CHAPTER

RHEOLOGY

7

CHAPTER OUTLINE

When we talk about rheology in food, we are specifically looking at the flow or deformation of a particular food. Despite the word "flow," rheology is equally applied to solids, gases, and liquids, in other words the phases and textures of food. Having said that for the most part in the past, food rheology was restricted to liquid foodstuffs. Nowadays, rheology is more aptly applied to materials like solutions, emulsions, suspensions, foams, gels, and melts as well as semisolids like creams and pastes (McKenna and Lyng, 2003). This means that the food rheologist deals with many food phases that are often substantially inhomogeneous. By way of example, take the humble "ketchup" sauce; if an open bottle is held upside down, it will not flow unless it has been shaken or tapped vigorously—this is due to its rheological properties. In the same way, rheological properties describe the behavioral properties and the perception of certain foods. This occurs either on touching, or it can be felt in the mouth. Such properties depend not only on the rheological flow but also on the solid particles within the food (Belitz et al., 2009; Adebowale, 2012).

Rheology is important for many aspects of food production and consumer consumption: it involves the physical characteristics of fluids and semisolid foods, the engineering and process design, the development of new products, and their testing including as mentioned earlier their sensory properties. While food rheology is not directly equated with food texture, there is, however, some considerable overlap. Taking the International Standards Organization (ISO), for example, we can define food texture as

> all the rheological and structural (geometrical and surface) attributes of a food product perceptible by means of mechanical, tactile, and, where appropriate, visual and auditory receptors.
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> **Redgwell and Fischer, 2002**

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Rheology has its own vocabulary. In lay terms, food rheology defines the consistency of the many different food products used in the kitchen and without.[1] In turn, consistency is defined by the elasticity (springiness) and viscosity (thickness) of these items (*see next section*). This knowledge is important in the making of pasta, bread, cereal, chocolate, and salad dressings, among many others (Vaclavik and Christian, 2014).

Isaac Newton thought that at a given temperature and shear stress, the viscosity of a fluid would remain constant regardless of changes to the shear rate. Although, in reality, he was only partly right. For example, a few fluids like water and honey do in fact behave this way—these fluids are called Newtonian fluids. Most fluids, though, have viscosities that fluctuate depending on the shear rate of the substance—these are called non-Newtonian fluids (Barnes et al., 1989).

7.1 ELASTICITY, VISCOSITY, AND VISCOELASTICITY

Elasticity—is the tendency of materials to return to their original shape after any deforming force is withdrawn. Examples might include bread dough, gummy bears, etc.

Viscosity—is an internal property of a fluid that offers resistance to flow. For example, pushing a spoon through a bowl of water takes little effort—little resistance—but through honey, the same force moves the spoon very slowly. An important point here is the consistency of resistance. In such compounds as water, honey, or cooking oil, the resistance is uniform and independent of any applied force. That is to say, whether a spoon is pushed through honey or not, the viscosity is the same—this property as described above is called Newtonian fluids. By contrast, in non-Newtonian compounds, viscosity increases or decreases with the increasing application of force (Adebowale, 2012).

The viscosity of a liquid then is a measure of the difficulty that molecules exhibit when passing each other in a fluid, like our ketchup example previously. Therefore, viscosity in liquids corresponds to the informal concept of "thickness." It is the fluid resistance to "shear" forces that arise from forces that exist between the molecules.

Plasticity—this type of fluid will generally behave like a solid when under little or no stress. As in the ketchup example, a force must be used to overcome the apparent solid sauce's viscosity in order for it to flow freely, and once the force is removed, so the ketchup returns to its apparent sold state (Barnes et al., 1989).

Pseudoplastic—is the type of fluid whose viscosity decreases with increased shear rates. These are perhaps the most common of the non-Newtonian fluids and include starches and pastes and are sometimes referred to as shear thinning.

Shear thinning—Most foods show a decrease in viscosity with increased forces such as chewing, kneading, or spreading. Such non-Newtonian materials include melted chocolate, peanut butter, and concentrated tomato juice, for instance. In the example of peanut butter, if one were to mix a spoonful in a bowl, the longer and faster one stirs, the thinner the peanut butter becomes. This is due to the shear-thinning effect of the compound.

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[1] Rheology is also applicable to nonfood items too.

Shear thickening—by contrast, viscosity increases with more rigorous force. A good example of this is the action of corn flour in water. When agitated with a small force, the resistance is noticeable; however, mix it with greater force and the resistance is also that much greater (Adebowale, 2012).

Viscoelasticity—is another rheological property of food substances in which certain solutions, suspensions, colloids, etc. exhibit both viscous and elastic[2] characteristics (Barnes et al., 1989). Examples include bread dough, peanut butter, and cream.

