of the critical temperature, and cooked on the right side.

On this same plot we could change the temperatures axis to something else, and then we could put the ingredients of Dave Arnold's drink on the uncooked side, i.e. all of the raw ingredients that Dave put into his drink. On the other side, on the cooked side, we would put the finished, or "cooked", drink. As the drink is being finished there are all of these different steps and transformations that occur, and you could imagine parameterizing those along the axis of this plot. Indeed, in this course what we will do is to try to take recipes like the drink that Dave made, and try to figure out what the essential features are that make them so delicious.

This is going to prove to be more complicated than it might seem at first sight, which is particularly evident with the egg. We mentioned that an egg went from being uncooked to cooked at a critical temperature. That was the way we interpreted the Oxford English Dictionary. But what we are going to find out, is that an egg cooks in different ways at many different temperatures. Indeed, there are different transformations that occur in an egg as you heat it from, say, 60 degrees to 70 or 80 degrees Celsius.

For example, as we will describe to you later on in this course, at 63 degrees there is a protein in eggs called ovotransferrin that unfolds, and this changes the texture of the egg (fig. 2.3). At around 80 degrees, other proteins unfold that also change the texture of the egg. Hence, cooking a simple egg has an entire range of different transitions that describe the changes in texture in the egg. When we say that the egg is going from

cooked to uncooked, it is actually a very gross simplification of all of the different things that are happening. And if one wants to be able to control the texture of an egg, or even the taste, one needs to be aware of and control these different transitions. This is one of the sorts of things that we are going to want to expose as we go through this subject in this class.

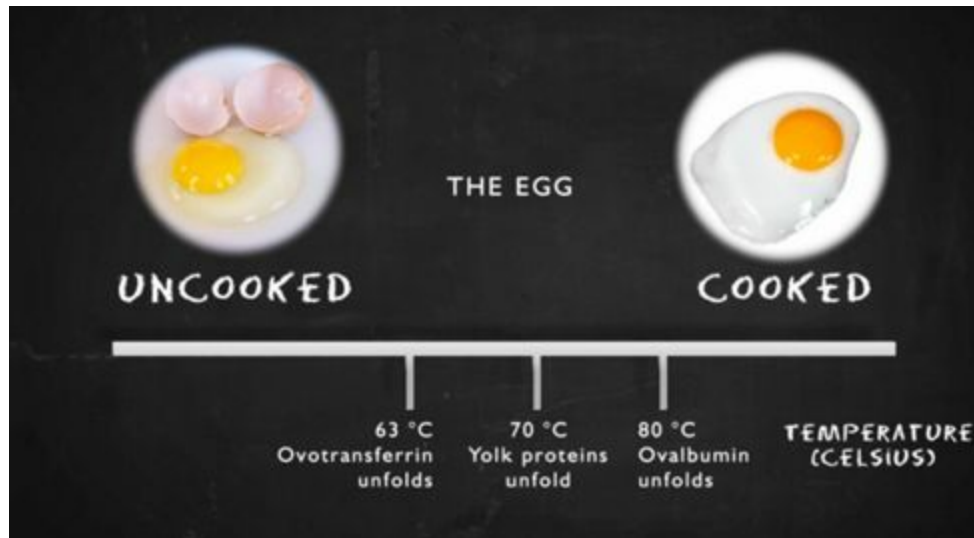


Figure 2.3 A more detailed phase diagram of an egg. Most foods have several critical temperatures, each corresponding to a component within the food. Ovotransferrin, several types of yolk proteins, and ovalbumin are examples of egg proteins that “cook”, or unfold, at different temperatures.

There are other ways of cooking besides changing temperature. We already mentioned Dave Arnold’s drink. But one can also think about this in the context of an egg. It turns out that one can cook an egg without applying any heat at all. By changing the acidity of the liquid that the egg is in, one can cause an egg to go from uncooked to cooked. An example of this is a so called “century egg” (fig. 2.4), which is a Chinese delicacy that is created by storing an egg in a basic solution for a very long time. We will talk more about acidic and basic solutions later on.

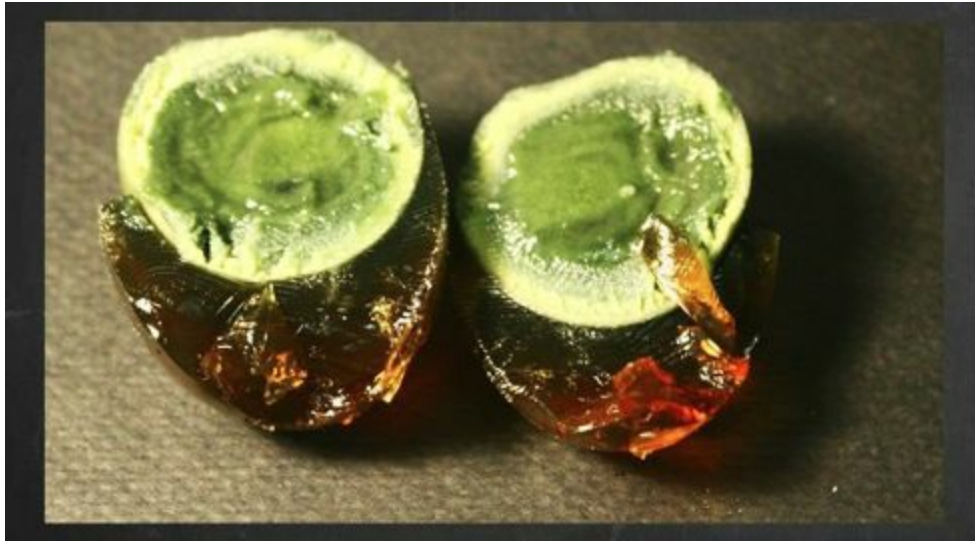


Figure 2.4 Century eggs, a Chinese delicacy, are created by immersing eggs in solutions with high pH for long periods of time

2.1.3 Looking Ahead

The goal of this class is to try to tease out these sorts of ideas in more detail. In the first two weeks of the class, we are going to focus on the very basic transitions that occur when one cooks, what we may refer to as, ordinary foods. We'll focus on the application of heat as the primary driving force, although we'll think a little bit about other things too.

This first week, we're going to take a more macroscopic view of the subject by discussing what heat is. What does heat do to food? How much heat does it take to cause an egg to cook?

In Chapter 3, we are going to start to delve into the microscopic processes that are happening inside of the egg, or any material, when you cook it. What are the underlying reasons for the change in texture or taste that make a food go from something which we consider "uncooked", and often less unappetizing, to being "cooked", and much more delicious?

2.2 Cooking with Heat

2.2.1 Energy Density of Fuels

How do we apply heat to food to cook it? Throughout the ages, human beings have done this in rather straightforward ways. We start with fuel, and we then take the fuel and either burn it, or use it in some other fashion, in order to create heat. And that heat then transforms food from being uncooked to being cooked. Perhaps the simplest way to do this is to use wood as your fuel. If you use wood, then you can just burn the wood. Burning the wood creates a fire, and you can then put your food on top of the fire and cook the food (fig 2.5).



Figure 2.5 Burning wood releases the energy of the wood as heat, which can be used to cook food.

Now suppose you have a pile of wood, perhaps a kilogram, and you would like to make a feast for all of your friends. How much food could you cook with this kilogram of wood? Clearly there is a limit to what can be cooked with a fixed amount of fuel. How do we think about this?

It turns out that wood, or any fuel, has what we call an energy density. This is an energy per unit mass, i.e. a measurement of how much energy can be liberated by burning a certain mass of the fuel. In the case of wood, the energy density is 14 megajoules per kilogram. That is 14 million joules per kilogram. Joules, as you probably remember, is an SI unit of energy. It's measured in kgm^2/s^2 .

Suppose you had a kilogram of wood. What this means is that you have 14 megajoules of energy that you can use to cook with. And the question then becomes, what can you cook with 14 megajoules? This is the thing that we want to start to learn how to think about.

Before we go into this in a little more detail, we should comment that there are other fuels that we commonly use. Charcoal is one example. It turns out that charcoal has a much higher energy density than wood — about 30 megajoules per kilogram. In other words, it is almost a factor of two more, which explains why you need less charcoal than wood to heat the same amount of food.

Natural gas has an even higher energy density: about 45 megajoules per kilogram. This is about a factor of three higher than the energy density of wood, which is why — if any of you have ever cooked on an outdoor grill with a propane tank — you don't need as much gas by weight to cook the same amount of food as you do with wood.

The question with all of these types of energy is: what can you cook with it? Can you cook an egg? Can you cook a chicken? Can you cook a steak? Can you cook a tofu burger? How many chickens or tofu burgers can you cook? This is a problem that home chefs face when having a half-full gas tank in their grill. And they wonder, how much can I cook with this? Am I going to get through the barbecue appropriately? What we now want to do in this chapter is to show you how, if you understand the physics, you can do some simple calculations to get a rough estimate of whether or not you will make it through your barbecue.

2.2.2 The Power of Ovens

Before doing so though, let's look at some other ways to cook food. For most of everyday cooking we don't burn any fuel at all, we use an oven of some sort. There are at least two types of ovens: There are electrical ovens, which have hot coils on them which heat the air within the oven. And there are microwave ovens which send radiation that interacts with and heats the food.

If you look at the specifications on an oven, you will notice that it does not report the energy in terms of the fuel that is used. It actually reports the energy in "watts". Watts is a unit of power, and its units are joules per second. What this means is that, if you put the food in the device for a certain period of time, you can calculate the total energy that was put out by the oven during that time by multiplying the power with the time.

$$\text{power} \cdot \text{time} = \text{energy}$$

$$\text{watts} \cdot \text{sec} = \left(\frac{\text{J}}{\text{sec}} \right) \cdot \text{sec} = \text{J}$$

This is the amount of energy you would hope also got absorbed by the food. As you probably already know though, all of the energy from the heating coils does not go into heating the food; a lot of it is lost to the "environment", i.e. it heats up the air, the oven itself, the dish in which you cook the food, and sometimes even the room. But this is a rough ballpark number to make sure that you are in the right range.

The typical energy of a microwave oven is about 400 watts. The typical energy of a bigger oven, a heat oven, is about 1,000 watts (fig. 2.6). How can we compare the amount of energy in an oven with the energy of a kilogram of wood? Suppose you put a piece of food in your oven for 10 minutes. Since every minute has 60 seconds, that is 600 seconds. If your oven has 1,000 watts, that means that the total energy you can possibly dump into the food is 1,000 watts times 600 seconds, which is 600,000 joules, or 0.6 megajoules. This is actually less energy than in a kilogram of wood, which is 14 megajoules.



Figure 2.6 Three basic cooking instruments: a fire, a microwave, and an oven.

Using these numbers, you can convert the weight of wood that you would need to burn in order to match the time that you leave something in an oven. It is not a perfect comparison, i.e. it is not true that the energy from wood is exactly equivalent to the energy from the oven because you are applying heat in different ways. This we will cover later on in this course. But this gives you a ballpark figure for what amount of energy is being used.

Another example of this, which is especially relevant when thinking about more environmentally friendly ways of cooking, is solar ovens (fig. 2.7). A solar oven consists of a large reflector shield, shaped in a way that focuses energy from the sun. The problem with solar ovens is that the energy, or the average solar radiance from the sun, is about 200 watts per square meter. This means that if we were able to capture all of the sunlight within a one square meter area, we would get about 200 watts, which is considerably less energy than that of an oven or a microwave oven. This is one of the reasons why making a solar oven is so difficult. Another reason is that it is quite hard to make a reflector that can focus all of the energy from the reflector shield into the food. These are some of the challenges that people are trying to solve as a way of having more environmentally friendly cooking devices.



Figure 2.7 Solar ovens, here showcased by Chef José Andrés (second from left), are an environmentally friendly way of cooking food.

2.2.3 What is Heat?

What is heat, anyway? When you apply heat to food, what are you actually doing to it?

One definition is that heat is the total energy that results in the temperature of the system being whatever it is. In other words, if a thing has a higher temperature, that means it has more heat.

At a molecular level, temperature is a measure of the motion of the molecules within a material. Imagine that at a certain temperature the molecules in a material are jiggling around at some rate. In scientific terms we would refer to this as the molecules having an average kinetic energy. When you heat up the material, the average kinetic energy of the molecules increases, or, expressed in simple terms, the molecules jiggle around faster. This is what temperature is. And it is this jiggling that causes changes to occur in the material, which is at the heart of what we do when we cook and try to make food delicious.

Imagine a box with lots of water molecules (Video 2.1). Initially, the water molecules are at a rather low temperature and so they are sitting, barely moving at all. As we gradually raise the temperature to a slightly higher level, the molecules start to jiggle a little bit and they start to move and bump into each other. If we raise the temperature a little more, the molecules start to move by each other. And if we raise the temperature a lot, you see the molecules whizzing around everywhere. That jiggling and whizzing of the molecules is the essence of temperature, and this is what we are actually doing to a material when we dump in heat.

The questions that arise now is: if we apply a given amount of energy to a system, namely some number of joules, how much does the temperature rise? We will discuss this next. And then, given a particular temperature rise, how does that relate, specifically, into the whizzing around of the molecules? This we will discuss properly in Chapter 3.

Sorry, it appears your system either does not support video playback or cannot play the MP4 format provided. However, you can view the video by clicking on this link:

[02_eth_slide_18-2_1.mp4](#)

Video 2.1 Simulation of the movement of water molecules at increasing temperatures. Seconds 0-10 represent a solid state, seconds 13-17 liquid, and seconds 19-23 gas. The bar in the top right corner indicates temperature.

2.3 The Equation of the Week

How much energy has to be given to food to heat it up? If you want to heat up an egg by 10 degrees Celsius, how many joules does it take to do that?

The answer to this, it turns out, is contained in a simple mathematical equation, which is the equation of the week for our first week of the course. The equation says that:

$$Q = mc_p \Delta T$$

Before we tell you what the symbols in this equation mean, let us tell you a little bit about the philosophy of using such equations in this course.

Some of you may be uncomfortable with the idea of using equations, and it is not our intent to make you uncomfortable with them. Instead, we hope to convince you throughout this course, that there are simple equations that represent the essential idea of a given concept in cooking. And if you read the equation as an expression of how different things depend on each other you will hopefully develop more intuition for what is going on in materials. And moreover, as you will see, using equations can also turn out to be rather useful.

For example, later on we will show you how the equation of this week,

$Q = mc_p \Delta T$ can help you cook a perfect egg without investing in an expensive immersion heater. That is, by understanding the equations that we give you, you will have the opportunity to use them to invent new recipes if you so desire. Now having said that as introduction, let's go into the equation.

Let's start by looking at what the various symbols in the equation mean (Table 2.1). Q is the amount of heat that you dump into the food. It is measured in joules. For example, if you burn a kilogram of wood, and somehow manage to dump all of the resulting heat into the food, then Q will be 14 megajoules.

The mass of the food is denoted by m . Every food has some mass, and you would weigh it with a scale to figure out how much. For the purposes of this

equation, m should be measured in kilograms.

ΔT is the temperature difference, i.e. the final temperature of the food minus the initial temperature of the food. If, for example, you have a chicken and it starts out at 20 degrees Celsius and you heat it up to 40 degrees Celsius, then ΔT is 40 minus 20, which is 20. ΔT should be measured in either degrees Celsius or degrees Kelvin.

Finally, c_p is a number that we call the specific heat of a material. It is the number that characterizes how much something heats up when you apply a specific amount of heat, and it is measured in units of joules per gram per degree Celsius or degree Kelvin (J/g°C or J/gK). This number is different for different foods, and we will typically give it to you so you don't need to remember the exact values. We will discuss this number in more detail later on.

EQUATION OF THE WEEK		
Symbol	Description	Units
Q	heat	J
m	mass	g
c_p	specific heat	J/gK or J/g°C
ΔT	change in temperature	K or °C

Table 2.1

The point of this equation, is that there is a direct relationship, which is very well understood, between the amount of heat that you put into a food and how much the temperature will rise. In the next section, we are going to use this equation to try to understand, and get some intuition for, the relationship between the energy that you put into a food and the temperature rise.

2.4 Applications of the Equation of the Week

2.4.1 Boiling a Cup of Water

It is now time to use the equation of the week to calculate how much energy you have to add to heat various things so that we can start to see how it works.

One thing we need to know before we can use the equation is the values for specific heat, c_p . As we mentioned, the specific heat changes from material to material.

It turns out that the specific heat for water, an important cooking material, is 4.18 J/gK. The specific heat of eggs is about 3.18 J/gK. The specific heat of milk is closer to water, 3.85 J/gK. For beef, depending on the cut of beef, the specific heat is somewhere between 2.5 and 3.5 J/gK. The specific heat of air is considerably lower at 1 J/gK. And, finally, the specific heat of olive oil, another item that is useful for cooking, is about 1.97 J/gK, i.e. about half that of water (fig. 2.8). Since one degree Celsius is equivalent to as one degree Kelvin, the unit J/gK is interchangeable with J/g°C.

	Specific Heat (J/g K)	Density (g/cm ³)
Water	4.18	1
Eggs	3.18	1
Milk	3.85	1.1
Beef (rump)	2.6	~0.9
Beef (shank)	3.18	~0.9
Air	1	0.001
Olive Oil	1.97	0.91

Figure 2.8 Specific heat and density of common foods. (Source Wolfram Alpha)

As you can see in Figure 2.8, eggs, milk, and beef all have specific heats between those of olive oil and water. This actually turns out to be true for most foods, and it is not an accident by any means. In fact, the main ingredient of all food is water. This is something that we are going to have to think about constantly throughout this course. It will come up again and

again in one context or another. Another important ingredient of food is fat. Eggs, milk, and beef all contain fat. Fats, just like olive oil, which, of course, is a fat, tend to have a specific heat around 2. So the fact that most foods have specific heats between water and oil can, somewhat simplified, be explained by a large percentage of them being made up of both water and oil

Having learned about c_p , we are set for using the equation of the week. Let's say we want to make a cup of tea. You want to heat the water by putting it in the microwave, and you are wondering how long you have to put it in the microwave for until the water boils. To figure this out, we first have to calculate the energy it takes to boil one cup of water (and let's assume in this case, that you are boiling not just an arbitrary cup of tea, but exactly 1 cup, i.e. 237 mL). One cup of water weighs 237 grams — you could find this number by weighing or by knowing that the density of water is 1g/ml and simply calculating. We can assume that we start out with water at room temperature, i.e. about 23 °C, and we want to heat it to the boiling point, which is 100°C. Hence the variables in the equation are as follows:

$$m = 237 \text{ g}$$

$$c_p = 4.18 \text{ J/gK} = 4.18 \text{ J/g}^\circ\text{C}$$

$$T_{\text{final}} = 100^\circ\text{C}$$

$$T_{\text{initial}} = 23^\circ\text{C}$$

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 100^\circ\text{C} - 23^\circ\text{C} = 77^\circ\text{C}$$

How much energy do we have to dump in? Plugging these numbers into the equation of the week, we get:

$$Q = mc_p\Delta T = (237 \text{ g}) \cdot (4.18 \text{ J/g}^\circ\text{C}) \cdot (77^\circ\text{C}) = 76300 \text{ J}$$

So the amount of energy it takes to boil a cup of water is 76,280 joules.

Unless you have a very well developed sense for what a joule actually is, it's hard to know what this means.

One way to put this number into context, is to ask how much wood it takes to make this much energy? You already know that the energy density of wood is 14 MJ/kg, so the amount of wood needed is 76,280J divided by 14MJ/kg, which is 5.4 grams.

Another way to put the number into context is to figure out how long you would need to put the cup of water in the microwave for it to boil. You could go to your microwave, if you have one, and find its power output — usually it is about 400 watts. Using this number, how long does it take to generate 76,280 joules with your microwave oven?

Once you have calculated how long it takes, we also recommend you go and do the experiment. Namely, try putting a cup of water in your microwave for that amount of time, and see if it actually starts to boil? And if it does not work, you should try to think about why.

2.4.2 Heating a Cup of Oil

What if we were going to try to heat up oil instead of water? Oil, like water, is an important cooking material. For example, when you fry something on a pan you often coat it with oil. How would the calculation we did above change if we heated up olive oil from room temperature to 100°C instead of water?

First, the density of olive oil is slightly different than water. It is about 0.9 g/ml for oil rather than 1 g/ml for water. So they are comparable, but slightly different. This means that the mass of 1 cup of olive oil is going to be a little bit less than the mass of 1 cup of water, more specifically 213 g according to the calculation below.

$$m_{oil} = (237 \text{ mL}) \cdot (0.9 \text{ g/mL}) = 213 \text{ g}$$

But the main difference between the two is the specific heat. The specific heat of water is 4.18 J/gK, whereas the specific heat of olive oil is 1.97 J/gK.

Plugging the numbers into the equation of the week, we get:

$$Q_{oil} = m_{oil} c_p \Delta T = (213 \text{ g}) \cdot (1.97 \text{ J/g}^\circ\text{C}) \cdot (77^\circ\text{C}) = 32400 \text{ J}$$

So the amount of energy it takes to heat up a cup of olive oil is about 32,355 joules. This is less than water by about a factor of 2. In other words, heating up a cup of oil would require about half as much wood or about half as long in the microwave as a cup of water.

2.4.3 Heating an Oven

Another interesting question you might ask yourself is, how much energy is stored in an oven? An oven consists of air, and air, we already know, has a specific heat of 1 J/gK. When you heat up an oven to some temperature, how much energy have you stored?

To keep the comparison the same to the examples above, let's say that we are heating up the temperature in the oven from 23°C to 100°C, so our ΔT is the same. The only thing we are missing is the weight of air in the oven, which we can find by knowing its volume and the density of air.

Let's say that the volume of an oven is about 10 liters. This is not a very big oven, but it is a reasonable volume for an oven. As for the density, air is much less dense than water. Water, we saw in the example above, has a density of 1 g/ml. The density of air, it turns out, is only 1/1,000 of that — it is 0.001 g/ml.

Using this information we can find the mass of the air in the oven by multiplying the density with the volume.

$$m_{air} = (10000 \text{ mL}) \cdot (0.001 \text{ g/mL}) = 10 \text{ g}$$

So the mass of air in an oven is about 10 grams.

Using the equation of the week, we can calculate the energy that is stored in the oven:

$$Q_{air} = m_{air} c_p \Delta T = (10 \text{ g}) \cdot (1 \text{ J/g}^\circ\text{C}) \cdot (77^\circ\text{C}) = 770 \text{ J}$$

So the energy stored in the heated oven is 770J. This is a much smaller energy than could be stored in a cup of water or oil. If you think about it, you knew this intuitively. If you are cooking something and you open the oven, you probably don't hesitate for a second putting your hand in the air in the oven, but you would never put your hand in boiling water which is a lower temperature than the oven. Part of the reason for this is that there is much less energy stored to damage you, or in a sense to "cook" you.

2.4.4 Cooking an Egg

Let's conclude these sample calculations with an example of heating an actual food. How much wood does it take to cook an egg? Just as above, we can calculate this by using the equation of the week, the difference being that we must use the mass and specific heat of an egg instead of water, oil, or air.

Chef Dave Arnold, and many chefs with him, claim that a perfect egg has been cooked to 64°C. So let's cook our egg to this temperature. This means that ΔT is 64°C-23°C, which is a 41°C. We know from Figure 2.8 that the specific heat of an egg is 3.18 J/gK, and the mass of an egg is about 50 grams. According to the equation of the week, the energy required to cook an egg is 6520 J.

$$Q_{egg} = m_{egg} c_p \Delta T = (50 \text{ g}) \cdot (3.18 \text{ J/g}^\circ\text{C}) \cdot (41^\circ\text{C}) = 6520 \text{ J}$$

How much wood does this correspond to? Not a lot. Knowing that the energy density of wood is 14 MJ/kg, we find that only 0.5 g of wood is needed to cook a perfect egg.

2.5 Molecular Origins of Specific Heat

Why do some materials have a higher specific heat than others? What is it about water, with a specific heat of 4.18 J/gK , that makes it have a specific heat about twice as high as that of olive oil, at 1.9 J/gK ?

We can begin to answer this question by looking at the units, joules per gram Kelvin. The units tell us that somehow water is able to store more energy per gram and more energy per degree of temperature. And as is often the case in this class, the reason for this, can be discerned by understanding what happens on a molecular level.

Water has three atoms that are bonded to each other, two hydrogens and one oxygen. The hydrogens and oxygens on each water molecule are also interacting with hydrogens and oxygens on other water molecules. What happens as you start to heat up water is that you are adding thermal energy. You already know that eventually this energy will make the water molecules move around faster and faster, and this is what we detect as an increase in temperature. However, before this happens, there is a certain amount of energy that can be absorbed by the molecules themselves. Somewhat simplified, this energy goes into making the atoms in the molecule vibrate and rotate around their bonds and it is referred to as vibrational and rotational energy. This subtle absorption of energy does not contribute to a temperature increase.

Naturally then, the more energy a molecule can absorb in rotation and vibration, perhaps by having more ways in which it can vibrate and rotate, or perhaps by needing more energy to rotate and vibrate in the first place, the more energy you can store in the molecule before the temperature starts to increase. And this is what gives us the specific heat.

Based on its higher specific heat, water molecules clearly have a greater capacity to store energy than oil. The main reason for this is that the bond between oxygen and hydrogen is an unusually strong bond, much stronger than the bonds that occur in most fats. This is the reason water can store so much more energy before you start to see an increase in temperature, and this, in turn, is the reason the specific heat of water is relatively high, even

if you compare to other materials.

Since most foods contain a lot of water, its high specific heat has important implications for cooking and for this class. As Figure 2.9 shows, it is often the moisture content of a food that determines what its specific heat is. Oranges, for example, which are mostly made of water (90%), have a specific heat that is not much lower than that of pure water (3.9 vs 4.18 J/gK). Fresh figs, with a water content of ~80% water, have a slightly lower specific heat than oranges, but if you remove most of the water by drying, the specific heat decreases even further from 3.6 to 2.3 J/gK. Similarly, the low specific heat of flour, can partly be explained by its low water content.

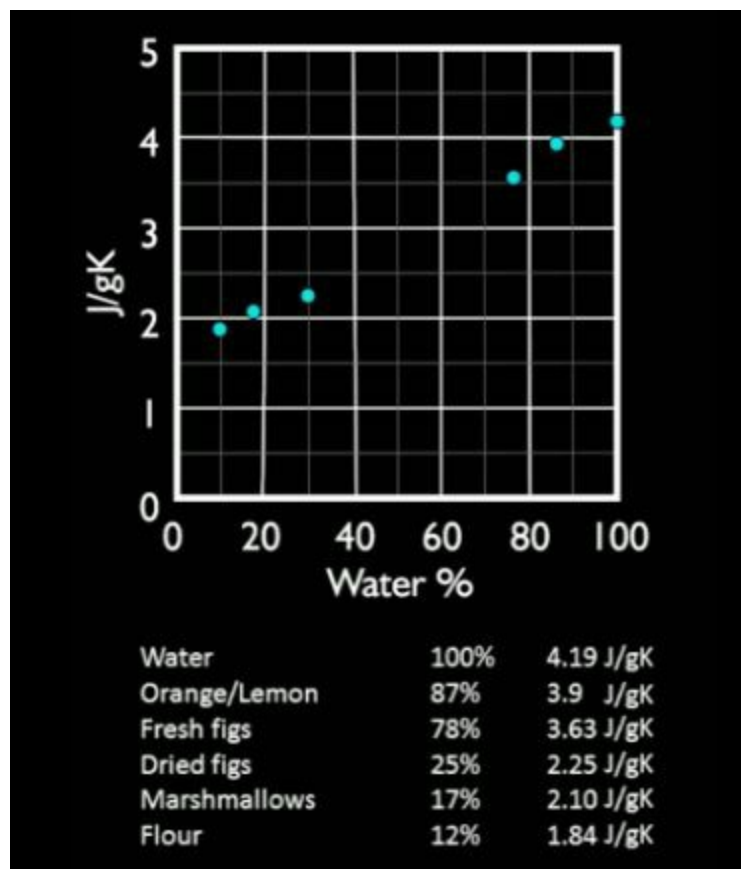


Figure 2.9 The specific heat of a food is often related to its water content.

2.6 Specific Heat

2.6.1 Burning a Hamburger

Many of us are interested in the calorie content of food. When we go to the supermarket, or when we eat food, we often look at the nutrition label to see how many calories it contains. It turns out there is a surprising connection between the caloric content of a food and its specific heat.

So far we have talked about how much heat it takes to cook a given amount of food. We did this by discussing how much energy was released when burning some fuel, say wood. But you don't have to burn wood. You can burn anything you'd like. In particular, you could imagine just burning your food.

Imagine you took a hamburger and instead of burning wood to make heat, you burn the hamburger. A reasonable question then is, how much energy would be liberated from burning a hamburger?

We can actually do this experiment in a rather simple way: We can take a jar with a well defined amount of water in it, perhaps a liter of water. We can light a hamburger on fire, place it under the water jar, and measure how much the temperature of the water increases (fig. 2.10).

Using the equation of the week, $Q = mc_p \Delta T$ and plugging in the mass of the water, the specific heat of water, and the measured temperature difference, we could then calculate the amount of heat that was released by the food when you burned it.



Figure 2.10 The caloric content of a hamburger can be estimated by burning a hamburger below a jar of water and measuring the resulting temperature increase.

2.6.2 What is a Calorie?

With this simple thought experiment as background, let's turn to what a calorie actually is. The definition of a dietary calorie, i.e. the type of calorie you see on food labels is:

The energy it takes to heat up one kilogram of water by one degree Celsius.

This is essentially the same as specific heat. In fact, we can use the

equation $Q = mc_p \Delta T$ to relate the definition of a dietary calorie to joules. To do this, we simply take the mass of one liter of water, which is a kilogram, we multiply by c_p , which is $4.18 \text{ J/g}^\circ\text{C}$, and then we multiply by one degree Celsius:

$$Q = mc_p \Delta T = (1000 \text{ g}) \cdot (4.18 \text{ J/g}^\circ\text{C}) \cdot (1^\circ\text{C}) = 4180 \text{ J}$$

We find that 1 dietary calorie is 4,180 joules, or 4.18 kJ. Dietary calories are typically written with a capital C, i.e. Calories. This is a way to distinguish them from another type of calorie known as a gram calorie. Gram calories are not capitalized, and denote the energy it takes to heat up one gram of water by one degree Celsius, instead of a kilogram. The energy content reported on nutrition labels is always given as Calories, and this is usually the unit we will be interested in for the purposes of this class.

The relationship between Calories, calories, and joules is as follows:

$$1 \text{ Cal} = 1000 \text{ cal} = 4.18 \text{ kJ}$$

2.6.3 Bomb Calorimeter: A Precise Way to Measure Calorie Content

When food scientists measure the calorie content of different foods, for example in order to make the nutrition label that you usually find on packaged foods, they actually use an apparatus that builds on the same principle as the water jar contraption we just discussed. These apparatuses are called bomb calorimeters (fig. 2.11). They have a little hole in which you put your food, the food gets burned, some known mass of water is heated up, and the calorimeter measures the temperature increase very precisely.

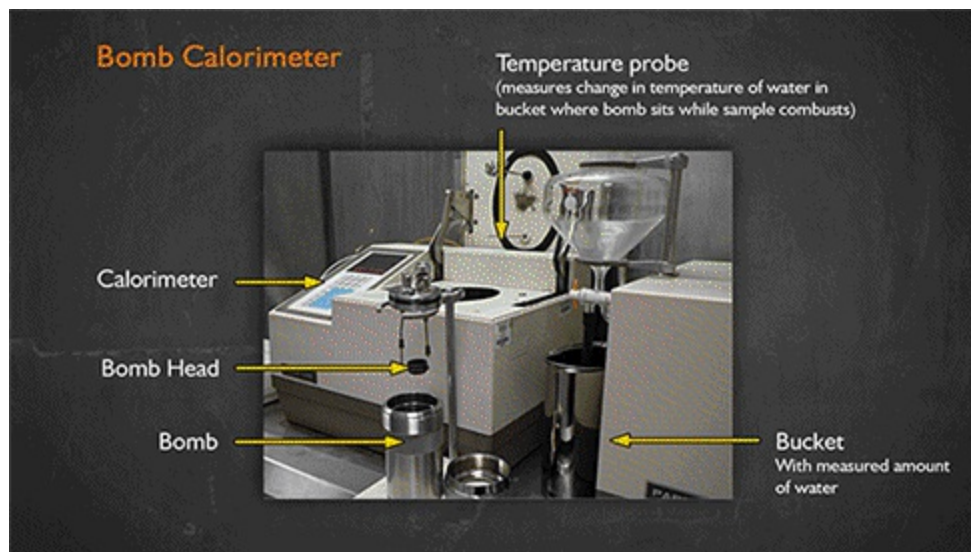


Figure 2.11 A Bomb calorimeter can measure the calorie content of foods very accurately. A small food sample is placed in a cup on the “bomb head”, and placed inside the combustion chamber, aka the “bomb”, which is then sealed tightly. The entire combustion chamber is then immersed in a bucket with a pre-measured amount of water. As the food sample combusts, the temperature probe measures the change in temperature of the water, and automatically outputs the calorie content on the display. The instrument is highly insulated so that no heat from the food sample is lost to the surroundings.

The one difference between a bomb calorimeter and the water jar contraption is that the bomb calorimeter is highly insulated. None of the heat from burning the food is lost. It all goes into heating the water. Hence, the calorimeter gives a much more accurate measurement of how much energy the food actually contains, than if you had just burned your hamburger and done the experiment yourself.

2.6.4 The 4-4-9 Rule

A bomb calorimeter is ultimately the most precise way of measuring the calorie content of foods. But there happens to be another, much easier, way of estimating the calorie content which is very useful. This is a simple rule of thumb that is usually referred to as the 4-4-9 rule. It goes like this: Food, as you know, is composed of three main ingredients, carbohydrates, proteins, and fats. It turns out that the calorie content for both carbohydrates and proteins is about 4 Calories per gram. The calorie content for fats is about 9 Calories per gram. Hence the 4-4-9 rule (fig. 2.12).

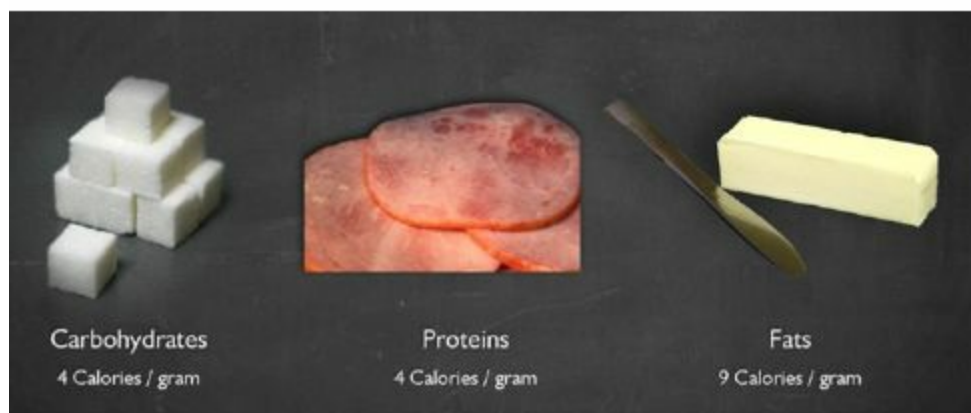


Figure 2.12 The 4-4-9 rule describes the energy density of the three main food components: carbohydrates and proteins have 4 Cal/g, and fats have 9 Cal/g.

The consequence of this is that if a food label says that it has a certain number of grams of proteins, carbohydrates, and fats in a serving, you can, from these three numbers alone, calculate the calorie content of the food. If you go into your pantry and look at the food labels, you will discover that this works extremely well. And if you find instances where the number of Calories reported disagrees with this calculation, we wouldn't blame you if you distrust the label...

As an example, look at the nutrition label from the Nestle Toll House chocolate chip cookies below (fig. 2.13). One serving of Nestle Toll House chocolate chip cookies has 4 grams of protein, 49 grams of carbohydrate, and 19 grams of fat.

Nutrition Facts	
Serving Size 1 cookie (78.0 g)	
Amount Per Serving	
Calories 370	Calories from Fat 171
	% Daily Value*
Total Fat 19.0g	29%
Saturated Fat 9.0g	45%
Cholesterol 20mg	7%
Sodium 340mg	14%
Total Carbohydrates 49.0g	16%
Dietary Fiber 2.0g	8%
Sugars 28.0g	
Protein 4.0g	
* Based on a 2000 calorie diet	

Figure 2.13 Nutrition label of Nestle Toll House chocolate chip cookies.

If we want to calculate the calorie content in one serving, we need to multiply the grams of protein by 4, the grams of carbohydrates by 4, and grams of fat by 9. When we add these up, we find that the calorie content of a cookie is 378 Calories, which is very close to the 370 Calories reported on the label.

Total calorie content of a serving:

$$(4 \text{ g}) \cdot (4 \text{ Cal/g}) + (49 \text{ g}) \cdot (4 \text{ Cal/g}) + (19 \text{ g}) \cdot (9 \text{ Cal/g}) = 378 \text{ Cal}$$

2.7 Molecular Origins of the 4-4-9 Rule

2.7.1 Digesting Sugar - The Chemical Reaction

It is really very curious. Carbohydrates and proteins have a general calorie content of 4 Cal/g. And fats have a general calorie content of 9 Cal/g. Why is that? After all, there is a large number of different types of carbohydrates, proteins, and fats. You would have thought, at least initially, that there must be some variation of calorie contents.

To answer this question, we need to introduce a little bit of chemistry. Of course, chemistry is very important for cooking. All of cooking is the transformations of the chemicals in food from one form to another. So this will also serve as an initial example of how to think quantitatively about chemical reactions.

Let's start by looking at the chemical structure of a sugar molecule. The chemical name for sugar is sucrose, and its structure is depicted in Figure 2.14.

Every blue dot represents a carbon atom. By counting all of the atoms we find that there are 12 carbons, 11 oxygens, and 22 hydrogens. In other words, the molecular formula of sucrose is $C_{12}O_{11}H_{22}$. The bonds between atoms are colored red, purple, light blue, and green. The red bonds are carbon-carbon bonds, and there are 10 of those. Similarly, there are 8 purple oxygen-hydrogen bonds, 14 blue carbon-hydrogen bonds, and 14 green carbon-oxygen bonds.

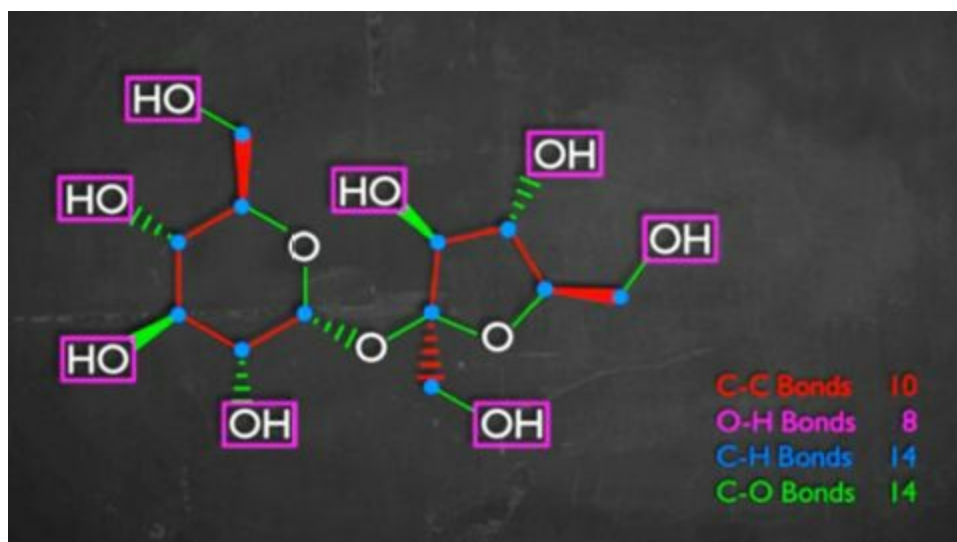


Figure 2.14 Chemical structure of a sucrose molecule. Bonds of the same type have the same color.

When you eat sugar, you are actually eating lots of these molecules. Your body then digests the molecules, which means it breaks them into pieces and converts each molecule to carbon dioxide and water. In order for this to happen you also need oxygen from the air. Expressed in words rather than chemical formulas, the reaction looks like this:



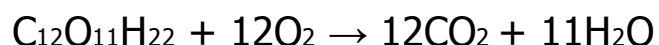
If we want to understand how much energy your body gains when you eat sugar, we have to think about the digestion process in two steps. First we have to ask, how much energy is released when the sucrose and oxygen molecules break apart? And then we have to ask, how much energy does it take to reform the molecules of carbon dioxide and water?

Before we can proceed to calculate the energies however, we need to know how many carbon dioxide and water molecules can be made from one sucrose molecule. This can be figured out by using a principle called stoichiometric balance. It tells us that if we start out with a molecule that contains 10 carbon atoms, then the molecule(s) we end up with after the chemical reaction takes place will also have 10 carbon atoms. In other words, you cannot change the number or type of molecules on either side of a reaction.

In this case, since sucrose has 12 carbon atoms, there will still be 12 carbon atoms after digestion. There is no way around it. The carbon atoms cannot

go anywhere else. Since water (H₂O) contains no carbons, the only way to end up with carbons after the reaction is done is by making carbon dioxide (CO₂). Because of this, we know that we must make 12 CO₂ molecules. Similarly, since the sucrose molecule had 22 hydrogens in it, we know that we must end up with 11 H₂O molecules because there are no hydrogens in carbon dioxide. So now we know that one sucrose molecule is broken down into 12 CO₂ and 11 H₂O.

But we still have not considered the oxygens. In the final product we have 24 oxygens from CO₂ and 11 from H₂O, ie 35 total. Since sucrose only has 11 oxygens, we are lacking 24 oxygens on the side of the reactants. This corresponds to 12 molecules of oxygen (O₂). We now have a chemically balanced equation, telling us that one molecule of sucrose and 12 molecules of oxygen result in 12 carbon dioxide and 11 water molecules:



2.7.2 The Calorie Content of Sugar -Breaking and Forming Bonds

Now let's return to our two questions: How much energy is released when sucrose and oxygen molecules break apart? And how much energy does it take to reform carbon dioxide and water?

In order to answer these questions, we have to introduce the idea of chemical bonds. Chemical bonds, of course, themselves contain energy, and this is because the molecules in the substance attract each other with some energy of interaction. The amount of energy a bond contains changes depending on the type of interaction.

All of the bonds in the sucrose molecule are covalent bonds. They are the strongest type of bond we will discuss in this course, and have relatively high energies that are fairly similar to each other. Below is a list of the different energies of the different bonds.

$$\text{C} - \text{C} = 346 \text{ kJ/mol}$$

$$\text{C} - \text{H} = 411 \text{ kJ/mol}$$

$$\text{O} - \text{H} = 459 \text{ kJ/mol}$$

$$\text{C} - \text{O} = 358 \text{ kJ/mol}$$

If we want to find out how much energy is stored in the sucrose molecule, we have to calculate the total energy stored in all the bonds. According to the calculations below, this equals 17,898 kJ/mol.

$$\text{C} - \text{C} = (346 \text{ kJ/mol}) \cdot 10 \text{ bonds} = 3460 \text{ kJ/mol}$$

$$\text{C} - \text{H} = (411 \text{ kJ/mol}) \cdot 14 \text{ bonds} = 5754 \text{ kJ/mol}$$

$$\text{O} - \text{H} = (459 \text{ kJ/mol}) \cdot 8 \text{ bonds} = 3672 \text{ kJ/mol}$$

$$\text{C} - \text{O} = (358 \text{ kJ/mol}) \cdot 14 \text{ bonds} = 5012 \text{ kJ/mol}$$

$$\hline = 17898 \text{ kJ/mol}$$

To this we have to add the energy stored in the oxygen molecules. There are 12 oxygens, and it turns out that breaking one oxygen-oxygen bond

releases 485 kilojoules per mole. Hence the total energy from oxygen is:

$$\text{O} = \text{O} = (485 \text{ kJ/mol}) \cdot 12 \text{ bonds} = 5820 \text{ kJ/mol}$$

Next let's compute the energy for reformation. A carbon dioxide molecule contains carbon-oxygen double bonds and there are 24 of them because there are 12 CO₂ molecules with two double bonds per carbon. A water molecule contains 2 oxygen-hydrogen bonds, each with an energy of 459 kJ/mol. So in order to form these molecules we need the following amounts of energy:

$$\text{C} = \text{O} = (803 \text{ kJ/mol}) \cdot 24 \text{ bonds} = 19272 \text{ kJ/mol}$$

$$\text{O} - \text{H} = (459 \text{ kJ/mol}) \cdot 22 \text{ bonds} = 10098 \text{ kJ/mol}$$

By taking the energy gained from breaking apart sucrose and oxygen and subtracting the energy that is needed when forming carbon dioxide and water, we find that the total energy from the reaction is:

$$17898 \text{ kJ/mol} + 5820 \text{ kJ/mol} - 19272 \text{ kJ/mol} - 10098 \text{ kJ/mol} = 5652 \text{ kJ/mol}$$

$$= 5652 \text{ kJ/mol}$$

This is how much energy your body gains when you eat a mole of sugar. It still does not sound like 4 Cal/gram, so let's convert the unit kJ/mol to Cal/gram so we can compare the two numbers. By looking up that the weight of sucrose is 342 grams/mol, and using the fact that one dietary calorie is 4.19 kJ, we find that this corresponds to 3.95 Cal/gram

$$(5652 \text{ kJ/mol}) \cdot \left(\frac{1 \text{ mol}}{342 \text{ g}} \right) \cdot \left(\frac{1 \text{ Cal}}{4.18 \text{ kJ}} \right) = 3.95 \text{ Cal/g}$$

This is indeed very close to 4 Calories per gram, which, of course, is exactly the amount of energy the 4-4-9 rule predicts sugar, a carbohydrate, should have.

2.8 Latent Heat

2.8.1 Adding Heat at a Phase Transition

One of Dave Arnold's demos shows what happens to the temperature of a drink as it is shaken in a cocktail shaker. The demo is done as follows: Dave starts out with two beakers, one with water at room temperature, and one with ice. He measures the temperature of the ice to be 0°C . He then adds the water and ice together in a cocktail shaker with a thermometer inside, and shakes hard for about 30-60 seconds. Remarkably, as he does this, the temperature of the ice water mix goes down to below 0°C , usually between -5°C to -8°C , i.e. below the freezing point of water.

Think about this for a moment. It makes no sense. Why would a mixture of two things end up having a temperature that is below the temperature of either of the two things before mixing?

The reason this happens is one additional idea that is important for understanding how adding heat influences a material. This idea goes under the name of latent heat — latent heat of fusion and latent heat of evaporation.

Imagine that you have some material, let's just say it is water. You start out with the water as ice, at a temperature that is well below the freezing point of water, perhaps minus 20°C . You want to start adding heat to the ice and you want to track what happens to the temperature as you do this.

Ice, like all materials, has a specific heat. If you were to plot heat as a function of temperature, it would go up from minus 20 degrees with the slope depending on the specific heat (fig. 2.15). It would continue to go up until you hit the freezing point of water, at which point, it would change phase. Since the specific heat of water is different from the specific heat of ice, the slope would change as the phase changes.

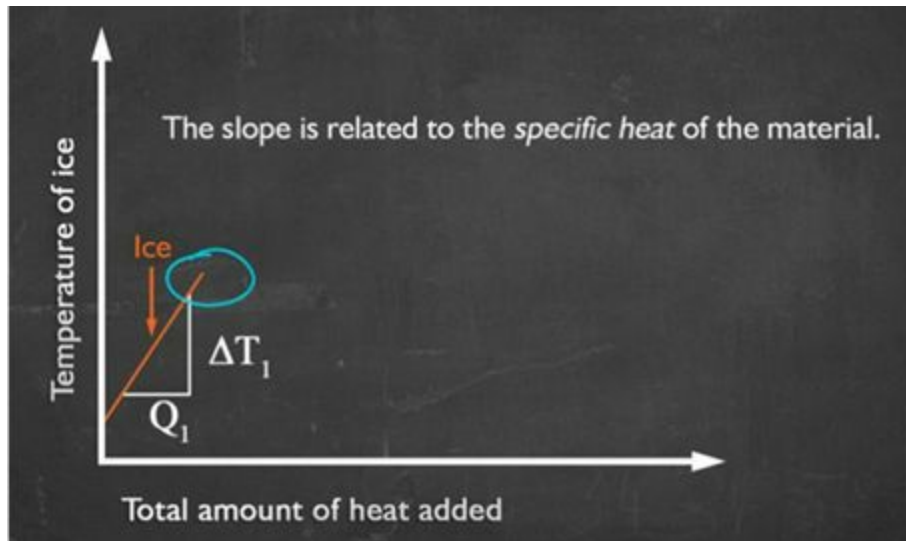


Figure 2.15 Graph showing temperature as a function of heat for a piece of ice. As heat is added to the ice, the temperature increases until it reaches 0°C (blue circle).

However, before the phase change actually happens at 0°C , there will be a plateau region where you will keep adding heat without the temperature increasing (fig. 2.16). It will stay at 0°C until you have put in a certain amount of heat, and only after this, will the solid ice become a liquid and the temperature will start to go up again as you add more heat.

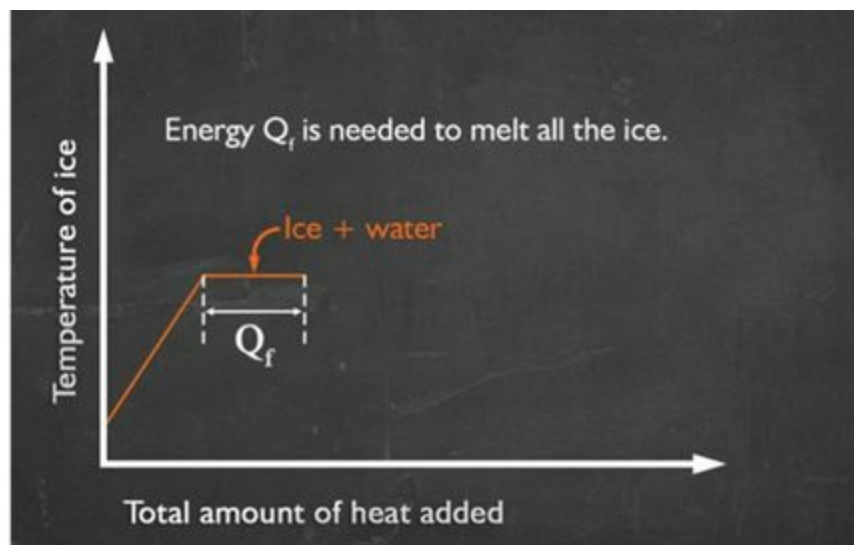


Figure 2.16 At the freezing point, a certain amount of heat has to be added for the solid-to-liquid transition to occur. This occurs without an accompanying change in temperature and is called the latent heat of fusion.

The extra heat that you have to add to cause the solid to become a liquid is called the latent heat of fusion. It is essentially the extra heat that you have to add to change the molecular structure of the material from that of a solid to that of a liquid. We will discuss this in more detail in the next chapter on

molecular interactions.

Returning to the plot and our piece of ice that has now turned to water, this behavior continues as we add more heat. If we continue to heat up the water, the temperature will increase from 0°C until it gets to 100°C degrees. Again, the slope of the line will depend on the specific heat of water. At 100°C you know that the liquid water will turn to gas, but, again, there is some amount of heat that you have to add to the water in order for that to occur. You add heat and the temperature stays at 100°C. You add more heat, and the temperature still stays at 100°C. Finally, you have added enough heat and the liquid is now a gas and the temperature of the gas will start increasing again (fig 2.17).

The heat you have to add to cause liquid water to change into gaseous water, is called the latent heat of evaporation.

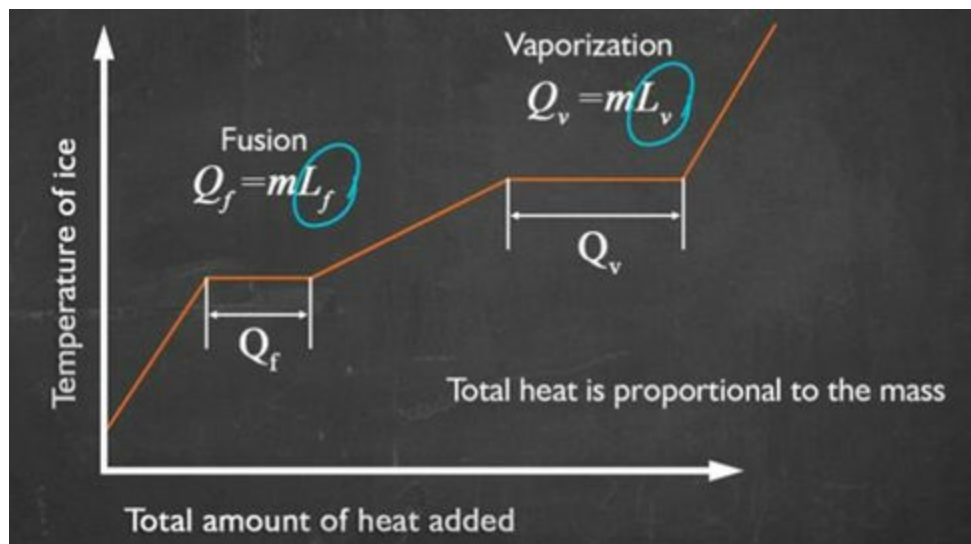


Figure 2.17 Once the ice has melted, the temperature of the water increases until it reaches the boiling point. Again, some amount of heat needs to be added for the liquid-to-gas transition to occur. This is called the latent heat of vaporization.

These numbers, the latent heat of fusion and the latent heat of evaporation, are actually rather large. The latent heat of fusion for water is 335 joules per gram. The latent heat of evaporation is 2,260 joules per gram. The fact that they are so large is one reason that explains water's peculiar ability to act very efficiently both as a cooling agent and as a heating agent. They are also at the heart of the reason why the ice water mixture in Dave Arnold's demo went below the freezing point, and additionally they explain several other phenomena, as we will see below.

2.8.2 The Equation for Latent Heat

The behavior we just explained can be described with a version of the equation of the week that is reserved for phase transitions, i.e. when a material changes between being a solid/liquid and between being a liquid/gas. This is the equation:

$$Q_{v,f} = L_{v,f} \cdot m$$

In this equation, Q , is the amount of heat we have to add for the phase transition to occur. That is to say, this is the heat we have to add without detecting a corresponding increase in temperature. $L_{v,f}$ is the latent heat of fusion or evaporation depending on whether the material is changing between liquid and solid (L_f) or between liquid and gas (L_v). The mass, m , is the mass of the material that is undergoing the phase change.

2.8.3 Steam Burns: Latent Heat of Evaporation

Hopefully you have not had this experience, but even if not, you probably know that the steam above a boiling pot of water is very, very hot. So hot, that if you put your hand in it, you could get a very nasty burn. What is so peculiar about this is that if you were to put your hand in the air of a hot oven, you probably would not get a burn, even if the air in the oven is much hotter than the temperature of the steam. The question is, why? And the answer, of course, is related to the latent heat of evaporation.

Let's imagine that you put your hand in steam, and that 10 grams of steam happen to condense on your hand. In condensing on your hand, the water is going to release heat. This makes sense since it is the reverse process of what we learned about above, in which we had to add heat for the water to go from a liquid to a gas. When the water condenses backwards from a gas to liquid, it will release heat instead. So how much heat will it release? Let's find out.

If the latent heat of evaporation is 2,260 J/g, and if the mass of water is 10 grams, then the total energy needed to transform the liquid to gas corresponds to 22,600 joules according to the calculation below.

$$Q_v = L_v \cdot m = (2260 \text{ J/g}) \cdot (10 \text{ g}) = 22600 \text{ J}$$

So this is how much energy we have just dumped into your poor hand. The question now is, how much will the hand heat up from this energy dump? Again, we can use the equation of the week. We know what Q is 22,600J. This is how much heat was released from the condensation of the steam onto your hand. We can assume that your hand weighs, perhaps, 100 grams. As for the specific heat, let's say that your hand is the most similar to beef, which we happen already to know the specific heat of. The specific heat of beef is about 3.18 J/gK (fig. 2.8). Solving for ΔT in the equation of the week, we then have:

$$\Delta T = \frac{Q}{mc_p} = \frac{22600 \text{ J}}{(100 \text{ g}) \cdot (3.18 \text{ J/g}^\circ\text{C})} = 7^\circ\text{C}$$

So the temperature of your hand would go up by 7°C . This is a lot if you consider that in order for this temperature to be distributed over your entire hand, it will initially have to heat up the thin surface layer of your hand to a much hotter temperature. We will discuss this aspect of heat in Chapter 6.

2.8.4 Ice Water: Latent Heat of Fusion

Next, let's think about the latent heat of fusion. The principles are the same as with latent heat of evaporation; in order to cause ice to turn into water, heat has to be added. What this means, is that if you put ice into water, you have to suck heat out of the water in order to make the ice melt. As the ice is taking up heat from the water, the temperature of the water will drop. Just as with the steam burn example above, we can calculate how much the temperature of the water will drop using our equations.

For the sake of argument, imagine that you have a cup with 10 grams of ice, a similar mass to the steam above. Since the latent heat of fusion is 334 J/g and you want to melt 10 grams of ice, this requires 3,340 joules according to the calculation above.

$$Q_f = L_f \cdot m = (334 \text{ J/g}) \cdot (10 \text{ g}) = 3340 \text{ J}$$

This is how much energy is required to melt the ice, and hence this is the amount of energy that is going to be taken out of the water causing a temperature drop. How much would the temperature drop?

Let's assume that we have a glass of water, which is about 800 grams. Using the equation of the week, and plugging in the value for Q that we just calculated, 3,340 J, and the specific heat of water, 4.18 J/gK, we can calculate ΔT :

$$\Delta T = \frac{Q}{mc_p} = \frac{3340 \text{ J}}{(800 \text{ g}) \cdot (4.18 \text{ J/g}^\circ\text{C})} = 1^\circ\text{C}$$

So 10 grams of ice drops the temperature of 800 grams of water by about 1°C. If we instead had used 100 grams of ice, then it would have dropped by about 10°C, at which point it is starting to get significant. This explains why, if you dump a lot of ice in your water, it can cool it quite a bit. And it also explains what happened in Dave Arnold's peculiar demo at the beginning of this section. This is something to think about the next time you shake a cocktail!

2.8.5 Summary

In summary, the latent heat of evaporation and the latent heat of fusion describe the fact that extra heat is required to cause a phase transition in a material. Understanding what they are is important for understanding how a material behaves when heat is applied, and we will talk more about the underlying molecular reasons in the next chapter. But the latent heat of fusion and evaporation are also important practically when cooking. We have shown you two examples here, and we will see more of them as we continue in this course.

CHAPTER 3

Phase Transitions

TABLE OF CONTENTS: 3

3.1 Introduction to Phase Transitions

[3.1.1 Phase Transitions of Eggs vs. Water](#)

[3.1.2 One-dimensional Phase Diagrams of Simple Materials: Nitrogen, Ethanol, Carbon Dioxide](#)

3.2 Phase Diagrams

[3.2.1 Pressure and Phase Transitions](#)

[3.2.2 Two-dimensional Phase Diagrams](#)

[3.2.3 How Chefs Manipulate Phase Diagrams](#)

[3.2.4 One-dimensional Phase Diagrams Revisited: Carbon dioxide](#)

3.3 Equation of the Week

[3.3.1 Molecular Basis of Phase Transitions](#)

[3.3.2 A Competition Between Energy and Entropy](#)

[3.3.3 A Competition Between Sticking & Jiggling or Interaction Energy & Thermal Energy](#)

[3.3.4 Molecular Bonds](#)

3.4 The Science of Rotovaps

[3.4.1 A Molecular View](#)

[3.4.2 Manipulating Pressure](#)

[3.4.3. The Different Parts of a Rotovap](#)

[3.4.4. Distilling Alcohol](#)

3.5 Phase Transitions of Fats

[3.5.1 Saturated and Unsaturated Fats](#)

[3.5.2 Chain length](#)

3.6 The Science of Supercooling

[3.6.1 Nucleation](#)

[3.6.2 Crystal Growth](#)

[3.6.3 Homogeneous and Heterogeneous Crystallization](#)

3.7 Solubility

[3.7.1 Solubility and Phase Transitions](#)

[3.7.2 The Equation of the Week Applied to Solubility](#)

[3.7.3 Solubility and Candy Making](#)

3.8 Phase Transitions of Solutions

[3.8.1 Freezing Point Depression and Ice Cream](#)

[3.8.2 Boiling Point Elevation and Candy Making](#)

3.9 How to Derive the Equation of the Week

CHAPTER 3

3.1 Introduction to Phase Transitions

We began this class with the definition of cooking from the Oxford English Dictionary. The definition said that cooking was the transition of foods under the application of heat, and we readily recast this definition as a plot. The plot consisted of a horizontal line for temperature, and somewhere along this line we drew a vertical line, indicating the critical temperature where the food on the diagram cooked. We said that below the critical temperature, the food is uncooked, and above it the food is cooked. In the case of an egg, we also discussed that there are several critical temperatures. In fact, if you are trying to control the texture of an egg, you have lots of choices. If you like slightly runny eggs, you want temperatures of about 60-61°C, thoroughly cooked eggs occur at 68-70°C, and the perfect egg happens around 64°C. As we will see throughout this course, the different temperatures correspond to different molecular transitions in the food. For example, with respect to an egg, at 63°C a protein named ovotransferrin unfolds, and this causes the change in texture that you observe when you go through that temperature boundary. As you increase the temperature, there are more and more transitions, each corresponding to the unfolding of different proteins.

Different foods have different critical temperatures. Whether you are trying to cook a turkey, or a pie, or cake, there are many different types of phase transitions taking place that cause the food to taste and feel different in your mouth when cooked to different temperatures. One of the goals of this class is to explain what those transitions are, why they occur, and how to control them.

3.1.1 Phase Transitions of Eggs vs. Water

In order to start our investigation of phase transitions in food, we will first study materials that are slightly simpler than eggs, turkey, or pie. While these are the foods that we ultimately would like to know more about, they are a bit complicated in their physical behavior, and it makes sense to look at some less complex materials first.

A simple material that is highly relevant, not only to cooking, but to life in general, is water. We are mainly composed of water. The primary component of food is water. It is perhaps the most ubiquitous substance around us in our daily lives, and it also plays an important role in cooking – when you cook a hard-boiled egg, a typical way to do it is to put it in hot water. And since food is composed of water, when you heat up the food, you are also heating up the water. For all of those reasons, the phase behavior of water is an important backdrop to this entire course. And if all of this were not enough, it also turns out to be a simple enough material to start comparing and contrasting different phase behaviors. So with that as an introduction, here is a phase diagram for water (Fig. 3.1).

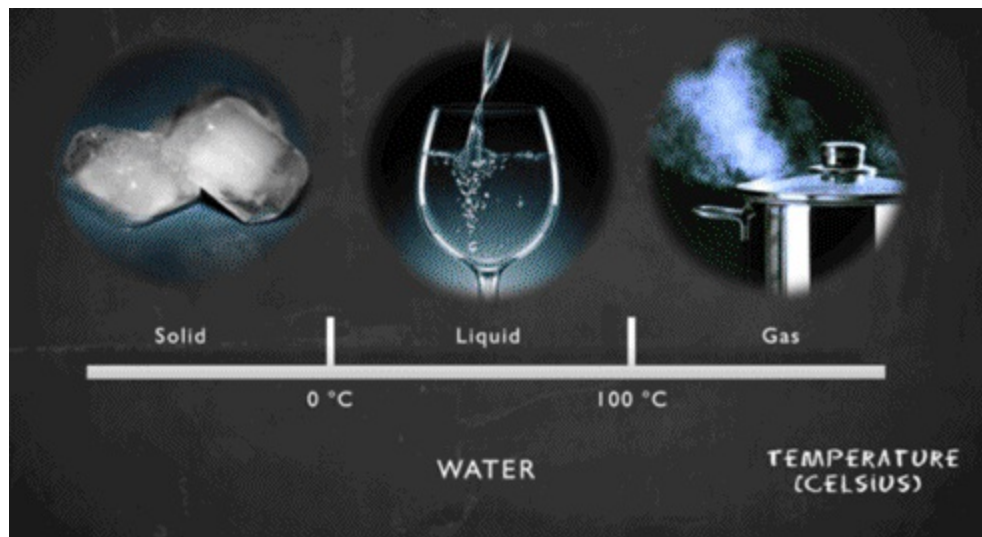


Figure 3.1 The phase diagram for water. Water melts at 0°C and boils at 100°C.

The purpose of Figure 3.1 is only to make you think about what you already know in the context of phase diagrams. Namely, there is a critical temperature, which is about 0°C, below which water is a solid. It's ice. And there is another critical temperature at 100°C, above which water transforms from a liquid to a gas. In between these two temperatures, water is a liquid.

Interestingly, when you compare the phase diagram of water to the phase diagram of an egg, they are reversed. Whereas water is a solid at low temperatures and turns into a gas when heated, an egg becomes a solid when heated. Moreover, eggs and water are also different in the sense that water will readily go back to a liquid after having been ice, whereas an egg, once cooked, will remain solid. There is no way to uncook an egg by changing the temperature. This is true for most foods. A cooked turkey, or pie, never reverts back to the uncooked state. If, by contrast, you place an egg in the freezer, it will also turn into a solid. It will feel cold when you take it out, but in every other way it will feel more or less like a hard-boiled egg. This egg, however, will return back to being a liquid at ambient temperatures. So there is something peculiar about the fact that heating the egg makes it become a solid. How can this be? How is it that the phase behavior of an egg, which is primarily composed of water, can be so different than the phase behavior of water itself? The reason, as we will see, is because of the special molecular transitions inside the egg, and we will discuss this in more detail later on.

First, let's look at a few more simple materials. As opposed to eggs, and most other foods, these are pure materials in the sense that they are composed of a single substance.

3.1.2 One-dimensional Phase Diagrams of Simple Materials: Nitrogen, Ethanol, Carbon Dioxide

The first material is nitrogen (Fig. 3.2). Though you may not be aware of this, nitrogen is an important aspect of your daily life, because it is the major component of air. It may not surprise you therefore to learn that at room temperature, nitrogen is a gas. You have to cool it quite a bit, to -195°C , in order to turn it into a liquid, and if you cool it a just a little more to about -210°C , then it becomes a solid. So in many ways, the phase behavior of nitrogen looks a lot like that of water. At high temperatures, it is a gas. At low temperatures, it is a solid. The difference is just that the critical temperatures are different, and that nitrogen becomes a liquid at much colder temperatures. The fact that it is so cold, allows it to cause very unusual phase transitions in food, and for this reason many chefs use it in their kitchens in a number of interesting ways.

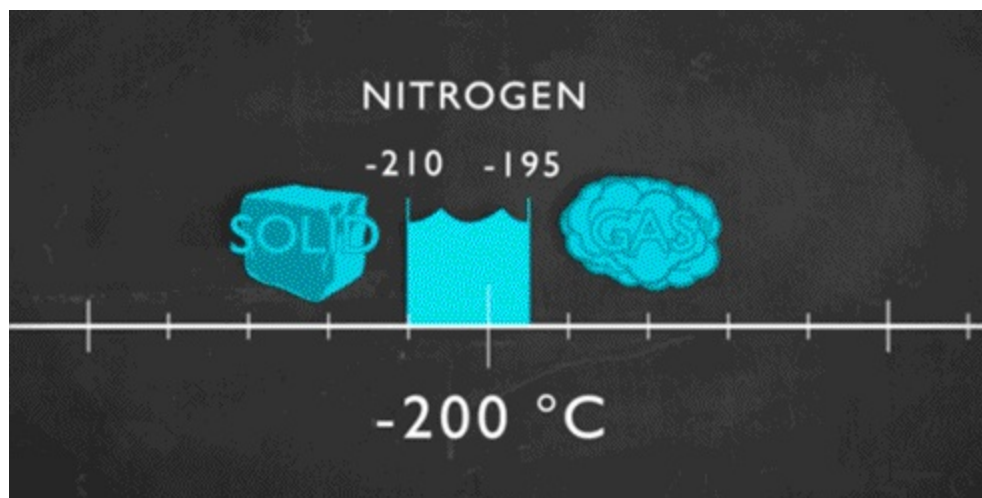


Figure 3.2 The phase diagram for liquid nitrogen. Nitrogen in liquid form is very cold and is often used by chefs and scientists as a cooling agent. It becomes a solid below -210°C and boils at -195°C .

Another simple material that is important for cooking is ethanol. It will not surprise you that ethanol is a liquid at room temperature, otherwise there would not be liquid ethanol in wine or other alcoholic beverages. The temperature at which ethanol transitions from being a liquid to a gas occurs at a slightly lower temperature than that of water, around 78°C (Fig. 3.3). If you are ever using wine to make sauces, this is the reason alcohol boils off more quickly from the sauce than water. In order to turn ethanol into a solid, you have to cool it more than what is needed for water, down to

about -114°C . Other than the different transition temperatures though, the general phase behavior of ethanol is exactly like that of water and nitrogen. And, in particular, it looks nothing like that of an egg. In fact, it seems like the peculiar substance is not water, nitrogen, or ethanol. It is the egg.

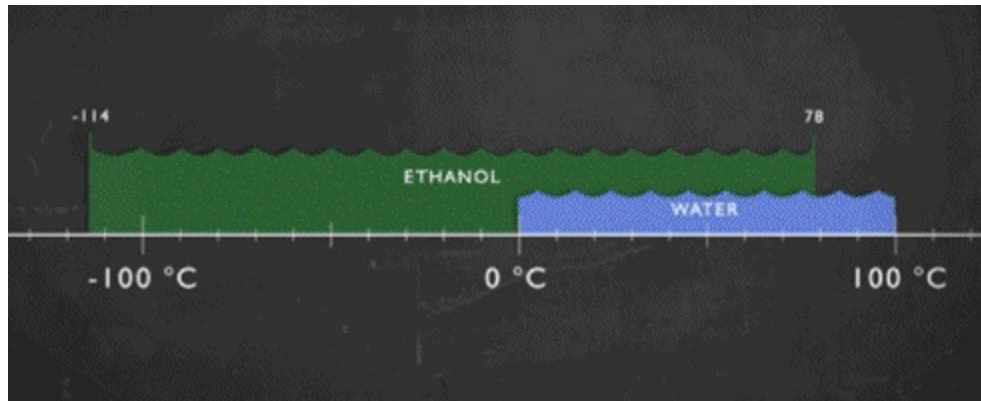


Figure 3.3 The phase diagram for ethanol as compared to water. Ethanol is a liquid over a larger temperature range than water. The lower boiling point of ethanol compared to water can be utilized to separate ethanol from ethanol-water mixtures.

An example of a simple material that has a different phase diagram from the ones we have seen above is carbon dioxide. You know that carbon dioxide is a gas at room temperature. Every day in the newspaper, there seems to be another article about the ever-increasing concentration of carbon dioxide in the atmosphere. The curious fact about carbon dioxide is that at standard pressure, it has no liquid phase at all. It goes straight from being a gas to a solid, and this happens around -80°C (Fig. 3.4). So the phase diagram of carbon dioxide appears strikingly different from that of water. Namely, at high temperatures it is a gas and at low temperatures it is a solid, but there is no liquid phase in between.

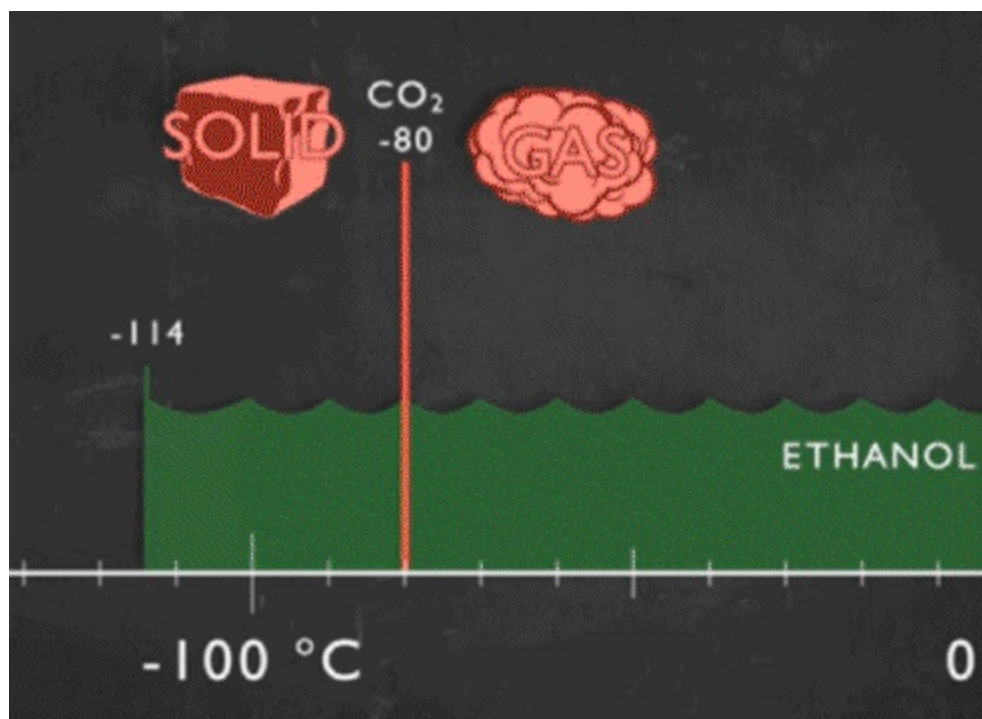


Figure 3.4 The phase diagram of carbon dioxide. At standard pressure, carbon dioxide has no liquid phase. It transitions from a solid to a gas at -80°C .

Video 3.1 shows how the phase diagrams of the materials we have seen so far relate to each other. All of these phase diagrams, including the one for the egg, pose a very important question about physics, which is, why is it that the different materials have transitions at the places that they do? Why is it that water transitions from a liquid to a gas at 100°C ? Why does it transition from a liquid to a solid at 0°C ? Why do these numbers change for nitrogen? What we would like to do is to develop an understanding of why materials have the phase behaviors they do. And the reason for this is that this will help us understand the physics, not only of these simple materials, but ultimately of the materials that we cook with.

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[movie_1_phases_slide-11-13_1.mp4](#)

Video 3.1 The phase diagrams of water, nitrogen, ethanol and carbon dioxide as seen along one temperature axis.

3.2 Phase Diagrams

Up until this point, we have talked about the behavior of phases as a function of temperature. That is, we have talked about what happens if you heat a material or cool a material, and how it changes phases when you do that. But there are many ways to change phases in cooking other than playing with temperature. Another natural knob is pressure. Similar to temperature, you can cause the phase behavior of a material to change by changing the pressure.

3.2.1 Pressure and Phase Transitions

What exactly is pressure? Pressure is the effect of the air that surrounds us. We are so used to this force that is constantly squeezing in on us that we usually do not notice it, but it is actually pretty high. At sea level we say that the pressure is 1 atmosphere of pressure. If you go up to higher altitudes though, the pressure decreases. In fact, at about 16,000 feet, the air pressure decreases by a factor of about two. The reason for this is simply that there is less air around to squeeze on you (Fig. 3.5).



Figure 3.5 The pressure at high altitudes is lower than the pressure at sea level. Since pressure affects the phase behavior of materials, this turns out to be relevant for cooking in a number of ways. For example, water boiling at high altitudes will be at a temperature that is lower than the familiar 100°C , affecting any recipes involving boiling, such as making pasta etc.

Another way to illustrate pressure is with a balloon. The air inside a balloon is pushing outwards, and the air on the outside is pushing in. Both pressures are exerting forces on the balloon, and in order for it to stay inflated the pressure from the inside needs to be higher than the pressure on the outside. On first thought, balloons may not seem to be related to cooking at all, but it turns out that they are a great analogy when thinking about the physics of air bubbles or liquid droplets. We will return to them in Chapter 8 when discussing emulsions and foams, and again in Chapter 9 in the context of baking and leavening.

Pressure can be reported in many different units. A common unit is

atmospheric pressure, or atm, but you may also have encountered psi, bar, and torr. We will primarily use the international standard unit for this class, which is force per unit area. Force, of course, is measured in units of Newton, so the units of pressure end up being Newtons/m². This unit is so common that it has a special name, Pascals (Pa), after the philosopher Blaise Pascal. The pressure at sea level, 1 atm, corresponds to 105 Pa.

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

3.2.2 Two-dimensional Phase Diagrams

With this information as background, let's see how pressure affects the phase transitions of materials. You may already be familiar with the fact that cooking at high altitudes can be very challenging, and the reason for this is precisely the lower pressure. So let's start by looking at how the phase transitions of water, the most common ingredient in food, are altered at different pressures (Fig. 3.6). At 1 atm, we already know that water freezes at 0°C and boils at 100°C. If the pressure is increased to about 1.5 atm, it turns out that the solid-liquid transition still occurs at around 0°C, but the liquid-gas transition takes place at a higher temperature of about 112°C. In contrast, at lower pressures, say at 0.75 atm, we see a similar pattern: the liquid-solid transition temperature stays about the same, but the liquid-gas transition temperature decreases to about 92°C.

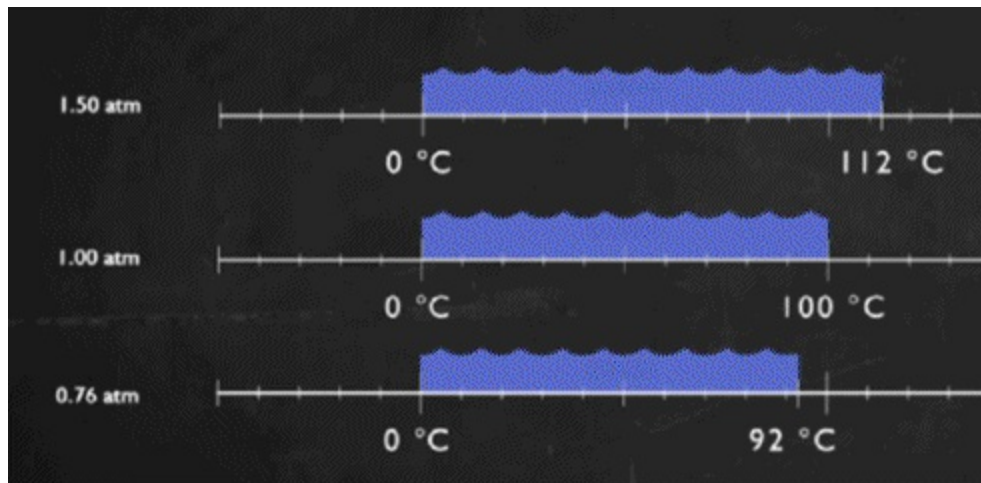


Figure 3.6 Pressure affects the phase behavior of all materials including that of water. At a standard pressure of 1.0 atm, water boils at 100°C. At pressures lower than 1.0 atm, it boils at lower temperatures, and at higher pressures it boils at higher temperatures.

We can start to organize the information above into a single diagram by introducing a y- and x-axis, with temperature on the x-axis and pressure is on the y-axis (Fig. 3.7).

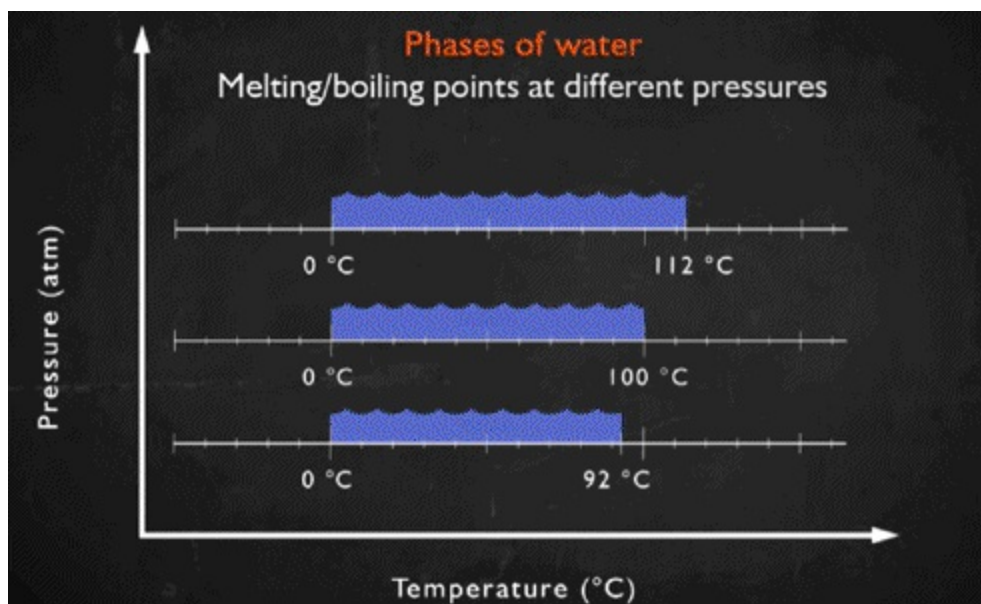


Figure 3.7 We can take the pressure dependence of phase transitions into account and create a two-dimensional phase diagram with temperature on the x-axis and pressure on the y-axis.

If we then go and figure out what the transition temperatures are at several other intermediate pressures as well, we can create what scientists refer to as a two-dimensional phase diagram. We simply connect the dots where the material changes from a solid to a liquid and from a liquid to a gas with lines, and we add labels to the different phases (Video 3.2). Note: Video 3.2 erroneously indicates that Standard Temperature and Pressure, usually referred to as “STP” by scientists, occurs at 100°C and 1 atm. In reality, STP occurs at 0°C and 1 atm, although in the context of cooking it is often convenient to think of “standard” to be occurring at room temperature, 25°C, and 1 atm.

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Video 3.2 Video illustrating the creation of a two-dimensional phase diagram of water, with temperature on the x-axis and pressure on the y-axis.

As you can see in Figure 3.8, there is a large region in the phase diagram where the material is a solid, a middle region where it is a liquid, and another large region where the material is a gas. The useful thing with this type of diagram, is that at any given temperature and pressure, you can find

out what the phase of the material is simply by reading off the diagram. So, for example, by looking at the phase diagram we can see that at room temperature, which is about 23°C , and standard pressure, 1 atm, water is a liquid.

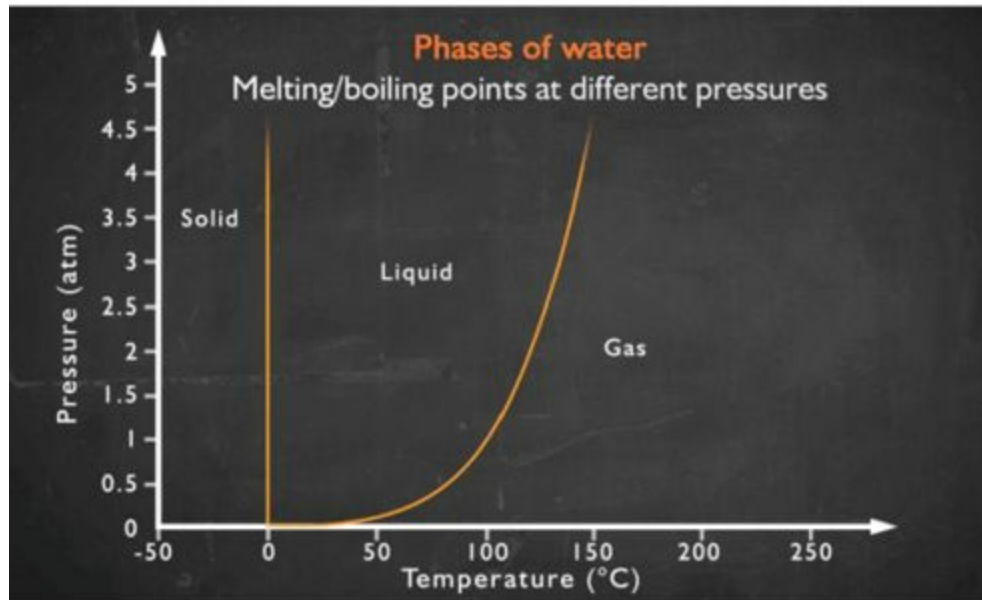


Figure 3.8 Two-dimensional phase diagram of water.

What if we wanted to use this plot as a way to cook the perfect egg, the challenges of which we have talked about at length in previous chapters. Recall that one of the problems with cooking perfect eggs is that at 1 atm, the boiling temperature of water is 100°C , and this is well above 64°C , which is the temperature that happens to result in perfect eggs. One possible solution that presents itself based on this plot, is to take the egg and go and climb a tall mountain. If the mountain is at exactly the right height, so that the pressure happens to correspond to a boiling point of 64°C , then you could boil your egg on top of the mountain and it would come out perfectly. By reading off the phase diagram we can find out that a 64°C boiling temperature occurs when the pressure is about one fourth of the atmospheric pressure, i.e. 25 kPa. So all we have to do is find a mountain where the pressure is 25 kPa. This, unfortunately, has one small caveat, which is the fact that even on the very top of Mount Everest, the pressure is as high as 34 kPa and the boiling point of water only decreases to 71°C . So we would have to find an even taller mountain than Mount Everest in order to cook the perfect egg, and this, of course, poses some challenges.

3.2.3 How Chefs Manipulate Phase Diagrams

Chefs, not wanting to climb mountains in order to cook perfect eggs, instead use various pieces of equipment to manipulate phase diagrams. One such piece of equipment is the pressure cooker (Fig. 3.9). Pressure cookers work by raising the pressure in the environment in which something is being cooked, and thus according to the phase diagram, cause the boiling point to increase. A typical pressure cooker will roughly double the atmospheric pressure, so that it ends up at about 2 atm. Reading off the diagram this corresponds to a temperature of about 120°C. So the water will boil at a higher temperature, and this, of course, accelerates the cooking time.

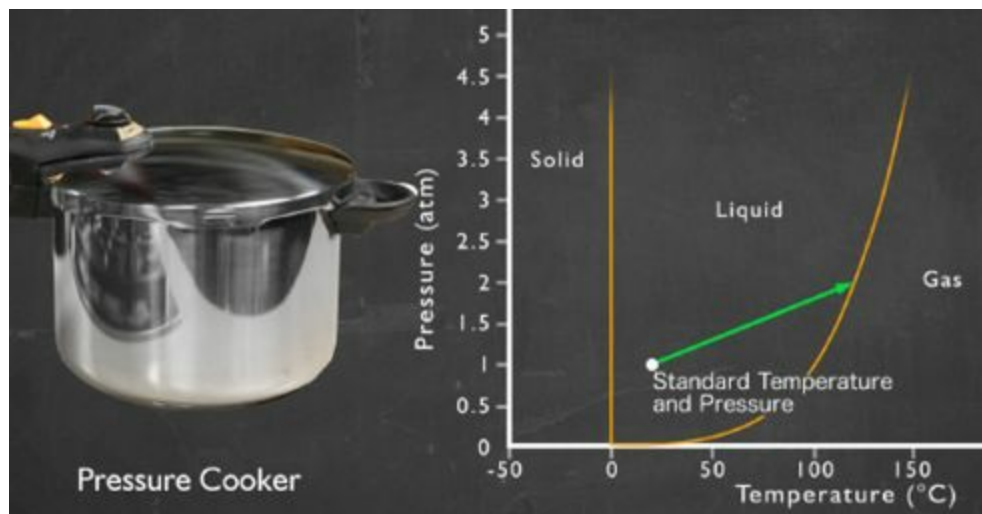


Figure 3.9 Phase diagram of water with an arrow indicating the effect of a pressure cooker. Since the pressure in a pressure cooker is higher than 1.0 atm, the temperature at boiling is higher, thus allowing for foods to be cooked faster.

As a way to admire the speed with which pressure cookers cook food, let's look at a recipe. Figure 3.10 shows a recipe for cooking potatoes in boiling water. Doing this the normal way takes a long time; you have to bring the water to a boil and then wait for the potatoes to cook – all in all the entire process probably takes about 15-20 minutes. On the other hand, according to this recipe, the potatoes are done in 6 minutes. The reason it is so accelerated is because the high pressure causes a higher boiling temperature, and this in turn causes the relevant phase transitions within the potato to be reached much more quickly.

6 medium potatoes
1 cup water

Place potatoes and water in pressure cooker. Cook on high pressure for 3 min. Let steam rise for 3 min. Quickly release pressure and open cooker.

Figure 3.10 Recipe for pressure cooked potatoes.

Another type of equipment that chefs commonly use to manipulate the phase transitions of food is the immersion heater (Fig. 3.11). This is what Dave Arnold, and many chefs with him, use to cook perfect eggs. The great advantage with immersion heaters is that they allow you to cook an egg, or any other piece of food, at a very specific temperature. They consist of a waterbath and a motor element, which carefully controls the temperature of the water to be whatever you want it to be. This is very powerful, because it allows you to sit wherever you want on the phase diagram of water and not be so dependent on its boiling point. You can just set the immersion heater to whichever temperature you want to reach for the food to be cooked perfectly, and then leave the food in the water bath for as long as you want. The food will not overcook, because the temperature will never get too high. So you can prepare your eggs or meat several hours in advance, and simply remove them when you are ready to eat.

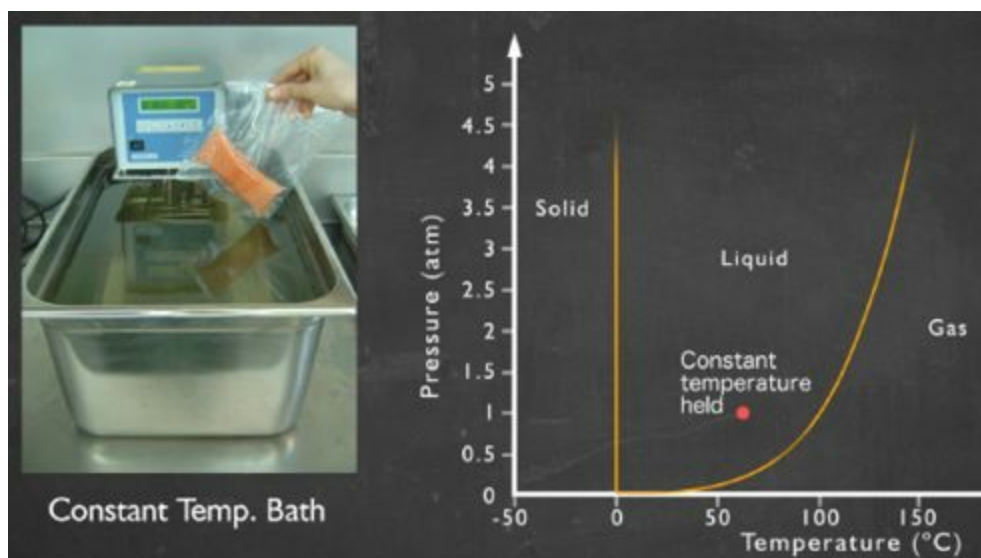


Figure 3.11 Phase diagram of water with a dot indicating the effect of a temperature controlled water bath. The pressure is not changed when cooking with this method. Rather, the temperature is held constant at a temperature lower than 100°C for long periods of time, allowing for foods to be cooked at

the precise temperature required.

The final piece of apparatus that chefs use in the context of phase transitions is the rotary evaporator. For short, it is usually referred to as a rotovap. Instead of raising the pressure the way pressure cookers do, rotovaps operate by lowering the pressure. A typical rotovap lowers the pressure by about 25% (Fig. 3.12). We will discuss the science of rotovaps in much more detail later on in this chapter, but the basic idea is that since the pressure is lower, the boiling points of materials go down. As a result, it actually takes longer for things to cook, but the great benefit with this approach is that the food cooks much more gently, and for that reason chefs tend to use rotovaps quite a lot, and often in very creative ways.

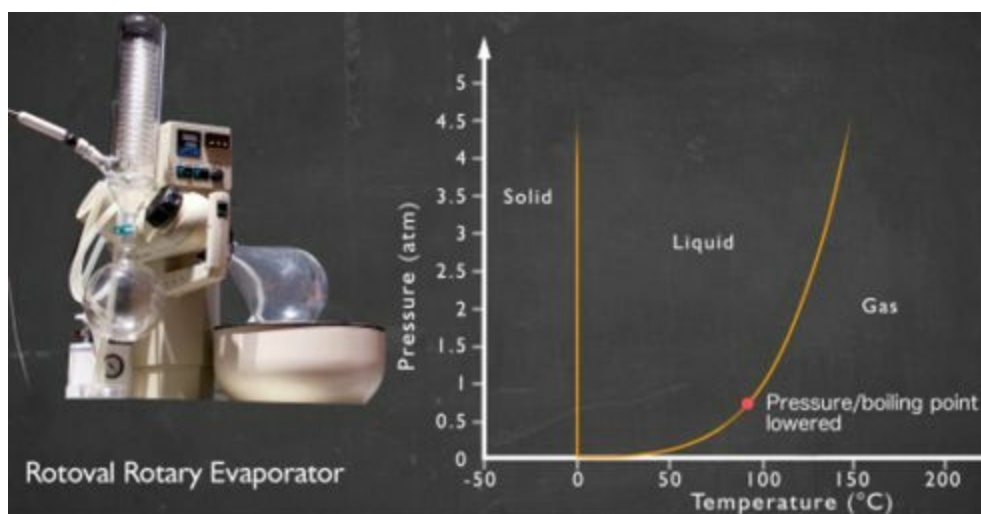


Figure 3.12 Phase diagram of water with an arrow indicating the effect of a rotovap. Since the pressure in a rotovap is lower than 1.0 atm, liquids will vaporize at lower temperatures.