Before describing some of the agents of rheology, it is worth looking at the various states of foods—that is, solutions, colloids, suspensions, gums, gels, and thickeners.

7.2 SOLUTIONS, COLLOIDS, SUSPENSIONS, GUMS, GELS, AND THICKENERS

Central to food rheology are colloids; in particular hydrocolloids. Colloids are microscopically dispersed substances evenly distributed throughout another substance—a sort of cross between a solution and an emulsion. Hydrocolloids often make up the gums, gels, and thickeners; they are hydrophilic (water-loving) colloids that can be polysaccharides or proteins of vegetable, animal, microbial, or synthetic origin and either are naturally present or are added to foods to control physical and functional properties of aqueous (water-based) foodstuffs. Technical jargon aside, food rheology is essentially the study and application of these hydrocolloids (gums, gels, and thickeners) (Vaclavik and Christian, 2014).

Gums, gels, and thickeners display several important properties and are used for foam, liquid, and emulsion stabilization; for the prevention of ice and sugar recrystallization; and for textural and other organoleptic properties. That is to say, when added to an aqueous mixture, gums, gels, and thickeners increase viscosity without substantially modifying other properties, such as taste. Such thickening agents tend to provide stability too and may also improve the suspension of other ingredients or additives. In understanding hydrocolloid science, there are two properties of particular importance that these gums, gels, and thickeners display; these are their gel and flow properties (their viscosity and viscoelasticity).

7.2.1 SOLUTIONS

A solution is a homogeneous mixture of two or more substances. The dissolving agent is the solvent, and the component that is to be dissolved is the solute. Components of a solution are atoms, ions, or molecules that make them very small at 10^{-9} m or smaller in diameter. A good example of a solution is sugar and water. That said, it does not have to be a liquid; gases, for instance, can dissolve in liquids, and even solids can be dissolved in solids. The science is fairly easy on this one; when an atom loses or gains an electron, it becomes an ion with a charge (positive or negative) (see Appendix B). Everyday table salt is an ionic compound with positively charged sodium ions and negatively charged chlorine ions. Because of this, the opposite charges are attracted to each other; however, salt becomes ionized when the chlorine atoms in salt attract electrons from the sodium. Once salt is dropped into some water,

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[2] Elastic materials are those that strain when stretched then return to their original state once any stress is removed.

the positive and negative ends of water molecules are attracted to the sodium and chlorine ions. As the water molecules exert a stronger pull on the salt ions, so they are pulled into the water—they are dissolved (Vaclavik and Christian, 2014).

Another example of a solution is carbon dioxide that dissolves in water to form carbonated water. Examples of solutions are endless and include sugar, salt, soluble proteins, acetic acid, and certain soluble vitamins too. Solutions are not always either liquid or gas; take candy canes, for example, these are simply a solid solution of sugar, water, and flavorings. Liquids can also be dissolved in other liquids as well, such as water and ethanol. Because of this, alcohols can be made to any strength required from 1 to 100 percent. Even nonpolar oils can be dissolved in a strong alcohol solution (Vaclavik and Christian, 2014; Field, 2011). By design, homogeneous mixtures are solutions with particle size dimensions between 0.1 and 2 nm.

7.2.2 COLLOIDS

(See also Section 2.2)

A colloid is an intermediate phase between a solution and a suspension. Colloids are varied systems in which one substance is dispersed (called a dispersed phase) as fine particles in another substance (called the dispersed medium or the continuous phase). The dispersed phases are particles bigger than molecules and are in the range of 2–1000 nm in size and are termed colloidal particles or simply colloids. They are too large to dissolve and far too small to settle out naturally (McKenna and Lyng, 2003). Good examples of colloids are milk, fog, clouds, and smoke. These microscopically dispersed insoluble particles that are suspended in say milk, for example, are known as the colloids, whereas the whole milk (the overall mixture) is known as the colloidal suspension. Unlike a solution too (described previously) whose stable solute-solvent mixture constitutes only one phase, the colloid's suspended particles are considered multiphasic (Dickinson, 1992). Furthermore, to qualify as a true colloid, the mixture must be one that does not separate or settle out too easily. Colloids can be distinguished from solutions and suspensions using the Tyndall effect. That is—as light is passed through a colloidal dispersion, so it will be reflected or scattered by the larger particles within the colloid. There are three subclasses of colloids: hydrocolloids (gels and sols), emulsions, and foams.

7.2.2.1 Hydrocolloids: Gels and sols

There are two types of water-based colloids (hydrocolloids) often encountered in the kitchen; these are the gels and the sols (liquids made of colloidal suspensions of very small solid particles) (Field, 2011). Sols are described in Section 2.2.

Gels in the kitchen are types of mixtures involving water and solids. One of the most common forms of gel is perhaps the panna cotta, a mixture of milk and milk protein molecules that bond together to form a jelly. Another type of gel is aerated mixture in which water or cream is trapped in cell-like matrices of separate pockets as in a fruit mousse (Talarczyk, 2009). Gelatin (the agent used in both the previous examples) in fact is a prime example of a hydrocolloid, and it is also one that sits in both gel and sol categories. When cold, gelatin is a gel, yet when warmed, it becomes a sol. This strange set of affairs is also true of jellies made of other reversible gelling agents like agar, carrageenan, and pectin (Field, 2012). Gels are formed when particles are cross-linked through chemical bonding into three-dimensional shapes that behave somewhat like solids. Other gelling agents include starches (polysaccharides) and agar. Agar though has certain advantages over other gels and starches in that it has a higher melting point (85°C/ 185°F) and a higher setting point (32°C/90°F). Agar is also used as a vegetarian option to gelatin (made from red algae or seaweed) although the varied mouthfeel and textures of the two are quite different. Carrageenan (extracted from red seaweed) is another gel that acts similar to agar, only this gelling agent is viscoelastic and liquefies under "shear" stress and returns to a solid once the stress is removed. Pectin, a soluble dietary fiber, is another gel used mainly for making jams and jellies. Pectin is usually extracted from citrus fruits like oranges or lemons or harder fruits like apples. Pectin can also be found in the softer fruits although usually in much smaller quantities. Commercially, most pectin is extracted from the apple pulp after it has been squeezed for juice. Protein gels too, like those found in egg whites, while not reversible, are nevertheless also very common in the kitchen.

7.2.2.2 Emulsions

(See also Section 15.3)

An emulsion is another form of colloid. While it is a common fact that by themselves oils or fats and water do not mix well, with a little help, they can be joined in an emulsion such as milk and milk fats or a good salad dressing. Emulsions with fats such as these are quite easy to make (if following certain rules *see below*) as the chemical bonds between them are really quite weak. The trick is to use molecules that both attract and repel oil and water—in this case, a double-ended molecule; these are called emulsifying agents. Luckily, these molecules are very easy to come by as most organic cells' membranes contain a water-loving side and a water-repelling side. These are known as phospholipids. Once ground up and introduced to oil, they form a coating around small droplets of oil, thus preventing it from combining with other small droplets of oil. A common emulsifying agent is lecithin. This is obtained commercially from soybeans, but there is another source readily available to the cook and that is egg yolks. Egg yolks contain lecithin and protein that help bind oil and vinegar together; also if mustard is used, the phospholipids present will also strengthen the emulsion (Field, 2011). Egg yolks can be used to thicken all sorts of emulsions. This is because of the various yolk components, two in particular: the proteins of low-density lipoproteins (LDL) (phospholipids and cholesterol), and secondly, the larger yolk granules (containing both LDL and high-density lipoproteins (HDL)) are both effectively strong emulsifying agents. That said, the large yolk granules are at this stage simply too big to coat any dispersed droplets; however, add some salt and it helps break down the large granules into their more effective subcomponents—LDLs, HDLs, and proteins (in particular phosvitin).

Gums (Section 7.2.4) can also be used as a stabilizer in the emulsifying process. Gums are large starch-like molecules that when in the presence of water form colloidal suspensions. Adding a pinch of xanthan gum, for instance, into a hollandaise or a mayonnaise at the right moment will stabilize the emulsion very effectively, making it very difficult to separate. Apart from lecithin, there are other emulsifying agents, most important of which is "fat" surprisingly. Fat molecules are triglycerides, i.e., made up of three fatty acids. Break these fats down into their component parts monoglycerides or diglycerides and one has more emulsifying agents to play with.

7.2.2.2.1 Emulsifiers and stabilizers

When it comes to emulsifiers, these can best be described as molecules that lower the surface tension of the dispersed phase (e.g., in mayonnaise). What happens is as the surface tension of the oil is lowered so it is easier for the egg yolks lecithin content (or other emulsifying agents) to coat the oil droplets, helping to keep them apart from each other. Furthermore, emulsifying agents must be partly soluble in both liquids. They do this by the chemical makeup of the particular agent. Each agent must have two different regions within the same molecule, one soluble in water and the other soluble in fat. Lecithin, as mentioned, is a good emulsifier as it contains molecules with both a fat- and water-loving area. Other good emulsifiers are the larger protein molecules with their long chains of amino acids that too contain both fat- and water-compatible molecular regions. All in all, though, it can be said that the best natural emulsifiers in the cook's kitchen are lecithin (in egg yolks) and casein proteins (in milk and cream).