3.2.4 One-dimensional Phase Diagrams Revisited: Carbon dioxide

Before ending this section, let's return to the phase diagrams of carbon dioxide and nitrogen. We already discussed the temperature dependence of these diagrams at 1 atm. Figure 3.13 also includes the effect of pressure. As you can see, at 1 atm there is no liquid phase at all for carbon dioxide. In other words, if you take solid carbon dioxide, which is very cold at about -80°C but otherwise has the look of ice, and put it in room temperature, it will go straight from a solid to a gas. In fact, scientists often casually refer to solid carbon dioxide as dry ice because of this convenient tendency to simply evaporate into gas and not make everything wet the way melting ice does.

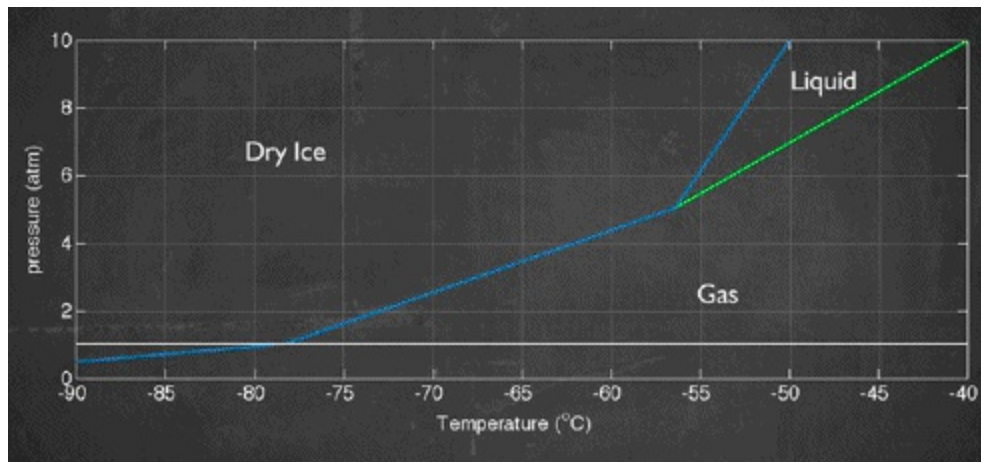


Figure 3.13 Two-dimensional phase diagram of carbon dioxide.

If you want the carbon dioxide to turn into a liquid, you have to increase the pressure to as high as about 8 atm. Once you do this though, there is a sharp transition temperature where the solid turns into a clear liquid, and another temperature where the liquid turns into a gas. The transition temperatures are -54°C for the first and -46°C for the second transition. So if we were to draw a one-dimensional phase diagram at a pressure of 8 atm, we would get something that looks very much like a typical phase diagram where all three phases are represented (Fig. 3.14).

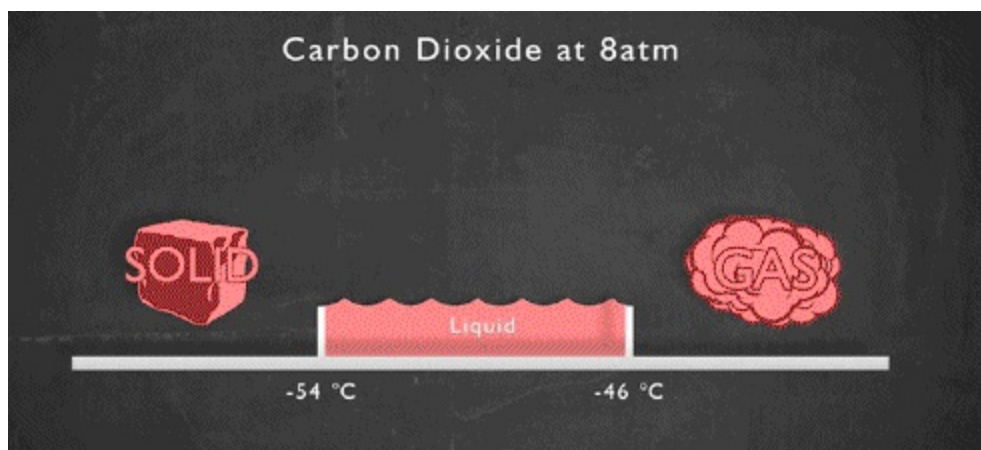


Figure 3.14 One dimensional phase diagram of carbon dioxide at a pressure of 8 atm. Though carbon dioxide has no liquid phase at standard pressure, it looks very similar to a typical phase diagram at 8 atm.

To demonstrate that carbon dioxide does indeed turn into a liquid at high pressures Daniel Rosenberg, our Science and Cooking demo guru, designed the following very simple, but illustrative, experiment. You put a couple of small pieces of solid carbon dioxide into a small vial. You then seal the vial, so that no gas can escape, and you put it in a vice grip so that the cap cannot easily fly open. Because the gas cannot escape, the pressure inside of the tube is going to go up, and when the pressure gets high enough, the dry ice reaches a point where instead of going directly to gas, it melts. If you release the pressure by loosening the cap, the liquid condenses straight back into a solid.

3.3 Equation of the Week

We have seen that many simple materials have phase diagrams that are qualitatively similar to each other. There is a liquid phase, a solid phase, and a gas phase. The phase a material finds itself in depends on the temperature and the pressure. We now want to ask why. What is it about these materials that make their phase behaviors so different?

3.3.1 Molecular Basis of Phase Transitions

The answer should not be that surprising to you – it has to do with the molecules that make up the materials. The molecules in the materials interact with each other, and it is the nature of the interactions that lead to the different phase behaviors. To illustrate this, Figure 3.15 shows the now familiar phase diagram of water, and on top of it are placed sketches of what the solid, liquid, and gas phases look like on a molecular level.

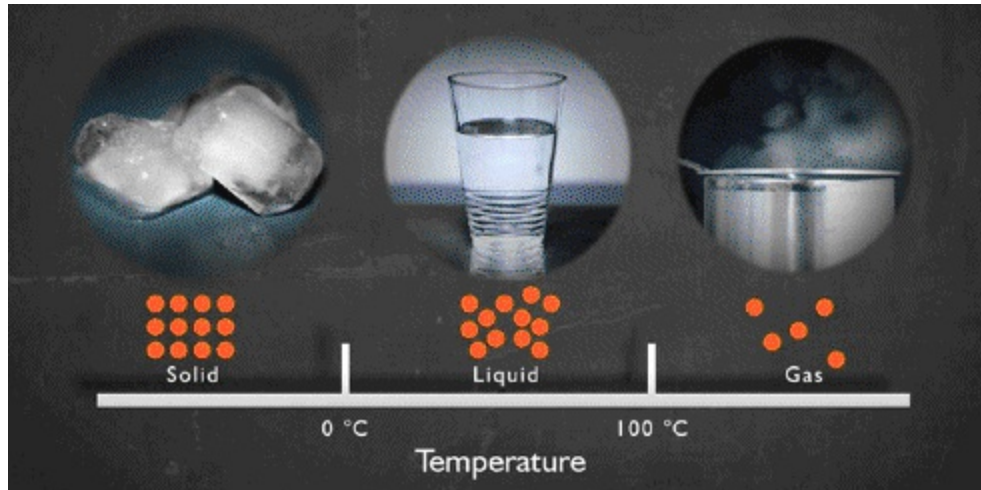


Figure 3.15 The phase diagram of water with cartoons indicating the molecular behavior at each phase.

The solid phase is very ordered, and the molecules are arranged in some sort of a lattice. The liquid phase, in contrast, has a much more disordered configuration and the molecules can move by each other. The density of molecules is comparable to that of the solid phase though. By contrast, the molecules in the gas phase are everywhere and far apart, and they are also very disordered.

To illustrate this further, below are three videos with molecular simulations of each of the three phases of water. In the first video, the water molecules are whizzing around all over the place (Video 3.3). What phase is it? It's a gas. The molecules are moving very fast, they are far apart, and they are filling the entire space, exactly what we would expect of a gas.

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[movie_3_gas_water_16_sec_1.mp4](#)

Video 3.3 Simulation of water molecules in the gas phase.

In the second simulation, the molecules are not whizzing around, but they are still moving by each other (Video 3.4). They're not fixed in space. This behavior is typical of a liquid.

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Video 3.4 Simulation of water molecules in the liquid phase.

Finally, in the last simulation, the molecules are not moving at all, they just sit in one place and vibrate (Video 3.5). The temperature is also much lower as you can tell by the temperature gauge in the upper right. As you might expect, this simulation represents a solid.

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Video 3.5 Simulation of water molecules in the solid phase.

For simple materials, like water, these simulations actually give a fairly accurate picture of what is going on at the molecular level of a solid, liquid, and a gas. For complex materials, like an egg, something very different is going on, and we will only briefly touch on this later on in this chapter and go into it in more depth in Chapter 5. For the purposes of understanding phase transitions though, the simulations nicely demonstrate the two basic factors that are at play in determining the phase behavior of a material. On one hand, the molecules interact with each other. They stick to each other in some fashion. Whereas on the other hand, molecules have motion. It is the competition between the molecules moving around on one hand and sticking to each other on the other that leads to the phase behavior of simple materials.

This reasoning also gives some insight into the pressure dependence of

phase transitions. If you squeeze on a material, which is the equivalent of increasing the pressure, the molecules come closer together and it is harder for them to move apart. If you squeeze enough, you can imagine that a gas will become a liquid. The phase diagrams in the previous section show that this is exactly what happens. If a material is in the gas phase and you increase the pressure at a fixed temperature, it will transition to a more condensed phase, and for many cases eventually from a gas to a liquid, or from a liquid to a solid.

What we now want to do is see if we can take these qualitative ideas about phase transitions and turn them into a mathematical description explaining why materials have the phase behaviors they do. In the process, this should help us get a better understanding of the different factors at play and how they relate to each other.

3.3.2 A Competition Between Energy and Entropy

There are two ways, both quite powerful, of looking at this problem scientifically. The first way focuses on the free energy of the system. At any given point in the phase diagram, the system is trying to minimize its free energy. An analogy would be if the energy of the system were a very hilly valley, and the goal of the system were to find the lowest point in the valley. If we placed a ball on the hill, it would roll down to the bottom. In other words, the position of the ball would be determined by the fact that it is located in equilibrium at the bottom of the hill. In the same way, scientists would say that a material minimizes its free energy, and there are two main factors that influence it. One is the sticking of the molecules to each other. This is what we call the internal energy. The other factor relates to the motion of molecules. This is called entropy. Entropy is the notion that the molecules in a material, to maximize their entropy, would like to be as far apart as they possibly can. They would like to be as free to move as possible. It is the competition between the interaction energy that holds molecules together on the one hand, and the desire to be as free to move as possible on the other hand, that ultimately determined the free energy and leads to the different phase behaviors of materials.

3.3.3 A Competition Between Sticking & Jiggling or Interaction Energy & Thermal Energy

The second way of looking at this problem is microscopic. This is the perspective we will discuss in more detail here, because it gives physical insight into what is going on that is more easily generalizable to many cooking materials. For this perspective, we simply focus on the behavior of a single molecule and ask what is happening to it at any given point.

Generally what is happening, is that the molecule is sticking to other molecules and also moving around due to thermal energy. So we are going to think about phase behaviors as the competition between, on one hand, sticking, and on the other hand, motion.

To express the balance between sticking and motion quantitatively, we need to be able to quantify both of them. Let's start with the motion, or the jiggling. Recall the equation from Chapter 2, $Q = mc_p\Delta T$, which relates how much heat needs to be put into a material in order for the temperature to rise by an amount ΔT . Remember that the heat, Q , in this equation is an energy. It has the units of joules. If we could find some way of characterizing this energy as being per molecule, we would have a good estimate of the jiggling energy. And indeed, Ludwig Boltzmann, a great physicist in the late 19th century found a way to do just this. He invented a formula which basically says that the thermal energy of a molecule is proportional to the temperature of the molecule when measured in units which we call degrees Kelvin. The Kelvin temperature scale is especially pertinent in this context because it is set to be zero where the molecules do not move at all. In other words, the temperature can never go below 0 degrees Kelvin, and the molecules cannot possibly be any more stationary. You may already know that the Kelvin and Celsius scales relate to each other according to the conversion formula below, so that 0 degrees Kelvin corresponds to -273°C .

$$\text{Kelvin} = \text{Celsius} + 273 \text{ K}$$

Based on this, Boltzmann derived a formula that says that the thermal energy of a molecule is given by $Ck_B T$, where C is a constant, T is the temperature as measured in degrees Kelvin, and k_B is a universal constant

of nature that has been named the Boltzmann constant in Boltzmann's honor. It has a value of $1.38 \cdot 10^{-23}$ joules per Kelvin. The constant, C , depends on the atmospheric pressure, but for simple materials at 1 atm the value is about $3/2$, so this is what we will use in this discussion.

Let's use this formula to evaluate the thermal energy of a molecule at room temperature. For simplicity, let's say that room temperature is 27°C , which turns out to be 300 K. If we plug the numbers into the formula, we find that the thermal energy of a molecule at room temperature is $6 \cdot 10^{-21}$ J. This is a very small number.

$$C = \frac{3}{2}$$

$$k_B = 1.38 \cdot 10^{-23} \text{ J/K}$$

$$T = 27^\circ\text{C} = 300 \text{ K}$$

$$U = Ck_B T$$

$$U = \frac{3}{2}(1.38 \cdot 10^{-23} \text{ J/K})(300 \text{ K}) = 6.2 \cdot 10^{-21} \text{ J}$$

In order to understand what this small number means for the phase behavior of a material we need to compare it to something. We have to compare the jiggling to the sticking, the motion due to thermal energy to the interaction energy holding molecules together.

One way to think about this is by the following analogy: Imagine that you were in a room with very sticky walls, and you were bouncing around the room with a lot of energy. Would you end up sticking to the walls or not? The answer would depend on whether or not you have more energy than the walls have sticking power. If you do, then you will not stick to the walls. If you don't, then you will stick to the walls. This is exactly what happens to the molecules in a material. When a molecule is in a liquid, it sticks to the other molecules, whereas if its motion is strong enough it will escape.

Figure 3.16 summarizes these ideas on a phase diagram. The molecules in a material will be in a condensed phase when their interaction energy is much bigger than the thermal energy, $Ck_B T$. By contrast, when the interaction energy is much smaller than the thermal energy, the molecules will be free to move around, and the material will be a gas. The point at which these two quantities are exactly equal to each other is where the phase transition

occurs.

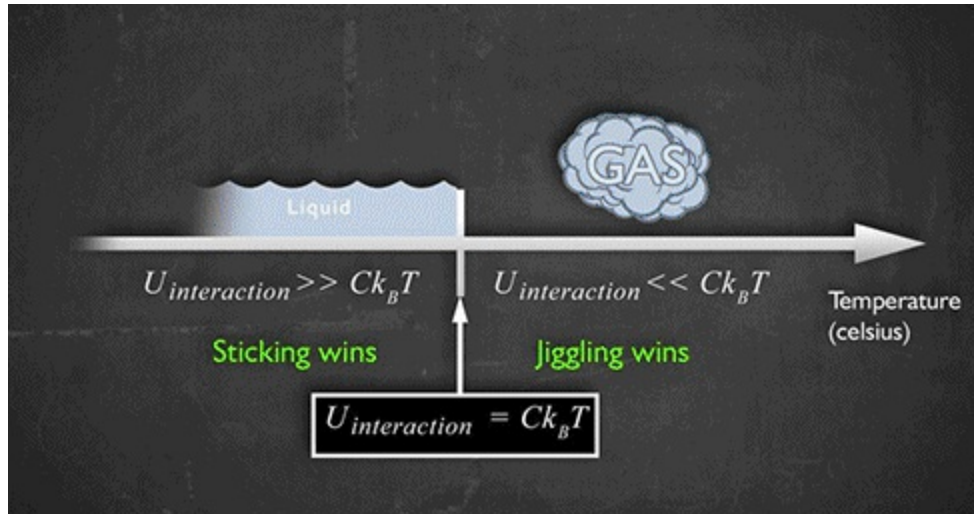


Figure 3.16 On a molecular level, the two factors determining the phase behavior of materials is on the one hand the strength of the sticking interactions, ie the bonds holding molecules together, and on the other hand the kinetic energy, ie the jiggling that breaks the molecules apart. In a liquid, the sticking interactions are stronger than the jiggling, and in a gas the opposite is true. At a phase transition sticking and jiggling are equal to each other.

This notion gives us the equation of the week, which is $U_{int} = Ck_B T$ (Table 3.1). The reason this is our equation of the week is because in a single equation, it contains all of the physics that we have talked about so far, and accurately predicts the phase transitions between condensed and non-condensed phases.

EQUATION OF THE WEEK		
$U_{int} = Ck_B T$		
Symbol	Description	Units
U_{int}	Interaction energy	J
C	Constant	–
k_B	Boltzmann constant ($1.38 \cdot 10^{-23} \text{J/K}$)	J/K
T	Phase transition temperature	K

Table 3.1

3.3.4 Molecular Bonds

But we are not done yet, because in order to use the equation of the week, we have to be able to quantify the interaction energy of the molecules. And this, of course, depends on the materials. Some materials have high interaction energies, and the equation of the week would predict that they would also have a high boiling point. Yet other materials have lower interaction energies between the molecules, and would be expected to have a lower boiling point. We would for example expect that ethanol, which boils at a lower temperature than water, has weaker bonds between individual molecules than water. And indeed, this turns out to be the case.

There are four different types of molecular interactions that are important to cooking, and they all have different energies that are associated with them. The weakest bonds are called van der Waals interactions. They are the dominant interaction in ethanol. Slightly stronger, but still by comparison fairly weak, are hydrogen bonds. These occur in water. The second strongest bonds are electrostatic bonds. They occur between two molecules or atoms that are charged. And, finally, the strongest type of bond is covalent bonds. Covalent bonds are so strong that they do not tend to break for most cooking unless a lot of heat or a significant pH change is involved. Figure 3.17 lists the energies per molecule for each type of bond. Van der Waals and hydrogen bonds are at about the same order of magnitude, whereas electrostatic and covalent bonds have between ten to forty times higher energies.

Type of Interaction	Interaction Strength	Interaction Energy
Van der Waals	Very weak	2×10^{-20} J/molecule
Hydrogen bonds	Weak	4×10^{-20} J/molecule
Electrostatic	Pretty strong	2×10^{-19} J/molecule
Covalent	Very strong	8×10^{-19} J/molecule

Figure 3.17 A list of common molecular bonds and their respective energies.

In the context of the equation of the week, a material with hydrogen bonds is going to boil at higher temperatures than a material with van der Waals interactions. For example, the reason liquid nitrogen turns into a gas at room temperature whereas water and ethanol do not, is that it primarily consists of van der Waals interactions. Water is entirely made up of

hydrogen bonds and will stay liquid the longest, whereas ethanol, which consists of a mix of primarily van der Waals interactions, but also some hydrogen bonds, will boil at temperatures between those of water and liquid nitrogen.

The equation of the week is so powerful because it summarizes all of the physics that we have discussed so far. It relates the motion of molecules, and thus the temperature that you are imparting on the system, with the interaction energies between the molecules, and hence explains why different materials have different phase behaviors. It also explains why a material with stronger bonds will have higher boiling or melting temperatures than a material with weaker bonds. Moreover, it also explains why increasing the pressure leads to a lowering of the transition temperatures for any given material, and why, as a result, you have to heat the material to a higher temperature for the transition to occur. All of this is at the core of the structure of the phase diagrams that we discussed in the previous section.

The equation does not apply directly to complex materials such as eggs, but the general principle of balancing energy and entropy will turn up again and again in this course. For example, later on in this chapter, we will discuss the melting behavior of fats, which is slightly more complicated than that of simple molecules, but can still be completely explained by the principles we discussed here. Further, in our discussion on cheese making, you will find that the same idea applies: the molecules in the milk fall apart when heat is applied, and then reaggregate into cheese under different conditions, and this is also a competition between sticking and jiggling, or energy and entropy.

3.4 The Science of Rotovaps

A classic example of how traditional scientific tools can be used to amazing effect in the kitchen is the rotary evaporator. Commonly referred to as a rotovap, this instrument is typically used in synthetic chemistry labs as a gentle way to evaporate solvent after a chemical reaction. More recently, chefs are using rotovaps to create novel and delicious liquids, and you will see them being used again and again in this course. The principles of operation of a rotovap are completely explained by the physical principles of this week, and the purpose of this section is to describe them in some depth.

The culinary idea behind using a rotovap is the following: Imagine your favorite drink, be it Coca Cola, orange juice, or wine. And imagine that you want to make the delicious flavor of it even more concentrated. In other words, you want to find a way to keep all the characteristic flavor molecules, while getting rid of the diluting water. Alternatively, imagine that there is a particular aspect of the drink you like, and you would like to isolate that flavor away from the other flavors, and create an entirely new type of liquid altogether. The rotovap, it turns out, would accomplish just these kinds of things for you.

3.4.1 A Molecular View

Recall the equation of the week, $U_{\text{int}} = Ck_{\text{B}}T$, which represents the balance between the molecules sticking together, the interaction energy, on the one hand, and the jigglng due to thermal energy on the other hand. Next, imagine a liquid which consists of different materials. For the sake of argument, let's imagine that it consists of red molecules and blue molecules (Fig. 3.18). The red and blue molecules interact with each other, but they stick to each other with different strengths. Let's say that the red molecules bind weakly to other molecules, and that the blue molecules bind strongly. How can we separate the red molecules from the blue molecules using only the principles of the equation of the week?

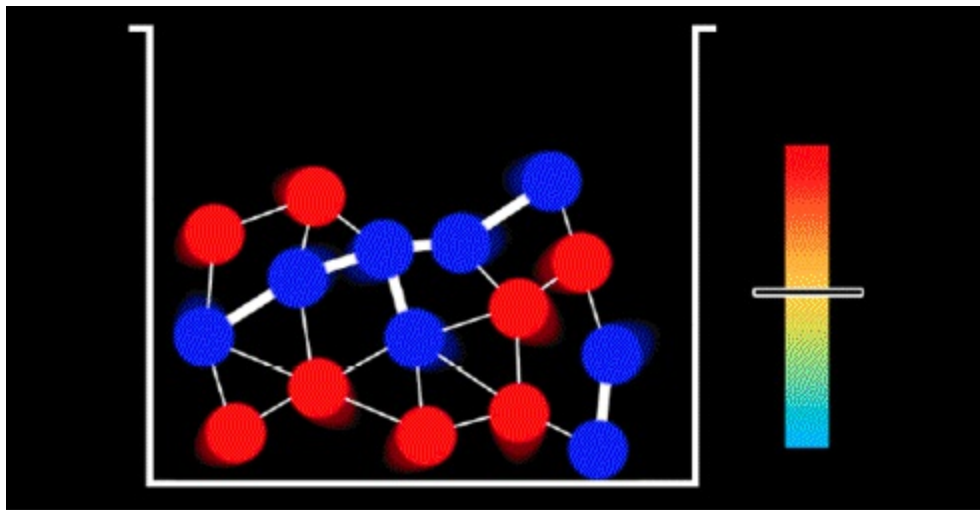


Figure 3.18 A cartoon of a solution made of blue molecules and red molecules. The red molecules bind to each other with weaker bonds (thin lines) than the blue molecules (thick lines).

If the liquid consisted only of red molecules, it would start to boil at some temperature which would be determined by the interaction energy between the molecules. Similarly, a liquid containing only blue molecules would start to boil at some different temperature, which would also be determined by the interaction energy, except in this case the interaction energy would be that of the blue molecules. Since the interaction energy is stronger for blue molecules than for red molecules, the boiling temperature for the blue solution will be higher. Given this, you could imagine that if you are at a temperature between the temperature at which the red molecules boil and the temperature at which the blue molecules boil, then only the red molecules will be boiling off. The blue ones will stay behind because the thermal energy is not yet strong enough to break the bonds between them

(Fig. 3.19). Of course, the red and blue molecules also bind to each other so it is a little more complicated than that, but this is the general principle. As a result, at this intermediate temperature, the vapor above the solution will consist of more red than blue molecules.

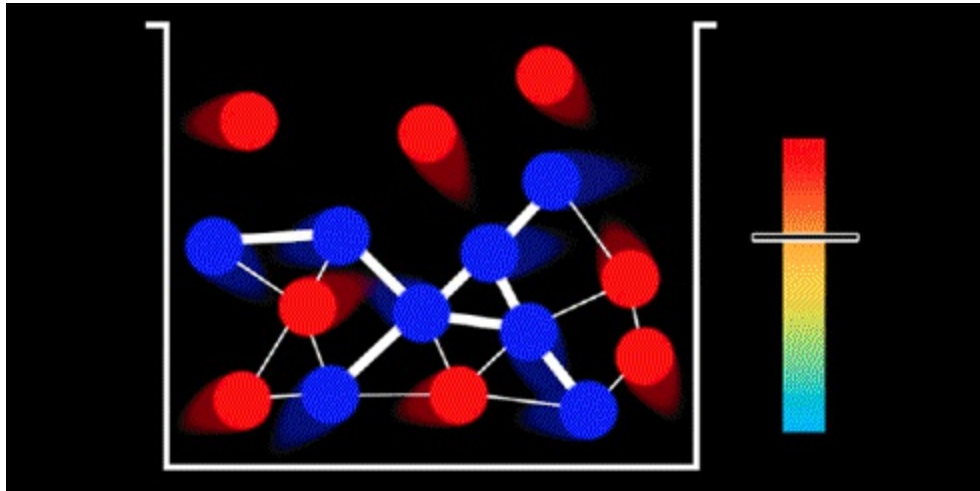


Figure 3.19 When the temperature is raised just enough to break the weak bonds between the red molecules, but not so much that the stronger bonds between blue molecules are broken, the red molecules will vaporize but the blue molecules will stay liquid. If the red molecules can then be captured and isolated, the two kinds of molecules can be separated. This is the idea behind a rotovap.

If we could now capture the gas above the solution and turn it into a liquid, we would end up with a solution that has many more red molecules than blue molecules, and we would have succeeded in our quest to separate the two types of molecules. This is exactly what rotovaps are able to do.

There is one caveat to this method though, which is the following: Imagine that you were a famous chef, and you wanted to capture the very essence of eucalyptus or chocolate, and serve it to the diners in your restaurant. Based on the above, you would do this by trying to find the perfect temperature at which the desired molecules would boil off, and then heat the solution to that temperature. The problem is that the moment you start to apply heat to the flavor compounds in the solution, chemical reactions start taking place, and this changes the flavor and makes it different from the original taste. We all know that foods that have been heated or cooked tend to taste different from when they are uncooked, and this is the same idea. So if you are trying to preserve the essence of the material, you want to avoid heating, because that will change the flavor.

3.4.2 Manipulating Pressure

Is there some way to cause the same phase transition without heat? Yes, indeed, and we have learned exactly how to do it earlier in this chapter. Recall the phase diagram of water, and remember that liquid water can turn into a gas by increasing the temperature from 23°C to 100°C at 1 atm. But we can achieve the same phase transition by changing the pressure and keeping the temperature fixed.

If we isolate the part of a phase diagram that illustrates the liquid-gas boundary, we get what is called a vapor pressure diagram. The vapor pressure of a material is the pressure at which a material vaporizes at a given temperature. By isolating the vapor pressure curve, we can add curves for several materials to the same chart for easy comparison. Figure 3.20 shows the vapor pressure curves for water, ethanol, and a few other materials. As you can see, different materials, and even mixtures of different materials, have different positions on the diagram. Ethanol, for example, consists of molecules that are bound more weakly together than water molecules, and hence has a higher vapor pressure than water at any given temperature.

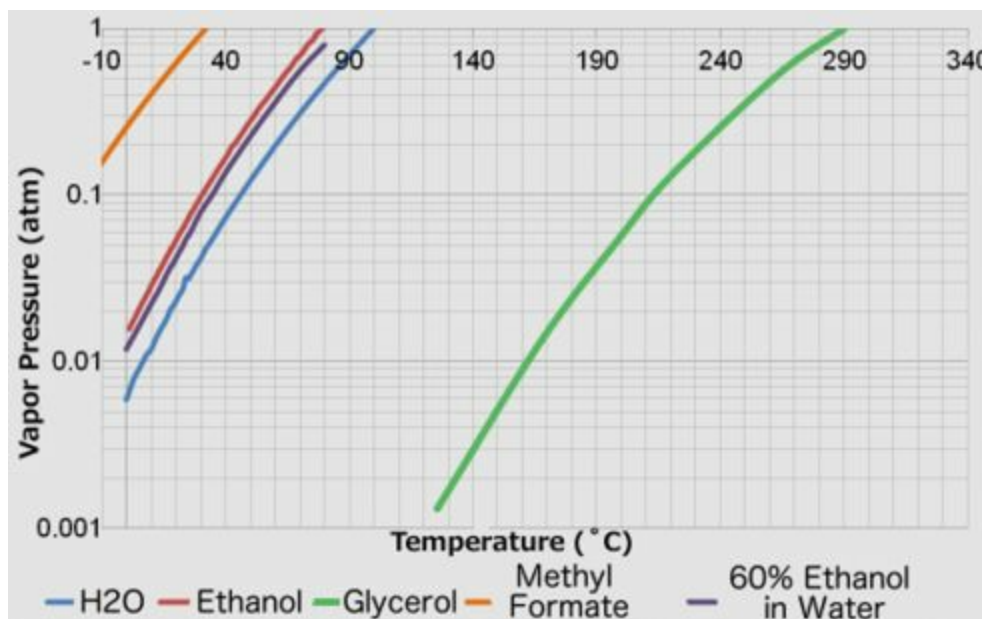


Figure 3.20 Vapor pressure chart for common substances

Given the above, we should be able to decrease the pressure instead of increasing the temperature and cause the more volatile compounds to come off that way. If we are careful enough and hit just the right pressure, i.e. the

pressure between the vapor pressure of the molecules we want to collect and the vapor pressure of the molecules we want to leave behind, we should still be able to get our liquid separated the way we intended.

3.4.3. The Different Parts of a Rotovap

With this in mind, let's return to the rotovap. For the purposes of this discussion, a rotovap consists of two main parts: a flask for the original solution that you are planning to rotovap, and a second flask for collecting the vaporized solution. To operate the rotovap, you add the original solution, be it Coca Cola, a eucalyptus infusion, or something else, to the flask on the right in Figure 3.21, and attach it to a vacuum pump. As the pressure is lowered, the most volatile compounds in the flask will start boiling off and create a vapor above the solution. The vapor is pulled away by the vacuum into the other side of the rotovap, and since this side is kept very cold, either with condenser coils, ice, or even dry ice, the gas will readily recondense and collect as a liquid at the bottom of the other flask.

So this is how we would go about separating one component of a liquid from another, and chefs have employed this method in numerous creative ways in their restaurants. Chef Joan Roca even uses the rotovap to collect the unique compounds in soil from a pine forest, thus creating a liquid that evokes memories of walking through a fragrant forest. As you can see, the physical principles of these types of rotovap creations are perfectly explained by the science of this week.

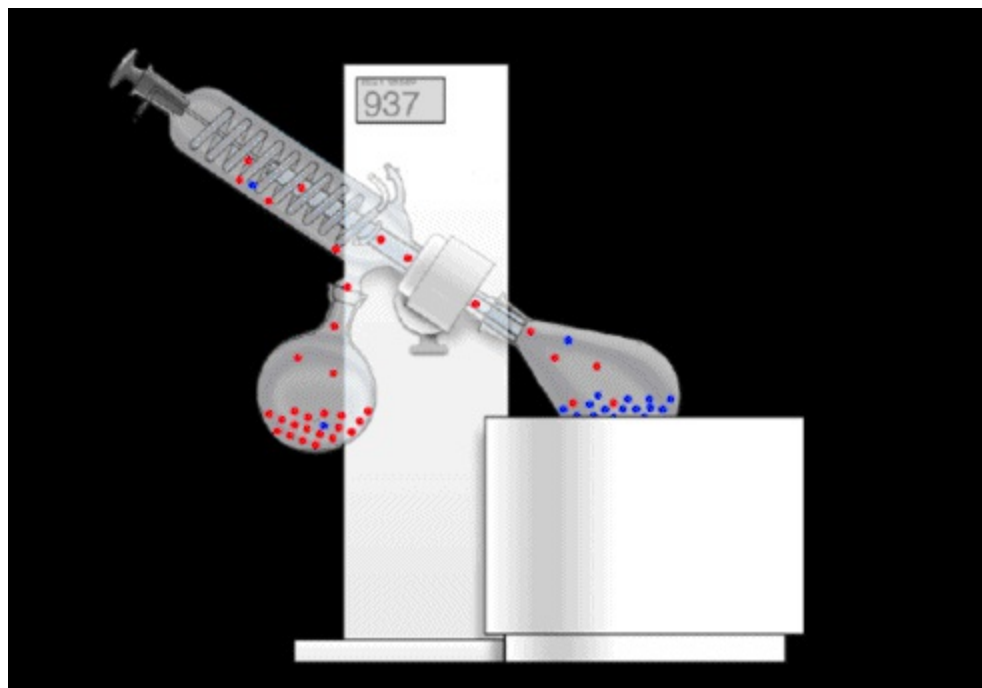


Figure 3.21 A rotovap has two main components: an evaporation flask that is lowered into a temperature controlled water bath (right) and a receiving flask that is attached to a condenser, which in turn is attached to a vacuum source (left). As a vacuum is applied, molecules will evaporate from the

evaporation flask and recondense in the receiving flask.

3.4.4. Distilling Alcohol

Before leaving this discussion, let's touch upon one other important process in cooking that is related to this concept, which is the general process of distillation. Later on in this course, we will discuss fermentation, and as a part of that discussion we will study the chemical reaction that microbes use to convert sugar into ethanol. For various reasons that we will discuss in more depth later on, it turns out to be almost impossible to get the alcohol content of a fermentation reaction to go above 20%. One reason for this is that the alcohol content is determined by the sugar content in the grapes, which has some upper limit. Another reason is that above 20%, the ethanol becomes so toxic for the microbes that they die, thus being unable to continue increasing the amount of alcohol. These are the reasons that the alcohol percentage of wine typically is in the range of 10-15%.

You all know though, that many alcoholic beverages exist where the ethanol content is much higher than that of wine. So, how is this possible? The answer is the process called distillation. In many ways distillation works similarly to rotovaps. It uses the fact that ethanol molecules are more volatile than water molecules, and thus, either by decreasing the pressure or increasing the temperature, the two types of molecules can be separated. Just like rotovaps, distillers have a cool part where the ethanol vapor, or the vapor consisting primarily of ethanol since unavoidably some water molecules vaporize too, can recondense into a liquid.

If you are hoping to create a beverage with a very high alcohol content, or for that matter, with very strong flavors from the rotovap, you may need to repeat the process several times. The reason is that the condensate from both the distiller and the rotovap, is not going to be a pure substance. There is also going to be water and other compounds within it, because the gas above the liquid always contains molecules other than the ones you are trying to collect. But if you repeat the process, you will increase the concentration of the molecules you want more and more, and eventually get a very pure substance. There is a limit though. If you go to a liquor store, you will notice that even the purest-grade ethanol is not 100% ethanol. It is usually something like 96%. That is because of the peculiar properties of ethanol and water, which make it very, very difficult to get that last couple percent of water out.

In summary, we hope this discussion has made it clear how the principle of balancing the interaction energy, the sticking, with the thermal energy, the jiggling, is at the heart of the process of both rotovaps and distillations. Hopefully it also explains how some of the remarkable creations of the chefs work.

3.5 Phase Transitions of Fats

We will now extend our discussion of phase behavior to cooking materials, so that you can see how the ideas that we have discussed so far generalize to food. A good food to start out with is fats. They are important for cooking, and they undergo readily visible phase transitions that are relatively easy to understand conceptually. Figure 3.22 shows four phase diagrams. Two of them are of water and ethanol, which we have already discussed at length. They are contrasted with two cooking materials, namely coconut oil and olive oil. Since the primary phase transition important to cooking in this case is the solid to liquid transition, this is what we will focus on here.

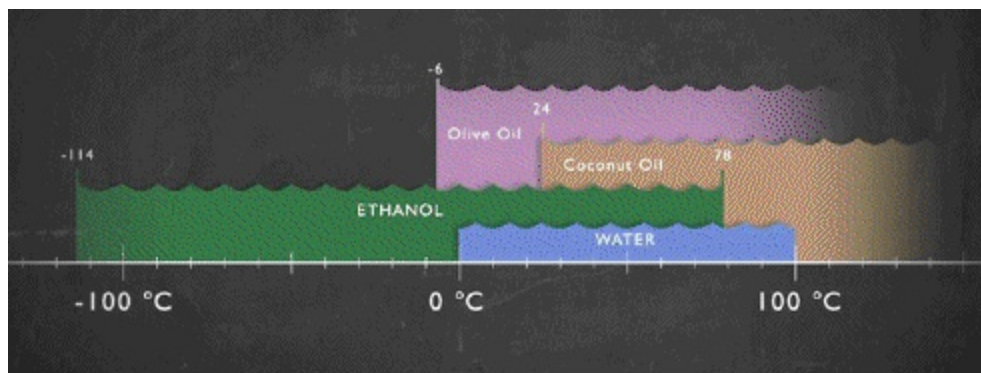


Figure 3.22 Phase diagrams of two common fats, olive oil and coconut oil, as compared to the phase diagrams of water and ethanol.

Coconut oil has a solid to liquid phase transition at about 24°C at 1 atm. This means that if you take coconut oil and put it in the refrigerator, it will solidify and become a solid gook, whereas if you keep it out on the counter on a warm day, it will become a liquid. Olive oil tends to be a liquid over a much wider temperature range, but if you put it in the freezer or cool it to below -6°C, it will also become a solid. These are just two examples, but virtually any fat, ranging from shortening to cocoa butter to canola oil, turn out to have their own unique melting temperature. The question we now want to ask is why these transitions occur, and how to think about them scientifically.

You will probably not be shocked to learn that the same principles that apply to simple materials also apply to cooking materials. Namely, cooking materials consist of molecules, and the molecules both stick to each other and jiggle around. The varying phase behaviors of different fats are due to

the different ways that the fat molecules interact with each other. In order to understand this, let's study the molecules of fat in a little more detail.

3.5.1 Saturated and Unsaturated Fats

The main component of fats are molecules that are called triglycerides. The name stems from their chemical structure; they consist of three fatty acid chains connected by a glycerol molecule at their base (Fig. 3.23). The fatty acid chains are in themselves simply long carbon chains, but small differences in their structure end up playing an important role in determining the phase behavior.

There are two main types of fatty acid chains: saturated and unsaturated. Saturated fats get their name from the fact that all of the carbon bonds have been saturated with hydrogen atoms. As a result there are only single carbon-carbon bonds in the molecule. It turns out that it is in the nature of single bonds to result in straight carbon chains, so as a result, saturated fats have fatty acid chains that are straight. In contrast, the carbon atoms in unsaturated fats have not been saturated with hydrogen atoms, so instead of binding to hydrogens, some of the carbons will be forming double bonds with each other. Depending on how the double bonds form, they are referred to either as *cis*- or *trans* bonds, each contributing in their own way to the overall geometrical structure of the fatty acid. *Cis*-bonds, for example, are notorious for making the fatty acid chains have a bent structure

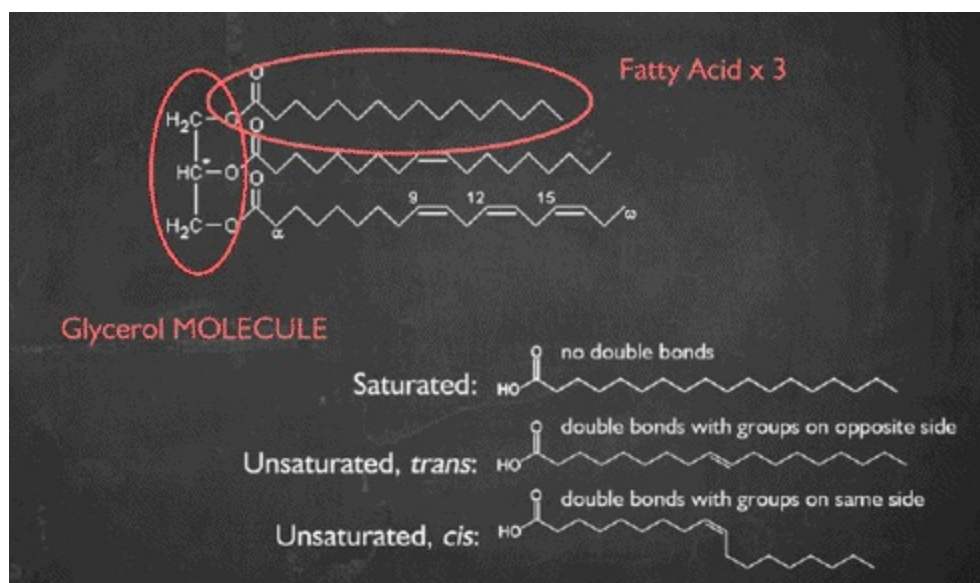


Figure 3.23 Fats are made of triglycerides, which in turn are made of three fatty acids connected via a glycerol molecule. The fatty acids can be either saturated or unsaturated, referring to whether the carbon chains contain any double bonds or not. Unsaturated fatty acids are further divided into two groups based on whether the bonds are *cis* or *trans*, which refers to the relative positions of the carbon

chains at either side of the double bond. Cis-bonds have a straight chemical structure, but trans-bonds result in a kinked structure, and this ultimately affects the phase behavior of the fat.

Ultimately it is the geometrical structure of the fatty acid chains that is responsible for the different phase behaviors that we observe in fats. Imagine that you take two saturated fatty acid chains and try to push them closely together. Since they are both straight, you will be able to align them closely so that they contact each other more or less along the entire carbon chain. As a result, van der Waals interactions between them will be strong and they will stick to each other. In contrast, instead imagine the same exercise between two unsaturated fatty acid chains (Fig. 3.24). Since they are bent, you will not be able to pack the chains as closely together, and van der Waals interactions will not be as strong. So comparing saturated and unsaturated fatty acid chains, the interaction energy, U_{int} , will be higher for saturated fats.

Based on this information, you should already have an opinion about what the different melting temperatures are going to be in these different materials. Since saturated fatty acids have a higher interaction energy, we would expect them to have a higher melting temperature than unsaturated fatty acid chains. This is because we know that it takes more thermal energy, more jiggling energy, to rip the molecules apart if the interaction energy is high.

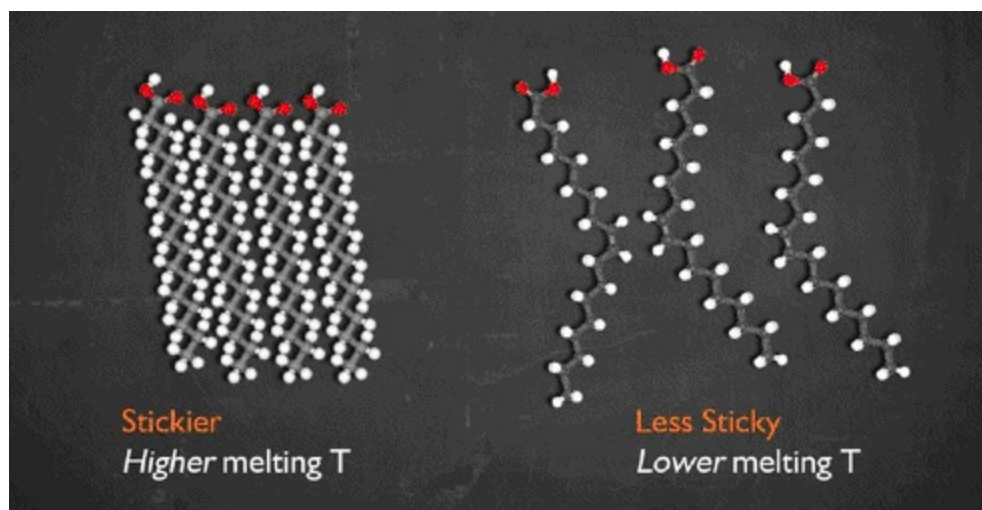


Figure 3.24 The chemical structure of the fatty acids in a fat molecule affects the phase behavior. Saturated fatty acids are straight, which allows them to pack densely and form strong intermolecular bonds. Unsaturated fatty acids have a kinked structure and therefore cannot pack as densely. It takes higher temperatures to break the intermolecular bonds of a saturated fatty acid compared to an unsaturated fatty acid, and this results in a higher melting point.

3.5.2 Chain length

In addition to saturation, there is one other property that plays an important role in the melting behavior of fats, which is the fact that the length of the chains can vary. Two very long saturated fatty acids are going to have much stronger van der Waals interactions overall, than two short ones, and this is also going to affect the melting temperature (Fig. 3.25). You can imagine then, that between the chain length and the saturation, it can sometimes be hard to predict the interaction energy and melting behavior. A very long, though bent, unsaturated fatty acid, may very well have a higher interaction energy than a short and straight saturated fatty acid chain, but the relationship may also very well be reversed and it is hard to predict which property will win.

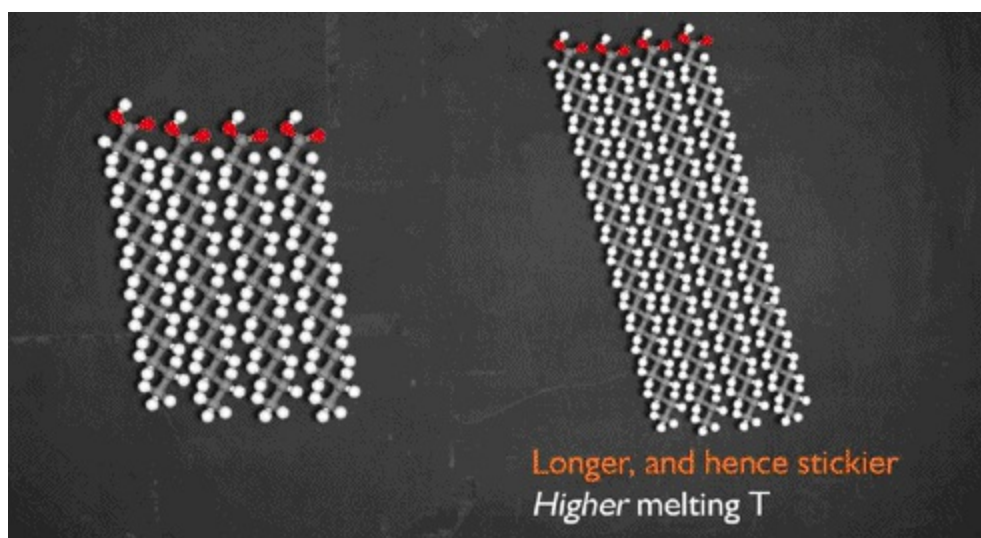


Figure 3.25 Fatty acid with long carbon chains form stronger intermolecular bonds than those with short carbon chains. As a result the melting point of fats made up of fatty acids with long carbon chains is usually higher.

Video 3.6 shows a simulation of the melting behavior of a fat. This is an analogous simulation to the ones illustrating the melting of water that we have previously seen. For simplicity, the fat molecules are represented by long carbon chains, without the connecting glycerol molecule. At low temperatures the carbon chains are all stuck to each other, and as the temperature goes up, they come apart.

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Video 3.6 Simulation of fatty acid chains going from solid to liquid to gas as the temperature increases. Temperature gauge is in the upper right hand corner.

To see if our prediction about saturation and melting temperature holds true, we can study the saturated fat composition of several types of cooking fats. Figure 3.26 shows the fat composition of olive oil, coconut oil, cocoa butter, and shortening. They all have different amounts of saturated fats. Olive oil has the lowest at about 14%, whereas cocoa butter is much higher at about 61%.

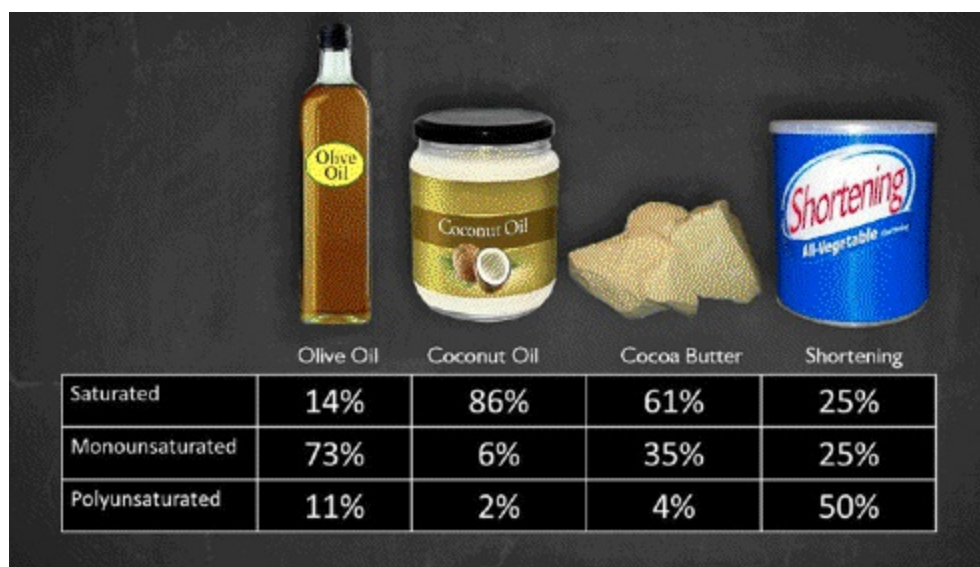


Figure 3.26 Fat composition of four common types of fat.

Based on the discussion above, it would not be surprising if cocoa butter has a somewhat higher melting temperature than that of olive oil. It is difficult to predict how much higher it would be, since the melting point also depends on chain length, but nevertheless this seems like a reasonable prediction to make. And indeed, if we plot the melting temperatures on a phase diagram, this is exactly what we see (Fig. 3.27). Cocoa butter has melting temperatures in the range of 27-35°C. Whereas olive oil has a melting temperature around -6°C. This is a temperature difference of between 30-40°C, most of which can probably be explained by the different compositions of fatty acids.

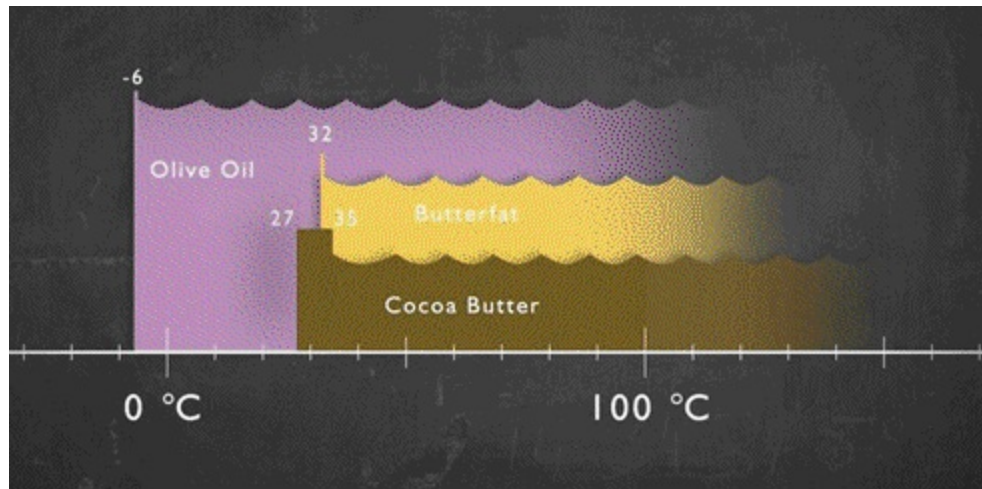


Figure 3.27 Phase diagrams for olive oil, butter fat, and cocoa butter. Cocoa butter has a higher melting point than olive oil, a fact that can be explained by it being composed of higher percentage of saturated fats.

One interesting fact about the phase diagrams of fats is that the transition is usually not an abrupt event. Rather, it occurs over a range of temperatures. The reason for this is that typical cooking fats, such as cocoa butter and olive oil, are not composed of a single type of fat molecule. There are usually several different types of fat molecules in them, which means that the melting temperature is going to reflect the range over which the different fat molecules melt. This is actually not unlike what happens in an egg. An egg is composed of many different types of molecules, all undergoing phase transitions at different temperatures. In contrast, a pure substance, like water, will not behave like this. It goes from a liquid to a gas at exactly 100 °C at 1 atm. It is never a range between 95 and 105 °C. So in a more complex material like cocoa butter, we start to see the beginnings of what happens in materials that contain many different types of molecules.

3.6 The Science of Supercooling

Possibly one of the most remarkable desserts by Chef Joan Roca includes the following steps: a liquid is taken from a rotovap, cooled in a freezer to a temperature below 0°C , and then poured on a dish. As the liquid hits the plate, it solidifies, and grows into a tall, glistening ice sculpture.

On the surface of it, this violates several laws of physics that we have described so far. How can a substance that in every way looks to be made of water, be cooled below 0°C at 1 atmosphere of pressure, and still remain a liquid? Up until this point we have insisted that water should be a solid below 0°C at 1 atm. Further, why is it that when this liquid is poured on the plate, a big mound of ice forms? This, after all, is what should have happened at 0°C and 1 atm in the first place? The curious phenomenon we observe in Joan Roca's dessert has a name, supercooling, and we will explain the physics behind it in this section.

It turns out that it is possible to violate the phase diagrams that we have so carefully studied so far. The way in which this happens is very interesting and important in its own right, and will also play an important role for some of the cooking we will do later on in this course. Figure 3.28 shows the standard phase diagram of water that you are already familiar with. The green arrow indicates what we observe in Joan Roca's dessert, namely that it is possible to cool a material to below its freezing point and still have it remain a liquid.

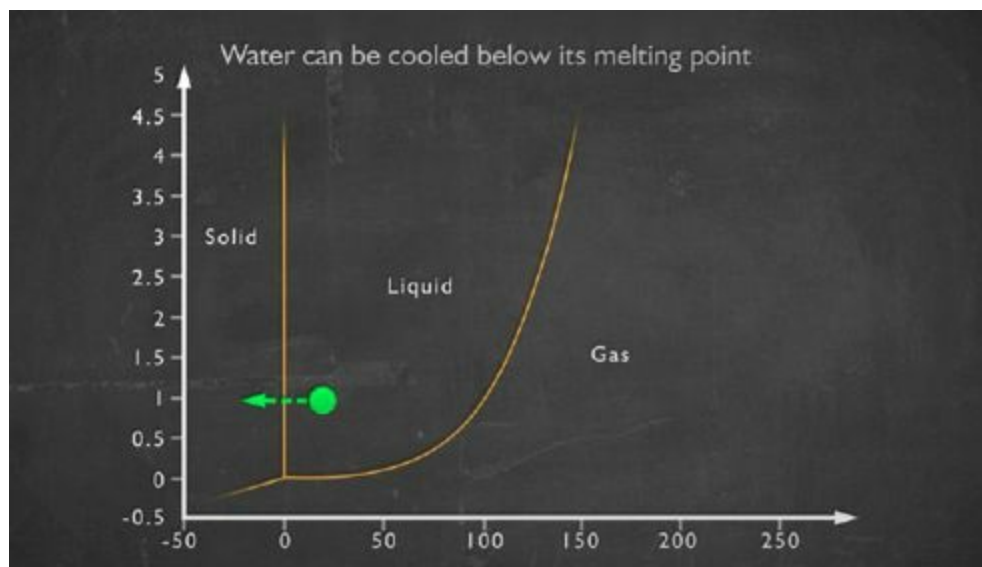


Figure 3.28 Phase diagram of water indicating the phenomenon of super cooling, i.e. the ability to cool

a liquid below its freezing point without having it turn into a solid.

How can this happen? We know that at temperatures below 0°C and 1 atm water wants to become a solid. The crux of the matter is that this does not happen spontaneously. Something has to happen before the solid can form.

3.6.1 Nucleation

Let's first think about this in terms of an analogy: Imagine that you are at a sporting event, and something really great happens. Some play occurs where the team you are rooting for wins, and you want to start clapping spontaneously. So you start clapping and your friend sitting next to you also starts clapping, but it is very loud in the stadium and the noise of the clapping is drowned out. Gradually, though, as more and more people start clapping, the noise from the clapping increases so that eventually the entire auditorium erupts in applause.

A similar scenario takes place when a liquid turns to solid. As the temperature starts going below the freezing point, imagine that one of the molecules decides it no longer wants to be liquid. It wants to become ice. So it says to its friend, hey, let's be ice. And the two molecules stop moving about in liquid-like fashion, and stick together. Once this happens, more and more molecules start sticking together into lots of little mini-solids, and eventually there is a lot of ice. Scientists call this a nucleation event (Video 3.7). In order for ice to form, there has to be a nucleation event, and it is the control of the nucleation events that is the essence of the remarkable ice structure in Joan Roca's dessert.

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[movie_7_phases-rotovap_slide-036_1.mp4](#)

Video 3.7 Simulation of crystal formation. Crystals form in two steps: nucleation and crystal growth. In nucleation, a small number of molecules gather into tiny clusters. Once the clusters are stable, they provide a site for crystal growth as new molecules add on.

3.6.2 Crystal Growth

One might think that it is easy for the tiny clump of molecules that are stuck together to start growing into more ice. After all, we learned that at temperatures below freezing, the “sticking” between molecules wins out over the “jiggling”, i.e. the energy is lower for molecules that are solid than liquid. But imagine that the tiny ice crystal really has two types of molecules: the molecules at the center, and the molecules at the boundary. The molecules at the center are surrounded by other molecules which are also in solid form, whereas the molecules at the boundary have a bit of a conundrum. On the one hand, they are next to other molecules in solid form. But on the other hand, they are next to the background liquid. So they are neither bound nor free. They are in an intermediate state and because of this they are neither minimizing their energy, nor maximizing their entropy. For this reason, it actually costs more energy to put molecules on the surface of the ice crystals than it takes to put them either in the middle of the ice crystal or in the middle of the liquid. In other words, having a boundary costs energy, and the more of a boundary you have, the more energy it costs.

In terms of the clapping analogy, the same principle can be explained as follows: Imagine that a group of you and your friends start to clap in a crowded stadium. Maybe you are in the center and you are surrounded by all of your friends who are also clapping. So most people in the group are on the outside. You are the only one who is in the middle. But as the group of clapping people grows, there are more and more people on the inside and fewer and fewer people on the outside. At that point, it becomes more favorable to begin to clap.

3.6.3 Homogeneous and Heterogeneous Crystallization

But this is not the whole story. It turns out that in very, very pure water, without any impurities or dirt in it at all, it is possible to calculate how big a crystal needs to become in order for the influence of the molecules at the boundary to no longer be significant enough to stop the crystal from growing. Surprisingly, crystals of that size are big enough so that they do not tend to form with reasonable probability until about -5°C , i.e. much below the freezing point of water. Even though it is energetically favorable for ice crystals to form, the process that triggers them to form does not actually occur until well below the freezing point of water. That, of course, contradicts all of our experiences. If you take a glass of water and stick it in the freezer, you expect it to turn into ice. The fact that resolves this conundrum is that most nucleation of solids takes place on dirt. In other words, the impurities in the liquid end up serving as nucleation sites for ice crystal formation. This is usually referred to as heterogeneous nucleation, as opposed to homogeneous nucleation which is what takes place in a very pure liquid around -5°C (Video 3.8).

It is very hard to get water that is pure enough so that you can cool it below the freezing point. It will almost invariably form ice. And even if the impurities in water are removed, the container you are using needs to be of a very smooth material so that any irregularities cannot serve as nucleation sites either. Joan Roca managed to by-pass all of these obstacles in his amazing dessert with the ice sculpture.

In summary, the basic physics that governs the violation of the phase diagram that made Joan Roca's dessert possible is the idea that crystals need to nucleate in order to grow, and that nucleation of crystals is much more unfavorable than the actual growth of crystals. We will revisit this idea fairly soon in the chapter on chocolate, and you will see that the creation of chocolate is all about controlling the nucleation events of the correct type of crystals.

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[movie_8_phases-rotovap_slide-040_1.mp4](#)

Video 3.8 In heterogeneous nucleation, small clusters form from molecules in the solution, whereas in homogeneous nucleation dirt, or other impurities, provide the sites for crystal growth.

3.7 Solubility

Soda tends to taste incredibly sweet and delicious, and if you look at the nutrition facts label you will find that it usually has large amounts of sugar in it. With this in mind, here is a question for you: What is the sweetest drink you can possibly make?

Suppose you take a jar which has a pound of water in it. And then suppose you take another jar which has a pound of sugar. Do you think you can dissolve the pound of sugar into the pound of water? In other words, if you pour the sugar into the water and stir, will the sugar disappear into the water or will it pile up on the bottom? Next, imagine that you were to do the same thing with salt. Do you think all the salt would dissolve?

It turns out that all of the salt would not dissolve. In fact, the solubility of salt is about $\frac{1}{3}$ of a gram per gram water, which means if you took a pound of salt and tried to pour it into a pound of water, $\frac{1}{3}$ of it would dissolve, and the other $\frac{2}{3}$ would come out at the bottom. If you don't believe us you should go try it. Just take some salt, measure out the weight of the water, measure out the weight of the salt, pour it in, and you will see that only about $\frac{1}{3}$ of the mass of water will actually dissolve.

If you do the same with sugar, on the other hand, something completely different happens. The pound of sugar will dissolve perfectly in a pound of water. But it is even worse than that. The solubility of sugar is actually 2 grams per gram water, which means that you can actually take 2 pounds of sugar and pour it into one pound of water, and it will still dissolve perfectly.

At first glance, this exercise may seem unrelated to the theme of this chapter. But it is not. If you think about it, many things that we eat or drink, involve dissolving one substance in another substance. Often the two substances have different phases. For example, if you like to drink coffee or tea, this involves pouring hot water over coffee grounds or tea leaves so that some of the molecules get into the water. Similarly, if you add spices to a soup or a stew, you expect them to dissolve into the fluid and flavor the food. There are many other examples of the importance of solubility throughout cooking. And the question that we want to ask in this section is what the physics of this is. What determines how much of one substance can be dissolved in another? Why is the solubility of sugar so much more

than the solubility of salt?

3.7.1 Solubility and Phase Transitions

If you look at the shape of sugar under a microscope, you see that it has the shapes of little square crystals (Fig. 3.29). When you pour the sugar crystals into water, they come apart and the individual sugar molecules of the crystals dissolve and spread all through the liquid (Fig. 3.30).



Figure 3.29 Table sugar is composed of crystals, i.e. highly ordered lattices of sugar molecules.

This should remind you of something that we have already discussed. We have taken a solid, poured it into another substance, and the molecules then fill the space like a gas. This is reminiscent of what happens when a liquid undergoes a phase transition and turns into vapor. And, in fact, the solubility of any compound, whether sugar, salt, or anything else, is very much like the phase transition that occurs between a liquid and a gas. And, indeed, the physical principle that governs the dissolution is also analogous to that of a phase transition.

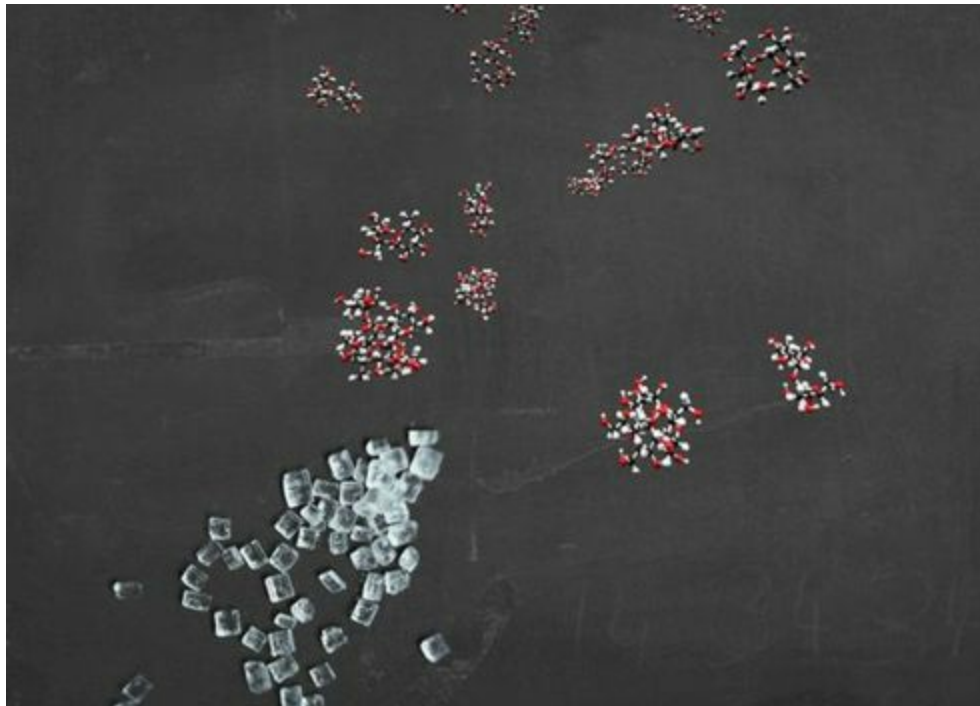


Figure 3.30 When table sugar is added to water, the sugar crystals dissolve and go into solution.

We previously discussed that the liquid to gas transition can be described by the formula $U_{\text{int}} = Ck_{\text{B}}T$, where U_{int} is what we have casually been referring to as “sticking”, and $Ck_{\text{B}}T$ is the “jiggling”. We can apply this same idea to the sugar molecules that are coming off of the crystal. The molecules in the crystal have some interaction energy that holds them together. When they come off of the crystal, two things happen. The first is that they are surrounded by water molecules which is not as favorable as being in a crystal, but it is not altogether unfavorable either. Second, and even more importantly, the molecules can now jiggle. They have entropy. And it is this competition between the favorable jigging, on one hand, and sticking, on the other hand, that is relevant to the question of how much sugar you can dissolve.

Another way of expressing the same idea, is in terms of the competition between energy and entropy. On one hand, when a sugar molecule is in a crystal, it is binding to its neighboring molecules, and it gains some energy from that relative to when it is released in the water. On the other hand, when the molecule is released, it has entropy. It has the freedom to explore volume, and this creates a driving force that makes it favorable to move around in the liquid. So the question of dissolution is the same competition between energy and entropy that we have already discussed. For that reason, we can literally apply the same equation of the week that we did for

the phase changes. Namely, the solubility limit occurs when the interaction energy is equal to some constant times kBT . The physics is the same. The only thing that is different is the constant. In the case of phase transitions, the constant was $3/2$, but in the case of dissolution, the constant is going to depend on the situation.

3.7.2 The Equation of the Week Applied to Solubility

There is a way to find the constant for dissolution, which exposes the physics in more detail. The formula for the constant says that it is the logarithm of the volume that each sugar molecule takes up when it is released into the liquid divided by the volume that each sugar molecule takes up when it is in the solid, and this number in turn is divided by a number that we call z , which represents the number of neighbors that the sugar molecule has when it is in the crystal (Fig. 3.31).

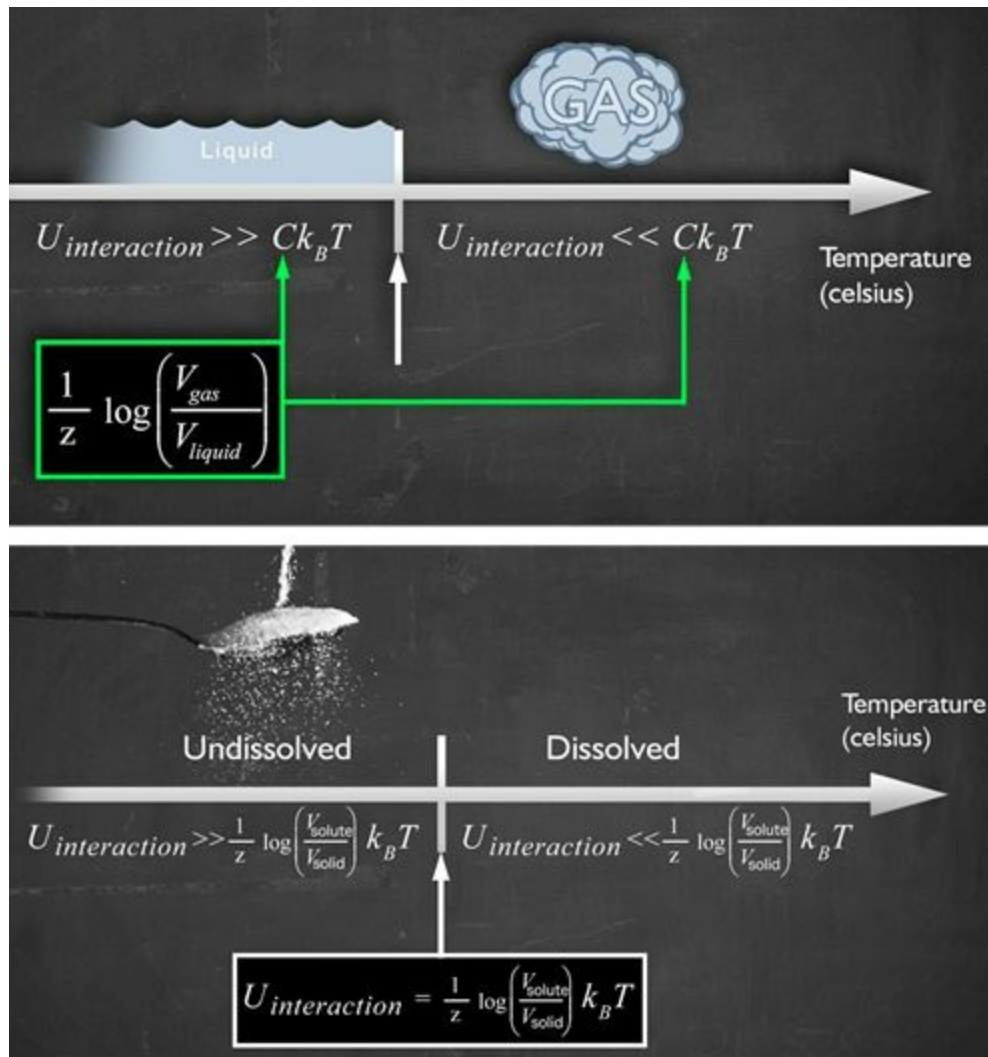


Figure 3.31 The dissolution of sugar in water is similar to a phase transition in that it is a competition between energy and entropy. Thus, the equation of the week can be applied, and the constant, C , can be expressed in terms of the volume the sugar molecules take up before and after dissolution.

The purpose of showing this formula is not so much to understand it in any detail, but rather to show the different factors that are involved. It is also

particularly useful if we wanted to take this one step further and find out what the concentration of the sugar in the water is, which is the question that prompted this discussion in the first place. That is, if you are drinking some type of soda, and most sodas are primarily sugar dissolved in water, what is the concentration of sugar in the soda? Could you make the soda even sweeter and, if so, how sweet could you make it? If we want to find the answer to the last question, we can solve for the concentration of solute in this formula and it gives us the expression below.

$$\text{Concentration}_{\text{solute}} = \text{Concentration}_{\text{solid}} e^{\frac{(-U_{\text{interaction}})(\# \text{ contacts})}{k_B T}}$$

This formula was first invented by Ludwig Boltzmann, a great physicist in the 19th century. It shows that the concentration of the dissolved sugar depends on the concentration of solid sugar, which is basically the density. And it also depends on the temperature and the interaction energy between molecules.

3.7.3 Solubility and Candy Making

It turns out that one aspect of this formula is particularly important for candy making, which is the fact that the concentration of the solute, i.e. the dissolved sugar, goes up quite substantially as the temperature increases. Figure 3.32 shows this same idea on a graph; it plots solubility of sugar as a function of temperature (Fig. 3.32). If you were chocked to learn earlier in this section that you can dissolve 2 pounds of sugar in 1 pound of water, you will be even more chocked when you study this plot and learn that if you increase the temperature to the boiling point of water, you can actually dissolve 4 pounds of sugar in 1 pound of water. The solubility actually goes up by a factor of two. And as the temperature increases even more, the solubility continues to go up further, until eventually, at some critical temperature, there is just sugar.

The fact that the solubility curve looks the way it does, and has the temperature dependence that we have described, is very important for candy making. Without this, we would not have candy as we know it. We will delve into the science of candy making further later on in this chapter.

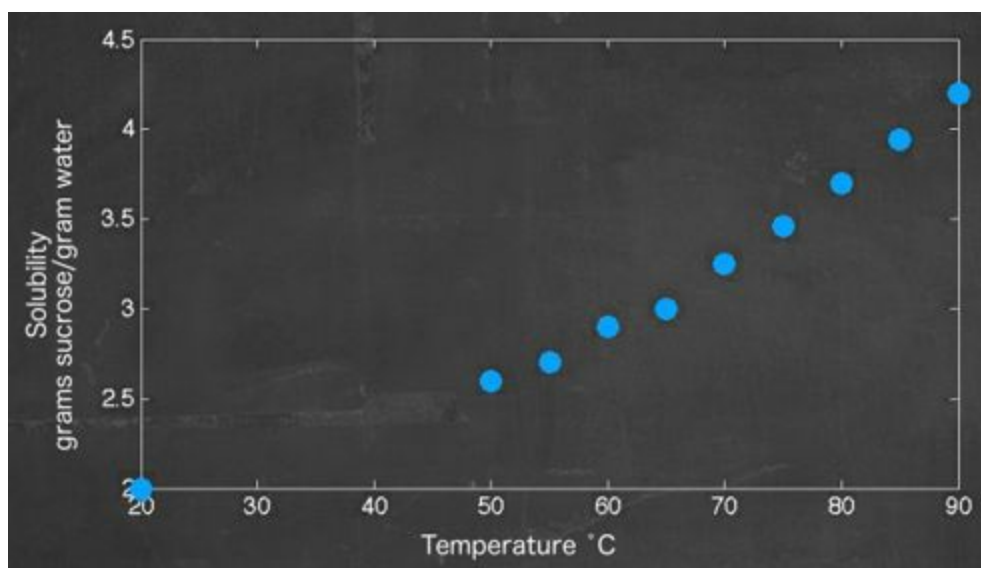


Figure 3.32 Solubility of sugar as a function of temperature.

Before leaving this topic, there is one final observation to make. We started out comparing the solubilities of sugar and salt, noting that whereas you can dissolve 2 gram of sugar per gram water, you can only dissolve $\frac{1}{3}$ grams of salt. Why are these numbers so different?

The reason in this case is peculiarly simple. Recall that the weight of 1 mole

of sugar is about 342 grams. And the weight of 1 mole of salt is about 58 grams. There is about a six-fold difference between the molecular weight of sugar and salt. Coincidentally, 2 grams and $\frac{1}{3}$ grams also differ by a factor of six. This means that when the maximum amount of sugar and salt is dissolved in water at room temperature, there is actually the same number of molecules in a given volume of each. Both solutions have the same number of molecules. This indicates that the difference in solubility is primarily an entropic effect, as opposed to an energetic effect. Interestingly, at higher temperatures than room temperature the difference in solubility is no longer six-fold. If you increase the temperature to 100°C the solubility of sugar doubles, whereas the solubility of salt does not. So at higher temperatures, the energetic effect starts playing a role in setting the solubility limit as well.

3.8 Phase Transitions of Solutions

When you dissolve one material in another, the properties of the final mixture will differ from the original. Even if you are nowhere near the solubility limit, a sugar-water or salt-water solution is going to have different properties than water alone. An important place where this comes up in cooking is when making ice cream.

The making of ice cream involves the dissolution of both sugar and salt. The actual ice cream is made by dissolving sugar in milk, where the milk primarily consists of water. The ice cream solution is then cooled to below freezing by immersing it in a solution of salt and water while blending. You can, of course, simply put the entire batch of ice cream mix in the freezer instead of using a salt-water solution, but it turns out that there are limitations in allowing the ice cream to freeze without simultaneously stirring related to the rate at which ice crystals form. For this reason a salt-water solution is often used, and it also perfectly illustrates the scientific concepts at work. So, how do the different properties of these two solutions, the sugar-water and the salt-water, affect the ice cream making process?

We already discussed the striking fact that you can dissolve six times more sugar than salt in water as measured by weight. We explained this difference as being caused by the different molecular weights of sugar and salt, and claimed that the number of molecules dissolved in both cases is the same.

3.8.1 Freezing Point Depression and Ice Cream

Imagine that you have two solutions, one of sugar and one of salt. They are both saturated so you cannot dissolve any more sugar or salt in them. Next imagine that we try to have these solutions undergo a phase transition of some type. Since we are focusing on ice cream at the moment, let's imagine that we are freezing them. We know that without the sugar or salt, the temperature at which the water becomes a solid is 0°C . This is the temperature at which the entropy of the water molecules is balanced by the sticking energy between the water molecules in the ice crystals (Fig. 3.33).

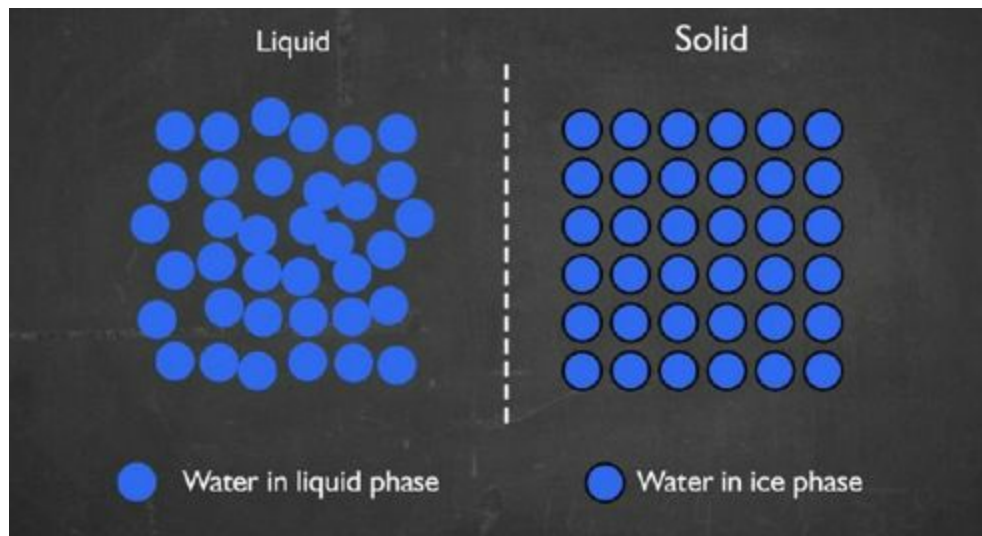


Figure 3.33 With no solutes, such as salt or sugar, added, water freezes at 0°C . In other words, this is the temperature at which entropy and energy are balanced.

If salt or sugar is added to the water, the solute molecules have an additional entropy. In other words, the total entropy of the solution is the entropy of the water molecules plus the entropy of the salt or sugar molecules. Hence, when you freeze the mixture, you have to stop the motion both of the water molecules and of the solute molecules. This requires a little extra energy than you would have had to give it otherwise. This extra energy leads to a phenomenon called freezing point depression. It is the notion that if you try to freeze a solution of salt or sugar water, you have to go to a lower temperature than if there were no salt or sugar. The lower temperature is needed to counteract the additional entropy and stop the solute molecules from moving (Fig. 3.34). The freezing point depression depends on the entropy of the solute, and, as such, the amount that the freezing point is depressed depends on the number of solute molecules per unit volume. The more solute molecules, the more the freezing point is

depressed.

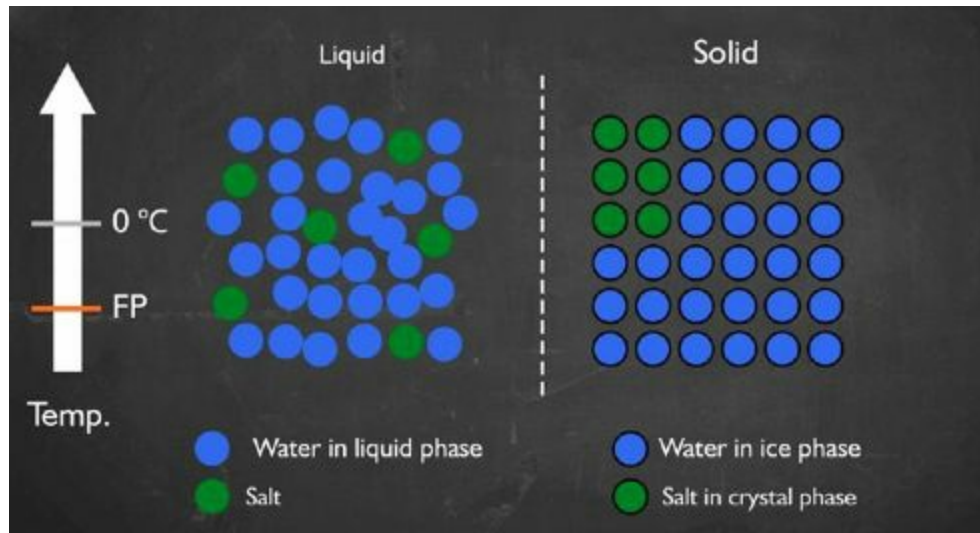


Figure 3.34 With solutes present in the water, the entropy will be larger than the entropy of a pure water solution. Thus it takes a greater reduction in energy to counteract the entropy, i.e. the temperature needs to be lowered below 0 °C for the solution to turn solid.

Freezing point depression is an important phenomenon in cold weather climates during the winter, where salt is frequently poured on the roads as a way to stop precipitation from freezing. Sprinkling salt on the roads tends to lower the freezing point enough so that roads and sidewalks don't freeze over and become slippery.

In the context of making ice cream, this raises a bit of a conundrum in the following sense: We add sugar to milk in order to make the ice cream sweet, but this lowers the freezing point. If you then try to freeze the sweet milk by surrounding it with ice, it will not freeze because the ice cream mixture has a lower freezing point than the melting ice. Somehow you have to get the material that surrounds the ice cream to have a lower freezing point than the ice cream itself. A way to do that is to add salt.

If you add salt to water, the freezing point will be depressed. Given that you have added enough salt, the salt-water solution, when frozen, will be at a lower temperature than the freezing point of the milk-sugar mixture. This is because there are more salt molecules per volume in the salt-water solution than there are sugar molecules in the sugar-water solution – recall that it is the number of molecules that determines the extent of the freezing point depression. In order to make sure that the freezing point for the salt-water solution is low enough, ice cream recipes typically make you saturate the water with salt. So you add $\frac{1}{3}$ grams of salt per gram of water, and this

ensures that the temperature of the salt-water gets lower than the freezing point of the sugar-water solution. The amount of sugar needed for our taste buds to detect something as being sweet is considerably lower than the solubility limit of sugar. Even a can of soda, which tastes incredibly sweet, contains much less sugar than the maximum amount that could be dissolved. So the amount of freezing point depression that results in the ice cream mix will not be nearly as much as that of the salt water. And that is why ice cream recipes tend to work.

3.8.2 Boiling Point Elevation and Candy Making

Solutes not only lower the freezing point of mixtures, they also raise the boiling point. The underlying physics is very similar, and the phenomenon is equally important for cooking. Let's return to the example where we dissolved 2 pounds of sugar in 1 pound of water. If we boil that mixture, the water molecules are going to boil off, and the sugar molecules are going to stay behind. Thus, the number of water molecules that the sugar is dissolved in is going to decrease. So the entropy decreases since there is less space for the sugar molecules to occupy (Fig. 3.35). This has the consequence that in order to boil the solution, it has to be heated to a hotter temperature than if there were no sugar in the water. The phenomenon is called boiling point elevation. It is analogous to freezing point depression, and it occurs in all cases where solutes are dissolved in a solvent.

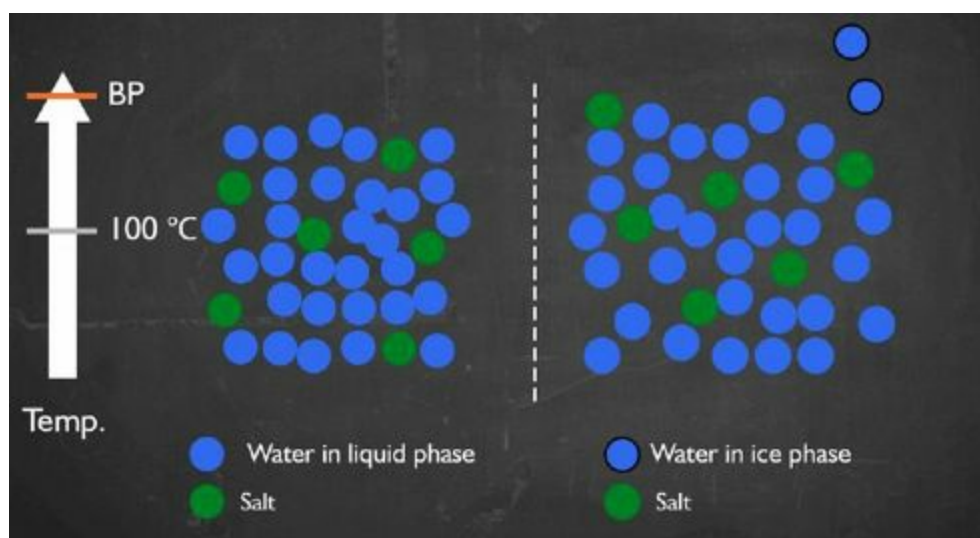


Figure 3.35 In a sugar-water solution, only the water molecules will boil off, leaving the sugar molecules behind. Hence, as the temperature increases, the sugar molecules have less and less space and the entropy decreases. As a result, you have to add more and more energy, i.e. increase the temperature, to make the solution boil.

How is boiling point elevation important for cooking? In order to examine at least one instance of this, let's observe a plot of the boiling point of a sugar-water mixture as a function of the concentration of dissolved sugar (Fig. 3.36). With no sugar dissolved, the boiling point, as predicted, is 100°C. But as the mass of sugar increases, the boiling point goes up dramatically. When around 80% of the weight of the solution is sugar, the boiling point has gone up to 110°C. As you continue to increase the weight percent of

sugar, the boiling point goes up more and more until at about 100% sugar, the boiling point is 150°C. So the boiling point was elevated by about 50°C between solutions with no sugar and essentially all sugar.

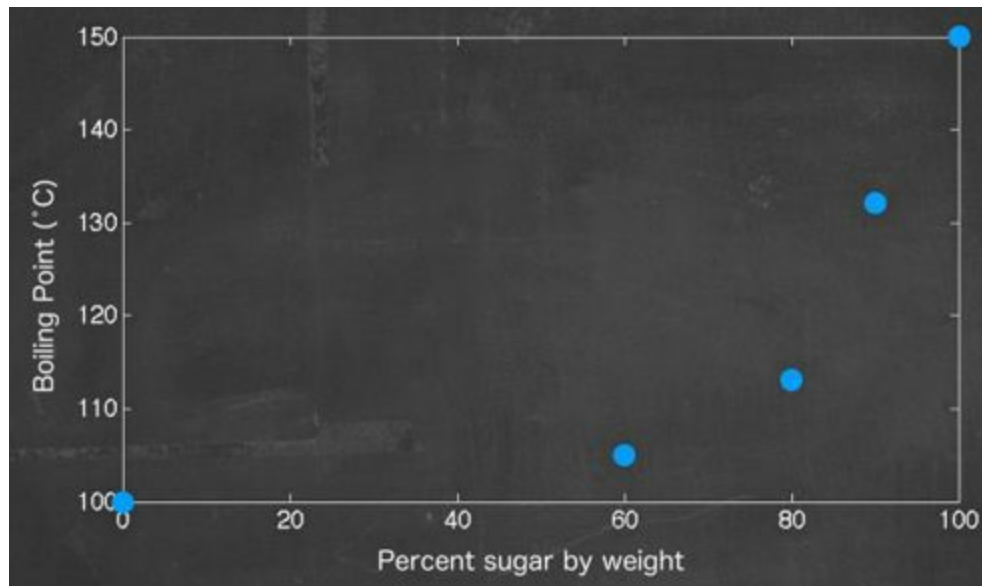


Figure 3.36 The boiling point of a sugar water mixture as a function of sugar concentration.

This plot contains within it the secrets of candy making. Why? Typical candy recipes involve adding large amounts of sugar to water and then boiling the mixture. When the mixture boils, some of the water evaporates and the percentage of the sugar in the mixture increases. As a result the boiling point is elevated according to the plot in Figure 3.36, which has the effect that even more water boils off, which in turn raises the boiling point even more, causing even more of the water to boil off, and so on and so forth. So over time, the mixture will get hotter and hotter, and you can essentially tune the percentage of sugar in the water by closely monitoring the boiling point. Indeed, when cooking candy you typically use a candy thermometer to very accurately measure the temperature of the mixture. What the plot in Figure 3.36 shows you is that what you are really controlling with the temperature is the weight percent of sugar that is in the mixture. The weight of sugar controls the texture of the sugar, which in turn controls what can be made out of the sugar, and this is at the very core of candy making.

3.9 How to Derive the Equation of the Week

We will end this chapter on a more advanced note by revisiting and re-deriving the equation of the week. Our strategy will be to apply the bulk perspective of balancing energy and entropy, in order to see if we can arrive at the same equation, and, in the process, see if we cannot gain a new perspective on the equation itself.

The first step in this derivation is to equate the following two quantities: The change in entropy of a system when it undergoes a phase transition from a liquid to a gas. And the change in energy of the same system when it undergoes the same phase transition.

Let's focus on the energy first. In a liquid, the molecules are close to each other and touching, whereas in a gas, the molecules are far from each other and not touching. The total energy, E_{liquid} , in a liquid is the number of molecules, N , times the number of bonds per molecule, z , times the interaction energy per bond, U_{int} .

$$N = \text{\#molecules}$$

$$z = \text{\#bonds/molecule}$$

$$U_{\text{int}} = \text{interaction energy/bond}$$

$$E_{\text{liquid}} = NzU_{\text{int}}$$

The total energy, E_{gas} , in a gas is essentially zero, because the molecules are whizzing around, and essentially do not touch each other at all. So the change in energy, ΔE , is just given by the energy from the liquid.

$$E_{\text{gas}} = NzU_{\text{int}} = 0$$

$$\Delta E = E_{\text{liquid}} - E_{\text{gas}} = NzU_{\text{int}}$$

We now have to set the change in energy equal to the change in entropy. The entropy at any given time can be obtained by multiplying kBT times the number of molecules, N , times the logarithm of the number of

configurations that are available to each molecule.

$$\Delta \text{Entropy} = Nk_B T \cdot \ln(\# \text{ configurations})$$

How do we find out the number of configurations available to each molecule? This is admittedly tricky. Luckily, what we really need to find is the in entropy between the gas and the liquid. And thanks to the fact that the difference between the logarithms of two numbers is the same as the ratio of the numbers, we find the following expression for the change in entropy.

$$\begin{aligned} \Delta \text{Entropy} &= Nk_B T \cdot [\ln(\# \text{ configurations}_{\text{gas}}) - \ln(\# \text{ configurations}_{\text{liquid}})] \\ &= Nk_B T \cdot \ln \frac{(\# \text{ configurations}_{\text{gas}})}{(\# \text{ configurations}_{\text{liquid}})} \end{aligned}$$

Finally, setting the change in energy and the change in entropy equal to each other, we get the following expression.

$$NzU_{\text{int}} = Nk_B T \cdot \ln \frac{(\# \text{ configurations}_{\text{gas}})}{(\# \text{ configurations}_{\text{liquid}})}$$

If we just cancel out the number of molecules, N, we get a formula that starts to look a lot like our equation of the week.

$$U_{\text{int}} = \frac{k_B T \cdot \ln \frac{(\# \text{ configurations}_{\text{gas}})}{(\# \text{ configurations}_{\text{liquid}})}}{z}$$

The only difference between the equation of the week and the expression above, is the ratio, the logarithm divided by z. And, in fact, this is exactly what we were previously referring to as the constant, C.

$$C = \frac{\ln \frac{(\# \text{ configurations}_{\text{gas}})}{(\# \text{ configurations}_{\text{liquid}})}}{z}$$

What if we wanted to calculate the constant, C ? The most difficult step would probably be to estimate the ratio of the number of configurations in the liquid versus the gas. There may be a way around this though if we think about it in terms of volume. In a liquid a molecule is confined to where it is, whereas in a gas it can move around everywhere. A good proxy for the ratio of configurations would therefore be the ratio of the volumes of the liquid and the gas. So what we need to do is to calculate the volume of a fixed number of atoms of the gas and divide it by the volume of a fixed number of atoms of the liquid.

$$\ln \frac{(\# \text{configurations}_{\text{gas}})}{(\# \text{configurations}_{\text{liquid}})} = \ln \frac{(V_{\text{gas}})}{(V_{\text{liquid}})}$$

Let's consider a mole of each. It turns out that at 1 atm, the volume of a mole of gas is 22.4 liters, which corresponds to 22,400 cm³. The corresponding volume for a liquid can be obtained by dividing the molecular weight, 18 g/mol, by the density of water, 1 g/cm³. This tells us that 1 mole of liquid water has a volume 18 cm³. If we want to compute the constant, C , in our formula, we need to take the logarithm of the ratio of 22,400 cm³ divided by 18 cm³. It turns out that this number is about 7.

$$\ln \frac{(\# \text{configurations}_{\text{gas}})}{(\# \text{configurations}_{\text{liquid}})} = \ln \frac{(V_{\text{gas}})}{(V_{\text{liquid}})} = \ln \frac{(22,400 \text{ cm}^3)}{(18 \text{ cm}^3)} \approx 7$$

So the constant, C , is ~ 7 divided by z , which is the number of contacts per particle. The number of contacts per particle varies, but it is usually something like 5, 6, or 7, which is why the constant turns out to be about 1. The number we gave you was 3/2, which is what you would find with a slightly more careful accounting of the various factors.

$$C = \frac{\ln \frac{(\# \text{configurations}_{\text{gas}})}{(\# \text{configurations}_{\text{liquid}})}}{z} \approx \frac{7}{\sim 5,6,7}$$

Hopefully this derivation shows you the essence of the physics behind the equation of the week. An important point to make is that the constant, C , is

going to depend on the conditions. For example, in the discussion above we used the volume that gas occupies at 1 atm, but if the pressure changes, the volume of the gas will also change, which ultimately changes the constant.

Chocolate

TABLE OF CONTENTS: CHOCOLATE

C.1 The Different Phases of Chocolate

[C.1.1 Structure and Melting Behavior of Cocoa Butter](#)

[C.1.2 Packing and the Six Crystalline Phases of Cocoa Butter](#)

C.2 The Science of Chocolate Tempering

[C.2.1 The Challenge of Making Phase Five Chocolate](#)

[C.2.2 Seeding with Phase Five Nuclei](#)

CHOCOLATE

C.1 The Different Phases of Chocolate

C.1.1 Structure and Melting Behavior of Cocoa Butter

The science of chocolate has much in common with the science of fats, which we discussed in Chapter 3. This is because the primary component of chocolate is a fat: cocoa butter. Similar to other common fats in food, cocoa butter is a triglyceride, which means it has three fatty acid chains connected by a glycerol molecule (Fig. C1). It is the interactions between these molecules that give rise to the phase behavior of fats in general and, as we will see, of chocolate. As opposed to other common food fats though, cocoa butter has a number of interesting and special characteristics. We will highlight these below.

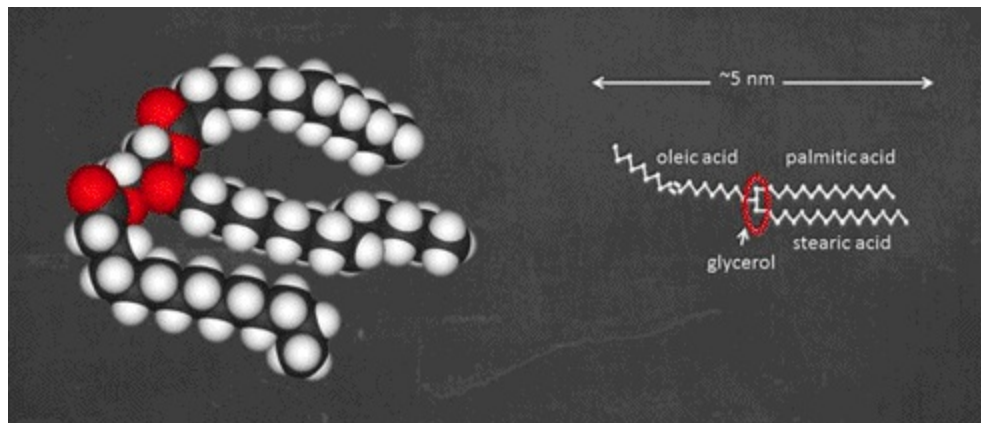


Figure C1 Cocoa butter consists of triglycerides, which are built by a number of different fatty acids such as oleic acid, palmitic acid, and stearic acid.

Chocolate as we know it is usually a solid – if you hold a piece of chocolate in your hand, it does not melt, and if you break it, it snaps. However, if you put the chocolate in your mouth, it tends to melt and turn into a liquid. So one of the essential properties of chocolate is that it melts in your mouth, but not in your hand. This is possible because the melting temperature of chocolate happens to occur right between the temperature of your hand and your mouth. If you are healthy, your mouth is around 37°C , and your hand, touching the colder air, tends to be colder, maybe around 28°C . So there is a 10 degree temperature difference between your mouth and your hand,

and the melting temperature of cocoa butter falls in this window.

As you recall, a fat's melting temperature has its origin in the molecular structure of the triglycerides it is composed of. We learned that fats made of saturated fatty acid chains as a general rule have higher melting points than unsaturated fats since they are able to pack more closely together (Fig. C2). The triglycerides in cocoa butter consist of palmitic, stearic, and oleic acid. Palmitic and stearic acid are both saturated fatty acids and tend to make up two parallel arms of the molecule. Oleic acid is unsaturated, and tends to point away from the two arms of stearic and palmitic acids (Fig. C1). Ultimately, it is the packing behavior of these molecules as a function of temperature that gives rise to the science of chocolate.

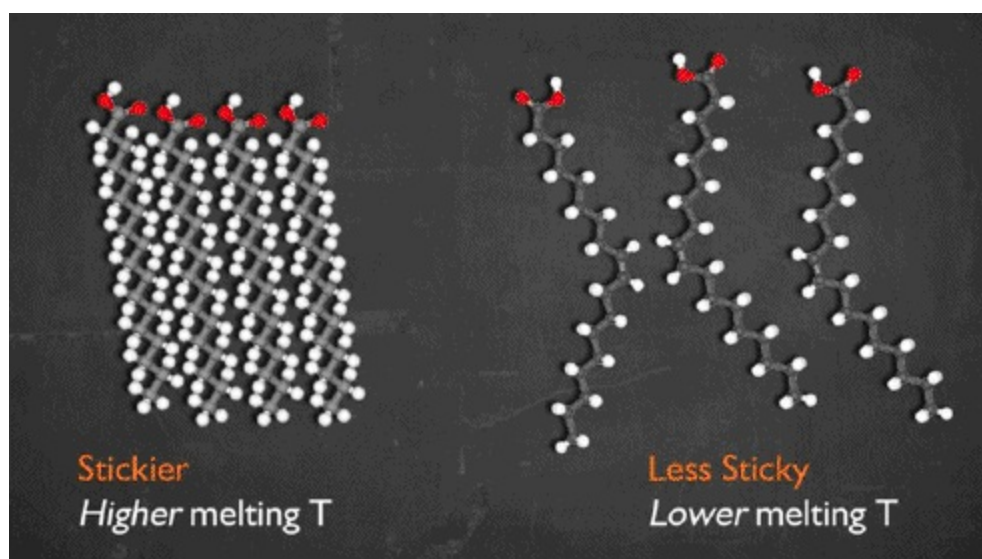


Figure C2 The chemical structure of the fatty acids in a fat molecule affects the phase behavior. Saturated fatty acids are straight, which allows them to pack densely and form strong intermolecular bonds. Unsaturated fatty acids have a kinked structure and therefore cannot pack as densely. It takes higher temperatures to break the intermolecular bonds of a saturated fatty acid compared to an unsaturated fatty acid, and this results in a higher melting point.

Figure C3 shows a phase diagram of cocoa butter compared to other common fats. Olive oil, as discussed in Chapter 3, becomes a solid at about -6°C ; butter at around 32°C . Unlike these two fats, cocoa butter does not have a sharp melting temperature, but rather a range from 27 to 35°C . This range is due to cocoa butter being a much more complex material than olive oil, a property that also ends up leading to a much richer phase behavior. We have talked about fats having a liquid phase and a solid phase, and most fats only have one solid phase. Cocoa butter on the other hand, has no less than six different solid phases, each corresponding to a different

crystalline structure. Thus, in order to make the chocolate that we know and love, we not only need to make the cocoa butter undergo a simple liquid to solid transition. We must also understand and manipulate all of the different crystalline phases.

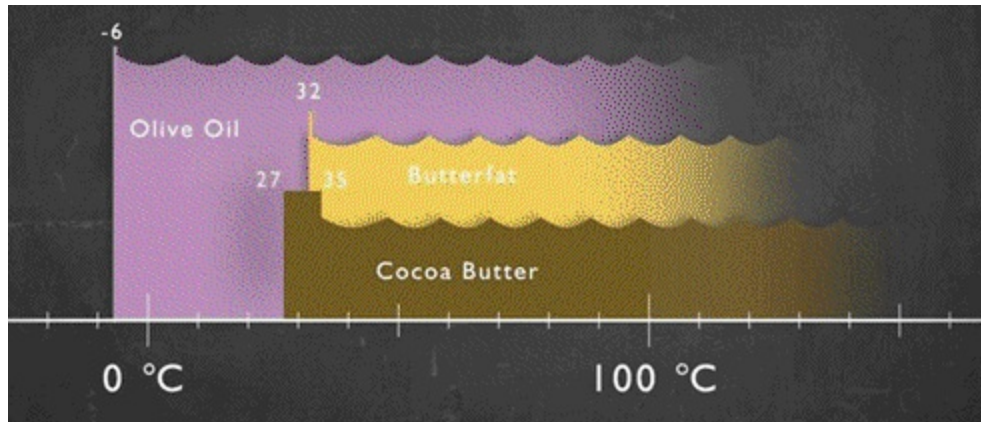


Figure C3 Phase diagrams for olive oil, butter fat, and cocoa butter.

C.1.2 Packing and the Six Crystalline Phases of Cocoa Butter

How are all of these different solid phases possible? The answer lies in the different ways the fat molecules can be packed together. If you recall that a triglyceride molecule tends to have two fatty acid chains pointing in the opposite direction of a third one, you can imagine different ways that the molecules could be stacked together. There are at least two ways to do it. One would be to stack the single chain adjacent to the double chains in the layer before it. Thus the single chain would line up with the double chains, and this pattern would alternate from layer to layer as seen in Figure C4. This is called double chain packing.

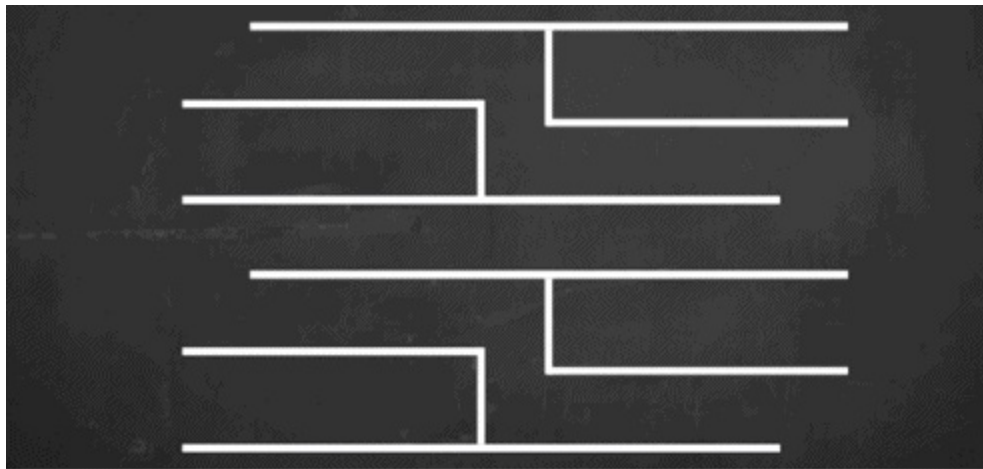


Figure C4 Cartoon of double chain packing of the triglycerides in cocoa butter.

Another way to stack the triglycerides is where the double arms from two different triglycerides are stacked, and the left-over single arms are stacked on top of each other (Fig. C5). This is called triple chain packing. Each different way of packing results in different interaction energies. Double chain packing will have a different overall interaction energy than triple chain packing, and which of the interaction energies ends up being higher depends on the properties of the fatty acid chains. For example, if the single fatty acid chains are saturated, this will lead to a different interaction energy in double versus triple chain packing. As true as this reasoning is though, the actual stacking behavior in a piece of chocolate is complicated to predict based on the nature of the fatty acid chains alone. It is really best determined empirically by studying the phases of fats under a very powerful microscope.

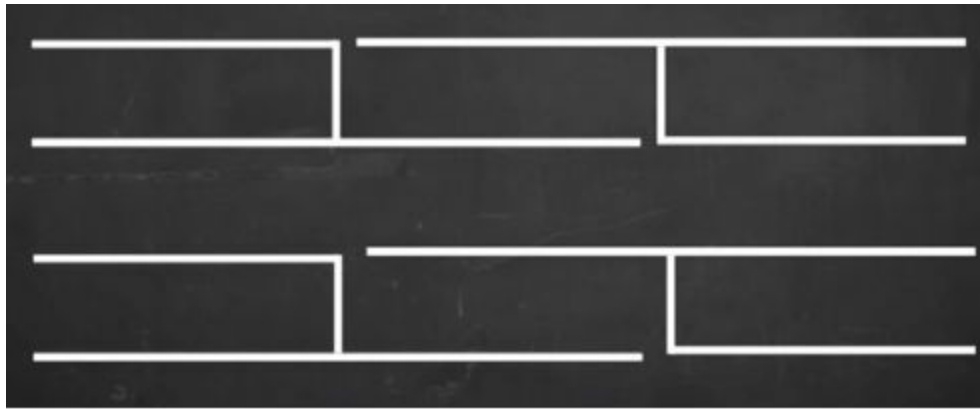


Figure C5 Cartoon of triple chain packing of the triglycerides in cocoa butter.

Figure C6 shows the phase diagram of chocolate. Each of the six temperatures corresponds to the melting point of a different crystal phase. Phase 1 has the lowest melting temperature, phase 2 the second lowest and so on. Each phase is composed only of triglyceride molecules that are packed in a certain way. Since each packing corresponds to a unique interaction energy, the melting temperatures end up being different as well. So each phase will melt entirely at its unique melting temperature, and the transition is sharp, rather than occurring over a range of temperatures.

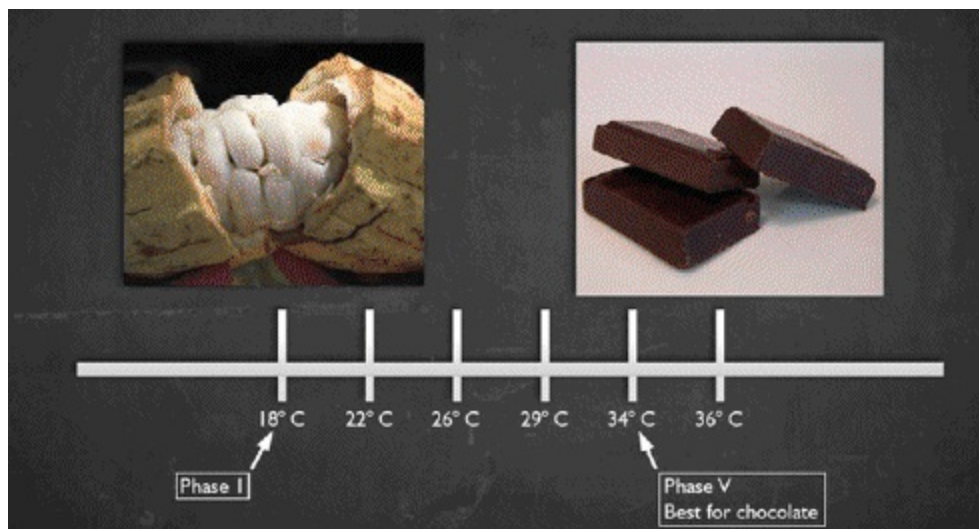


Figure C6 Phase diagram of chocolate. There are 6 different crystalline phases of cocoa butter, each corresponding to a different type of packing of the fat molecules. Each crystalline phase has a unique melting point.

Based on this phase diagram, if you wanted to make a material that melts in your mouth, which is at 37° C, but not in your hand at about 28° C, you would be left with phases five and six. Phase four might also work, but only barely. It turns out that phase five indeed is the phase that chocolate as we know it is usually made from. The other phases do not produce the same

desirable glossy appearance and snap when you bite into it.

You can see then why it might be hard for inexperienced home chefs to make good chocolate in their kitchens: once the chocolate is melted, you have to find a way to crystallize it into phase five only, without contaminating it with any of the other phases. The complexities of making chocolate are all associated with this issue, and this is what we will discuss next.

C.2 The Science of Chocolate

Tempering

C.2.1 The Challenge of Making Phase Five Chocolate

Before looking at an actual recipe, let's think about how we would go about making chocolate that is made only out of phase five and none of the other phases. One way might simply be to melt chocolate and cool it down to a temperature just below 34°C , i.e. the temperature at which it is supposed to transition to phase five, and then wait for it to solidify. If left at this temperature for long enough, one would imagine that the right phase would eventually form. This, it turns out, is not a bad prediction.

One problem with this method, though, is that it takes a very long time. It can take days or longer to make phase five chocolate this way. By contrast, water turns solid much more quickly when cooled to below 0°C . So why does phase five chocolate take so much longer? Once again, the reason can be found in the six different crystalline phases. The fact that there are so many ways for the triglyceride molecules to arrange themselves, makes it take much longer for them to find the best arrangement at any given temperature. The "best way" is determined by the arrangement that results in the overall lowest energy of the system at a given temperature. Eventually, the chocolate will find this lowest energy, but it may take a very long time to get there.

The molecular search for the lowest energy is similar to the following scenario: Imagine that you were deposited randomly somewhere in a big mountain range, and told to go and find the lowest point. With no elevation map available, you would look around and go to the lowest point you saw. Once there, you might realize that there are other mountains close by and possibly other, even lower, valleys hidden among them. In order to get to another valley you would need to climb up the other mountains and down into the valley. Once there you would check if the height were lower or higher than the first valley, and you would keep doing this until you found the lowest valley. If you were in a very rugged mountain range, this would

take a while, whereas if you were in a range with only one tall mountain and one valley, it would be easy. The mountain range represents the energy landscape of all the different conformations the cocoa butter molecules might find themselves in. The mountain peaks correspond to very unstable, high energy conformations, and the valleys correspond to stable, low energy conformations. Using this analogy, cocoa butter is a molecule with a rather rugged mountain range, whereas the mountain range of water is not as rugged. Hence it takes longer for the cocoa butter molecules to search for the lowest point, whereas for water the process is much faster.

Other than taking a long time, there is another problem with the method of simply cooling chocolate to below 34°C and waiting. If you don't wait long enough, phase five will indeed form, but once cooled to room temperature, which is the temperature at which we normally store chocolate, it will transition to phase four. Phase four is a much softer material than phase five, but more importantly it isn't nearly as stable. Hence, over time, phase four slowly transitions back to phase five. This, of course, was exactly what we wanted in the first place, and all should be well. However, it turns out that phase five is not only more stable, it is also a much denser material than phase four. The molecules are more tightly packed together. Thus, as the molecules contract in going from phase four to phase five, the material excretes a liquid form of cocoa butter which ends up on the outside of the chocolate. The liquid is visible as a white coating on the surface, and is usually referred to as fat or chocolate bloom (Fig, C7). This is another reason home cooks may have difficulty making chocolate – it is hard to keep it at the right temperature for long enough that phase five forms stably.

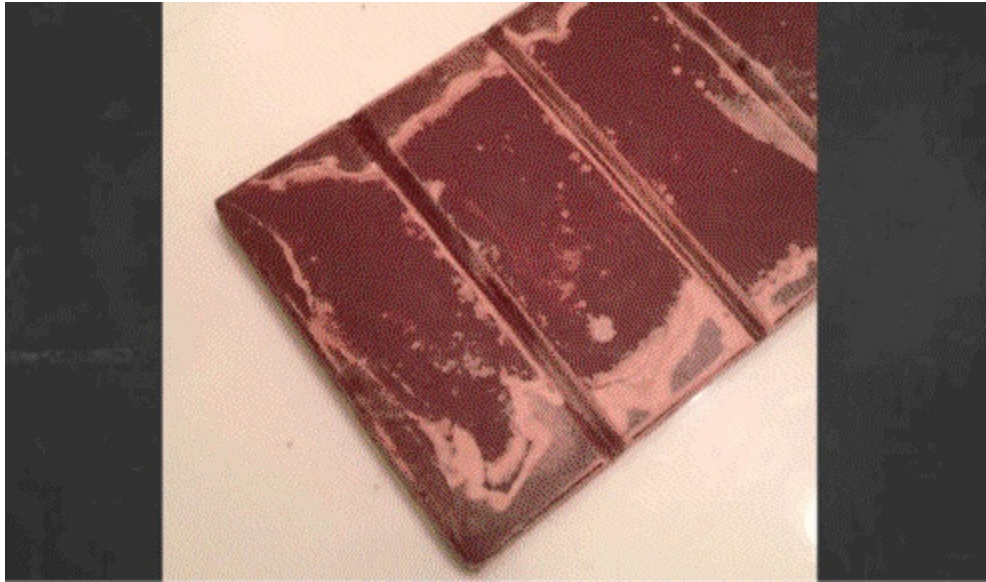


Figure C7 Over time a piece of chocolate may develop chocolate bloom.

C.2.2 Seeding with Phase Five Nuclei

Chocolate making, as done in practice, is closely related to the kinetics of crystal formation which we discussed in the context of phase transitions in Chapter 3. We learned then that simply being in the range of a phase diagram where crystals are supposed to form, doesn't necessarily mean they will. Crystal formation takes time. It takes time because the nuclei of crystals are difficult to form. Once that has happened, the nuclei quickly grow into much larger crystals. We can speed up this process by introducing nuclei to a solution, thus by-stepping the time consuming nucleation process. In the context of chocolate, each of the six crystalline phases corresponds to a different type of nuclei. If you were to take nuclei of a certain phase and introduce them to chocolate, you would, as long as the temperature were not such that it were completely disadvantageous for that phase to form, promote the formation of that phase of chocolate.

This suggests a strategy of how to make stage five chocolate in a robust enough fashion that it can be done quickly in your kitchen or on an industrial scale. If we can only make lots of little nuclei of phase five, introduce them to a solution of molten chocolate, and let it cool, the nuclei will form bigger crystals of phase five, until, eventually, all of the chocolate is in that phase.

There are two ways of getting phase five crystals. One way is to heat up chocolate, cool it to the temperature range where phase five is favored, and let it sit for a while so that lots of little nuclei of stage five form. If you cool this solution, the nuclei will grow into larger crystals of phase five chocolate at a rate that is much faster than if you had left the solution at the higher temperature. The issue with this strategy is that there must be enough nuclei of phase five and no contamination by any of the other phases. If there are not enough crystals, you get the scenario described above where the chocolate will transition to phase four at the lower temperature, only to transition back to phase five while producing undesirable fat bloom.

A second way of getting phase five crystals is to melt chocolate and then, while keeping it in the right temperature window, add solid chocolate pieces of the type you want. You can get a nice chocolate bar and crumble it into the molten chocolate so that it forms little nuclei that larger crystals can grow from. Many chocolate tempering recipes, both industrial and for the home cook, often involve a combination of both of these methods.

There are other complexities to manipulating crystal formation that we will not emphasize here. It is necessary, for example, to stir the chocolate as the crystals are forming because it both accelerates the growth of the crystals, and also tends to break apart weaker crystals that would result in less stable large crystals.

All in all, if the tempering recipe is followed correctly, you will end up with phase five chocolate. The small caveat to this is that phase six is actually even more stable than stage five. So if chocolate in phase five sits around for long enough without being stored according to protocol, it will eventually form phase six. Both phase five and phase six are triple chain packings, which is the most stable packing there is for cocoa butter. So one strong solid is transformed into another strong solid, and that takes a long time to happen. It is a much slower process to go from phase five to six than from phase four to five because phase five is already a low energy phase. Once the transition does occur though, you will see the same evidence in the form of fat bloom that we discussed above. This is again because phase six not only is more stable than phase five, but also more dense. So as the chocolate transforms from one phase to another, it excretes liquid cocoa butter that coats the surface while the chocolate itself also changes into a much harder, less appetizing texture. You will have seen it if you ever kept chocolate around the house for too long.

CHAPTER 4

Elasticity

TABLE OF CONTENTS: 4

4.1 What is Elasticity?

[4.1.1 Mouthfeel and Elasticity](#)

[4.1.2 Elasticity of a Spring](#)

[4.1.3 Elasticity of Foods](#)

4.2 Microscopic Origins Of Elasticity

[4.2.1 The Units](#)

[4.2.2 Equation of the Week](#)

4.3 Applications to Steak

[4.3.1 Elasticity of Raw and Cooked Steak](#)

[4.3.2 Cross-link Distances in Raw and Cooked Steak](#)

4.4 The Elasticity of Strudel Dough

[4.4.1 The Gluten Network](#)

[4.4.2 Deconstructing the Strudel Recipe](#)

4.5 Elasticity of a Candy Apple

[4.5.1 Three Important Facts About Sugar](#)

[4.5.2 The Candy Thermometer](#)

[4.5.3 A Microscopic View](#)

[4.5.4 The Role of Glucose](#)

[4.5.5 Lower Temperature Thought Experiment](#)

4.6 Summary

[4.6.1 Steak](#)

[4.6.2 Chocolate](#)

[4.6.3 Candy](#)

4.6.4 Strudel

CHAPTER 4

4.1 What is Elasticity?

4.1.1 Mouthfeel and Elasticity

Imagine you eat a piece of food, and, in doing so, you are trying to decide if you like it. Whether you are aware of it or not, you are probably considering a whole range of different aspects of the food. Taste may be the most obvious one, but a food's mouthfeel, smell, and visual appeal are just some of the other characteristics you are taking into account as you are trying to make up your mind.

Each of these characteristics is complex and can be discussed at length. A food's mouthfeel, for example, can be described in a myriad of ways. If we wanted to describe it scientifically though, we could do so rather effectively by looking at just a few properties that scientists typically use when describing soft matter materials. In the case of solid foods, this property is elasticity, the topic of this chapter. In the case of liquid foods, it's viscosity — we will turn to this in Chapter 7.

All foods have a texture, and as we cook a food, the texture often changes. A good example of this is cooking a steak. The texture of a steak changes as it goes from raw to cooked. A rare steak is typically relatively easy to chew, a medium steak is a little tougher, and a well-done steak is much harder to chew. For reasons that we will discuss in this chapter, the meat becomes tougher and harder to bite down on as we cook the steak for longer periods of time, i.e. the elasticity changes. In scientific terms, we say that the elastic modulus of the food increases as we cook it.

Sometimes, changing the texture of a food is one of the main objectives in cooking it (using our broader definition of cooking from Chapter 2). We often closely associate a particular texture with a particular food. Chocolate is an excellent example of a food we manipulate in many different ways to achieve different textures, each needing to be just right for the particular version of chocolate we have in mind. Chocolate mousse, for example, is supposed to be light and airy. It's supposed to have such a low elastic modulus that you hardly have to chew it at all. A chocolate bar, however, is supposed to be much stiffer, and real chunk chocolate, a really good Belgian chocolate, is supposed to be yet stiffer, i.e. have an even higher elastic

modulus.

So the elastic modulus is a measurement of how stiff or squishy a material is. The higher the elastic modulus, the stiffer the material. It is worth noting that this definition of elasticity may seem unintuitive at first glance. The everyday usage of the term elasticity implies objects that are stretchy, springy and pliable. Thinking in scientific terms though, these flexible objects will have smaller elastic moduli than objects that are typically, in common terms, not thought of as elastic at all. Thus a piece of firm tofu will have a higher elastic modulus than a piece of soft tofu, an ice cube will have a higher elastic modulus than a piece of jello, and so on (Fig. 4.1). In the next section, we will discuss the origin of elasticity in more detail.

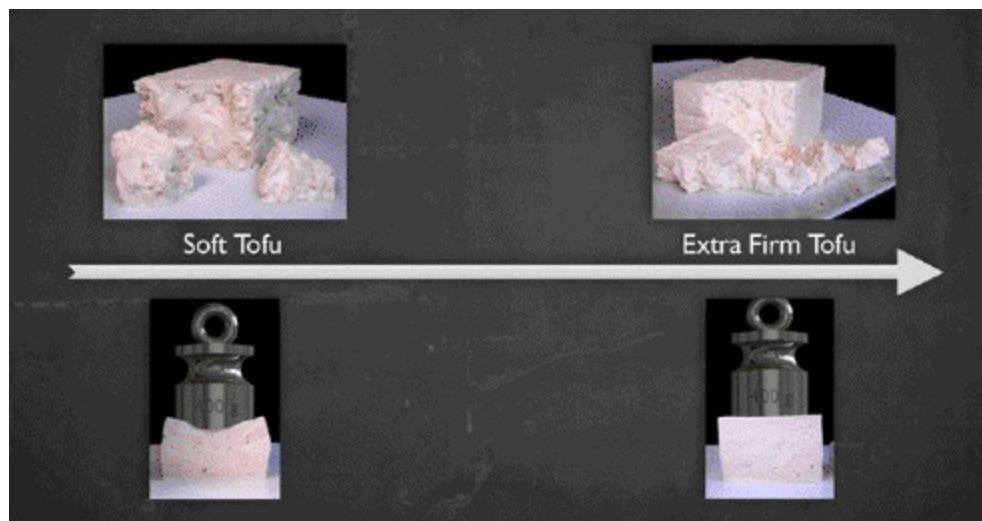


Figure 4.1 Tofu has different elasticities, ranging from soft tofu to extra firm tofu. Firm tofu has a higher elastic modulus than soft tofu, and consequently compresses less than soft tofu.

4.1.2 Elasticity of a Spring

To understand elasticity, let's start in the simplest way. Let's start with a spring. If we take a spring of a certain length, L_0 , and we hang a weight on the end of it like in Figure 4.2, the spring lengthens. It becomes longer by a certain amount. The change in length, the ΔL , is determined by two things: how heavy the weight is, and how springy the spring is.

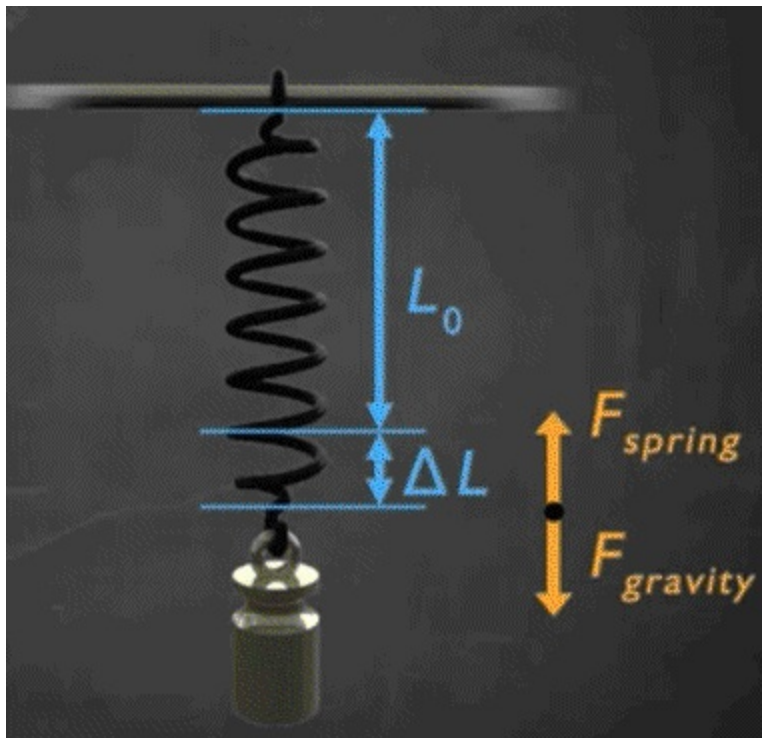


Figure 4.2 Hanging a weight from a spring with length, L , causes it to elongate by some distance, ΔL . The weight is experiencing a downward force, $F_{gravity}$ and an upward force, F_{spring} . The forces are equal but opposite so that the net force on the weight is zero.

When placing the weight on the spring, it may initially bounce up and down a little, but once it stops moving, the forces on the weight are balanced. This means that there is no net force on the weight. I.e. if we add up all the forces acting on it, they would equal zero. In this case, the weight is being pulled down by the force of gravity, and the spring is exerting an equally large force upwards, preventing the weight from falling to the ground. If we know the mass of the weight, we can figure out what the downward force from gravity is; remember that force equals the mass times gravity, $F_{spring} = mg$. And since the forces are balanced, the upward acting force from the spring must be the same but opposite, i.e. $-mg$, the minus sign indicating that the force is acting in the opposite direction.

$$F_{spring} = -F_{gravity}$$

$$F_{spring} = -mg$$

The same reasoning applies if we, instead of lengthening the spring, compress it by putting the weight on top of it like in Figure 4.3. Now, the spring gets shorter. It gets shorter by a given amount, ΔL . Again, ΔL is related to how heavy the weight is and how springy the spring is. Since the forces must be balanced, the force due to the weight must exactly equal the force pushing upwards from the spring. The spring always exerts a restoring force. It always tries to bring itself back to its original length.

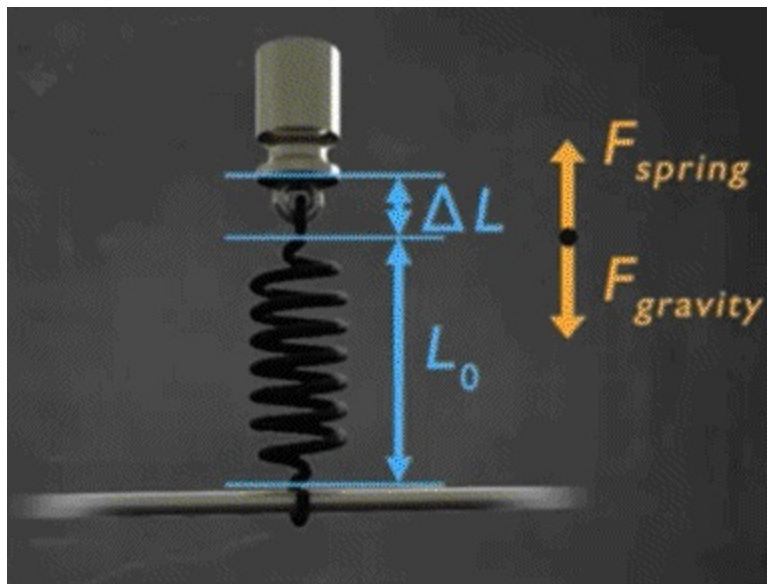


Figure 4.3 When a weight is placed on top of a spring, instead of hanging below it, it causes the spring to compress rather than elongate. The weight is still experiencing a net force of zero.

Some springs are more flexible than others. A very stiff spring will be able to push back on the weight without a very large difference in ΔL . By contrast, if the spring is loose and flexible, the spring will extend or compress by a large amount when placing a weight on it. The forces in these cases are the same, but the effect on the length of the spring varies depending on the inherent ability of the spring to push back. We call this the spring constant. The larger the spring constant, the larger force it takes to extend the spring by a given length. So a stiff spring has a very large spring constant, and a flexible spring has a small spring constant.

This relationship between the force of the spring and the change in length is expressed by Hooke's Law:

$$F_{spring} = -k\Delta L$$

Hooke's Law says that the force acting on the weight from the spring is linearly proportional to the change in length and to the spring constant, k . Just as above, the minus sign arises since the force from the spring is a restoring force acting in the opposite direction of gravity.

As you see, we now have two equations for the force from the spring,

$$F_{spring} = -mg$$

$$F_{spring} = -k\Delta L$$

By setting the forces equal to each other, we can calculate what the spring constant of a particular spring is. All we have to do is determine what the mass of the weight is by weighing it, and then measure the change in length as we hang or place the weight on the spring. We can then solve for the spring constant, k , by dividing the force by the change in length:

$$-k\Delta L = -mg$$

$$k = \frac{mg}{\Delta L}$$

4.1.3 Elasticity of Foods

The elastic modulus of a food is the equivalent of the spring constant for a spring, and we can use the same reasoning as above to figure out what it is.

For example, if we want to measure the elastic modulus of a piece of steak, we would place some weight on it and measure how much the steak compresses. In the case of food, there are two additional considerations though. The first consideration is that the area of the food matters. You probably know this intuitively: if you place the weight on a small piece of food it will compress a lot, but if the food is larger and the weight can be absorbed by a larger area, then the food will compress less (Fig 4.4).

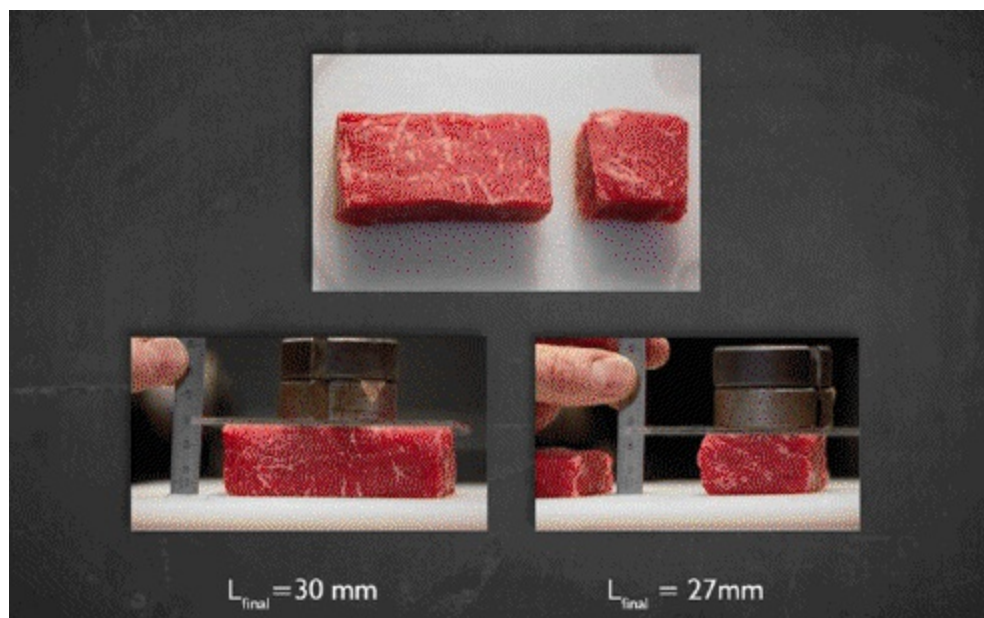


Figure 4.4 A steak with a large area will not compress as much as a steak with a small area under the same weight.

When reporting the elastic modulus of the steak, we want it to be independent of its size. So to do this, we normalize the force from the applied weight by dividing it by the area. The resulting quantity is referred to as the stress.

$$\text{Stress} = \frac{\text{Force}}{\text{Area}}$$

The second consideration, is that the thickness of the steak matters. A very thick piece of steak will compress more than a very thin piece of steak. A thick steak may compress by several millimeters, but a piece of steak that is

only a few millimeters thick to begin with, will not compress as much. You can try this for yourself the next time you eat steak, or any elastic food for that matter, by cutting pieces of different heights and putting weights on them. So what we are interested in then, is how much the steak compresses compared to its original thickness. Just as with the area, we normalize the compression distance, by dividing it by the original thickness, L . This quantity, the relative change in thickness, is referred to as the strain:

$$\text{Strain} = \frac{\Delta L}{L}$$

Now we can calculate the elastic constant (or elastic modulus) the same way that we calculated the spring constant. To arrive at the spring constant, we divided the force by the change in length. For the elastic constant, we take the normalized force and divide it by the normalized length, we divide the stress by the strain. This gives us the following expression for the elastic constant:

$$E = \frac{F / A}{\Delta L / L}$$

4.2 Microscopic Origins Of Elasticity

4.2.1 The Units

Let's try to understand elasticity by looking more closely at the equation we just arrived at. Let's start with the units. From the equation we see that elasticity is a stress divided by a strain. The strain is a relative change in length; it's a length divided by a length. There are no units to that. The stress is a force divided by an area. A force divided by an area is a pressure. So the units of elasticity are pressure (i.e. Pascals, or Pa). If we plug in SI-units into the equation, the same reasoning looks like this:

$$E = \frac{F / A}{\Delta L / L} = \frac{\text{N/m}^2}{\text{m/m}} = \text{N/m}^2 = \text{Pa}$$

This also makes sense if we think about elasticity on a molecular level. Food, of course, is made up of molecules. When we deform food, whether we squeeze it, stretch it, or deform it in any direction, we are changing the relative positions of the molecules. We are making the bonds between the molecules longer or shorter. Each of these bonds has some energy, and there is a certain number of bonds.

We can understand the intrinsic origin of elasticity by remembering that the elasticity has the same units as pressure, which is a force (N) per unit area (m^2). If we multiply both the force and the area by a length as we have done below, we end up with this expression:

$$E = \frac{\text{N}}{\text{m}^2} \cdot \frac{\text{m}}{\text{m}} = \frac{\text{Nm}}{\text{m}^3}$$

The nominator is a force times a length (Nm). This is the same as an energy, i.e. we can think of this as the energy of a bond. In the denominator we end up with an area times a length, which is the same as a volume. And the inverse of volume is density. So this expression is telling us that elasticity is an energy per a certain volume, or the energy density of the bonds. As the number of bonds per unit volume goes up, the elasticity goes

up. As the energy between the bonds goes up, the elasticity goes up. Typically, the energy of the bonds don't change that much for different types of foods, or for different types of materials. So the dominant cause of elasticity is the density of the bonds. The densities of the bonds can change quite dramatically, and that's why you can get very, very different elasticities.

4.2.2 Equation of the Week

The energy density gives us another way of understanding the elasticity.

There is an energy for each bond, U , and there's a density of bonds, $\frac{1}{l^3}$, where l is the bond length (Fig. 4.5). So the elasticity can be written as

$E = \frac{U}{l^3}$, which is also the equation of the week (Table 4.1):

EQUATION OF THE WEEK		
$E = \frac{U_{\text{int}}}{l^3}$		
Symbol	Description	Units
E	Elastic modulus	Pa
U_{int}	Interaction energy	J
l^3	Crosslink distance	m

Table 4.1

So the physical origin of elasticity is basically the amount of energy it takes to deform all the bonds. When you place a weight on a piece of food, and it compresses, you are changing the dimensions of the food (Fig. 4.6). And, as a result, you are deforming all the bonds, i.e. you are changing the energy density. So you can understand elasticity not as how you deform the food, but how you change the length of the bonds.



Figure 4.5 A cartoon of the cross-links in a steak, each having an average bond energy, U , and an average bond length, l .

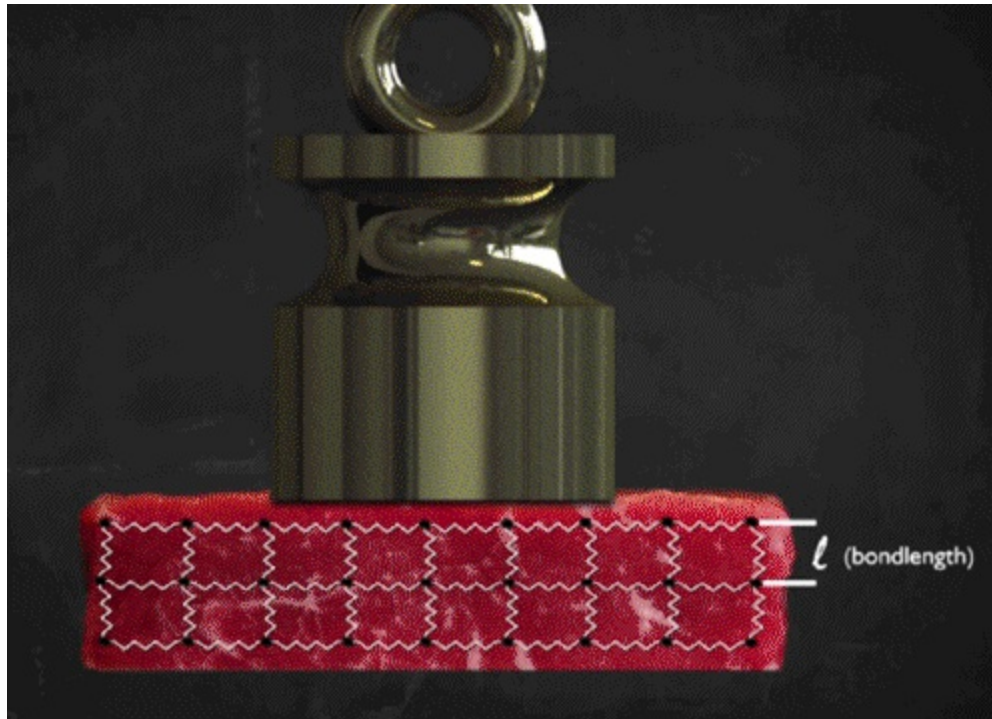


Figure 4.6 The energy and the length of the bonds give rise to the elasticity of the steak, thus determining how much the steak will compress.

4.3 Applications to Steak

4.3.1 Elasticity of Raw and Cooked Steak

Let's see if we can apply what we just learned about elasticity and how to measure it by cooking a steak. We originally did this experiment with the help of Daniel Rosenberg when preparing this part of the course. It's an exercise in how to calculate the elasticity of a food, and you can do it with any food – steak, bread, angel food cake, or Ferran Adria's spherified olives.

In order to be as precise as possible, we cut out little pieces of steak, all with the same dimensions: 4 cm by 4 cm, and with the same heights. We then applied a weight to the steak pieces before and after cooking, and used the

equation $E = \frac{F/A}{\Delta L/L}$ to calculate the elastic moduli.

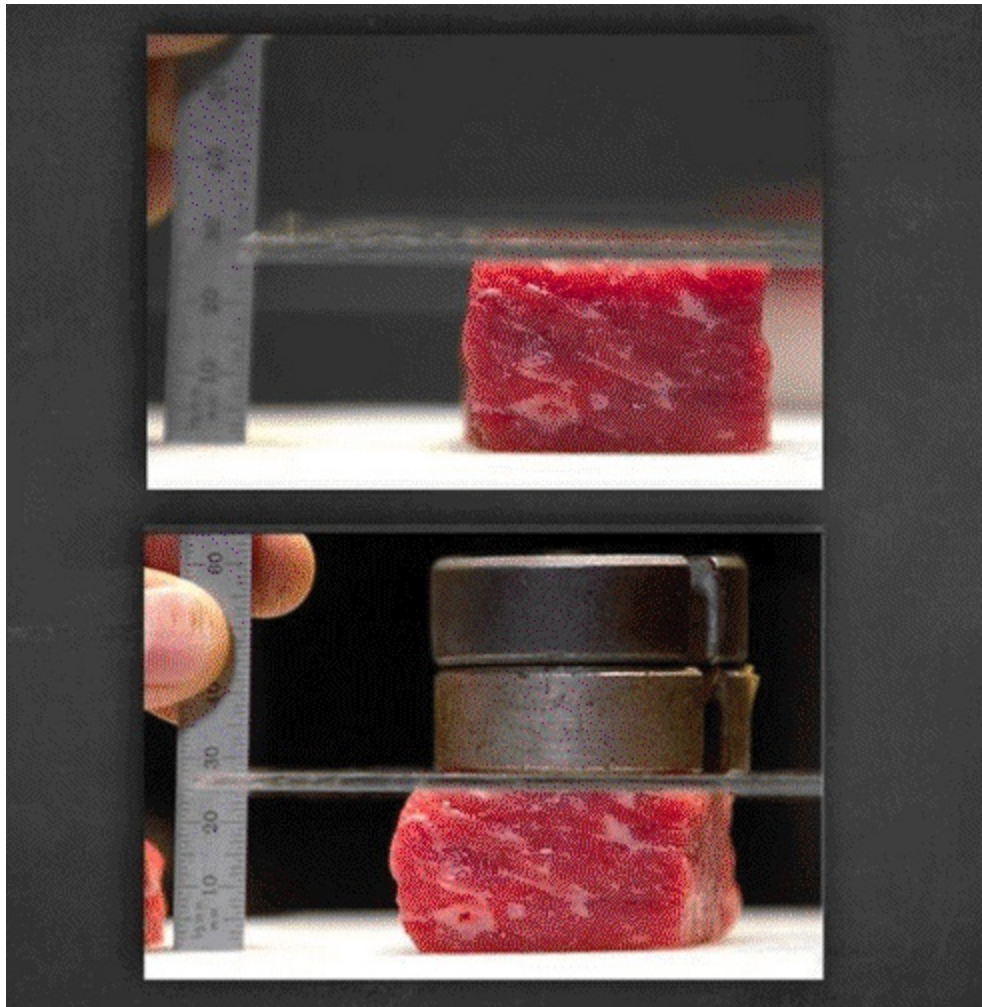


Figure 4.7 Measuring the compression for a raw piece of steak.

Figure 4.7 shows the measuring tools we used. They are very simple, just a plastic plate that we place on top of the food, a ruler, and weights. We used a 200 gram weight. As you can see, the initial measurement for the raw steak was 30 mm. As we applied the weight, the steak compressed to 26 mm. So ΔL is 4 mm. In order to figure out the elasticity, we also need to know the area of each piece of steak. We told you that each piece had sides of 4 cm, so the area is $4 \text{ cm} \cdot 4 \text{ cm} = 16 \text{ cm}^2$. And we need to know the force. The force is the mass times the gravitational constant, i.e. 0.2 kg times 10 m/s^2 . Here is a summary of what we know:

$$\Delta L = 4 \text{ mm} = 0.004 \text{ m}$$

$$L = 30 \text{ mm} = 0.03 \text{ m}$$

$$F = mg = 0.2 \text{ kg} \cdot 10 \text{ m/s}^2 = 2 \text{ N}$$

$$A = 4 \text{ cm} \cdot 4 \text{ cm} = 16 \text{ cm}^2 = 0.0016 \text{ m}^2$$

After having converted all units to SI-units, we can plug into the equation and solve for the elastic modulus:

$$E = \frac{F / A}{\Delta L / L} = \frac{(2 \text{ N}) / (0.0016 \text{ m}^2)}{(0.004 \text{ m}) / (0.03 \text{ m})} = 9,400 \text{ N/m}^2$$

So the elastic modulus for our raw piece of steak is $9,400 \text{ N/m}^2$.

Now, let's compare to the cooked steak. This steak was cooked to about medium well, and as you can see the original height was the same as for the raw steak, 30 mm (Figure 4.8). In fact most of our variables are the same as above. The force is the same, 2 N, and the area is the same 16 cm^2 . As we applied the weight, you can see how the steak compressed to 28 millimeters. So ΔL is 2 millimeters, about half as much as the raw steak.

$$\Delta L = 2 \text{ mm} = 0.002 \text{ m}$$

$$L = 30 \text{ mm} = 0.03 \text{ m}$$

$$F = mg = 0.2 \text{ kg} \cdot 10 \text{ m/s}^2 = 2 \text{ N}$$

$$A = 4 \text{ cm} \cdot 4 \text{ cm} = 16 \text{ cm}^2 = 0.0016 \text{ m}^2$$

Plugging into the equation we get:

$$E = \frac{F/A}{\Delta L/L} = \frac{(2 \text{ N})/(0.0016 \text{ m}^2)}{(0.002 \text{ m})/(0.03 \text{ m})} = 18,700 \text{ N/m}^2$$

The elastic modulus of our cooked piece of steak is $18,700 \text{ N/m}^2$, which is twice as much as for the raw steak. Given that the only thing that changed was that ΔL doubled, this is exactly what we would expect. It also fits well with experience — a cooked steak is usually tougher to chew than a raw steak, so it makes sense that its elastic modulus is higher.

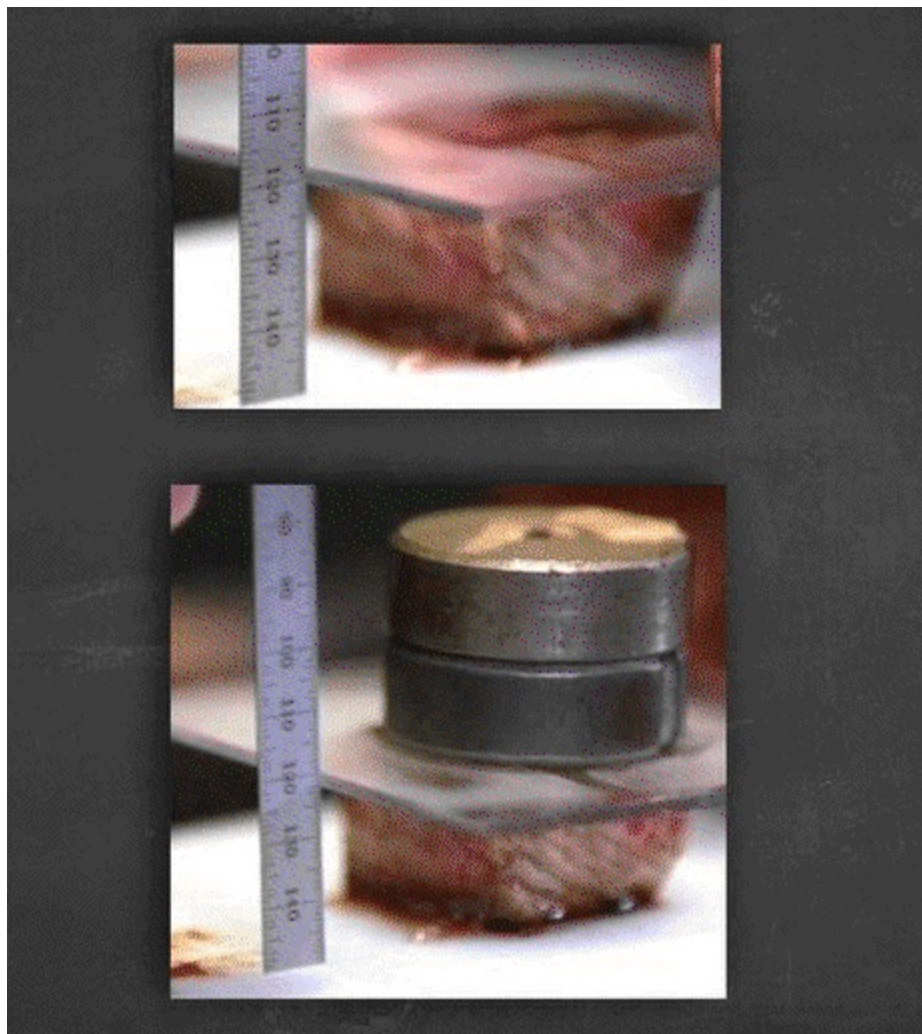


Figure 4.8 Measuring the compression for a piece of steak cooked to medium-well.

4.3.2 Cross-link Distances in Raw and Cooked Steak

So far we have talked about elasticity on a macroscopic level. Next let's see what these elastic moduli tell us about what goes on at a molecular level in the two steaks. Figure 4.5 shows a highly simplified picture of a steak on a molecular level. The cross-link distance, l , is just an average, so the cross-links are indicated as all having the same lengths, which in reality they are not. Each cross-link has an average interaction energy, U .

Since we observed an increase in elastic modulus, we would expect an increase in energy density of the bonds. We mentioned before that the interaction energy typically does not change much in materials, so we are going to focus on calculating the cross-link distance.

By using the equation $E = \frac{U}{l^3}$, and solving for l , we can calculate the cross-link distance both for the raw steak and for the medium well steak.

$$E = \frac{U}{l^3}$$
$$l = \sqrt[3]{\frac{U}{E}}$$

The bond energy, we know from Chapter 3, can be obtained from the

equation: $U = Ck_B T$. For the raw steak, we can assume that the temperature is 23°C, and for the cooked steak, we can assume it's a little higher, about 30 degrees higher since this is the temperature at which the majority of the proteins coagulate, although the temperature really doesn't affect the outcome much. Plugging into the equation, we find that the crosslink distances for the raw and cooked steaks are 7.6 mm and 6.2 mm respectively.

$$l = \sqrt[3]{\frac{(1.38 \cdot 10^{-23} \text{ J/K}) \cdot (300 \text{ K})}{(9,400 \text{ N/m}^2)}} = 7.6 \text{ nm}$$

$$l = \sqrt[3]{\frac{(1.38 \cdot 10^{-23} \text{ J/K}) \cdot (330 \text{ K})}{(18,700 \text{ N/m}^2)}} = 6.2 \text{ nm}$$

Just as we would expect, the cross linked distance has decreased as we cooked the steak. It's about 20% shorter. This isn't a huge change, but it's enough to tell us that the change in elasticity that we observe on a macroscopic scale is reflected in the cross-link distance on a molecular scale.

4.4 The Elasticity of Strudel Dough

Moving on from steak, which is only one of many elastic foods, we are now going to see how this concept applies to a delicious recipe for strudel that Chef Bill Yosses cooks. In this recipe, four ingredients, water, flour, salt, and a little oil are mixed in a mixer until they form a tight ball of dough. The dough is then stretched out into a large, thin sheet, a stuffing of apples and other ingredients is spread on top, and it is then rolled up and baked in the oven.

Strudel dough has a lot in common with other doughs, the general principles of which we will talk more about when covering baking in general in Chapter 9. But our discussion of elasticity would not be complete without discussing its role in baked goods, and to do this we need to understand what gluten is.

4.4.1 The Gluten Network

Gluten is a protein component of flour that gives strudel dough its very special characteristics. The protein content of flour is usually about 10% (the rest is primarily carbohydrates in the form of starch), although the exact percentage of protein actually depends on where in the world, and even where in the US, you buy your flour. Of the protein, a majority is composed of large protein molecules called glutenins and gliadins. These are the molecules that make up the gluten network.

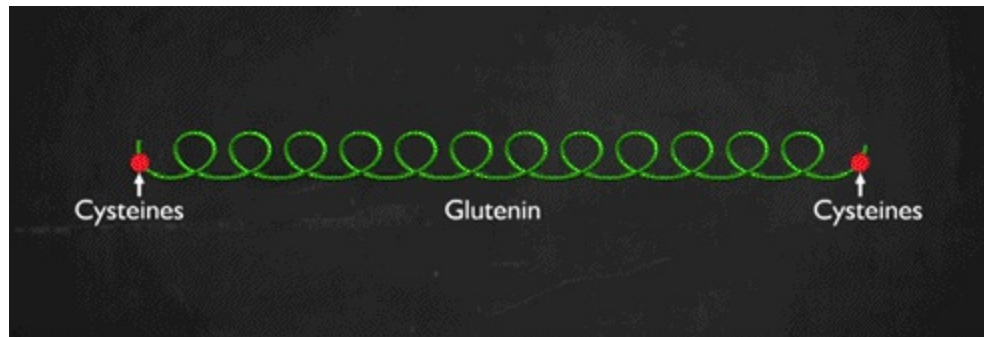


Figure 4.9 Glutenin is an elongated molecule with cysteine residues on both ends.

It is ultimately the structure of the glutenin molecules that contribute to the elasticity of the gluten network. Glutenin is a long and relatively large molecule with a coiled structure. Since it's a protein, it's composed of amino acids, some of which have a charge, although most of them don't. The ends of each glutenin molecule contain the amino acids cysteine (Fig. 4.9). Cysteines contain a sulfur atom, which can bond with sulfur molecules on other cysteines on other glutenins (Fig. 4.10). This sulfur-sulfur bond is a strong covalent bond, and tends to be important for the structure of many proteins, not just glutenins. So the cysteine molecules bind to other cysteines, thus linking the glutenin molecules together, eventually resulting in a large and intricate network, the gluten network (Fig 4.11).



Figure 4.10 The cysteines on different glutenin molecules form strong bonds, thus linking the molecules together.

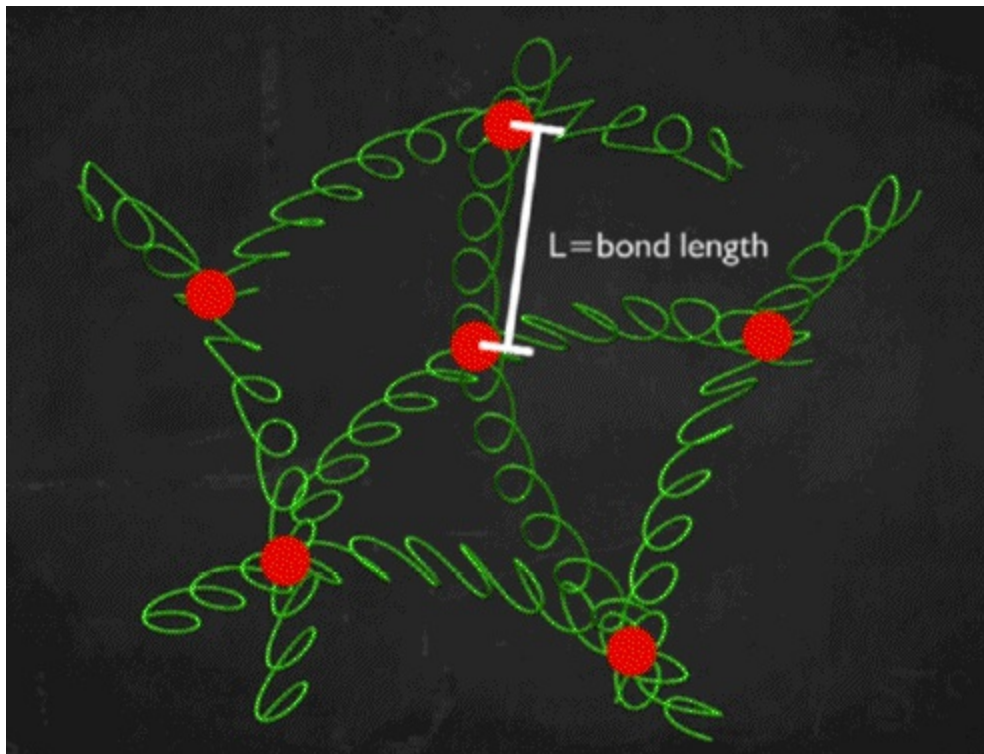


Figure 4.11 Ultimately the many long strands of linked glutenin form a messy network. Similar to the steak, the gluten network consists of bonds which have an average bond energy, U , and an average bond length, l .

When we first mix flour and water to make a dough, all of the glutenin

molecules in the network are originally messy and all over the place. Then, as we start to knead the dough, we are slowly unfolding and aligning the long glutenin molecules, and van der Waals interactions can start to form between them (Fig. 4.12). Van der Waals bonds, as you know, are weaker bonds, but since there are so many of them they end up having an overall strong effect. As we knead the dough, the aligned molecules can slide along each other, and this is what is giving the dough its elastic properties. The more we knead the dough and align the molecules, the more elastic the dough gets. We're essentially forming more and more cross-links.

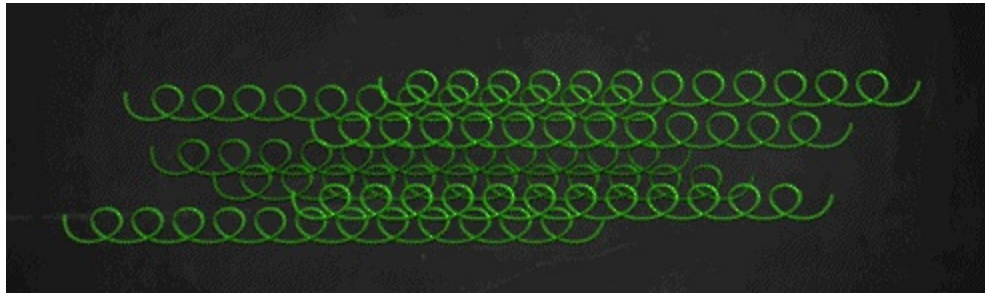


Figure 4.12 When kneading the dough, the glutenin molecules align, thus allowing for stronger bonds to form between them.

The dough is not only elastic though, it also has a property called plasticity, which is closely related to elasticity. As you may know, when you stretch strudel dough, it will first stretch out, and then relax back a little before staying partly stretched out. The reason it stays stretched out is that as the glutenin molecules slide along each other, new van der Waals bonds can form between different parts of the molecule. This phenomenon is called plasticity. When you stretch or compress something and it doesn't completely recoil to its original shape, that's plasticity. When the object does recoil to its original shape, it's elasticity. In the strudel dough, and in fact in many other types of foods, both of these phenomena can be observed.

4.4.2 Deconstructing the Strudel Recipe

Strudel dough is amazing in its ability to stretch incredibly thin. Figure 4.13 shows a microscope image of the dough Bill Yosses made when we prepared this chapter, and you can see that the dough is stretched so thin that you can almost see through it. In fact, bakers sometimes use this as a test to tell if they have kneaded their dough enough, it's referred to as the windowpane test. If they can stretch a small piece of dough really thin like this, without having it break, then the gluten is well-developed and the dough ready to rise.

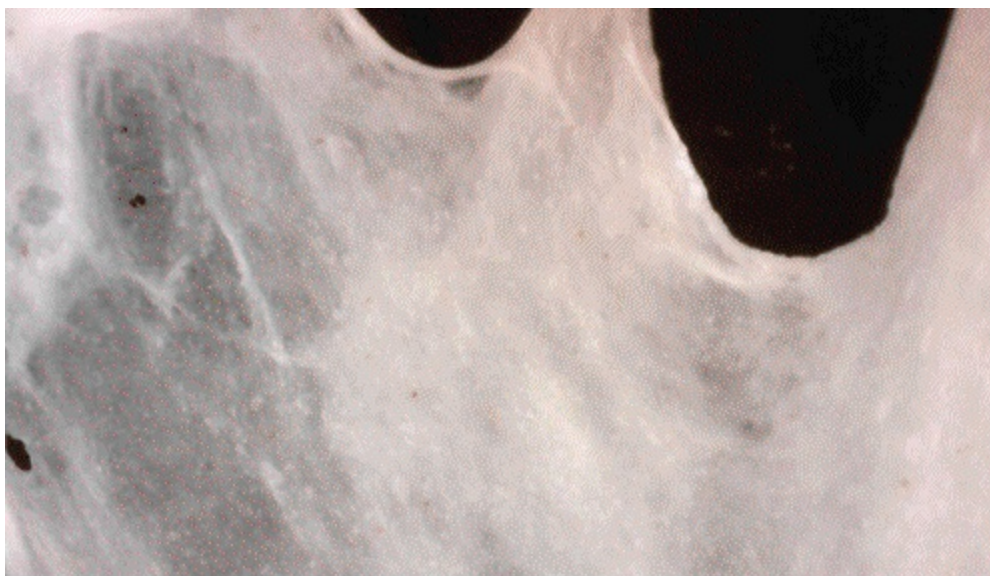


Figure 4.13 A microscope image of a piece of very thinly stretched strudel dough.

Bill has a number of things he pays special attention to as he works his way through this recipe. Below we are going to see if we can figure out what the scientific reasons for these special considerations are.

First, when Bill makes strudel, he always makes sure either to use bread flour, or some other flour that has a high protein content, when he makes this recipe. This is because if the flour is high in protein, it is also going to be high in gluten, and this is what's contributing to the strong network. Bill also emphasizes that he always wants to make sure that he "works" the gluten enough. By this he means that he wants to make sure that all of the glutenin molecules unfold and align as much as possible. This way they will be able to slide along each other better and the dough will be more elastic.

Another observation Bill makes, which is a little less obvious, is that when he adds salt to the mix of flour, water, and oil, he notices an increase in the

elasticity. This sounds curious at first, but if we think about the underlying structure of the gluten network, we can understand why. As mentioned, a few of the amino acids along the glutenin molecules are charged. When you add salt, which consists of positive sodium ions and negative chloride ions, these charged amino acids attract the salt ions (Fig 4.14). The positive sodium ion will be attracted to negatively charged amino acids and vice versa. This has the result that the charges on the glutenin molecules get neutralized, which leads to the glutenin molecules stacking more closely since the charged amino acids are no longer trying to form electrostatic bonds that disrupt the aligning (Fig 4.15). So the overall effect is that the van der Waals interactions get stronger, which allows us to stretch the dough more.

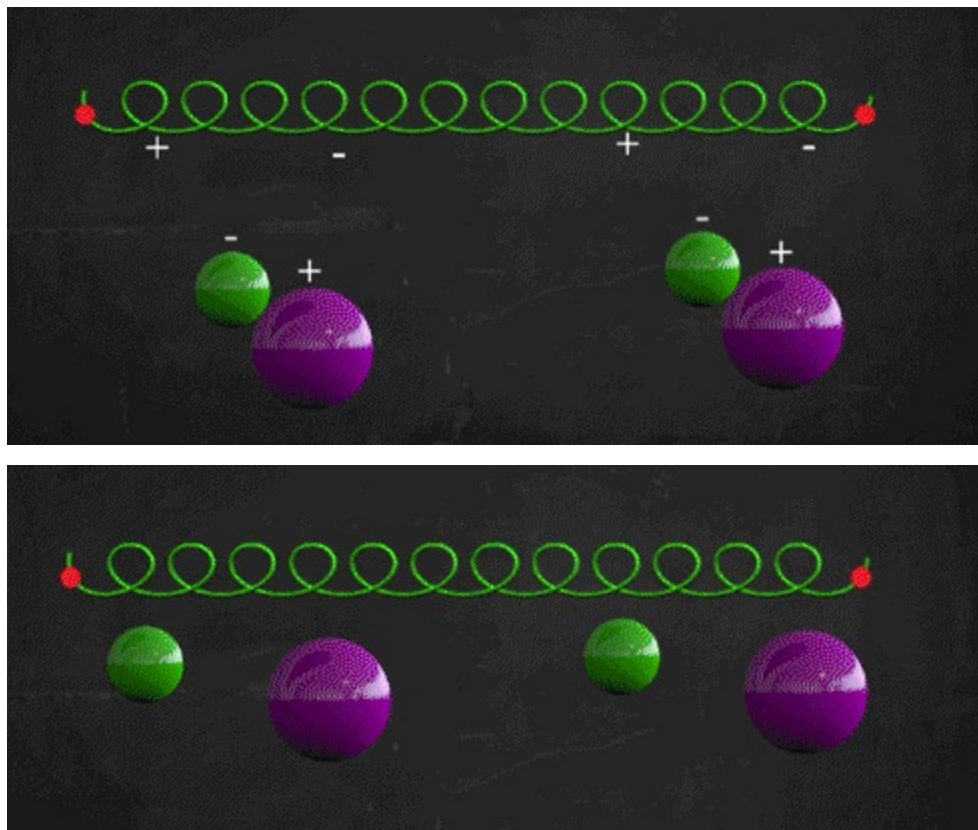


Figure 4.14 and 4.15 The positive and negative charges on sodium chloride neutralize the charged amino acids on the glutenin molecules, thus allowing them to align more closely and form stronger interactions with each other.

Finally, Bill states that he wants to let the dough rest for a while before spreading it out thinly so that it can absorb water. It turns out that water absorption also helps develop the gluten network. You can imagine that if the glutenin molecules are not dissolved in water, they will not as easily be able to stretch out and form bonds with each other. In addition, when flour

absorbs water, the starch granules in the dough swell. Since starch makes up the majority of flour, this is essentially what's contributing to the bulk of the dough. The gluten network is primarily contributing a scaffold; remember that only about 10% of flour is protein, and only some of that consists of glutenin. So the development of the starch granules is of equal importance in creating the ultimate final product, and this is what Bill is concerned about when he lets it rest.

4.5 Elasticity of a Candy Apple

4.5.1 Three Important Facts About Sugar

Bill Yosses has in his repertoire a remarkable demonstration in which he heats seemingly simple ingredients, sugar, water, and a little bit of glucose until they reach a certain temperature. He then pours the resulting viscous sugar solution onto the counter and starts to mold it into a thin shell of candy, shaped perfectly like an apple. A lot of care and skill is required to make this happen, and behind every step there is an enormous amount of science.

We are now going to go through the important scientific elements of this recipe and explain how it fits into the learning goals of this chapter. In order to do this, there are three important facts about sugar, sugar water, and heated sugar water that we want to emphasize.

The first is that the sugar that you put in sugar water is sucrose. Sucrose is a disaccharide, which is made out of glucose and fructose (Fig. 4.16). So sucrose is bigger than both glucose and fructose alone. Bill also adds glucose to the mixture, and one of the things we are going to think about is what different roles sucrose and glucose are playing within the recipe.

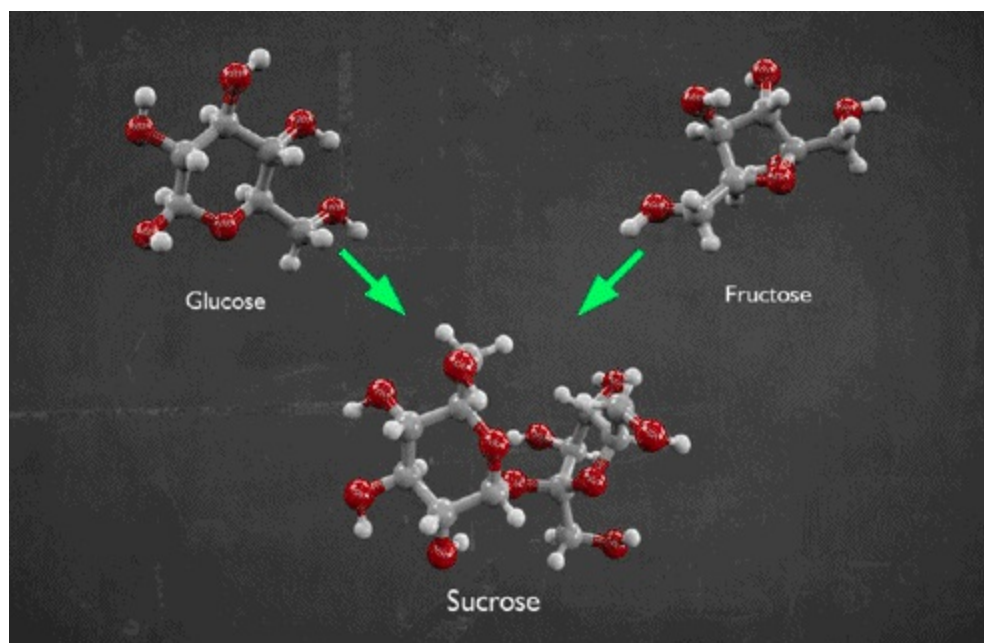


Figure 4.16 Sucrose is a disaccharide consisting of a glucose and fructose molecule.

The second important fact is the idea that the solubility of sugar in water increases dramatically as a function of temperature (Fig. 4.17). Whereas at room temperature, you can dissolve approximately two grams of sugar for every gram of water, which is already a lot, you can dissolve about twice as much, four grams for every gram, when you increase the temperature to 100°C. The solubility goes up more and more as you increase the temperature.

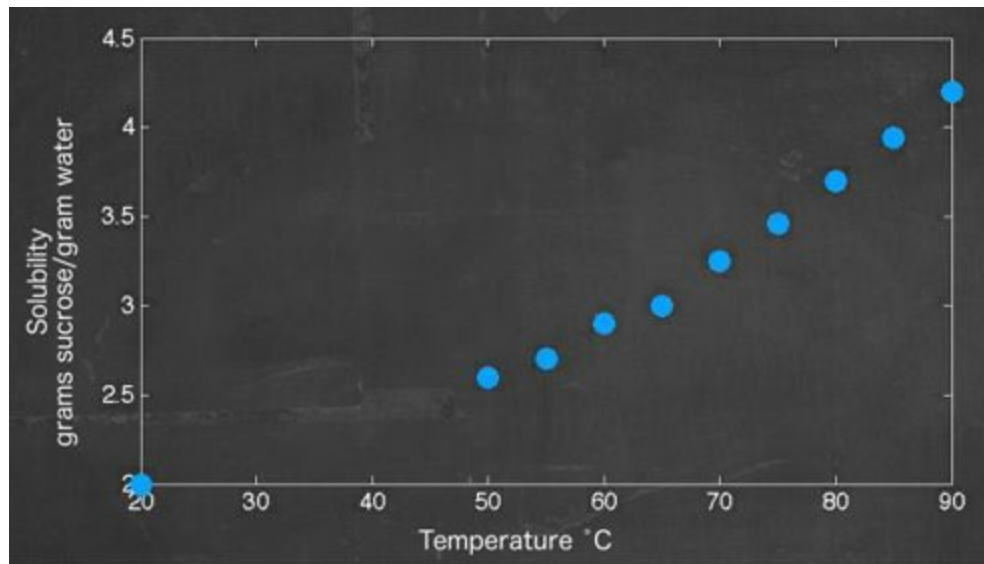


Figure 4.17 Solubility of sugar in water as a function of temperature.

And finally, the third important fact, is that the boiling point of the sugar water mixture depends critically on the mass fraction of sugar (Fig. 4.18). What this means is that the higher the percentage of sugar in the mixture, the higher the boiling point. It increases from 100°C, the boiling point of pure water, to around 150-160°C once the mixture is almost entirely made of sugar. The way to think about this relationship, the boiling point as a function of the sugar concentration, is that it is really a way of dialing in the mass fraction of sugar. In other words, if you were to heat the mixture up to 110°C, then you know that that corresponds to a mass fraction of sugar of about 60-70%. If you heat it up to 140°C, then that corresponds to a mass fraction in the range of 80-90% sugar, and so on.

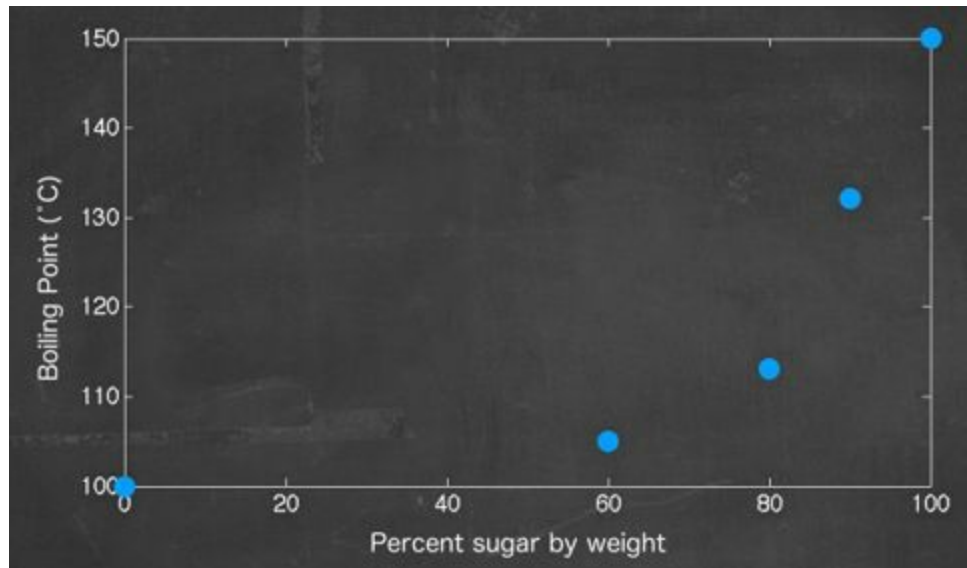


Figure 4.18 The boiling point of a sugar-water solution as a function of the mass fraction of sugar.

When Bill makes his candy apples, he is very, very careful to tune the temperature. He says the temperature needs to be within the narrow range of 151-152°C before he pours it on the counter and starts to mold it into an apple. If you go any lower or any higher it doesn't work. The way to think about it, is that between this very narrow range of temperatures, you're actually very carefully controlling the water content of the sugar mixture. And it's the very sharp dependence of the boiling point on the mass fraction of sugar that gives rise to the need for this exquisite temperature control when you make candy.

4.5.2 The Candy Thermometer

As context, let's just say a couple of words about candy making. On a traditional candy thermometer, there are words that go with the temperature ranges. There is thread, soft ball, hard ball, firm ball, soft crack, and hard crack (Fig. 4.19). The range Bill was trying to hit at 151-152°C, was within the hard crack range.



Figure 4.19 A candy thermometer not only shows a range of temperatures, but also indicates the texture of the sugar at several temperature ranges.

All of these words actually come from part of the candy making process itself. They refer to the fact that if you heat up sugar water to certain temperatures, and you then quench it (quenching is a scientific word that means to cool rapidly to a cooler temperature), then the mixture feels like something which is hard crack, soft crack, hard ball, soft ball, and so on. In fact, if you watch Bill making a candy apple, you will see how before he starts molding the sugar glass, he takes a spoonful of the sugar water out of the pan as a test, and then he pours it on the counter. And the sugar then solidifies like glass, and gives off a crackling sound. This is the sign it's in the hard crack range. So the words just describe the properties of sugar when you do this procedure.

The reason you see this crackling effect, is that when the hot sugar water from the pan touches the much cooler counter, it will very rapidly cool, or

quench, to a much lower temperature. The effect of this is that the amount of sugar that is dissolved in the mixture is much higher than what it should be at this new temperature. The sugar is at the concentration that, according to the plots in Figure 4.17 and 4.18, you would expect it to have at the higher temperature. It's not at the concentration you would expect at the lower temperature on the counter.

So the question is, what happens? The answer is that the sugar tries to form crystals. You essentially have too much sugar in the solution, in scientific terms we would say that the solution is supersaturated, and the excess sugar tries to come out of solution by forming crystals. The crystals will continue to form until the amount of sugar left dissolved in the liquid corresponds to the amount there should be at the cooler temperature according to the plot. Depending on how much sugar there was to begin with, more or less sugar will crystalize, resulting in the different textures of hard ball, hard crack etc.

The same thing that happens for the hard crack test, also happens when Bill pours the entire sugar water mixture onto the counter to start forming the candy apple. As the mixture cools, and as Bill starts to shape it with his hands, crystals are forming, and it's the crystals that are basically making up the material. As the number of crystals increase, they are starting to jam into each other and making the solution more and more viscous, until it's eventually a solid. So while this chapter covers elasticity, this is an example of how closely connected viscosity and elasticity are. Viscosity is about pouring things. And elasticity is about squishing things. In the case of the sugar water, we have both. The solution starts out as a liquid with a certain viscosity, and eventually ends up as a solid with an elastic modulus. We will talk more about viscosity in Chapter 7, but this will serve as a very brief introduction, and we'll come back to some of these ideas later on.

4.5.3 A Microscopic View

In order to make a candy apple, Bill Yosses needs to have two things happen. First, when the candy apple solidifies, it needs to form an actual solid, it needs to have some rigidity to it, an elastic modulus. It can't be a liquid or too brittle, or he can't serve it at a state dinner or in whatever context he would like to serve it in. Second, when the material is hot, Bill needs it to be a liquid, he needs it to flow, otherwise he can't mold the candy apple with his hands and form the shape he wants.

Now let's think through what has to happen to the molecules in the sugar water solution for this to occur. Let's walk through this scenario, and then we will discuss how the scenario would change if you were to change the initial temperature of the sugar water solution so that instead of 150°C it were at a lower temperature.

Suppose the sugar water mixture is at 150°C, and you pour it onto a cold counter. As we just discussed, the material starts to cool, and since the amount of sugar in solution is much more than it should be at the new temperature, crystals start to form. Even at the higher temperature there were little nuclei of crystals floating around, although not very many because most of the sugar was dissolved. These small nuclei can now serve as nucleation sites as the sugar crystals start to grow. It's the same principle that we explained for the super cooling that took place in Joan Roca's beautiful dessert earlier in the course. The presence of little crystals can speed up crystal formation because they can serve as nucleation sites, thus by-passing the step of forming the initial little crystal which is much harder to do.

Since the sugar water mix was very hot, there was a large excess of sugar, which is now rapidly coming out of solution and the crystals grow quickly. We then have these big solid chunks of sugar floating around in the liquid (Fig. 4.20). They are solid, they have an elastic modulus and they obey the equation of the week. The amount of liquid there is left is also determined by the temperature. At 150-152°C a certain fraction of the liquid has boiled off. So the crystals are floating around in what is really a rather small amount of liquid, and this is what determines the material.

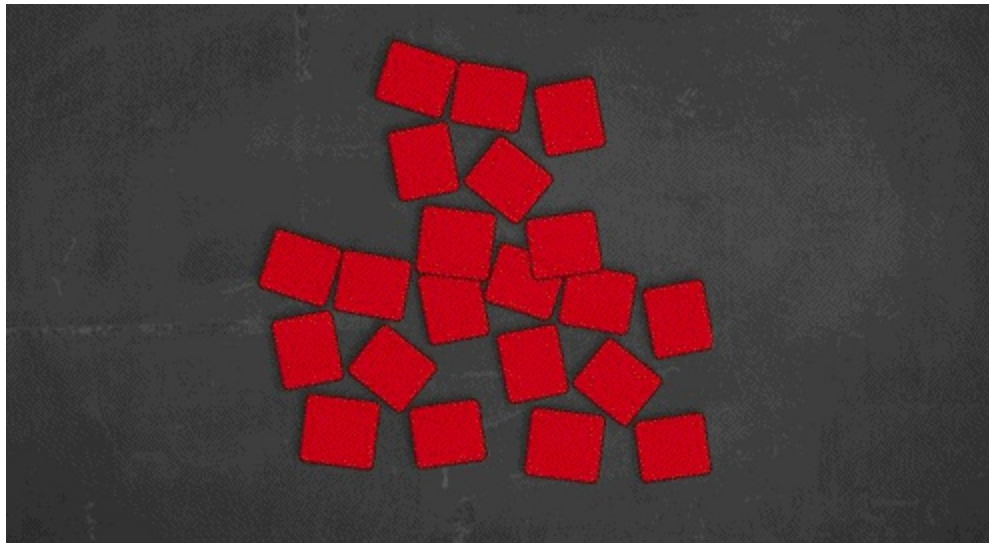


Figure 4.20 A candy mixture prepared at the right temperature will contain a small number of crystals that are relatively large in size. They will be floating in a relatively small amount of water.

4.5.4 The Role of Glucose

If at this point the only ingredient in the solution were sucrose, then it would simply reform the sugar that it was in the first place; it would just reform sugar crystals. This would be all fine, if it weren't for the fact that sugar crystals don't actually flow. They don't have the malleable property that Bill needed in order to mold the candy apple. In order for that to happen, the system has to form a glass. And glass formation requires that you put something in the solution to impede the crystallization of these nuclei that are growing. This turns out to be the role of the glucose.

Glucose, as already mentioned, is one of the two components of sucrose, the other one being fructose. Glucose is smaller than sucrose, it basically has the shape of just a part of sucrose. This ends up being important for glass formation for the following reason: Imagine you took a bunch of perfectly square blocks and stacked them up to make a block wall, similar to a brick wall that might make up part of your house. The blocks would make a perfect lattice. But now suppose somebody came along and broke off little parts of some of the bricks. If you tried to build a house out of these bricks they wouldn't stack as well. In the same way, if you add into the sugar water solution small pieces of sucrose, namely glucose, it won't form as strong or as rigid a solution, and it will be better able to flow. This is the role of glucose. It's essentially an inhibitor of crystallization.

Other ingredients than glucose could play a similar role. Corn syrup, for example, is sometimes used when making other types of candy. Corn syrup is not a piece of sucrose, it's actually many sucroses that are stuck together, making long chains of sugars. They basically play the same role, although the detailed behavior is different.

4.5.5 Lower Temperature Thought Experiment

Lastly, let's think about what would have happened if we had started out at another temperature. Since 150-152°C is pretty much the hottest a sugar solution can get without burning, let's imagine that the mixture was at a lower temperature. Suppose you were in the firm ball or soft ball stage, where, when you dunk a scoop and quench it, the mixture actually has an elastic modulus.

Let's say you are starting out at 120°C instead of 150°C. As you pour the solution onto the counter, it will spread out and start to cool. Just as before, the mixture is super saturated. Since the temperature is slightly lower, you will have more nuclei in the initial pouring. This is because it will be easier for the nuclei to form when there is not as much heat to agitate them and break them apart. However, these nuclei will grow more slowly than in the high temperature version, because there is not as much sugar dissolved. As a result there will be very many little crystals as opposed to a few bigger crystals (Fig. 4.21). There is also going to be more water around because at the boiling point of 120°C, the mass fraction of sugar is much lower than at 150°C. This solution of many small crystals in a relatively larger amount of water ends up making the mixture more squishy. It has an elastic modulus but it is not as hard as the candy mixture we got from the higher temperature. It turns out you can't use it to make the shell of a candy apple at all, because as you try to mold it, it does not remain a solid mass, and it will not be able to hold its final shape.

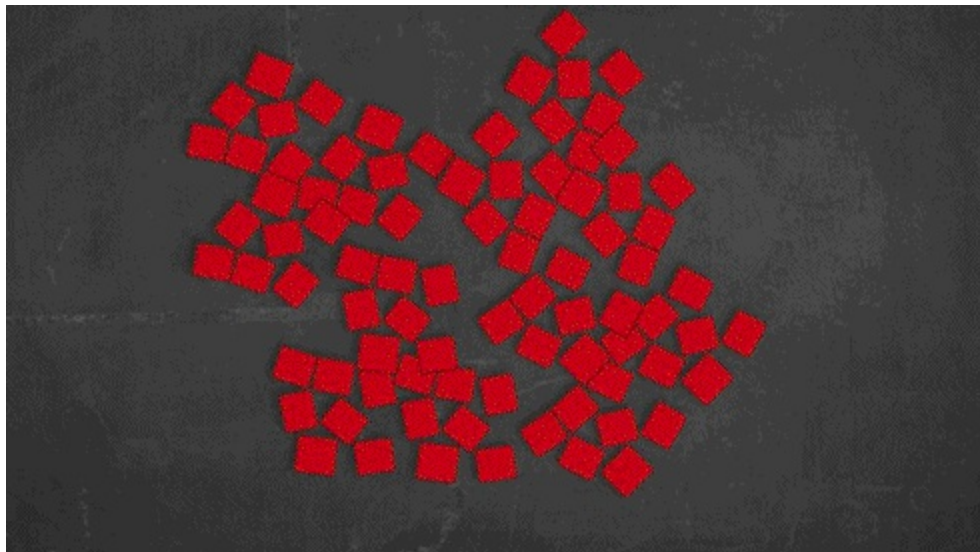


Figure 4.21 A candy mixture prepared at sub-optimal temperatures will contain a large number of

crystals that are relatively small in size. The crystals will float in a solution with relatively more water than the correctly prepared candy.

In Chapter 7, we will return to this fascinating story of sugar water mixtures in the context of viscosity. But for now we just want you to focus on the elastic parts of what is happening. You should see that with these very simple molecular ingredients and the interactions between them, one can create remarkable solid bodies, like, for example, Bill Yosses' candy apple.

4.6 Summary

We have spent this chapter looking at a delicious array of different types of foods: everyday foods like steak, and less common ones like Bill Yosses' delectable strudel and candy apple. All of these foods have different properties. They have their unique tastes and textures. But the reason that we are showing them all to you now is because we are focusing on the scientific idea of elasticity, which is the scientific way of measuring how stiff or soft a material is.

We have introduced you to the quantity that scientists measure to find out what the elasticity of a food is: the elastic modulus. And we have discussed

the equation of the week, $E = \frac{U}{l^3}$, where U is the interaction energy between the bonds in the material, and l is the characteristic distance between them. Using this equation, we explained that the elastic modulus can be thought of as a network of springs that are underlying the material, each having different stiffnesses and lengths.

Why is this idea so powerful? By using this one equation, $E = \frac{U}{l^3}$ we can start to get an understanding of why this diverse array of different foods have such different elastic moduli. It not only explains why foods have the properties they do, but it also gives you an idea as a chef of how you would go about changing the elastic moduli of the different foods that you are trying to cook.

As a summary of this chapter, let's go through the several different types of foods that we have talked about and see how the equation applies.

4.6.1 Steak

As we discussed, when you cook a steak it gets stiffer. We even use this property to test its done-ness by using the famous thumb test. Turning to the equation of the week, we see that there are two ways to increase E , the elastic modulus. One is to increase U , the strength of the bonds between the molecules in the steak. And the other is to decrease l , the distance between the bonds.

Indeed, when you cook a steak, it turns out that you affect both of these quantities. You affect U , the energy of the bonds, by heating the steak. The heat causes strong covalent bonds to form between the molecules of the steak, which essentially makes the proteins stiffer. You also affect the bond length, l . You can get a sense for this by thinking about what happens to a steak on a macroscopic scale when you cook it. You may recall that its weight decreases and it shrinks a little. This happens because the water of the steak is evaporating and it dries out. When the water evaporates, the distances between the springs are shrinking. For example, if a piece of steak starts off weighing a quarter pound when raw, and as you cook it, it loses half of its mass, then this means that l^3 in the denominator has shrunk by a factor of two. Hence, the elastic modulus has increased by a factor of two just from the water loss, even if the bonds have not strengthened at all.

4.6.2 Chocolate

In the introduction to this chapter we briefly mentioned chocolate and the different textures it can have. Chocolate exists in various forms. On the one side, the stiff side, there are chocolate bars, and on the other side, there is chocolate mousse. We'll look more closely at chocolate later, but for now you should know that chocolate is actually a crystal. There are six crystalline phases of chocolate, although only one of them has the properties of the chocolate we like to eat. The chocolate crystals consist of fat molecules that are stuck to each other by bonds, and the bonds have some strength and some energy. The bond distance, l , is pretty small because the fat molecules have sizes on the scales of nanometers. So in terms of the equation of the week, since l is small, the elastic modulus of the chocolate ends up being high. This makes sense because we all know that a chocolate bar is a pretty stiff material.

What about chocolate mousse? Chocolate mousse is also made out of chocolate, but it is much, much softer. How can you make something with such a low elastic modulus with a substance which itself is so stiff? The reason is apparent if you cut open a chocolate mousse and see what it is made of – lots of little air bubbles. All of these bubbles were incorporated into the chocolate cream when the mousse was made, essentially making a chocolate foam. We will discuss foams later in the course, but for now let's focus on how this gives rise to an elastic modulus. What are U and l ? U , the energy scale, is essentially set by how much energy it takes to form one of the bubbles in the chocolate mousse. This is not nearly as much energy as it takes to deform a solid crystal with lots of atoms that are densely packed. Similarly, the cross-link distance, l , is the size of the bubbles. And as you can tell just from looking at them, they are much, much larger than the nanometer scale in solid chocolate. Since U is smaller and l is larger, the mousse has a much lower elastic modulus than solid chocolate.

4.6.3 Candy

Just like chocolate, candy is a crystal and has a very high elastic modulus because the atoms in sugar crystals have very strong bonds between them. But we also talked about how the sugar water mixture had to be soft enough for Bill to mold it. And, also, we talked about the fact that when you heat sugar water to various temperatures and then quench it, the resulting material has different stiffnesses. We refer to them as hard ball, firm ball, soft ball, hard crack, and so on.

What is happening in these different materials in terms of the equation,

$E = \frac{U}{l^3}$? To understand this, we have to remember that the temperature of a sugar water mixture is essentially a surrogate for the volume fraction of water in the solution. The more water there is, the farther apart the sugar molecules will be on average and fewer bonds will form. So the average bond energy, U , is lower, and since the molecules are farther apart l is larger. Overall this has the effect of decreasing E as the sugar water mixture goes from hard ball to firm ball to soft ball.

4.6.4 Strudel

Our last food example for this week was a baked good, strudel. We discussed how the elastic modulus of the strudel dough was determined by the glutenin molecules. In terms of the equation of the week, U is the interaction energy between the glutenins, and l is whatever the characteristic distance between them is.