Emulsions, while able to help create sauces or accompaniments, are inherently unstable, and they can readily "split" or coalesce into their preemulsified fractions. This is not too much of a problem if using handmade emulsions in the home or the professional kitchen. But for longer shelf life—especially in the manufacturing industry, one also needs to consider the stability of the emulsion. Having said that, more and more professional kitchens are becoming familiar with industrial stabilizers and emulsifiers. As mentioned, while emulsifiers ease the process of making an emulsion, it does not necessarily translate into a stable emulsion. For a stabilizer to work, it must be able to "get in the way" of the droplets that are trying to rejoin (coalesce). Luckily though, there are numerous molecules and particulates that can help in this respect. Proteins, starch, pectins, gums, and fine pieces of plant tissue all stabilize emulsions well. Even tomato paste, with its substantial protein content (approximately 3%), is a useful emulsifier and stabilizer.

Making emulsions. From the above text, it might seem that emulsions are quite easy to make; in reality, a few rules must be followed if one wishes to create a stable product. In the first instance, in all cases, the dispersed phase is added to the continuous phase and not the other way around. Take mayonnaise, for example, the steps include the following:

- The liquid- or water-based mixture (water and vinegar) is mixed with suitable emulsifying agents like egg yolks and any stabilizing agents being used.
- The dispersed phase (the oil) must be added very slowly/gradually to begin with (*see below*) while the mixture is whisked or blended vigorously.
- It is prudent, too, not to add too much dispersed phase—no more than three times the volume of the continuous phase (the vinegar and water solution) should be adequate; otherwise, the final emulsion becomes too thick and less stable.

Split, coalesce, separation of emulsions. Every cook in the kitchen knows that when making an emulsion, it is important to start slowly although many perhaps do not know why beyond increasing the chance of the mix "splitting." This means adding the dispersed phase (in the case of mayonnaise, it is oil and in hollandaise, it is clarified butter) slowly. This is because, in the early stages of an emulsion, if too much dispersed phase (oil) is added too quickly, too soon, the oil cannot be dispersed into the growing emulsion quickly enough. This leaves droplets of oil unemulsified before more oil is added. This phenomenon is known as "splitting," "coalescing," or "separation." An emulsion has to grow and grow slowly at first; once the emulsion has achieved a little volume and developed some viscosity, its increased stability then allows oil to be added more quickly.

7.2.2.3 Foams

A foam is simply any liquid or solid that has a gas suspended in it. They form an important aspect of cooking, especially in baking. Foams can also take many forms including marshmallows, meringues, Genoese sponge cakes, whipped cream, foam sauces, and some cookie recipes. They are formed in several different ways, and in many but by no means all cases, protein plays an important part in the process (Field, 2012). For the most part, many proteins are partly or wholly water-soluble and are made of long chains of amino acids curled up tight in small ball-like structures. These are held together by weak chemical bonds. That said, not all proteins are the same; instead, some are attracted to water (hydrophilic) and are repelled by oils and fats, while others are attracted to oils and fats and are repelled by water (hydrophobic). Despite these differences, when heat is applied or when proteins are physically agitated (e.g., by beating), they begin to denature (see Chapter 4). As described, denatured proteins are proteins whose weak bonds have been broken, and as a result, they have a tendency to uncurl or unravel. Denaturing can occur in three different ways: physically or mechanically as in beating, whisking, or pounding with a meat hammer; chemically/biologically through the addition of acids in lemon juice, cream of tartar, and acidic marinades; or through heat by cooking, etc. As these unraveled proteins encounter other uncurled proteins, so two things generally happen. Firstly, the untangled protein is not fully untangled; this allows it to tangle or snag onto other proteins creating physical or mechanical bonds. The second thing than can occur is new chemical bonds that are formed allowing the two proteins to bind together at the molecular level. The bonds between these proteins are stronger and more stable if the proteins are not fully uncurled or unraveled. Ultimately, as more and more proteins bind together, they form a protein web—a network that traps some of the water or oil in which the proteins reside and any air that was also incorporated as the mixture was being beaten or cooked. In other words, bubbles of air are surrounded by a tough layer (the skin) of interconnected denatured proteins. In whipped egg whites, these bubbles of air are surrounded by a film made of protein to which some water is still attached. In whipped cream, the air bubble is surrounded by a film of protein to which some fat is still attached; also, because of the different nature of the proteins in cream (being hydrophobic), so the water within the cream is pushed out and held outside this bubble (Gardiner et al., 1998; Field, 2012).