If we compare strudel to other baked goods, we will see that the gluten network is not always the only contributor to elasticity. If you compare it to angel food cake, for example, you will notice that it is much softer than strudel. Both contain flour, i.e. gluten, so our discussion of the gluten network still applies. But how can such different textures be created from the same material? Just as with the chocolate mousse, it is the foam-like interior that gives us the answer to this. Thus, when you push on angel food cake, you are really compressing the air bubbles. So U is the energy it takes to compress an air bubble, and l is the size of one of the bubbles. Since, angel food cake has a smaller U , and a larger l than strudel, it ends up having a lower elastic modulus.

To summarize, the real power in a scientific concept, as exemplified this

week by the equation $E = \frac{U}{l^3}$, is that it takes disparate phenomena, from strudel to chocolate, from steak to candy, and shows, in a unified way, why they have the properties they do. If you think about elasticity from the point of view of this equation, you will start to see how different phenomena in cooking, which at first may seem very far apart, are all just manifestations of the same basic principle.

CHAPTER 5

Diffusion, Gelation and Spherification

TABLE OF CONTENTS: 5

5.1 Introduction to Gelation

[5.1.1 The Principles of Gelation – Spaghetti and Hand-holding](#)

5.2 Gels made with Proteins

[5.2.1 The Molecular Basis of Protein Folding and Unfolding](#)

[5.2.2 The pH Dependence of Protein Unfolding](#)

5.3 Gels made with Hydrocolloids

[5.3.1 The Molecular Basis of Spherification](#)

[5.3.2 Cooking with Hydrocolloids](#)

5.4 Spherification

[5.4.1 The Movement of Calcium Ions](#)

[5.4.2 Making Cheese on a Microscope Slide](#)

5.5 Random Walk

[5.5.1 Pearson, Einstein and Bachelier on the Random Walk](#)

[5.5.2 The Equation of the Week](#)

5.6 Osmosis

CHAPTER 5

5.1 Introduction to Gelation

5.1.1 The Principles of Gelation – Spaghetti and Hand-holding

One of the most important phase transitions that occurs in cooking is gelation. It occurs in many of the things that you might cook every day, and it also occurs in some of the more esoteric types of cooking that we will talk about this week. When you cook an egg, for example, it transitions from being a liquid at room temperature to being a solid when heated up for a long enough time. This is an example of gelation. Another example is Jell-O, which can be made very easily by adding some boiling water to a box of Jell-O powder, leaving it in the refrigerator to cool down, and voila, out comes a gel. A third example of gelation is spherification, Ferran Adria's remarkable culinary creation that consists of a thin layer of gel around a delectable drop of liquid food. It turns out that all of these different phenomena, when looked at from a physical perspective, are very similar. For one thing, they all involve the concept of a phase transition in that they go from liquids to solids. But they also share some key underlying scientific principles, which we will discuss in this chapter.

Imagine that you have long strands of polymers that are all interwoven with each other, similar to a bowl of spaghetti, where the individual spaghetti strands represent the polymers (Fig. 5.1). The spaghetti can slide by each other and you can pull out individual strands from the bowl. Next, imagine that some of the places where the spaghetti strands overlap, get glued together (Fig. 5.2). Now the polymers are stuck. What was initially a liquid, because the polymers could flow by each other, is now a solid. In other words, the spaghetti strands have formed a gel and the glued places correspond to the cross-links in the gel.

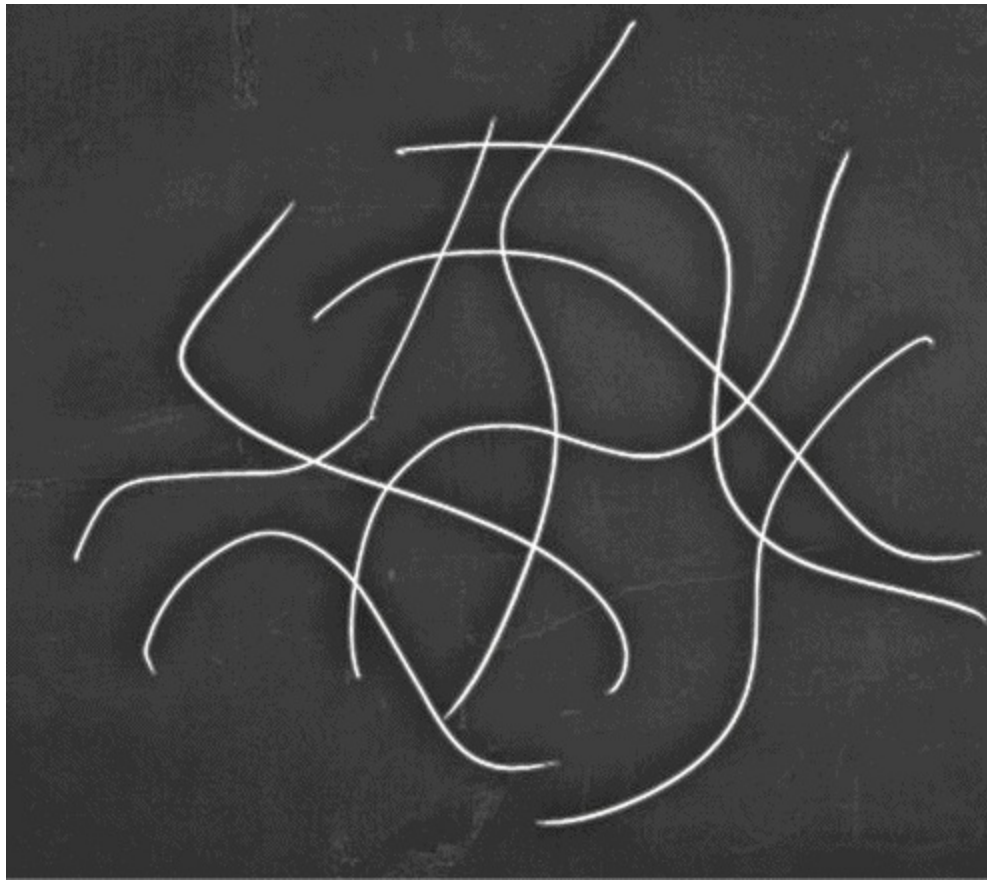


Figure 5.1 A cartoon depicting a solution of interwoven polymer strands

You can get a sense for the same concept with the following exercise: get a group of friends together in a room and ask everyone to start walking around in the room. Since they are moving by each other they are behaving like a liquid. If you then ask your friends to randomly choose two different neighbors to hold hands with, you will essentially have formed the physical structure of a gel, with the hand-holding corresponding to the crosslinks. Everyone will be stuck and unable to move, unless they let go of the hands.

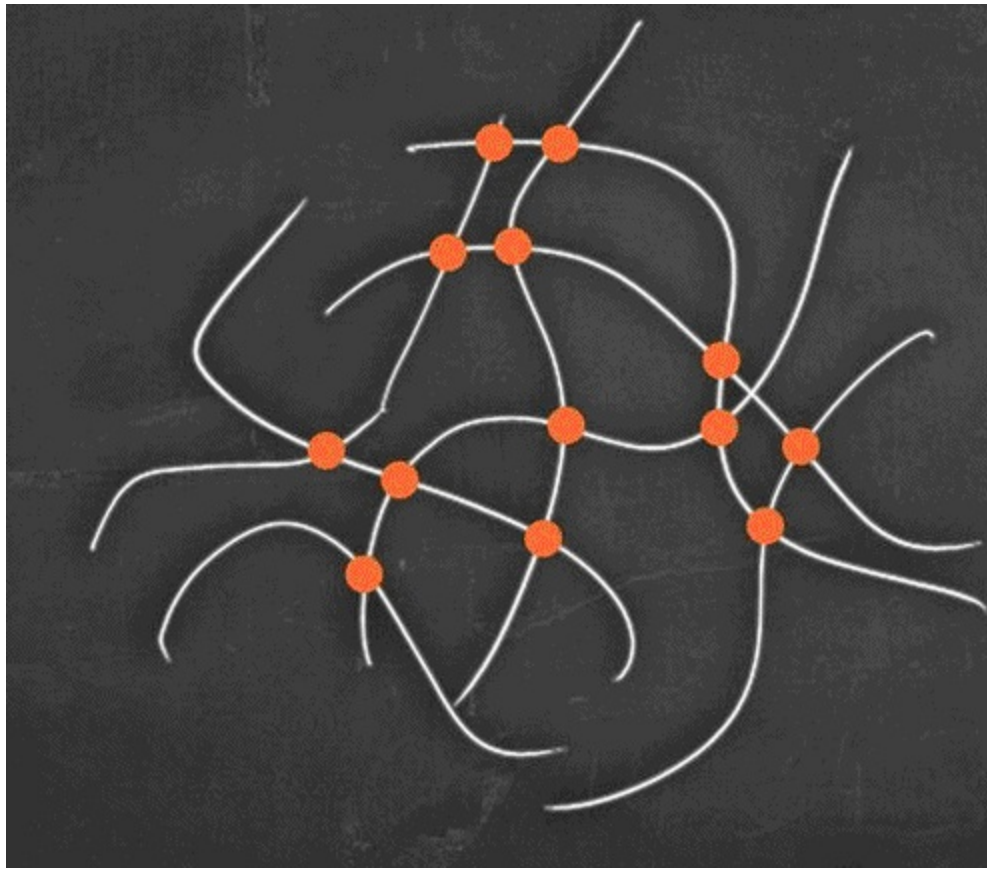


Figure 5.2 A cartoon of polymer strands that have been glued together in the places where they overlap.

In both of the examples above, there is some average distance between the cross-links. In the spaghetti bowl the distance is on the scale of centimeters, and in the hand-holding exercise it is on the scale of meters. This is also the case for real gels, such as eggs or Jell-O, except in these cases the cross-links are much, much shorter. If we call the cross-link distance l , then we

can use the equation that we described last week, $E = \frac{k_B T}{l^3}$ to find out what the elasticities of the gels are (Fig. 5.3).

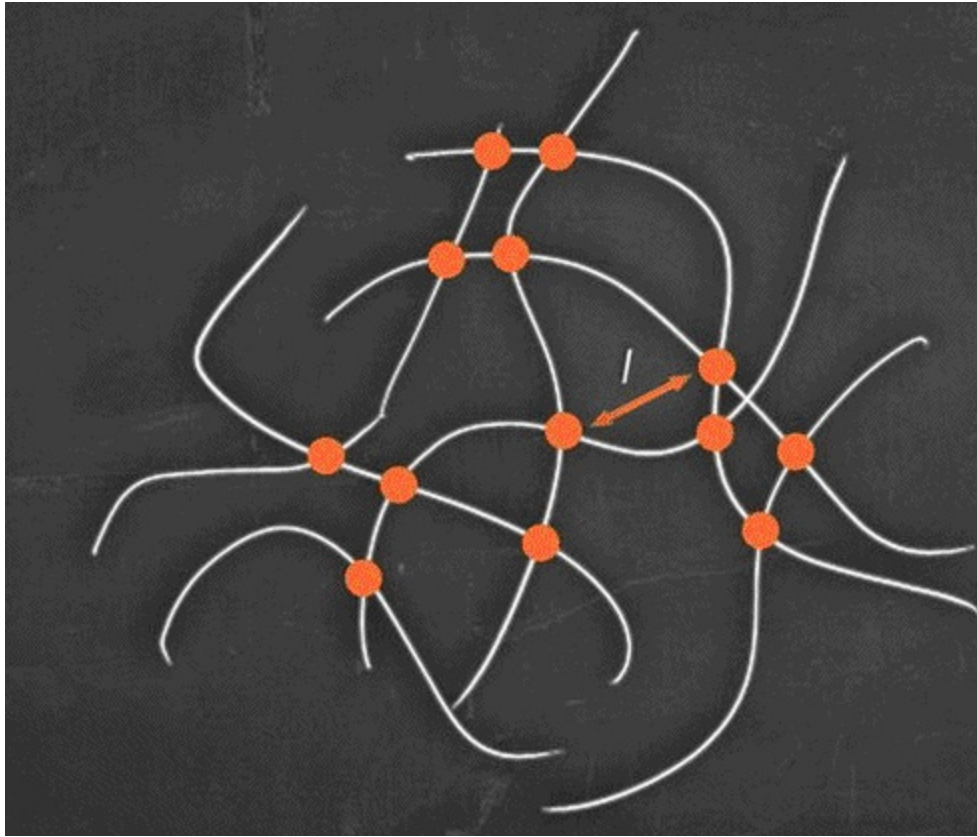


Figure 5.3 Cross-linked polymer strands cause the formation of a gel, where the average cross-link distance, l , can be used to calculate the elasticity of the gel with the equation $E = \frac{k_B T}{l^3}$.

What is interesting about gels in general is that, as opposed to other solids, such as a piece of wood or an ice cube, only a very, very small portion of the molecules in the material is causing the solid to hang together. In the case of the spaghetti, it was the relatively few places where the spaghetti strands were glued. In the case of the hand-holding, it was the small area of the hands, the rest of the person was able to move freely. So most of the material in a gel is actually a liquid. You only need to add a small amount of the cross-link forming polymers to make the material form a solid.

How do cross-links form in real gels? It turns out that there are essentially two different chemical ways that this can happen. One way is that the polymers come from some protein component of the food. This is what happens with eggs. The proteins unfold because of heating, and then they stick to each other forming cross-links. Another way is to add some other polymer to the food, which forms the cross-links that contribute to gel formation. We will cover each of these in the next two sections.

5.2 Gels made with Proteins

5.2.1 The Molecular Basis of Protein Folding and Unfolding

Recall the phase diagram of an egg, and how, as you increase the temperature, the proteins unfold and bind to each other to form cross-links. Let's examine in a bit more detail how this actually happens.

At room temperature, the egg white consists of a sea of proteins that are tightly folded into compact structures (Fig. 5.4). When you heat the egg, at some critical temperature, the proteins unfold and adopt shapes that are more like long, stringy polymers. The unfolding exposes parts of the polymer that were previously buried in the structure, some of which are "sticky" in the sense that they easily form bonds with other parts of the polymer. This is essentially what's causing the cross-links in the egg to form, and as a result the eggs solidifies. Since the bonds are so strong, they don't break at lower temperatures, which is why the egg does not revert back to a liquid when cooling down.

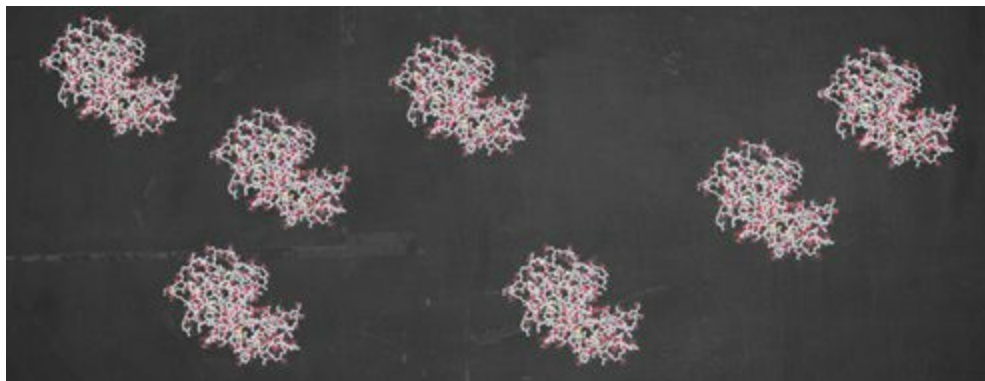


Figure 5.4 On a molecular level, the interior of an egg consists of a sea of proteins dissolved in water. While still uncooked, the proteins are carefully folded into their characteristic three-dimensional structures.

To understand in more detail how all of this happens, we need to look more closely at the molecular level. Proteins, as you recall, are long chains of amino acids (Fig. 5.5). There are twenty different amino acids, and the sequence in various proteins varies depending on the protein. Figure 5.6 shows the amino acid sequence of chicken ovalbumin, with each letter corresponding to a specific amino acid.

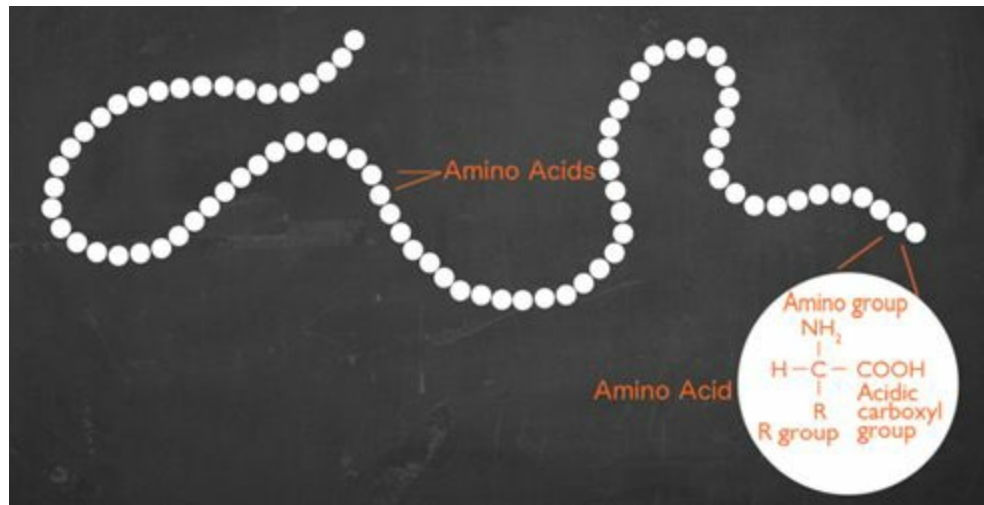


Figure 5.5 Proteins are polymers of amino acids.

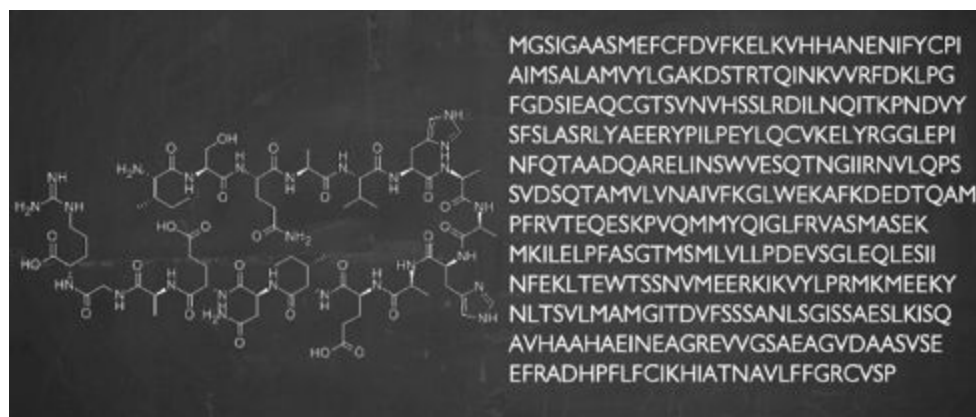


Figure 5.6 The sequence of amino acids in a protein is typically written as a list of the capital letters that denotes each of the amino acids. The picture shows the chemical structure (left) and the amino acid sequence (right) of the protein ovalbumin.

Different amino acids have different chemical and physical properties, but two properties in particular turn out to be especially important for understanding the processes at work here: how hydrophobic or hydrophilic the amino acids are (Fig. 5.7). Hydrophilic amino acids tend to be solvable in water. Hydrophilic comes from a Greek word that means “water loving”. “Hydrophobic” amino acids, on the other hand, are not solvable in water, but instead tend to dissolve in oil. Hydrophobic means “water fearing”. Since hydrophilic and hydrophobic amino acids dissolve in such different liquids, you can imagine that they also do not like being in close contact with each other (Fig. 5.8).

POLAR AMINO ACIDS				NONPOLAR AMINO ACIDS			
AMINO ACID	3-Letter	1-Letter	Charge	AMINO ACID	3-Letter	1-Letter	Charge
Aspartic acid	Asp	D	negative	Alanine	Ala	A	nonpolar
Glutamic acid	Glu	E	negative	Glycine	Gly	G	nonpolar
Arginine	Arg	R	positive	Valine	Val	V	nonpolar
Lysine	Lys	K	positive	Leucine	Leu	L	nonpolar
Histidine	His	H	positive	Isoleucine	Ile	I	nonpolar
Asparagine	Asn	N	uncharged polar	Proline	Pro	P	nonpolar
Glutamine	Gln	Q	uncharged polar	Phenylalanine	Phe	F	nonpolar
Serine	Ser	S	uncharged polar	Methionine	Met	M	nonpolar
Threonine	Thr	T	uncharged polar	Tryptophan	Trp	W	nonpolar
Tyrosine	Tyr	Y	uncharged polar	Cysteine	Cys	C	nonpolar

Figure 5.7 A list of all 20 amino acids. Polar and charged amino acids are hydrophilic, whereas non-polar amino acids are hydrophobic. Each amino acid can also be identified either by its three-letter abbreviation (i.e. Asp, Glu. etc), or by its assigned capital letter (i.e. D, E, etc).

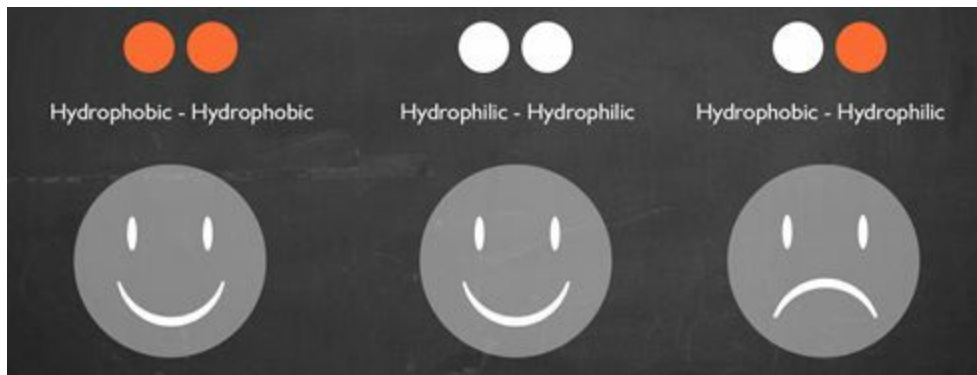


Figure 5.8 Hydrophilic amino acids favorably interact with other hydrophilic substances (such as water or other hydrophilic amino acids). Similarly, hydrophobic amino acids favorably interact with other hydrophobic substances (such as oil or other hydrophobic amino acids). Hydrophobic and hydrophilic substances do not favorably interact.

The result of these different solubility preferences is that hydrophobic amino acids on a protein chain will try to assemble together and stay away from water as much as possible. Similarly, hydrophilic amino acids are also assembling together, but will stay close to the water. Thus, when a protein polymer folds up, something like the following scenario will take place: If the temperature is low enough so that the protein doesn't jiggle a lot, it will try to fold into a compact structure. It will try to assemble all of the grey dots in Figure 5.9, i.e. the hydrophobic amino acids, in the interior of the protein, where they are away from the surface and thus don't touch water. The white dots, the hydrophilic amino acids, will assemble on the surface, in contact with water and away from the hydrophobic interior. It's not possible to do this arrangement perfectly because the amino acids are also attached to the polymer string, but the idea is to minimize exceptions to this rule as

much as possible. By doing this you are following the principle of minimizing the free energy of the protein, and the configuration that is the most favorable will win. Recall that since water is the main constituent of all living cells, we can almost always think of proteins as existing in water as opposed to oil. If proteins were dissolved in oil instead, the opposite arrangement would happen, i.e. the hydrophilic residues would be on the inside and hydrophobic residues on the outside.

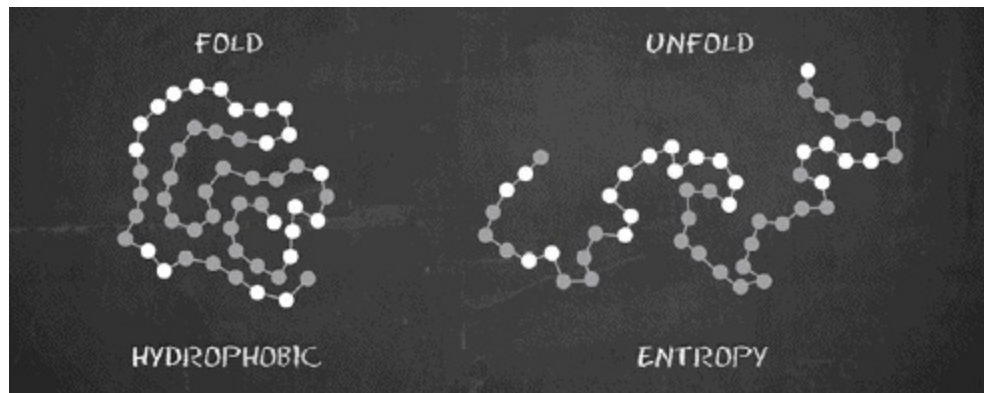


Figure 5.9 Left: At low temperatures a protein polymer will attempt to fold so that hydrophobic residues (grey) cluster in its interior away from water, and hydrophilic residues (white) are on the surface. Right: At higher temperatures entropy plays an increasingly important role. The polymer unfolds and, as a result, hydrophobic residues from the interior are exposed.

At high temperatures, the situation is different because entropy starts to matter. Entropy, as we discussed before when describing phase transitions, competes with energy and causes the protein to unfold. And once it does that, all of the grey hydrophobic amino acids that were initially buried inside are exposed (Fig. 5.9, right). Instead of neatly assembling in the interior, they will randomly stick to other hydrophobic amino acids. This is the origin of the cross-links, which is what forms the gel when you cook an egg.

Video 5.1 shows a more accurate model of what the unfolding of a protein may look like. It is a molecular dynamics simulation that was done on a real protein, the egg protein albumin to be precise, and shows how the protein unfolds as the temperature increases. Simulations like this one includes estimates of all forces and bonds that we know of, and thus gives a fairly accurate picture of how unfolding happens. Initially in the video, the protein is in its compact state, the helices and bends you see are characteristic structures that occur in various ways in all proteins. And when the temperature increases, the bends slowly straighten out and the protein starts to unfold.

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Video 5.1 A molecular dynamics simulation showing the denaturation of albumin as temperature is increased. (Video courtesy of the Greg Verdine Lab, Harvard University)

5.2.2 The pH Dependence of Protein Unfolding

Heating is not the only way to cook an egg. It turns out there are two other ways of causing similar transitions of the proteins. One is by changing the salt concentration, and the other is by changing the pH. Let's look at the role of pH by studying a recipe for poached eggs. Figure 5.10 shows a recipe, and as you can see, it calls for one tablespoon of vinegar and four large eggs. Before cooking the eggs, you are supposed to pour the vinegar into the water. The boiling time is given only as 2-3 minutes, which is a surprisingly short cooking time. The reason you get a boiled egg even with this short cooking time, is that the vinegar changes the pH of the solution. The pH of vinegar is about 2.5, which means that the number of hydrogen ions in the water is dramatically increased. Why does this make a difference? Returning to the list of amino acids in Figure 5.7, you can see that in addition to amino acids being hydrophilic and hydrophobic, there is also a small number that have a charge. Aspartic acid and glutamic acid have negative electric charges, whereas arginine and lysine have positive electric charges.



Figure 5.10 Recipe for poached eggs.

Electric charge is yet another way in which the amino acids on a protein can interact with each other. Like charges are going to repel and unlike charges are going to attract each other. Similar to hydrophobicity and hydrophilicity, these properties will affect the folded structure of the protein. For example, if two positive charges come in proximity with each other, they are going to push that part of the protein structure apart, and vice versa. There is in fact an electrostatic energy of the system, i.e. of the protein structure as a

whole, which is proportional to the square of the charges, and this energy contributes to the free energy of the protein in solution just like the hydrophobic and hydrophilic properties did (Fig. 5.11). When the protein is in its folded state, it has already compensated for the charges, and when the protein is heated and unfolds, it will also try compensating for the charges, the result being the formation of cross-links that contribute to the gel.

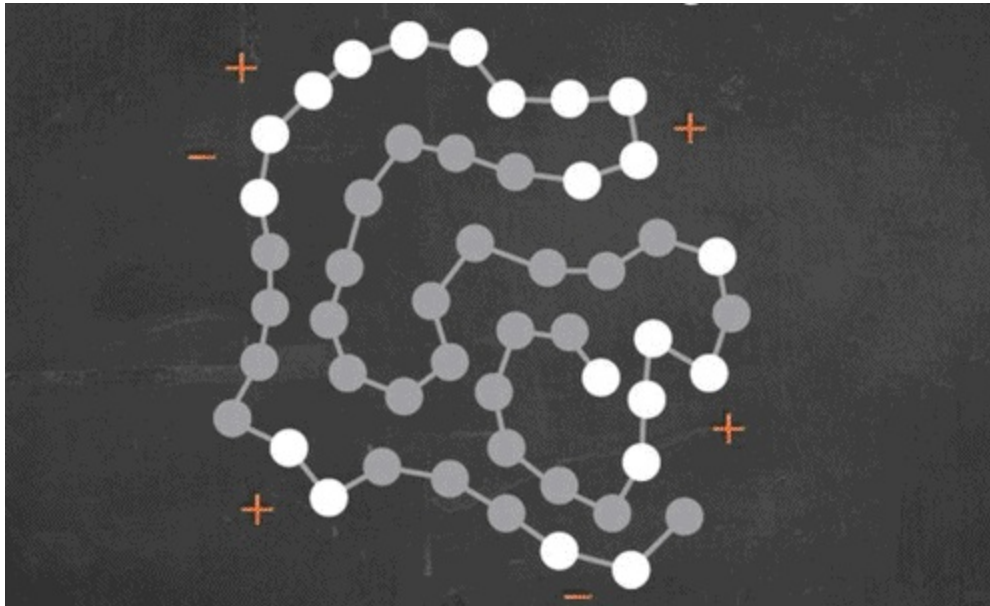


Figure 5.11 The charged amino acids in a protein sequence contribute to an overall electrostatic energy of the protein. The electrostatic energy is proportional to the square of the net charge, i.e. $U_{\text{electrostatic}} = CQ^2$, where U is the electrostatic energy, C is a constant, and Q is the net charge of the protein. In the picture above $Q=4-2=2$ since there are 4 positive and 2 negative charges.

It turns out that one thing one can do to manipulate the folding and unfolding of a protein is to change the charges of the protein, and the way to do that is to change the pH of the solution. This works because charged amino acids actually change their charge depending on the pH that they are in. At low pH, the excess hydrogen ions will bind to the amino acids and increase their charge, and at high pH, the amino acids will release protons to the large number of hydroxide ions (OH^-) in the solution. So if a protein is in an acidic solution, the charges will be even more dramatic than they were before, and this will make the proteins easier to unfold. Similarly if the solution is basic, the charge and unfolding behavior will also be affected.

Figure 5.12 shows a plot of the pH dependence of protein unfolding. The idea behind it is that by knowing the pH dependence of all of the charged amino acid in a protein, we can calculate the total pH dependence of the

protein. In the figure, the protein is fish myosin, one of the major proteins in fish. You can see that at neutral pH, the charge is overall negative, but when the solution is highly acidic, say around 2, the charged state of the protein increases dramatically. In fact, it becomes positive overall. This, of course, makes the protein much more unstable and much more likely to unfold. In other words, the proteins are much more likely to transition from uncooked to cooked.

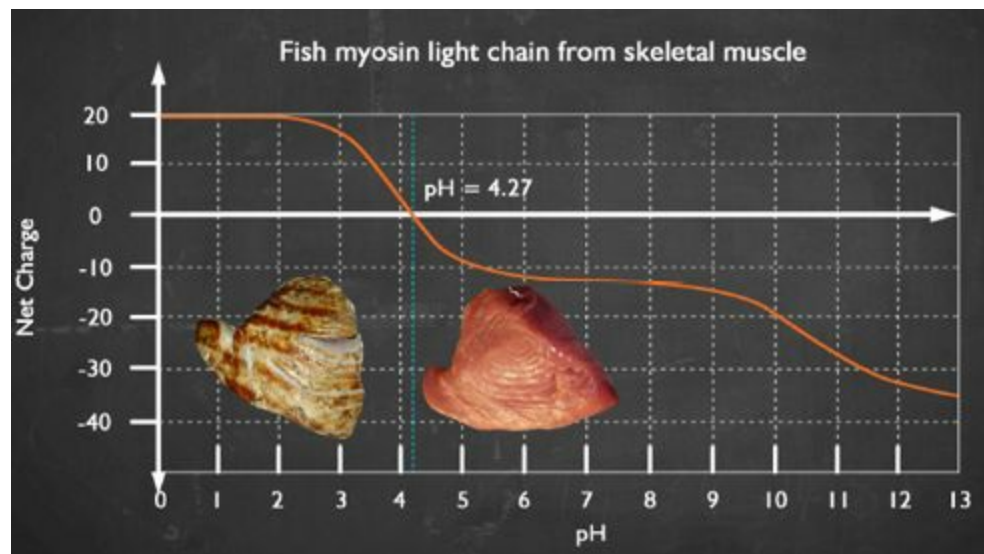


Figure 5.12 Plot of the pH dependence of myosin protein unfolding. Between pH 5 and pH 9, i.e. neutral pH, myosin has a net negative charge. When the pH reaches below 4 the protein quickly takes on a large positive charge, which destabilizes the protein and causes it to unfold.

This very same effect is the secret behind the surprisingly short cooking time in the poached egg recipe. By adding vinegar to the water before boiling, the net charge on the proteins increased, making the proteins more likely to unfold (Fig. 5.13). As a result the egg did not need to boil for as long to cause the same changes to occur. There are many, many other examples of how manipulating the pH is used to great effect when cooking. Vinegar with a pH of 2.4 is used in recipes for home-made ricotta cheese. Lemon juice at pH 2.2 is used for cooking ceviche. Baking soda, at pH 8.4, can be used to change the pH to basic when browning onions and baking cookies. These are but some examples, and we encourage you to be on the look-out for more in your everyday food experiences.

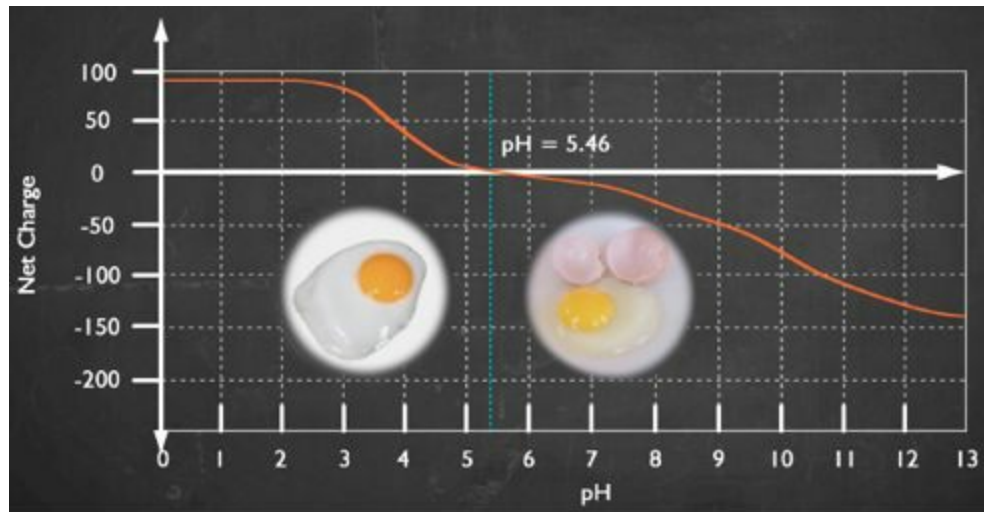


Figure 5.13 Plot of the pH dependence of protein unfolding in serum albumin. At pH 7, the albumin has a net charge of about zero, but at high and low pH the net charge is either very high or very low, thus destabilizing the protein and causing it to unfold.

The challenge with manipulating the pH while cooking, is that while we often want to cause the proteins to unfold and coagulate, we also don't want to ruin the taste. Too much vinegar or lemon juice in a recipe isn't going to taste very good, as anyone who has had a spoonful of vinegar can attest to. One of the balances between, on the one hand, causing transitions by changing the acidity; and on the other hand, causing them with temperature, is that when changing the acidity, the taste also tends to be affected.

5.3 Gels made with Hydrocolloids

5.3.1 The Molecular Basis of Spherification

In the previous section we covered the first of two chemical ways that cross-links can form in food. In this section we will discuss the second way. As opposed to the first mechanism, this one does not involve proteins folding and unfolding. Instead it involves situations where the goal is to make carbohydrate polymers stick to each other.

Let's start by studying a recipe for spherification (Fig. 5.14). The recipe is a classic by Ferran Adria, who is the inventor of this modernist dish in which a thin shell of gel is created around a liquid food. In this case the food is a delicious juice made from tea, sugar and lemons, hence the name, spherical tea ravioli, but the inside of the sphere can be made of any liquid food (Fig 5.15). We will talk about the physics of how the outside of the gel forms in the next section, but first let's take a closer look at the ingredients. You will notice that there are two ingredients that seem a little unusual. One is sodium alginate, and the second is calcium chloride.



Figure 5.14 Spherified peas. (Photo: ElBulli Foundation).

Spherical Tea Ravioli

Setting Bath:

500 grams of water
 3.25 grams of calcium chloride (0.65%)

Ingredients:

475 grams of water
 16 grams Earl Grey tea
 25 grams of sugar
 50 grams of lemon juice
 1.5 grams of sodium alginate (0.3%)

Preparation:

1. Mix 400 grams of water, the tea and 20 grams of sugar while cold and steep in the refrigerator for 24 hours. Strain.
2. Combine the lemon juice with 5 grams of sugar and freeze in an ice tray.
3. Blend the sodium alginate with 75 grams of water.
4. Dilute the calcium chloride in 500 grams of water.
5. Mix the tea infusion with the sodium alginate base and allow to rest. Place in the freezer to chill but do not allow it to freeze.
6. Place a lemon cube in a 3cm dosing spoon and fill the rest of it with the tea base. Place in the calcium chloride bath for 30 seconds.
7. Rinse the ravioli in cold water.

Figure 5.15 Recipe for spherical tea ravioli

Calcium chloride is a type of salt, and the sodium alginate is a carbohydrate polymer that comes from seaweed. The key characteristic of the alginate polymers is that they are negatively charged, which means that they will repel each other (Fig. 5.16).

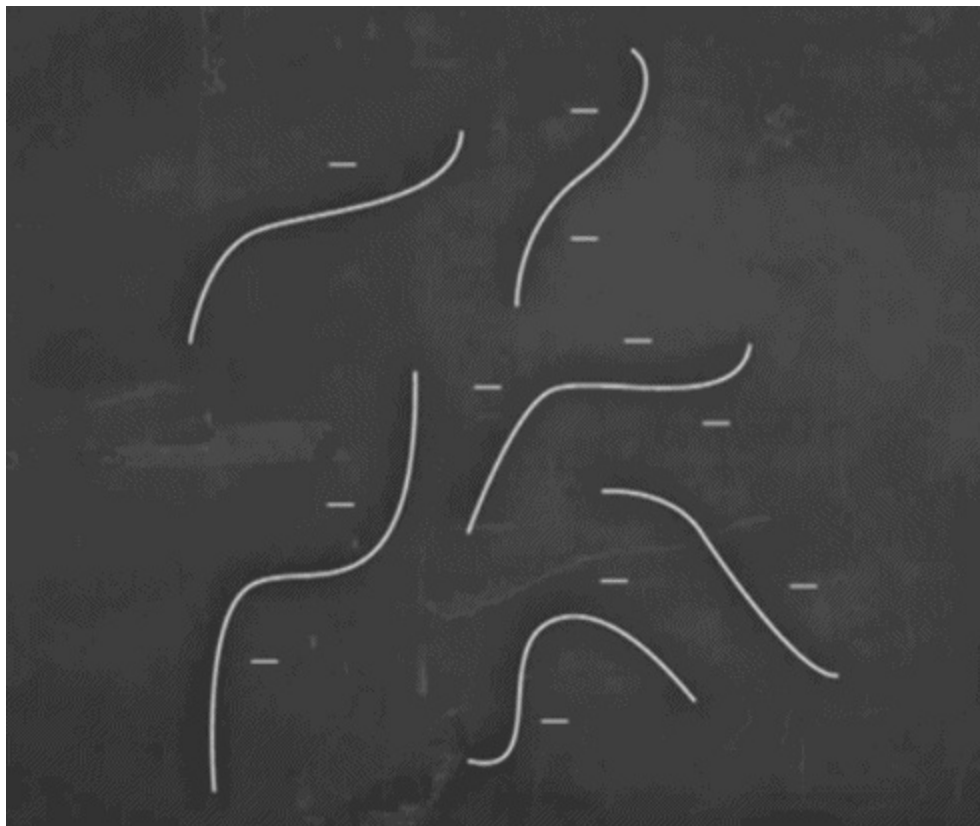


Figure 5.16 Alginate polymers are negatively charged, causing the polymers to repel each other.

If we are in the business of trying to make a gel, this is somewhat problematic. After all, we need to make the polymers stick to each other, not repel each other. How could we do that? One thing to try would be to add positive charges. We will find this in the form of table salt in the kitchen. Table salt consists of positively charged sodium ions and negatively charged chloride ions. When poured into a solution of water and alginate, the ions will disassociate, and the positive ions will stick to the negative polymer strands and neutralize them (Fig. 5.17). As a result the polymers will repel each other less than they did before, but they probably still won't stick to each other.

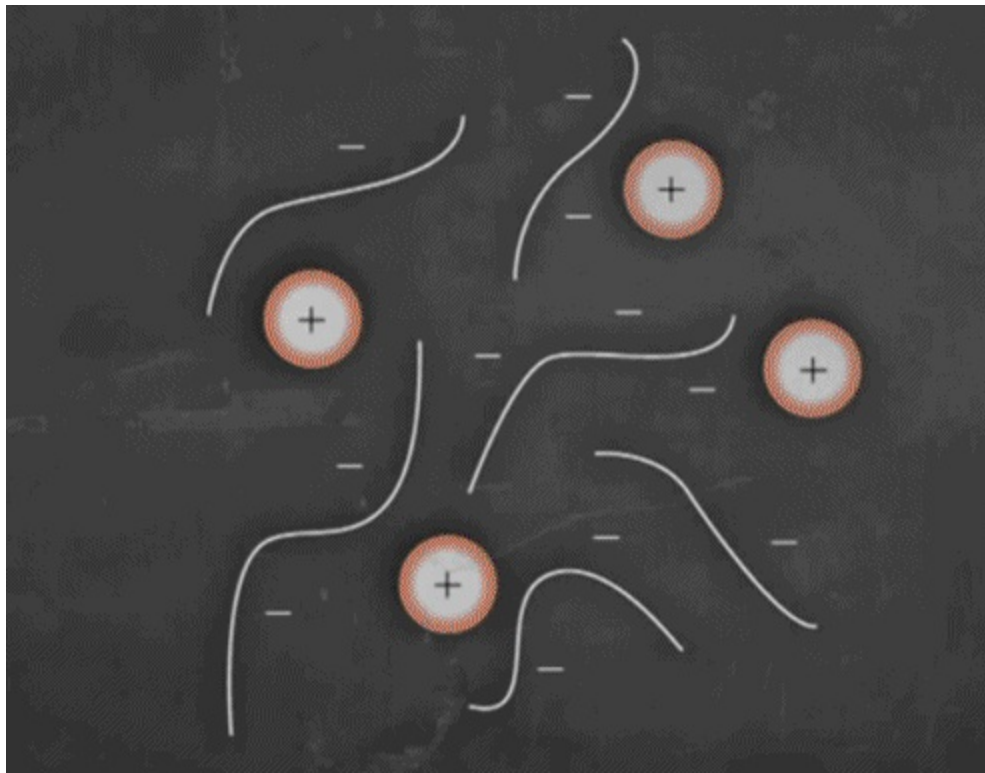


Figure 5.17 The positively charged sodium ions in sodium chloride (table salt) can neutralize the negatively charged alginate polymers. However, they are not sufficient to make the polymers cross-link to each other.

It turns out though, that by using a different type of salt, calcium salt, one can make the polymers stick. This is because calcium ions have two charges instead of one, so after binding to and neutralizing one negative charge, it can also bind to another alginate molecule with the other charge. This links the polymers together (Fig. 5.18). The situation is similar to the demonstration where we asked you to gather a group of friends and randomly hold hands, thus essentially creating a gel. The calcium ion essentially corresponds to one person who, with his or her two hands, has

the ability to hold hands with two friends, as opposed to just one friend.

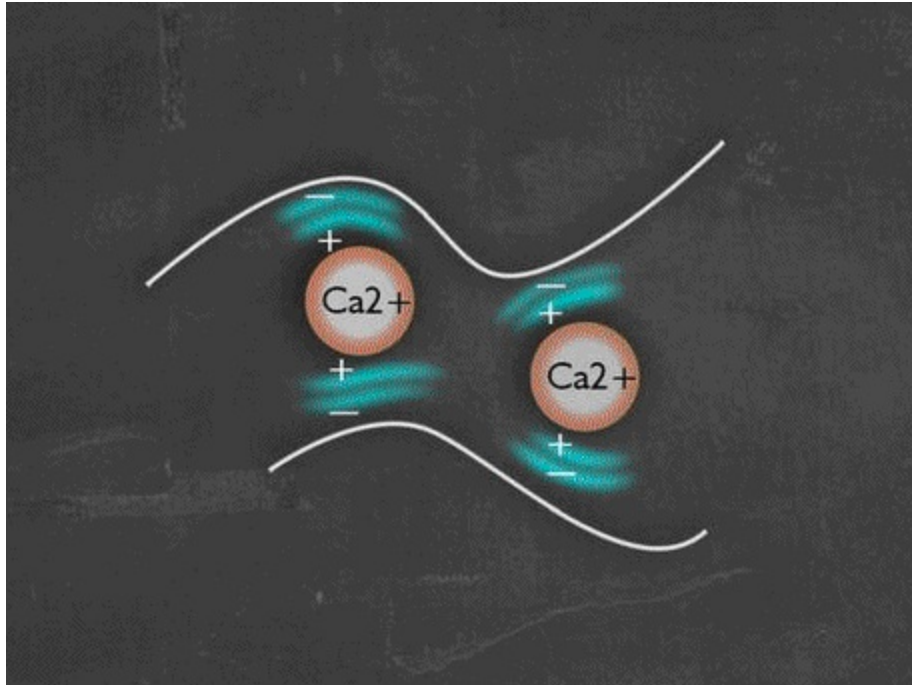


Figure 5.18 Calcium ions from calcium chloride have two positive charges, and can therefore link two different alginate polymers together.

Figure 5.19 shows what this scenario looks like on a chemical level. The alginate molecule has a chemical structure with places within it where the calcium molecules can bind, thus causing two alginate polymers to be attached to each other.

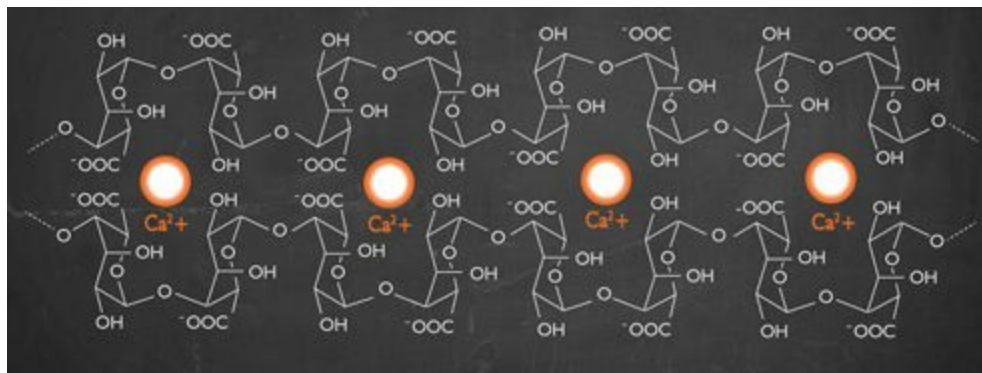


Figure 5.19 Chemical structure of two alginate polymers with bound calcium ions. (Source: ElBulli Foundation)

5.3.2 Cooking with Hydrocolloids

Sodium alginate is an example of a hydrocolloid, i.e. a substance that forms a gel in the presence of water. There is a long list of other hydrocolloids that can be used in various contexts in the kitchen (Fig. 5.20). Gellan, guar gum, and xanthan gum are some other examples. The properties of the different hydrocolloids vary slightly, and a skilled chef carefully selects which one to use depending on the desired outcome for the food.

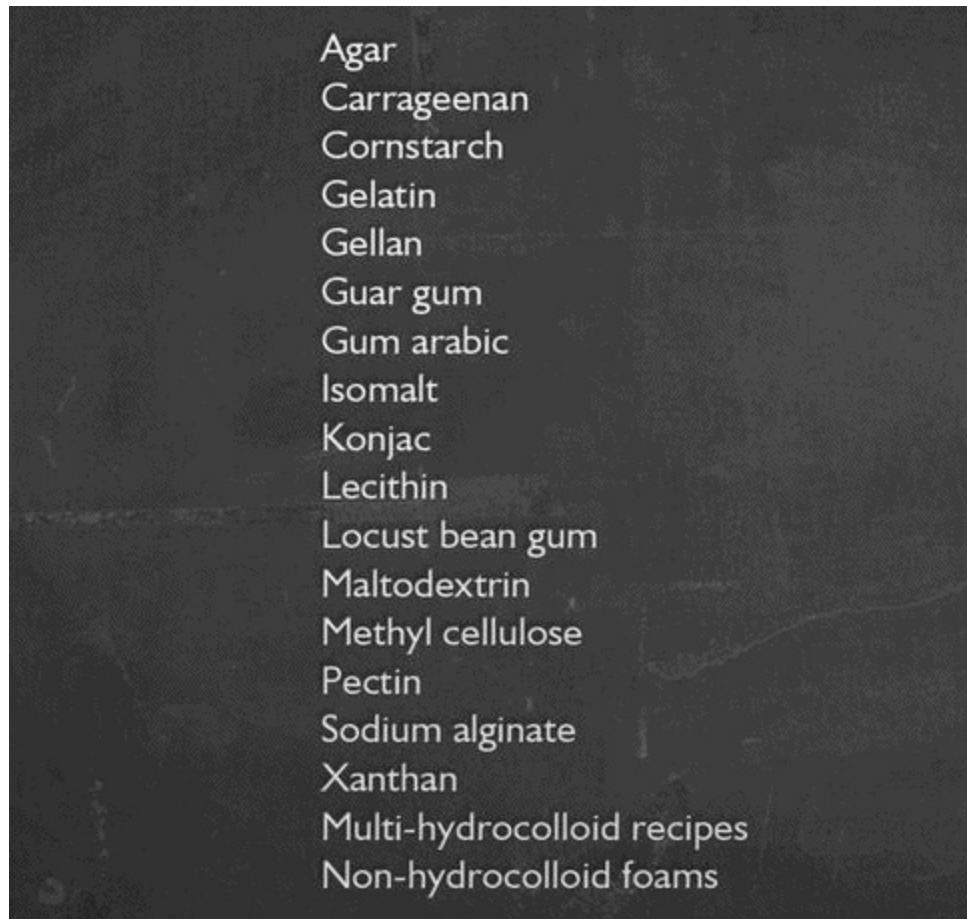


Figure 5.20 List of common hydrocolloids used for cooking.

One remarkable example of how hydrocolloids can be used to create novel dishes, is a recipe for Hot and Cold Tea by Chef Heston Blumenthal, owner of the restaurant The Fat Duck in the UK. In this recipe, tea is served hot and cold at the same time; one side of the cup is hot and the other is cold, and the two sides are vertically, and invisibly separated. Thus upon drinking, one side of the mouth feels the hot temperature and the other side feels the cold temperature (Fig. 5.21). The challenge in making this recipe, is that both the hot and cold tea need to be solid enough so that they do

not easily mix with each other across the vertical line. But they also need to be liquid enough so that they are experienced as tea, not Jell-O. And, perhaps most importantly, they need to have about the same elasticities at the hot and cold temperatures. It turns out Heston Blumenthal was able to achieve all of these things by using a hydrocolloid called gellan. Just like alginate, gellan is a carbohydrate, but unlike alginate, its gelation mechanism is less based on charge and more reminiscent of the gelation mechanism of an egg.

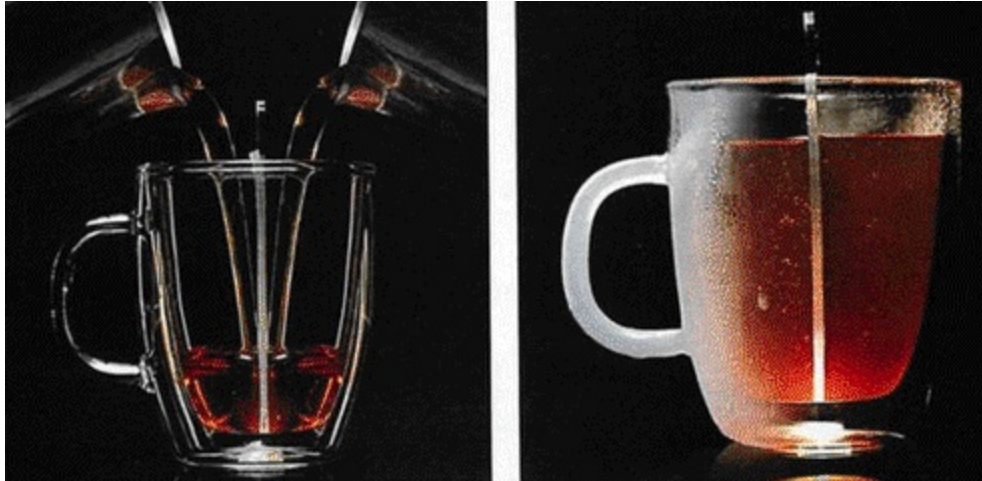


Figure 5.21 Hot and cold tea as created by Chef Heston Blumenthal. One side of the cup contains hot tea and the other side contains cold tea.

Another example of a remarkable dish made possible by the use of hydrocolloids is hot ice cream. This is another of Ferran Adria's creations. It uses methyl cellulose, which has the special property of being able to cause gelation even at relatively high temperatures. Thus you can use it to create ice cream that has the texture of cold ice cream even when served at temperatures up to about 50-60°C.

5.4 Spherification

5.4.1 The Movement of Calcium Ions

In a typical recipe for spherification, you start out with some juice, be it mango, pea, or olive juice, and then add a small amount of alginate to it (Fig. 5.22). If you could zoom in you would see long strands of alginate polymers floating around in the juice. Since they are negatively charged they float around without getting too close to each other. The next step is to take a spoonful of this solution and carefully submerge it into a calcium bath. The ions from the bath start to move into the sphere and, since they are doubly positively charged, they cross-link the alginate strands by the mechanism we just discussed. The result is that a thin gel starts to form around the juice sphere (Fig. 5.23). The gel grows thicker over time, but if done right, the final gel layer is just thick enough to contain the juice, but so thin that, when eaten, it pops open in the mouth and releases the delicious juice on the tongue all at once.

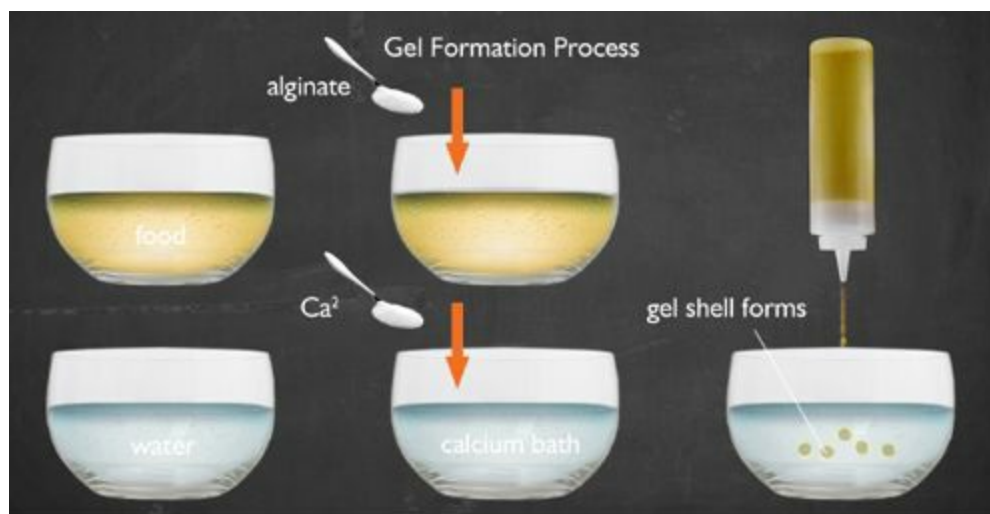


Figure 5.22 Spherification involves dissolving a small amount of alginate in a liquid food of your choice. The liquid is then submerged or dripped into a solution made from calcium chloride and water. The calcium ions cross-link the alginate polymers, causing a thin gel to form around the liquid food.

Other than the cross-linking mechanism of the calcium ions, the key process that makes this recipe possible is the movement of calcium ions into the juice sphere. Without this happening no cross-links between alginate and calcium could form in the first place. We will describe this process in detail in the next section, but let's first look at a few other examples where this

same process plays an important role, because interestingly, the process that governs the motion of calcium ions is not only important for spherification, but also occurs throughout cooking, and indeed, throughout everyday life in various other ways.



Figure 5.23 An alginate droplet submerged in a calcium solution will form a thin shell encapsulating the liquid.

One example of the same process is cooking a steak. A nicely cooked steak will be less cooked in its interior, have a texture similar to well-done close to the surface, and have a crispy, brown layer right at the surface (Fig. 5.24). In order for the steak to develop this brown layer, heat has to move from the grill, or the stove, into the meat, and transform the initially flaccid meat into a nice, crispy, brown layer. This layer is physically analogous to the gel layer that forms around the sphere in the calcium bath, and it actually occurs through the same physical process. Both the steak and the spherification also have in common something you already know about cooking, which is that time matters. If you leave the steak on the grill for too long, it will be cooked and dry all the way through. If, on the other hand, you cook it too briefly, the interior will be raw. Similarly, how long you leave a droplet of olive juice in a calcium bath matters. If you leave it for too long, maybe as long as an hour, the sphere will be made of solid gel all the way through, and the dish will be a very different eating experience altogether. If left for too short, the gel will be too thin and the sphere will fall apart.



Figure 5.24 The process of cooking a steak is physically analogous to the process that occurs in spherification.

5.4.2 Making Cheese on a Microscope Slide

The process that underlies the movement of calcium ions, also occurs in recipes for ricotta cheese. Recall that when we added vinegar to milk and heated it to about 90°C, the milk curdled. It coagulated, and formed what we now know to be a gel. It is a different type of gel than occurs in spherification, but it is still a gel. Daniel Rosenberg has in his repertoire a demonstration that essentially involves making ricotta cheese under a microscope slide. It illustrates the process at work in the context of ricotta cheese, but it is also a great demonstration of the underlying physics of steaks and spherification. The idea of the demonstration is to add a drop of milk to a microscope slide and then, next to it, add a drop of vinegar. When you put a thin cover glass slip on top of the drops, they mix, and you can observe what happens under a microscope.

To understand what happens on a macroscopic scale, recall the phase diagram from Chapter 3, where pH was plotted on the y-axis and the temperature on the x-axis (Fig. 5.25). At 90°C only a small amount of vinegar had to be added for the milk to curdle. However, if you instead wanted to make cheese at room temperature, you would have to add a lot more vinegar. So as the milk and vinegar drops mix on the microscope slide, we are essentially making cheese at room temperature and watching as it happens.

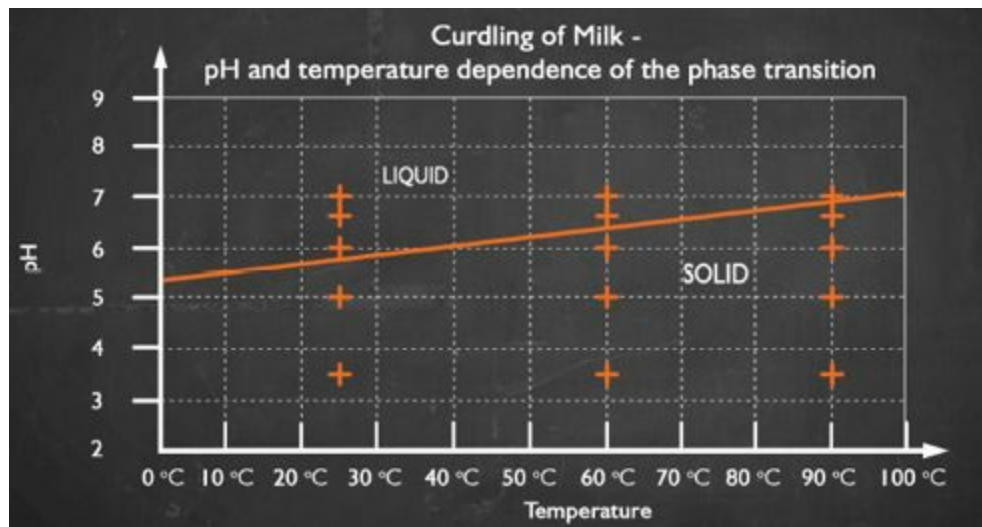


Figure 5.25 Plot showing the pH and temperature dependence of the curdling of milk

Before the drops have mixed at all, the microscope image will reveal how the fat globules in the milk are jiggling around, or undergoing what seems

like random motions in all directions (Video 5.2). When the vinegar starts mixing with the milk it does so by traversing in from the side of the image, causing the proteins in the milk to unfold and coagulate. As a result, the jiggling stops, and the image under the microscope becomes stationary. As time passes, a larger and larger region under the microscope turns stationary as the vinegar continues to spread through the milk. This process, the growing of the stationary cheese-like layer is physically exactly analogous to what is happening in the alginate when it is cross-linked by the calcium ions. The vinegar is invading the milk, unfolding the milk proteins, and causing them to form cross-links. Similarly, in spherification, the calcium ions invade the alginate solution, causing the alginate molecules to stick to each other. In both cases, the resulting immobilization leads to the formation of a gel.

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Video 5.2 Cheese making on a microscope slide. The fat globules in the milk are initially jiggling around, but immediately stop when the vinegar moves in from the bottom of the slide. The vinegar causes the proteins in the milk to denature and form a gel. (Video courtesy of Daniel Rosenberg)

5.5 Random Walk

5.5.1 Pearson, Einstein and Bachelier on the Random Walk

The physical mechanism that underlies the processes we just described, goes under the name of the random walk. The idea of the random walk, to our knowledge, was first introduced into the scientific literature by a great statistician named Karl Pearson (Fig. 5.26). He described it in a letter to the journal *Nature* in 1905. The journal *Nature* was then, and is today, one of the great scientific journals that exists. Apparently it was permissible at that time to ask questions in the articles published there, rather than propose answers as is the case today, because Pearson described the process and then asked the readers of the journal for help trying to understand it mathematically. The process he described was the following: Suppose that a person flips a coin, and depending on how the coin lands, the person either takes a step to the right or to the left. For example, if the coin comes up heads, the person takes a step to the right, and if the coin comes up tails, the person takes a step to the left. This process of randomly moving to the right or to the left, Pearson called the random walk, and he asked the readers of the journal if anyone could help him understand the mathematics that underlies this process.

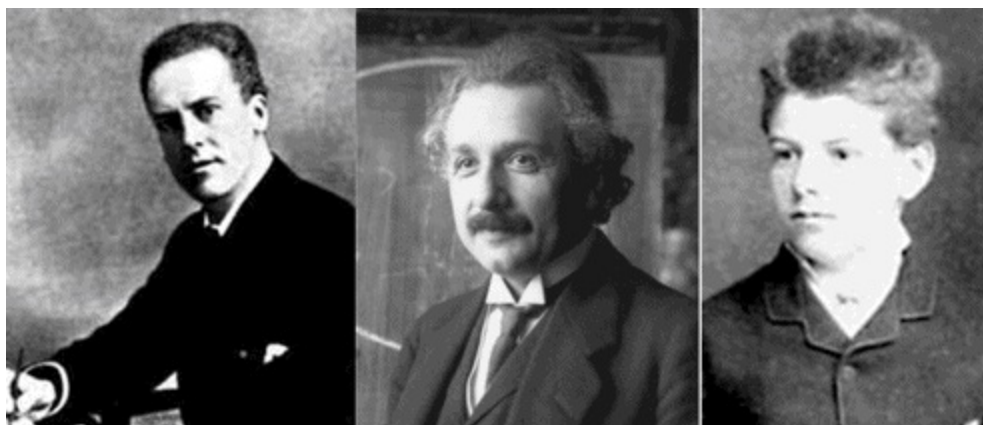


Figure 5.26 Karl Pearson, Albert Einstein, and Lois Bachelier, three scientists who all studied the phenomenon of random walks

Pearson wrote this letter in 1905, and it turns out that if he had been a careful reader of the literature, he would have realized that this question had already been answered in the literature not once, but twice, by two

different people in the years that preceded.

One of the people was a young man whose name was Albert Einstein. He wrote a paper in 1904, it was one of the three great papers that he wrote that year, and the paper had the title "On the Movement of Small Particles Suspended in Stationary Liquids Required by the Molecular Theory of Heat". This is perhaps not the most captivating title, and the content, at first glance, does not look much different. But what Einstein did in this paper was actually closely related to the demo of making cheese on a microscope slide, except instead of adding vinegar, Einstein just studied the milk. Recall how the fat globules of the milk were moving around randomly under the microscope before the vinegar was added? Einstein noted that the reason the fat globules move around is because they are being buffeted by the other molecules in the milk. And he asked himself what the characteristics of this process could be.

If you think about it, the process is actually very much like the random walk that Pearson described. Namely, imagine a fat globule surrounded by other molecules and fat globules. Sometimes the molecules on the right will push the fat globule the left, and sometimes the molecules on the left will push the fat globule to the right. The fat globule will get pushed randomly in both directions. Einstein worked out the mathematics of this behavior in his paper, and we will introduce the central formula soon. As an aside, he also used the answer to this question to calculate what the size of the buffeting molecules in the milk must be, which, of course, is something we also tried to do at the beginning of this class.

The other person who answered Pearson's question is someone you have probably not heard of. He was also a young man at the time and his name was Louis Bachelier. He was a student of Poincaré, who was one of the great mathematicians at the time. Bachelier was interested in a very different phenomena, namely, the movement of stock prices. He wanted to make a model, a mathematical description, for how stock prices change with time. If you pick a stock and watch it, you will see that some days it goes up and some days it goes down. The price is buffeted by random factors that are moving it up and down. On the surface of it, it looks like it is undergoing a random walk, and this was indeed Bachelier's hypothesis. We now know that the movement of stock prices is a bit more complicated than

this, but nonetheless, the formula he invented was a mathematical description, which was identical to the one Einstein had invented. It also answered Pearson's question, and it will be of great use to us now in our description of the random walk.

5.5.2 The Equation of the Week

How is all of this relevant to spherification and steaks? It's relevant because the question in all of the cases above becomes: how far does the thing in question move after a certain amount of time? In the case of the person flipping a coin, imagine that the flipping is repeated a hundred times, and each time the person steps either to the right or left. How far has the person moved in the end? In terms of stock prices, we might like to know how a certain stock will be valued after a certain number of days or weeks. Similarly, whether we are cooking a steak or spherifying something, we would want to know how long we should let the process go on for the steak or sphere to be done just right.

Recall how the juice and alginate sphere was submerged into a calcium solution. An enlarged view of what this would look like at the interphase of the sphere and the solution can be seen in Figure 5.28 (top). On a molecular level, each calcium ion, just like the fat globule in the milk, is buffeted by the molecules on all sides, and will randomly be pushed one way and then the other. If the calcium is pushed into the alginate sphere, and if the polymers are arranged right, it will bind to the negative charges and form a cross-link (Fig. 5.28, bottom). And this, of course, is what forms the gel. If the calcium ions have time to move far into the sphere, then the gel will be thicker than if they don't move as far. So what ultimately decides the thickness of the gel is the distance the calcium ions move, and this, of course, is determined by the random walk. So by understanding how random walks work, we can predict how long we should leave the sphere in the alginate bath, in order to get just the right thickness for the sphere to pop just right in your mouth.

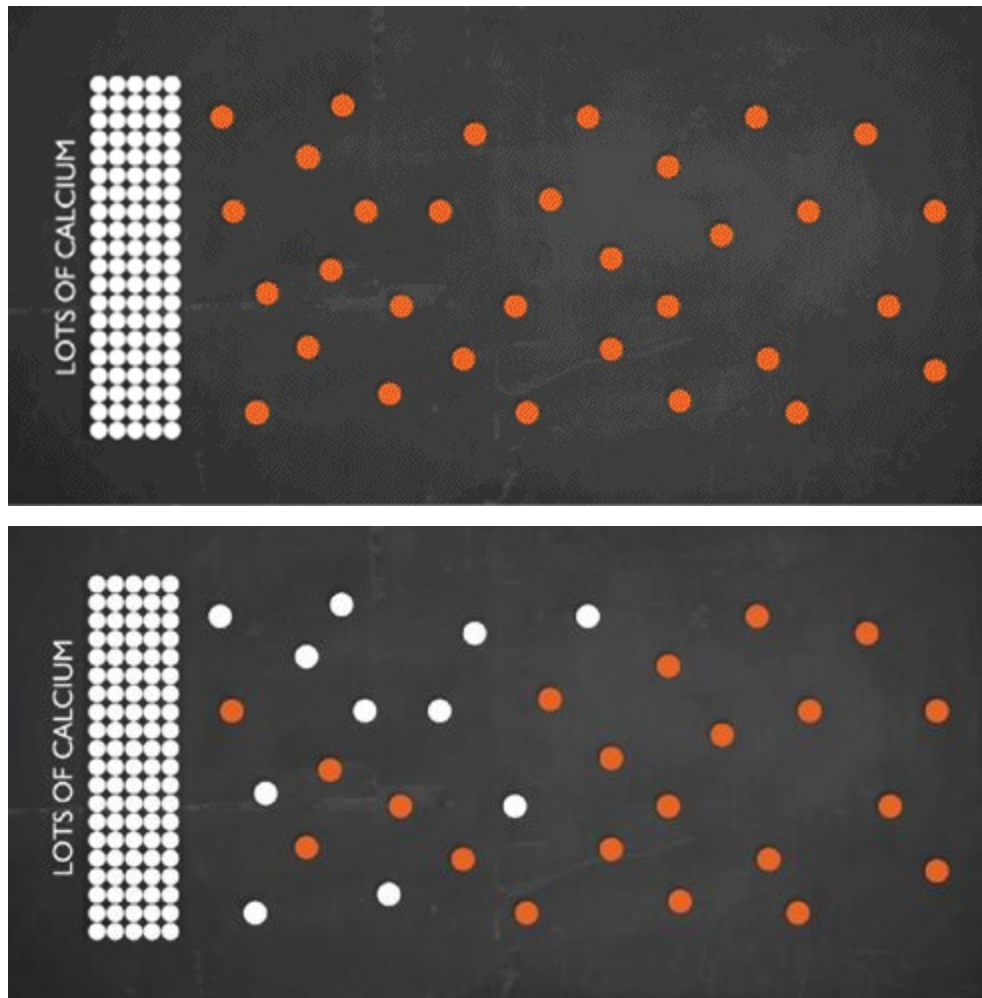


Figure 5.28 A cartoon of the boundary between the alginate sphere (right) and the calcium solution (left). Calcium ions are shown in white and alginate is indicated in orange. Initially there are no calcium ions in the alginate (top), but over time the calcium ions move into the alginate solution by performing a random walk (bottom).

The same reasoning applies to cooking a steak. If you were trying to cook a steak so that it had a thin brown layer on the outside, while still being slightly rare in the middle, you would want to make sure that the heat from the stove or grille moved just the right distance into the steak. And the question for you as a cook would be, how long does it take for that to happen?

The answer to the question of how long a random walk takes is in the form of an equation. This is the same equation that both Bachelier and Einstein found, and it is the equation for this week (Table 5.1). The equation says that L , which is the distance that the calcium ions move, or the distance that heat moves, or the distance that the vinegar diffuses through the milk, is equal to the square root of 4 times D times t . D is a number that varies from material to material. It is called the diffusion coefficient, and is usually

given in units of cm^2/sec , and t is the amount of time elapsed.

$$L = \sqrt{4Dt}$$

Now that we have an equation that describes this process, let's try to use it in answering one of the questions above. Imagine you wanted to spherify a drop of mango juice. How long should you let the droplet sit in the calcium bath for the thin shell to form? In order to use the equation, we first need to know what the diffusion constant, D , is. It turns out that this number is $8 \cdot 10^{-10} \text{ m}^2/\text{sec}$, i.e. for every second that you leave a calcium ion in water, it randomly moves over a very small area of $8 \cdot 10^{-10} \text{ m}^2$. Next let's suppose that we want a half a millimeter-thick shell. Since D is given as m^2/sec , we will convert this variable to meters, half a millimeter is the same as 0.0005 meters. Now we can solve for the time, t , and plug the numbers for L and D into the equation.

$$t = \frac{L^2}{4D}$$
$$t = \frac{(5 \cdot 10^{-4} \text{ m})^2}{4(8 \cdot 10^{-10} \text{ m}^2/\text{sec})} = 78 \text{ sec}$$

So according to these calculations you should wait a little over a minute for the shell to form in the recipe. And indeed, this time is very similar to the time that is usually proposed in spherification recipes.

EQUATION OF THE WEEK

$$L = \sqrt{4Dt}$$

Symbol	Description	Units
L	Distance of diffusion	m
D	Diffusion coefficient	m ² /sec
t	Time to diffuse	s

Table 5.1

5.6 Osmosis

A concept that is closely related to diffusion, and also very important for cooking, is osmosis. It's a key concept in brining and pickling of vegetables, for example, and America's Test Kitchen takes advantage of it in a recipe for making the perfect coleslaw. In this recipe they add a healthy amount of salt to chopped cabbage, and let it drain over a colander for a while before finishing the recipe the traditional way. Why do they do this and what happens on a molecular level? Let's see if we can explain this by learning a little about how osmosis works.

The underlying physical principle of osmosis, just like that of diffusion, is the idea of the random walk. The two concepts differ though in that osmosis involves the presence of a membrane, which obstructs the movement of the random walk for certain molecules but not for others. A membrane of this kind is usually referred to as semi-permeable or selectively permeable. It is the type of membrane that encloses the cells of all plant and animal cells, helping them to regulate what enters and exits the cell. Water can flow freely across a semi-permeable membrane, but large molecules or molecules with a charge, ions, cannot move across without actively being transported by the cell.

Video 5.3 starts out showing a cell membrane. We can pretend that this is the membrane of one of the coleslaw cells from the America's Test Kitchen recipe. There is water both on the inside and outside of the cell, and when adding the salt, there will be a high concentration of sodium ions and chloride ions on the outside. Since the salt ions are charged and hence cannot move across the membrane, they will stay on the outside. The water molecules, however, can move across the membrane freely, and will be crossing it in both directions. When they find themselves on the side of the membrane that has a higher salt concentration, it turns out that they have a higher probability of staying there. As a result, there is an increase of water flux towards the side of the higher salt concentration. This is the process at the heart of osmosis: water molecules will move, overall, in a direction that equilibrates the salt concentration on one side of a semi-permeable membrane to be similar to that of the other.

Sorry, it appears your system either does not support video playback or

cannot play the MP4 format provided. However, you can view the video by clicking on this link:

[video_3_osmosis_03.mov](#)

Video 5.3 The process of osmosis as observed over a cell membrane.

This explains what happens in the coleslaw recipe. By mixing the chopped cabbage with salt and waiting for a while, the water in the coleslaw cells move out of the cells, and ends up in the bowl under the colander. If you try this for yourself, you will see that quite a bit of water comes out of the cabbage even after just 15 minutes. The result is that the coleslaw is now deliciously crunchy since it contains less water, and, in addition, since we have already drawn out a lot of water that may otherwise leak out and dilute the sauce, the final result will be less watery. So understanding osmosis is the trick to making perfect coleslaw.

CHAPTER 6

Heat Transfer

TABLE OF CONTENTS: 6

6.1 Introduction to Heat Transfer

[6.1.1 Heating Protocols and Target Temperatures of Common Recipes](#)

6.2 Browning Reactions

[6.2.1 Maillard Reactions Create the Flavorful Crust on Cooked Foods](#)

6.3 Why it is Hard to Cook a Steak

[6.3.1 The Challenge of Hitting Different Target Temperatures](#)

[6.3.2 Cooking Protocols that Address the Challenges](#)

[6.3.3 The Final Challenge: Food Continues to Cook](#)

6.4 Heat – Microscopic Perspective

[6.4.1 Heat Diffuses by a Random Walk](#)

[6.4.2 Heat Diffusion Constants of Food](#)

[6.4.3 Example: Cooking a Tuna Steak](#)

6.5 Heat – Macroscopic Perspective

[6.5.1 Heating as a Transfer of Thermal Energy: Deriving an Equation for Heat Transfer](#)

[6.5.2 Comparing the Equation with Experimental Data](#)

6.6 Calculating Temperature Profiles

[6.6.1 Finding the Temperature of a Food as a Function of Space and Time](#)

[6.6.2 CookMyMeat Software](#)

6.7 Rules of Thumb I: Cooking Times

[6.7.1 Using the Diffusion Equation as an Estimate](#)

6.8 Rules of Thumb II: Cooking Times

[6.8.1 Applying the Diffusion Equation to Cooking a Turkey](#)

6.8.2 Limitations of the Diffusion Equation

CHAPTER 6

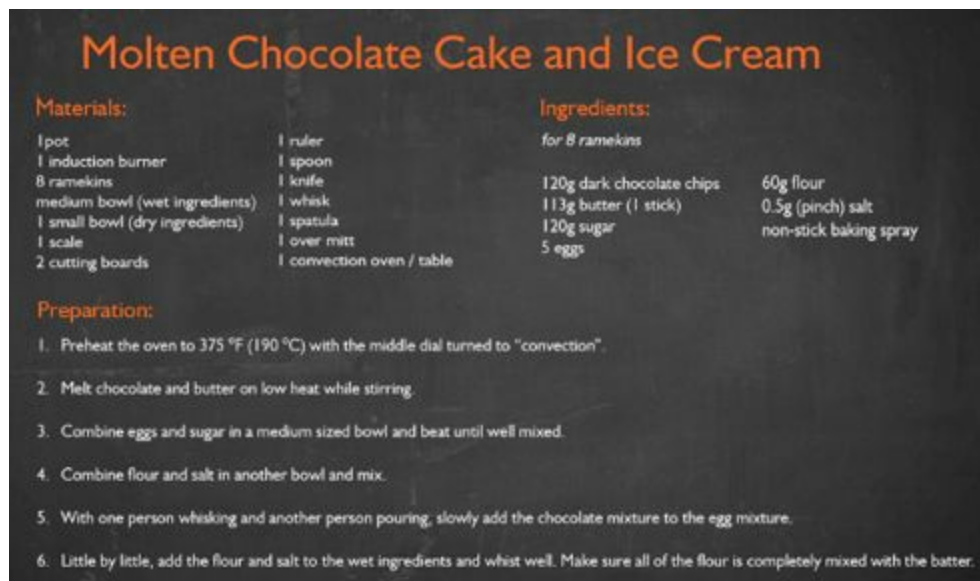
6.1 Introduction to Heat Transfer

A critical component of cooking is the application of heat to food. Indeed, as you likely recall from Chapter 2, the Oxford English Dictionary uses the word heat in the very definition of what cooking is. It says that cooking is to make a food “fit for eating by due application of heat, as by boiling, baking, roasting, broiling, etc”. Although the definition of cooking in this class is much broader than this, heating is obviously very important for cooking. We now want to talk about the physics behind it.

We have discussed cooking food with heat before in this course in the context of cooking an egg. We pointed out that when adding a certain amount of heat, an egg goes from being uncooked to cooked. The transition happens at a certain temperature, which, depending on how you like your eggs, is somewhere between 60 and 70°C. The perfect egg, as defined by many chefs, is at about 64°C, and we identified this as being near a transition where some of the critical egg proteins unfold and then coagulate with each other. Similarly, cooking chocolate also involves critical temperatures. We learned that chocolate has five crystalline phases in the range of 18-36°C, and that the art of tempering chocolate involves hitting one of the phases and making the chocolate stay in that state.

6.1.1 Heating Protocols and Target Temperatures of Common Recipes

With this in mind, let's look at some recipes and see how various heating protocols are implemented. Figure 6.1 shows a recipe for molten chocolate cake, which is one of our favorite labs for this course. One of the beauties of this recipe is that you don't cook the chocolate cake all the way through, so the center remains uncooked and deliciously molten. As it turns out, you can use this fact to study the physics of heat transfer. The recipe looks much like how one would expect a cake recipe to look: it asks for flour, eggs, butter, sugar, salt, and, of course, chocolate. After mixing, you are supposed to pour the batter into ramekins and bake in an oven at 375°F, or 190°C.



Molten Chocolate Cake and Ice Cream

Materials:

- 1 pot
- 1 induction burner
- 8 ramekins
- medium bowl (wet ingredients)
- 1 small bowl (dry ingredients)
- 1 scale
- 2 cutting boards
- 1 ruler
- 1 spoon
- 1 knife
- 1 whisk
- 1 spatula
- 1 oven mitt
- 1 convection oven / table

Ingredients:

for 8 ramekins

- 120g dark chocolate chips
- 113g butter (1 stick)
- 120g sugar
- 5 eggs
- 60g flour
- 0.5g (pinch) salt
- non-stick baking spray

Preparation:

1. Preheat the oven to 375 °F (190 °C) with the middle dial turned to "convection".
2. Melt chocolate and butter on low heat while stirring.
3. Combine eggs and sugar in a medium sized bowl and beat until well mixed.
4. Combine flour and salt in another bowl and mix.
5. With one person whisking and another person pouring, slowly add the chocolate mixture to the egg mixture.
6. Little by little, add the flour and salt to the wet ingredients and whisk well. Make sure all of the flour is completely mixed with the batter.

Figure 6.1 Recipe for molten chocolate cake.

What are the transitions that occur in the cake as it bakes? As with the egg, there are many of them. Not all of them are well understood, but most occur in the range of 60-80°C (Fig. 6.2). Around 70 or 80°C the egg proteins that help give the cake some solidity unfold. Around 60°C carbon dioxide gas is emitted by reactions that we will discuss later on in the course. Noticeably, all of these transition temperatures occur well below the 190°C of the oven. In fact, they are even well below the boiling point of water. This is a bit strange. Why would we bake a cake at an oven temperature that is much higher than the target temperatures we are hoping to reach?

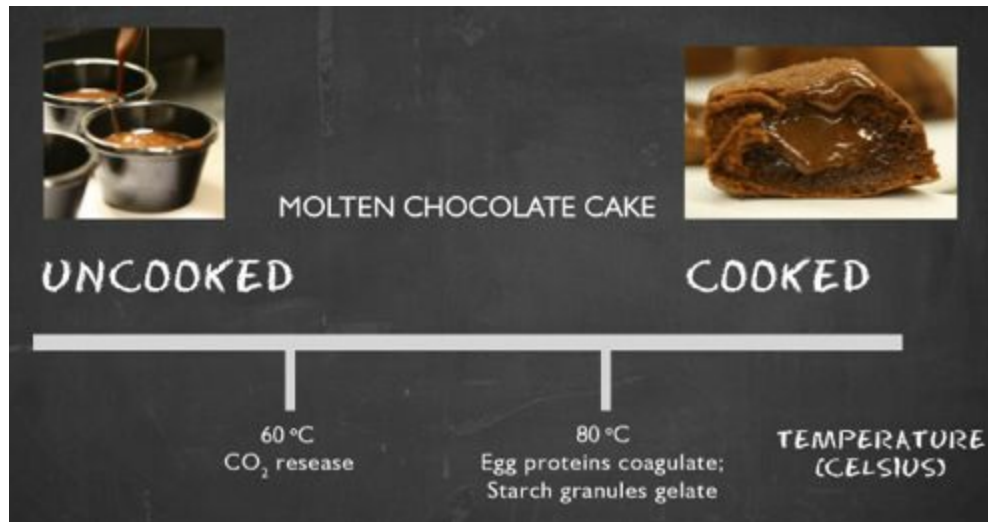


Figure 6.2 Phase diagram for molten chocolate cake. Most of the phase transitions in molten chocolate cake occur in the range of 60-80°C.

Let's look at the heating protocols of a few other recipes and see if there is a similar difference between the target temperatures of the food and the oven temperature. First, here is a recipe for meatloaf (Fig. 6.3).

Meatloaf

Ingredients:

2 pounds ground beef	1 cup dried breadcrumbs
1 egg	2 tsp salt
1 onion	1 tsp white pepper
2 cloves garlic	2 tsp soy sauce
3/4 cup milk	1Tbsp honey
1/2 cup heavy cream	

Preparation:

1. Preheat the oven to 350°F (175°C).
2. Combine the top nine ingredients in a bowl and mix well. Shape into three loaves and place in a lightly greased baking pan.
3. Combine soy sauce and honey in a small bowl and brush onto the meat loaves.
4. Bake at 200°C for 40 min.

Figure 6.3 Recipe for meat loaf.

Meatloaf consists of ground meat and several other ingredients that are shaped into a loaf and then baked in an oven. The recipe says to set the oven to about 350°F, or 175°C, again well above the boiling point of water. The critical temperatures required to cook meat, on the other hand, are much lower: between 50 and 70°C (Fig. 6.4). This is the range in which myosin and other proteins denature and coagulate, and the collagen dissolves.

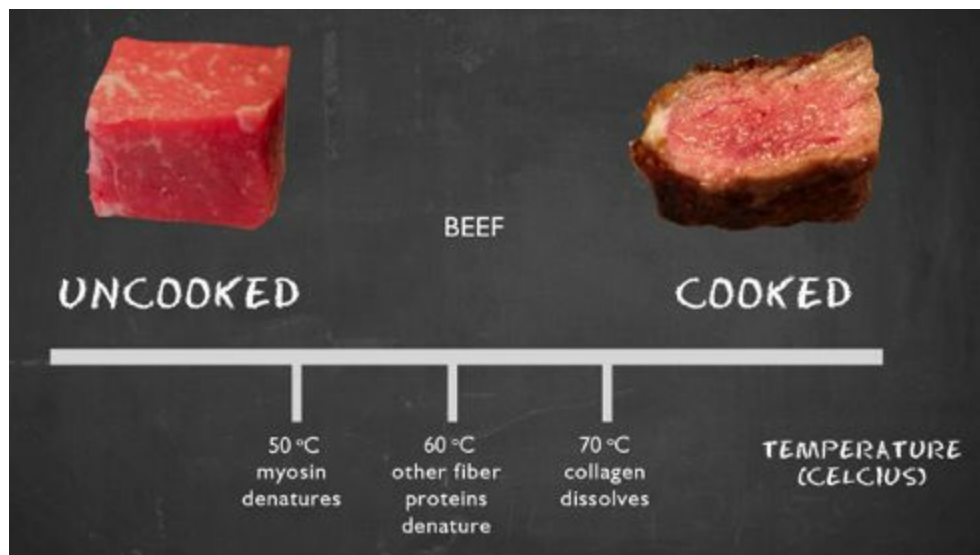


Figure 6.4 Phase diagram for beef. Most of the phase transitions in beef occur in the range of 50-70°C.

So, both molten chocolate cake and meatloaf are cooked at oven temperatures that are much higher than their respective target temperatures. How about cooking fish?



Figure 6.5 Recipe for baked tuna steak.

A typical recipe for tuna steak usually has the oven a bit warmer than that of meatloaf, maybe around 450°F, or 230°C (Fig. 6.5). It won't shock you at this point to learn that the critical temperatures for cooking tuna are much lower than this, more specifically they are in the range of 40 to 60°C. This is a little lower than the transition temperatures of beef, and, again, much below the boiling point of water (Fig. 6.6).

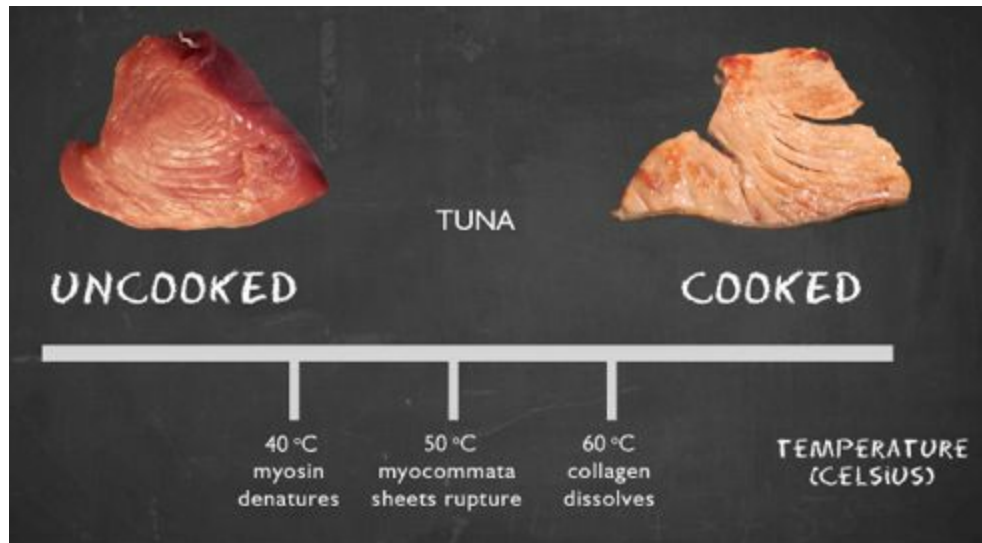


Figure 6.6 Phase diagram for tuna. Most of the phase transitions in tuna occur in the range of 40-60°C.

The reason that the transition temperatures of these foods are all in about the same range is not that hard to understand qualitatively. Fish, meat, and cake all consist of biological materials, and cooking them usually involve the unfolding and coagulation of proteins. Biological materials do not tend to do very well in boiling water and it makes sense that the transition temperatures occur well below that. Still, the fact that the recipes call for oven temperatures that are so much higher than both the boiling point of water and the target temperatures of the foods is somewhat of a mystery.

The answer to this mystery is at the heart of why it can be so difficult to cook food by heating. It turns out that in order to properly cook a food so that it turns out delicious, one often needs to cook the inside to one target temperature, and the outside to another, much higher, target temperature. The outside target temperature is usually much higher than the boiling point of water and the inside is considerably lower. The very essence of why it is so hard to cook a steak, for example, lies in this difficulty of simultaneously hitting both target temperatures (Fig. 6.7). In the following sections we will first discuss the chemical reactions that call for such high target temperatures on the outside of foods, and, second, we will discuss different heating protocols that attempt to solve the dilemma of cooking the insides and outsides of foods to different temperatures.

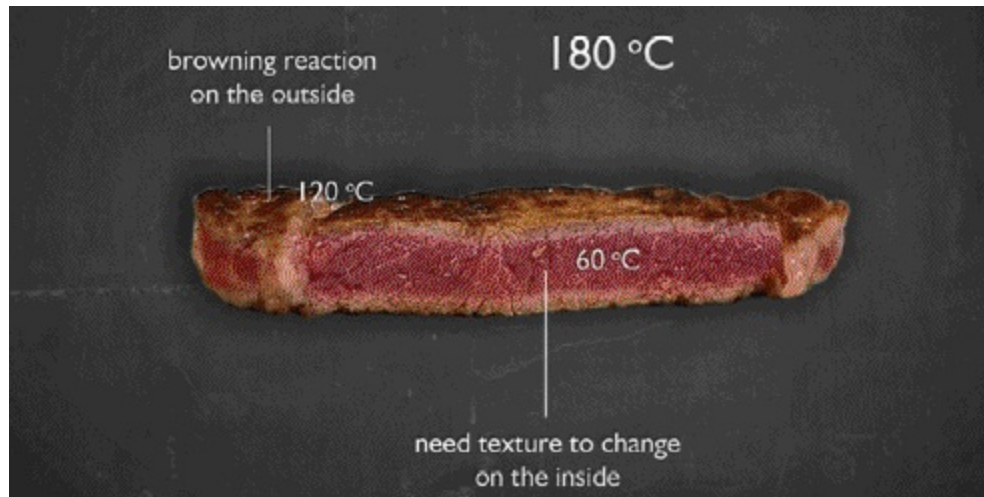


Figure 6.7 In order to cook the perfect steak, different target temperatures must be reached on the inside and outside of the steak. This can be very difficult to achieve.

6.2 Browning Reactions

6.2.1 Maillard Reactions Create the Flavorful Crust on Cooked Foods

The reason you have to cook the outside of foods to temperatures that are higher than the boiling point of water is because of a set of chemical reactions. Arguably these reactions are some of the most important in cooking, at least if you like how your food tastes. The reactions are usually referred to either as browning or Maillard reactions – browning, because in addition to being tasty, they also tend to make foods brown, and, Maillard, after a great chemist, Louis Maillard, who, in the 19th century, discovered and described them (Fig. 6.8). Maillard reactions are really a cascade of reactions, but they have in common that they always start out with a carbohydrate molecule, like a sugar, reacting with an amino acid on a protein. At high temperatures, say around 120-130°C, this initial reaction leads to hundreds of small molecule byproducts. Some of these byproducts are brown color compounds and some are flavor molecules. The brown colored surface that develops as you cook a steak, and the accompanying rich flavors, are all due to Maillard reactions. In fact, since the molecules are often volatile, which means that they easily spread in the air and reach your nose, they are also responsible for the mouth-watering smell that arises when cooking a steak.

The flavor cocktail that arises from these reactions is incredibly complex and hard to reproduce, and while you can buy all kinds of different spices in a store, the rich flavor on a well-done grilled vegetable or steak is not sold in the supermarket. In fact, the only way to produce that flavor is to induce Maillard reactions on the surface of the food, and this requires a temperature above 120°C.



Figure 6.8 Louis Camille Maillard, a 19th century chemist, discovered and described the browning reactions that take place on the surface of a steak.

So how do you achieve a temperature above 100°C on the food surface? After all, we have previously told you that food is mostly made of water, and we know that water cannot reach a temperature higher than its boiling point of 100°C . Once the temperature goes above this, the water will turn into gas. It turns out that this is exactly what happens in a thin layer around the surface of the steak. The resulting dry layer no longer contains any water, and subsequently the temperature can go high enough for Maillard reactions to take place. So having some of the water boil off is critical for the browning to occur, and the reason you only form a very thin crust on meat or fish is because water only tends to boil off at the very surface of the food (Fig. 6.9).

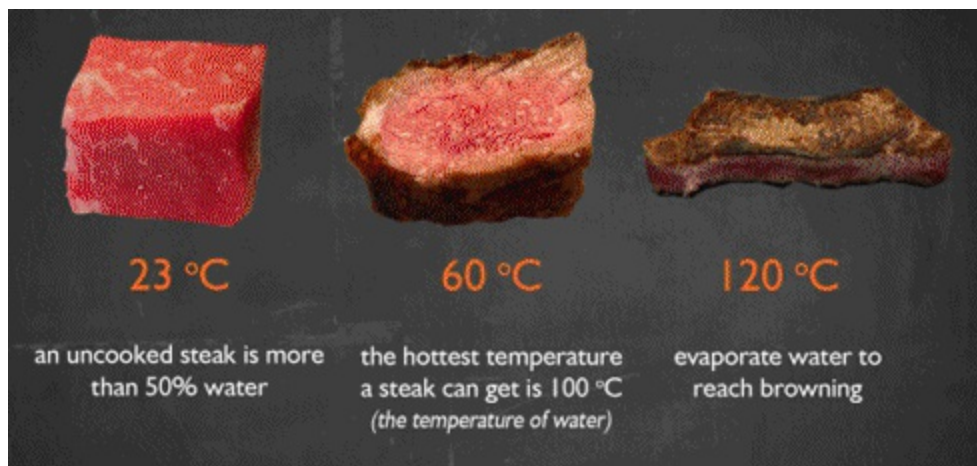


Figure 6.9 Maillard reactions occur at temperatures above 120°C . Since food mostly consists of water, which has a boiling point of 100°C , this higher temperature can only be reached if the water in the food is allowed to evaporate. This is indeed what happens on the surface of a steak as it cooks.

6.3 Why it is Hard to Cook a Steak

6.3.1 The Challenge of Hitting Different Target Temperatures

Given what we have learned about browning reactions and target temperatures, we are presented with an interesting dilemma. On the one hand, the outside of a steak requires temperatures higher than 120°C in order for Maillard reactions to occur. We discussed how this occurs in the previous section. And, on the other hand, the inside requires a temperature of about 60°C , because this is the critical temperature that corresponds to the perfect texture. We discussed before how chefs use the thumb test to gauge the elasticity and determine when a steak is done (Fig. 6.10). Elasticity, of course, is simply a surrogate for the internal temperature. The higher the temperature, the more proteins denature and coagulate, and the stiffer the steak tends to get.

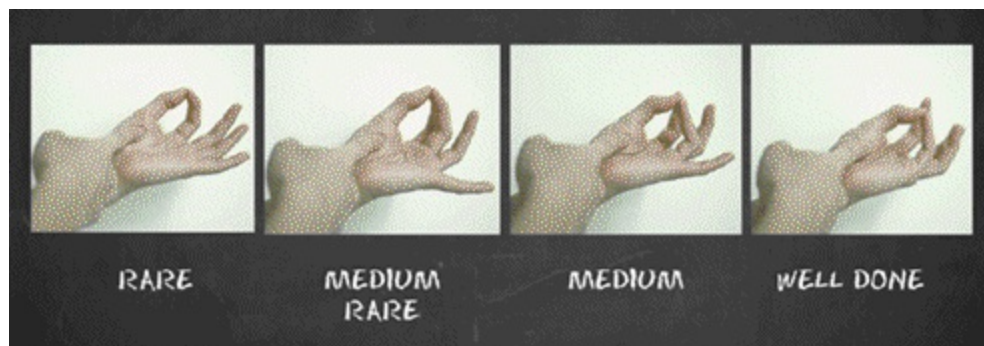


Figure 6.10 The thumb test is a popular way to gauge if a steak is cooked to the desired done-ness. By touching the thumb to the index, long, ring, and little fingers, and comparing the resulting elasticity of the flesh to that of the steak, the cook can get a sense for whether the steak is cooked to rare, medium rare, medium, and well done respectively.

The subsequent dilemma that arises from trying to balance these two requirements is illustrated in Figure 6.11 which shows a cross-section of a steak. The steak has a very thin, brown, and flavorful crust that has been produced with the help of Maillard reactions. The center, however, is still pink and has a tender texture. Given that temperature is a continuous variable, i.e. it decreases continuously from the edge to the middle, the result of this temperature distribution is that most of the meat is either undercooked or overcooked.

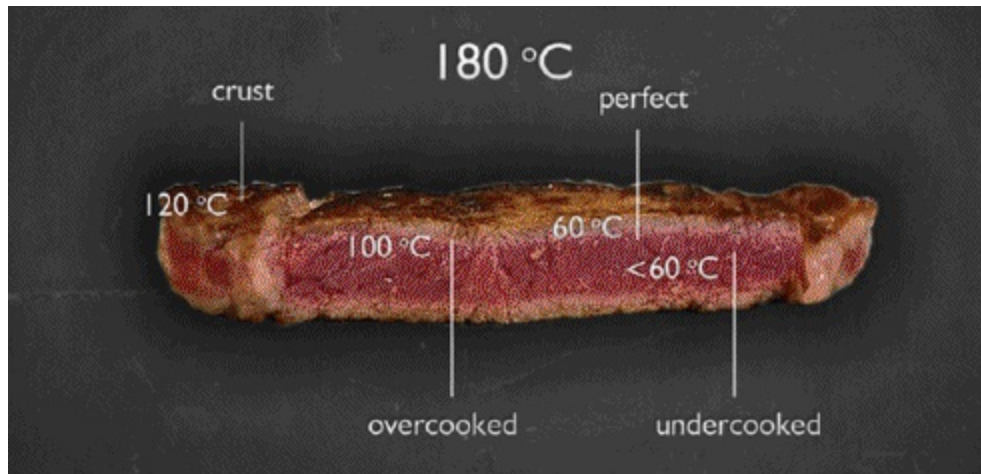


Figure 6.11 Temperatures of a cooked steak. A perfectly cooked steak will have reached an interior temperature of about 60°C . Moving from the center to the surface, the temperatures are increasingly higher, having the effect that the meat is slightly overcooked. Just below the surface, water will have evaporated, allowing the temperature to go higher than 100°C , in turn enabling for Maillard reactions and the formation of a nice crust.

The same idea is illustrated in Figure 6.12, which shows the corresponding temperature distribution as drawn on a graph. Right at the very edge of the steak, the temperature is the same as that of the oven, which, in this case, is set to 180°C . Then there is a very thin layer above 120°C where Maillard reactions can occur. Still a little deeper into the steak, the temperature decreases to 100°C , the boiling point of water. If the steak is perfectly cooked, the middle of the steak will be at about 60°C , and in between, you can imagine a curve which goes from 100°C close to the edge, down to 60°C in the middle.

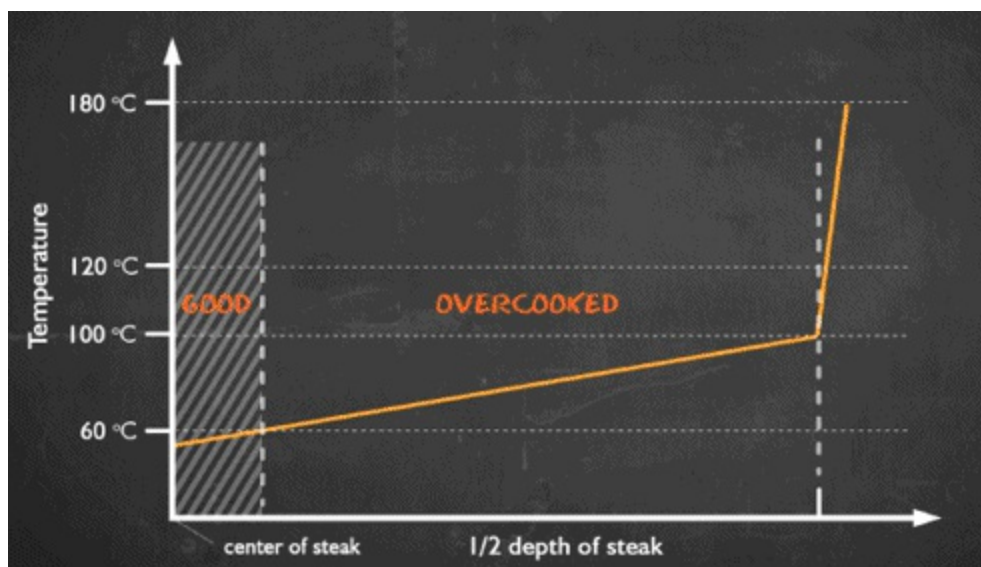


Figure 6.12 The temperature profile of a steak as described in Figure 6.13. The x-axis describes the steak from the center, at $x=0$, to the surface. The dotted line to the left indicates the small cross-section that is cooked to within $\sim 60^{\circ}\text{C}$, i.e. the target temperature for beef. The dotted line to the right

indicates the thin layer that has a temperature higher than 100°C .

As you can see on the graph, if you achieve the target temperature of 60°C in the center, most of the steak is necessarily at a temperature that is higher than 60°C , because otherwise you will not hit the temperature you need on the outside to create the flavor molecules you want. So most of the steak is overcooked. And that, in essence, is one of the reasons it is so hard to cook a steak. Namely, it is essentially impossible, using a standard cooking method, be it an oven, stove, or similar, to get the exact target temperature in the middle, whereas at the same time getting the browning reactions on the surface to occur.

To further complicate this, recall from Chapter 4 that the elasticity is not only determined by the protein state at a certain target temperature, it also depends on how much water the steak contains. In the context of the equation where elasticity, E , equals $k_{\text{B}}T/l_3$, the more water there is, the larger l is, and consequently the softer the steak will be. It won't surprise you to learn that if you put a steak in a very hot oven, more water will be lost than if you put it in a slightly cooler oven. So if you put your steak in a 120°C oven, you could get browning reactions on the outside of the steak while losing much less water than in a 180°C oven. This would have an effect on the final texture. So another part of the art of cooking a steak is also to balance the amount of water loss compared to the desired amount of browning reactions.

6.3.2 Cooking Protocols that Address the Challenges

You can imagine many different ways of cooking a steak that tries to solve the challenges we have just discussed. For example, you could imagine cooking a steak at either 120°C or 190°C and getting completely different outcomes even though the target temperature in the middle of the steak is the same. You might also imagine first cooking the steak in an oven at 120°C, and then finishing it on the stove for a nice crust. Further, you might imagine cooking the steak only on the stove, and even in this case there are many different options: you could let the steak cook on one side for a couple minutes and then turn it over and cook it on the other side until done. Or you could imagine flipping the steak back and forth every 15 seconds. Over time you would transfer roughly the same amount of heat to the steak this way, but since each side would have a chance to cool off between each flip, it would lead to a different temperature distribution than only flipping once.

There is one particular cooking method that deserves special attention in this context because it gets at the challenges we have discussed in a very powerful way. It also explains why this method has become so popular. The method is that of sous vide. You simply cook the piece of food to the exact target temperature in a constant temperature water bath. Since the food is sealed in a plastic bag, no water is lost and the temperature is just right (Fig. 6.13). The resulting meat or fish will be quite bland though, since there have not been any Maillard reactions, but this can easily be fixed by quickly searing the food on both sides. As long as the searing is brief enough, the heat will not penetrate deeper into the food and overcook it. So you will have a delicious crust with a perfect texture in between. This is a very robust and reliable way of cooking a steak.



perfect texture
(but doesn't taste good)

YOU WANT
BROWNING
REACTIONS!

Figure 6.13 Sous vide is one option when trying to cook the perfect steak. By using a temperature controlled water bath, the entire steak is allowed to reach the desired target temperature. By briefly searing, a nice crust can be added before serving.

If these were all the complexities there were to cooking a steak, it would be hard enough. But it turns out there is one more challenge that makes it even harder than what we have described so far.

6.3.3 The Final Challenge: Food Continues to Cook

Suppose you have found the perfect way of cooking your steak and it is exactly at the correct target temperature. Let's say it is at 62°C . You are ready to serve it to your guests. You take the steak off of the grill, put it on a plate, and invite the guests to sit down. Imagine that the guests then say that they'd like to go wash their hands. This takes a while, but they come back, sit down, and take a bite out of the steak. Disappointingly, it turns out that by the time the guests do this the temperature is no longer at 62°C .

What happened? Well, there is some amount of thermal energy stored in the steak. Recall the equation from Chapter 2, $Q = mc_p\Delta T$. That thermal energy needs to escape in order for the steak to cool down to room temperature. One might think that the heat will simply go into the air and disappear. But air, it turns out, is a very lousy thermal conductor. It is very bad at transmitting heat. This is actually the reason you can stick your hand in a hot oven without having it burn. For the same reason, if you take a cooked steak off the heat source and leave it on a plate, it tends to retain its heat. Very little heat escapes into the air. Instead, the heat redistributes itself within the steak. The heat from the hot edge diffuses towards the center, so the part that is 120°C will decrease in temperature and the 60°C center will increase. Thus, over a relatively rapid period of time, the temperature distribution in the steak will become flat. The entire steak will be overcooked (Fig. 6.14). After having so carefully tried to cook the steak to a perfect temperature center, this is a real bummer. The only way around it is to cook your steak to below the target temperature, because once you take it off the stove or out of the oven, it will continue cooking.

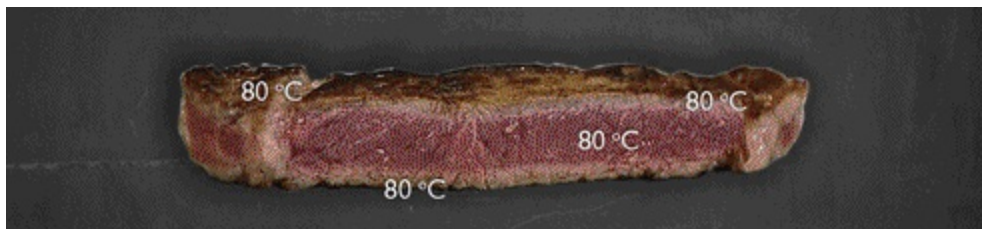


Figure 6.14 A steak continues to cook even after it is taken off the stove or grille. This can lead to the entire steak being overcooked as the hot temperatures from the exterior heat up, and cook, the interior.

To summarize, there are four main reasons why it is hard to cook a steak, a

turkey, a piece of tofu, a potato, or whatever you would like to cook (Fig. 6.15). First, you want to hit the correct texture on the inside of the food. This is why you are applying heat in the first place. That perfect texture requires a typical temperature in the range of 50 to 70°C, which are the typical temperatures at which proteins unfold.

Second, you want browning reactions to occur on the surface of the food. Browning reactions require a much higher temperature, around 120°C or more, and this can be difficult to achieve. In particular, and this brings us to the third reason, there is no way, short of sous vide cooking, to achieve an outside temperature of 120°C in combination with an inside temperature of 60°C, without having most of the food be at neither 60°C nor 120°C. That is, most of the food is going to be at a temperature much higher than the target temperature, and thus be overcooked.

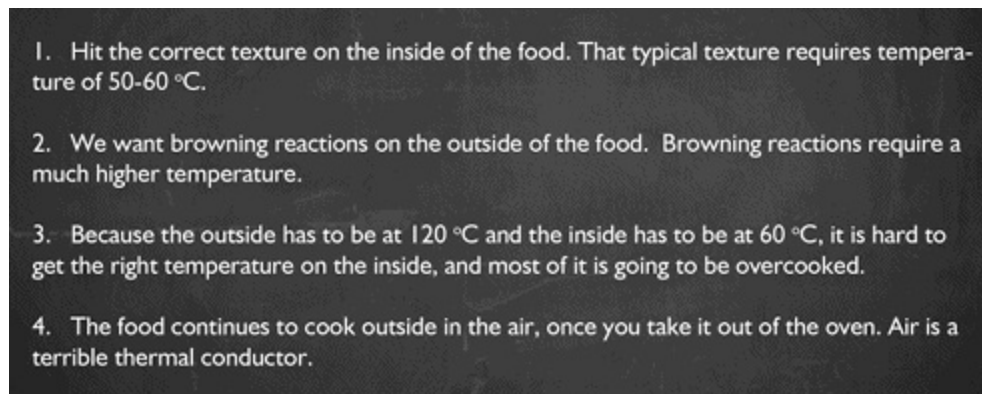
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1. Hit the correct texture on the inside of the food. That typical texture requires temperature of 50-60 °C.
 2. We want browning reactions on the outside of the food. Browning reactions require a much higher temperature.
 3. Because the outside has to be at 120 °C and the inside has to be at 60 °C, it is hard to get the right temperature on the inside, and most of it is going to be overcooked.
 4. The food continues to cook outside in the air, once you take it out of the oven. Air is a terrible thermal conductor.

Figure 6.15 A summary of the four main reasons for why it can be so hard to cook a steak.

Fourth, if this were not bad enough, when you have cooked the food to the perfect temperature, and take it off the heat source, the food continues to cook. So the middle temperature rises, the outer temperature falls, and the entire food ends up at a much higher temperature than you originally wanted.

6.4 Heat – Microscopic Perspective

Having covered the challenges of cooking with heat, we now want to delve into the physics of how heat is transferred into food. There are two ways of understanding this concept, microscopically and macroscopically, and we are going to look at each in turn in the next two sections.

6.4.1 Heat Diffuses by a Random Walk

Microscopically, what happens is that the molecules in the hot air have a high kinetic energy, they whizz around very fast, and as they bump into the molecules in the food they cause them to whizz and vibrate as well. So, gradually, the thermal energy of the food increases and the food gets hotter. The next step is that heat somehow moves from the edge of the food all the way to the center, thus heating up the food. This happens by much the same process: as the molecules on the edge of the steak start to vibrate, they randomly bump into the molecules around them, and as those molecules in turn start to vibrate, they randomly bump into other molecules and the temperature front moves deeper and deeper into the steak. Thus the overall physical process is really the same as what we discussed last week in the context of diffusion. Namely, heat diffuses into food like a random walk.

You will recall that a random walk can be characterized by the equation

$$L = \sqrt{4Dt}$$

where L is the distance of diffusion, D is the diffusion constant that is governing the random walk, and t is time. Whereas last week, the diffusion was, for example, the diffusion of calcium ions in a solution, this week, it is the diffusion of heat. Subsequently, the one thing that changes in the application of this equation compared to last week is the value of D . This week, D is the heat diffusion constant of the food. Other than this number the basic physical process is exactly the same.

6.4.2 Heat Diffusion Constants of Food

What, then, is the heat diffusion constant of food? The exact number, it turns out, varies somewhat between different foods. In the case of chicken, it even depends on the type of meat you cook: white meat has a diffusion constant of $1.36 \cdot 10^{-3} \text{ cm}^2/\text{sec}$, which is similar to that of beef, and dark meat is a little lower at $1.28 \cdot 10^{-3} \text{ cm}^2/\text{sec}$. Fish in turn is even lower than this at $1.1 \cdot 10^{-3} \text{ cm}^2/\text{sec}$, and vegetables tend to vary between 1.1 and $1.8 \cdot 10^{-3} \text{ cm}^2/\text{sec}$.

What's so curious about these numbers is that they are almost all the same. Whether we are talking about meat or potatoes, they all have a heat diffusion constant somewhere around one and a half times $10^{-3} \text{ cm}^2/\text{sec}$. Why is that? Well, the major ingredient of food, of course, is water. And the heat diffusion constant of water is $1.4 \cdot 10^{-3} \text{ cm}^2/\text{sec}$. Indeed, all of the heat diffusion constants in Figure 6.16, and, for that matter, in general, are just manifestations of the heat diffusion constant of water.

Food	Diffusion Constant ($\times 10^{-3} \text{ cm}^2/\text{sec}$)
Beef	1.35
Chicken	1.36 (white meat)
Chicken	1.28 (dark meat)
Fish	1.09
Apple	1.12
Strawberry	1.27
Peas	1.82
Potato	1.23
Water	1.4

Figure 6.16 Heat diffusion constants of common foods. Most foods have heat diffusion constants that are very similar to that of water at $1.4 \cdot 10^{-3} \text{ cm}^2/\text{sec}$.

If the fundamental law for how heat propagates in food is the equation

$L = \sqrt{4Dt}$, and if the heat diffusion constant, D , is essentially the same for all foods, what we have really discovered is that the distance heat travels into a food in a certain time is more or less the same for all foods. This is a remarkable fact that permeates much of cooking.

6.4.3 Example: Cooking a Tuna Steak

Let's apply this equation and see if we can estimate how long it takes to cook things. Imagine that you are cooking a steak in a skillet. The skillet is hot and heat is diffusing into the steak. How far would the heat diffuse in, say, a minute? Using the equation and the diffusion constant for beef from the table above, the diffusion distance L turns out to be 0.6 cm. So in a minute, the heat diffuses by about half a centimeter.

$$t = 1 \text{ min} = 60 \text{ sec}$$

$$D = 1.35 \cdot 10^{-3} \text{ cm}^2 / \text{sec}$$

$$L = \sqrt{4Dt} = \sqrt{4 \cdot (1.35 \cdot 10^{-3} \text{ cm}^2 / \text{sec})(60 \text{ sec})} = 0.6 \text{ cm}$$

If we instead were to cook the steak for four minutes, then the diffusion distance would double because of the square root. Instead of 60 seconds, the time, t , would be 240 seconds, and this would result in a diffusion distance of 1.3 cm. This is a good rule of thumb for how long it takes for heat to move into a food: one minute corresponds to about half a centimeter, and four minutes to about one full centimeter.

$$L = \sqrt{4Dt} = \sqrt{4 \cdot (1.35 \cdot 10^{-3} \text{ cm}^2 / \text{sec})(240 \text{ sec})} = 1.3 \text{ cm}$$

You can test this idea by going into your kitchen and cooking a steak. Even better, you may want to cook a tuna steak, because tuna has the useful property of dramatically changing color when it cooks. It goes from a translucent red to a cloudy white color when the proteins denature, and hence the heat diffusion distance can very easily be visualized (Fig. 6.17). So you can cook a tuna steak on a skillet, and every couple of minutes you can remove a piece and measure the thickness of the increasingly thick cooked layer, and see how it compares to our prediction above. When performing this experiment ourselves, we found that the thickness of the white layer after the first minute was about 7 mm, after two minutes it was 8mm, after three minutes 10 mm, and after four minutes it was about 12 mm. So the equation did a fairly good job predicting the heat diffusion

distances that we calculated above.

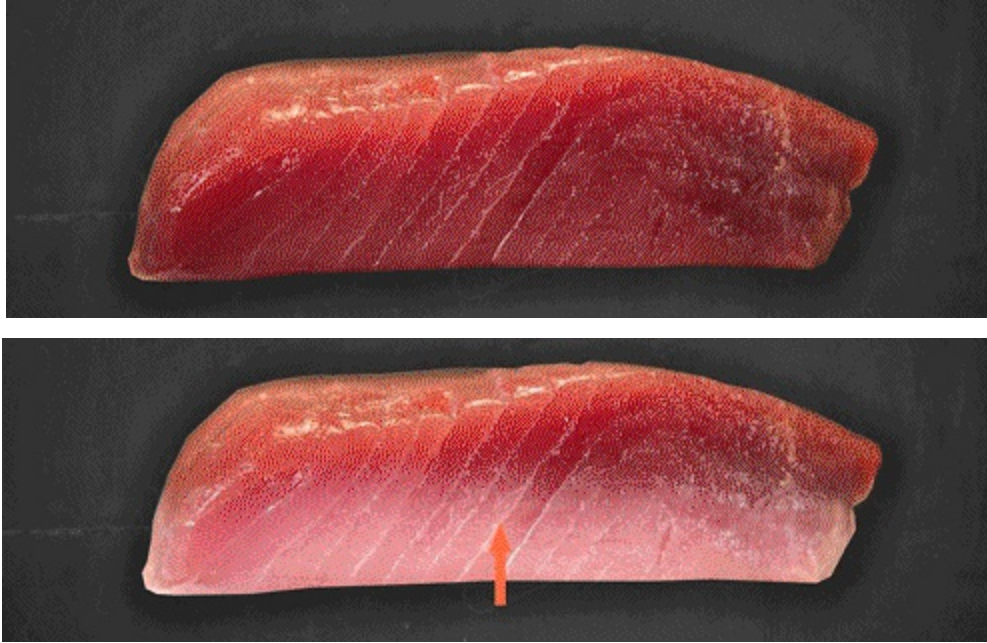


Figure 6.17 Raw tuna steak is red in color, but takes on a whiter shade when cooked. This can be used as a way to approximate how far heat has diffused into the fish.

If you cook a tuna steak, you may also notice some of the other reasons why it is hard to cook a steak. Namely, you may notice that if you don't measure the thickness of the white, cooked layer immediately, but instead let the piece of cooked tuna sit on the counter for a while, then the thickness of the cooked layer actually increases. The tuna steak keeps cooking. Instead of escaping into the air, the heat continues to move further into the steak. When we cooked a piece of tuna for one minute, and then let rest for ten minutes, we found that the original cooked layer of 7 mm had increased to 11 mm, which is a quite significant increase.

6.5 Heat – Macroscopic Perspective

6.5.1 Heating as a Transfer of Thermal Energy: Deriving an Equation for Heat Transfer

In addition to the microscopic view of heat transfer that we just discussed, which is based on the idea that heat moves into food by way of a random walk, there is also a second way, which is more quantitative in nature. This idea is related to our discussion of energy and heat in Chapter 2. Recall from that chapter that if you want to heat a piece of food so that its temperature increases by some temperature, ΔT , then you have to add a certain amount of energy. The amount of energy is given by our very first equation of the week, $Q = mc_p\Delta T$, where m is the mass of the food and c_p is the specific heat. With this equation in mind, consider putting a piece of food in the oven. Initially, no energy has been transferred to the food at all, whereas over time, the oven will transfer its energy and the food will heat up, eventually reaching the same temperature as the oven. If we use this very simple idea in a mathematical equation, we can come up with a quantitative formula that describes how food tends to heat up. Here is how we would go about this:

First let's express the equation in words, and then we will change the words in the equation to mathematical symbols. This is the equation:

$$\begin{array}{ccc} \text{Rate of change of the} & & \text{The heat transferred to} \\ \text{thermal energy of the food} & = & \text{the food from the oven} \end{array}$$

In order to make that into a mathematical formula we need to know the rate of change of thermal energy, on the one hand, and the amount of heat that is transferred into the food, on the other.

Let's start with the rate of change of thermal energy. Thermal energy is just $mc_p\Delta T$, and the rate of change can be expressed mathematically by taking what's called the time derivative of $mc_p\Delta T$, which is written d/dt :

$$\begin{array}{l} \text{Rate of change of the} \\ \text{thermal energy of the food} \end{array} = \frac{d}{dt}(mc_p \Delta T)$$

Now we have to express the other side of the equation, which is how much heat is transferred to the food. To understand this, imagine putting a piece of food in an oven that is the same temperature as the food. Of course, no energy is going to be transferred because the temperatures are the same. In order to transfer energy, the oven has to be hotter than the food. So, intuitively, you know that the amount of energy that is being transferred is going to depend on the difference in temperature of the oven and the food, i.e. $T_{\text{oven}} - T_{\text{food}}$.

There is also going to be some proportionality constant that depends on the size of the food. A large food will have a larger area through which heat can be absorbed, compared to a piece of food with a very tiny area. So the proportionality constant is going to be proportional to the surface area, A , of the food. It is also going to be proportional to another constant, which depends on the type of food. Engineers call that constant the heat transfer coefficient, h .

$$\begin{array}{l} \text{The heat transferred to} \\ \text{the food from the oven} \end{array} = Ah(T_{\text{oven}} - T_{\text{food}})$$

If we organize all of these variables into a single equation, we get the following formula:

$$\frac{d}{dt}(mc_p \Delta T) = Ah(T_{\text{oven}} - T_{\text{food}})$$

This equation can be solved using ideas from calculus, and we then get an equation for how the temperature of a food varies over time:

$$T(t) = (T_{\text{food}} - T_{\text{oven}})e^{-t/\tau} + T_{\text{oven}}$$

The equation has two terms in it. The first term is proportional to the temperature difference, i.e. the initial temperature of the food minus the

temperature of the oven. The second term is a constant in the form of an exponential function, where t is how much time has elapsed, and τ is the amount of time over which the temperature of the food changes. The variable τ is related to all the quantities that we just mentioned and essentially captures the idea that certain properties of the food determine how long it takes to heat it up: the area, the specific heat, the heat transfer coefficient, the mass of the food, and so on. Finally, the temperature of the oven, T_{oven} , is added.

6.5.2 Comparing the Equation with Experimental Data

The best way to understand this formula is to plot it, and the grey line in Figure 6.18 does just that. It shows the temperature of a food as a function of time. The orange dots represent data that we took in our labs to convince ourselves that this formula was true. We simply put tofu in an oven at some temperature, and we then measured the temperature of the tofu as a function of time. As you can see, the temperature increases just the way you would expect based on the formula. It increases from the initial room temperature of the food to the temperature of the oven, which was 100°C . After 8-10 minutes, the interior of the tofu has reached $60\text{--}70^{\circ}\text{C}$, which we consider to be done based on our discussion about what the target temperatures of foods usually are.

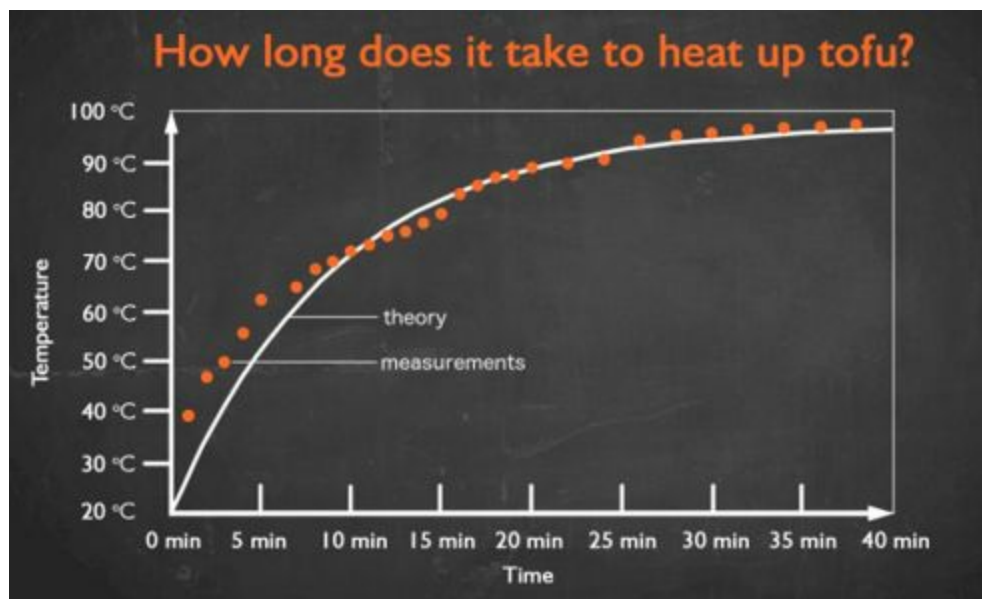


Figure 6.18 Plot of the interior temperature of a piece of tofu as a function of time while baking in an oven.

6.6 Calculating Temperature Profiles

In section 6.4 we discussed heat transfer from a microscopic perspective. We learned that since its underlying principle is that of a random walk, we

can apply the diffusion equation, $L = \sqrt{4Dt}$, to find the distance, L , that heat travels in a certain time, t . In section 6.5 we proceeded to discuss heat transfer from a macroscopic perspective, and we found an expression that allows us to estimate the temperature inside a cooked food based on the temperatures of the food and the oven, as well as a number of other properties of the food.

6.6.1 Finding the Temperature of a Food as a Function of Space and Time

What if we wanted an accurate way of predicting the temperature distribution within a food for any given heating protocol? We already discussed how chefs apply different heating protocols when cooking a steak, and the reason for this was that they wanted to control the temperature distribution in a precise way. They wanted to hit a particular target temperature in the middle of the steak, while also making sure that the surface temperature was hot enough for Maillard reactions to occur. If you were able to calculate the temperature distribution inside of a steak as a function of space and time for any given heating protocol, then it may also be possible to figure out how to control it. Of course, this would not only apply to steak, but to the heating of any type of food.

Scientists have actually known how to solve this problem for a long time, more than 100 years. So when Nathan Myhrvold cooks a steak sous vide, then dunks it in liquid nitrogen, and subsequently sears it, it is possible to calculate from first principles how the temperature changes inside. The same goes for any other heating protocol.

Understanding the formula for this requires a bit of mathematics that is beyond the level of this course, so we will not discuss it in detail. However, the physics is actually very similar to the physics in the previous section. Namely, in the previous section we said that the rate of change of thermal energy inside of a food comes from the energy of the pan or oven. In this case, we do something very similar, but instead we imagine breaking the food into little bits, and argue that the change of thermal energy of every little bit comes from the flow of heat into or out of its neighboring bits. Using this argument, one can derive an equation that scientists call the diffusion equation. It looks like this:

$$\frac{dT}{dt} = D \nabla^2 T$$

There may be several symbols in this equation that are unfamiliar to you. That's ok. The point of showing it to you is not to make you understand it in detail, but rather to point out that it exists. If you can solve it, you can

determine the temperature of a food as a function of space and time as it cooks.

6.6.2 CookMyMeat Software

We asked a group of MIT students, along with their faculty advisers, to write a piece of software that solves the diffusion equation for different types of food. The software allows us to visualize the temperature distribution inside a food as it cooks without having to solve the equation for each point in time and space ourselves (Fig. 6.19). It is tremendously valuable in getting an intuition for how foods cook. Moreover, the software is written in such a way that you can put in your own cooking protocols for several different types of meat and get a sense for how they cook. Here is a link for you to try it out: <https://groups.csail.mit.edu/uid/science-of-cooking/home-screen.html>.

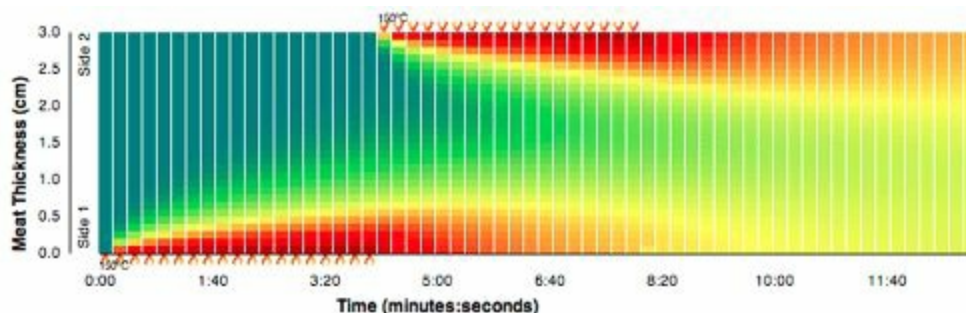


Figure 6.19 Temperature distribution inside a steak according to the CookMyMeat software.

In addition to showing the temperature, the software also shows an estimate for how the protein state of the meat changes while cooking (Fig. 6.20). This is incredibly useful because the reason you care about temperature in the first place is because of the effect it has on the state of the different proteins in the food. As we saw in the many phase diagrams in Chapter 3, once we hit the critical temperature for certain proteins to denature, we consider the food to have reached a certain state of doneness. And so the software also allows you to see the doneness. It basically compares the temperature profile of the steak to a table of data that estimates what the states of the proteins are at any given temperature. Once the temperature hits a certain threshold, the program shows a change in the protein state.

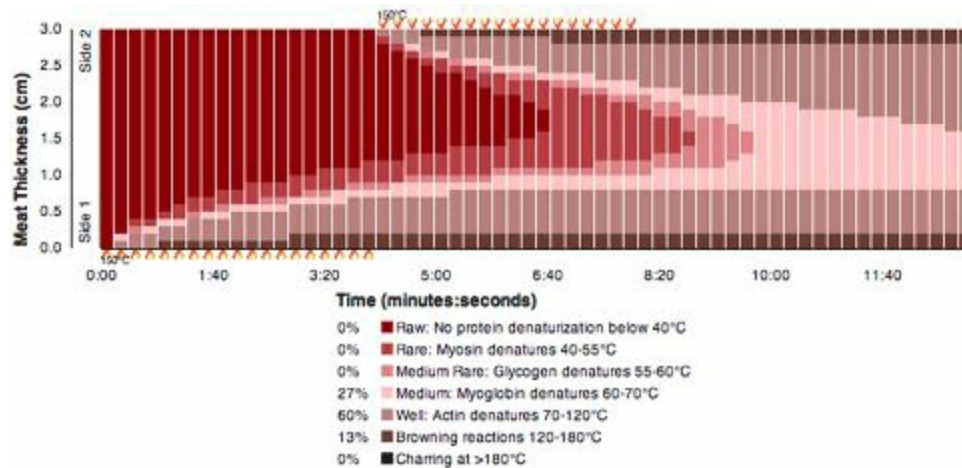


Figure 6.20 Protein state within a cooked steak according to the CookMyMeat software.

The protein transitions in the program were all taken from two tables in Harold McGee's book *On Food and Cooking*. They show the protein transitions that occur in beef and fish (Fig. 6.21 and 6.22). For example, at about 120°F, the myosin in beef denatures, and this corresponds to a certain done-ness in the steak. At other temperatures, other molecular events happen, each corresponding to further states of done-ness.

The Effects of Heat on Meat Proteins, Color and Texture							
Meat Temperature	Doneness	Meat Qualities	Fiber Weakening Enzymes	Fiber Proteins	Connective-Tissue Collagen	Protein-Bound Water	Myoglobin Pigment
100°F 40°C	Raw	-Soft to touch -Slick, smooth -Translucent, deep red	Active	Beginning to unfold	Intact	Begins to escape from proteins, accumulate within cells	Normal
110°F 45°C	<i>Bleu</i>						
120°F 50°C	Rare, 120-130°F	-Becoming firmer -Becoming opaque	Very active	Myosin begins to denature, coagulate		Escape and accumulation accelerate	
130°F 55°C	Medium rare, 130-135°F	-Resilient to touch -Less slick, more fibrous -Releases juice when cut -Opaque, lighter red	Denature, become inactive, coagulate	Myosin coagulated	Collagen sheaths begin to weaken		
140°F 60°C	Medium, 130-145°F	-Begins to shrink -Losing resilience -Exudes juice -Red fades to pink		Other fiber proteins denature, coagulate	Collagen sheaths shrink, squeeze cells	Flows from cells under collagen pressure	Begins to denature

Figure 6.21 The effects of heat on meat proteins, color and texture. (Adapted from *On Food and Cooking*, Harold McGee).

The Effects of Heat on Fish Proteins and Texture

Fish Temperature	Fish Qualities	Fiber Weakening Enzymes	Fiber Proteins	Connective-Tissue Collagen	Protein-Bound Water
70°F 20°C	-Soft to touch -Slick, smooth -Translucent	Active	Beginning to unfold	Beginning to weaken	Beginning to escape
100°F 40°C	-Soft to touch -Slick, smooth -Translucent -Wet Surface	Active	Myosin begins to denature, coagulate	Collagen sheaths shrink, rupture	Escape accelerates; leaks from cells
110°F 45°C	-Begins to shrink -Becoming firmer -Becoming opaque -Exudes juice				
120°F 50°C	-Continuous to shrink -Resilient -Less slick, more fibrous -Opaque -Exudes juice when cut or chewed	Very active	Myosin coagulated	Thick myocommata sheets begin to shrink, rupture	Leakage at maximum

Figure 6.22 The effects of heat on fish proteins and texture. (Adapted from *On Food and Cooking*, Harold McGee).

You should realize that the output in this program is approximate, since the critical temperatures at which the transitions occur in meat are also approximate. The actual transition temperatures are going to depend on the type of meat, the particular cut, how the fat is arranged, etc. Still, by providing a visualization of the diffusion equation in combination with some basic estimates of the protein states in foods at different temperatures, we believe that this software is useful in trying to get a better understanding of the physics of heat transfer.

6.7 Rules of Thumb I: Cooking Times

6.7.1 Using the Diffusion Equation as an Estimate

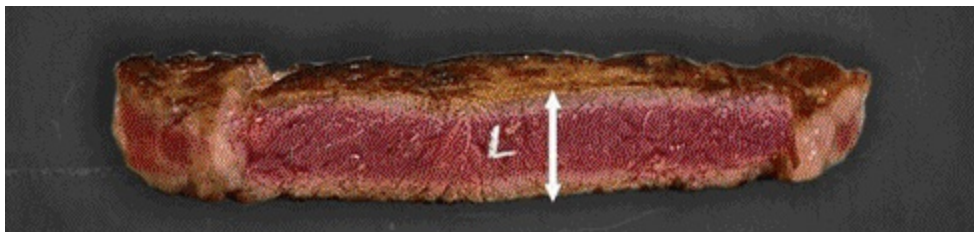
What if you don't have access to the diffusion equation software, but still want to know how long you should cook a piece of food? Usually the recipe will tell you, but you may have had the experience of needing to cook a familiar recipe in a different sized dish, and in this case, estimating the cooking time can be rather difficult.

There is a simple rule of thumb that will give you an approximate cooking time without using the software. It is simply a rearrangement of the

diffusion equation $L = \sqrt{4Dt}$, that has been solved for time so that $t = L^2/4D$.

So a simple rule of thumb for estimating cooking time is to find the shortest dimension that heat has to diffuse into the food you are trying to cook. Plug it into the formula, and compute $L^2/4D$.

The variable D is just the heat diffusion constant of the food, which is about the same as the heat diffusion constant of water, because all foods are primarily made of water. L , of course, is some length of the food. In particular, it is the shortest length of the food because heat will move through the shortest dimension first. So, when cooking a steak it is the thickness of the steak that matters, and when cooking a lasagna, the L is the depth of the lasagna dish, not the width or length (Fig. 6.23).



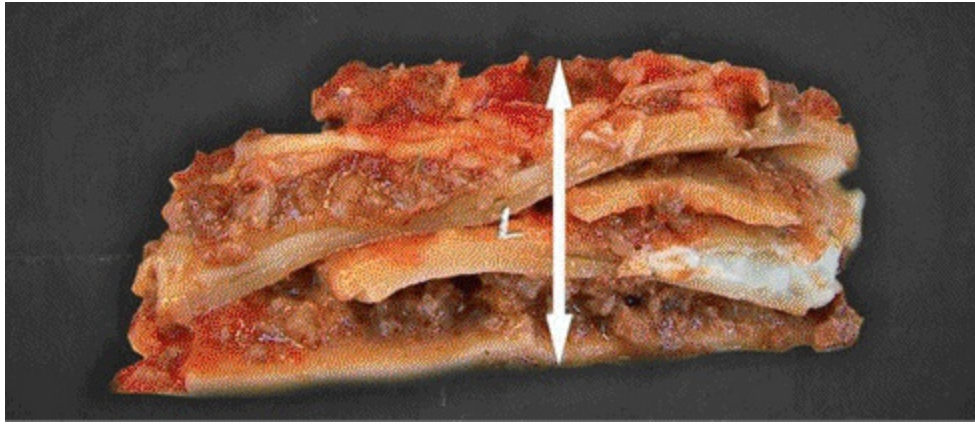


Figure 6.23 When calculating the time it takes for heat to diffuse into food, the shortest distance the heat has to travel must be taken into account. Thus, the diffusion distance, L , for a steak, or a lasagna, is estimated by the respective thicknesses.

When estimating L , you also have to take into consideration which way you cook the food. If you cook it in an oven, heat will diffuse from both the top and bottom, so you should use $L/2$ as the distance of diffusion instead of L , because heat only has to travel half the distance in order to cook the center. If, on the other hand, you were cooking the steak on a stove top, the heat is only coming from the bottom and heat needs to diffuse through the entire L of the steak (Fig. 6.24). This explains why cooking times are different depending on whether you cook something on a stove or oven.

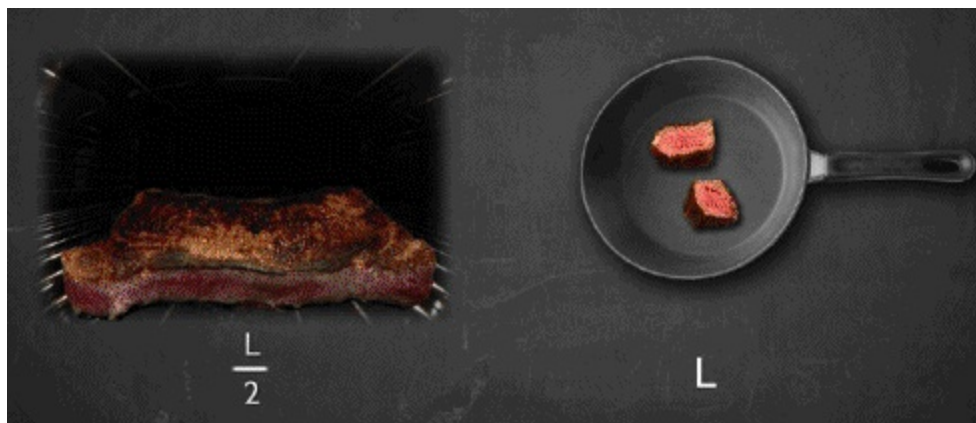


Figure 6.24 The diffusion distance, L , of a food depends on the cooking method. For a steak cooked in the oven, heat diffuses both from the top and bottom, and the diffusion distance is therefore half the steak thickness. A steak cooked on a stove top, on the other hand, will only have heat diffusing from the bottom. Thus, the diffusion distance is the same as the thickness of the steak, provided, of course, that the steak is not flipped half-way through cooking, in which case L is half the thickness.

How would we apply this formula to something like a turkey? A turkey does not have an obvious thin direction, and, moreover, cooking tables tend to quote the cooking times for turkeys in terms of mass, not length. We can solve this dilemma by making a very simple physicist's approximation and

saying that the amorphous shape of the turkey is more or less a sphere. If we do this, we can express the radius of the turkey in terms of its volume, the volume of a sphere being $\frac{4}{3}\pi r^3$. Further, since volume is density times mass, we can substitute these variables in the equation and get an expression for mass in terms of the radius, r , and density, ρ (Fig. 6.25). The density of turkey is about the same as water, 1 g/cm^3 , because the primary ingredient of turkey is water. From here, all you have to do is solve for the radius, r , and you have the length in terms of mass and density. The radius is the length scale you should use when computing the cooking time. This is the distance that heat will need to diffuse until it reaches the center.

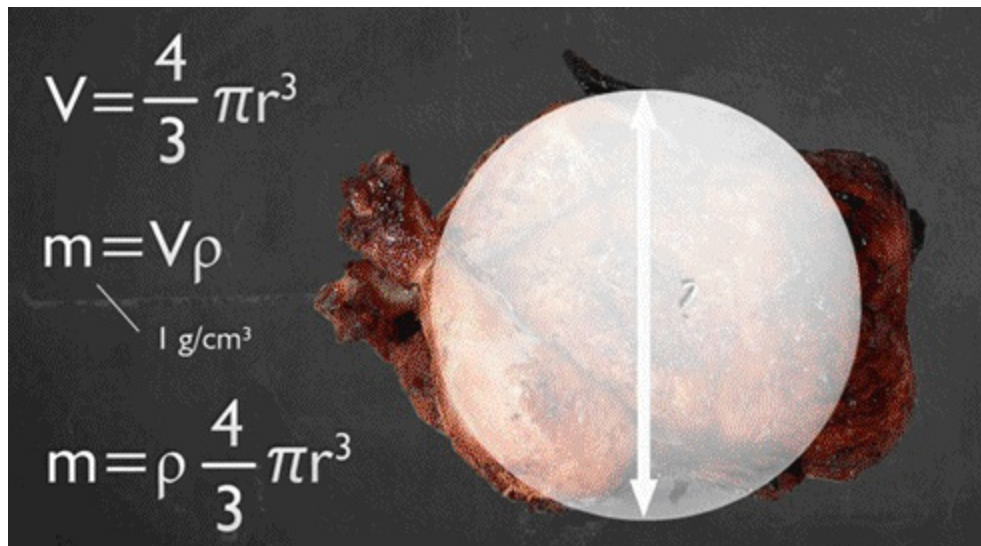


Figure 6.25 We can estimate the heat diffusion in a turkey by approximating it as a sphere, and using its mass to solve for the radius. The radius is then equal to the shortest distance of diffusion, L .

6.8 Rules of Thumb II: Cooking Times

6.8.1 Applying the Diffusion Equation to Cooking a Turkey

Let's put our formula for cooking times to the test by comparing it to some cooking times given in a cookbook. Figure 6.26 shows a table with cooking times for turkey, which assumes that the temperature of the oven is set to 325°F. As the mass increases, the suggested cooking times get longer.

Weight	Approximate Cooking Time
8-12 lbs	2 3/4 - 3 hours
12-14 lbs	3 - 3 3/4 hours
14-18 lbs	3 3/4 - 4 1/4 hours
18-20 lbs	4 1/4 - 4 1/2 hours
20-24 lbs	4 1/2 - 5 hours

Figure 6.26 Turkey cooking table. Approximate cooking times are given as a function of the mass of the turkey.

The table says that an 8 pound turkey is supposed to cook for about 2.75 hours. Let's see how a prediction from our formula compares to this. Assuming that a turkey more or less has the shape of a sphere, we can approximate the length, L , by solving for the radius, r , in the equation below where the mass is given in grams and the density is the same as that of water. The radius turns out to be 9.7 cm.

$$m = \rho \frac{4}{3} \pi r^3$$

$$m = 8 \text{ lbs} = 3,900 \text{ g}$$

$$\rho = 1.0 \text{ g/cm}^3$$

$$r = \sqrt[3]{\frac{3}{4} \frac{m}{\pi \rho}} = \sqrt[3]{\frac{3}{4} \frac{(3,900 \text{ g})}{\pi (1 \text{ g/cm}^3)}} = 9.7 \text{ cm}$$

Next let's plug this radius into the formula, $t=L^2/4D$. The length, L , is 9.7 cm, and the diffusion constant, D , is the same as that of water, $1.4 \cdot 10^{-3} \text{ cm}^2/\text{sec}$. This turns out to be 4.7 hours.

$$t_{\text{cook}} = \frac{L^2}{4D} = \frac{(9.7 \text{ cm})^2}{4(1.4 \cdot 10^{-3} \text{ cm}^2 / \text{sec})} = 4.7 \text{ hours}$$

This, of course, is a bit longer than the 2.75 hours stated by the recipe. Still, this calculation should be regarded as a success, because it correctly gives the basic order of magnitude of the cooking time just from simple laws of physics.

6.8.2 Limitations of the Diffusion Equation

Moreover, there are many reasons why this formula should lead to a cooking time that is too long relative to that given in the recipe. First, this formula contains no information on the temperature. Not the temperature of the oven, nor the initial temperature of the turkey, nor the final temperature you are trying to reach inside the turkey. If you have ever cooked a turkey, you know that you pay a lot of attention to all of these variables. In fact, it is critical to use a thermometer to monitor the temperature inside the turkey so that you can tell when it has reached a certain target temperature. By contrast, the cooking time in our formula was only dependent on the radius of the turkey and the heat diffusion constant of water.

In addition, in section 6.5 we discussed how the temperature as a function of time changes exponentially from the initial temperature of the turkey to the final temperature of the oven. And we mentioned that the temperature of the oven is always many times higher than the target temperature of the turkey. In fact, the target temperature is usually somewhere in the beginning or middle of the plot in Figure 6.18. This is in fact the true cooking time, and it is going to be less than $L^2/4D$, which is the typical time scale of the entire heating process.

The second reason that the cooking time from our formula was a bit short has less to do with mathematics, and more to do with the shape of turkeys. Turkeys, at least once they are prepared for cooking, tend to have a big hole in the middle. Thus, unless you stuff the turkey, the hole will be filled with air, and the temperature of that air will be the temperature of the oven. So the turkey is really being cooked from two sides, the inside and the outside. This is different than our calculation, where we assumed that the turkey was a sphere made through and through of turkey. So our calculated cooking time is more like that of a stuffed turkey.

Although our formula is a little off, it is not off by a lot. In fact, it is off by what is essentially a constant factor. In order to explain what we mean by this, let's ask the following question: How much longer would it take to cook a turkey that weighs twice that of the 8 lbs turkey we just discussed? Just as before, we can use the equation that relates the mass of a sphere to the radius and density, and thus find the length, L , that heat needs to diffuse.

As you can see in the calculations below, since the mass is a factor of 2 larger, the radius of the turkey goes up by a factor of $2^{1/3}$, which is about 25% larger. If we use this in the formula for cooking time, where L is squared, we get a time that is $(2^{1/3})^2$ times larger, which is the same as 1.6. So the cooking time, according to our theory, should be about 60% longer for a 16 lbs turkey compared to an 8 lbs turkey, or, really, whenever the weight is doubled. If we multiply the cooking time given for the 8 lbs turkey with 1.6, we get a predicted cooking time for the heavier turkey of 4.4 hours. According to the cooking table in Figure 6.24 this is very close to the suggested cooking time for a 16 lbs turkey.

$$L_{8\text{lbs}} = \sqrt[3]{\frac{3 m_{8\text{lbs}}}{4 \pi \rho}}$$

$$L_{16\text{lbs}} = \sqrt[3]{\frac{3 \cdot 2m_{8\text{lbs}}}{4 \pi \rho}} = \sqrt[3]{2} \sqrt[3]{\frac{3 m_{8\text{lbs}}}{4 \pi \rho}} = \sqrt[3]{2} L_{8\text{lbs}}$$

$$t_{\text{cook}} = \frac{L_{16\text{lbs}}^2}{4D} = \frac{(\sqrt[3]{2} L_{8\text{lbs}})^2}{4D} = 2^{2/3} \frac{L_{8\text{lbs}}^2}{4D} = 1.6 \cdot 2.75 \text{ hours} = 4.4 \text{ hours}$$

According to the same reasoning, a turkey that is 10 times heavier, has a little more than double the radius, and will hence take a little more than four times longer to cook. Not ten times longer, as one might initially expect, but four times longer.

In summary, while the formula for cooking time, $L = \sqrt{4Dt}$, is systematically off because of the reasons that we have discussed, it does predict the right trend with size. In many ways that is the most interesting part of the formula. If we want to calculate a more precise cooking time, it is best to turn to a computer program like the one we discussed in section 6.6 that can solve the complex diffusion equation and give a precise temperature at any point in time. In the absence of that, our predictions will involve some hand-waving. Nevertheless, the physical principles we have discussed do a fairly decent job explaining and predicting how long you should cook things.

CHAPTER 7

Viscosity and Polymers

TABLE OF CONTENTS: 7

7.1 Introduction to Viscosity

[7.1.1 Definition of Viscosity](#)

[7.1.2 Temperature Dependence of Viscosity](#)

[7.1.3 Estimating Viscosity of Water](#)

7.2 Measuring Viscosity

7.3 How Thickeners Work

[7.3.1 Four Ways Chefs Increase Viscosity](#)

[7.3.2 Volume Fraction](#)

7.4 Modernist Thickeners

[7.4.1 Polymers Spread Out Like a Random Walk](#)

[7.4.2 Calculating the Volume Fraction of a Polymer in Solution](#)

[7.4.3 Polymers Entangle](#)

7.5 Viscoelasticity

7.6 Equation of the Week

[7.6.1 Summary and Background](#)

[7.6.2 An Equation for Viscosity](#)

[7.6.3 Equation of the Week: Volume Fraction](#)

[7.6.4 Equation of the Week Applied to Modernist Thickeners](#)

7.7 Glasses and Candy Apple Viscosity

[7.7.1 The Role of Time Scale for Creating Culinary Glasses](#)

[7.7.2 Molecular Origins of Glasses](#)

CHAPTER 7

7.1 Introduction to Viscosity

A common problem in cooking is that you have some liquid food, be it a sauce, a dressing, a soup, or a liquid drink such as a milkshake, and you want to make it thicker. Sometimes the reason for this is one of mouthfeel – you want the food to have a thick and satisfying consistency. A thick milkshake is an altogether very different type of food than a tall, sugary glass of milk, and a thick and creamy soup is very different, and more filling, than a clear soup made of stock. Other times, you want the liquid to be thicker because you want it to cling to some other food that it is served with. A flavorful sauce that clings to the food it is eaten with, will be able to flavor that food much more effectively than if it is too thin to hold on. For example, a thicker salad dressing will be able to cling to the ingredients in a salad and make them more flavorful than a thin dressing that collects at the bottom of the salad bowl. Similarly, we want a cheese sauce to cling to the accompanying macaroni and a meat sauce to cling to the steak.

7.1.1 Definition of Viscosity

The scientific term for the thickness of a liquid is viscosity. All fluids have viscosity. It is defined as the resistance of a fluid to flow, the larger the resistance, the higher the viscosity. If you imagine walking through water, you know that it is much more difficult than walking through air. For every stride you take, the water imparts resistance that you must push through in order for the water to flow aside so that you can walk through it. Walking through honey, which has a higher viscosity than water, is even more difficult, because the honey imparts an even larger resistance.

The resistance of fluids is due to the molecules or particles they contain. When we first introduced liquids in Chapter 3, we saw that the molecules in liquids move around. They don't move quite as fast as the molecules in gases, but they still have some motion compared to solids where the molecules are completely stationary. As the molecules move around in a liquid, they bump into each other, and this impedes their movement. Thus, the more the molecules in a fluid bump into each other, the higher the viscosity.

An effective analogy by Nathan Myhrvold explains this further: Imagine a subway platform with almost no one on it. If you want to walk from one end to the other, it will be fast and easy. Next, imagine a very crowded subway platform. Now walking from one end to the other will take much longer because you will keep bumping into people and having to walk around them. The same is true for viscosity: the more molecules in the fluid, the slower the fluid will move. Similarly, the larger the molecules in the fluid, the slower the movement – imagine walking through a crowded subway platform where everyone is carrying large suitcases. It will be even slower!

With this analogy in mind, if you walk through water, the molecules need to move away and over each other in order for the water to flow to the side and let you through. The easier they can move over one another the easier it will be for you to walk. Fluids containing very small molecules, like water, whizz by each other relatively easily, making the viscosity low. Large molecules, though, like those in oil or honey, take much longer to move over one another, making the viscosity higher.

If we wanted to describe the resistance of a fluid in scientific terms, we

would say that the fluid imparts a force, or a stress, that prevents the flow. Recall the force pushing back on your legs as you walk through water. The stress is the viscosity times the rate at which the fluid flows over itself. A rate is measured in units of 1/sec, and based on this we get the following relationship between the viscosity, the stress, and the flow rate:

$$\text{stress} = \frac{\text{viscosity}}{\text{time}}$$

rearranging gives us:

$$\text{viscosity} = \text{stress} \cdot \text{time}$$

So the viscosity is the stress times a time, where the time is often referred to as the relaxation time. If we substitute the text for the appropriate Greek letters, we get the following relationship:

$$\eta = \sigma \cdot \tau$$

where:

$$\eta = \text{viscosity (Pa} \cdot \text{sec)}$$

$$\sigma = \text{stress (Pa)}$$

$$\tau = \text{time (sec)}$$

And if we plug in the units for stress (Pa) and time (sec) in this equation, we find that the units of viscosity are Pa · sec.

7.1.2 Temperature Dependence of Viscosity

From what we have learned about the role of molecular motion for viscosity, we can understand that temperature must have an important effect. As the temperature of a fluid increases, the molecular motion also increases, and this makes it easier for the molecules to move by one another. Oil, for example, has a viscosity that changes very strongly with temperature. If you increase the temperature of oil, the viscosity can become as low as the viscosity of water. You may also have experienced the same phenomenon when cooking: a sauce with a perfect consistency served hot right off the stove, will become thick and gooey when allowed to cool on the dinner table for too long.

7.1.3 Estimating Viscosity of Water

We can use what we have learned so far to estimate an actual number for the viscosity of one of the most important materials in this course, and arguably for life in general, namely water. One way to define viscosity in a fluid is by how fast the molecules in the fluid move past each other. The higher the speed of the molecules, the faster they move past each other. Similarly, the smaller the molecules, the faster they move past each other. We also know that the concentration is important, the higher the concentration, the higher the viscosity because there are more molecules to bump into. We will use density as an approximate variable to describe concentration for now, but in section 7.3 we will find a more accurate expression. With size, speed, and density in mind, a reasonable estimate for the viscosity of water is the density, ρ , times the speed, v , times the size of the molecules.

$$\eta = \rho \cdot v \cdot \text{size}$$

The speeds of molecules are usually about the same independent of different kinds of fluids, about $1.5 \cdot 10^{-2}$ km/sec. The densities of fluids are also fairly similar, about $10\,000 \text{ kg/m}^3$ or 1 g/ml . What tends to change the most is the size of the molecules. The size of a water molecule is about $3\text{\AA}$, or $3 \cdot 10^{-10} \text{ m}$. Plugging these values into the equation, we get a viscosity of $4 \cdot 10^{-3} \text{ Pa} \cdot \text{sec}$, or $4 \text{ mPa} \cdot \text{sec}$, and this, it turns out, is very close to the value you get if you measure the viscosity of water experimentally, which is about $1 \text{ mPa} \cdot \text{sec}$.

$$v = 1.5 \cdot 10^{-2} \text{ km/sec}$$

$$\rho = 10,000 \text{ kg/m}^3 = 10^4 \text{ kg/m}^3$$

$$\text{size} = 3 \cdot 10^{-10} \text{ m}$$

$$\eta \approx (10^4 \text{ kg/m}^3)(1.5 \text{ km/sec})(3 \cdot 10^{-10} \text{ m}) = 4 \cdot 10^{-3} \text{ Pa} \cdot \text{sec}$$

7.2 Measuring Viscosity

There are many ways to measure viscosity, ranging from simple methods using materials available at home, to the very precise and sophisticated equipment that is used in laboratories. In some way or other, all methods measure a fluid's resistance to flow.

One of the most advanced ways of measuring viscosity is to use a rheometer (Fig. 7.1). This is the instrument of choice in scientific laboratories and other contexts where very precise measurements of viscosity are required. Rheometers work by placing the fluid of interest between two plates. When the upper plate is rotated, the fluid exerts a force on the lower plate, and that force can be measured. The faster the upper plate is rotated, the larger the force. By measuring the force and knowing the rotation rate, the viscosity can be determined.



Figure 7.1 A rheometer precisely measures the viscosity of fluids. It works by rotating a metal cylinder over a sample placed on the black area in the picture, and measuring the resisting force from the sample.

Another instrument scientists use to measure viscosity is a capillary (Fig. 7.2). A capillary is a very thin tube, and it works by simply letting a fluid

flow through it under the force of gravity and measuring how long it takes. The more viscous the fluid, the longer the flow time. This method also allows for very accurate viscosity measurements.

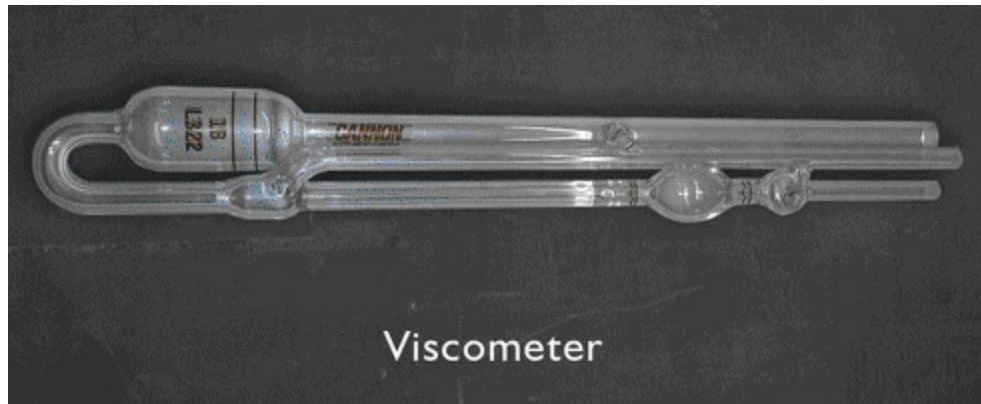


Figure 7.2 A capillary viscometer measures viscosity by measuring the time it takes for a given liquid to flow through a narrow capillary within a U-shaped glass tube.

There are many other ways of measuring viscosity that are really just variations on the same principles. For example, you can measure how long it takes for a fluid to flow through a funnel. Or, you can make a hole in the bottom of a plastic cup and measure how long it takes for a certain amount of fluid to flow through it. Or, you can fill a graduated cylinder or glass with fluid, drop a metal ball through it, and measure how long it takes for the ball to reach the bottom. Finally, our favorite, is to measure the viscosity of a cheese sauce by filling a tall glass with cooked macaroni and measuring how long it takes for the sauce to flow through it. In fact, this is how we measure viscosity in the mac and cheese lab which typically accompanies this chapter. It may not be as precise a method as some of the other ones, but in a culinary context it gets at the very essence of why we would want to make the cheese sauce viscous in the first place, namely to make it cling to the food so that it tastes better. In all of these cases, the more viscous the fluid, the longer the time is for these events to happen.

7.3 How Thickeners Work

From our discussion on the molecular origins of viscosity you can understand that if you want to increase the viscosity of a liquid, you somehow have to increase how much the molecules or particles bump into each other. One way to do this is simply to add more particles. Another is to decrease the amount of liquid in the mixture so that the concentration of particles increases. The main ways in which we thicken foods in culinary contexts usually involve some version of one or the other of these two.

7.3.1 Four Ways Chefs Increase Viscosity

The many ways in which chefs can control the viscosity of liquid foods, can, according to Nathan Myhrvold, be grouped into four main categories. The first is by reduction. This method involves increasing the concentration of particles in a fluid by boiling off some of the liquid. The reduction of wine that you may do as one of the steps in the preparation of a red wine sauce is one example of this. A disadvantage of this method is that it can take a very long time to boil off enough liquid for the food to become thicker. In the case of a red wine sauce, for example, since there are not very many particles in wine to start with, it is not uncommon that 90% of the liquid must be boiled off for substantial thickening to occur, and this takes time. If a liquid contains even fewer particles than wine, then the method of reduction is not very effective at all at increasing viscosity.

The second way to thicken a liquid food is by adding starch. When you add starch to a liquid, the number of particles increases by way of the starch granules, and this alone increases viscosity. In addition, the starch granules not only swell, increasing the size of the particles, but also have a tendency to clump together. We will discuss the mechanism of how this increases viscosity in more detail toward the end of this section. In general, starch based thickeners are effective and come in many different versions, ranging from flour to cornstarch to arrowroot, each having their own unique properties. Their main disadvantage is that they need to be added in rather large quantities in order for substantial thickening to occur – a typical thick white sauce requires about $\frac{1}{4}$ cup of flour for every cup of milk. As a result, the food is diluted and often becomes much less flavorful. This sometimes makes starch a less attractive choice for some types of thickening.

The third way to thicken a liquid food is to turn it into an emulsion. Since most foods are water based, this usually involves adding some fat such as oil or butter. The fat droplets end up behaving just like particles, so again, we have essentially increased viscosity simply by increasing the concentration of particles. The downside of thickening with emulsions is that they usually involve adding large amounts of fat. Mayonnaise, for example, contains about a cup of oil for every quarter cup of water-based liquid.

Finally, the fourth way of thickening liquid foods is with modernist thickeners. Modernist thickeners have the unique property of effectively

being able to thicken a fluid even when added in very small amounts. Thus they do not dilute the flavor of the food the way starch based thickeners do. They also do not involve the lengthy preparation times of thickening by reduction, nor the addition large amounts of fat involved in thickening with emulsions.

7.3.2 Volume Fraction

We can understand the thickening in all of these cases if we think about the fluids on the level of the particles. Just as with the molecules, when the fluid flows, the particles also flow. And similar to the particles, the particles have to move over one another in order for the entire fluid to flow. The higher the concentration, and the larger the particles, the more difficult this is.

In fact, the concentration and the particle size are so important for viscosity that if we could find a way to express these two quantities together in one variable, we would have an effective way of predicting the viscosity. The way to do this is to find the total volume that the particles occupy in the fluid. If the concentration and particle size is large, then the total volume of the particles is large, and if the concentration is small and the particles very tiny, then the total volume of particles is very small. We can calculate the total volume of the particles by finding the volume of each of the particles and multiplying it by the number of particles there are. If we then divide this by the total volume of the fluid, we have a quantity that is called the volume fraction.

$$\phi = \frac{\text{\#particles} \cdot V_{\text{particles}}}{V_{\text{fluid}}}$$

The volume

fraction is the most important variable for determining how the particles impact the viscosity of a fluid. When there are very few particles in the fluid, or their volume fraction is very low, then they have almost no effect at all. When the fluid flows, the particles just flow with the fluid and the viscosity of the fluid is just the viscosity of the fluid itself. The particles play no role whatsoever (Video 7.1).

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[movie_1_07_viscosity_slide_13_1.mp4](#)

Video 7.1 A fluid containing a small amount of particles will flow very easily, i.e. the viscosity is low. However, when the volume fraction of the particles increases they become

crowded and interfere with each other, hence making it more difficult for the particles to flow over one another. In this case, the particles really impact the flow of the fluid and increase the viscosity (Video 7.2). For this to happen, the volume fraction of particles has to be sufficiently high, usually on the order of 50%, i.e. about half of the volume of the fluid must be occupied by particles in order for the viscosity to be considered substantial.

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[movie_2_07_viscosity_slide_12_1.mp4](#)

Video 7.2 A fluid with many particles will not flow very easily, i.e. the viscosity is high.

Knowing that the volume fraction is so important explains why starch is such an effective thickener. There are two reasons for this. First, not only do the starch granules occupy their initial volume, they also absorb water and swell considerably when heated, and this, of course, increases the volume fraction (Video 7.3). So if you add 15% of starch to a sauce, i.e. the initial volume fraction is 15%, then the final volume fraction after swelling will be much larger, and the viscosity will increase.

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[movie_3_07_viscosity_slide_15a_1.mp4](#)

Video 7.3 Starch granules swell as they absorb water, and therefore contribute considerably to the viscosity of a solution

The second reason that starch is such an effective thickener is that the granules stick together into tenuous structures (Video 7.4). The volume of these structures is the volume of the structures themselves plus all the water that they enclose, as shown by the circle in Video 7.4. This increases the effective volume fraction of the particles further, because it allows them to occupy even more volume by also including the enclosed water. So the viscosity increases further. Hence, even if the volume fraction of the particles is not greater than 50%, the fact that they are bundled together

makes the effective volume fraction large enough to significantly increase the viscosity.

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[movie_4_07_viscosity_slide_15b_1.mp4](#)

Video 7.4 Starch granules not only swell in solution, they also form aggregates. The aggregates contribute to increasing the volume fraction of the solution and hence also the viscosity.

In summary, all of these different ways of thickening a liquid food have in common that they increase the volume fraction to 50% or higher. We have already discussed how starch granules do this. A reduction accomplishes the same thing by boiling off the surrounding liquid. Similarly, an emulsion only becomes viscous if the droplets occupy at least 50% of the total volume. This can happen either by adding enough drops, or by having the drops be sticky and form larger, tenuous structures in exactly the same way that the starch granules did. In the next section we will discuss how modernist thickeners accomplish the same thing, although in a slightly different way.

7.4 Modernist Thickeners

Modernist thickeners are special in that they can provide effective thickening even with very small amounts of material. Even so, as you will soon see, the way they increase viscosity is in many ways similar to how particles work. The difference is that modernist thickeners are very long polymers and therefore have the unique feature that they can occupy a huge volume with very little mass.

7.4.1 Polymers Spread Out Like a Random Walk

To understand this, we have to look at how a polymer behaves in solution. A polymer is a very long molecule that is made up of many, many much smaller monomers. Polymers also have the special characteristic that they are very flexible. The reason for this is that the bond between each of the monomers can bend in more or less any direction, and they do this with equal probability (Fig. 7.3). It should be mentioned that this is somewhat of a simplification, and in reality the bending depends on the specific molecule, but the overall effect is not so far from this, and it is helpful in trying to understand what is going on.

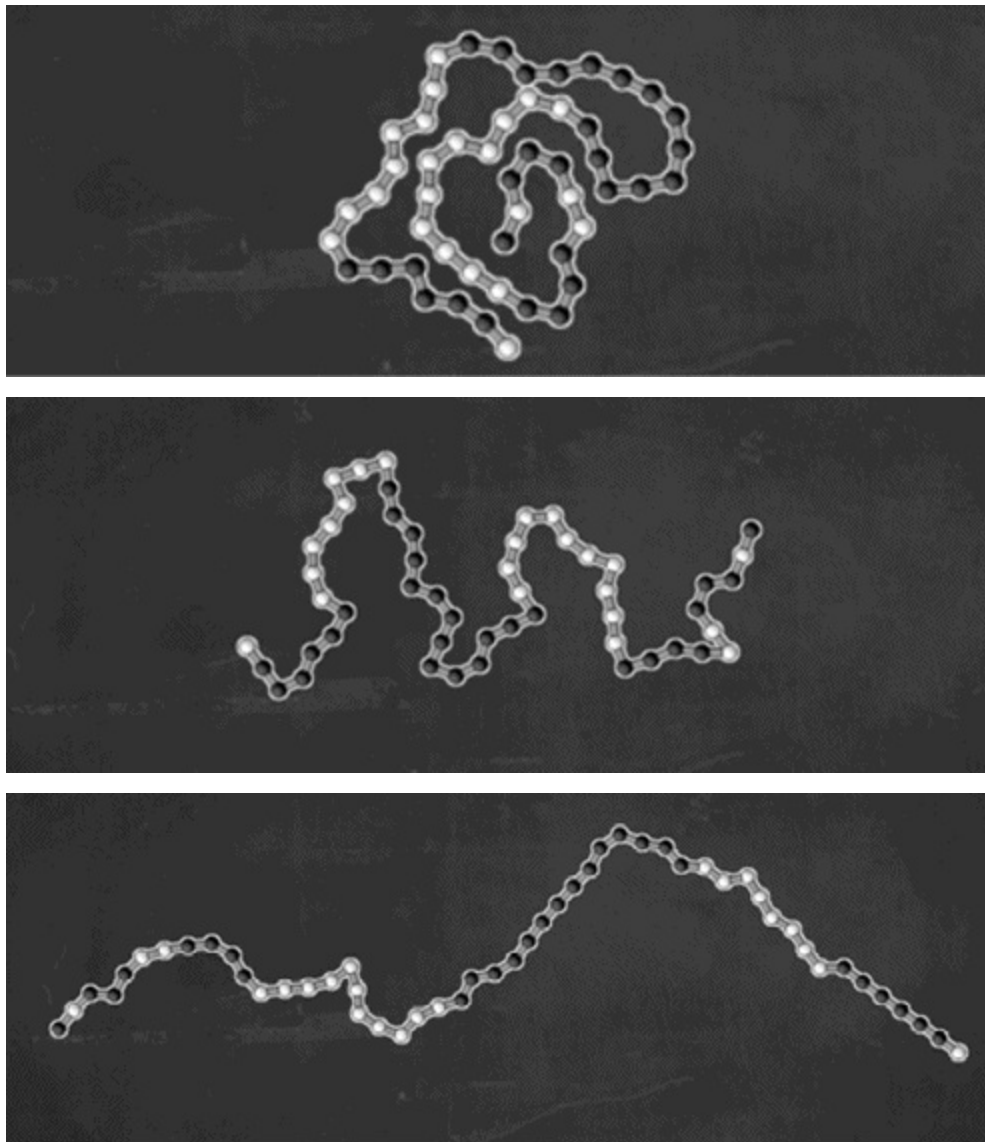


Figure 7.3 A polymer is a long flexible molecule composed of individual monomers. At each monomer, the polymer can turn in any direction, resulting in an overall structure that has the shape of a random walk. A polymer can take on a large number of different configurations, ranging from very small and

compact, to long and flexible.

When you think about it, this random bending in any direction sounds very similar to the concept of a random walk, which we discussed at length in the context of diffusion. We said that the way a molecule moves in a solution, say, a calcium ion in an alginate solution, is by repeatedly moving randomly in any direction over an extended period of time. It turns out that a polymer dissolved in a liquid will look very similar to the movement of such a molecule. In fact, you can imagine tracing the random walk of a calcium ion and ending up with the structure of a polymer, where each step in the random walk corresponds to one of the monomers. The video below illustrates this point by showing the random walk of a calcium ion (Video 7.5). As you can see, at the end of the walk, the ion has covered a large volume. In the same way, a long polymer will occupy a large volume simply by the way it arranges itself in the solution.

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[movie_5_07_viscosity_slide_19_1.mp4](#)

Video 7.5 Random walk of a calcium ion. A line drawn along the path of the ion illustrates what the shape of a large polymer might look like.

7.4.2 Calculating the Volume Fraction of a Polymer in Solution

We can calculate just how much space the polymer takes up by applying the principles of random walks. It turns out that the radius of a random walk depends on the distance of each step times the square root of the number of steps. With the same reasoning, the radius of the polymer will depend on the length of each monomer times the square root of the number of monomers (Fig. 7.4).

N = number of monomers

a = monomer size

$$\text{radius polymer} = \sqrt{N} \cdot a$$

Thus we can approximate the volume that the polymer occupies simply by cubing the radius of the polymer from above. If we wanted to be more precise, we would plug the radius into the equation for the volume of a sphere, $4/3\pi R^3$, but cubing it is close enough for our purposes.

$$\text{Volume}_{\text{polymer}} = a^3(\sqrt{N})^3$$

The volume fraction of each polymer, then, is the actual volume occupied by the polymer molecule itself, divided by the total volume occupied by the molecule in solution. The volume occupied by the polymer molecule itself is simply the volume of each monomer, a^3 , times the number of molecules, N . Hence the volume fraction of each polymer ends up being:

$$\text{Volume fraction}_{\text{polymer}} = \frac{a^3 \cdot N}{a^3(\sqrt{N})^3} = \frac{1}{\sqrt{N}}$$

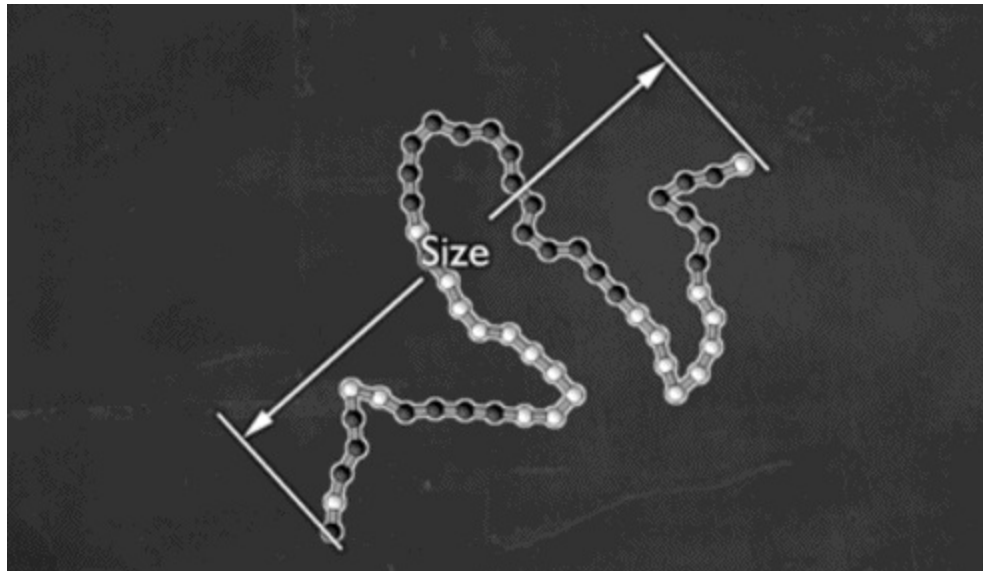


Figure 7.4 The size of a polymer molecule can be thought of as a sphere that occupies a certain volume in space. By estimating the radius of the sphere, we can obtain an approximation of the polymer size.

Let's apply this equation to an actual example. If a typical polymer has, say, 10 000 monomers, i.e. N is 10,000, then, according to the equation above, the volume fraction ends up being $1/100$, or 1%. This is a very low volume fraction, i.e. the actual polymer volume is very small compared to the effective polymer volume. So from this you can see that the effective space that the polymer occupies is very large despite its mass being very small, and this is the secret to its huge effect on viscosity. Since the polymer can spread out and fill the solution it can change the viscosity considerably (Video 7.6).

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[movie_6_07_viscosity_slide_36_1.mp4](#)

Video 7.6 Polymers spread out in the liquid in which they are dissolved, allowing them to increase the viscosity significantly despite their small volume fraction.

7.4.3 Polymers Entangle

Polymers have an additional unique feature in that they entangle with each other. In other words, not only do they spread out and fill large volumes, they also entangle with other polymers, and this increases the viscosity further. The increase in viscosity happens because, just like the particles in a viscous solution must move by each other in order for the fluid to flow, the polymers also have to move past each other. If the polymers are intertwined, they first have to disentangle, and the only way they can do this is by slithering along their lengths as shown in Video 7.7. This process is called reptation, and it is a very slow process. It is not unlike what would happen if you had a bowl of spaghetti and tried to pull out one long spaghetti strand from the rest. Since the spaghetti strand is long and intertwined, this would take a while. So the reason modernist thickeners are effective at increasing the viscosity is not only because they are polymers and thus have a large effective volume fraction. It is also because, by virtue of being polymers, they have the ability to entangle with each other and this increases the viscosity further.

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[movie_7_07_viscosity_slide_37_1.mp4](#)

Video 7.7 Polymers are highly entangled and the only way to separate them is by reptation.

7.5 Viscoelasticity

Many aspects of viscosity can be understood by looking at the level of the particles and molecules. One such aspect is the close relationship between the viscous and elastic characters of a fluid. At very short time scales the molecules or particles do not have time to get out of the way so that the fluid can flow. The result is that the material behaves like a solid.

One example of a material where this effect is particularly apparent is corn starch. If you have not seen this before, we recommend you go into your kitchen and dissolve a small bowlful of corn starch in water. If you then try to run a spoon through the dissolved cornstarch very slowly, you will notice that it flows just fine. The cornstarch is thick and very viscous, but it still flows. However, if you instead try to move the spoon through the cornstarch very quickly, you will notice that it gets stuck. The fluid jams up, and behaves just like a solid. So at short time scales cornstarch behaves like a solid instead of a liquid.

Video 7.8 illustrates what is going on at the level of the cornstarch particles. Initially the particles are naturally moving about due to thermal motion. If the particles are then suddenly moved very rapidly, they don't have enough time to move over one another and they jam together and become solid-like. It takes some time for them to relax again and recover their flow, again due to thermal motion, and this time is called the relaxation time. In very concentrated fluids, or in fluids where the molecules are somewhat sticky, the relaxation time is even longer.

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[movie_8_07_viscosity_slide_26_1.mp4](#)

Video 7.8 At short time scales, the molecules in a complex fluid may not have time to move past each other and they jam. This leads to the material behaving like a solid rather than a liquid.

Simple fluids, like water and oil, contain no particles. Instead it is the molecules themselves that jam. However, since the molecules are moving very fast and thus can move around one another very quickly, the time scales have to be very short in order for you to see the jamming.

Nevertheless, even simple fluids behave like elastic materials if you look at short enough times. In fact, if you have ever jumped into a pool and done a belly flop instead of a dive, you have probably experienced first hand the pain that comes from the molecules not moving out of the way quickly enough. The pain is due to the water behaving like a solid at the short time scale it takes for you to hit the water.

Modernist thickeners also have viscoelastic properties. In their case the solid-like properties are due to the polymers not being able to disentangle and move away from one another at short time scales. Video 7.9 shows a cartoon illustrating this idea.

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[movie_9_07_viscosity_slide_28_1.mp4](#)

Video 7.9 At short time scales, polymers in solution will not have time to disentangle in a way that allows them to flow like a fluid, and they will behave like solids.

The fact that all fluids, be it simple fluids, complex fluids with particles, or polymeric fluids, all acquire solid-like properties at short time scales allows us to express a relationship between the viscosity of the fluid on the one hand and the elasticity of the solid-like material on the other hand. The one variable that relates them to each other is just the relaxation time, which we can call τ . The formula says that the elasticity, E , is equal to the viscosity, η , times the relaxation time, τ .

$$E = \eta \cdot \tau$$

With this equation, we can get a sense for why different fluids have different viscosities. For example, for a simple fluid, the elasticity is large, but since the relaxation time is very short, the viscosity is quite low. By contrast, for a solution with modernist thickeners, the polymer network has a relatively low elasticity, but since the relaxation time is long, the viscosity must be large.

7.6 Equation of the Week

7.6.1 Summary and Background

As a way to provide the necessary background to the equation of the week, let's briefly summarize the concepts we have discussed so far. We have talked about viscosity in simple fluids and in complex fluids. Examples of simple fluids are water or liquid nitrogen, which have single molecules of the same type that are whizzing by each other. And we told you that viscosity was essentially a measurement of the resistance of the molecules to flow. Or, expressed differently, it was caused by how long it took and how difficult it was for the molecules to move around each other.

Most of manipulating viscosity when cooking requires putting various types of other stuff into a simple fluid. This is what we mean by complex fluids. You might add starches, solid particles, or polymers, and when you pour the fluid, these things also have to move around each other and this increases the viscosity.

We have talked about three different types of things that can be added to simple fluids when cooking (Fig. 7.5). The first are what we might call simple particles. These are rigid particles such as the sugar crystals in a sugar syrup. In a sugar-water mixture, the sugar crystals are much larger than the water molecules, and when moving by each other, they make a concentrated sugar-water mixture very viscous.

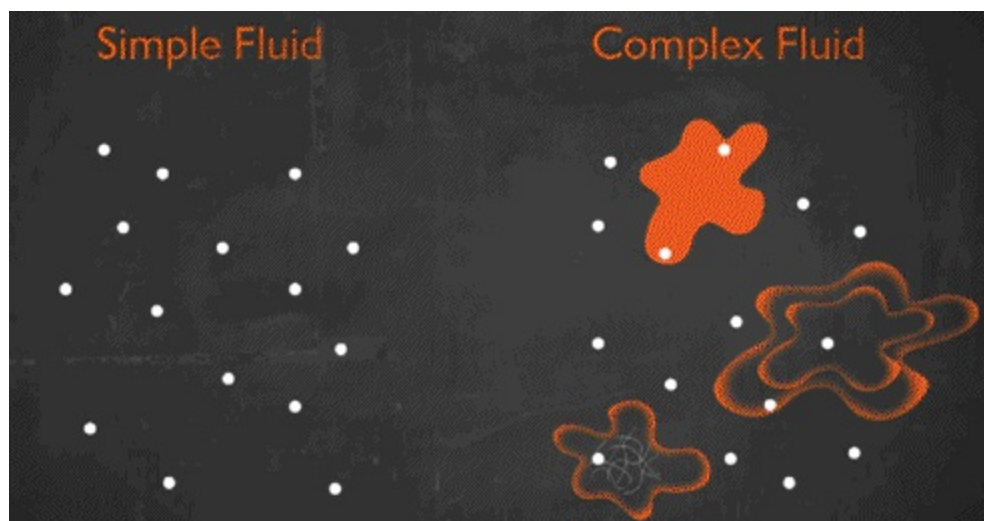


Figure 7.5 There are two types of fluids: simple fluids and complex fluids. Simple fluids, such as water, are composed of a single type of atom or small molecule. Complex fluids also contain other types of

substances such as for example (1) solid particles, i.e. saturated sugar or salt solutions (2) solid particles with complex behaviors , i.e. starch solutions where the starch swells, or (3) polymers, i.e. solutions with modernist thickeners.

The second category of complex material that can be added when cooking is starches. This is a common way to thicken sauces. Starch granules are also small solid particles, but they have the remarkable property that when heated in a liquid, they expand. Amazingly, the radius of a starch granule can expand by a factor of three, which means that the volume goes up by a factor of 30. So, even if you add a relatively small amount of starch, the effective amount of material that you end up with in the mixture is 30-fold larger. Thus it can have a big effect on the viscosity because the volume fraction is much larger.

The final type of complex material that can be used to thicken liquid foods is modernistic thickeners. As we already mentioned, modernistic thickeners are polymers, which themselves have a relatively low molecular weight, but because they arrange themselves as random walks in the fluid, they take up a large volume fraction. They essentially turn into large blobs, which, having to move around each other, end up increasing the viscosity substantially.

In general when you cook, you put combinations of all of these things in. Depending on the recipe, you may add solid particles, starch granules, and maybe even modernist thickeners. It is the cooperation of all of these materials that leads to increased viscosity in most thickened liquid foods.

7.6.2 An Equation for Viscosity

At first thought you might think that a good equation of the week to summarize these ideas would be an equation for viscosity itself. If we were to write such an equation, it would look something like the following: Let's call the viscosity of the simple fluid that you are adding material to η_0 . For most of cooking η_0 would be the same as the viscosity of water. Then, let's call the final viscosity of the mixture of materials η . The viscosity of the final mixture will then depend on the initial viscosity and the volume fraction, ϕ , in the following way:

η = Viscosity of complex fluid

η_0 = Viscosity of simple fluid

$$\eta = \eta_0 \cdot f(\phi)$$

The volume fraction, ϕ , in this equation will be composed of all of the different things you add: particles, swelled starch granules, polymers, etc. Thus, this equation essentially says that the viscosity of a mixture depends on the amount of stuff you put into it. And the critical feature of the stuff is the volume fraction, i.e. how much volume did the stuff fill up.

If one were to plot the viscosity, η , as a function of volume fraction, it would look something like the plot in Figure 7.6. When the volume fraction is small, the viscosity is the same as that of the simple fluid. As more and more other materials are added, the viscosity increases, i.e. $f(\phi)$ increases dramatically. Eventually $f(\phi)$ gets so large that the viscosity essentially becomes infinite. The reason this happens is that there are so many blobs around that they cannot move by each other and they become stuck. For the sorts of things that you cook with, where the materials essentially have random shapes, the critical volume fraction where this happens is somewhere between 60% and 70%. Below that, the mixture will flow. But at volume fractions higher than 50% or 60% the viscosity is usually considered significant. This is where a sauce or liquid food will be substantially thickened and rich.

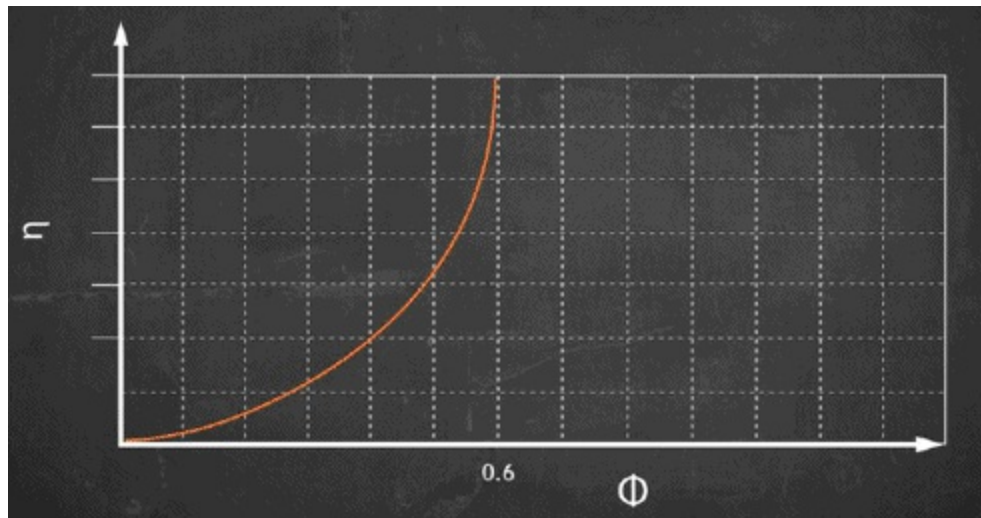


Figure 7.6 Plot of viscosity as a function of volume fraction. When the viscosity is about 50-60%, the fluid has considerable viscosity. At volume fractions above 60-70%, the viscosity is so high that the material becomes stuck.

7.6.3 Equation of the Week: Volume Fraction

With this as background, it should make sense that the equation of the week is not the equation for viscosity. Instead it is the equation for the volume fraction, ϕ , because the volume fraction is the most important variable to control when you want to control the texture of a sauce.

How do you calculate the volume fraction? The volume fraction is the volume of the material you add, divided by the volume of the liquid you started with (Table 7.1).

ϕ = Volume fraction

$$\phi = \frac{\text{Volume}_{\text{dispersed}}}{\text{Volume}_{\text{total}}}$$

There are two things to remember about this equation. First, in the numerator, the volume of the dispersed material has to include not the dry volume, but the volume it acquires in the liquid. Thus, the effective volume fraction of starch is the volume after the starch granules have absorbed water and expanded. Similarly, the effective volume fraction of a polymer is that of the random walk. The denominator should include the total volume. Usually it is sufficient only to include the volume of the liquid because this tends to be the main contributor to volume, but if you want to be precise it should include everything added to the mixture.

EQUATION OF THE WEEK		
$\phi = \frac{V_{\text{dispersed}}}{V_{\text{total}}}$		
Symbol	Description	Units
ϕ	Volume fraction of dispersed phase	Unitless
$V_{\text{dispersed}}$	Volume of dispersed phase	L
V_{total}	Total volume	L

Table 7.1

The reason this equation represents the physics of this week so well, is that it beautifully connects a culinary phenomenon with the underlying science. Whenever you are presented with a recipe, you can compute the volume fraction of the dispersed phase and this will give you an idea of whether or not the sauce will be thick before you even cook it!