7.2.2.3.1 Egg whites

As is true for the gelling or coagulation of heated eggs (see Section 11.4), the key to a stable egg foam is the propensity of albumin proteins to unfold and bond with each other when they are being exposed to physical stress. By whipping the egg whites, we exert physical stress on the proteins. As the whisk forces itself through the white, so it drags some of the white with it creating a pulling force that physically unfolds the compacted protein molecules. As a result, egg whites readily form physical bonds with each other, and a continuous solid matrix of proteins holds both water and air in place. There are several things that we need to consider in this scenario. By increasing the connections or bonds between proteins, we can make our egg white foam more stable. Because of the predominantly hydrophilic proteins within egg whites, any oil present—whether from the yolk itself or whether introduced by accident (greasy bowl or utensils)—will adversely affect the ability of the whites to whip. Interestingly, in this respect, the type of equipment used also affects the whip; for instance, fat readily sticks to plastic, so even if it appears clean, the chances of some residual fat being present are higher in plastics than other materials. This is why metal or glass bowls are usually preferred for whipping egg whites in.

Whites can also be overwhipped. This results from the overbeaten proteins uncurling or unraveling too much, encouraging too many bonds to form, which then ends up drawing the proteins closer together effectively squeezing out bubble-trapped air rather than containing it. What happens then is egg whites look grainy and dull and will eventually collapse back on itself (McGee, 1997; Gardiner et al., 1998). So, to help stabilize egg whites and reduce excessive bond formation, we can use a few tricks. Using copper bowls to whip the whites is one trick, for instance. This is not a housewife's tail; instead, this helps stabilize the foam because ions in the copper bowl react with the proteins that contain sulfur. In turn, this allows them to form stronger bonds with other amino acids that also contain sulfur (Field, 2011). Another trick is to add a small amount of acid such as lemon juice, vinegar, or cream of tartar into the egg white mix. This can also help stabilize foams by allowing the proteins to unravel a little and tangle together with other lightly unraveled proteins even before the whisking starts (Gardiner et al., 1998; Field, 2012). However, one thing, as cooks we see a lot of is overbeaten egg whites. In this case, by simply adding another egg white and beating it until the mixture forms peaks again can often salvage the mixture.

When it comes to optimum whipping techniques, whites at room temperature are easier to whip due to decreased surface tension that also allows the proteins to expand that much easier. Also, adding sugar at the correct stage during beating makes a positive difference. Adding sugar too soon however means the sugar molecules obstruct and slow down the egg white's proteins ability to find each other and form bonds (Gardiner et al., 1998).

Lastly, while the albumin protein allows egg whites to foam in the first place, when a meringue, for instance, is in the oven, another protein ovalbumin gives the structure rigidity upon cooking.

7.2.2.3.2 Gelatine foams

As well as the albumin of egg whites, so other proteins can also make foams. Another simple protein foam is made with gelatin. Gelatin is a protein obtained either from stock or by the acid and alkaline processing of collagen (found in animal bones, tendons, hides, etc.). It is used, among other things, to make marshmallows. Marshmallows are made by several methods, but one method involves cooking a sugar syrup to the firm ball stage (116°C/240°F) and beating the mixture into gelatin that has softened in cold water. As with other protein foams, the gelatin will denature as the hot syrup, and whisking causes it to form links with itself, forming a sturdy net, with the syrup attracting the water-loving parts of the protein, leaving the oil-loving parts facing the air in the bubbles.

7.2.2.3.3 Milk foams

Milk foams tend to be more fragile than other foams and as such are generally made shortly before serving. Milk foams too need to be heated with steam in order to foam naturally. As per the above examples, milk owes its foaming power mainly to its proteins. There are two different types of proteins in milk: the caseins responsible for around 80% of all proteins in milk and the whey proteins. While casein plays a role in the functional properties of whipping/foaming, it is the whey proteins that offer far superior foam stabilizing properties. In doing so, it creates a more rigid film at the air/water interface of the foam. As proteins amass (either by mechanical whipping or through the use of steam injection), so a thin layer around of proteins forms around the pockets of air. Milk foams, however, are more fragile and short-lived than other foams because milk's proteins are scarce (just 3% of the milk's weight compared with egg whites' 10%). On top of this, casein proteins are tough little proteins to denature making it difficult to unfold and coagulate/gelate into a solid network. This is why milk can be boiled and boiled evaporating to a fraction of its original volume without curdling. However, if we heat the milk to around 70°C/160°F, the whey proteins (just 1% of milk's weight) do unfold to some extent. If these proteins unfold at the air-water boundary of a bubble wall, then whey proteins do bond to each other and at the same time moderately stabilizes the foam. Some milks are more convivial than others at producing foams, especially those skimmed milks with reduced fat and/or fortified with proteins. However, be aware that skim milk foams lack flavor and mouthfeel, whereas full fat foams are somewhat fuller in texture and flavor. One other point to consider is that very hot milk does not hold its foam well. Although, when it comes to fat, it must be said that, as is the case of egg whites, the addition of fat will destabilize and minimize the formation of foam. In this respect, as fats in milk increase, so foam stability decreases. This is so up to about 5% and then after close to 10% fat, so the opposite occurs, and milk foams are once again stabilized. At this point, highly more stable cream-type foams are formed.

7.2.2.3.4 Cream foams

Cream, the layer of butterfat on top of milk, is liquid at body temperature yet solidifies when chilled. There are a variety of cream types that are usually distinguished by their fat content. Ranging from 18% fat content for single creams in the United Kingdom to 30%–35% for whipping creams, and richer still at 48%, there are the double creams; moreover, some creams, especially clotted creams, can have as much as 55%–60% fat content.

Unlike foams of egg whites and milk, proteins do all the foaming; however, in whipped cream, proteins share the task with fat; that is, cream foams are mostly stabilized by fat (McGee, 2004). Also, unlike egg whites where fat inhibits the whipping process, if cream is to be whipped—only cream with a minimum 30%–35% fat content can be whipped into a foam. This is why "single" creams cannot be whipped (Field, 2012). The process of whipping cream foams works like this. Firstly, the cream must be chilled to keep the fats solid. Then as cream is whipped, so proteins are denatured and which then surround the fat globules (triglycerides) in the cream. Along with these proteins, cholesterol and molecules called phospholipids[3] work together surrounding the globules of fat. Phospholipids' unique structure comprises both water-loving (hydrophilic) and water-repelling (hydrophobic) components. This special arrangement helps keep the triglycerides floating around separately, not only from one another but also from the liquid water in the cream (Field, 2011). As part of "fats," protective membranes are exposed or stripped away so the "naked" fat globule settles in one of two regions in the cream. Either they face the pocket of air in the bubble, or they stick to another destabilized fat globule. Collectively, the fat globules (just like the proteins) stick together or, more precisely, coalesce. At this point, pockets of air are surrounded by films of solid fat and protein with trapped air inside and with the water on the outside in between the bubbles. This creates a continuous fatty network. In the process and as mentioned above, the temperature of the fat is important—that is to say, only chilled fat can coalesce; warm fat will simply not adhere to each other, and one ends up with a split cream, a demulsified solution. Additionally, cream with a higher fat content like the UK double cream (38%–40% fat) will actually whip faster while forming a stiffer, denser, and less voluminous foam.

If the whisking continues past the point at which a stable foam has been made, the congregation of fat globules continues until the process actually begins to destabilize the foam. At this point, more fat globules coalesce with each other into ever coarser clumps of butterfat. At which point, air and liquid that was held together inside the pockets of fat begin to weep; the fat loses volume, and the cream becomes granular (in kitchen parlance, it is "split"). Further whipping still and we can turn the whole thing about face, that is, instead of having a water-based solution with tiny films of fat and protein with air trapped inside; overbeating will eventually break down the membranes further forcing the fat to clump tighter together and forcing the air and water out. In this situation, we have made butter.

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[3] Phospholipids, special biological "fatlike" molecules that possess hydrophilic (water-loving) and hydrophobic (water-fearing) regions.

As has been labored, to keep the whipped cream stable, the temperature of the fat needs to be kept low enough that the fat stays quite solid. Another solution to help stabilize the foam is to add more protein, such as gelatin or certain vegetable gums. In fact, as cream is inherently unstable in itself, after 24–48 h, water will naturally start to leach out of the cream, making any cakes or buns coated with it slightly soggy. One common solution is to add a small amount of gelatin that helps hold the foam together and by extension keeps the fat in place (Field, 2011; McGee, 2004). Further, if cream has already been whipped successfully (straight out of the fridge) and held at room temperature the same as above, the butterfat will soften, and bubbles will collapse leading to leakage of the liquid. If using homogenized cream, the fats are generally smaller; this gives rise to creams that are lighter in texture

7.2.2.3.5 Sugar foams

One can make foam without proteins, emulsifiers, or surfactants although as a general rule they are usually less stable. But if we make the foam out of something that hardens when it cools and before the air can escape, then we don't require proteins to stabilize the foam. One kind of confection—honeycomb or cinder toffee—does just that. One starts by cooking a saturated sugar syrup (sucrose and simple sugars) to about 150°C/302°F, to the hard-crack stage of sugar boiling. This is the stage just before the sugar starts to burn (caramelizes) and turns brown (Field, 2011). To this mixture, bicarbonate of soda is added, and then, the mixture is quickly beaten. The high heat causes the baking soda to decompose into sodium carbonate and carbon dioxide bubbles which, upon cooling, entrap the bubbles causing a sweet sugary foam that is popular around the world.