Our argument on the relationship between volume fraction and viscosity illustrates another point, namely that of how closely related the concepts of viscosity and elasticity are. The viscosity of a mixture gets very large just before getting stuck, and once it is stuck the material becomes elastic. So once something becomes very viscous, it is just on the verge of becoming elastic, at which point, its properties change dramatically.

7.6.4 Equation of the Week Applied to Modernist Thickeners

Finally, let's conclude by discussing one subtlety in the use of the equation of the week, which illustrates something very important about the use of modernist thickeners and their viscosity.

Let's imagine that we wanted to compute the effective volume fraction of a modernist thickener. You know that only a tiny amount leads to large increases in viscosity, so how is this reflected in the equation of the week? For example, imagine adding 1% xanthan gum by weight to a liquid food. This is enough to change the texture of the food by a lot, making something with the viscosity of milk turn into a milkshake. If we wanted to find the effective volume fraction of xanthan gum in the liquid we would have to find the effective volume of all of the polymers and divide it by the total volume. The way to compute the effective volume of the polymers for xanthan gum, or for any modernist thickener, is to recall that the radius of the random walk is $\sqrt{N}$, where N is the number of monomers, times the radius of a single monomer, a . Hence the volume of each random walk, is either the cube of that, which is an approximation, or $\frac{4}{3}\pi r^3$, which is the volume of a sphere.

$$\text{radius}_{\text{random walk}} = a \cdot \sqrt{N}$$

$$\text{Volume}_{\text{random walk}} = (a \cdot \sqrt{N})^3$$

or

$$\text{Volume}_{\text{random walk}} = \frac{4}{3}\pi R^3 = \left(\frac{4}{3}\pi (a \cdot \sqrt{N})^3\right) = \frac{4}{3}\pi a^3 \sqrt{N}^3$$

This means that the volume of each random walk will be quite large. If we then were to multiply this number by the number of polymers in order to get the total volume occupied by xanthan gum, it may actually turn out that the tiny amount of xanthan gum you added ends up having a volume fraction larger than 1. Now, there is no way the volume fraction can ever be larger than 1. That would mean that the volume of the polymers in the dispersed phase is larger than the volume that you started out with in the first place. This makes no sense, but it does tell us something important about what is

going on.

When the volume fraction is larger than 1 it means that the polymer spheres overlap with each other. And when they overlap, they start to entangle. So instead of being spheres, they unfold and tangle up with each other like a bowl of spaghetti, which makes it even harder for the polymers to move by each other. This makes the viscosity go up even more than if the polymers were spherical. The critical idea that explains the behavior of modernist thickeners is that even with a very small weight of polymer, the total volume fraction can easily go above 1, at which point the polymers become entangled, and viscosity is increased by a lot.

7.7 Glasses and Candy Apple Viscosity

7.7.1 The Role of Time Scale for Creating Culinary Glasses

The viscosity of a fluid is related to the time scale that it takes to relax its structure. As the viscosity increases, the time scale to relaxation gets longer. If the time scale gets long enough, we say that the liquid has become a glass, the longer the time the more solid-like the glass. Window glass, for example, is a liquid, but the relaxation time is so long, that in our lifetime, we do not see a relaxation. If the relaxation time is not quite as long as that, we may still be able to see the very slow flow of the fluid.

We can take advantage of this property to make various materials, such as window glass or bottle glass, but also culinary materials. For example, Chef Bill Yosses makes a thin-shelled candy apple much the same way one would blow glass. He starts out by making a sugar solution out of water and sugar. By letting the liquid solution cool somewhat, it gets so viscous that it can be shaped into a ball and put on top of a small blow-pipe. He can then carefully inflate and mold the sugar into a hollow apple by making sure he keeps the temperature just right – not so cold that the sugar solidifies and cannot be molded, and not so warm that its viscosity decreases and it cannot retain its shape. By having a fan and a heat source handy he can make sure that the temperature can be adjusted quickly. When the apple has obtained the desired shape, he quenches it by lowering the temperature and the apple turns completely solid with a hard, glass-like texture. You can imagine that in order for the viscosity at each step of the recipe to be as desired, the initial sugar concentration needs to be just right.

7.7.2 Molecular Origins of Glasses

We can understand the behavior of glasses by looking at the molecular origin. For fluids, the relaxation time is very rapid. They flow because molecules can move over one another. However, when the fluid is cooled down, the molecules become much slower and the relaxation time gets larger (Video 7.10). As a result, the viscosity increases. Eventually, viscosity gets so large that relaxation can no longer occur, and the liquid becomes a solid. At high concentrations of particles in a fluid, such as sugar molecules in water, it also becomes harder and harder for individual molecules to move over one another. So instead of moving by each other individually, they have to move collectively, and this takes a much longer time. So as the temperature decreases, the number of molecules that have to move together increases, and the viscosity increases.

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[movie_10_07_viscosity_slide_09_1.mp4](#)

Video 7.10 Whether a material behaves like a liquid or a solid depends on the time scale. At long time scales, molecules have time to flow by each other and the material behaves like a liquid. However, if the time scale is short enough, molecules will not have time to flow by each other, and the material will behave like a solid.

Different types of glasses will vary in their behavior depending on how their viscosities change with temperature. For some materials, small changes can lead to very large changes in viscosity. Other materials change relatively slowly in viscosity as the temperature changes. This is the case with the sugar solution for the candy apple. The viscosity changed slowly enough for Bill to work it into a beautiful glass structure, and only when he was done did he change the temperature more dramatically so that the flow stopped completely and it solidify into a glass. It is this relatively slow approach to the solid-like state that enabled the molding of the apple. And whether the material is made of sugar and water, like the candy apple, or of silica, like window glass, the underlying physical principles are the same – the properties of the materials change slowly enough with temperature that they can be worked with, and as the materials cool completely they solidify.

CHAPTER 8

Emulsions and Foams

TABLE OF CONTENTS: 8

8.1 Introduction to Emulsions

[8.1.1 Making an Emulsion](#)

[8.1.2 Surfactants Stabilize Emulsions](#)

8.2 Surface Energy

[8.2.1 Energy of the Oil-Water Interface](#)

[8.2.2 Energy of the Interface for Surfactants](#)

8.3 LaPlace Pressure

[8.3.1 The Pressure that Keeps the Droplets Inflated](#)

[8.3.2 Volume Fraction](#)

[8.3.3 Equation of the Week](#)

8.4 Packing

[8.4.1 Random Close Packing of Spheres: Bubble Gum Balls](#)

[8.4.2 Hexagonal Packing of Spheres](#)

[8.4.3. Packing of other Shapes: M&M's, Chocolate Chips and Flour](#)

8.5 Failure of Emulsions

[8.5.1 Creaming](#)

[8.5.2 Coalescence](#)

[8.5.3 Ostwald Ripening](#)

[8.5.4 Phase Inversion](#)

8.6 Foams

[8.6.1 Making Foams](#)

[8.6.2 Failure and Stabilization of Foams](#)

8.7 Colloids

8.8 Ice Cream

[8.8.1 A Foam, Emulsion, and Dispersion](#)

[8.8.2 Microscopic Structure of Ice Cream](#)

CHAPTER 8

8.1 Introduction to Emulsions

The foods in Figure 8.1 are all examples of either emulsions or foams. Mayonnaise is an emulsion and the cappuccino and beer have foams on top. The reason we arrange these foods in the same image, and indeed, in the same chapter, is that even though emulsions and foams differ in many ways, they are similar enough that by understanding the scientific principles of one, we can also understand the scientific principles of the other. The principal way in which these two materials are similar is in their composition: An emulsion consists of drops of one immiscible fluid in a second fluid. Mayonnaise, for example, consists of drops of oil in water. A foam is the same thing, except instead of the droplets consisting of a fluid, they are made of air or a gas. In the case of the cappuccino foam, the droplets are made of air and the fluid is milk, and in the case of beer foam, the droplets are gas and the fluid is the beer fluid itself.

Emulsions and foams are common throughout cooking, with examples ranging from whipped cream and aioli, to salad dressings, ice cream, various sauces, and even bread. We will start this chapter by learning more about the science of emulsions, and will then continue on to foams and other suspensions.





Figure 8.1 Three examples of emulsions and foams: mayonnaise (an emulsion), and cappuccino and beer (the heads of both are examples of foams).

8.1.1 Making an Emulsion

Let's start by trying to make an emulsion. If you happen to have some olive oil and water nearby, we invite you to follow along by doing this experiment for yourself. Start by pouring about equal parts of oil and water into a glass or bottle, and you will notice that the two fluids separate into two layers. The oil will be on top because it is lighter, it has a lower density, and the water will be on bottom. The only way to try to mix the two layers is by shaking the bottle or glass vigorously. When we do this, the layers initially look like they have mixed, but when looking closer we see that in reality the mixing is a matter of small droplets of one fluid having formed in the other. This is an emulsion. In this case it is an emulsion of oil in water, i.e. the drops are made of oil and they are floating in the water. If we then just watch the emulsion for a while without shaking, the oil drops, being lighter than the water, will start floating to the top, packing closely together at the surface. Eventually the bubbles will pop, and, over time, the two fluids will separate into two layers again. We say that the emulsion has phase separated. Video 8.1 shows a cartoon of this entire sequence of events.

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[movie_1_08_emulsions_slide_7-8-9-2.mp4](#)

Video 8.1 An emulsion forms when droplets of one liquid form within another liquid. Eventually, the droplets in the emulsion recombine and the two liquids separate again. Various methods can be used to prevent an emulsion from failing in this way.

When discussing emulsions, the fluid that is in the drops is usually referred to as the dispersed phase, and the fluid in which the drops float around is called the continuous phase. In the example, oil is the dispersed phase and water is the continuous phase (Fig. 8.2). This type of emulsion is sometimes referred to as a direct emulsion, and includes foods like mayonnaise and aioli.

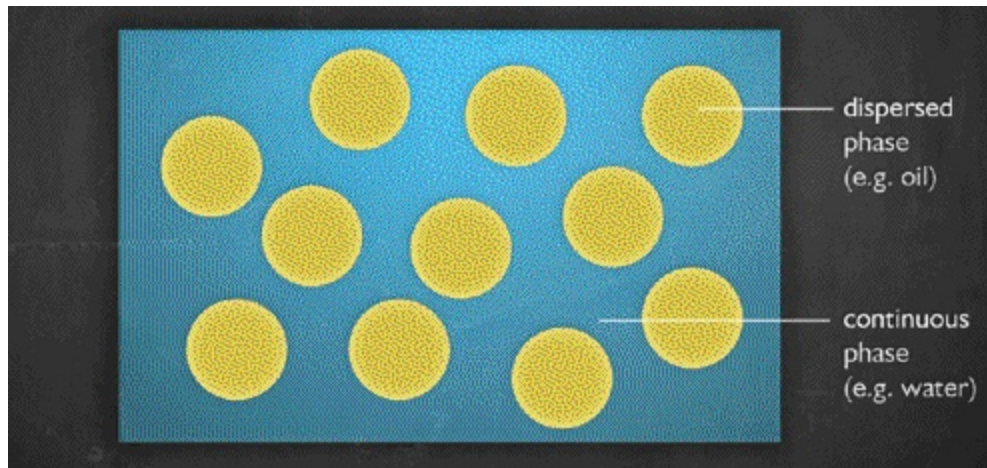


Figure 8.2 Emulsions consist of drops of one liquid (the dispersed phase) dissolved in another liquid (the continuous phase). In the image above, and for the remainder of this chapter, water is blue and oil is yellow.

An emulsion can also be made the other way around, by having water make up the dispersed phase and oil the continuous phase. When made this way, the emulsion is an indirect emulsion (Fig. 8.3). Butter is an example of this type of emulsion.

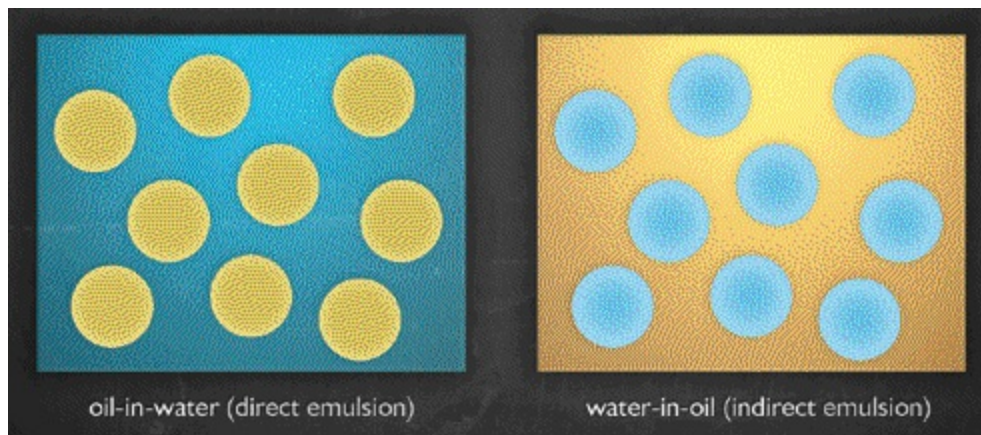


Figure 8.3 There are two types of emulsions: oil-in-water, and water-in oil emulsions.

What happened in the experiment above highlights one of the problems with emulsions: they are often rather unstable. If left alone for long enough, they will eventually separate into an oil and a water phase. To make them stable, you somehow have to prevent the drops from joining together. You have to prevent the smaller drops to coalesce into larger drops, which is what eventually leads to phase separation. This can be done by stabilizing the interface between the drops and the continuous phase. Molecules that are able to do this are called surfactants.

8.1.2 Surfactants Stabilize Emulsions

A surfactant is a surface active molecule (Fig. 8.4). It is amphiphilic, which means it has both water- and oil-like properties. Part of the molecule is water-like, or hydrophilic, and the other part is oil-like, or hydrophobic. What makes surfactants so special is that the two parts are joined together into one molecule, so that part of the molecule likes to dissolve in water and the other part in oil. Since the surfactant does not dissolve well in its entirety in neither oil nor water, it ends up sitting at the interface of the two liquids. So when you add surfactant to an emulsion it naturally goes to the surface of the drops, orienting itself so the hydrophilic part points into the water and the hydrophobic part points inward toward the oil drop. If the emulsion is an indirect emulsion, the surfactant will be arranged in the opposite way, with the hydrophilic part pointing inwards and the hydrophobic part pointing outwards.

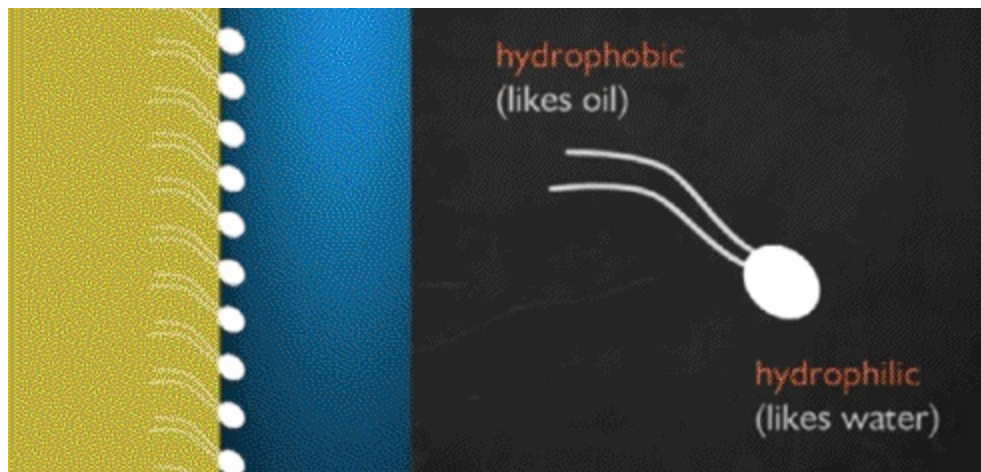


Figure 8.4 Cartoon of a surfactant. Surfactants stabilize the interface of oil and water by having their hydrophilic ends pointing in direction of the water, and the hydrophobic ends reaching into the oil.

If you add enough surfactant to an emulsion, the amphiphilic molecules completely coat the entire surface of all of the drops. When the drops come close together, the surfactant acts almost like a shield preventing the two drops from coalescing (Fig. 8.5). As a result, the drops do not merge as easily, and subsequently the emulsion remains stable.

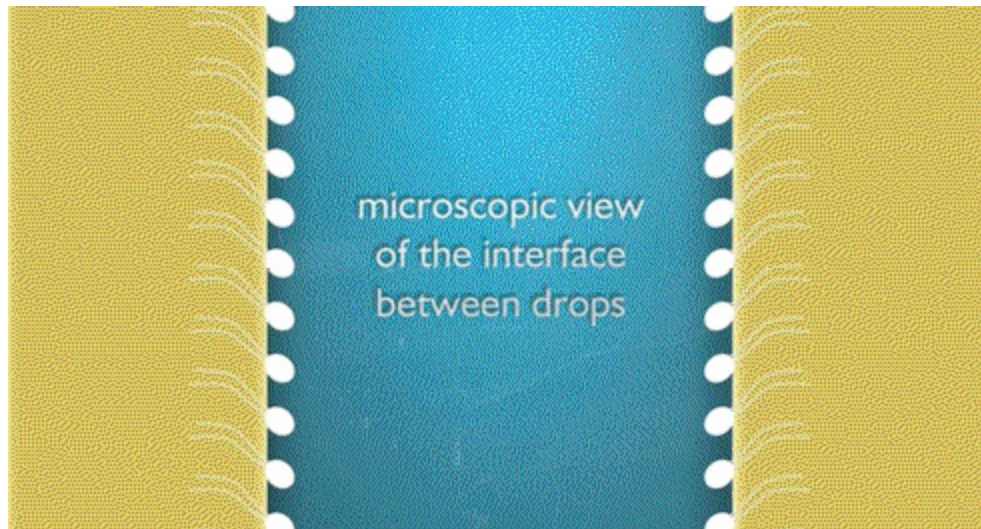


Figure 8.5 Surfactants will coat the surface area of the droplets in an emulsion. When two droplets get too close to each other, the hydrophilic part of the molecules will repel, thus preventing the droplets from coalescing.

When making an emulsion, you typically add the surfactant to the continuous phase. So if you are making an oil-in-water emulsion you add the surfactant to the water. Usually, you also add excess surfactant to ascertain that it will coat the surface area of all the drops you create as you are emulsifying. For the surfactant to have effect, it has to come out of the water and go to the interface. However, since part of the surfactant is oil-like, it does not easily dissolve in water. Instead, the molecules arrange themselves so that the tail groups, the oil-like part of the surfactants, face toward each other in spheres, thus excluding the water. We call these aggregates micelles (Fig. 8.6). This arrangement allows the surfactant to exist in the water without exposing its tail groups to the water. From here the micelles act as a reservoir of surfactant. They easily break up and bring new surfactant to the interface as more drops are created.

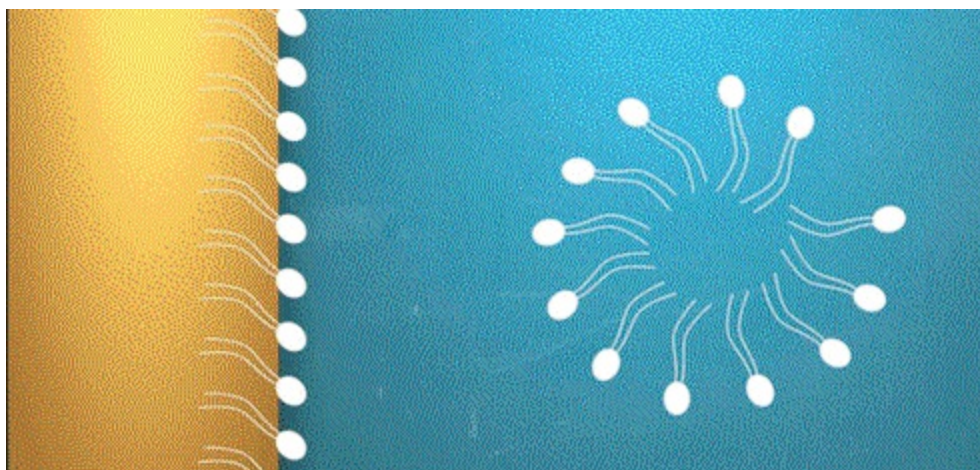


Figure 8.6 Excess surfactant molecules form micelles by clustering their hydrophobic tail groups away from the water.

A commonly used surfactant in cooking is egg yolk. This is the ingredient that makes mayonnaise stable, for example. The stabilizing properties of egg yolk come from phospholipids, which have long hydrophobic “tails” and a hydrophilic “head”. Many plants also contain surfactants that can be utilized in cooking – garlic, for example, provides the surfactants in aioli.

8.2 Surface Energy

8.2.1 Energy of the Oil-Water Interface

An essential feature of emulsions is the fact that you have lots and lots of interface between two fluids. If the oil and water in the experiment above were allowed to stay in two separate layers the way they were before shaking the bottle, the interface would only be the relatively small area of the cross-section of the glass or bottle. But once we shake the bottle, the surface area of the interface increases dramatically. It is now the total surface area of all of the drops.

So when you make an emulsion you are creating large amounts of new interface. And whenever you create new interface, you have to put energy in. The reason for this is that an interface between two fluids always has an energy associated with it. This is the energy that leads to the surface tension, which is the force that tries to pull the fluids together. In the case above, the added energy came from shaking the bottle.

Surface tension and surface energy are really the same thing, and one way to understand this is by comparing their units. The units of surface tension are force per length. By multiplying both the nominator and denominator by a length, we end up with force times length in the nominator, which is the same as energy, and length by length in the denominator, which is the same as area. And this, it turns out, is exactly the units of surface energy.

Surface tension = surface energy

$$\text{Surface tension} = \frac{\text{Force}}{\text{Length}}$$

$$\text{Surface energy} = \frac{\text{Force}}{\text{Length}} \cdot \frac{\text{Length}}{\text{Length}} = \frac{\text{Energy}}{\text{Area}}$$

As an example, the surface tension between oil and water is typically 70 millinewtons per meter (mN/m). This is a force per length. But you can also think of it as an energy, in which case it is 70 millijoules per meter squared (mJ/m²), which is an energy per area, or an energy density.

Another way to understand surface tension and surface energy is by thinking about the oil-water interface on a molecular level. From this perspective, the interface is made up of individual oil and water molecules. As with all molecules, there is a certain interaction energy between them, and this gives us the energy term in the nominator. The area is simply the area of the molecules, which can roughly be estimated as the side of each molecule squared. So the surface tension is just the energy per unit molecule (Fig. 8.7).

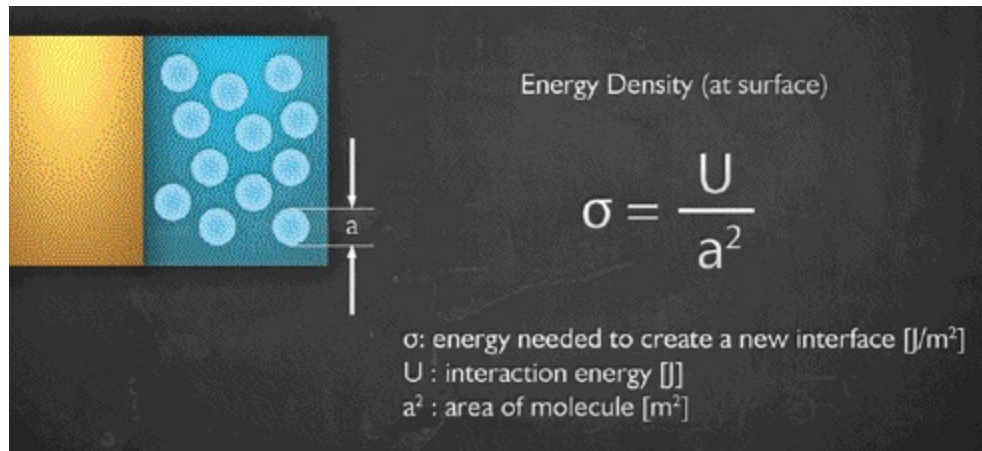


Figure 8.7 The surface energy between two molecules is the interaction energy, U , between them, divided by the area of each of the molecules.

We can use this molecular understanding of surface tension to get a numerical estimate for a typical oil-water interface. The surface tension due to the water alone, would just be the interaction energy between the water molecules divided by the area. We know that the water molecules move around, so the energy between them probably isn't very large. A simple estimate would be to use the thermal energy as the energy of interaction, which we already learned is $k_B T$. With regard to the area, a good estimate for the side of a water molecule is about 2 Ångstroms. Using these numbers, we end up with a surface tension equaling 100 mN/m or 100 mJ/m². This is very close to the measured value for an oil-water interface, which is 70 mJ/m².

$$\sigma = \frac{U}{a^2}$$

$$\sigma = \frac{k_B T}{a^2} = \frac{(1.38 \cdot 10^{-23} \text{ J/K})(300 \text{ K})}{(2 \cdot 10^{-10} \text{ m})^2} = 100 \text{ mN/m}$$

8.2.2 Energy of the Interface for Surfactants

What happens to the surface tension if a surfactant is added? Surfactants typically have a larger dimension than the water and oil molecules. So even if the interaction energy between molecules is about the same, the area is larger, which means the surface energy will be smaller.

For example, if we assume that a surfactant molecule has a dimension of about 3 Ångstroms and that the interaction energy is the thermal energy, the surface tension will be approximately 50 mN/m, or 50 mJ/m², according to the calculation below. So surfactants lower the surface tension, and they primarily do this because they are larger molecules (Fig. 8.8).

$$\sigma = \frac{U}{a^2}$$

$$\sigma = \frac{k_B T}{a^2} = \frac{(1.38 \cdot 10^{-23} \text{ J/K})(300 \text{ K})}{(3 \cdot 10^{-10} \text{ m})^2} = 46 \text{ mN/m}$$

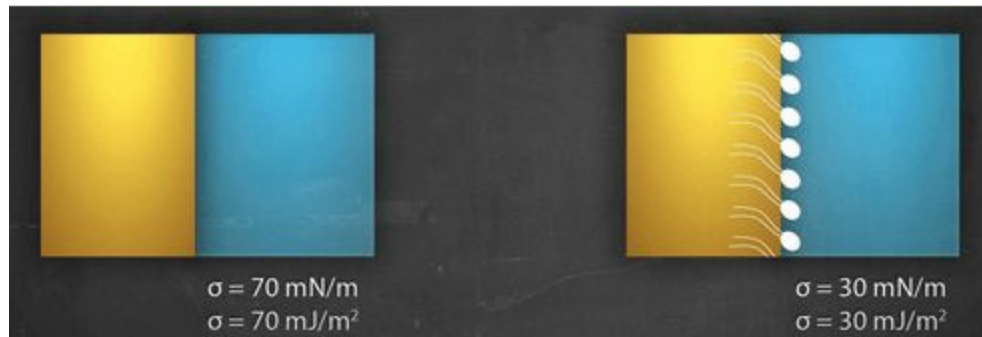


Figure 8.8 Surfactant molecules tend to be larger than water or oil molecules, thus providing a larger area, a , over which the interaction energy, U , can be distributed. As a result, they lower the surface energy, σ .

While it is true that surfactants lower the surface tension, this is not the main mechanism by which they stabilize emulsions. The foremost way they do this is by coating the drops and preventing them from coalescing.

8.3 LaPlace Pressure

8.3.1 The Pressure that Keeps the Droplets Inflated

The effect of surface tension on a fluid is that it pulls the fluid together. Recall the shape of raindrops on a window or small amounts of water spilled on a table – the water usually does not float out over a large area, but collects in rounded half-spheres, or droplets. This is due to the surface tension. The reason the water takes on a spherical shape is that this is the most effective way to minimize the surface energy. A sphere has the least surface area for its volume compared to any other shape, and by adopting this shape, the excess energy at the interface is minimized. This is the reason the dispersed phase in an emulsion is made of spherical drops as opposed to having any other shape.

Since the surface tension pulls in on the drops, it needs to be resisted by an opposing force for the drops not to shrink. This force comes from the internal pressure of the drop. The internal pressure pushes outwards and the surface tension pulls inwards. The principle is not unlike that of a balloon. A balloon is made of elastic material, which pulls inwards and plays a similar role as the surface tension around a droplet. In order to get the balloon blown up, you have to add excess pressure on the inside otherwise the balloon would collapse. This excess pressure is called the Laplace pressure (Fig. 8.9). It is the pressure that provides the force that pushes outwards and keeps the drop blown up.

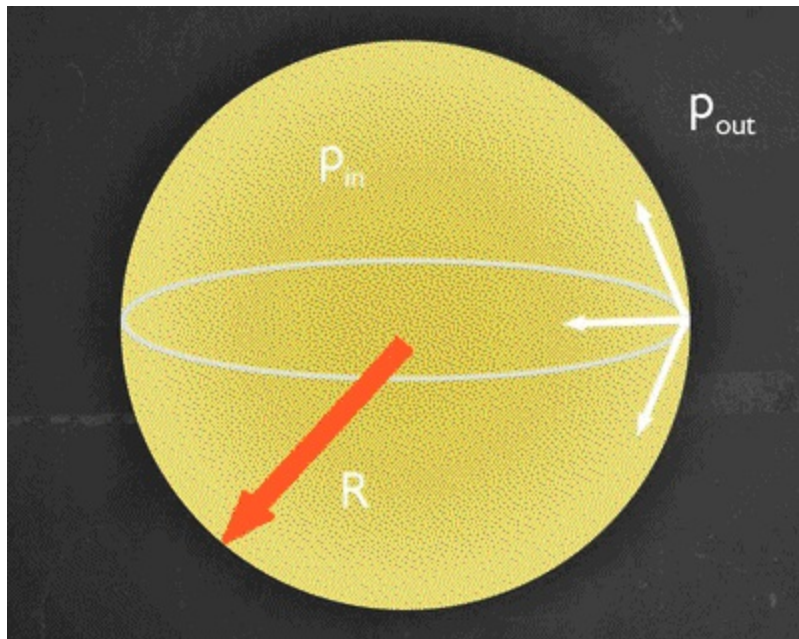


Figure 8.9 A droplet in an emulsion has two opposing pressures acting on it: a pressure from the surroundings pushing inwards, p_{out} , and a pressure from the inside preventing the droplet from closing in on itself, p_{in} . The difference between these two pressures, $p_{in} - p_{out}$, is called the LaPlace pressure.

When a drop is neither expanding nor shrinking, the inward force from the surface tension and the outward force due to the pressure difference are equal to each other. So we can calculate what the LaPlace pressure is by setting these two forces equal to each other. On one side of the equal sign is the force due to the surface tension, which is $2\pi R$, or the circumference of the drop times the surface energy. On the other side of the equal sign is the force due to the pressure difference, which depends on the area of the drop, so it is the pressure difference multiplied by the area of the drop, πR^2 :

$$2\pi\sigma R = (p_{in} - p_{out})\pi R^2$$

If we solve for the pressure difference in the equation above, we get an expression for the Laplace pressure, Δp . It is dependent on the surface tension, σ , and the radius, R , of the sphere.

$$\Delta p = \frac{2\sigma}{R}$$

As you may be able to infer from our analogy with the balloon, the LaPlace pressure is closely related to how easily deformable a drop is. A balloon that has only been partly filled with air, is very easy to deform. It also has a

small LaPlace pressure because the pressure on the inside is not very high compared to the pressure on the outside. On the other hand, a balloon filled with a lot of air, is very firm and you have to apply more force to deform it. The LaPlace pressure is large because the pressure on the inside is much larger than the pressure on the outside.

This becomes important for emulsions because if an emulsion contains a lot of drops they will pack closely together and push on each other. Imagine that you try to push two balloons together. If they are firm you have to squeeze harder than if they are soft for the same deformation to occur. The same is true for fluid drops (Fig. 8.10). The higher the LaPlace pressure, the more force has to be applied to squeeze them together. If the drops are very closely packed and very firm, you have to apply a considerable amount of force to get them to deform at all. In fact, collectively, the drops will almost behave like a solid. And it turns out this is exactly what happens. With enough drops in it, the emulsion becomes a solid. Imagine a very stiff mayonnaise – it is much more like a solid than a liquid. This is a very interesting effect. Somehow, by mixing two fluids, oil and water, or oil and vinegar in the case of a mayonnaise, the resulting material is a solid.

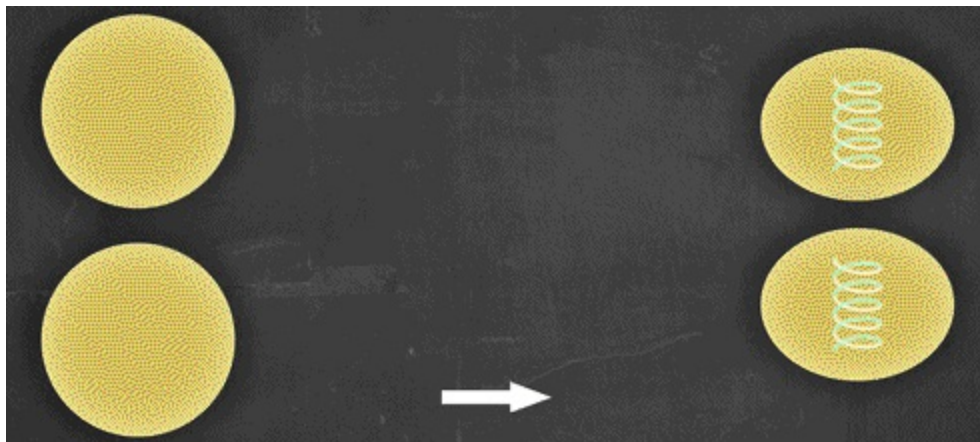


Figure 8.10 It requires energy to deform the droplets in an emulsion.

8.3.2 Volume Fraction

To show you how the density of drops in an emulsion affects the consistency, we looked at two different emulsions under the microscope: a very firm aioli, and a much more fluid mayonnaise. Below is a picture of the aioli (Fig. 8.11). The drops are so small and densely packed that they are hardly visible at the shown magnification.

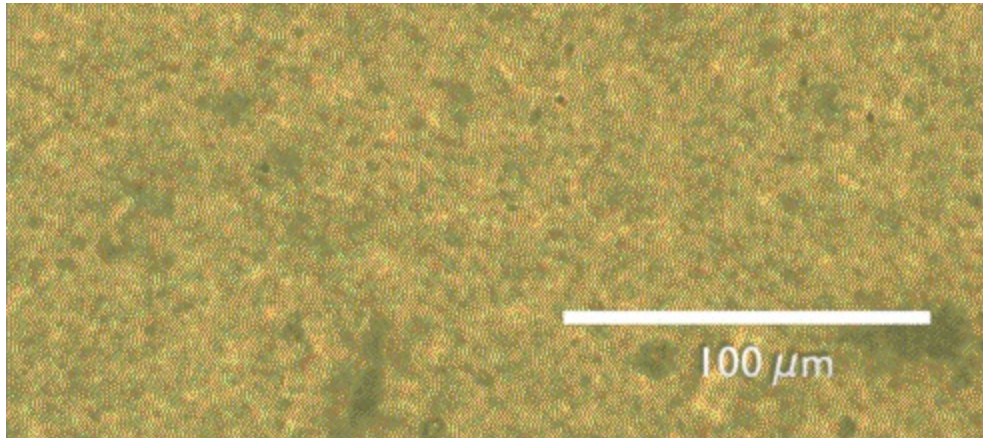


Figure 8.11 Microscope image of aioli. The drops are small and densely packed and can hardly be discerned.

By comparison, the figure below shows a microscope image of mayonnaise, where the drops are much larger and less densely packed (Fig 8.12). Just as expected, the fluid-like consistency of the mayonnaise corresponds to sparsely packed drops, while the solid-like aioli consists of very densely packed drops.

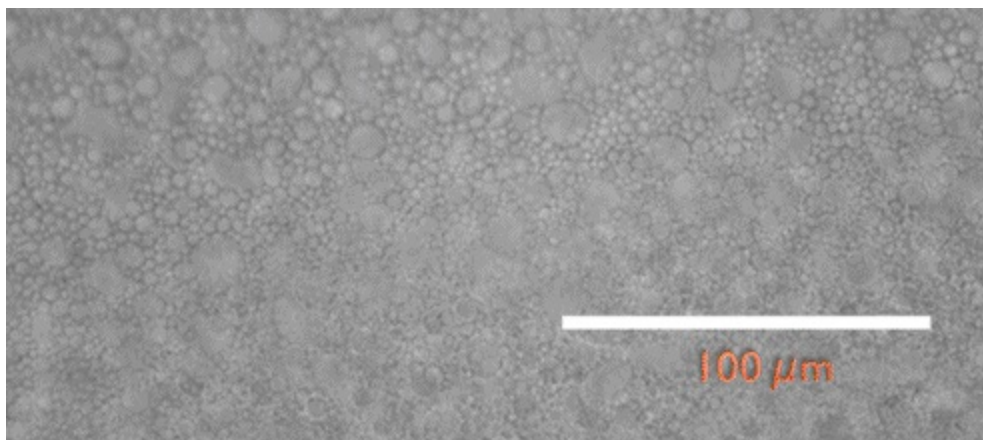


Figure 8.12 Microscope image of mayonnaise. The drops are larger and less densely packed than in the aioli.

How does this happen? When making an emulsion, we increase the concentration of drops, and we decrease the drop size. We are making more

and more drops of a smaller and smaller size. As a result, we are making more and more surface area and thus storing more and more interfacial energy. The energy comes from the energy we add by mixing or stirring. As you increase the number of oil drops in the water, you are essentially adding more and more of the dispersed phase into the continuous phase. In other words, you are increasing the volume fraction of the dispersed phase compared to the continuous phase. So a good way to parameterize the number of drops in an emulsion is by finding the volume fraction. It is simply the volume of the dispersed phase divided by the total volume of the dispersed and continuous phase. So if the drops are many and densely packed, the volume fraction will be large, whereas if the drops are few and far between, the volume fraction will be small (Fig. 8.13).

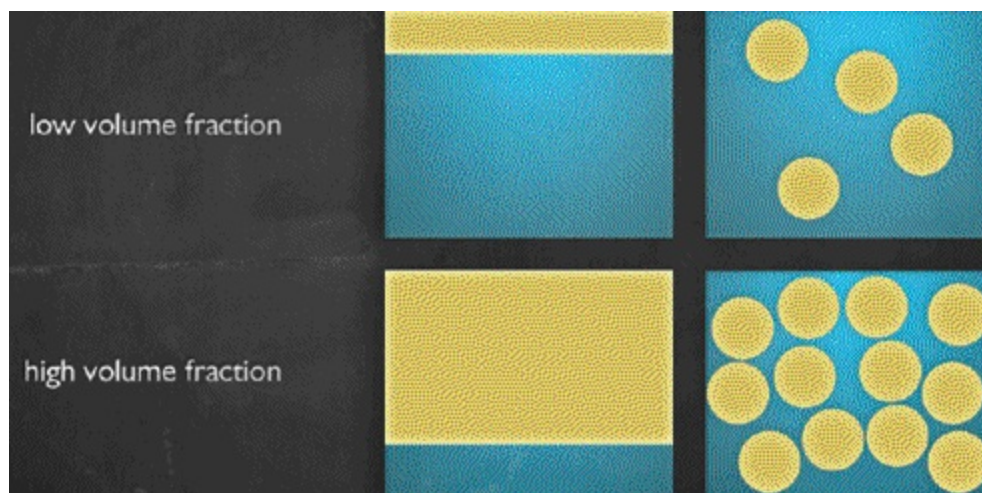


Figure 8.13 The volume fraction of an emulsion is an expression of the percentage of dispersed phase it contains. The higher percentage of dispersed phase, the higher the volume fraction.

When the drops are far apart, they can remain spherical. But as the concentration increases, the drops have to start squeezing together. There is a critical volume fraction where the drops begin to deform one another, which is the volume fraction where the emulsion turns from being a fluid to being a solid. This occurs when the volume of the dispersed phase constitutes about 64% of the total volume. Above that concentration, the drops can no longer coexist as spheres, they have to squeeze on one another (Fig. 8.14). This volume fraction, 64%, may seem like a random number at first, but it is actually not random at all. The reasons behind it will become clear later on in this chapter when we discuss the principles behind how spherical objects pack. For now, let's focus on what happens as the drops in an emulsion squeeze together. Ultimately, the force that

squeezes the drops together comes from the surrounding continuous phase, which, in the case of a direct emulsion, is water. The water is holding the drops together, and it is putting enough force on the drops that they have to deform. As a result, the drops are trying to push apart, but they cannot do this because they are held in place by the water. It is this force, and the resulting deformation, that makes the emulsion into a solid-like material.

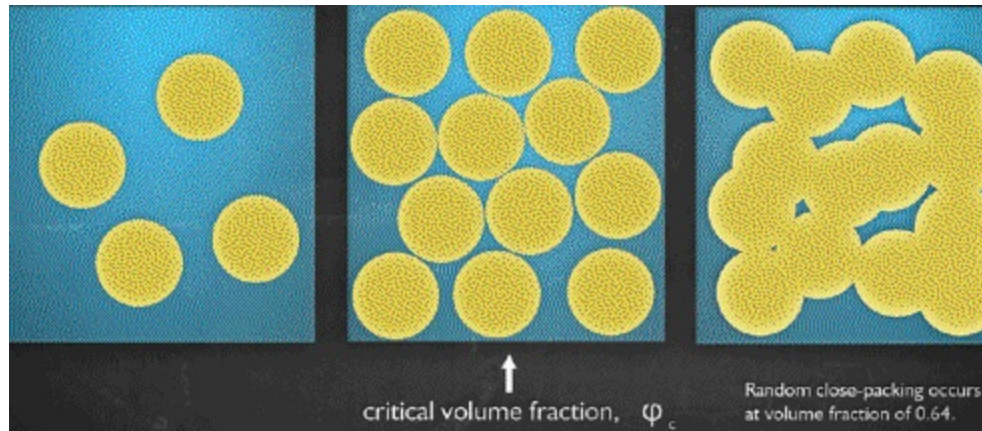


Figure 8.14 When the volume fraction of an emulsion is above the critical volume fraction of 64%, the droplets can no longer pack as spheres and start squeezing into each other. As a result the emulsion takes on a solid-like consistency.

At low concentrations of oil, when the volume fraction is less than 64%, the emulsion will flow just as if it is water. As the volume fraction increases, the resistance to flow gradually increases, until eventually, at 64%, the emulsion can no longer flow at all. It becomes a solid.

8.3.3 Equation of the Week

Once an emulsion becomes a solid, it also acquires a corresponding elasticity. We can calculate what the elasticity is based on what we just learned about the volume fraction. First, we know that the elasticity has to be zero below the critical volume fraction, since a material that flows cannot be elastic. As the volume fraction increases, the elasticity also increases. In fact, it increases linearly with the volume fraction, as shown in Figure 8.15. The slope of the line is set by the LaPlace pressure, which we know depends on the surface tension and the radius of the drop. If the LaPlace pressure is high, it will require a lot of force to deform the drops, so the elastic modulus is high and it is a very stiff emulsion. Conversely, if the LaPlace pressure is low, it is much easier to deform the drops and the emulsion is less stiff and has a low elastic modulus.

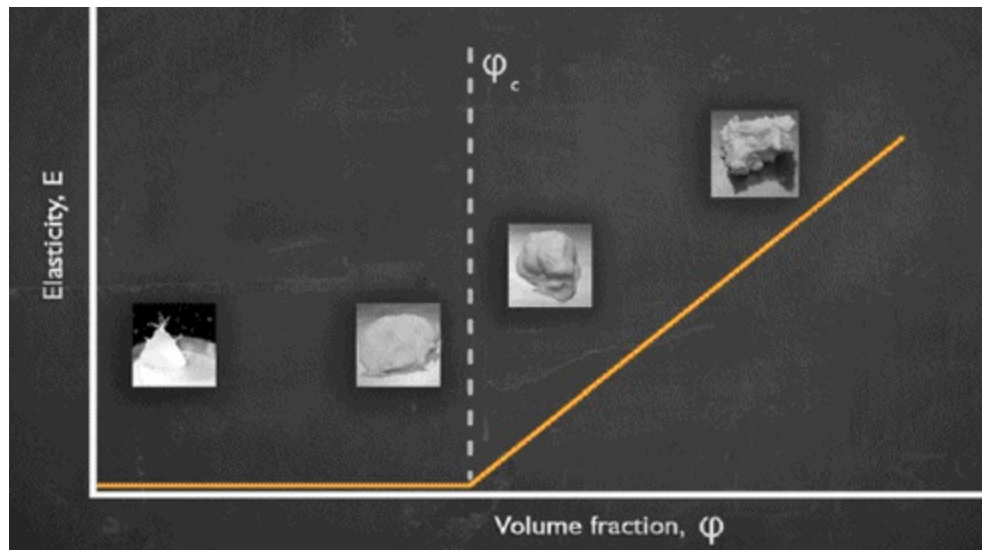


Figure 8.15 Elasticity, E , as a function of volume fraction, ϕ . Emulsions are elastic above the critical volume fraction, ϕ_c .

The scientific principles we just discussed are succinctly expressed in the equation of the week, which describes the relationship between the volume fraction, LaPlace pressure, and elasticity (Table 1). According to the equation, as the volume fraction increases, the elastic modulus of the emulsion will increase, which is consistent with our discussion above. Similarly, as the surface tension increases, the elastic modulus will also increase. Based on this you might think that surfactants decrease the elastic modulus of emulsions, since they decrease the surface tension. But this is actually not the case. Surfactants do the opposite, they increase the

elasticity of emulsions by stabilizing the drops, and the stabilizing effect is large enough to off-set the small increase in surface tension. The equation also predicts an inverse relationship between the radius and the elasticity. We already know that this must be the case since many, many small drops contribute a large overall interface area between oil and water, which can store more energy. So as the drop size decreases, the elastic modulus increases.

EQUATION OF THE WEEK		
$\phi = \frac{V_{dispersed}}{V_{total}}$		
Symbol	Description	Units
ϕ	Volume fraction of dispersed phase	Unitless
$V_{dispersed}$	Volume of dispersed phase	L
V_{total}	Total volume	L

Table 8.1

8.4 Packing

The concept of packing is highly related to the scientific principles underlying emulsions and foams. It describes how non-overlapping objects can be arranged in three-dimensional space, which of course is of great interest if we want to understand how the drops in an emulsion are arranged within the continuous phase.

To help us think about the concept of packing, let's put emulsions aside for a while and instead imagine a bowl filled with bubble gums balls, the spherical candies that usually come in an assortment of different colors. What we are about to discuss applies not only to them, but also to much smaller particles such as sugar and flour. In fact, it applies to any particles, regardless of their size, that would only fill a fraction of the volume they are in. How much of the volume do they fill? Well, this is exactly what we are interested in finding out.

8.4.1 Random Close Packing of Spheres: Bubble Gum Balls

If we wanted to estimate the volume fraction occupied by the bubble gum balls in the bowl, we would first calculate the volume of one sphere, which is $\frac{4}{3}\pi r^3$ and then count and multiply by the number of spheres to get the total volume of all of the spheres. We would then divide this by the volume of the bowl, assuming it is filled all the way to the top. This would be the volume fraction occupied by the spheres.

Bubble gum balls in a bowl pack the way they do because each of the spheres has to support itself by resting against its neighbors. It turns out that for spheres randomly poured into a bowl like this, the volume fraction is about 58% to 60% of the total volume. Or, expressed differently, it has a volume fraction between 0.58 and 0.6. The spheres are very disordered. If we shake the bowl gently, the spheres will actually start to pack more efficiently, and as a result, the volume fraction increases. The spheres will sink slightly in the bowl and occupy a smaller volume, and thus the number of spheres per volume goes up.

It has been determined that the absolute best packing that can be achieved for randomly arranged spheres like these is 64%. This is if there is no order in the structure of the spheres, no predictable relationship between one sphere and the next one. We refer to this as random close packing. This is where the critical volume fraction in the Equation of the Week comes from. Scientists actually don't know how to calculate this number analytically, but every time it is measured and every time a computer simulation is done, the volume fraction turns out to be 64%. This is the case for all spherical objects regardless of size and material. So when we use this number in the Equation of the Week, it is because we know that the drops in an emulsion, even with the absolute best random close packing, cannot exceed 64%.

8.4.2 Hexagonal Packing of Spheres

The only way the volume fraction can increase beyond 64% is if the spheres become ordered. If each layer forms a flat layer that is exactly stacked on top of the next layer, we get what is referred to as hexagonal packing. You may recall the pattern from how oranges are sometimes stacked in stores. This type of packing turns out to be the most efficient packing possible. In fact, the volume fraction increases all the way to 74%. Moreover, because of its predictable nature, this volume fraction can be calculated exactly, as opposed to the one resulting from random close packing.

8.4.3. Packing of other Shapes: M&M's, Chocolate Chips and Flour

So far, we have discussed bubble gum balls, which are perfectly spherical in shape. But what happens if the particles are not spherical? After all, this is the case for many things, M&M candies, for example, are not spherical, but ellipsoidal in shape. How do they pack? Interestingly, although scientists in general understand packing fairly well, it is only recently that the volume fraction of M&Ms has been measured. It turns out that ellipsoidal particles like M&Ms pack much more efficiently than spheres. Their random close packing has a volume fraction of 74%, quite a bit higher than the 64% of spheres. Surprisingly, this is not only the case when comparing spheres to M&M's. Spheres are actually anomalous in the sense that they pack the least densely of any shape.

What about other shapes? Staying in the domain of candies, what about the much less uniformly shaped chocolate chips we used for the cookies in Chapter 1? If you have some chocolate chips in a bowl you will see that they pack to a much higher volume fraction than spheres. But exactly what the volume fraction is, is much harder to predict. It would have to be measured.

So far, we have been talking about candies that have exactly the same size. But often, particles come in many different sizes. If you want to study this, you can mix chocolate chips of two different sizes, a large and a small size, together and see what happens. You will probably find that the small chocolate chips are able to fit in some of the spaces between the large chocolate chips. As a result the volume fraction is relatively high. This tends generally to be true: particles of different sizes can pack more efficiently and thus have a higher volume fraction. This is important for emulsions because, as you may have noticed in the microscope images above, the drops in an emulsion are often different sizes. For the most part we can ignore this in our calculations, but it is an important feature of emulsions that affects their behavior.

Generally speaking, different shapes pack to different volume fractions. In addition, it is almost always the case that gentle shaking gets objects or particles to pack more efficiently. This happens because even though objects always have to be supported by their neighbors, they can usually

find new pockets and configurations that are more favorable and this increases the volume fraction.

8.5 Failure of Emulsions

An emulsion requires there to be drops of one fluid in a second fluid. However, since the two fluids do not naturally mix, they will eventually separate into two separate layers. The emulsion will fail. Some emulsions fail more easily than others. A small change in temperature can be enough to make a béarnaise or hollandaise sauce almost instantly go from being a creamy thick sauce, to a thin soup of two separate liquids. The precarious nature of emulsions is something even the best of chefs are acutely aware of, so let's look at the science behind what it means to have an emulsion fail.

8.5.1 Creaming

In order for an emulsion to fail, the drops of the dispersed fluid must somehow be lost. There are several ways that this can happen. The first way is due to the fact that oil and water have different densities. Oil is less dense than water, and over time the oil drops will float to the surface. The oil will cream (Video 8.2). This will particularly be the case if the volume fraction is relatively low. As the oil drops collect close to the surface, they pack more closely and the volume fraction increases. The top part of the emulsion will be more solid-like. This is the beginning of one failure mechanism.

Sorry, it appears your system either does not support video playback or cannot play the MP4 format provided. However, you can view the video by clicking on this link:

[movie_2_08_emulsions_slide_53.mp4](#)

Video 8.2 An emulsion can fail by any combination of a number of different mechanisms: Ostwald ripening, coalescence, creaming, and sedimentation.

8.5.2 Coalescence

For the emulsion to fully fail though, the drops eventually have to break and recombine, ultimately forming two separate layers, and there are several ways that this can occur. The most obvious way is through coalescence, which is where two drops come close to one another and join together to form a larger drop (Video 8.3). For an emulsion to fail, you have to lose the drops, which means the drops have to become larger.

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[movie_3_08_emulsions_slide_55.mp4](#)

Video 8.3 Coalescence involves two droplets combining to form one droplet. The resulting droplet will be larger and have a lower surface energy than each of the original droplets.

8.5.3 Ostwald Ripening

A second way that drops can grow is through a mechanism called Ostwald ripening (Video 8.4). This is a very pervasive process in emulsions, and it is almost impossible to eliminate it completely. Fortunately, it is a relatively slow process, so unless an emulsion is stored for a very long time, it does not play a significant role. Ostwald ripening is the transfer of fluid from one drop to another drop. Recall that drops are at a higher internal pressure than the outside, and that the internal pressure, the Laplace pressure, increases as the drops get smaller. Because of this, there is a driving force to transfer the fluid from the small drops into the large drops.

The transfer of liquid between two drops occurs through the continuous phase, which is possible either because the dispersed phase is slightly soluble in the continuous phase, or, alternatively, it happens via the micelles. The micelles have oil-like interiors and can swell slightly by absorbing more oil, which can then be transferred across the continuous phase from smaller drops to larger drops. As a result the small drops get smaller, and the large drops get larger. Eventually, the small drops disappear, and the large drops become very large, and this leads to failure of the emulsion.

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[movie_4_08_emulsions_slide_56.mp4](#)

Video 8.4 Ostwald ripening involves the transfer of fluid from one droplet to another. As the droplets decrease in size, the Laplace pressure increases, and this speeds up the transfer of liquid from smaller droplets to larger droplets.

Coalescence can be avoided with a proper choice of surfactant. To prevent Ostwald ripening, though, any transport of fluid from one drop to a second drop has to be avoided. This can partly be achieved by controlling the micelles and by using a continuous phase that does not allow easy dissolution of the dispersed phase. However, since Ostwald ripening takes a longer time, it is typically not the origin of the failure of emulsions in foods.

8.5.4 Phase Inversion

When Nandu Jubany made aioli and hollandaise sauce in one of the lectures for this course, he worried about a different type of failure of the emulsion. He referred to it as breaking the emulsion. The reason this is so prevalent, is that as the emulsion is close to completion, the volume fraction of the dispersed phase is very, very large. Sometimes there is a much larger volume of dispersed phase than there is continuous phase. This is what gives the emulsion the thicker texture, and eventually, in the case of an aioli or a mayonnaise, makes it into a solid. But this large volume fraction is very difficult to maintain, and the emulsion easily phase inverts at which the dispersed phase, which is the larger fraction, becomes continuous, so that there are small drops of the continuous phase in the dispersed phase. This is referred to as breaking the emulsion.

As a way to quickly correct an emulsion that is about to phase invert, Chef Nandu always keeps excess water nearby when making his emulsions. In fact, when making aioli with a mortar and pestle, he even listens to it as a way of catching early signs that it is about to break. At the slightest hint that this is about to happen, he adds a tiny amount of water, which is the continuous phase, to avoid the breakage of the emulsion.

8.6 Foams

8.6.1 Making Foams

Foams are similar to emulsions, except instead of having drops of one fluid inside a second fluid, they have bubbles of air or gas inside a fluid (Fig. 8.16). The head of a beer or a cappuccino are examples of foams – they consist of bubbles of gas dispersed in the liquid from the beer, and bubbles of air dispersed in milk. Other examples are whipped cream, soufflé, chocolate mousse, marshmallows, and meringues. Foams are also a common element in modernist cuisine. The menu at ElBulli used to feature foams ranging from savory potato and basil foams, to sweet coconut foams as part of dessert. As part of his lectures in this course, Chef Joan Roca made foams of Comte cheese and Chablis, and Nandu Jubany, chef and owner of restaurant Can Jubany in Vic, Spain, makes a delicious foam using sea water, which he serves on top of an oyster on a shell.

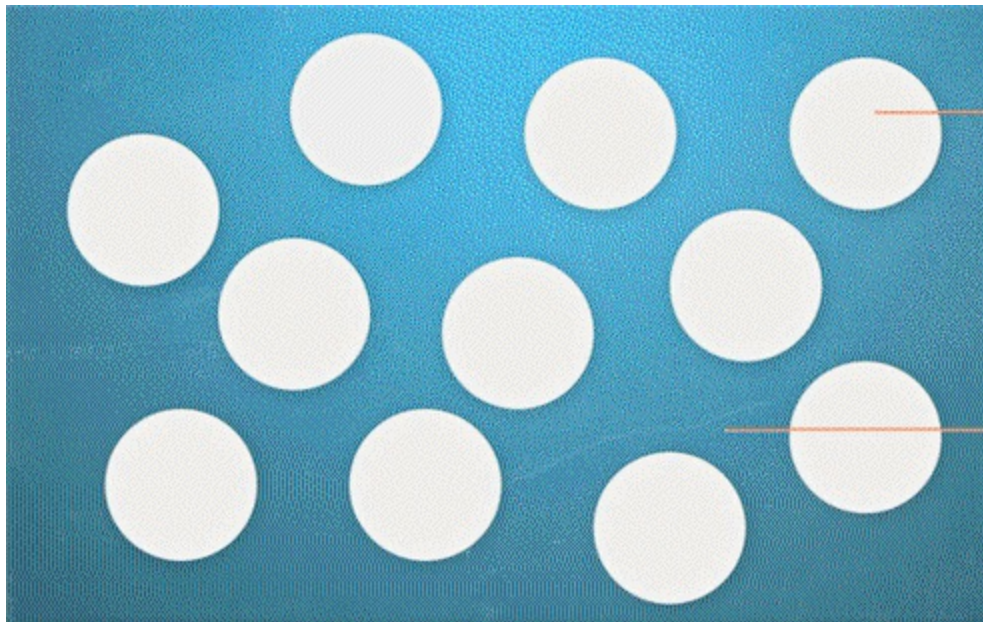


Figure 8.16 Foams are similar to emulsions, but differ in that the dispersed phase consists of air rather than a liquid.

The amazing thing about foams is that they are made by mixing a fluid and a gas, two materials which obviously have very different properties. A fluid collects at the bottom of a bowl, whereas a gas wants to expand everywhere. By mixing them together, the gas is captured as bubbles inside the liquid, and the result is a material that is a solid. In this regard foams

are just like emulsions, and they can be understood by applying the same scientific principles. For example, just like emulsions, the volume fraction of the dispersed phase determines if the foam will have the consistency of a liquid or a solid. The higher the volume fraction, the more solid-like is the foam. Whipped cream, for example, can turn into a very thick elastic solid if enough air is incorporated by heavy whipping.

Air can be incorporated into foams using various methods, the most common being simple whisking by hand or with a mixer. Another way that is common in restaurants is the use of a whipped cream maker. This tends to be how coffee shops add whipped cream on top of coffee or hot chocolate (Fig. 8.17).



Figure 8.17 There are several methods for incorporating air in the production of a foam. Examples include kitchen aids, which incorporate air by consistent whipping, and whipped cream makers, which use chargers of high-pressure gas such as nitrous oxide.

Whipped cream makers work by inserting high pressure gas, typically nitrous oxide because it is soluble in milk, into a can containing the liquid intended for foaming. The gas is under such high pressure that it is actually a liquid, and thus the two liquids mix into what is essentially an emulsion, where the compressed gas is the dispersed phase. When the emulsion is sprayed out of the can the pressure decreases and the liquid droplets expand into bubbles. The result is a very light and delicate foam. Figure 8.18 shows the consistency of whipped cream made with a whipped cream maker compared to one made with a mixer.

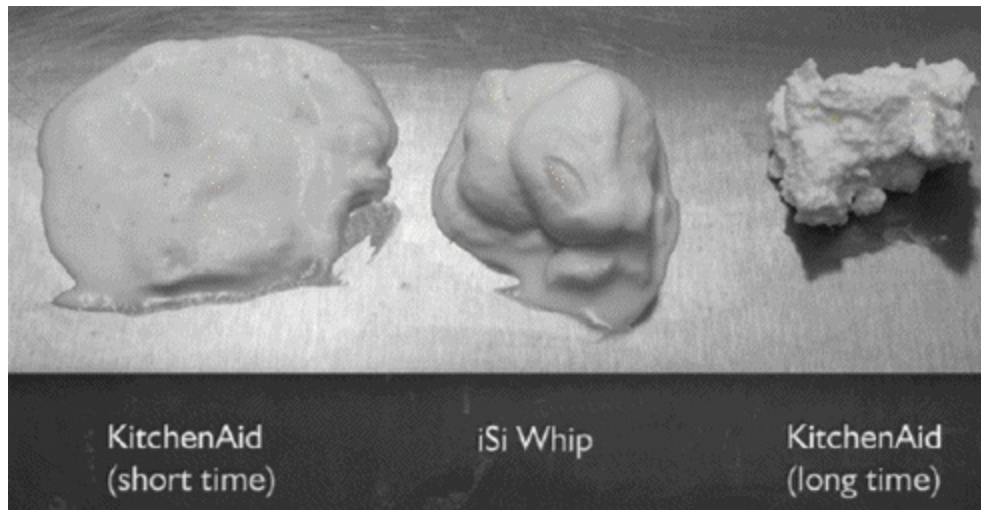


Figure 8.18 Depending on the time and method used, the texture of foams vary.

The same two foams as seen under a microscope are shown below. The air bubbles in the whipped cream made with the whipped cream maker, or iSi Whip as it is also called, are much sparser than the air bubbles made with the KitchenAid mixer (Fig. 8.19).

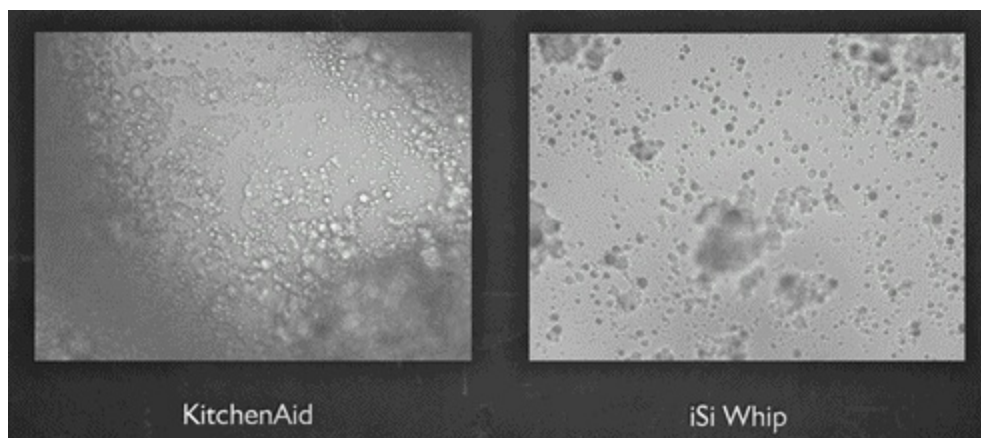


Figure 8.19 Microscope image of whipped cream made with a kitchen aid (left) and and an iSiWhip (right).

8.6.2 Failure and Stabilization of Foams

The bubbles in foams get destabilized in some of the same ways that the drops in emulsions do. Coalescence, Ostwald ripening, and creaming are all contributing to foam failure. However, in the case of foams, the creaming that occurs as a result of drainage is much more severe because of the greater density difference between the air and liquid in a foam compared the density difference between two liquids in an emulsion (Fig. 8.20). So the bubbles in a foam tend to cream, rise to the top, while the liquid is pulled down by gravity, and thus contribute more significantly to the destabilization of foams.

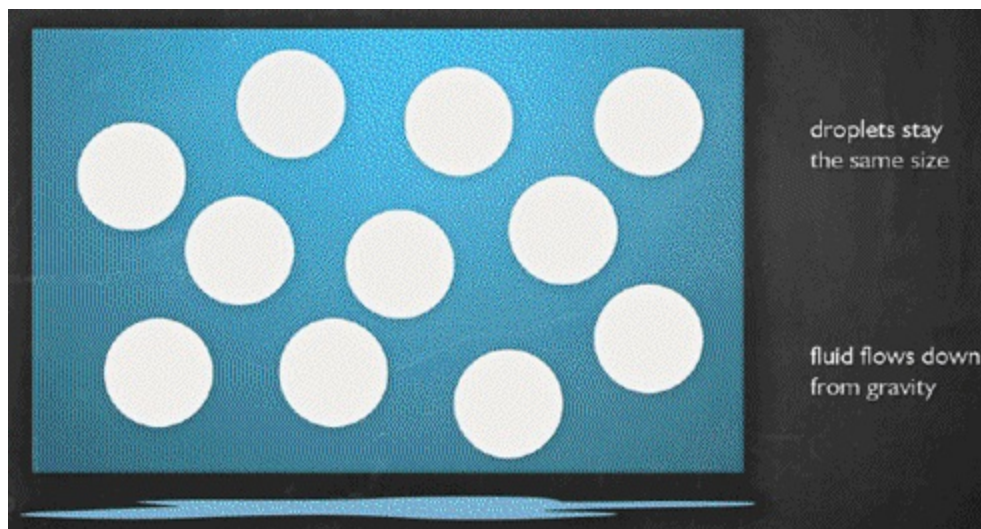


Figure 8.20 Foams tend to fail by drainage: air bubbles float to the top and the liquid is pulled down by gravity.

Just as was the case with emulsions, foams can be stabilized with a surfactant. The surfactant molecules sit at the interface between the dispersed and the continuous phase, and prevent the bubbles from coalescing. Milk and beer contain a lot of natural surfactants, which is the reason they foam so well. Similarly, some culinary vegetable foams can be made without additives because of naturally occurring surfactant. For example, Nandu Jubany makes a foam from the juice of carrots without having to add any surfactant, while for his oyster foam, the addition of a small amount of lecithin is necessary for stability. There is a number of different surfactants that can be utilized for the purposes of foam stabilization, all having in common that they sit at the interface and stabilize the bubbles (Fig. 8.21).

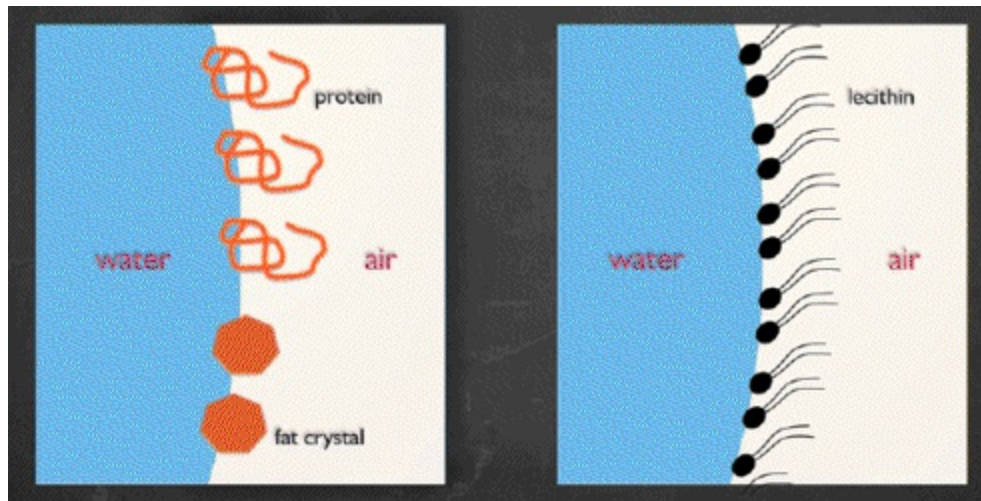


Figure 8.21 Foams, just like emulsions, can be stabilized with surfactants. Proteins, starches, and fats can act as surfactants. Lecithin is an example of a surfactant that consists of molecules with hydrophobic fatty acid tails and hydrophilic head groups.

There are other ways of stabilizing foams in addition to using surfactant. One way is to make the continuous phase elastic by turning it into a gel (Fig. 8.22). A mousse is a foam where the continuous phase has been gelled. This can be done by adding gelling agent to the liquid that is about to get turned into a foam. Another option is to turn the continuous phase into a solid either by freezing, or by incorporating fat that solidifies at slightly lower temperatures. With a solid continuous phase, the air bubbles are prevented from creaming, and the foam does not break as easily.

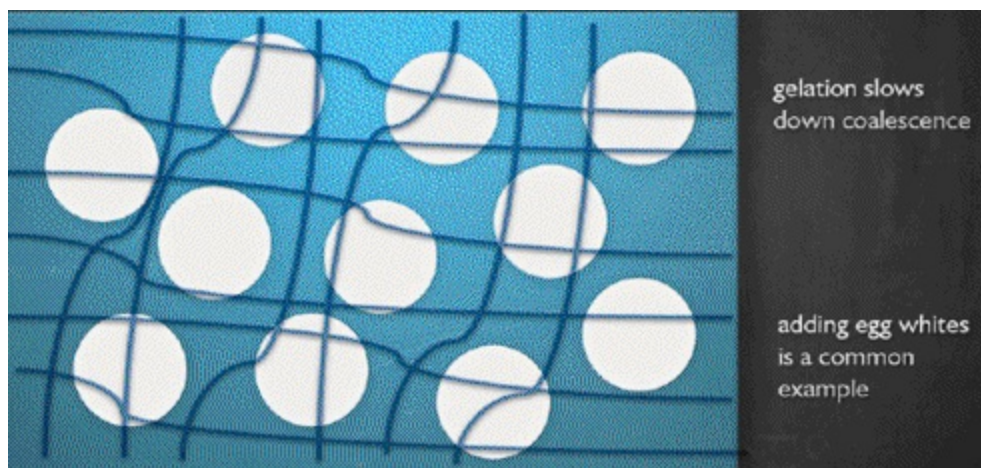


Figure 8.22 A foam can be stabilized by addition of a gelling agent. This causes the continuous phase to gel, which slows down coalescence.

Just like an emulsion, a foam can become elastic, and this happens when the bubbles pack at such a high density that they must deform (Fig. 8.23). The equation for the foam becoming elastic is also exactly the same as that for the emulsion. It depends on the surface tension, the inverse of the

radius, and the volume fraction, i.e. the difference of the volume fraction as compared to the critical volume fraction. As you make the bubbles smaller, the LaPlace pressure goes up, which in turn means that the elastic modulus of the foam goes up.

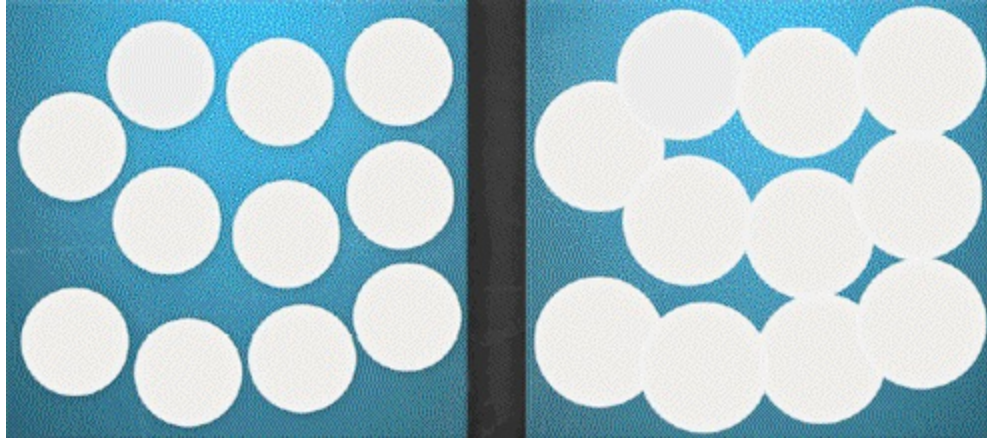


Figure 8.23 A foam, just like an emulsion, can become elastic if enough air is incorporated. A wet foam has a low volume fraction, and a dry foam has a high volume fraction of air.

8.7 Colloids

There is one additional type of dispersion that we have not yet discussed. We have talked about foams, which are air bubbles in a fluid. We have talked about emulsions, which are fluid drops in a fluid. A third type of dispersion is made of solid particles in a fluid. This is called a colloid, or a colloidal suspension (Fig. 8.24). Colloids are similar to emulsions and foams, but the drops or bubbles are replaced with solid particles.

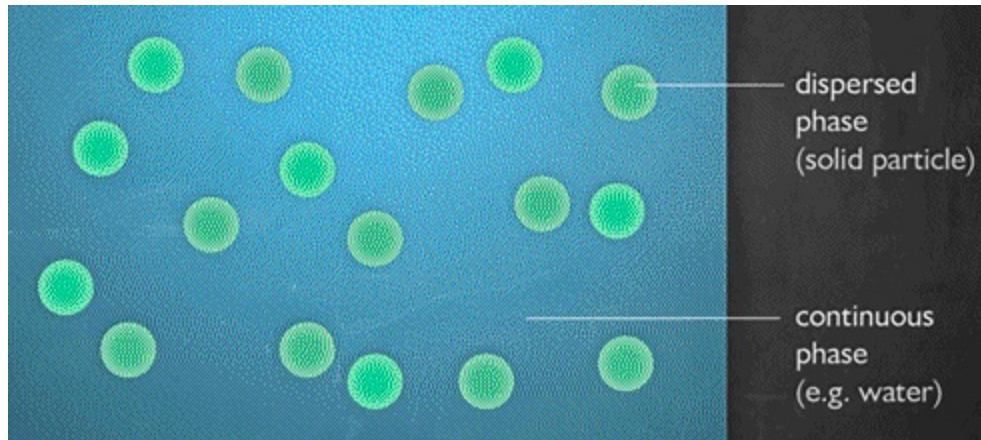


Figure 8.24 In a colloidal suspension, the dispersed phase consists of solid particles.

Colloidal suspensions are also commonly occurring in food. One of Dave Weitz's favorite examples is coffee (Fig. 8.25). Coffee consists of a continuous phase, which is water, with small coffee particles, or colloidal particles, that are suspended in the coffee and give it its black color. Purees are also colloids. A puree of potatoes, for example, is made of small particles of potato dispersed in a fluid of water and milk. The particles can move and flow within the fluid, so even though the particles are solid, the coffee or puree as a whole acts like a fluid because it is predominantly made of continuous phase.



Figure 8.25 Coffee and a puree made of potatoes are both examples of colloidal suspensions.

Interestingly, colloidal particles can also act as a surfactant for emulsions and foams. The particles can sit at the interface between two fluids or between a gas and a fluid, just like a surfactant molecule would, and stabilize the interface (Fig. 8.26). Their role, just like the role of surfactants, is to keep the two interfaces apart and prevent the drops from coalescing. When an emulsion is stabilized by colloidal particles, it is referred to as a Pickering emulsion, after the British chemist Spencer Pickering, who was the first person to recognize that colloidal particles can act as surfactants.

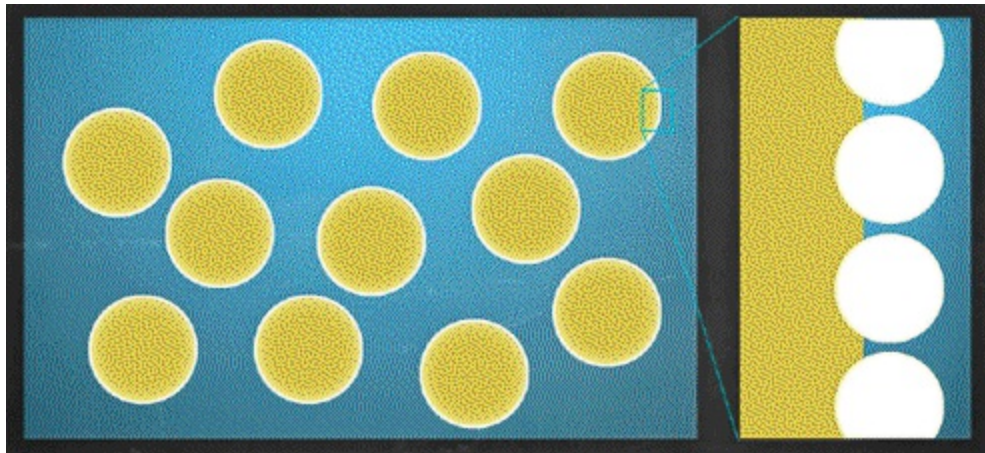


Figure 8.26 Colloidal particles can act as surfactants by existing at the interface of the to liquids in an emulsion or between the air and the liquid in a foam.

8.8 Ice Cream

8.8.1 A Foam, Emulsion, and Dispersion

An excellent example that encompasses all the types of dispersions that we discussed in this chapter is ice cream. Ice cream is a foam, an emulsion, and a colloidal suspension (Fig. 8.27).



Figure 8.27 Ice cream is an example of all three types of dispersions we have talked about in this chapter. It is an emulsion, a foam, and a colloidal suspension.

Ice cream is a foam, because it contains lots of air bubbles. It is an emulsion, because it is made of milk, and milk itself is an emulsion of fat drops in water. It is a colloidal suspension, because some of the fat drops are solid-like objects, and they sit at the interface of the air bubbles and stabilize them (Fig. 8.28).

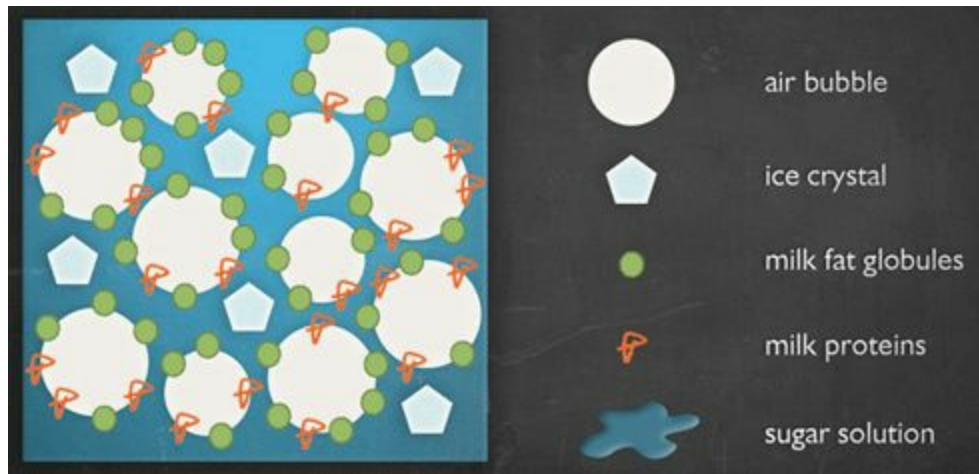


Figure 8.28 Cartoon of the microscopic structure of ice cream.

The first step of making ice cream, is to mix all of the ingredients together. This step not only incorporates air to create the foam, but it also brings the stabilizing fat globules to the interface of the air bubbles. Next, the ice cream mixture is frozen, at which point the continuous phase is solidified, and this has a further stabilizing effect. Since the continuous phase is made of milk, it becomes a solid emulsion of fat drops in water.

The stability of ice cream arises both because the interface is stabilized by colloidal particles, but also because the continuous phase is frozen. Since the foam itself is a solid, the air bubbles cannot move around and hence cannot as easily come close to each other and coalesce. There is also no drainage of the continuous phase, which would also cause the foam to fail.

8.8.2 Microscopic Structure of Ice Cream

We can study the structure of ice cream with an electron microscope. Under most microscopes ice cream would quickly melt, but this type of microscope allows for us to look at it when frozen so the structure is clearly visible.

Figure 8.29 shows a cross-section of ice cream with the length of the bar under the image corresponding to 100 μm . The air bubbles are clearly visible as round structures, and looking more closely we can see that they have a dotted surface. These are the colloidal fat particles that are stabilizing the interface of the bubbles. The emulsion itself is not visible other than as the solid continuous phase.

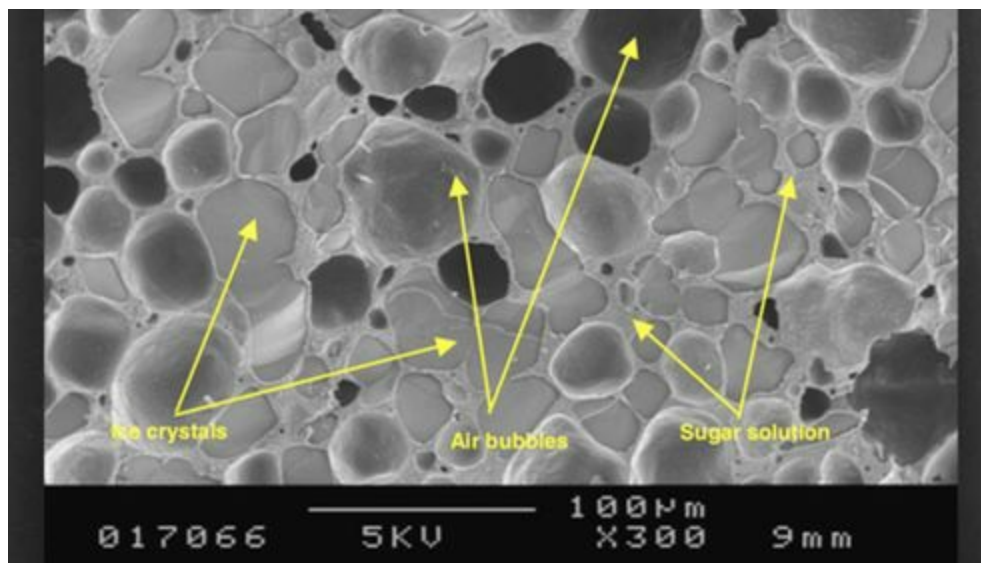


Figure 8.29 Electron microscope image of ice cream. Source: C Clarke, Physics of Ice Cream, Physics Educ. 2003.

CHAPTER 9

Baking

TABLE OF CONTENTS: 9

9.1 Introduction to Baking

[9.1.1 Summary of the Main Scientific Ideas that Underlie Baking](#)

9.2 Elasticity and Baking

[9.2.1 The Ingredients of Baking: Bakery Phase Diagrams](#)

9.3 Yellow Birthday Cake and Baking Soda

[9.3.1 Measuring the Amount of Gas Produced](#)

[9.3.2 Calculating the Amount of Gas Produced](#)

9.4 The Role of Acids in Baking

9.5 Baking Networks Glutenin

[9.5.1 Finding the Cross-link Distance of Glutenin](#)

[9.5.2 Comparison of Cross-link Distances in Different Baked Goods](#)

9.6 Modulating Glutenin Networks

[9.6.1 Ingredients Influencing the Interaction Energy of Cross-links](#)

9.7 Baking Networks: Eggs and Starch

[9.7.1 Calculating the Cross-link Distances of Ovalbumin](#)

[9.7.2 Elasticity Contributed by Starch](#)

9.8 Browning Reactions

[9.8.1 Caramellization](#)

[9.8.2 Maillard Reactions](#)

[9.8.3 Increasing Maillard Reactions](#)

9.9 Gas Production Yeast

[9.9.1 Estimating the Amount of Gas Produced](#)

9.10 Making Bubbles 1

[9.10.1 A General Introduction](#)

[9.11 Making Bubbles 2](#)

[9.11.1 Bubbles Formed by Carbon Dioxide](#)

[9.11.2 The Solubility of Carbon Dioxide in Batter](#)

[9.11.3 Finding the Velocity of Bubble Growth](#)

[9.11.4 Complexities of Bubble Growth](#)

CHAPTER 9

9.1 Introduction to Baking

Baking has arisen on several occasions in this course already. In Chapter 1 we introduced the Nestle Toll House chocolate chip cookie recipe and discussed the number of molecules there were of the different ingredients. In Chapter 6 we learned about heat transfer in the context of molten chocolate cake. But so far we have not been able to go into the science of baking in much detail. The reason is that it involves many, in fact, if not most, of the ideas that we have discussed up until this point. It involves elasticity, viscosity, emulsions, heat transfer, and solubility, to name just a few. This chapter will, on the one hand, be a review of the concepts that we have discussed up until this point. On the other hand, it will introduce how these concepts apply to baking.

Before we begin, we need to make one important point. We are not professional bakers. We are scientists. Our intent in this chapter is not to go through every method and technique required to make a baked good delicious. Instead, we are going to expose the basic scientific ideas that underlie baking, and by doing so we will hopefully also help you make sense of different baking recipes.

9.1.1 Summary of the Main Scientific Ideas that Underlie Baking

Before going into the concepts in detail, let's briefly look at how the physical ideas we have discussed so far apply to baking. Let's start with elasticity. In Chapter 4 we briefly discussed the science of strudel, which is made from a dough whose unusually stretchy properties are an integral part of the baking process. The elasticity of strudel dough, and any baked good for that matter, is given by three main factors. The first and second factors are the elastic networks of gluten and egg proteins respectively. Baked goods tend to involve both flour, which provides the glutenin, and eggs, which provide ovalbumin and other proteins that contribute to the gelation of an egg as it cooks. The third factor that contributes to elasticity is given by starches and sugars. Both of them increase the viscosity just by being present in the liquid. In addition, the starch granules will swell when heated, and if they swell enough they will end up contributing to an elastic modulus. The final elasticity of a baked good involves the interplay of all three of these factors in whatever configuration results from the specific baking protocol.

A second major idea that underlies baking is viscosity. This may not be obvious at first because, after all, most finished baked goods are solids, not liquids. But baked goods also have viscous properties. Without it, breads would not rise and cakes would not expand. Any time something expands and rises it involves the flowing of molecules by each other. So the viscous properties of batters are absolutely critical for their success.

A third scientific idea that is important in baking is emulsions and foams. Cakes themselves are emulsions and foams. To see this you just have to cut open a cake and look at the structure. You will see lots of little bubbles that are the result of gas expansions that occur during baking. Similar to the emulsions and foams we talked about in Chapter 8, the bubbles in batters and doughs will pack together and when the volume fraction reaches some critical point, they will start to squish into each other. That same process occurs during baking.

Yet another scientific idea is heat transfer. In this course, the classic example of this concept is molten chocolate cake, in which we study the diffusion of heat into a cake by measuring the thickness of the crumb during

baking. The heat transfer into baked goods do obey the laws of diffusion, but there is an additional complication, which is that baked goods rise. Because of this, heat not only moves by undergoing random walks, but also because of the rising itself. The rising changes depending on circumstances, and hence the law that governs heat transfer in a baked good is more complicated than what we discussed before.

Finally, a last set of scientific ideas that are important in baking involve chemical reactions. These include the reactions causing gases, which allow baked goods to rise. They also involve Maillard and caramelization reactions that give many baked goods their flavorful, golden crusts. In this category is also the general idea of solubility. After all, baking often involves dissolving ingredients of various kinds in some liquid batter, often made of water or milk. This is important for the baking process overall, and hence the ideas of solubility and the temperature dependence of solubility play an important role.

With this summary in mind, let's explore the details of how these different physical processes interplay with each other to make delicious cookies, cakes, and breads.

9.2 Elasticity and Baking

The elasticity in baked goods comes from two main components: protein networks and starches. If you cut open a baked good you may first notice that the interior is filled with air bubbles. The air bubbles, in principle, also contribute to elasticity in the way that we described in the chapter on emulsions. But around the air bubbles are layers of cake material, which contains proteins and starches, and this tends to be the dominant feature of the elasticity of baked goods.

The elasticity of baked goods is much more complicated than the elasticity we learned about in the context of gels. Gels involve straightforward pictures of cross-linked polymers where the elasticity is given by the equation $E=U/l^3$, and the only variables of interest are the cross-link distance and the interaction energy. Baked goods, on the other hand, involve many factors that are acting in parallel to create the elasticity. The starch granules and the networks from the glutenin and the eggs act together to create the overall elasticity and they are organized in some fashion which is very hard to know in detail. Their organization will depend on the cooking protocol, as well as any other ingredients that affect the fat, pH, or salt levels. It is very complicated, and there is no chance that we will be able to cover it in great detail, mainly because it just isn't very well understood.

Instead we are going to do a simple exercise that effectively illustrates what is going on. We will consider the batters for a variety of different baked goods, and by estimating the number of each type of molecule that contributes to elasticity, and then seeing how far apart the molecules are, we will create a mental picture of what is going on. This way, we will try to get a sense for the conditions under which one type of network is forming in favor of another, i.e. in which types of baked goods are either eggs, glutenin, or starch the main contributor of elasticity, and by how much.

9.2.1 The Ingredients of Baking: Bakery Phase Diagrams

In order to delve into this we need to know what the basic compositions of different types of baked goods are. You could find this by looking up specific recipes in a cookbook, or by using some rule of thumb. For example, it is commonly said that bread typically contains about 60% flour. However, different recipes, even when focusing on a particular type such as cookies or bread, are highly variable in the amounts of ingredients they contain. So in order to get actual numbers, we decided to study the ingredients of different recipes for baked goods more systematically. With the help of two computer science students, Elaine Angelino and Diana Cai, we collected data on as many recipes available online as possible and created a way to visualize the relative ratios of the ingredients. To explain, here is a simple example using bread.

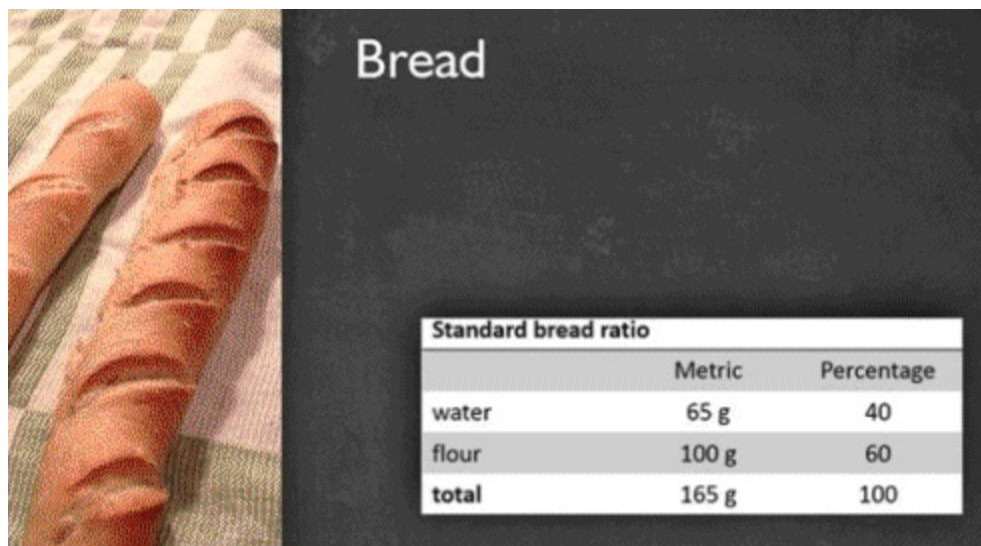


Figure 9.1 A typical recipe for bread contains about 40% water and 60% flour.

A typical recipe for bread contains 60% flour and 40% water (9.1). If we make a diagram with water content on the y-axis and flour content on the x-axis, we can represent this particular recipe by a dot (Fig. 9.2). A different bread recipe, with different amounts of flour and water, would be represented by different dot.

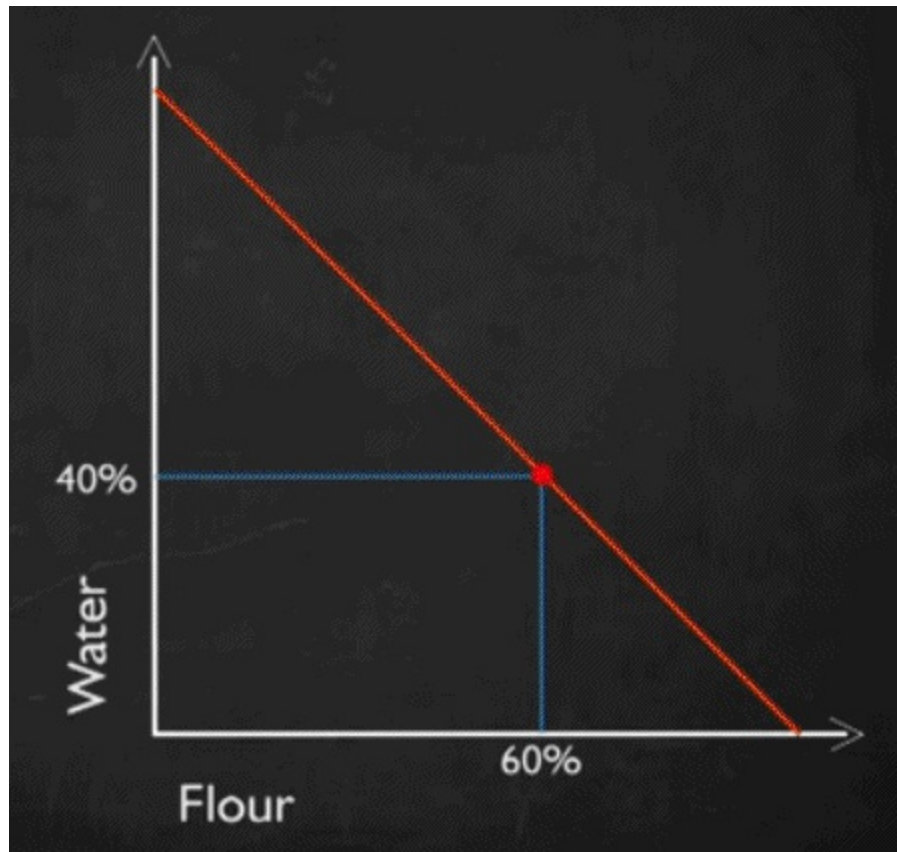


Figure 9.2 A two-dimensional recipe plot with water on the y-axis and flour on the x-axis. The bread recipe in Figure 9.1 is represented by a dot corresponding to 40% water and 60% flour. The red line indicates water and flour ratios that add up to 100%.

The same method can be used for more complex recipes, such as this recipe for baker's best brownies (Fig. 9.3).

Best brownie recipe			
	English	Metric	Percentage
butter	½ cup	115 g	24
sugar	1 cup	200 g	41
egg	2	70 g	14
vanilla	1 t	5 ml	1
cocoa powder	½ cup	30 g	6
all-purpose flour	½ cup	60 g	12
salt	¼ t	2 g	0.4
baking powder	¼ t	1 g	0.2
Total	27 oz.	754 g	100

Figure 9.3 A recipe for Best Brownies with ingredients given in English and Metric units, as well as by

percentage.