7.2.2.3.6 Leavening agents

Leavening (a raising agent) plays an important role in baking science. Specifically, leavening is the foaming action with the incorporation of either air or carbon dioxide bubbles, which helps to lighten and soften doughs and batters. Without leavening products, some traditionally leavened breads will be left dense. Leavening agents are the substances by which this is achieved, and they can take one of three forms—biological, chemical, or physical/mechanical (see also Section 10.1.6).

Biological leavening—Biological leavening is the process of using living organisms that characteristically release carbon dioxide to leaven things like doughs and batters, for example. Typical biological leaveners include sourdough starters, yogurt, buttermilk, and, more commonly, yeast. Yeast is a single-celled fungus that feeds on simple sugars and starch giving off by-products of carbon dioxide and alcohol, which give products made with yeast their distinctive flavor. In other naturally leavened breads such as certain sourdoughs, the flavor is further enhanced by various lactic acid bacteria (lactobacilli) or acetic acid bacteria (acetobacter). Unlike chemical leavening, however, biological leavening is a slower process requiring proofing times to allow the yeast time to react or ferment. Yeast comes in many forms and is known by many different names—fresh yeast, compressed yeast, active fresh yeast, cake yeast, baker's compressed yeast, wet yeast, active dry yeast, baker's yeast, bread machine yeast, brewer's yeast (aka beer yeast), and lastly nutritional yeast.

Chemical leavening—Chemical leaveners are compounds that, when the right conditions prevail, will release gases when they react with other chemical catalysts and/or moisture or with heat. Most are based on a combination of acid-like cream of tartar and a salt of bicarbonate (sodium bicarbonate or baking soda). After the reaction has finished, some say a saltiness can be detected, so it is wise to use chemical leavening agents prudently. Chemical leaveners are used in things like quick breads and cakes, as well as cookies and untold other applications where a long biological fermentation is undesirable or indeed impractical.

Mechanical—Mechanical leavening is the physical whisking or “creaming” to use kitchen parlance. This is no more noticeable than (as has been mentioned before) beating egg whites or whipped creams. It is also the method used in making nonchemical (raising agents) cakes like Genoese, where the only aeration introduced into the mix is that of beating/whisking.

7.2.2.3.7 Sauce and puree foams

These types of foams sit on the fence between protein and nonprotein foams in the culinary kitchen. It all depends on the ingredients used. Cooks will often aerate sauces and purees to make foams by whipping or blending liquids or purees at high speeds. As a result, almost anything can be foamed using this method. However, for the large part, most of these foams are very unstable as (depending on ingredients) there might be insufficient protein or stabilizing agents to hold the foam together. What usually happens then is once the foam forms, within seconds or sometimes minutes, the foam will collapse in on itself. One work-around solution that one might see cooks doing is to keep the sauce hot (if required) and as needed; the puree or juice foam is whipped to order, i.e., one dish at a time. Foams are so popular these days, however, that cooks often make foams with a stick blenders, but remember, for it to hold, one needs a stabilizer such as agar, gelatins (or other proteins), or lecithin and other emulsifiers and foaming agents (stabilizers).

Foaming agents or more commonly foam stabilizers are surfactants,[4] that is, when present in small amounts, they reduce the surface tension of liquids in turn facilitating the formation of a foam. Alternatively, to enhance a mixture, stability surfactants inhibit the coalescence of bubbles. Using gelatin as a foaming agent is very efficient as it is a good stabilizer in its own right; it is also worth noting the fact that different gelatins have different foam stabilizing properties and as such need to be carefully selected. Using the emulsifier lecite or lecithin (one among many) as a stabilizing agent is actually very good at converting juices and watery liquids to airs and foams. To produce a stable foam using soy lecithin, it is typically used at ratios between 0.25% and 1.0% ratio by weight. That is, for every 100 g of liquid, 0.25–1 g of soy lecithin would be used.