Brownie recipes tend to have two main characteristics. They tend not to contain any water. And they tend to have much more sugar than flour. The amount of sugar in this recipe is about 41% of the total ingredients, and the amount of flour is about 12%. Again, we can represent this on a plot with sugar on the y-axis and flour on the x-axis (Fig. 9.4). In what follows, we will refer to this type of diagram where the percentage of one ingredient is on one axis, and the percentage of the other ingredient is on the other axis, as a bakery phase diagram.

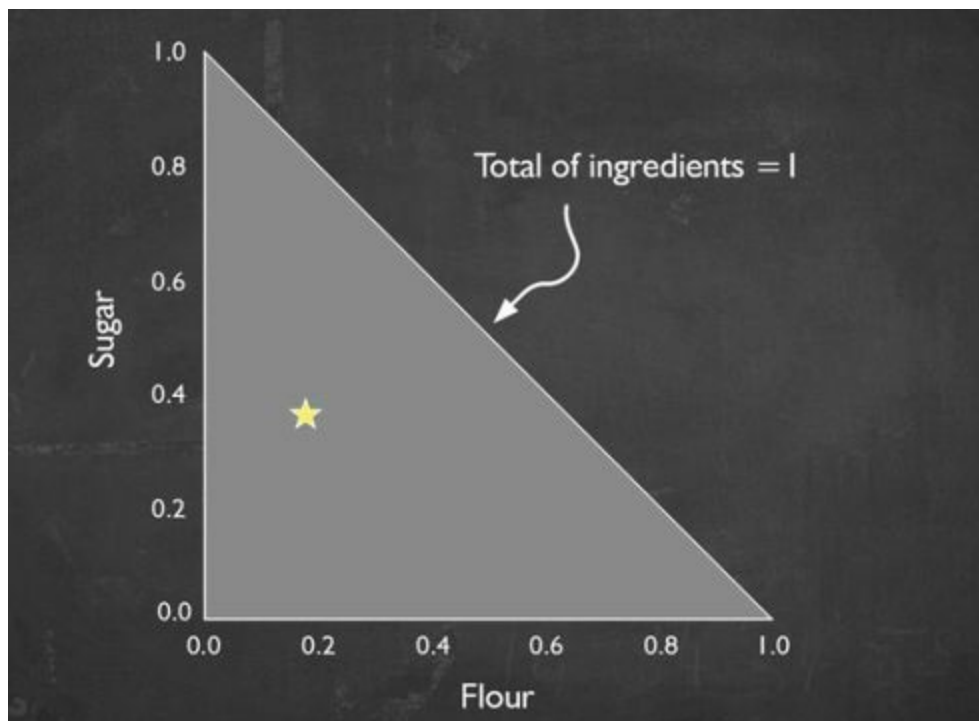


Figure 9.4 A recipe plot with sugar on the y-axis and flour on the x-axis. The Best Brownie recipe is indicated with a yellow star.

You probably know from experience that there will be some variation in the amounts of sugar and flour that different brownie recipes contain. Some will have 40% sugar, some only 35%. If we keep adding dots for other recipes to this phase diagram we will eventually get a sense for the region within this plot that represents brownie recipes. We know that it will occur in an area of the plot where there is more sugar than flour, because this is one of the signature traits of brownie recipes. But how do these data look, and how is that region different from that of cookie recipes or pancake recipes?

To get as complete a data set as possible, we downloaded as many recipes as we could from the web by scraping off recipes from webpages. We then

arranged the data in an Excel spreadsheet, where every row contains a recipe and every column has the ingredients in that recipe (Fig. 9.5).

	A	B	C	D	E	F	G	H	I	J	K	L
	names	applesauce	baking_powder	baking_soda	beer	butter	buttermilk	cake_mix	chocolate_chips	cinnamon	cocoa	cream
1	Absolutely Best Brownies	0	0	0	0	4	0	0	0	0	2.664	
2	Almond Coconut Brownies	0	0	0	0	12	0	0	0	0	0	
3	Amazingly Delicious Whole Grain Brownies	2	0.042	0	0	4	2	0	4	0	2.664	
4	Applesauce Brownies I	26	0	0.267	0	0	0	0	8	0.267	1	
5	Applesauce Brownies II	4	0.083	0.042	0	0	0	0	0	0	0	
6	Banana Nut Brownies	0	0.167	0	0	4	0	0	0	0	1.5	
7	Best Brownies	0	0.042	0	0	4	0	0	0	0	2.664	
8	Best Brownies Ever	0	0	0	0	0	0	0	0	0	10	
9	Better Brownies	0	0.167	0	0	0	0	0	0	0	6	
10	Better than Grandma's Brownies	0	0	0	0	6	0	0	0	0	0	
11	Bitterweet Chocolate Mousse Brownies	0	0	0.021	0	3	0	0	0	0	0	
12	Black & White Brownies	0	0.125	0	0	7.992	0	0	0	0	0	
13	Blonde Brownies	0	0.25	0	0	0	0	0	4	0	0	
14	Blonde Brownies I	0	0.083	0.021	0	2.664	0	0	5.328	0	0	
15	Blonde Brownies II	0	0.417	0	0	5.328	0	0	8	0	0	
16	Blonde Brownies III	0	0.167	0.042	0	0	0	0	16	0	0	
17	Blonde Brownies IV	0	0.125	0	0	4	0	0	0	0	2.664	
18	Bodacious Brownies	0	0	0.167	0	0	0	0	0	0	0	
19	Boyfriend Brownies	0	0.167	0	0	8	0	0	8	0	0	
20	Broadway Brownie Bars	0	0	0	0	8	0	0	8	0	8	
21	Brooks Best Bombshell Brownies	0	0	0	0	8	0	0	8	0	0	
22	Brownie Cups	0	0	0	0	8	0	0	8	0	0	
23	Brownie Mix 2	0	0.667	0	0	0	0	0	0	0	20	
24	Brownie Mix in a Jar II	0	0.167	0	0	0	0	0	0	0	5.328	
25	Brownie Mounds	0	0.083	0	0	2.664	0	0	0	0	0	
26	Brownie Tarts	0	0	0	0	4	0	0	0	0	0	
27	Brownies Allergy Free	0	0	0.083	0	0	0	0	0	0	4	
28	Brownies I	0	0.167	0	0	5.328	0	0	0	0	0	
29	Brownies IV	0	0	0	0	12	0	0	0	0	8	

Figure 9.5 Section of an excel spreadsheet containing ingredient lists from a large number of recipes that were downloaded from the web.

As you can imagine, there is a large number of different ingredients that can be used in brownies. But by focusing only on the flour and the sugar in every recipe, each recipe on the diagram can be represented with a dot showing the sugar percentage as a function of flour percentage (Fig. 9.6). Just as predicted, brownie recipes tend to cluster together in a certain region of the plot. In other words, a baked good called "brownie" will very likely have predictable amounts of sugar and flour within this range.

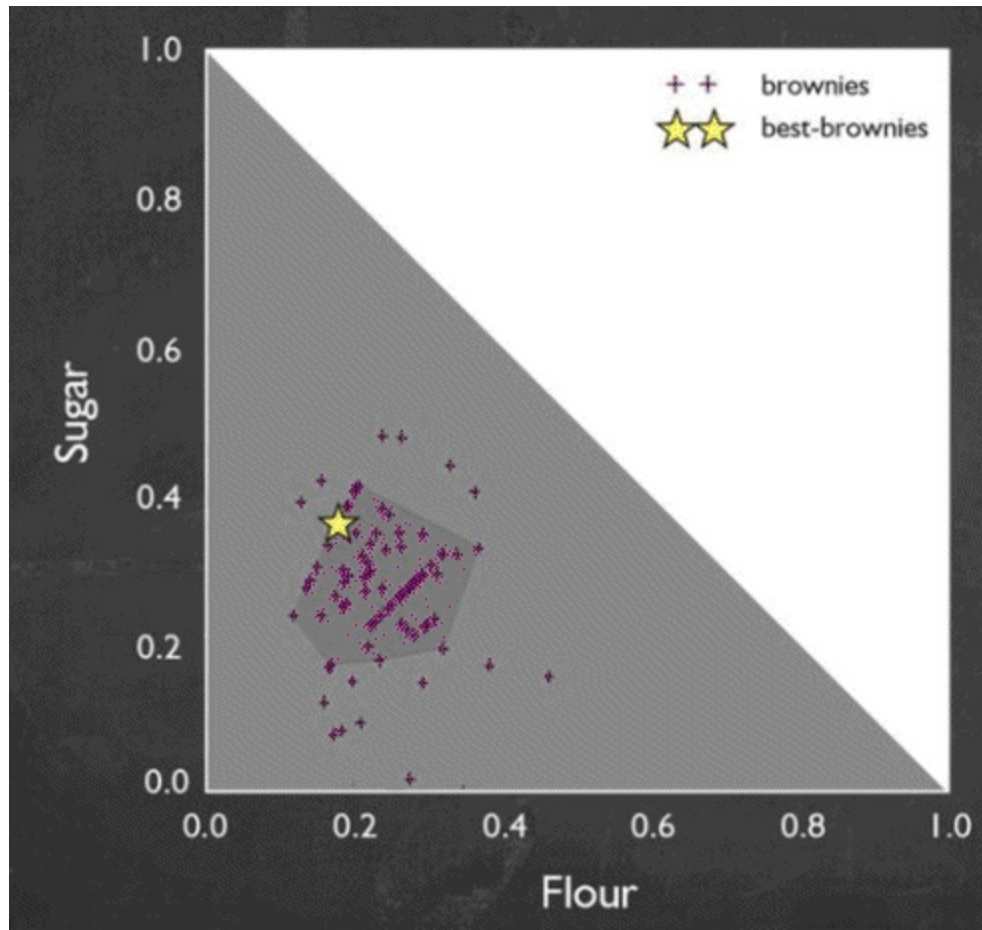


Figure 9.6 A recipe plot where all brownie recipes have been represented with a purple plus-sign based on their sugar and flour content. The general region in which brownie recipes tend to be found has been colored purple. The Best Brownie recipe is indicated with a yellow star.

Now let's consider cookies. Cookies tend to have different ingredient ratios from brownies. As an illustration, compare the two recipes for baker's best brownies and sugar cookies in Figure 9.7. Despite having the word sugar in the title, sugar cookies actually contain less sugar than brownies. They also contain much more flour.

Best brownie recipe				Sugar cookie recipe			
	English	Metric	%		English	Metric	%
butter	$\frac{1}{2}$ cup	115 g	24	butter	$\frac{1}{2}$ cup	115 g	15
sugar	1 cup	200 g	41	shortening	$\frac{1}{2}$ cup	100 g	13
egg	2	70 g	14	sugar	1 cup	200 g	27
vanilla	1 t	5 ml	1	egg	1	35 g	5
cocoa powder	$\frac{1}{2}$ cup	30 g	6	vanilla	1 t	5 ml	0.7
flour	$\frac{1}{2}$ cup	60 g	12	flour	2 $\frac{1}{4}$ cup	280 g	38
salt	$\frac{1}{4}$ t	2 g	0.4	baking powder	$\frac{1}{2}$ t	2 g	0.3
baking powder	$\frac{1}{4}$ t	1 g	0.2	baking soda	$\frac{1}{2}$ t	2 g	0.3
Total	27 oz.	754 g	100	Total	27 oz.	739 g	100

Figure 9.7 Ingredients in the Best Brownie recipe (left) as compared to the ingredients in a recipe for sugar cookies (right).

In the same way as we did with brownies, we can represent the flour and sugar ratios of different cookie recipes on our bakery phase diagram. When we do this, the difference between the two types of recipes becomes obvious (Fig. 9.8). The purple region of the brownie recipes and the blue region of the cookie recipes occupy completely different spaces. So when we give a baked good the name “brownie” it is because it has a different set of ingredients than a cookie, and chefs, as well as people in general, tend more or less to agree on what the different words mean.

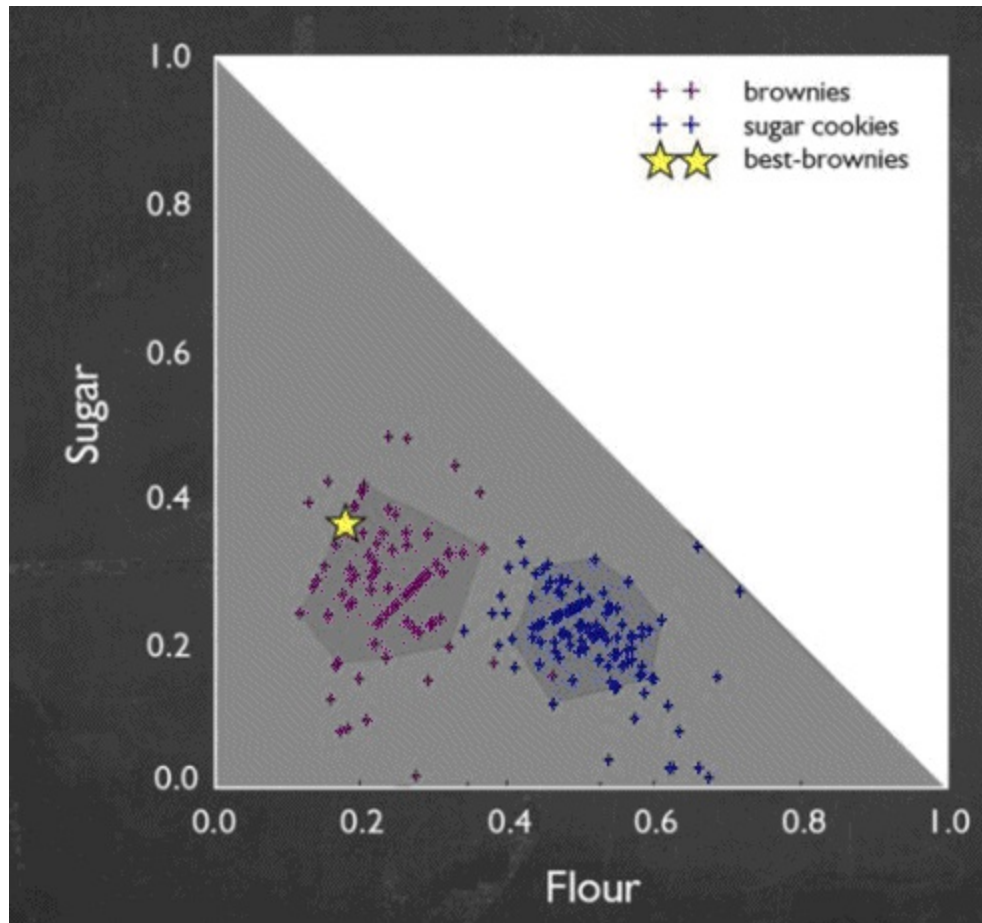


Figure 9.8 A recipe plot where all brownie and sugar cookie recipes have been respectively represented with a purple and blue plus-sign based on their sugar and flour content.

We can continue the same exercise with other types of recipes. Figure 9.9 shows cakes, breads, pancakes, cookies, etc, and each color corresponds to a different type of baked good. Pancakes, for example, are shown as light green crosses. They tend to have very little sugar, and the amount of flour tends to be between the amount of flour for brownies and cookies. Further, red crosses correspond to bread loaves. They also have less sugar than both brownies and cookies, and much more flour, usually between 50% and 75%.

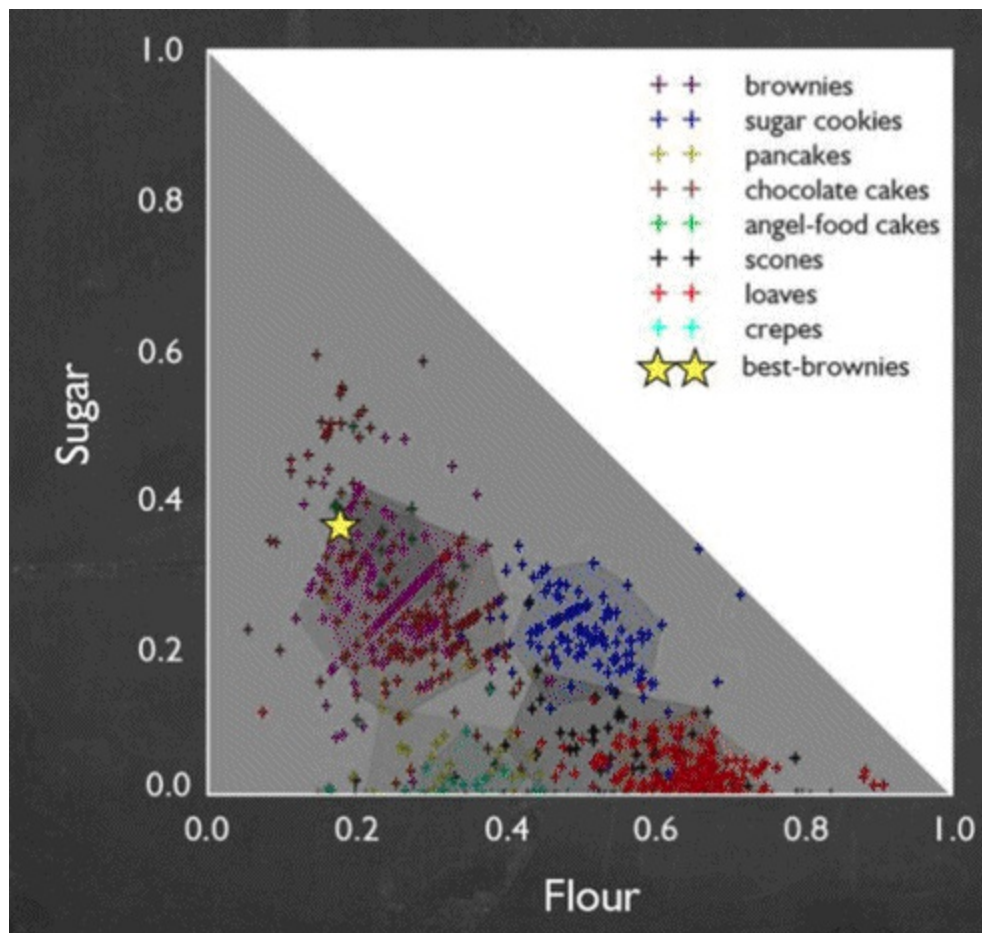


Figure 9.9 A recipe plot for a number of different baked goods based on sugar and flour content.

So far we have plotted sugar and flour, and, indeed, sugar and flour are very important ingredients in baked goods. But there are many other ingredients that are also important, including eggs, liquid, baking soda and baking powder to name a few. If we want to be able to visualize this, we would have to find a way to visualize the columns and rows in Figure 9.5 in a high-dimensional space (Fig. 9.10). This is difficult, though, because the human brain is not good at going beyond three-dimensional visualizations.

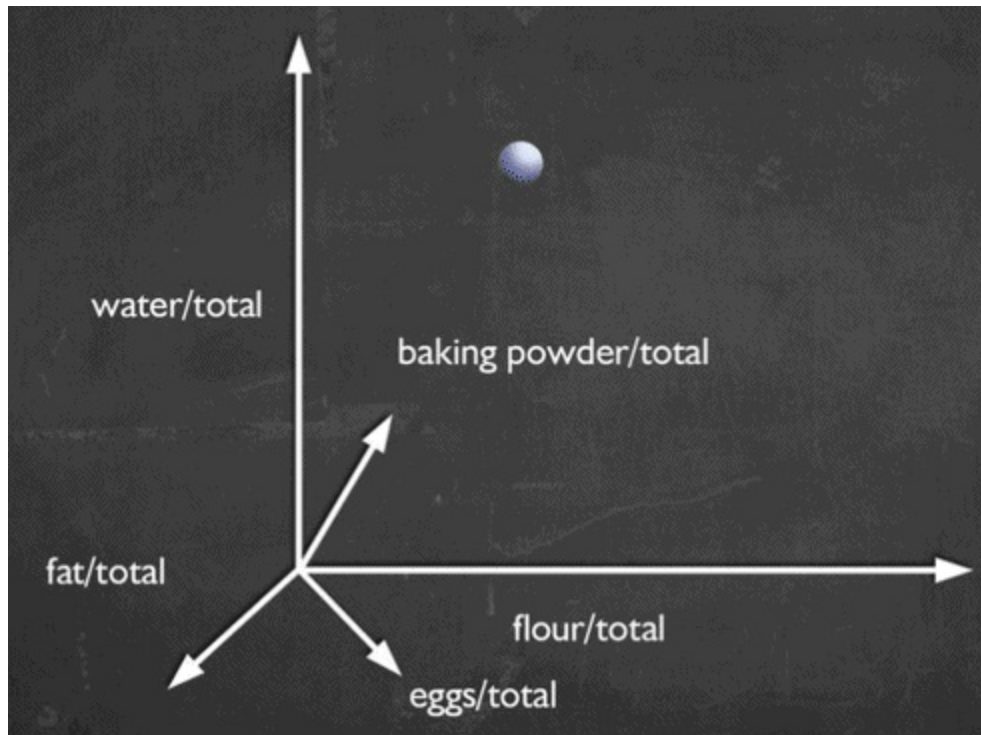


Figure 9.10 Recipes contain many different ingredients and an ideal recipe plot would somehow represent all of them.

The best we can do is to visualize these ingredients in four dimensions by printing them on the four faces of a tetrahedron. This way you can simultaneously look at the variation of flour, sugar, liquid and egg, which are arguably the four most important structural ingredients for baked goods. Figure 9.11 shows a representation of all of the recipes from the excel spreadsheet on the surfaces of a tetrahedron, and Video 9.1 shows what the tetrahedron would look like in 3-dimensional space. By studying it, you can start to get a sense for how different baked goods fill up ingredient space, and why they are so different.

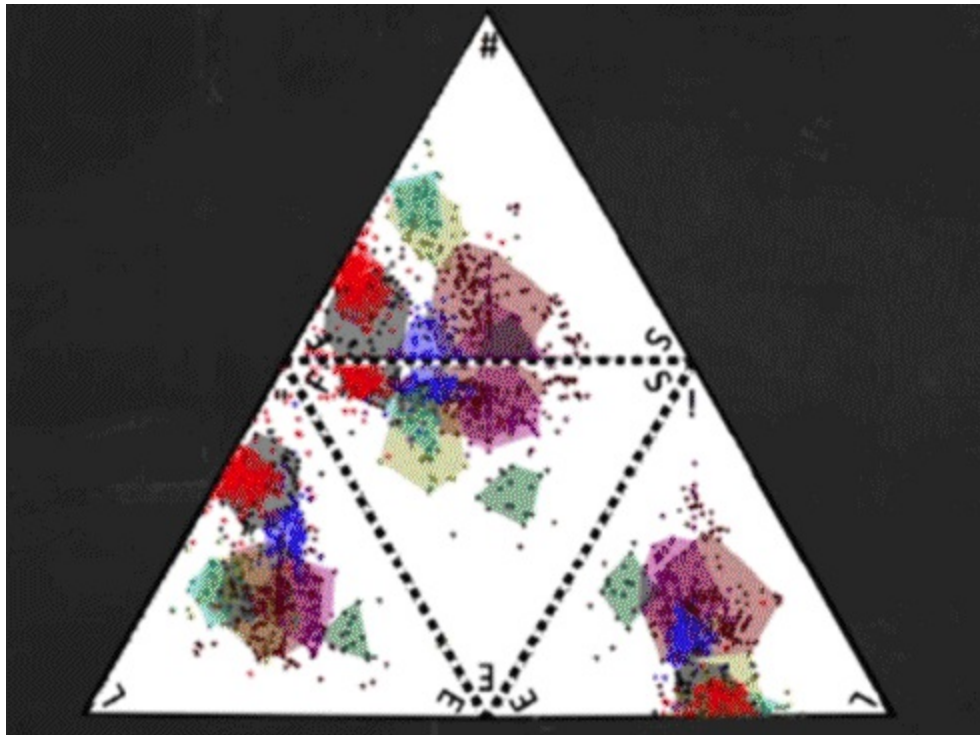


Figure 9.11 and Video 9.1 By using the shape of a tetrahedron, the main four ingredients in baked goods can be represented and visualized. Each side of the tetrahedron provides an axis for a recipe's percentage of either flour, sugar, liquid, or eggs.

Sorry, it appears your system either does not support video playback or cannot play the MP4 format provided. However, you can view the video by clicking on this link:

[movie_1_09_baking_slide_40_1.mp4](#)

Video 9.1

In sections 9.5-7, we will look more closely at some of these differences in ingredients and see if we can gain a better understanding of the microscopic origins of the elasticity for different types of baked goods.

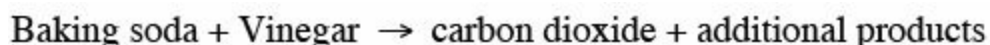
9.3 Yellow Birthday Cake and Baking Soda

One of the key ingredients in many baking recipes is baking soda or baking powder. Whether added separately or together, they are often the primary ingredients responsible for making a cake rise and developing a tender and fluffy texture. Let's look at how they do this in more detail.

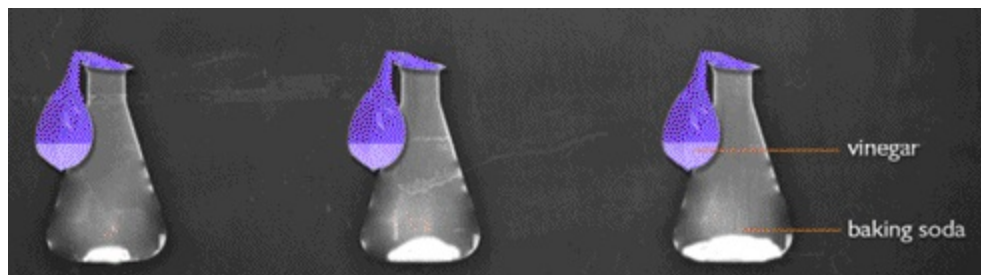
The first thing to note is that the central ingredient of baking powder is, in fact, baking soda. We will explain how the two substances differ later on, but for now, let's focus on the underlying science of baking soda since this will also help us understand baking powder.

9.3.1 Measuring the Amount of Gas Produced

The chemical name for baking soda is sodium bicarbonate. It is a basic substance, which means it has a pH above 7, and this makes it easily react with various acids in a recipe. In order to study how it works, we can imagine it reacting with a common household acid, vinegar. In fact, you can go into your kitchen and try this by putting a couple teaspoons of baking soda into a bowl and adding a little vinegar. What you will find is that the mixture immediately starts to fizz and bubble. A gas has been produced. And the gas, it turns out, is carbon dioxide. So, when baking soda reacts with an acid it creates carbon dioxide and some additional products.



If we wanted to study this reaction more carefully, we could design an experiment in which we are somehow able to capture the gas and measure how much there is. Then we could start to get a sense for how much gas corresponds to the amount of baking soda we typically put into a recipe when baking, and this in turn must be closely related to how fluffy the texture of baked goods with the same amount of baking soda ends up being. Figure 9.12 shows one way to do this. It shows three flasks which have baking soda in them. Each flask has a balloon attached to it with increasing amounts of vinegar. When the balloon is flipped, the two substances mix and the gas can be captured in the balloon. We can then estimate how much gas there is by measuring the radius of the inflated balloon and calculating the volume of the sphere.



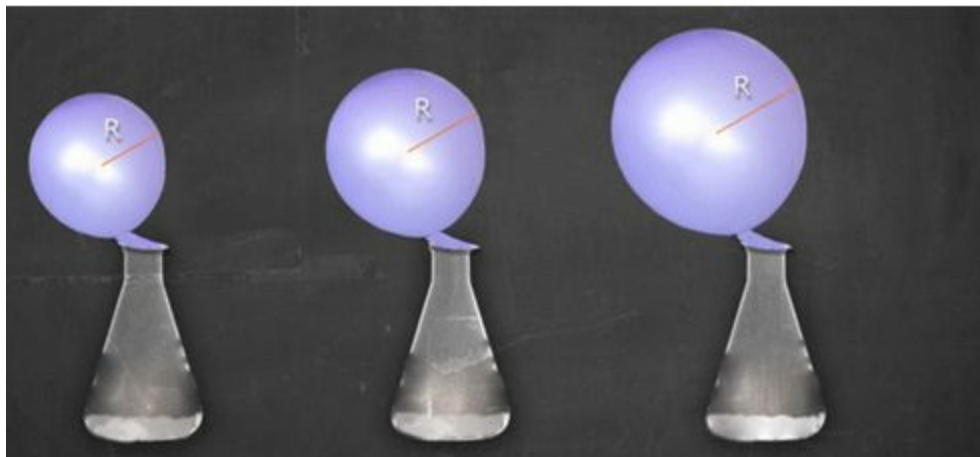
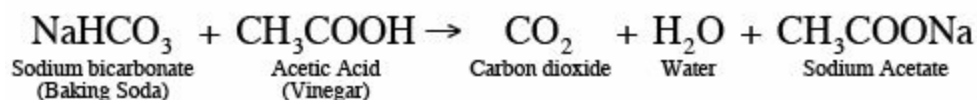


Figure 9.12 Experimental set-up to measure the amount of gas produced from the reaction of vinegar and baking soda. All three balloons contain the same amount of vinegar in excess, and the flasks contain 5, 10, and 15 grams of baking soda respectively. When the balloon is turned upside down, the vinegar pours into the flask and mixes with the baking soda. As a result the balloon is inflated and the amount of gas produced from the reaction can be estimated by measuring its radius.

When we performed this experiment, we found that 5 grams of baking soda resulted in a balloon with a volume of approximately one liter. This is probably slightly less than what the volume of gas would be outside the balloon because the pressure inside the balloon is higher than standard pressure, squeezing the gas into a smaller volume. Nevertheless this is a reasonable approximation. We can get a sense for just how reasonable it is by calculating the theoretical volume of gas we should have obtained based on the chemical equation.

9.3.2 Calculating the Amount of Gas Produced

The chemical equation tells us that one mole each of baking soda and vinegar, react to produce one mole each of carbon dioxide, water, and sodium acetate. The carbon dioxide comes from the bicarbonate (HCO_3^-) on the baking soda, and the water is made by one hydrogen on vinegar and a hydrogen and oxygen on the baking soda. This chemical reaction is the equation of the week (Table 9.1).



EQUATION OF THE WEEK		
$\text{NaHCO}_3 + \text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O} + \text{CO}_2$		
Symbol	Description	Units
NaHCO_3	Sodium bicarbonate (baking soda)	mol
CH_3COOH	Acetic acid	mol
CH_3COONa	Sodium acetate	mol
H_2O	Water	mol
CO_2	Carbon dioxide gas	mol

Table 9.1

Using this equation we can now estimate how much carbon dioxide gas we would get both in the balloon experiment and in a typical baking recipe. Let's start with the balloon.

The amount of baking soda in the flask was 5 grams, and the experiment was designed such that this was the limiting reagent. In other words, there was much more vinegar than baking soda, and thus the amount of baking soda determined how much carbon dioxide gas was produced. Since the molecular weight of baking soda is 84 g/mol, 5 grams correspond to 0.06 moles according to the calculation below.

$$5\text{ g} \cdot \left(\frac{1}{84\text{ g/mol}} \right) = 0.06\text{ moles}$$

Since the equation is stoichiometrically balanced, we will end up with the same number of moles of carbon dioxide as the number of moles of baking soda we put in, i.e. 0.06 moles. What is the volume of 0.06 moles of carbon dioxide gas? Well, it turns out that it is a law of nature that one mole of any gas takes up a volume of 22.4 L at standard temperature and pressure. So the gas produced in this experiment will occupy about 1.3 L in volume, which is not so far from our estimate of a liter based on the balloon experiment. So theory corresponds with our real-world observations, and this is a good thing.

$$0.06\text{ moles} \cdot 22.4\text{ L/mol} = 1.3\text{ L}$$

Now let's see if we can use the same chemical equation to predict the amount of carbon dioxide gas produced when baking a cake. Of course, most of you probably don't add vinegar to your cake batters. But it turns out you don't have to, because many other common baking ingredients are actually slightly acidic and they will react with the baking soda and produce carbon dioxide gas in a similar way as vinegar. For example, buttermilk, which is a common baking ingredient, has a pH of 4.5, and even sugar and butter are slightly acidic.

Let's put this in context by looking at an actual recipe. Figure 9.13 shows a recipe for yellow birthday cake by Joanne Chang, who is the chef and owner of Flour Bakery and Café in Boston.

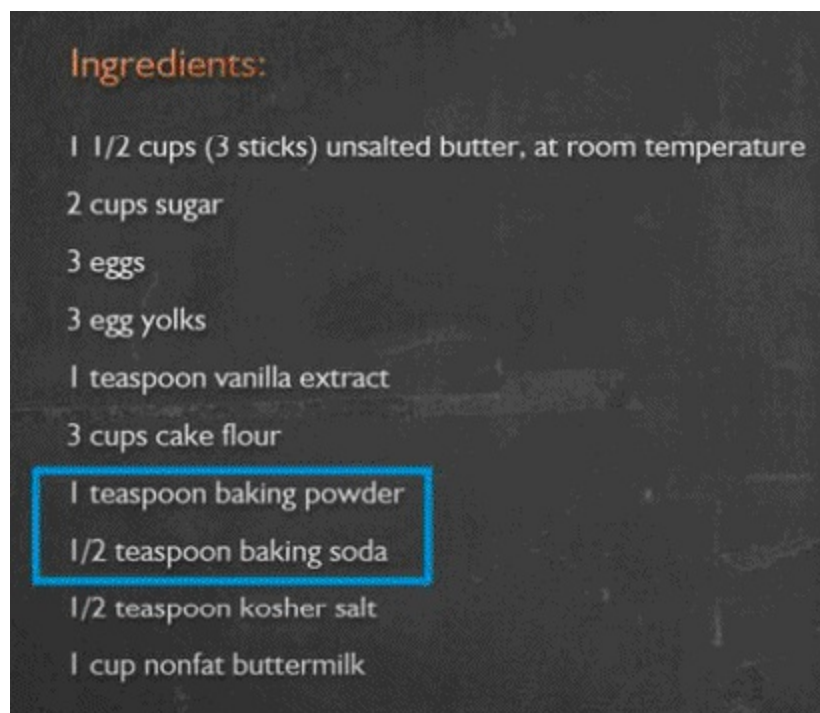


Figure 9.13 Recipe for Yellow birthday cake. (Source: Flour: Spectacular Recipes from Boston's Flour Bakery + Café, Joanne Chang.)

The recipe calls for one teaspoon of baking soda and half a teaspoon of baking powder. Baking powder, as we already mentioned, primarily consists of baking soda, and, conveniently, it also contains an acid for the baking soda to react with. The acid is commonly cream of tartar, and it is added in stoichiometric proportions, meaning there is the exact same number of moles of baking soda and cream of tartar.

How much carbon dioxide gas would we get from this recipe? First we have to find out how much baking soda there is in total. Knowing the stoichiometric ratio and the molecular weights of baking soda and cream of tartar, we can find out that about 1/3 of the mass is baking soda and about 2/3 is cream of tartar. So the baking powder is contributing 1/3 of a teaspoon of baking soda. Adding this to the half a teaspoon of baking soda in the recipe, we end up with 5/6 of a teaspoon of baking soda total. This is what will be contributing to the carbon dioxide gas that makes the cake fluffy.

Baking powder = $\frac{2}{3}$ cream of tartar + $\frac{1}{3}$ baking soda

Baking soda_{total} = $\frac{1}{3}$ tsp + $\frac{1}{2}$ tsp = $\frac{5}{6}$ tsp

$$\text{Baking soda} = \frac{5\text{g}}{1\text{tsp}} \cdot \left(\frac{5}{6}\text{tsp}\right) \cdot \left(\frac{1\text{ mol}}{85\text{g}}\right) = 0.05\text{ mol}$$

$$\text{CO}_2 = (0.05\text{ mol}) \cdot \frac{22.4\text{ L}}{1\text{ mol}} = 1\text{L}$$

One teaspoon of baking soda weighs 5 grams, so $\frac{5}{6}$ of a teaspoon corresponds to about 4 grams. Using the same molecular weights and calculations as above, this turns out to be 0.05 moles of baking soda, which then produces about 1 liter of carbon dioxide gas.

$$\text{Baking soda}_{\text{total}} = \frac{5\text{g}}{1\text{tsp}} \cdot \left(\frac{5}{6}\text{tsp}\right) \cdot \left(\frac{1\text{ mol}}{85\text{g}}\right) = 0.05\text{ mol}$$

$$\text{CO}_2 = 0.05\text{ mol} \cdot \frac{22.4\text{ L}}{1\text{ mol}} = 1\text{L}$$

So theoretically what this means is that as the yellow birthday cake bakes, it should puff up by about 1 liter. Does it? One way to find out is to go and bake the cake and compare the volume of the batter before baking to the volume of the finished cake. When Joanne Chang bakes the cake, the unbaked batter usually ends up having a volume of about two liters; you can also find this number by adding up the volumes of all the ingredients in the recipe. After baking, Joanne's cakes typically increase in volume by about 50% to 3 liters. This, of course, makes perfect sense based on our prediction that there is one liter of gas. So again, theory seems to agree with real life.

At least, at first. After closer scrutiny, there is a small problem with this, which is that air is also incorporated in many other places in the recipe. For example, the creaming of butter and sugar creates small air pockets in the butter, which then expand into larger bubbles when baking. There is also the whisking of the eggs, which incorporates air, and the release of water vapor during heating, all of which contribute to the fluffiness of the cake. Based on this, the increase in volume should be even more than one liter.

The reason it is not, is because gases have a tendency to dissipate very easily. The cake batter is not able to contain all of the gas the way the balloons did, and it therefore spreads in the room and disappears. In some batters, such as pancake batter, you can even watch this process happen as little bubbles pop on the surface. Some batters and doughs are better than others at containing gas bubbles. Bread dough for example, has a strong gluten network that allows bubbles to expand quite a bit without bursting, and is thus able to hold more gas. We will discuss the intricacies of this further toward the end of this chapter.

9.4 The Role of Acids in Baking

We mentioned briefly in the last section that many of the ingredients in baking recipes are acidic and thus provide something for the basic baking soda to react with. Figure 9.14 shows a list of other common acidic ingredients and their pHs. They range from quite acidic such as lemon juice, fruits, and honey, to just slightly acidic ingredients such as chocolate, sugar, butter, and milk. Eggs are one of few cooking ingredients that are actually basic.

Eggs	pH 8.5-9.5	Buttermilk	pH 4.5
Milk	pH 6.2-7.3	Sour cream	pH 4.5
Butter	pH 6.1-6.4	Honey	pH 3.5-6
Brown Sugar	pH 6	Vinegar	pH 2-3.4
Chocolate	pH 5-6	Apples	pH 3.1
Sugar	pH 5-6	Lemon Juice	pH 2
Molasses	pH 5.5		

Figure 9.14 The pH of common acids found in recipes for baked goods. (Adapted from: *Bakewise* by S.O. Corriher, pg. 68.)

Each of the ingredients in the table contain an acid that lowers the pH. In buttermilk the acid is lactic acid, the same acid as in sour cream and other dairy products. Fruits such as apples contain malic and tartaric acid. Coffee and chocolate contain yet other acids. All acids serve a similar role as vinegar in that they donate a proton, react with baking soda, and thus help in the creation of carbon dioxide. The rate at which this happens is going to depend on how easily the proton is given up, and this is determined by the pH of the acid. The rate is also going to depend on the temperature, since chemical reactions in general often are temperature sensitive. You can imagine studying the different reactions in detail by doing a version of the balloon experiment in the previous section and seeing how much gas is produced by different acids at different temperatures.

The temperature dependence of different acids is also the secret behind double-acting baking powders. You may have looked at a can of baking powder in your kitchen, and noticed that the ingredient list contains many other things than cream of tartar. Calcium phosphate and sodium aluminum sulfate are some examples. These are all different types of acids, some of

which release their protons at room temperature, and others not until they are in the higher temperature of the oven. Thus carbon dioxide gas is produced at several steps in the baking process, and this makes for a fluffier cake or cookie.

Figure 9.15 shows a table of acids that are commonly found in baking powder. As you can see, there is quite a difference in what percentage of the carbon dioxide is released at different points in the baking process. You can imagine that different combinations at different ratios would result in different textures. Commercial baking powders usually contain such combinations that have been carefully tried out for the best effect. In theory though you could imagine many more, and if you get the combination just right, you may be able to get that perfect texture you are looking for in your cake or cookie.

Leavening Acid	% Carbon Dioxide Released		
	2 min mixing	Bench Action	10-15 min During Baking
Monocalcium phosphate (MCP)	60	0	40
Anhydrous monocalcium phosphate (AMCP)	15	35	50
Sodium acid pyrophosphate (SAPP)	28	8	64
Sodium aluminum phosphate (SALP)	22	9	69
Sodium aluminum sulfate (SAS)	0	0	100
Dicalcium phosphate dihydrate (DCP)	0	0	100
Monopotassium tartrate (cream of tartar)	70	little	30
Glucono-delta-lactone (GDL)	25	40	35

Figure 9.15 Percent carbon dioxide released at different points in the baking process for common acids in baking powder. Adapted from LaBaw, GD, Bakers Digest 56 (1), 16 (1982).

9.5 Baking Networks Glutenin

Now that we have some idea of what contributes to the fluffy texture of baked goods, let's return to the ingredients in the batter and see how they contribute to the overall structure. We will start by using the different percentages of various baked goods from section 9.2 and seeing how they contribute to the elasticity.

Let's start with the molecule glutenin. We already touched upon how glutenin affects elasticity in Chapter 4 in the context of strudel dough, and we will now consider the effect on other types of doughs and batters. In particular, we are interested in finding out how much the glutenin in different types of doughs and batters contribute to elasticity by estimating the average cross-link distance.

9.5.1 Finding the Cross-link Distance of Glutenin

Glutenin comes from flour, and flour, of course, comes from the seeds of wheat. There are three main components to a wheat seed: the husk, the embryo, and the endosperm. The embryo is the part that will grow into a plant if allowed to, and the endosperm is essentially the nutrient pool feeding the embryo. The endosperm is also what all-purpose flour is primarily made of. Figure 9.16 shows a break-down of the components of wheat seeds as a whole and the endosperm alone. As expected, both wheat seeds and endosperm are primarily made of carbohydrates, and only about 10 grams of the endosperm is protein. Of the protein, in turn, approximately 60% consists of glutenin. In other words, about 60% of 10 %, i.e. 6% of the flour consists of glutenin.

Mass Per 100g (= 170 mL) of powdered wheat		
	Whole seed	Endosperm
Protein	13 g	10 g
Carbohydrate	72 g	76 g
Fat	2 g	1 g

Figure 9.16 The composition of wheat in terms of the whole seed and the endosperm.

What if, from these numbers, we wanted to find out how many glutenin molecules there are in a recipe? We could do this by multiplying the mass of flour with the percentage of glutenin, i.e 6%. Given that flour amounts in recipes often are given by volume, we may have to convert the volume to an approximate mass by multiplying by the density for flour which is approximately 0.6 g/cm^3 . Once we have the mass, we would divide by the molecular weight of glutenin, which is $75,000 \text{ g/mol}$ and multiply by Avogadro's number.

$$\text{\#molecules}_{\text{glutenin}} = \frac{m_{\text{glutenin}}}{75,000 \text{ g/mol}} \cdot 6.022 \cdot 10^{23} \text{ molecules}$$

$$\text{where } m_{\text{glutenin}} = m_{\text{flour}} \cdot \% \text{glutenin}$$

What really matters though is not the number of glutenin molecules, but how far they are apart. A good estimate for this is to find out how much

volume each glutenin molecule occupies in the batter. We can get this by dividing the total volume of the batter by the number of molecules. This tells us how much space each molecule has.

$$V_{glutenin} = \frac{V_{batter}}{\#molecules}$$

If we then imagine that space as being a cube, where each side has the same length, then the approximate distance between glutenin molecules is the same as the side of the cube. Let's call that distance l_g , denoting the length scale of glutenin. We can get this distance by taking the cube root of the volume that each of the glutenin strands occupies.

$$l_g = \sqrt[3]{V_{glutenin}}$$

9.5.2 Comparison of Cross-link Distances in Different Baked Goods

Now we can apply this reasoning to start to get a sense for how the distances between glutenin molecules vary in different recipes. In order to do this, we need approximate numbers for flour content in different types of recipes, and we can get this from the baking plot in Figure 9.9 earlier in this chapter. The plot tells us that pancakes are about 40% flour, bread about 60%, and cake about 30%. The exact percentages vary, of course, but these numbers will help us get some idea of the glutenin distances in baked goods, the textures of which we all know from experience are very different from each other.

Let's consider one kilogram of batter. Given the percentages from Figure 9.9, in a kilogram of pancake batter, the mass of flour would be about 400 grams, in bread dough it would be about 600 grams, and in cake batter about 300 grams. Applying our rule of thumb from above that glutenin makes up 6% of the flour, this corresponds to the following masses of glutenin in each batter:

$$m_{\text{glutenin,pancakes}} = 400 \text{ g} \cdot 0.06 = 24 \text{ g}$$

$$m_{\text{glutenin,bread}} = 600 \text{ g} \cdot 0.06 = 36 \text{ g}$$

$$m_{\text{glutenin,cakes}} = 300 \text{ g} \cdot 0.06 = 18 \text{ g}$$

Next, applying our formula above, these masses correspond to the following numbers of glutenin molecules:

$$\#\text{molecules}_{\text{glutenin}} = \frac{m_{\text{glutenin}}}{75,000 \text{ g/mol}} \cdot 6.022 \cdot 10^{23} \text{ molecules}$$

$$\text{Pancakes} = 1.9 \cdot 10^{20} \text{ molecules}$$

$$\text{Breads} = 2.9 \cdot 10^{20} \text{ molecules}$$

$$\text{Cakes} = 1.5 \cdot 10^{20} \text{ molecules}$$

As you can see, the number of glutenin molecules are not all that different from each other in the different batters. For all the talk of gluten in bread,

there are only twice as many glutenin molecules in bread than in pancakes. The huge numbers are not very helpful though, so let's calculate the volume that each glutenin molecule occupies by dividing the volume of the batter by the number of molecules. A kilogram of batter corresponds to about one liter, which is the same as $1,000 \text{ cm}^3$. This in turn is the same as 10^{24} nm^3 according to the conversion below. Having the volume in nm^3 will be more convenient since the distance between the molecules, as you might expect, is measured in nanometers.

$$V_{\text{batter}} = 1 \text{ L} = 1,000 \text{ cm}^3 = 1,000 \text{ cm}^3 \left(\frac{10^7 \text{ nm}}{1 \text{ cm}} \right) = 10^{24} \text{ nm}^3$$

Plugging this into the formula, we find that the volume per glutenin molecule in each batter is as follows:

$$V_{\text{glutenin}} = \frac{V_{\text{batter}}}{\# \text{ molecules}}$$

$$V_{\text{glutenin, pancakes}} = \frac{10^{24} \text{ nm}^3}{1.9 \cdot 10^{20} \text{ molecules}} = 5,260 \text{ nm}^3$$

$$V_{\text{glutenin, bread}} = \frac{10^{24} \text{ nm}^3}{2.9 \cdot 10^{20} \text{ molecules}} = 3,450 \text{ nm}^3$$

$$V_{\text{glutenin, cakes}} = \frac{10^{24} \text{ nm}^3}{1.5 \cdot 10^{20} \text{ molecules}} = 6,670 \text{ nm}^3$$

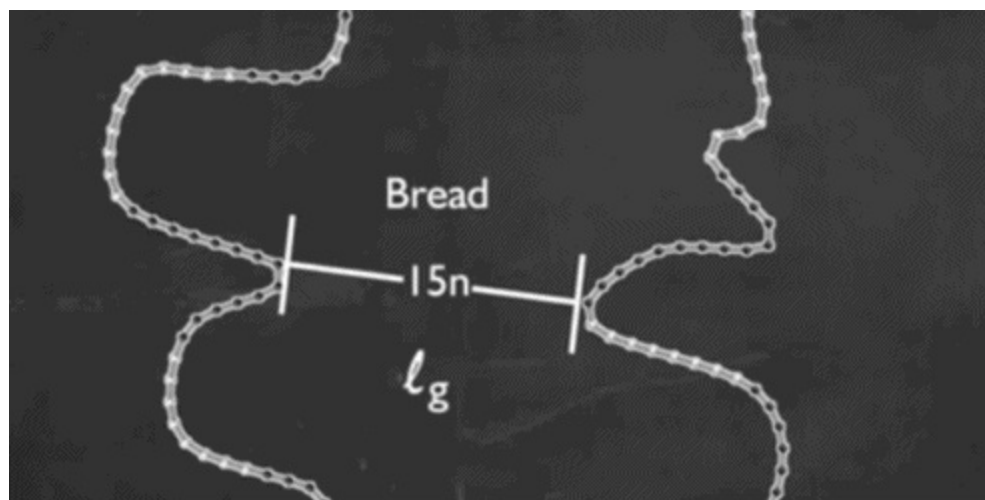
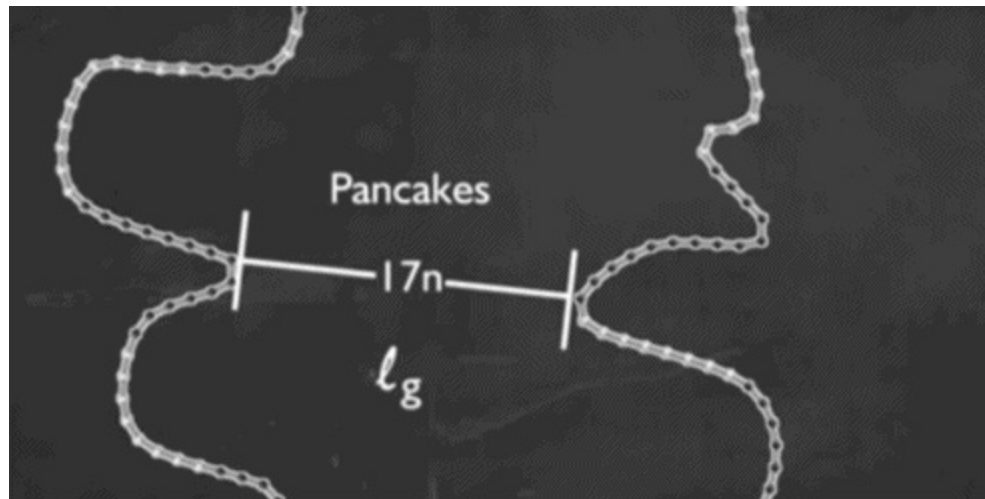
As you would expect, there is a larger volume per glutenin molecule in cake than in bread. But in order to get a better sense for what these numbers mean, let's convert the volume per molecule to a distance between molecules based on the reasoning that the volume is a cube and that the side of the cube is the distance between molecules. If we do this, and solve for l_g , it turns out that the distance between glutenin molecules in pancakes is 17 nm, in bread it's 15 nm, and in cake it's 19 nm (Fig. 9.17).

$$l_g = \sqrt[3]{V_{\text{glutenin}}}$$

$$l_{g, \text{pancakes}} = \sqrt[3]{5,260 \text{ nm}^3} = 17 \text{ nm}$$

$$l_{g, \text{bread}} = \sqrt[3]{3,450 \text{ nm}^3} = 15 \text{ nm}$$

$$l_{g, \text{cakes}} = \sqrt[3]{6,670 \text{ nm}^3} = 19 \text{ nm}$$



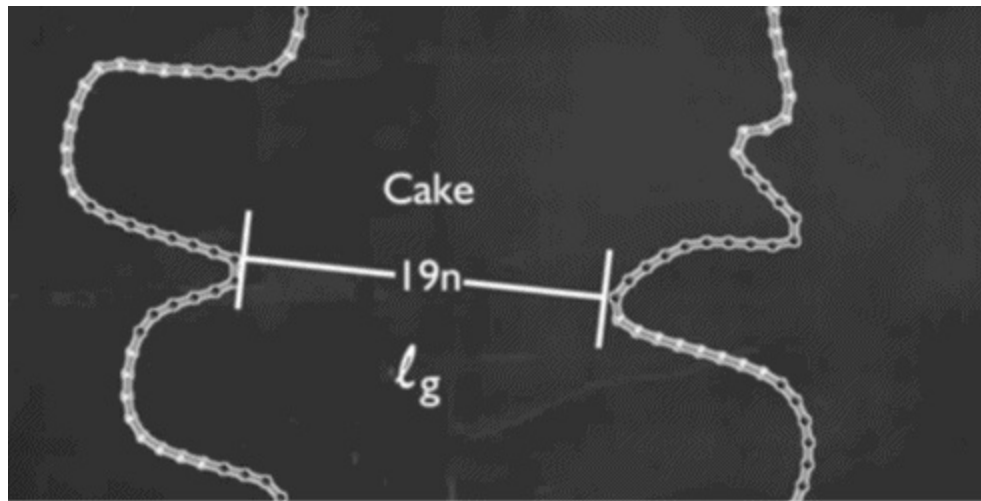


Figure 9.17 The distance between glutenin molecules, as based on our calculations, varies by a relatively small amount in various baked goods. In pancakes it is 17 nm, in bread 15nm, and in cake 19 nm.

There are two conclusions that can be drawn from these numbers. One is that there is actually a pretty insignificant difference between the distances in these different recipes. Knowing how different their textures are, it must be that something more than just the distance between glutenin molecules determines the texture.

The second observation to make is that all three distances are very short. In particular, they are much shorter than the length of a glutenin molecule, which we learned before is about 50 nm. This means that the glutenin molecules are actually close enough together that they could cross-link with each other and form an elastic network that provides the elasticity of the bread, cake, or pancake. So even though the glutenin network is not the only contributor to elasticity of the final baked good, it is at least conceptually possible, given the amount in the recipe, that it provides an elastic backbone, and this, of course, is just what we would expect.

9.6 Modulating Glutenin Networks

9.6.1 Ingredients Influencing the Interaction Energy of Cross-links

One of the reasons the different recipes in the previous section have such different textures despite the glutenin molecules being about the same distance apart, is that there is more to elasticity than the distance between molecules.

Recall the equation from Chapter 4, where $E=U/l^3$. Of course, the cross-link distance, l , is not the same as the distance between molecules, l_g , but the two must be in about the same range. In that sense, we have a fairly good estimate of the denominator in the equation. The other way to affect the elastic modulus is to change the interaction energy, U , in the nominator. There are several ways of doing this when baking, and our discussion of elasticity due to glutenin would not be complete without going through them.

One way to affect U is to coat the glutenin molecules with fat so that the hydrophobic residues of the fat weaken the interactions between the glutenin molecules. When a recipe contains butter, shortening, or other fats, you can expect the elastic network of the glutenin to be weaker for this reason. Indeed, the reason cakes are much more tender than bread is in part due to their higher fat content.

Another way to modulate the strength of interactions between glutenin molecules is to change the pH. We have talked about the role of pH in modulating protein interactions before, so this is not unexpected. At a lower pH, the glutenin molecules are more charged, and thus repel each other. This lowers their strength of interaction, leading to an elastic network with a lower elastic modulus. This effect is significant for many baking recipes since so many baking ingredients, as we have already learned, are acidic. So recipes involving any of the acidic ingredients in Figure 9.14, such as buttermilk (pH 4.5), sugar (pH 5-6), or various fruits, such as apples (pH 3), will have weakened gluten networks and different textures than if these ingredients were excluded.

9.7 Baking Networks: Eggs and Starch

9.7.1 Calculating the Cross-link Distances of Ovalbumin

Having considered the glutenin network, let's now think about other possible contributors to the elasticity of baked goods. In particular, let's talk about eggs. The questions we want to ask are similar to the questions we asked for glutenin. How many molecules of egg protein are there in a typical recipe? Is the distance between them short enough that they could contribute to the elasticity of the baked good?

Let's ask these questions in the context of a single egg. You will recall that there is a large number of different proteins involved in the gelation networks that form as an egg cooks, and all of them also play some role in baking. But for simplicity, let's focus on one of them, ovalbumin, which is the major protein of egg white.

How many ovalbumin molecules are there in an egg? If we assume that a typical egg weighs 34 grams with about two thirds of that being egg white, and, further, that about 60% of the egg white is composed of protein and 10% of the protein being ovalbumin, we can find the mass of ovalbumin according to the calculation below.

$$m_{\text{ovalbumin}} = 34 \text{ g} \cdot \frac{2}{3} \cdot 60\% \cdot 10\% = 1.36 \text{ g}$$

The molecular weight of ovalbumin is about 45,000 g/mol, so to find the number of molecules, we divide the mass, 1.36 grams, by the molecular weight and multiply by Avogadro's number. That turns out to be $1.8 \cdot 10^{19}$ molecules.

$$\begin{aligned} \# \text{molecules}_{\text{ovalbumin}} &= 1.36 \text{ g} \cdot \frac{1 \text{ mol}}{45,000 \text{ g}} \cdot \frac{6.022 \cdot 10^{23} \text{ molecules}}{1 \text{ mol}} \\ &= 1.8 \cdot 10^{19} \text{ molecules} \end{aligned}$$

Now let's compare this number to the similar number for glutenin from the previous section. For glutenin we considered a liter of batter. A reasonable number of eggs for a liter of batter will vary from recipe to recipe. For bread you typically use no eggs at all, whereas for pancakes or cakes you might use somewhere between 2-4 eggs. Let's assume we use four eggs, in which case we have four times as many ovalbumin molecules, i.e. $8 \cdot 10^{19}$ molecules. If we then convert this to an average distance between molecules using the same arithmetic as for glutenin, this turns out to correspond to about 20 nm or so. In other words, our estimate for the cross-link distance is very much in the same ballpark as that between glutenin molecules.

The ovalbumin molecules will only be able to form cross-links if they are longer than 20 nm though, otherwise they cannot stick to each other. Just like two people standing on opposite sides of a room cannot hold hands because their hands simply are not long enough, the ovalbumin molecules, on average, cannot cross-link if they are shorter than 20 nm. The size of a folded ovalbumin molecule is about 7x5x5 nm. This is a size that is estimated based on crystal structures, which is how scientists typically determine these things. This is much smaller than 20 nm, so if the ovalbumin molecules were in a folded state in the batter, no cross-links could form. Recall though that as an egg cooks, the proteins unfold and coagulate. In fact, this is a requirement for the gelation network to form, so the size of interest in this context is really the length of the unfolded protein. Assuming that the radius of the unfolded protein is about a nanometer, the length works out to be about 50 nm, which is basically the same basic length scale as that of glutenins. So, at least from the numbers alone, the ovalbumin molecules will indeed be able to cross-link with each other in a similar manner as the glutenins do. In fact, the bond energies are also about the same order of magnitude since they are all based on hydrophobic interactions between proteins modulated by electric charge. And so the resulting networks will have roughly the same consistency.

It should be emphasized again that the structure of baked goods is complicated. The glutenin and ovalbumin networks do not operate in isolation, but rather there is an interplay between all of the networks, and also including the starch granules, which we will discuss next. The elastic modulus is determined by complex interactions between all of these factors

which we can only imagine.

9.7.2 Elasticity Contributed by Starch

Lastly, let's consider how much the starch granules contribute to the elasticity of the three baked goods. You will recall from Figure 9.16 that all-purpose flour contains about 76% carbohydrates. Assuming that all of the carbohydrate is starch and recalling the flour percentages of pancakes (40%), bread (60%), and cake (30%), this corresponds to the following starch percentages by volume in each baked good:

$$\text{Pancakes} = 40\% \text{ flour} \cdot 76\% = 30\% \text{ starch}$$

$$\text{Breads} = 60\% \text{ flour} \cdot 76\% = 45\% \text{ starch}$$

$$\text{Cakes} = 30\% \text{ flour} \cdot 76\% = 22\% \text{ starch}$$

As you may recall from our discussion on emulsions, all of these percentages are below the critical percentage needed for the granules to jam into each other and contribute to elasticity. So on first thought, it looks like the starch network is not going to contribute to elasticity. However, we also know that the starch granules will swell up when heated in water, and this makes the liquid even more viscous. Eventually, the starch granules swell up so much that the network of grains contributes to the elastic modulus. Indeed, this is entirely within the ballpark of something that can happen in all three recipes. The fraction of starch is within a factor of two or three for the volume fraction to be such that it can form an elastic network, and this is a completely reasonable amount of swelling.

In summary, we have argued that the three main ingredients in cake, bread, and pancake recipes, namely glutenin, egg proteins, and starch, do indeed, based on our calculations, contribute to the elasticity of the final baked good in some way. The precise elastic modulus depends on other aspects of the recipe such as the way the ingredients are mixed, as well as other ingredients, such as acids, salts, and fats, which modulate the interactions between the main three ingredients.

The fact that all three of these ingredients turned out to play a significant role, at least partly explains why the bakery phase diagrams we discussed in section 9.2, are so robust. Based on our calculations, if you change the amount of flour in a recipe by 10%, you are actually not changing the cross-link distance between glutenin molecules by very much. And although the

10% change in flour content could affect the recipe, it is not obviously going to have a huge effect on the elastic networks.

9.8 Browning Reactions

We have referred to browning reactions previously in this course in the context of cooking a steak in Chapter 6. They were responsible for the brown, flavorful crust that develops on the surface of a steak at high temperatures. Browning reactions are also very important for baking. They provide the golden color we associate with the crusts of many cookies, cakes, and breads.

9.8.1 Caramelization

For steaks, the main set of browning reactions we discussed was Maillard reactions, which involved the reaction between an amino acid and a sugar as a first step. Maillard reactions are also important for baking, but in addition, baking also involves another prevalent set of browning reactions, namely those of caramelization. These reactions take place between sugar molecules at high temperatures, usually 160°C or above. The first step is the decomposition of the sucrose molecule into its two constituents, fructose and glucose. From here, the five-membered carbon ring of fructose, and the six-membered ring of glucose, decompose and re-react into hundreds of small molecules. As with Maillard reactions, many of these compounds are brown and/or flavorful, with the flavors in this case being nutty and buttery caramel flavors as opposed to some of the more meaty flavors of Maillard reactions.

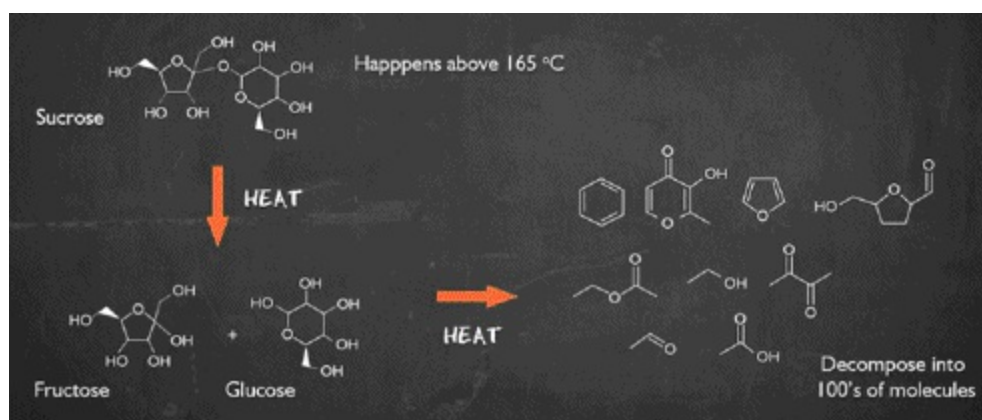


Figure 9.18 When sucrose is heated, it first falls apart into its two primary constituents, fructose and glucose, followed by further decomposition into a wide array of smaller molecules.

You can observe the process of caramelization, by simply pouring some white table sugar in a skillet and heating gently. In fact, you may have done this as the first step in making the caramel top of a crème caramel. The sugar will turn brown and start to melt into a thick golden brown syrup, and a delicious aroma of nutty and buttery caramel flavors will spread in the room. These are the signature flavors of caramelization reactions (Fig. 9.19). You know you have overheated the sugar if it turns from amber to dark brown or black, and start to smell unpleasantly bitter and vinegary. This is a sign that the reaction has gone too far.

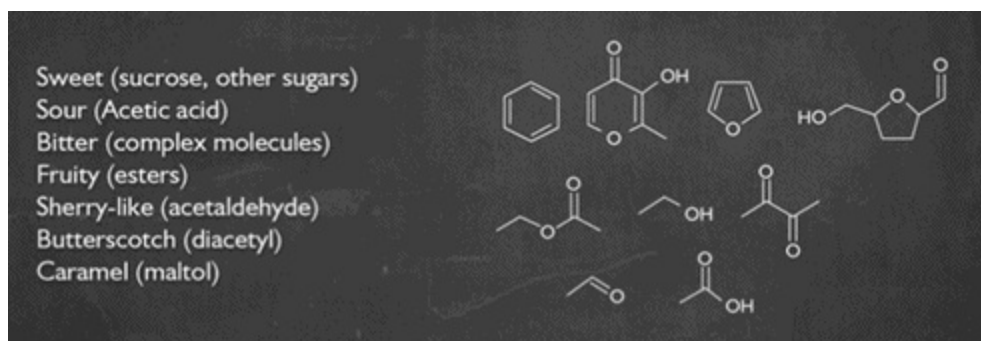


Figure 9.19 The typical flavors of caramelization, sherry, butter-scotch, and caramel, are caused by a large number of small molecules.

We can get a sense for the flavor space occupied by caramelization reactions by identifying them on a flavor wheel, which is what professional tasters use as a way to help them narrow down on and distinguish different flavors. As you can see, caramelization reactions primarily occupy a relatively limited number of flavor areas in the caramel, buttery, and fruity categories (Fig. 9.20).

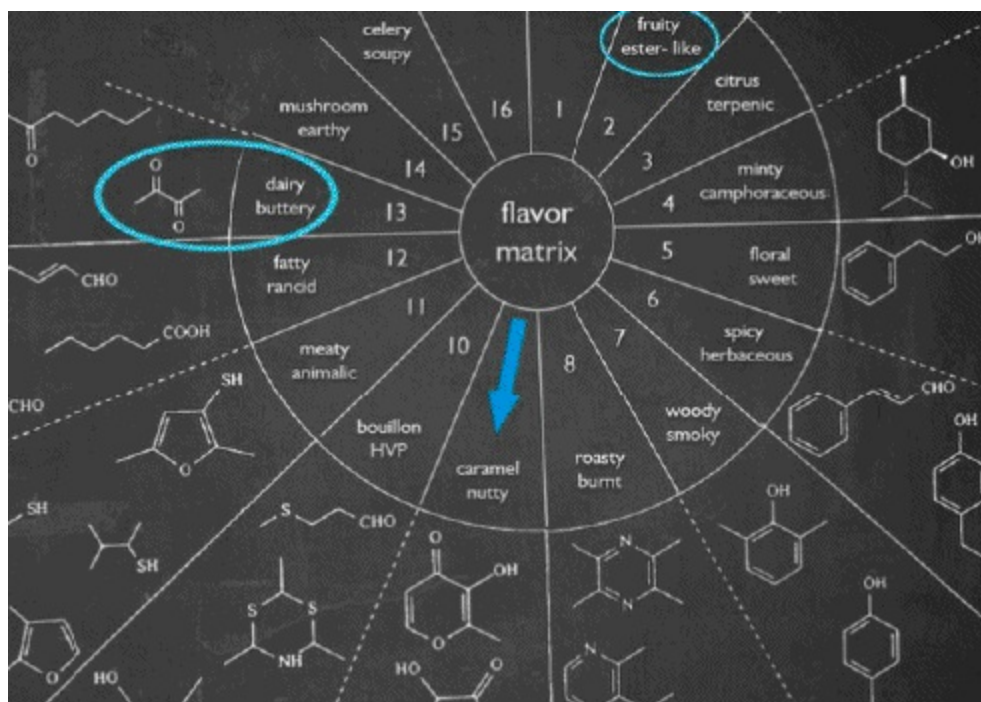


Figure 9.20 Flavor wheel showing the typical flavors of caramelization highlighted in blue.

9.8.2 Maillard Reactions

In contrast to caramelization reactions, which can occur by applying heat to sugar on its own, Maillard reactions also require the presence of proteins. This is because the first step involves an amino acid reacting with a sugar molecule. At temperatures above 120°C , the amino group on any of the 20 different amino acids on a protein can attack the carbon on a sugar molecule as shown in Figure 9.21. This leads to a bond between the sugar and the amino acid, and after this an array of different reactions can happen. The molecule can decompose further or react with other amino acids, sugars, or decomposition products. Given that there are 20 different amino acids, you can imagine that the number of different products is vast even though the reaction always starts out with the same step.

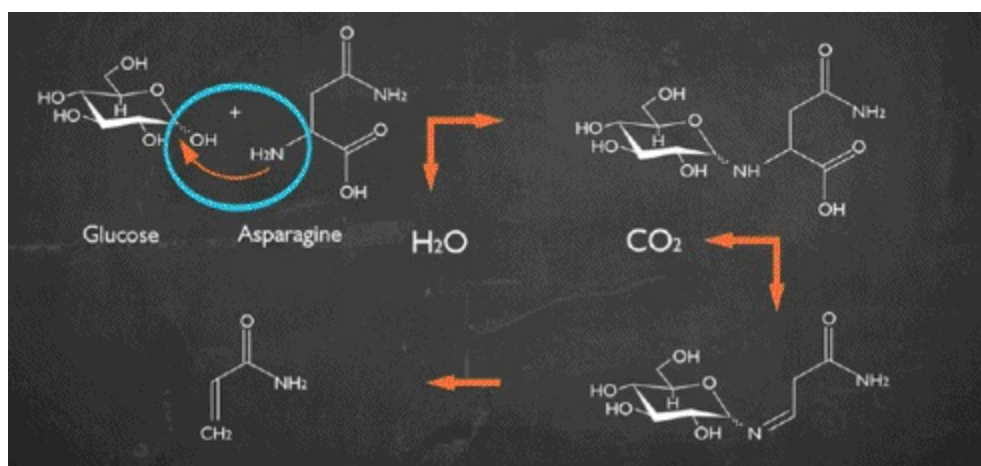


Figure 9.21 The first step of all Maillard reactions involve the nucleophilic attack of the amino group on an amino acid on the C-1 carbon on glucose. The resulting molecule can then decompose in a number of ways resulting in a wide array of small molecules.

The variety of molecules present in amino acids also explains the diverse flavor profile possible from Maillard reactions. For example, amino acids always contain nitrogen and sometimes sulphur compounds, which tend to contribute the meaty, earthy flavors that we associate with cooking a steak (Figure 9.22). Other flavor compounds are similar to those of caramelization reactions, such as the nutty caramel and butterscotch flavors that develop when heating milk. In this case, the lactose sugar and proteins in milk react and the milk turns into a rich, thick sauce. In fact, this is how to make dulce de leche, and it is also the principle behind several other caramel flavored candies and desserts.

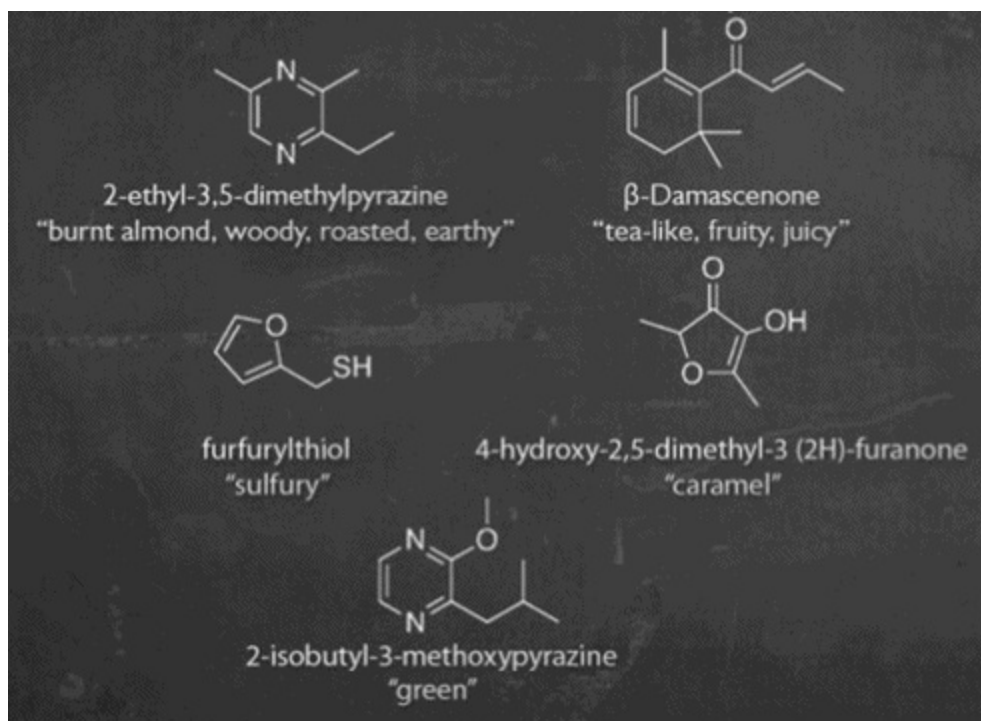


Figure 9.22 The diverse flavors of Maillard reactions, ranging from fruity to earthy to burnt, are caused by a large number of small molecules.

The diversity of flavors possible from Maillard reactions becomes even more obvious by marking them on a flavor wheel (Fig. 9.23). Almost any type of flavor is represented, ranging from earthy and meaty to woody, fruity, and floral. All of them are made possible by an initial reaction between a sugar and an amino acid molecule, which is quite remarkable.

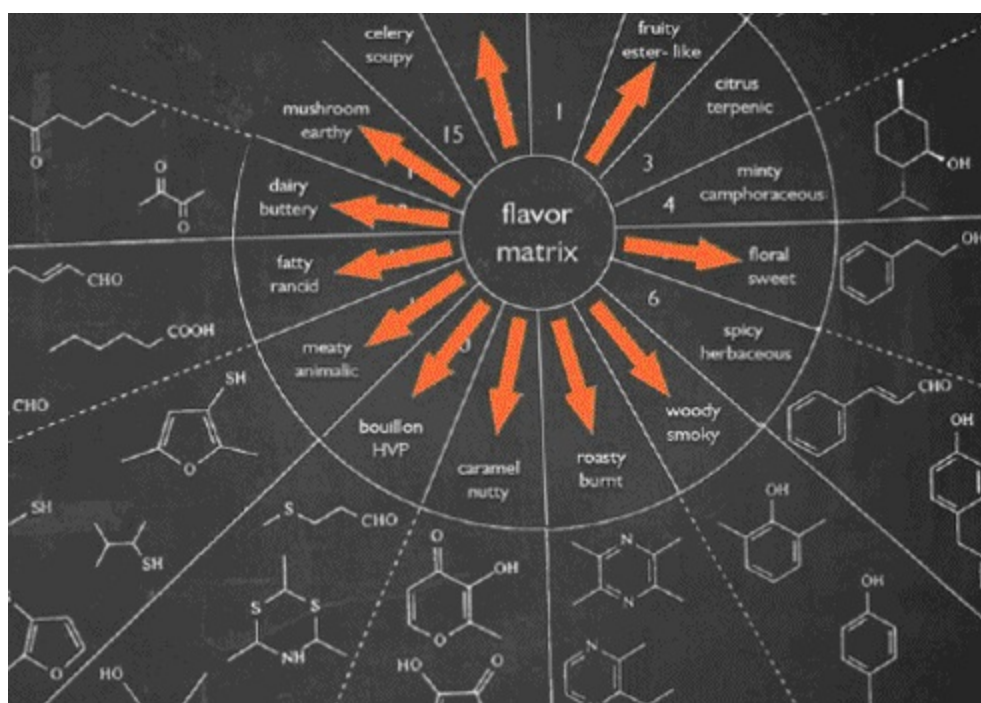


Figure 9.23 Flavor wheel showing the typical flavors of Maillard reactions highlighted in orange.

One feature of Maillard reactions that makes them interesting from a chemical perspective, and also quite tricky to control in a culinary context, is that they are so called exothermic reactions. An exothermic reaction is a chemical reaction that releases energy to its surroundings as it proceeds. This is in contrast to endothermic reactions, which instead absorb energy.

The exothermic nature of Maillard reactions has the following effect: In order to even get started, temperatures above 120°C are required. Once they start to occur, they produce energy in the form of heat, and this increases the temperature further, leading to even more reactions taking place. Thus the reactions quickly speed up once they start happening. Additionally, since many of the products of Maillard reactions are dark in color, heat absorption also increases as the reactions proceed and the color darkens. You may have experienced this in a culinary context in the context of making toast. You pop a slice of bread in the toaster and keep checking if it is done. Initially it seems to take forever, until then suddenly it is almost done, and then done, over-done, and burnt, seemingly very quickly. This is an example of how Maillard reactions speed up because of the exothermic nature of the reactions and the increased heat absorption as the color starts to darken.

Maillard reactions not only occur in baking. They contribute to the diverse flavors in an incredibly wide array of foods, from coffee and popcorn to champagne and cured meats (Fig. 9.24). Some of these foods, such as champagne and cured meats, are produced over such long time scales that Maillard reactions are able to take place even though the temperatures do not get very high. This is an interesting feature of chemical reactions which we will talk more about in Chapter 10.



Figure 9.24 Maillard reactions occur in a diverse set of foods, ranging from steak, to champagne, to popcorn.

9.8.3 Increasing Maillard Reactions

What if we wanted to speed up Maillard reactions? Clearly they add a lot of flavor to food, and it would hence be of culinary importance to have the ability to make more of them.

Looking back at the chemical reaction of the first step, let's see if we can figure out a way. The first step involved an amino group attacking and binding to the carbon on a sugar molecule. If we could speed up this reaction, we would also be speeding up the production of other downstream compounds. One way to speed it up would be to make the amino group a more effective attacker of the carbon. In chemistry language we say that we want to make it a better nucleophile. We can do this by adding a base that would remove one of the hydrogens on the amino group, thus making it have a negative charge. A negative charged amino group would more easily attack the slightly positively charged carbon atom on the sugar (Fig. 9.25).

One edible household base that comes to mind is baking soda. And, in fact, it turns out that if you add a pinch of baking soda to the skillet when browning onions, they actually do become brown faster. The same principle is applied when baking pretzels. The unbaked pretzels are brushed in basic sodium hydroxide before baking, and this gives them the typical dark brown exterior while still keeping the interior light.

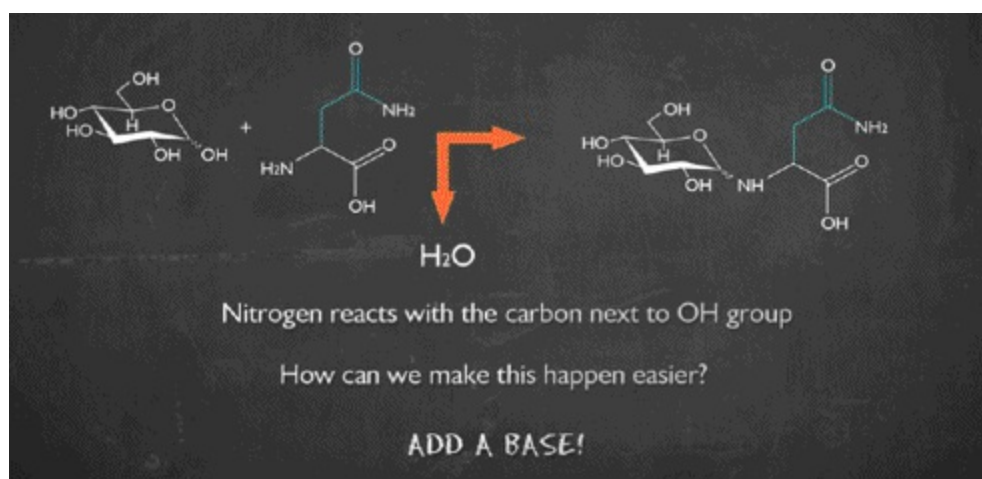


Figure 9.25 By adding a base, the rate of the nucleophilic attack of the amino group on glucose can be increased. This causes Maillard reactions to occur faster.

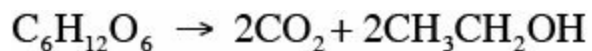
The same idea also applied to baking cookies. Some cookie recipes have a clear excess of baking soda compared to how much acid is provided. Any such excess baking soda will contribute to browning of the surface instead

of producing carbon dioxide gas. For example, white cookies often contain both baking soda and cream of tartar in about equal amounts. The cream of tartar reacts with the baking soda and produces carbon dioxide gas for leavening so that there is no baking soda left to contribute to browning. If the cookies are left long enough in the oven, they will of course eventually turn brown, but not nearly as quickly as if there is excess baking soda. In contrast, chocolate chip cookies is an example of a recipe without cream of tartar where the cookies turn brown much more quickly.

9.9 Gas Production Yeast

There are two ways of producing carbon dioxide gas when baking. The first way is with baking soda, which we have already discussed at length. The second way is by addition of yeast, which is the topic of this section.

Yeast are an important ingredient for many aspects of cooking. In fact, all of Chapter 10 focuses on the remarkable ways in which yeast and other microorganisms transform foods by the process of fermentation. Some of these processes have interesting overlaps. For example, the very same reaction that creates carbon dioxide gas when baking, is also responsible for converting grape juice into wine. The reaction is shown below: one glucose molecule is converted into two molecules of carbon dioxide and two molecules of ethanol. In wine-making the gas is allowed to evaporate, whereas in baking the gas is trapped in the dough, allowing it to rise.



9.9.1 Estimating the Amount of Gas Produced

Whereas gas production of baking soda is a straightforward chemical reaction, the reaction above is made possible by complex metabolic pathways of a biological organism. Yeast eat sugar, and by digesting it they are able to extract the energy needed to survive. The carbon dioxide is simply a by-product. Without going into the complexities of yeast metabolism, the reaction can still be understood simply by studying the reactants and products in much the same way that we studied the reaction of baking soda. So, just like we wanted to know how much carbon dioxide gas was produced from a teaspoon of baking powder or baking soda, we can ask how much carbon dioxide gas is produced from a teaspoon of baker's yeast.

One difference between the two reactions is that since yeast are living organisms they produce a continuous stream of carbon dioxide gas. Thus, the rate of carbon dioxide production is given by the number of yeast cells times the rate at which each yeast cell produces carbon dioxide gas.

$$\text{Rate of CO}_2 \text{ production} = \# \text{yeast cells} \cdot \text{rate yeast cell}$$

Let's look at each of these two factors in turn, starting with the number of yeast cells. A typical bread recipe calls for a teaspoon or so of yeast. One teaspoon has a volume of about 5 ml, so if we know the volume of one yeast cell, we can find out how many there are simply by dividing the total volume by the volume of one yeast cell. Yeast cells are tiny things. A typical volume is about $50 \mu\text{m}^3$, or

$50 \cdot 10^{-12} \text{ cm}^3$. This works out to be 10^{11} yeast cells in that little teaspoon of yeast that you put into your recipe.

$$1 \text{ yeast cell} = 50 \mu\text{m}^3 = 50 \cdot 10^{-12} \text{ cm}^3$$

$$\# \text{yeast cells in 5 ml} = 5 \text{ ml} \cdot \frac{1 \text{ cm}^3}{1 \text{ ml}} \cdot \frac{1}{50 \cdot 10^{-12} \text{ cm}^3} = 10^{11} \text{ yeast cells}$$

Each of the 10^{11} yeast cells is eating the sugar in the batter and producing carbon dioxide gas according to the reaction above. The rate at which they do this is essentially a question of how fast the yeast cells eat, and this

depends on a number of factors. Just like you would eat more food if you were very hungry and in a restaurant with food you love, as opposed to if you were full and in a restaurant with food you don't like, yeast also eat and grow based on the environmental conditions they are in. The two most basic environmental conditions that influence the rate of growth are pH and temperature. In addition, just like we have our favorite foods, yeast have their favorite foods too. I.e. while yeast are capable of metabolizing a variety of different sugars and carbohydrates, the growth rate depends on the type of sugar. In the case of glucose, which is one of the favorite foods, yeast cells eat so fast that they end up dividing every 1.5 hours. In other words, every 1.5 hours a yeast cell essentially doubles in weight. How much glucose is needed for this to happen? Well, at the very least each yeast cell would have to eat an amount of food that is equal to its weight, because otherwise where would the mass come from? Most likely, it would have to eat more than this, but this is a good rule of thumb. So in order to find the rate of gas production per yeast cell, we can ask how much carbon dioxide gas each cell would produce if it ate its own weight in sugar.

How much do yeast weigh? If you exclude the water, which is not important for our purposes since it depends on how much water is ingested, not how much sugar is consumed, then the dry weight of a yeast cell is 54 picograms, or $54 \cdot 10^{-12}$ grams. Using Avogadro's number and the fact that glucose has a molecular weight of 180 g/mol, we find that this corresponds to $1.8 \cdot 10^{11}$ glucose molecules per yeast cell. So in order for a yeast cell to eat its own weight in sugar, it needs to eat $1.8 \cdot 10^{11}$ glucose molecules. And according to our chemical reaction, these glucose molecules will be converted to twice as many carbon dioxide molecules, i.e. $3.6 \cdot 10^{11}$. And this all has to happen within a little more than an hour. So the rate of carbon dioxide production per yeast cell is $3.6 \cdot 10^{11}$ /hr.

$$\begin{aligned}
 m_{\text{yeast cell}} &= 54 \text{ pg} = 54 \cdot 10^{-12} \text{ g} \cdot \frac{1 \text{ mol}}{180 \text{ g}} \cdot \frac{6.022 \cdot 10^{23} \text{ molecules}}{1 \text{ mol}} \\
 &= 1.8 \cdot 10^{11} \text{ molecules} \\
 \text{rate yeast cell} &= 3.6 \cdot 10^{11} \text{ molecules CO}_2 / \text{yeast cell}
 \end{aligned}$$

Considering these two numbers together, the number of yeast cells in a

teaspoon (10^{11}) and the rate of carbon dioxide production by a single yeast cell ($3.6 \cdot 10^{11}/\text{hr}$), the total amount of carbon dioxide that can be produced by your teaspoon of yeast is about $3.6 \cdot 10^{22}$ molecules.

$$\text{Rate CO}_2 \text{ production} = \# \text{yeast cells} \cdot \text{rate per cell}$$

$$\text{Rate CO}_2 \text{ production} = 10^{11} \text{ yeast cells} \cdot 3.6 \cdot 10^{11} \text{ molecules CO}_2/\text{cell}$$

$$\text{Rate CO}_2 \text{ production} = 3.6 \cdot 10^{23} \text{ molecules CO}_2$$

How does this number compare to the number of carbon dioxide molecules that were released by a teaspoon of baking soda? It turns out it is essentially the same. We already saw that one teaspoon of baking soda corresponds to 0.06 moles of carbon dioxide gas, and this in turn corresponds to $3.6 \cdot 10^{22}$ molecules – exactly the same as the number of molecules one teaspoon of yeast can produce in an hour. Of course, yeast also have the feature that unless their growth is stopped in some way, they will keep producing more gas as time goes on.

These calculations are just estimates. But they can be tested with the same experiment we used for baking soda, where you could add yeast and batter to a flask, put a balloon on top, and measure how much gas is produced as a function of time. You could repeat the same experiment as a function of temperature, pH, the initial number of yeast cells, and so on, and eventually put together quantitative rules of thumb for what the rate of gas production for the yeast in your baked goods is.

9.10 Making Bubbles 1

9.10.1 A General Introduction

Another process that is central to baking is that of making bubbles. If you cut open a baked good you will find that it has an enormous array of bubbles, and you know from experience that the way the bubbles are structured affects the texture.

The air that fills the bubbles partly comes from the carbon dioxide produced by yeast or baking soda. It also comes from air that has been incorporated into the batter as part of the baking process. For example, one of the key steps in making Chef Joanne Chang's yellow birthday cake is to cream butter and sugar, which has the effect of the sugar crystals acting as shovels, digging out air pockets in the butter. Another common way to incorporate air when baking is to add whisked egg whites.

Now let's think about how these initial tiny bubbles that are placed into the batter grow and merge into the remarkable structure of bubbles in the finished cake. As a whole this is a complicated process – there is a large number of bubbles and their growth is affected by many different factors. But we will simplify the problem by focusing on a single bubble and considering the conditions under which it grows, how fast it grows, and how this depends on the recipe. At the end we will think about how the lessons learned from this single bubble apply to the structure of the entire cake or bread.

We discussed bubbles in the context of emulsions and foams in Chapter 8. In the case of foams, the air bubbles are surrounded by liquid instead of batter, but some of the same principles apply. In foams, we learned that the surface of a bubble costs energy, and the bubble wants to shrink due to the surface tension pulling inwards. In order for the bubble to remain in equilibrium it must be balanced by a higher air pressure inside the bubble than outside. We called this pressure difference the Laplace pressure and related it to the surface tension, σ , and the radius of the bubble, R , according to the following equation:

$$\Delta p = \frac{2\sigma}{R}$$

It is worth thinking about the Laplace pressure equation for a moment in the context of the bubbles in the batter. Like all surfaces, the bubbles in the batter must have a surface tension that is pulling inwards (Video 9.2). Given this, what is it about the bubbles that make them not close up upon themselves? In other words, what is resisting the energy of the surface tension? There are two possible answers to that.

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Video 9.2 The bubbles of air, water vapor, and carbon dioxide in the batter, all have a surface tension, which is contributing to the bubbles trying to close in on themselves. This action is offset by surfactants and the viscosity of the batter.

One is related to what we learned in the context of emulsions about how surfactants lower the surface tension of an interface. Cake batter naturally has lots of surfactants in it in the form of milk, butter, and eggs that may be preventing the bubbles from closing. Another possible explanation is that the batter is so viscous that it prevents the closing. The slow flow of the batter may outcompete the small inward force, making the closing action slow enough that the cake has time to bake before it happens.

9.11 Making Bubbles 2

9.11.1 Bubbles Formed by Carbon Dioxide

The previous section introduced the physics of bubbles in the context of baking more generally. What about in the context of carbon dioxide gas? In section 9.3, we found that the yellow birthday cake recipe resulted in 0.06 moles of carbon dioxide gas from the baking soda and baking powder. This corresponds to 2.36 grams. Where did all this carbon dioxide go?

There seem to be three possibilities. First, the gas could dissolve in the batter. The batter is made of liquid, and just like with any liquid the gas could dissolve in it. Second, the gas could go into the bubbles. We know that it must get into the bubbles eventually because that is what happened in the yellow birthday cake, but that does not mean that this happens initially. The third possibility is that the gas escapes.

Let's think about the third possibility first. It is certainly likely that some of the gas in the cake will escape. It is difficult to estimate how much, but you could imagine experiments that could help you find out. For example, you could prepare a batch of yellow birthday cake batter and compare the actual and predicted volumes of the final cake based on predicted carbon dioxide content as we did in section 9.3.

Different recipes most likely differ in the amount of gas that escapes. For example, you could imagine that a very viscous bread dough would be able to trap gas much more effectively than a more fluid batter would. The gluten of the bread dough would be strong enough that the bubbles would simply expand under the pressure of the gas, and only under very high pressure would they break and the gas escape.

9.11.2 The Solubility of Carbon Dioxide in Batter

Let's now ponder possibility number one, which is that the gas dissolves in the batter. To find out if it does this or not, we need to consider the solubility, which is simply a measure of how much of a certain type of molecules you can dissolve in a certain type of liquid. For example, in Chapter 3, we discussed the solubility of sugar in water. Since batter is mostly made of water, we can look up the solubility of carbon dioxide in water as a function of temperature and get some idea of what happens during baking (Fig. 9.26).

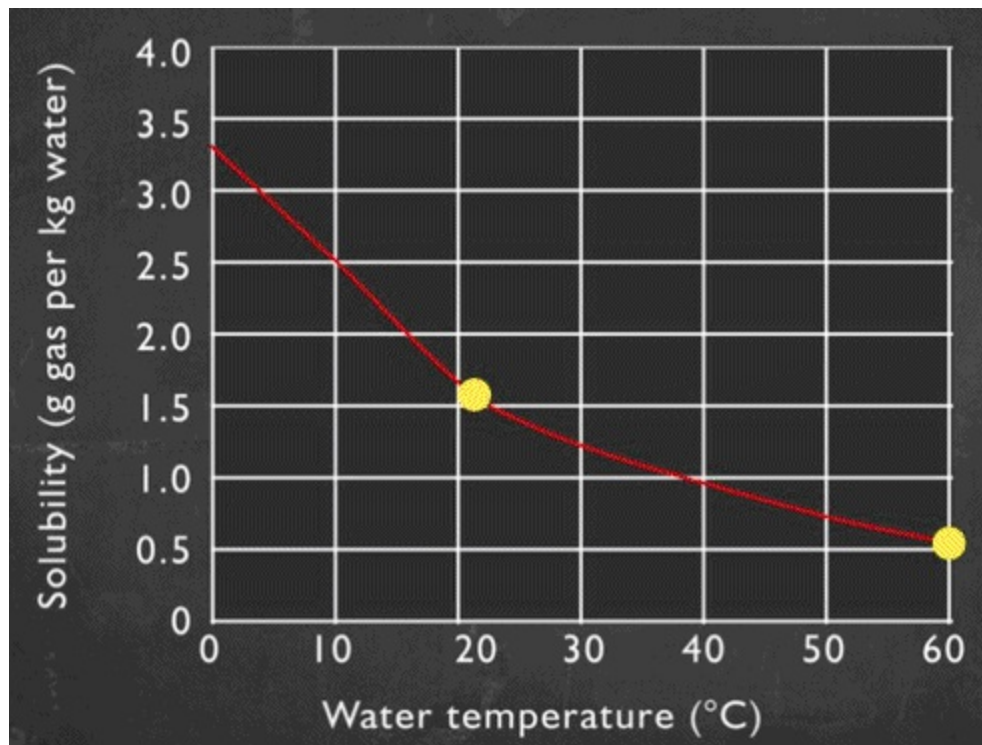


Figure 9.26 Plot showing the solubility of carbon dioxide in water as a function of temperature. The solubility of carbon dioxide decreases as the temperature increases.

The cake starts out at room temperature. It then heats up to between 60-80°C in the center depending on the exact recipe, and usually more than this closer to the edges. The plot shows that at room temperature about 1.5 grams of carbon dioxide can dissolve in a liter of batter. However, if the temperature increases to 60°C, which is the temperature at which some egg proteins start to denature, only about 0.5 a grams of carbon dioxide can dissolve.

What does this mean for the yellow birthday cake recipe? Recall that the batter added up to about 2 liters, which, according to the plot, would be

able to dissolve an entire 3 grams of carbon dioxide gas. But the recipe only produced 2.36 grams. So this means that initially all of the carbon dioxide gas from the baking soda would be dissolved in the batter. Of course, we can't know this for sure, but certainly this makes sense since the chemical reactions occur within the batter.

9.11.3 Finding the Velocity of Bubble Growth

Following this argument through, this means that initially the little air bubbles are not pressurized at all. They are simply hanging out in the batter. As soon as the cake is heated the situation changes though. The solubility of carbon dioxide goes down and it starts coming out of the batter and filling up the bubbles. As a result, the pressure inside the bubbles increases, and this causes them to expand. While the bubbles are expanding they are out of equilibrium. In other words, it is no longer true that the pressure difference between the inside and outside of the bubble is balanced with the surface tension. If that were true the bubble would not grow. Instead the pressure difference, Δp , is larger than $2\sigma/R$ in the Laplace equation.

As the bubbles grow, they are pushing the batter around them out, and in fact, it is the resisting viscous stress from the batter that is providing the balancing force to the unbalanced Laplace equation, thus slowing down the growth of the bubbles (Video 9.3).

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[movie_3_09_baking_bubblegrowth_slide_14_1.mp4](#)

Video 9.3 When the cake is heated, gas comes out of solution, causing the bubbles to expand. The growth of the bubble is counteracted by the viscous stress of the batter.

We can express this with an equation, where viscous stress is equal to the pressure difference, $p_{\text{out}} - p_{\text{in}}$, minus the force from the surface tension, $2\sigma/R$.

$$\text{Viscous stress} = p_{\text{out}} - p_{\text{in}} - \frac{2\sigma}{R}$$

We can rewrite this equation, if we consider that the viscous stress can be expressed in terms of the viscosity, η , the bubble radius, R , and the velocity, v , at which the bubble expands. You then get the following expression, where it turns out that v/R is what is called the sheer rate, and that viscosity times the sheer rate is the viscous stress.

$$4\eta \cdot v / R = \Delta p - \frac{2\sigma}{R}$$

If you solve for the velocity, v , you will have a formula that contains within it everything you need to know about how a bubble in the batter grows.

$$v = \frac{\Delta p R - 2\sigma}{4\eta}$$

We can use this equation to think about the various scenarios that might occur when baking. For example, in the context of carbon dioxide, where we are under the assumption that all of the carbon dioxide gas is initially dissolved in the batter and will come out of the batter when heated. By the time the temperature is 60°C, the solubility has been reduced by a factor of three, which means a lot of gas has been released and the bubbles have grown. All of the gas will not have come out at once though, but rather, it will be released gradually as the temperature increases (Video 9.4). What the equation tells us is that as Δp increases a little, the bubble will grow, and as it increases yet further, the bubble will grow some more. And this will continue until the end of the recipe when the cake is done.

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Video 9.4 The carbon dioxide produced in the recipe is initially dissolved in the batter. As the temperature increases the solubility of carbon dioxide goes down, and it gradually comes out of solution.

9.11.4 Complexities of Bubble Growth

The equation for the velocity of bubble growth is very useful, but it is even more complex than it may initially seem. As the batter is heated, not only is the carbon dioxide solubility going to change, the material constants themselves will also change. As the bubble grows, the radius will increase. In addition, the viscosity, η , will change as the batter is heated. Generally, the viscosities of materials decrease with increased temperature, meaning they become easier to expand. However, in the case of a cake the situation is complicated because in addition to the batter becoming less viscous, there are also elastic cross-links forming between glutenin molecules and egg proteins, and this has the opposite effect. Toward the end of baking the elasticity will win out and the cake will become solid. When this happens, the bubble growth will be significantly slowed down, and then eventually stop.

Baking gets even more complicated. In addition to the changing material constants and the decreasing solubility of carbon dioxide, we also have to consider the release of water vapor. This is well known to be an important part of baking and also occurs as the temperature increases. Since water has a different phase behavior than carbon dioxide, though, the release occurs at a different rate, making it additionally complicated to predict the growth of a bubble.

As a final note we should also point out that we have focused on the case of only one bubble in this discussion. In reality, there are lots of bubbles growing in a dough or batter, each going through a process like what we have just described, and each interacting with the other bubbles in some complicated way that goes beyond this discussion. Getting all of these variables right in a cake or bread recipe is absolutely critical in order to end up with the right texture, and this starts to explain why it can be so hard to bake a cake.

CHAPTER 10

Enzymatic Reactions and Fermentation

TABLE OF CONTENTS: 10

10.1 Introduction to Enzymatic Reactions

[10.1.1 The Mechanism of Enzymes](#)

[10.1.2 Enzymes and Food](#)

[10.1.3 Effect of Temperature on Chemical Reactions](#)

[10.1.4 Equation of the Week I](#)

10.2 Transglutaminase

10.3 Philosophical Introduction to Fermentation

10.4 Introduction to Microbes

[10.4.1 Diversity of Microbes and Fermented Foods](#)

[10.4.2 Microbial Metabolism and Competition](#)

[10.4.3 Foods Produced with Microbes](#)

10.5 Wine

[10.5.1 Calculating the Final Alcohol Content](#)

[10.5.2 Manipulating Sugar and Alcohol Content](#)

10.6 Vinegar

[10.6.1 Calculating the pH of Vinegar](#)

[10.6.2 Pineapple Vinegar: Decoding a Recipe](#)

10.7 Microbe Growth

[10.7.1 Exponential Growth of Microbes: Equation of the Week II](#)

[10.7.2 Example: Growth of Salmonella](#)

10.8 Microbe Growth Conditions

10.9 Microbe Death

[10.9.1 Food Safety and Microbial Death Rates](#)

[10.9.2 Pasteurization of Milk](#)

[10.9.3 Safety and Cooking Times of Meat](#)

CHAPTER 10

10.1 Introduction to Enzymatic Reactions

In the second half of this chapter we will delve into the scientific concept of fermentation and its various culinary applications. However, in order to fully understand fermentation, we first have to take a closer look at enzymatic reactions. The reason for this is that all fermentation processes are ultimately due to enzymes. It is the enzymes inside yeast or bacteria that are producing the molecules that give fermented foods their characteristic flavors and aromas. Enzymes are also highly related to food and cooking since they are responsible for the digestion of food in our bodies. They break down food components into small pieces and, in the process, extract energy that we need to live.

10.1.1 The Mechanism of Enzymes

You may already be familiar with enzymes in other contexts. For example, if you know anything about lactose intolerance, you may be aware that this is caused by a lack or deficiency in the enzyme that breaks down lactose in milk. The enzyme is called lactase. As is often the case with enzymes, its name combines the name of the molecule it breaks down with the ending “ase”. Peptidase and protease are other examples. A person with lactose intolerance can take a lactase pill just before eating dairy, and this artificially helps the body break down the lactose so that the person can avoid the uncomfortable symptoms associated with the intolerance.

Enzymes are proteins, which means that a lot of what we have already learned about proteins, is also true for enzymes. Just like other proteins, they will denature in the presence of heat, salt, or large changes in pH. Enzymes are very special proteins though. They work by speeding up or facilitating chemical reactions, each enzyme usually being uniquely designed for a particular reaction. Depending on the enzyme, they either help to break bonds or to make bonds form (Fig. 10.1). In either case, the first step is usually that the enzyme binds to the molecule or molecules in question. For bond breaking, the enzyme will then facilitate the bond breaking by affecting the molecule in some way. For bond formation, the enzyme often works by bringing two molecules closer together, and sometimes initializing a chemical reaction that leads to the two molecules eventually bonding to each other.

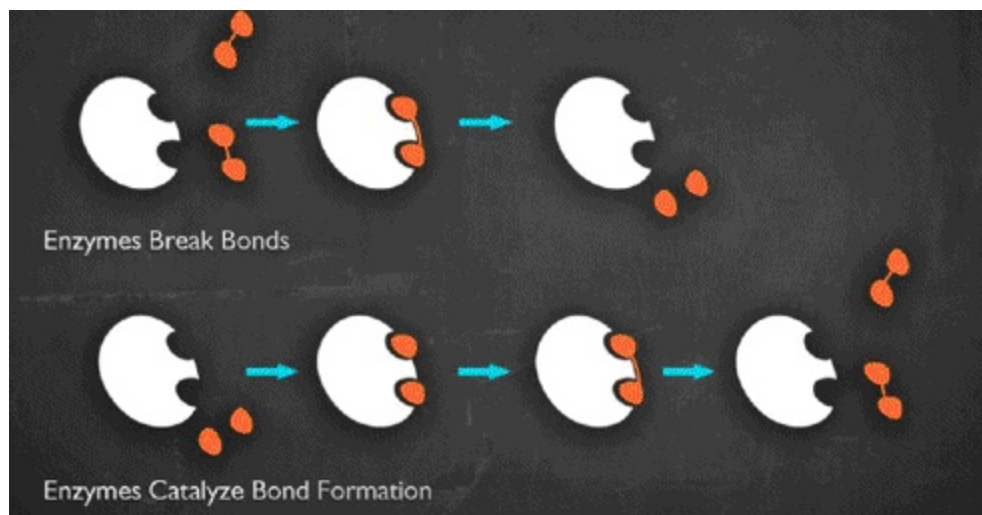


Figure 10.1 Enzymes speed up reactions either by helping to break (top) or make (bottom) bonds.

Since enzymes have such precise functions, it is understandable that they also have very specific three-dimensional structures that allow for the correct interaction with their substrates. If the structure is disrupted in some way, as would be the case if parts or all of the enzyme is denatured due to heat or altered pH, the enzymatic reaction is inhibited.

One way to think about enzymes is in terms of activation energy. This is the energy we need to put in in order to make the reaction happen. On the reaction energy diagram below, the activation energy is the “hill” of energy separating the reactants from the products (Fig. 10.2). Enzymes work by lowering this hill, or expressed correctly, by lowering the activation barrier, so that less energy input is required for the reaction to take place.

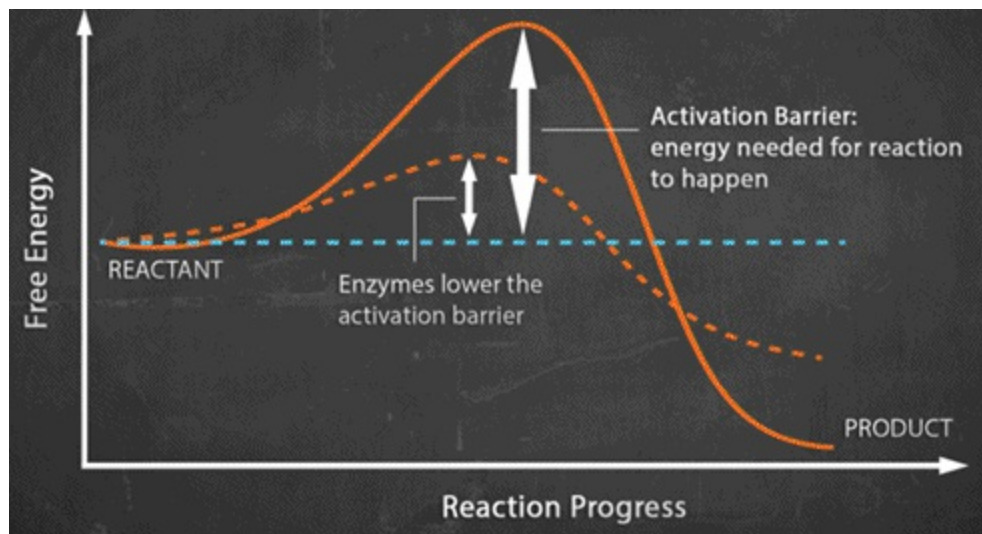


Figure 10.2 Energy profile for a hypothetical reaction in which a reactant is converted to a product. The most important way in which enzymes speed up reactions is by reducing the activation barrier. Both the uncatalyzed (orange solid line) and catalyzed (orange dotted line) reactions are shown as compared to the initial energy of the reactant (blue dotted line).

10.1.2 Enzymes and Food

Enzymes are important for food and cooking in many ways, often in contexts that we are not readily aware of. The enzyme rennin is critical to most cheese making, for example. It works by breaking one of the bonds in casein, which is an important protein in milk. As a result, casein loses its negative charge, which in turn causes the casein clusters in the milk to fall apart and coagulate. So rennin ultimately has the same effect on milk that heat and vinegar have when making ricotta cheese—it causes the milk to curdle, which, as you know, is the first step of cheese production (Fig. 10.3).

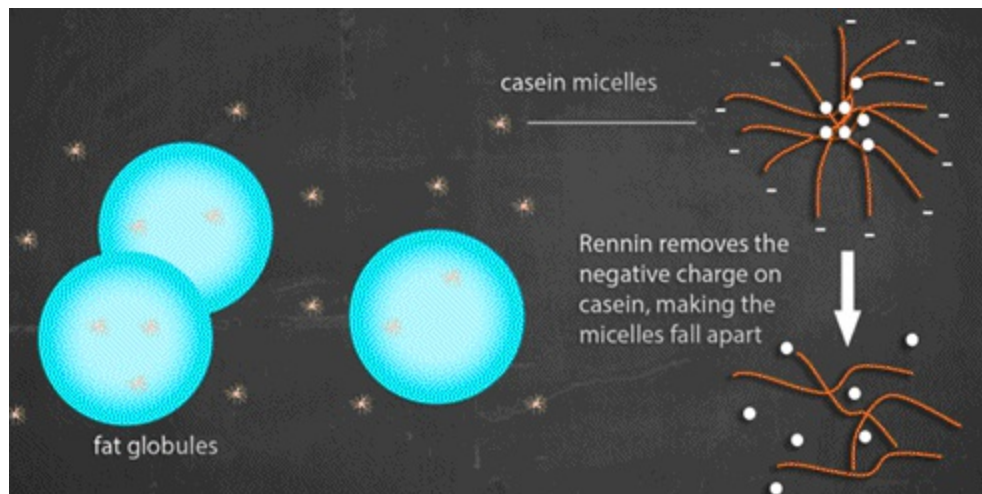


Figure 10.3 The enzyme rennin is widely used in cheese production. It works by cleaving the negative charges off the casein micelles in milk, which causes the micelles to fall apart and a subsequent formation of a network of new bonds. On a macroscopic level these chemical transformations are visible as the milk curdling.

The browning of fruits and vegetables is also due to enzymes (Fig. 10.4). Normally the enzymes that cause browning are stored in special compartments of the cells, but when you slice or bite into a fruit or vegetable, they are released and can interact with other molecules in a way that leads to browning.



Figure 10.4 The browning that occurs in fruit and vegetables is caused by enzymes.

In the case of fruit, the enzyme polyphenoloxidase interacts with phenolic compounds in the presence of oxygen, and causes the formation of large brown compounds (Fig. 10.5). Normally the polyphenoloxidase and the phenolic compounds are kept apart in the cells, preventing the reaction from taking place spontaneously. It is only when the cells are ruptured that the molecules mix and are exposed to oxygen. This can happen when humans bite or cut into the fruit, but it also happens as the result of attacks by insects, in which case the brown pigment acts as a deterrent. So the unappetizing brown color that develops on an apple or avocado after leaving it cut open on the counter is ultimately a matter of self-defense for the plant.

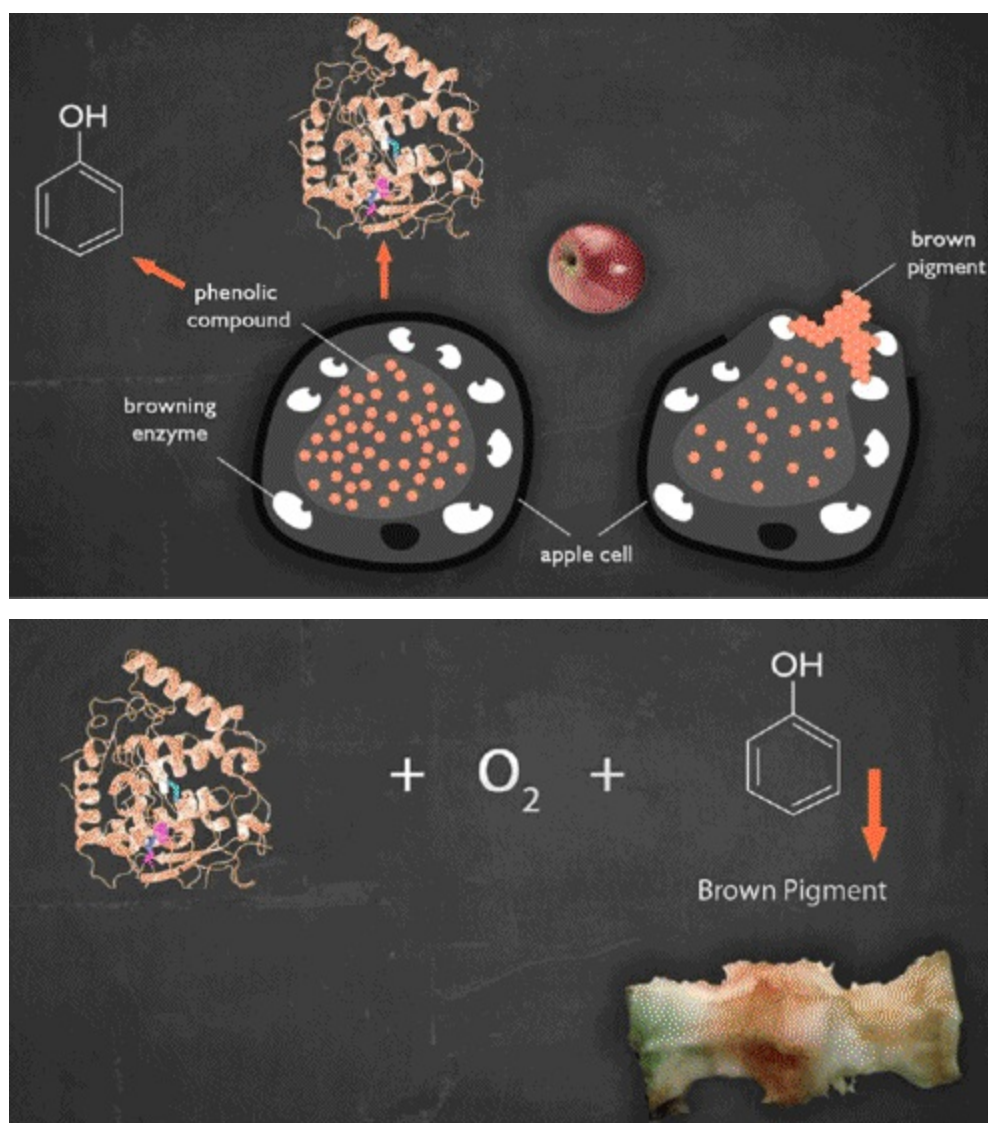


Figure 10.5 In an intact fruit cell, phenolic compounds and the enzyme that causes browning are separated. In a damaged cell, however, the two molecules are brought into contact with each other and with oxygen, causing large brown pigments to form. (Adapted from: On Food and Cooking, Harold

The effect of enzymes is sometimes desired when cooking, and sometimes unwelcome. Fortunately, since all enzymes are proteins, we can often use what we know about proteins to get the effect we are hoping for. For example, applying heat, or significantly altering the pH, will usually deactivate an enzyme if its effect is unwanted. This is actually a trick used when making pineapple jelly. If you have ever cooked pineapple jelly yourself, you know that one of the first steps is to heat the pineapple. The reason for this is that pineapple contains the enzyme bromelain, and bromelain, it turns out, breaks down proteins. This can be useful in some contexts. For example, along with papain in papaya, which has the same effect, bromelain is a common ingredient in meat tenderizers (Fig. 10.6). But in the context of making pineapple jelly, the enzymatic effect of bromelain is less desirable. Left unchecked, it will break down gelatin, the ingredient that is causing the jelly to gel, and the jelly will remain a fluid. Fortunately, this is easily fixed by quickly heating the pineapple, which denatures the enzyme so that it loses its activity.

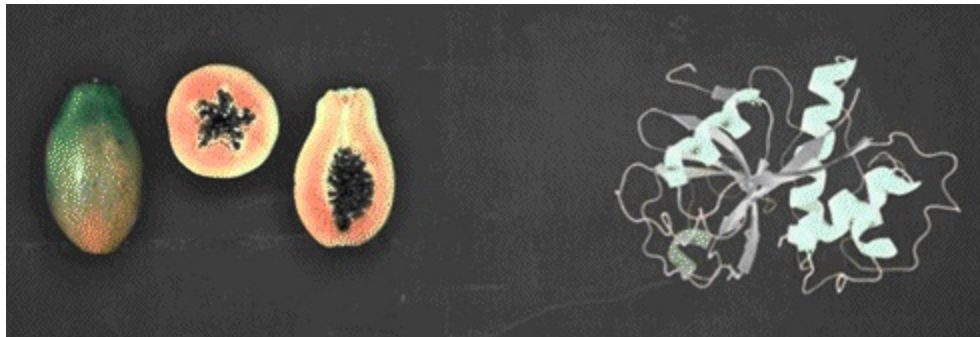


Figure 10.6 Papaya contains the enzyme papain, whose ability to break down proteins makes it suitable as a meat tenderizer. (Molecular structure adapted from Greg Verdine.)

America's Test Kitchen has some great tricks for how the power of enzymes can conveniently be turned off when making pesto. Basil, one of the key ingredients in pesto, quickly turns brown if damaged, resulting in pesto going from a rich green color to drab brown shortly after it is made. Not surprisingly, this is due to an enzyme. America's Test Kitchen advises that the enzyme can be inactivated by adding lemon juice or ascorbic acid to the pesto, and it will stay green for much longer. The same trick, just a few drops of lemon juice, also keeps avocado from turning brown for much the same reason.

10.1.3 Effect of Temperature on Chemical Reactions

All chemical reactions, regardless of whether they are facilitated by enzymes or not, tend to occur faster in the presence of heat. If an enzyme is involved, the temperature clearly cannot be increased so much that the enzyme is denatured, but even a small increase in temperature tends to speed up the reaction. If you have ever left fruit or vegetables outside the fridge in order to make them ripen faster, you already know about this intuitively. Similarly, when baking bread, you make sure not to put it to rise in a cold spot, as it would slow down the process.

Yet another example is collagen. If you slow cook meat, the temperature is kept relatively low, around 50-60°C for a long time. This has the effect that the collagen is slowly broken down to gelatin, something that would take a very, very long time if the meat were kept at room temperature. So temperature tends to increase the reaction rates of chemical reactions.

We can understand the same concept in terms of the energy reaction diagram in Figure 10.2. An increase in temperature essentially means that some of the activation energy is supplied by the environment in the form of thermal energy. For example, if the chemical reaction in question involves two molecules bonding to each other, you would want to increase the likelihood that they were in position so that they could react. One way would simply be to make the molecules move around more, and then the likelihood of them bumping into each other and reacting would increase. This could easily be accomplished by increasing the temperature, which increases the jiggling, or the kinetic energy, of the molecules.

10.1.4 Equation of the Week I

The effect of temperature on the rate of chemical reactions is described in an equation called the Arrhenius equation. The Arrhenius equation says that:

$$k = k_0 e^{-\Delta u / k_B T}$$

In this equation, k is the rate of the reaction, k_0 is the maximum rate each molecule would have if it had the maximum energy needed to get over the activation barrier in the chemical reaction diagram, and Δu is the energy barrier. In other words, the higher the barrier, the more energy is needed to make the reaction take place. And $k_B T$, of course, is just the thermal energy. The higher the thermal energy, the more the molecules move around, and the more energy is supplied for this reaction to take place. This is one of the two equations for this week (Table 10.1).

EQUATION OF THE WEEK		
$N(t) = N_0 e^{kt} = N_0 2^{t/\tau}$ where $k = \frac{\ln 2}{\tau}$		
Symbol	Description	Units
$N(t)$	Number of microbes at time t	Microbes
N_0	Initial number of microbes	Microbes
k	Rate of growth/death	s^{-1}
t	Time elapsed	s
τ	Doubling time	s

Table 10.1

The Arrhenius equation tells us that if the thermal energy, $k_B T$, is very large, then the exponent as a whole approaches 0. And e^0 , of course, is 1. This means that at high temperatures, the rate will be very similar to k_0 , which is the maximum rate. This would also be the case if the activation barrier, Δu , were very small. If, on the other hand, the temperature is very low, the exponent would be a large number, and consequently the reaction rate

would be much, much smaller than the maximum reaction rate. Similarly, if Δu is large, the reaction rate will also be a small fraction of the maximum rate.

The Arrhenius equation may look complicated at first glance, but it simply says that there is some maximum rate that a chemical reaction can have, and that the actual rate depends on two things: how much energy you need to put into a reaction, and how much energy you have available in the form of thermal energy. In the case of collagen, for example, applying heat at low temperatures, breaks down the collagen fibers into gelatin (Fig. 10.7). There are several steps to this, but one of them is hydrolysis of the peptide bond. You can imagine that as you slowly increase the temperature, the likelihood that this peptide bond will hydrolyze and break down into gelatin increases because the rate of the reaction increases. This is not only the principle underlying the breaking down of collagen, but of many other chemical reactions in cooking as well.

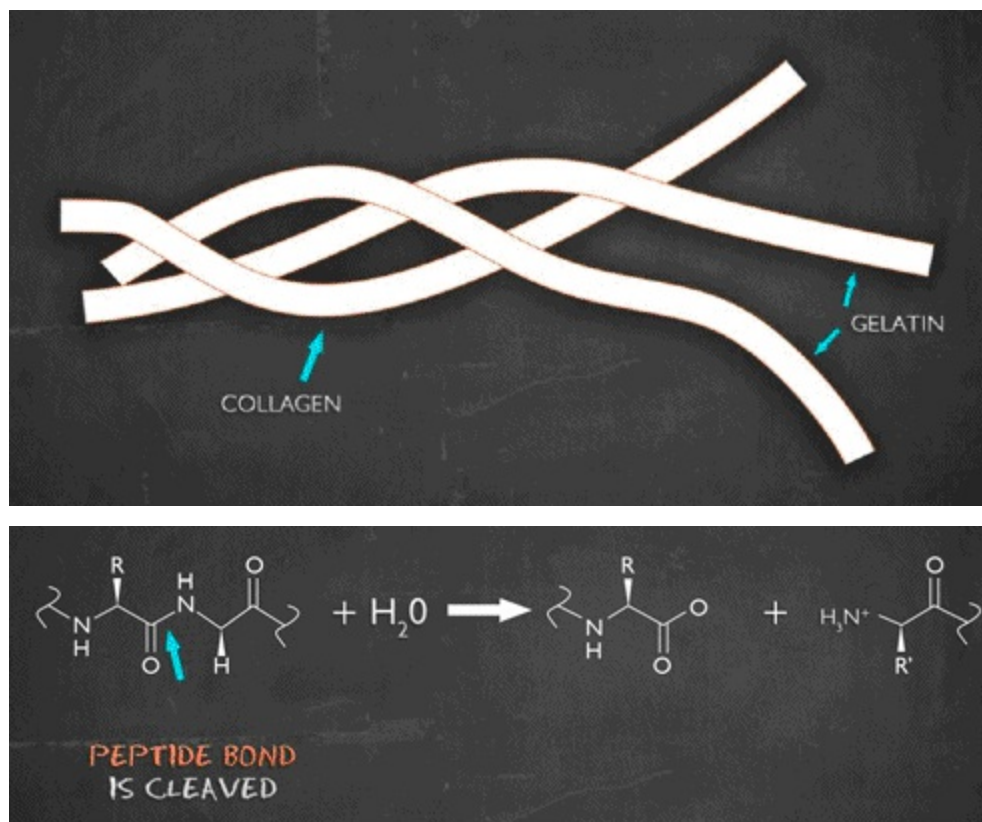


Figure 10.7 Collagen is a type of protein that consists of a triple helix of collagen chains. When heated, the helix is converted to gelatin by cleavage of the peptide bond.

10.2 Transglutaminase

An enzyme that is frequently used in the food industry is transglutaminase. It has the unique ability to attach pieces of meat to each other, acting almost like a glue, and is hence often referred to as “meat glue”. It is used in a variety of ways, such as joining small pieces of meat together into one larger piece that can more easily be cooked, or in the manufacturing of crabsticks. It is also used to great effect in haute cuisine. Chef Wylie Dufresne at restaurant wd~50, has been working closely with food scientist Ted Russin at the Culinary Institute of America for years to create a series of remarkable dishes involving this enzyme, such as noodles made purely out of shrimp or carrots.

Transglutaminase works by covalently cross-linking two aminoacids to each other. Covalent bonds, as you probably recall, are very strong bonds, and hence, even after the application of heat during cooking, the bonds are not broken and the meat sticks together.

Transglutaminase is a natural product and can be found in plants, animals, and even humans. For the purposes of cooking, it is harvested with the help of a soil bacterium, a procedure invented by a company named Ajinomoto. Both the process and the final product are natural. For those of you who are concerned with the safety of this particular food additive, Dave Arnold’s blog Cooking Issues features an informative discussion under this link:

<http://www.cookingissues.com/primers/transglutaminase-aka-meat-glue/>

There are different types of transglutaminase and knowing the difference between them is useful when studying recipes in which it is an ingredient, such as in the remarkable recipes by Chef Wylie Dufresne. The different types are all produced under the brand name Activa, each containing different mixtures of the enzyme and other ingredients that are commonly used in these recipes. There is Activa TI, Activa RM, and Activa GS.

Activa TI: Pure transglutaminase, some maltodextrin

Activa RM: Transglutaminase, maltodextrin, sodium caseinate

Activa GS: Transglutaminase, maltodextrin, gelatin, held at basic pH

Activa TI consists of pure transglutaminase and one additional component,

maltodextrin, which primarily acts as a filler.

Activa RM also contains a mixture of transglutaminase and maltodextrin, but in addition, it also contains sodium caseinate. This is a milk protein, which means it contains aminoacids. It provides an immediately available substrate for the transglutaminase enzyme to act upon when used in the context of food.

The third type, Activa GM, is a mixture of transglutaminase, maltodextrin, and gelatin. Similar to sodium caseinate, gelatin is a protein and contains readily available aminoacids for the enzyme. The other interesting feature about Activa GM is that it has a base added to the mixture.

Transglutaminase is inactivated at low pH, so the base ensures that the enzyme does not lose its potency before being added to the meat intended to be glued together. So the chef can prepare a solution of transglutaminase, also known as a slurry, and have it sit around the kitchen for some period of time. Since meat is slightly acidic, the slurry will not become active until it is added to the meat.

10.3 Philosophical Introduction to Fermentation

So far in this course, we have discussed proteins and cooking in terms of the various ways that proteins can be denatured. We have learned that you can cook proteins either by adding heat, by changing the pH, or by adding salt. All of these methods have in common that they, in some way or other, mess up the proteins, and this has led to our idea of what it means to cook food. So, for example, when we say that we cook ceviche by marinating fish in lime juice, we are really referring to the cooked appearance the fish gets from this procedure, which, as you have learned, is due to the denaturation of proteins.

This view of cooking has an interesting implication in the following sense: All of life depends on the function of proteins. In fact, all of the chemical reactions that are necessary to keep biological organisms alive, are executed by the vast number of proteins in the cells of those organisms. Hence, if you apply any of the cooking methods we have discussed so far to an organism, you not only destroy the proteins, you also kill the organism. For example, if you put yourself in 65°C for a long enough time, the proteins in your body will denature, and you will die. The same is true when cooking an egg. By cooking an egg, the life that was in the egg gets destroyed.

While we have so far been trying to destroy proteins, and thus indirectly destroying life, we have now come to the point in the course where we want to do the exact opposite. For the recipes in the remainder of this chapter, we absolutely do not want to mess with the proteins. In fact, we want to do everything we can to pamper them and cater to their needs. The reason for this is that in this chapter, the proteins, and indeed the organisms, are doing the cooking for us.

The whole point of this chapter is to use microbes, be it yeast, mold, or bacteria, to create small molecules that in some way transform the food, either by enhancing flavor and aroma, by acting as preservation agents, or by increasing the alcohol content. This means that when we cook with microbes we have to be very specific about the environmental conditions.

For example, when baking bread, we make sure that we are not letting the

dough rise at too low or too high of a temperature. Outside of a certain temperature range the yeast will not be happy, and we will end up with bread that has not risen properly. When reading recipes or watching chefs prepare recipes using microbes, you should pay special attention to how carefully the various environmental conditions are monitored, such as salt concentration, heat, the amount of oxygen, and so on. All of these parameters are important in order to keep the microbes alive so that they can do the cooking for us.

10.4 Introduction to Microbes

10.4.1 Diversity of Microbes and Fermented Foods

Figure 10.8 shows a picture of a diverse array of foods. If you were shown this picture out of context and asked to figure out what the foods have in common, you would probably be hard pressed to find an answer. The flavors of coffee, chocolate, wine, vinegar and yogurt are incredibly different from each other. Yet, these foods do have something in common, and the title of this chapter gives it away—they have all been produced with the help of microbes.

The use of microbes in food production is very common, perhaps much more common than many people realize. This is yet another example of how the scope of cooking is much broader than the traditional idea of it. The rest of this chapter is devoted to understanding the processes that give rise to these diverse flavors in more detail.



Figure 10.8 Microbes are used in the production of a wide variety of foods. Clockwise from top left: yoghurt, wine, beer, vinegar, chocolate, kimchi, coffee, olives, bread, and miso soup.

Figure 10.9 shows microscope pictures of some of the most commonly used microbes in food production. Yeast is used for baking bread or brewing beer. Molds are used in a variety of cheeses and in the production of soy sauce. Various bacterial strains have very broad applications; the picture shows lactic acid bacteria, which are used for making yogurt.

Microbes have been used for different purposes in the context of food and

drink for millennia. The most important objective has possibly been food preservation. Before refrigerators and freezers, fermentation was one of a very limited number of ways to preserve foods. Another aim of fermentation is flavor intensification. Soy sauce is a great example of the very intense flavors that can result from fermentation. Yet another goal has been intoxication. The earliest evidence of this is 8000 year old remains of wine found in wine jars in present day Iran. This is some of the earliest evidence we have of microbes being used to enhance food, but it is likely a practice that has been going on for much longer than this.

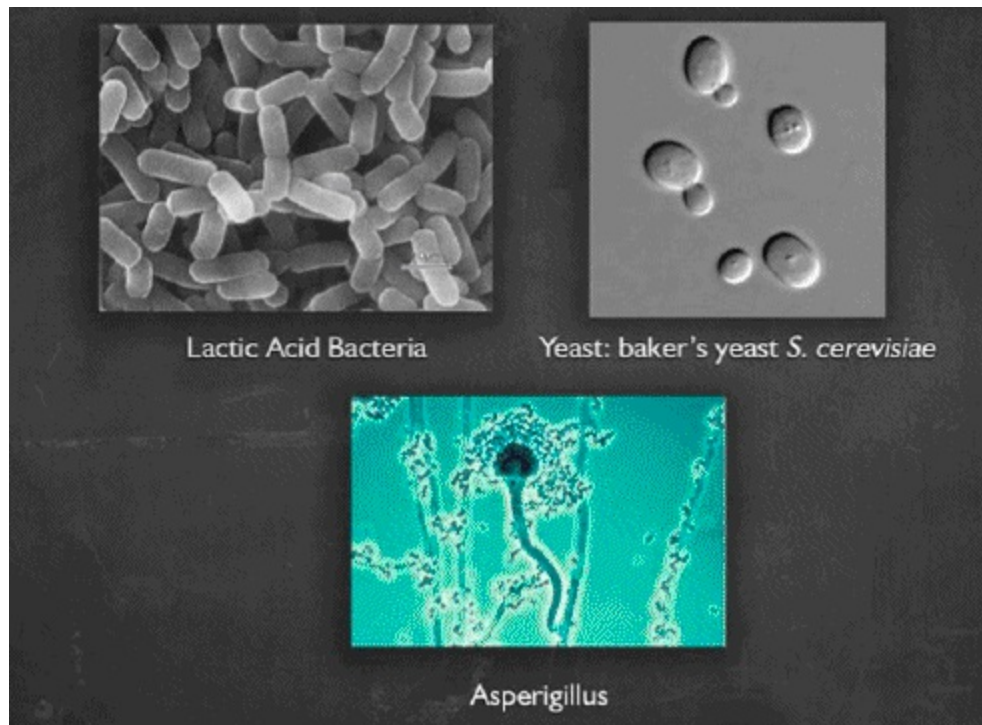


Figure 10.9 Microscope images of lactic acid bacteria, baker's yeast, and Aspergillus, a common mold.
(Source: US Department of Health and Human Services, <http://microbiologyglossary.wikispaces.com>)

Different cultures have employed fermentation in different ways and on different foods. Some examples are German sauerkraut, Italian preserved lemons, Japanese natto, Korean kimchee, pickles, soy souce, chocolate etc. The wide range of foods and flavors illustrate the diversity that is possible with fermentation.

10.4.2 Microbial Metabolism and Competition

Microbes are incredibly versatile organisms and various species can survive in environments that would be too inhospitable for all other living organisms. They are found on the bottom of oceans, near volcanic springs, and in your gut. They seem to be capable of turning just about anything into a food source. In general, they turn large molecules like carbohydrates and proteins into much smaller molecules (Fig. 10.10). You already know of an example of this from Chapter 9, where yeast turned the carbohydrates from flour, first into sugar, and then into carbon dioxide and ethanol, both of which are very small molecules.

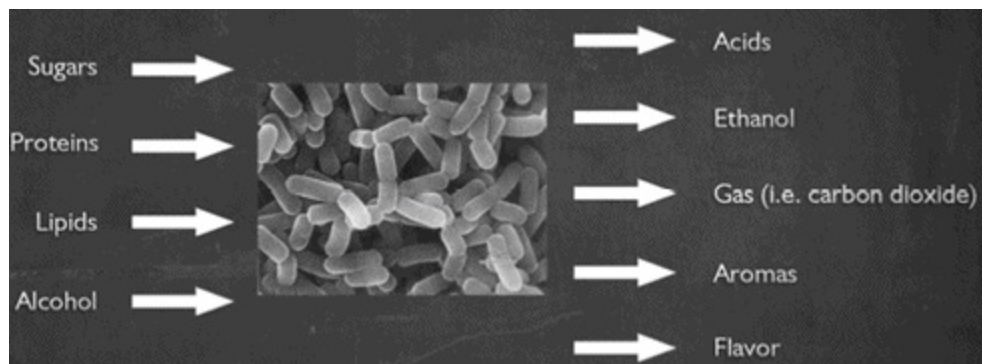


Figure 10.10 Microbes can utilize a diverse array of food sources to survive. Their digestive enzymes convert large macromolecules, such as proteins, fats, and carbohydrates, into small molecules, and derive energy in the process.

A lot of flavor and aroma compounds are also small molecules. Figure 10.11 shows some examples of compounds that give many foods their characteristic flavor or aroma. For example, 2-methyl propanol smells like bananas and benzaldehyde smells like almonds. Further, diacetyl is a molecule that is often produced during wine fermentation and gives some white wines their buttery flavor. Interestingly, the same molecule is also found in buttermilk, giving rise to the same buttery flavor there. All of these small molecules can be produced with microbial digestive enzymes. In fact, they are often the by-products of the digestive process in which microbes utilize various food sources and break them down to gain energy.

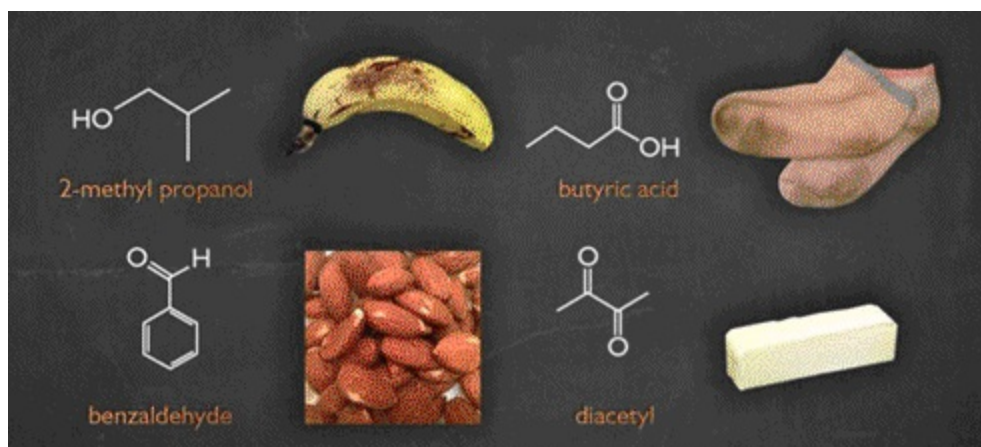


Figure 10.11 Many flavor and aroma molecules are small molecules. Some examples include: 2-methyl propanol which smells like bananas, benzaldehyde which smells like almonds, butyric acid which smells like wet socks, and diacetyl which tastes buttery.

Microbes are everywhere, and luckily, for the most part, they are harmless for humans. When they are used for cooking, we usually either add a specific microbe to the food in question, such as adding yeast when baking bread, or we simply utilize the microbes that are naturally occurring in the environment. In either case, the microbes start to use the food as a food source and the population grows. As part of the digestive process, the microbes produce small molecules, some of which act as poisons for other surrounding microbial strains. For example, brewer's yeast produces alcohol, which is toxic to most microbes. The result is that over time, one or a few of the microbial species will outcompete the others. They will take over the food source. The other microbes disappear and die, and this includes many harmful bacteria. So the food can be preserved for a long time because a harmless microbe has been allowed to take over and dominate the food source in a way that makes it impossible for harmful bacteria to live there. It is a pleasant coincidence that many of the molecules that result from the digestive processes, whether used for chemical warfare between different species or not, taste delicious to our taste buds, giving the characteristic flavor intensification of fermented foods.

10.4.3 Foods Produced with Microbes

Olives, kimchi, and sauerkraut are examples of fermented foods where the microbe responsible for fermentation is already naturally living on the vegetable and using the starches and proteins of it as a food source (Fig. 10.12). By having the recipe provide the right environment, the desired populations can thrive and grow. In the process, they produce an acid, and since low pH is harmful for most bacteria, other microbes are wiped out allowing the harmless, acid-producing bacteria to take over. Consequently, the foods last longer, and have also acquired new flavors.



Figure 10.12 Kimchi, a traditional Korean dish of fermented cabbage and other spices and vegetables, is made using the naturally occurring microbes on the raw vegetables.

Another example is brewer's yeast (Fig. 10.13). You probably know from experience that alcohol kills bacteria. For example, isopropanol is commonly used as a disinfectant in many first-aid kits. Brewer's yeast works the same way. It kills competing microbes by producing alcohol. Only a very small number of bacterial strains can survive around alcohol, and even to them, alcohol at high enough concentrations is very toxic. Depending on the specific yeast strain, the highest tolerable amount of alcohol varies, but the highest level is somewhere around 20%. This is the reason that whiskey, which has a very high alcohol percentage due to distillation, can sit open on your shelf for years and years without going bad, whereas a bottle of wine,

which contains 10-15% alcohol, is only going to keep for a couple of days.

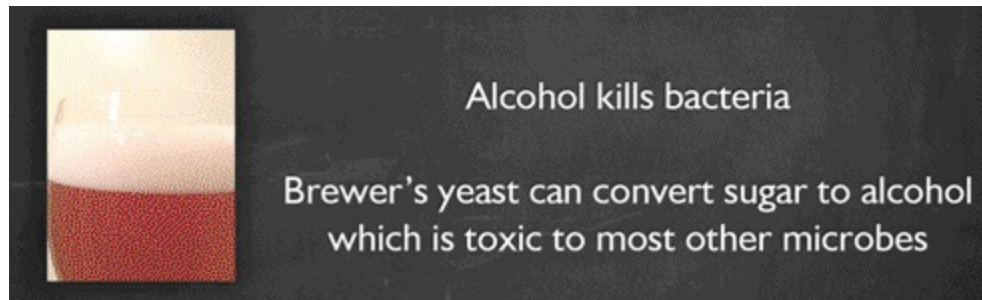


Figure 10.13 Brewer's yeast can convert sugar to alcohol, which is toxic to most other microbes. This is one example of how microbes secrete molecules as part of the chemical warfare between different species.

Another example is lactic acid bacteria, which is used to make yogurt, sour cream and other fermented dairy products (Fig. 10.14). These bacteria are able to use lactose as a food source and turn it into lactic acid. Lactose is actually a very uncommon sugar in nature, but it occurs in milk, and the bacteria that are able to metabolize it, have created a very special niche for themselves. The lactic acid lowers the pH, which wipes out all of the other bacteria. By making yogurt and sour cream, we are simply utilizing this process. The resulting products are delicious and slightly sour foods that keep longer than regular milk because of the inhospitable environment created by the lactic acid bacteria.

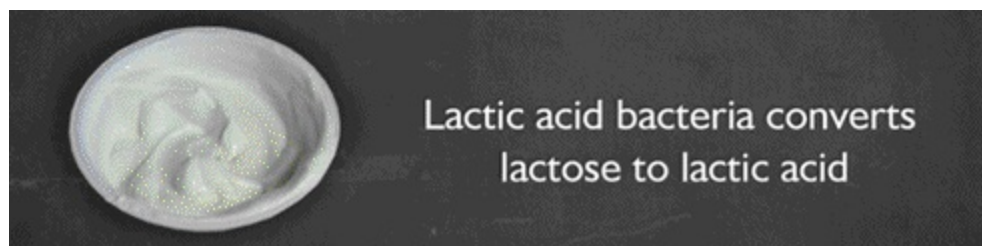


Figure 10.14 Lactic acid bacteria can convert lactose to lactic acid, which lowers the pH and thus creates an inhospitable environment for other microbes.

The miscellaneous varieties of cheese illustrate just how diverse the flavors of fermentation can be (Fig. 10.15). They range from mild to very strong and stinky. Typically, the longer a cheese has been aged, the stronger the flavors.



Figure 10.15 The variety of different cheeses available is a result of many different microbial communities, each producing a unique set of flavor and aroma molecules.

When making a particular type of cheese you want to leave as few things to chance as necessary, so you inoculate the milk with the bacterial strain known to produce the desired effect in the cheese you want to make. Figure 10.16 shows a table of the various microbial strains used for different cheese varieties. As the cheese ages, the initial culture usually becomes supplanted by others, and the microbial communities change. At any given time in the ageing process, a different set of microbial species is in majority. So the different species take turns outcompeting each other, each contributing their particular set of digestive molecules that contribute to the final taste and aroma of the cheese.

Species	Major known function	Product
<i>Propionibacterium shermanii</i>	Flavor & eye formation	Swiss cheese family
<i>Lactobacillus bulgaricus</i> <i>Lactobacillus lactis</i> <i>Lactobacillus helveticus</i>	Acid and flavor	Yogurt, kefir, Swiss, Emmental, and Italian cheeses
<i>Lactobacillus acidophilus</i>	Acid	Acidophilus, buttermilk
<i>Streptococcus thermophilus</i>	Acid	Emmental, Cheddar, Italian cheeses, and yogurt
<i>Streptococcus diacetylactis</i>	Acid	Sour cream, ripe cream, butter, buttermilk and starter cultures
<i>Streptococcus lactis</i> <i>Streptococcus cremoris</i>	Acid	Cultured buttermilk, sour cream, cottage cheese
<i>Streptococcus durans</i> <i>Streptococcus faecalis</i>	Acid and flavor	Cheddar, some Swiss cheeses
<i>Leuconostoc citrovorum</i> <i>Leuconostoc dextranicum</i>	Flavor	Sour cream, cottage cheese, ripened cream butter

Figure 10.16 Depending on the cheese being produced, milk is inoculated with specific bacterial species

Chocolate is yet another example of a fermented product. In this case the raw cocoa beans are fermented, creating the intense cocoa flavors that are so distinctive of chocolate (Fig. 10.17).



Figure 10.17 The first step in the production of cocoa powder and chocolate is fermentation of the raw cocoa beans.

Miso is an example of a fermented product that is actually created with two subsequent fermentation steps (Fig. 10.18). It starts by inoculating boiled rice with the fungus *Aspergillus oryzae* for a few days. The next step is to add the rice to soy beans and let the mixture continue fermenting. This is what gives miso its characteristic savory taste of salt and umami.

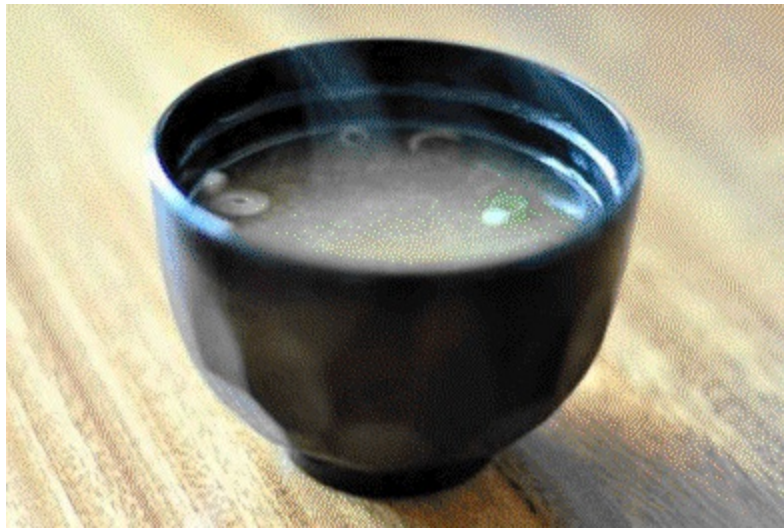


Figure 10.18 Miso is the result of a two-stage fermentation, the first using *Aspergillus* mold, and the second using lactic acid bacteria and yeast.

Chef David Chang of Momofuku in NYC has taken traditional fermentation recipes to a completely new level in his kitchen and food laboratory. He is applying traditional microbial strains to unexpected foods, thus creating entirely novel foods. Some of the most famous creations from the momofuku food lab is hozon and banji, David Chang's novel take on kimchi, and fermented pomegranate seeds.

10.5 Wine

Fermentation reactions can easily seem complicated and a little mysterious: small organisms that we cannot even see with the naked eye ingest certain molecules in a food and turn them into a diverse array of delicious molecular products. It is hard to know how we could predict or quantify a process that seems so vague and variable. Usually, though, an overall fermentation process can be simplified by studying the key reactants and products. For example, when studying the process that turns grape juice into wine, we can focus on the chemical reaction of sugar being converted into ethanol. Of course, as part of this process, many other delicious by-products are also formed by the digestive enzymes of the yeast cells, making the wine taste not just like alcoholic grape juice, but like wine. Nevertheless, by knowing the chemical equation for the primary chemical reaction, we can make some predictions about the final product. Let's see if we can use this strategy to predict the final alcohol content in a typical wine.

10.5.1 Calculating the Final Alcohol Content

Below is the balanced chemical reaction for how glucose is converted into ethanol and carbon dioxide. As you can see, for every one mole of glucose we get two moles of ethanol (Fig. 10.19).

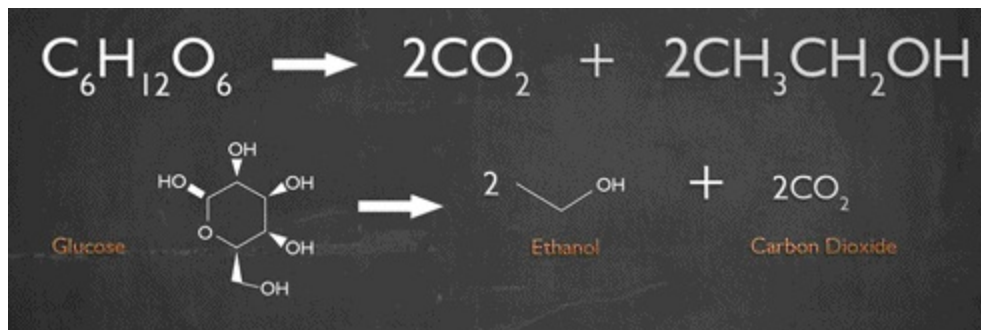


Figure 10.19 Balanced reaction of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, turning into carbon dioxide, CO_2 , and ethanol, $\text{CH}_2\text{CH}_2\text{OH}$. For every one mole of glucose there are 2 moles of carbon dioxide and ethanol produced.

To calculate the final ethanol content, the first thing we have to do is find out how much glucose there is in grape juice. If we assume that all of the sugar in grape juice is glucose, we can simply read the sugar content off any nutrition facts label in the store. It turns out that Welch's grape juice has approximately 20% sugar (Fig. 10.20).

Nutrition Facts	
Serving Size: 8 FL. OZ. (240mL)	
Servings Per Container: About 7	
Amount Per Serving	
Calories 150	
	% Daily Value*
Total Fat 0g	0%
Sodium 20mg	1%
Total Carbohydrate 37g	12%
Sugars 36g	
Protein 0g	
Vitamin C	20%

Figure 10.20 Nutrition label of Welch's grape juice. The sugar content is about 17%.

A typical bottle of wine contains 750 ml of liquid, and if we assume that the initial volume of grape juice is the same as the final volume of wine, the percentage of glucose corresponds to 150 g, which is the same as 0.8 moles according to the calculation below. Further, since there is a 1 to 2 ratio

between glucose and ethanol, the amount of ethanol produced will be twice that, i.e. 1.6 moles.

$$m_{\text{bottle}} = (750 \text{ ml}) \cdot (1 \text{ g/ml}) = 750 \text{ g}$$

$$m_{\text{C}_6\text{H}_{12}\text{O}_6} = 0.2 \cdot 750 \text{ g} = 150 \text{ g}$$

$$MW_{\text{C}_6\text{H}_{12}\text{O}_6} = 180 \text{ g/mol}$$

$$\text{Moles}_{\text{C}_6\text{H}_{12}\text{O}_6} = \frac{150 \text{ g}}{180 \text{ g/mol}} = 0.8 \text{ moles}$$

$$\text{Moles}_{\text{CH}_3\text{CH}_2\text{OH}} = 2 \cdot 0.8 \text{ moles} = 1.6 \text{ moles}$$

Knowing that the molecular weight of ethanol is 46 g/mol, we can convert the number of moles to grams. It turns out we have 73 grams of ethanol. And since the density of ethanol is 0.7 g/ml, this, in turn, corresponds to approximately 104 ml, which is 13.8% of the total volume.

$$MW_{\text{CH}_3\text{CH}_2\text{OH}} = 46 \text{ g/mol}$$

$$m_{\text{CH}_3\text{CH}_2\text{OH}} = 1.6 \text{ moles} \cdot 46 \text{ g/mol} = 73 \text{ g}$$

$$\rho_{\text{CH}_3\text{CH}_2\text{OH}} = 0.7 \text{ g/ml}$$

$$V_{\text{CH}_3\text{CH}_2\text{OH}} = \frac{73 \text{ g}}{0.7 \text{ g/ml}} = 104 \text{ ml}$$

$$\%_{\text{CH}_3\text{CH}_2\text{OH}} = \frac{104 \text{ ml}}{750 \text{ ml}} = 13.8\%$$

If you have a wine bottle close by, you can compare its alcohol percentage to the 13.8% above. You will most likely find that it is pretty close. In fact, most wines have an alcohol percentage somewhere in the range of 10-15%, and the reason it is not higher is because it is limited by the sugar content of the grapes.

10.5.2 Manipulating Sugar and Alcohol Content

For most table wines all or most of the sugar is converted to alcohol, so they tend not to be particularly sweet. But what if you wanted a sweet wine? Or what if you wanted a wine with a higher alcohol content than 10-15%? One way is simply to add a little extra sugar. You can then choose to stop the fermentation at 15% ethanol, but still get a sweet tasting wine since there is still unfermented sugar left. Alternatively, you could let the fermentation reaction continue, and, as long as the yeast did not get killed by the high alcohol concentration, continue making ethanol until the yeast ran out of sugar.

Cultures around the world have come up with various creative ways of increasing the sugar content of grape juice naturally. One way is just to let the grapes sit and dry on the vine, which over time leads to an increase in the sugar content. Another way is to leave the grapes on the vine until late in the season when temperatures go below 0°C, which also increases their sugar content. This is how icewines are made. Yet another way is to inoculate the grapes with a fungus, which causes the sugar concentration to increase. Wines made with this method are called noble rot wines, and include Tokajis in Hungary or Sauternes in France.

The caveat with producing highly alcoholic wines from very sweet grapes is that even the hardiest yeast strains cannot tolerate alcohol concentrations much above 20%. Ethanol is an effective weapon in the warfare against other microbes, but it is still a toxic substance, and depending on the yeast strain the upper limit that can be tolerated is somewhere in the range of 17-20%. So if you want to make a wine with a higher alcohol concentration than this, you would either have to distill the wine, or have some other way of adding alcohol to it. Port, sherry, and vermouth, are examples of fortified wines, and all hard liquors are distilled, including whiskey, rum, and vodka.

10.6 Vinegar

In the world of microbes, there is almost always some bug that can use food sources that other bugs cannot utilize or tolerate. It turns out that this is also the case for ethanol. While ethanol is poisonous for most microbes, there are also strains that can use it as a food source. Two examples are acetobacter and gluconobacter bacteria.

If you let wine sit around for too long, it will eventually turn into vinegar. If you have ever excitedly opened an old bottle of wine, only to find that it tasted sour and off, you know exactly what we are talking about. What has happened is that the bacteria have turned ethanol into vinegar, which is the same as acetic acid. This can happen under aerobic conditions, i.e. when there is oxygen present, and carbon dioxide is produced as a by-product (Fig. 10.21).

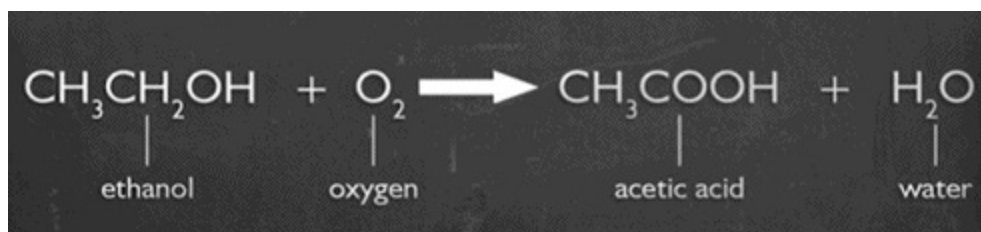


Figure 10.21 Ethanol is toxic to most microbes. Exceptions are Acetobacter and Gluconobacter, two bacterial species that are able to use ethanol as an energy source by converting it to acetic acid and water in the presence of oxygen.

Vinegar is a very powerful microbial agent. As little as 0.1% in a solution kills most microbes. This is why pickling is such a powerful preservation method; among other things it produces vinegar which keeps microbes at bay for long periods of time. Similarly, many fast-pickling recipes work by adding vinegar and brine, which together kill enough microbes to make the food keep for a long time in the fridge.

10.6.1 Calculating the pH of Vinegar

Given what we learned from our calculation of turning sugar into alcohol in wine, we can now use the same principle and figure out how much vinegar we would end up with if the bottle in the example above went bad. We already found out that the wine bottle contained 1.6 moles ethanol. Since the reaction is balanced, we would end up with 1.6 moles of vinegar as well. This corresponds to a final concentration of 2.1 mol/L according to the calculation below.

$$[\text{CH}_3\text{CH}_2\text{OH}] = \frac{1.6 \text{ mol}}{750 \text{ ml}} = 2.1 \text{ M}$$

From this we can figure out what the pH of the bottle is. Acetic acid is a weak acid and dissociates into an acetate ion and an H^+ ion in solution. The equilibrium constant is $1.8 \cdot 10^{-5}$, which corresponds to the concentration of the products divided by the concentration of the reactants.



$$k_a = 1.8 \cdot 10^{-5}$$

$$k_a = \frac{[\text{H}^+][\text{CH}_3\text{CH}_2\text{OO}^-]}{[\text{CH}_3\text{CH}_2\text{OH}]}$$

The concentration of acetate ions and H^+ ions is the same, so the nominator is $[\text{H}^+]^2$, and we already know that the concentration of acetic acid is 2.1 M, so we can solve for the H^+ concentration and find that it is 0.006 M. This corresponds to a pH of 2.2, which is actually a very good estimate for what the pH of lot of wine vinegars are.

$$[\text{H}^+] = \sqrt{(1.8 \cdot 10^{-5} \text{ M})(2.1 \text{ M})} = 0.006 \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log[0.006 \text{ M}] = 2.2$$

If the fermentation is not allowed to proceed all the way, which may be the case for balsamic and fruit vinegars, then the pH is usually higher and the vinegar is overall sweeter. Many fruit vinegars have a pH of about 4 or 5, for example. But for wine vinegar, assuming that all of the sugar turns into

ethanol, and that all of the ethanol then turns into acetic acid, a pH of around 2 is what we would expect.

10.6.2 Pineapple Vinegar: Decoding a Recipe

Below is a recipe for pineapple vinegar (Fig. 10.22). The only ingredients are sugar, water and pineapple. You mix them all together, cover with a cheesecloth, and store in a dark, cool place for six weeks to six months with intermittent sugar feedings every two weeks.



Figure 10.22 Recipe for pineapple vinegar. Adapted from Mary Karlin, *Mastering Fermentation*, 2013.

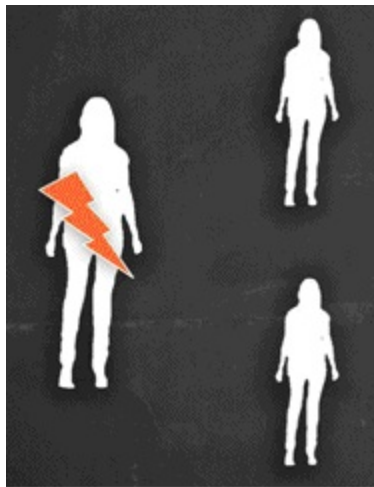
By now you know enough about fermentation to decipher the science of each of the steps in this recipe. For example, you know that every time you add more sugar, it is turned into ethanol, and the ethanol is then turned into acetic acid. Over time, the pH decreases, which means that fewer and fewer microbes can survive, and the microbes that are producing the acetic acid can thrive and take over the solution. You also know that covering the jar with cheesecloth, as opposed to some airtight material, ensures easy access to oxygen, which tells us that the chemical reaction requires aerobic conditions. On the contrary, you will see that many other fermentation recipes include steps to ensure exclusion of oxygen. The attention to particular environmental conditions is, of course, the important message

when dealing with all microbes. In all fermentation reactions we want to choose environmental conditions that meet the requirements for the particular microbe we are trying to favor. And the reason for this is that we want to tweak the environment so that it is just enough favorable for some microbes, so that they can take over and out-compete other potentially harmful microbes.

10.7 Microbe Growth

10.7.1 Exponential Growth of Microbes: Equation of the Week II

So far we have learned about some of the remarkable foods and flavors that microbes help us create. Now let's take a moment to think about how microbes multiply. But before venturing into microbes, let's start with something that might be a little more familiar to you, which is the multiplication of people. How is it that people multiply? You all know how this happens. You start out with one person, and that person divides and makes two people. The person who divided then dies, and you are left with two people. These two people divide, making four people. The original two people die, the four people divide, and you end up with eight people. In the next generation you have 16 people, then 32 people, and so on (Fig. 10.23).



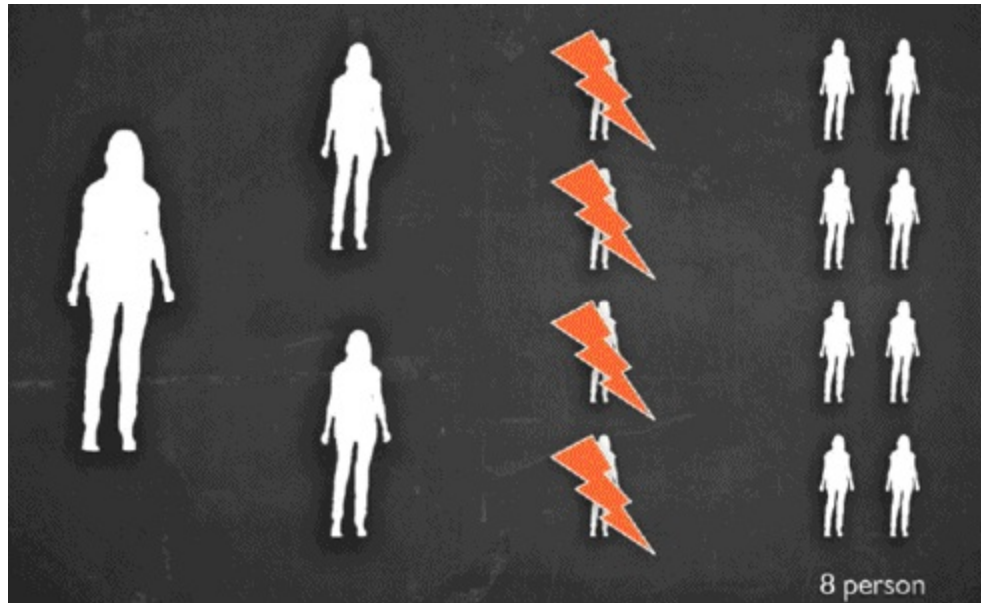


Figure 10.23 Populations, of people or bacteria, grow by exponential growth, which is the idea that every person or bacterium divides into two new persons or bacteria. With just a few generations, this leads to a huge increase in the population.



Mathematicians call this process where one gives rise to two, which give rise to four, and so on, exponential growth. Based on what we just told you, the process can easily be quantified with a formula for how many people, N , there are after n generations. The formula is:

$$N = 2^n$$

If we wanted to express the number of people in terms of time instead of in number of generations, we can convert this formula. We can say that every generation takes some amount of time. For humans the average generation time might be 20 or 30 years. This means that n , the number of generations, is the total time that has elapsed, divided by 30 years. We can

then rewrite the formula as

$$N = 2^{t/\tau}$$

where again N is the number of people, t is the time, and τ is the generation time, which in this case is 30 years.

Why is this called exponential growth? The reason is that mathematicians like to write this formula, instead of in the simple form above, in terms of the exponent e . When we do this, the very same formula looks like this:

$$N(t) = e^{kt}$$

where e is the exponential function and k is what we call the exponential growth rate. In this formula k is simply $\ln 2/\tau$. You can see that the two equations are interchangeable if you plug in $\ln 2/\tau$:

$$e^{\ln 2 \cdot t/\tau} = e^{\ln(2^{t/\tau})} = 2^{t/\tau}$$

This is the second equation of the week (Table 10.2).

EQUATION OF THE WEEK		
$N(t) = N_0 e^{kt} = N_0 2^{t/\tau}$ where $k = \frac{\ln 2}{\tau}$		
Symbol	Description	Units
$N(t)$	Number of microbes at time t	Microbes
N_0	Initial number of microbes	Microbes
k	Rate of growth/death	s^{-1}
t	Time elapsed	s
τ	Doubling time	s

Table 10.2

If you plot the number of people on the planet as a function of time, it looks very much like the numbers we saw above (Fig. 10.24). The number of

people started out very small, and over time it grew faster and faster. The issue this plot raises is that eventually the population might get so huge that it can't survive. Maybe it would get too crowded, or there would not be enough food, or something else. And indeed, one of the most important questions in the study of sustainability of the earth is how this process will proceed, namely, how many people can the earth support given the food resources available.

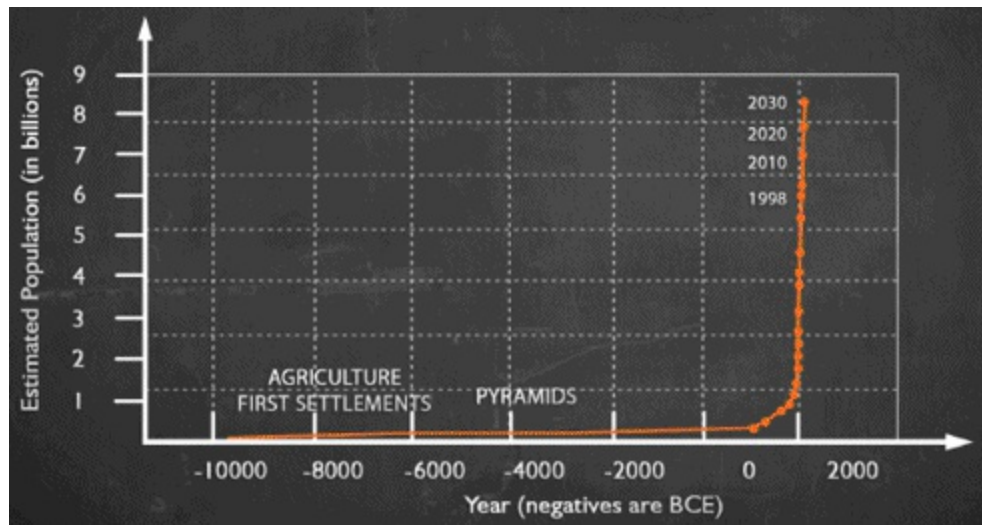


Figure 10.24 Plot of the population of the world as a function of time.

Why are we telling you this in the context of a cooking course? The reason, of course, is that the same issue occurs with microbes in cooking. A microbe really does start out as a single organism. And every generation, each bacterium divides. So one becomes two, two becomes four, four becomes eight, and so on and so forth. After 12 generations, there are 4 096 bacteria. After 22 generations, there are more than 4 million bacteria (Fig. 10.25).

Generation Number	Number of Bacteria
0	1
1	2
2	4
3	8
4	16
5	32
6	64
7	128
8	256
9	512
10	1024
11	2048
12	4096
13	8192
14	16384
15	32768
16	65536
17	131072
18	262144
19	524288
20	1048576
21	2097152
22	4194304

Figure 10.25 Exponential growth can lead to enormous increases in population over a relatively small number of generations. This is why trace contamination of microbes can very rapidly cause food to spoil.

10.7.2 Example: Growth of Salmonella

Let's work through an example to see how this works. Consider the bacterium Salmonella, which is relevant for cooking, because if there are too many Salmonella in your food, you will get sick. Salmonella has as a division time, which, under reasonable growth conditions, is about 20 minutes. This means that if you start out with one Salmonella on a piece of food, the number after time, t , would be $2^{t/\tau}$, where τ is 20 minutes. How many Salmonella will there be after 12 hours? Since each hour corresponds to three generations, 12 hours is enough time for 36 generations. So the number of Salmonella is 2^{36} , which is $7 \cdot 10^{10}$. So if you start out with one bacterium, there are 7 with 10 zeroes after it bacteria on your food after 12 hours.

$$t / \tau = \frac{720}{20} = 36 \text{ generations}$$

$$2^{36} = 7 \cdot 10^{10} \text{ bugs}$$

Will you be able to see them? Every bacterium is actually very small; it only weighs about 10^{-10} grams. But if you have $7 \cdot 10^{10}$ of them, there will be 7 grams of bacteria on your food. That is enough so that if we spread them out nicely, you'll be able to see them.

$$m_{\text{bugs}} = (7 \cdot 10^{10} \text{ bugs}) \cdot (10^{-10} \text{ grams/bug}) = 7 \text{ grams}$$

Indeed, this is exactly what happens when food spoils. If you place a piece of cheese or other food on the counter without refrigeration for some period of time, there will be films of bacteria or other microbes growing on top of it. The reason you can see them is that the generation time is sufficiently short that even after a relatively short time, there will be a visible number of them.

There are many different types of microbes on the earth, and even within the realm of food and cooking. It turns out that a division time of about 20 minutes is about the fastest there is. Another relevant division time for cooking is that of yeast, *Saccharomyces cerevisiae*, which divides in about two hours. In other words, there will be far fewer yeast cells in 12 hours

than there would be Salmonella (Fig. 10.26).

Microorganism	Incubation Temperature (°C)	Generation Time (Hours)
Bacteria		
Escherichia coli	40	0.35
Bacillus subtilis	40	0.43
Staphylococcus aureus	37	0.47
Pseudomonas aeruginosa	37	0.58
Clostridium botulinum	37	0.58
Treponema Pallidum	37	33
Protists		
Tetrahymena geleii	24	2.2-4.2
Chlorella gyrenoidosa	25	7.75
Euglena gracilis	25	10.9
Giardia lamblia	37	18
Ceratium tripos	20	82.8
Fungi		
Saccharomyces	30	2
Monilia fructicola	25	30

Figure 10.26 Examples of approximate generation times for common microorganisms at the indicated temperature. (Adapted from: Prescott's Microbiology, Wiley, Sherwood, Woolverton, 2011, p. 134.)

If we continue this further, we are going to run into trouble. If we wait 24 hours, starting from our single Salmonella, there will be about 10^{21} Salmonella on your food. Even if each of them only has a mass of 10^{-10} grams, this is still a total amount of 10^{11} grams. This number is absolutely crazy. One ton is 10^7 grams. So this means that there is about 10 000 tons of microbes on the food.

$$m_{\text{bugs}} = (5 \cdot 10^{21} \text{ bugs}) \cdot (10^{-10} \text{ grams/bug}) = 10^{11} \text{ grams} = 10\,000 \text{ tons}$$

There is no way, starting from a little piece of cheese or other food, and one single Salmonella, that you can possibly produce 10 000 tons of bacteria. The reason for this is that mass is conserved. The bacteria have to eat, and they are feasting on the food. Once the bacteria get to be too many, they will run out of nutrients and stop dividing. And indeed, if you were to plot the life cycle of bacteria growing on a piece of food, or really anywhere, there is a characteristic shape to it (Fig. 10.27). Initially, the bugs grow exponentially, and their number increases according to the laws that we have just described. But eventually the growth curve necessarily flattens out, in what biologists call, stationary phase. Here, the number of bacteria is more or less constant because they are crowding and interacting with

each other. At even later times, the population is running out of food and the number decreases.

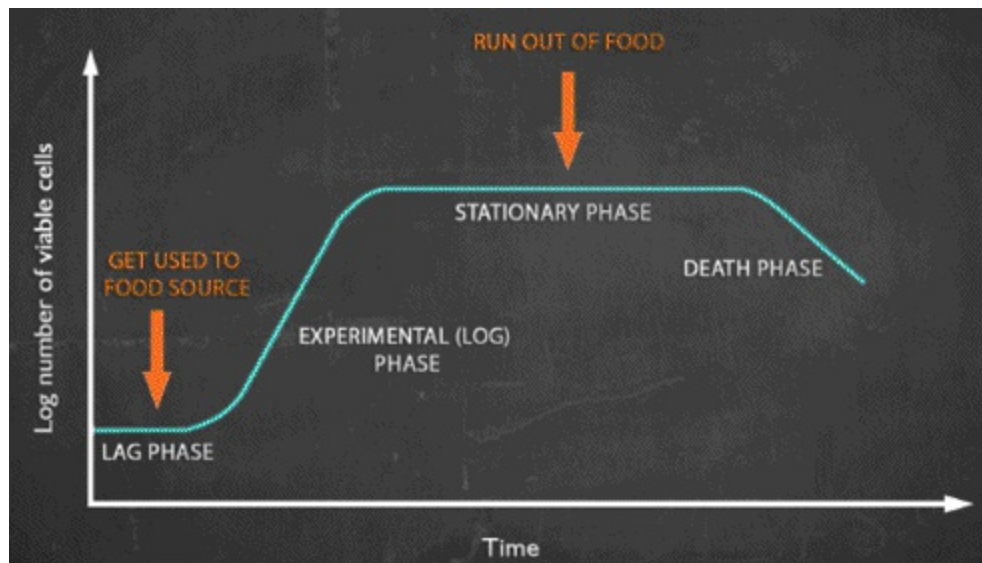


Figure 10.27 Plot of the logarithm of bacterial cells as a function of time. Bacterial growth has four distinct phases: lag, exponential, stationary, and death phase.

10.8 Microbe Growth Conditions

As we have learned, the growth of bacteria is very important for cooking, and the time it takes for bacteria to grow influences how we design recipes. So far we have simply assumed that the division time of bacteria is 20 minutes, which is a pretty good estimate. But in reality, the division time for microbes depends on the conditions they are in. Just like with all organisms, there is a set of environmental conditions at which a particular microbe can grow and thrive.

The two most important conditions for microbes in terms of cooking are the temperature and the pH of the environment. If we were to plot the growth rate as a function of temperature, it would look something like in Figure 10.28. There would be some minimum temperature at which the bacteria cannot grow. Below that temperature, they are unable to divide. Similarly, there would be a maximum temperature at which the bacteria can no longer divide. Outside this temperature range, the bacteria will not only stop dividing, but usually die altogether.

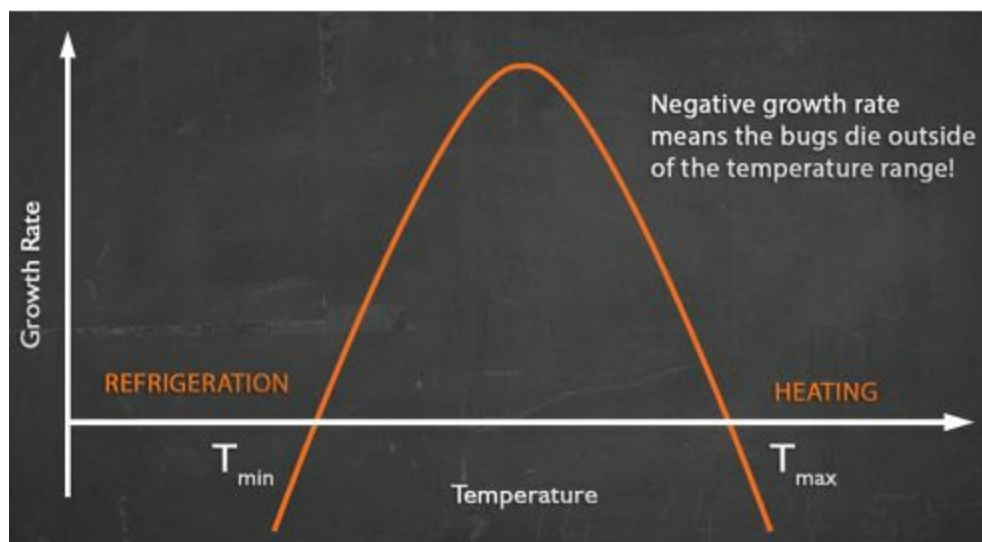


Figure 10.28 Bacterial growth rate depends on temperature. Bacterial division will be at its highest at some preferred temperature. Outside of this range, bacteria will stop dividing and die.

The lower temperature range for bacterial growth is the reason we put food in a refrigerator. If we make the temperature cold enough, bacteria will be unable to proliferate on our food. Similarly, when we pasteurize or sterilize food to get rid of microbes, we have to make sure the temperature is above the upper temperature. The implicit idea in many of our recipes is that if

you would like to get rid of microbe growth, you have to be outside of these temperature windows. And if you would like to facilitate microbe growth because you are trying to take advantage of the chemical transformations within microbes, you have to be within these bounds.

The same reasoning applies to pH. There is a range of pH where microbes can grow (Fig. 10.29). The reason for this is the same reason that we can cook food by manipulating the pH. In solutions where the pH is too high or too low, the proteins denature, and since microbes, just like all living organisms, depend on having functional proteins, they too can be manipulated by changing the pH.

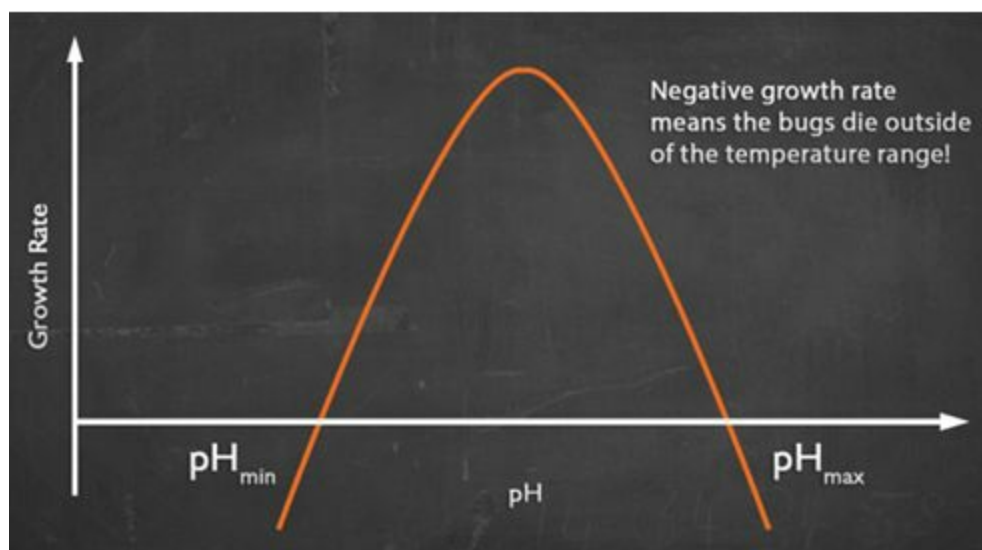


Figure 10.29 Bacterial growth rate depends on pH. Just as with temperature, there is a certain range of pH where bacteria will survive and divide.

As examples, let's look at the temperature bounds of two of the microbes that tend to be important in cooking: *E. coli* and *Saccharomyces cerevisiae*. It turns out that the bacterial strain *E. coli* can grow in a temperature range which is roughly between 10-40 °C (Fig. 10.30). The condition for maximum growth is very close to the upper temperature threshold—it's about 37°C, which, coincidentally or not, is very close to the temperature of human bodies. The yeast *Saccharomyces cerevisiae* tends to grow between a couple of degrees Celsius and 40°C. So in both cases, and, in fact, in the case of many microbes, if you want to eliminate growth, the temperature needs to be increased to about 40°C, or maybe, to play it safe, 50°C. Similarly, if the temperature is decreased to well below 10°C, most microbes also cannot grow.

Microorganism	Cardinal Temperature (°C)		
	Minimum	Optimum	Maximum
Nonphotosynthetic Procaryotes			
<i>Bacillus psychrophilus</i>	-10	23-24	28-30
<i>Pseudomonas fluorescens</i>	4	25-30	40
<i>Enterococcus faecalis</i>	0	37	44
<i>Escherichia coli</i>	10	37	45
<i>Neisseria gonorrhoeae</i>	30	35-36	38
<i>Thermus aquaticus</i>	40	70-72	79
<i>Pyrococcus abyssi</i>	67	96	102
<i>Pyrolobus fumarii</i>	90	106	113
Photosynthetic Bacteria			
<i>Anabaena variabilis</i>	unknown	35	unknown
<i>Synechococcus eximius</i>	70	79	84
Protists			
<i>Chlamydomonas nivalis</i>	-36	0	4
<i>Amoeba proteus</i>	4-6	22	35
<i>Skeletonema costatum</i>	6	16-26	>28
<i>Trichomonas vaginalis</i>	25	32-39	42
<i>Tetrahymena pyriformis</i>	6-7	20-25	33
Fungi			
<i>Candida scotti</i>	0	4-15	15
<i>Saccharomyces cerevisiae</i>	1-3	28	40

Figure 10.30 Different microbial species prefer different temperature ranges. The same is true for pH, salt concentration, and other environmental factors. (Adapted from: Prescott's Microbiology, Wiley, Sherwood, Woolverton, 2011, p. 143.)

10.9 Microbe Death

10.9.1 Food Safety and Microbial Death Rates

In terms of food safety, there are two different ways of eliminating microbes from food, and understanding the growth conditions for different microbes turns out to be key if we want to understand these protocols. The first is called sterilization, which means that you do something sufficiently severe so that all of the microbes in the food are killed. The second way is pasteurization, which means that you decrease the number of microbes substantially to put them below some safe threshold. The definition of what a safe threshold is depends on the type of bacteria. In the United States, the USDA has various standards of what needs to be accomplished in order for food to be declared to be safe.

For example, for the microbe *Listeria*, the standard says that whichever pasteurization procedure you use, the number of *Listeria* must be decreased by a factor of a million. In the case of *Salmonella*, the number has to be decreased by a factor of 10 million, whereas for *E. Coli*, the same number is 100 000.

The way the death of bugs works is very similar to the way the growth of bugs works. Namely, you could imagine that at a regular time interval, say every minute, half of the microbes die. So after one minute there are half as many as you started out with, and after another minute there will be half of that, which is a quarter (Fig. 10.31). Waiting yet another minute, there will be a half of that, which is an eighth, and then there will be a sixteenth, and so on and so forth. Thus, if the death time were one minute, the number of microbes at any given time would be the number of bacteria divided by 2^n , where n is the number of one-minute intervals that you waited. Applying this principle tells you whether you have met the USDA threshold for safety or not.

Number of Minutes	Fraction Remaining
1	1/2
2	1/4
3	1/8
4	1/16
5	1/32
6	1/64
7	1/128
8	1/256

Figure 10.31 The death rate of bacteria follows a similar principle as the growth rate. The table shows the fraction of bacteria that remains if half of the microbes die every minute.

The rule of thumb that the USDA uses for pasteurization procedures is referred to as the $6.5\log_{10}$ rule. This means that you are supposed to wait long enough for the number of microbes to decrease by a factor of $10^{-6.5}$. The number 10^{-6} is a factor of a million, which was how much the number of *Listeria* had to decrease, so the USDA essentially recommends going a little bit below that just in case. If you don't know what kinds of microbes are in your food, you want to kill the ones that are the hardest to kill to make sure that you got them all.

If we set $10^{-6.5}$ equal to 2^{-n} , then it turns out that n , the number of generations you have to wait to get this factor, is about 22. So the rule of thumb is that you need to wait for about 22 generations of bacterial death in order for the food to be fully pasteurized.

$$2^{-n} = 10^{-6.5}$$

$$\log_2 2^{-n} = \log_2 10^{-6.5} = -6.5 \cdot \log_2(10) = -22$$

$$n = 22$$

The death rate, just like the growth rate, is temperature dependent. Therefore, the time it takes until 22 generations of bacterial death have taken place and the food is safe to eat, depends on what τ is, i.e. what the characteristic time for the bacteria to die is, and that depends on the situation.

10.9.2 Pasteurization of Milk

Below is a table from the National Dairy Council with the pasteurization times required for milk (Fig. 10.32). If you perform the so called vat pasteurization, and heat the milk to 63°C, you have to wait about 30 minutes until the milk is safe to consume. On the other hand, if you do what is called high-temperature short-time pasteurization, you can get away with pasteurizing for only a second at a temperature of about 89-90°C. If you increase the temperature to 94°C, only a tenth of a second is needed. Finally, there is ultra-pasteurization, where you heat up the milk to 138°C for two seconds, which is long enough to make sure that every microbe is killed.

Temperature	Time	Pasteurization Type
63°C (145°F)	30 minutes	Vat Pasteurization
72°C (161°F)	15 seconds	High Temp Short Time Pasteurization (HTST)
89°C (191°F)	1.0 second	Higher-Heat Shorter Time (HHST)
90°C (194°F)	0.5 second	Higher-Heat Shorter Time (HHST)
94°C (201°F)	0.1 second	Higher-Heat Shorter Time (HHST)
96°C (204°F)	0.05 second	Higher-Heat Shorter Time (HHST)
100°C (212°F)	0.01 second	Higher-Heat Shorter Time (HHST)
138°C (280°F)	2.0 second	Ultra Pasteurization (UP)

Figure 10.32 The process of pasteurization uses the application of heat to destroy human pathogens in foods. The chart shows the pasteurization temperatures and times for different types of dairy pasteurization. (Source: National dairy Council)

We have already discussed in previous chapters what happens if you heat milk: the proteins start to unfold at about 64 degrees. You can imagine then that if you heat the milk for long enough, the proteins will unfold and cause phase transitions. It is obviously important that the pasteurization procedure does not let this happen, or the milk will no longer look like milk. Another thing that happens when heating milk to 138°C is that you initiate browning reactions. And, in fact, if you compare ultra-pasteurized milk to unpasteurized milk, you will notice that it has a slight brown color, and this is because even at the very short time scales of the pasteurization procedure, it is difficult to prevent browning reactions altogether.

10.9.3 Safety and Cooking Times of Meat

Below is an equivalent set of data for meat from Dave Arnold's blog Cooking Issues (Fig. 10.33). It plots temperature on the vertical-axis as a function of time on the horizontal-axis. At every temperature it tells you how long you have to cook something for it to become safe. The green regions are safe, and as you can see, below about 40°F, or a little above 0°C, it is safe to store meat without the proliferation of microbes. This is the reason we can store meat safely by putting it in a freezer. Above that there is a large red zone. This is the region in which microbes actually like to grow. There is no amount of time in this region that will kill off any microbes. And finally, at very high temperatures, there is another green zone. Above about 75°C the microbes cannot grow and your meat is safe. On the other hand, you also know that at 75°C the meat will cook, and eventually overcook, so hitting a safe temperature without overcooking the meat can be a delicate issue.

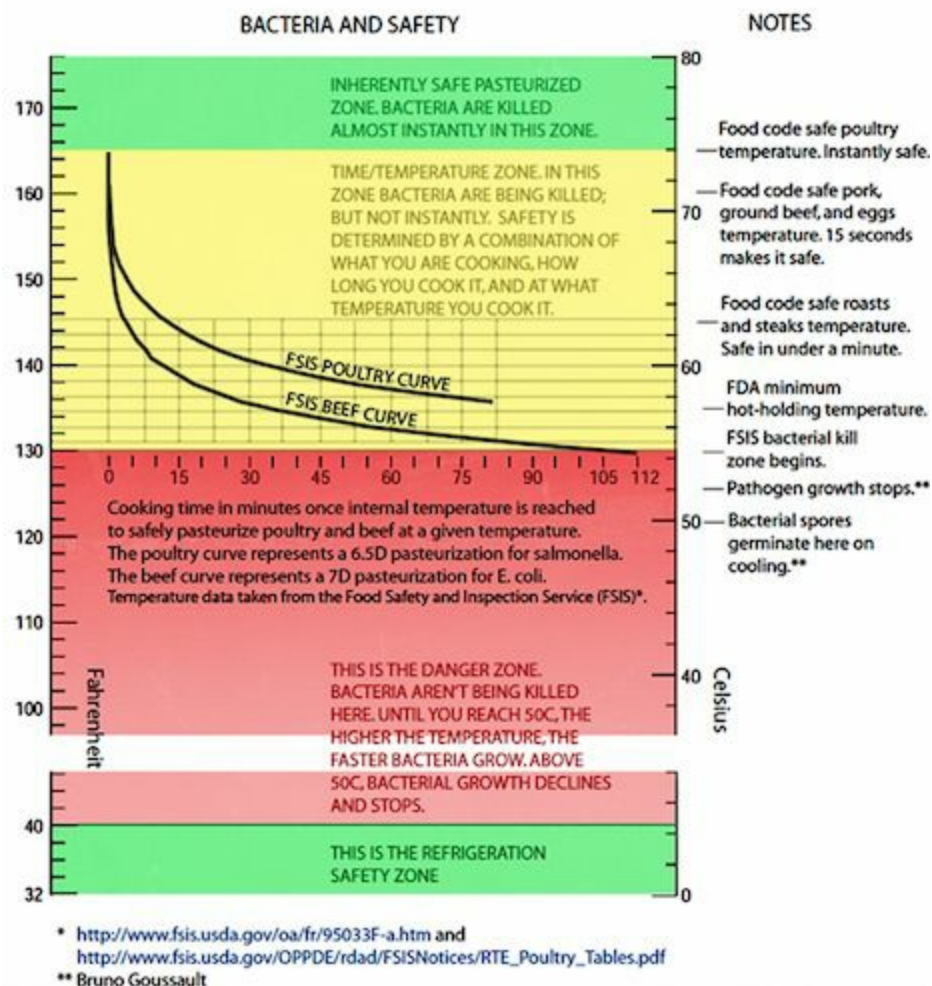


Figure 10.33 Plot showing how long to cook meat at different temperatures for it to become safe for

human consumption. Temperatures above 74°C and below 4°C are safe, whereas temperature between about 4°C–55°C promote bacterial growth. At temperatures between 55–74°C bacteria start to die off and the cooking time determines if the meat is safe or not. (Source: Dave Arnold Cooking Blog and USDA)

The zone we are particularly interested in is the yellow zone. Within it, there exists some temperature where as long as you wait long enough, the meat will be safe to eat. Notice on this plot there are two different curves: one for poultry and one for beef. It turns out that poultry has to cook slightly longer than beef for it to be safe to eat. For example, at 60°C poultry needs to be cooked for 30 minutes according to this standard, whereas beef only needs 5-7 minutes to be safe.

Why do you have to cook poultry longer than beef? This, of course, is a question of which environment provides more favorable conditions for growth, and although it is hard to predict what microbes like and don't like, there is one observation that we can make here, which is that the water content of poultry is slightly higher than that of beef. Poultry tends to contain close to 70% water, whereas beef tends to be in the low 60% (Fig. 10.34). Since microbes tend to want to be surrounded by water, poultry provides more space for the microbes to grow in, which in turn means that we need longer to get rid of all of them before the meat is safe to eat.

WATER CONTENT OF MEAT AND POULTRY		
Product Name	Percentage Water	
	Raw	Cooked
Chicken fryer, whole	66%	60%
White meat chicken, with skin	69%	61%
Dark meat chicken, with skin	66%	59%
Ground beef, 85% lean	64%	60%
Ground beef, 73% lean	56%	55%
Beef, eye of round	73%	65%
Beef, whole brisket	71%	56%

Figure 10.34 Water content of different types of meat and poultry.