7.2.3 SUSPENSIONS

Suspensions are created when particles of solid material are held within a fluid and are sometimes referred to as a coarse dispersion. A suspension will also have particles that are large enough to be seen under a microscope or with the naked eye. The particle size is generally larger than those found in solutions and colloids—usually greater than 1000 nm. Particles within a suspension may become distributed evenly throughout the suspension by shaking the contents vigorously or by mechanical means. They are also large enough not to dissolve in the fluid; instead, they separate out easily when disturbed. Although that said, the use of binding agents may prevent this from happening or at least slow the process down. Suspensions can either be heterogeneous[5] or homogeneous depending on the materials used. In short, we can say suspensions are types of mixtures in which solid particles do not dissolve in a liquid to form a solution and are too big to form a colloid. The large particle size gives the

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[4] A surfactant is a substance that aims to reduce the surface tension of a liquid in which it is dissolved.

[5] Heterogeneous suspensions have diverse, varied, or assorted particle sizes dispersed in a suspension liquid.

suspension a murky or opaque quality, and left long enough, some may separate out on their own or can be separated at will through filtration.

7.2.4 GUMS, GELS, AND THICKENERS

(See also Section 15.2.3)

Because thickening agents provide body, increase overall stability, and improve suspension within sauces, soups, stews, etc., so they are often used as food additives. Thickening agents then are materials used to thicken and stabilize solutions, colloids, emulsions, and suspensions. It is important to know too that some thickening agents are also gelling agents. Thickeners are often based on either polysaccharides[6] including starches, vegetable gums, pectins, and even proteins. The major types of thickeners, stabilizers, and gelling agents are discussed in the next sections.

7.2.4.1 Gums, gels, and gelation

Gums and gels work by taking a volume of liquid and stabilizing it in a solid matrix-like form through a network of partially dissolved long-chain polymer molecules. When they form a complete three-dimensional network throughout the system (usually as it cools), they become a gel. The most commonly known gel is gelatin although there are many other types of gels or gelling agents. For many, in the scientific world at least, it is reasonable in many cases to treat the network as a rubber-like system. Most gels start off in an aqueous medium although in certain cases some gels operate in an alcohol or oil-based environment. The gel works when the molecules form cross-linked connections that may be chemical or physical. As these molecules form, so further heating or gelation acts to create a three-dimensional network throughout the solution, at which point it forms a gel.

Methods of Gelation—There are a very wide and complex array of possible gelation mechanisms depending on the type of cross-links and their relative stability. However, for simplicity, we can divide the connections into two broad categories, chemical and physical. The main difference being that chemical connections are generally irreversible while physical connections can often be reversed. The prime example of chemical gels in food is well demonstrated in the cooking of eggs, both the egg whites and the yolks, whether in “floating islands,” “in brûlées,” or by themselves (see Section 4.2). That said, most gels encountered in the kitchen are of the physical variety rather than the chemical variety. As mentioned previously, the most common of these is gelatin[7], although it must be repeated that not all gels are equal. Gels originate from a variety of sources (animals, seaweeds, fruits, other foods, etc.) and have broadly differing molecular weights. This multiplies the range of possible junction types that may also significantly differ between products. This gives the cook a variety of gelling agents that he/she may play with. Other gels and thickeners include the following:

- *Agar*—is thermoreversible with high melting and setting temperatures.
- *Alginate*—is a polysaccharide made up of chains of sugar units (guluronate, mannuronate, or guluronate-mannuronate blocks), the proportion of which determines how strong a gel is formed.
- *Carrageenan*—gels when mixed with proteins.

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[6] Polysaccharides are carbohydrates (e.g., starches, cellulose, or glycogen) whose molecules consist of a number of sugar molecules bonded together.

[7] Gelatine is obtained by the thermal denaturation of collagen.

- *Cellulose derivatives*—various derivatives form gels by swelling or even wicking (the absorption or drawing off a liquid through capillary action).
- *Gelatin*—thermoreversible gels form on cooling.
- *Gellan gum*—is a water-soluble thermoreversible anionic[8] polysaccharide produced by the bacterium *Sphingomonas elodea*. It is a gelling agent developed specifically to replace agar and gelatin in conditions that are not ideal. There are two types of gellan gum: the first are gels made with low acyl, which tend to be brittle and firm. The second are made with high acyl, which are flexible and elastic.
- *Guar gum*—guar gum is a thickening agent derived from guar beans. It is especially useful as a binder in gluten-free baking.
- *Gum Arabic*—also known as acacia gum, is a natural gum made of the hardened sap of various species of the acacia tree—it also gels at high concentrations and in acidic environments too.
- *Locust bean gum*—also known as carob bean gum, is derived from the seeds of the carob tree; it is a cost-effective and simple way to stabilize certain foods.
- *Pectin*—is a naturally occurring polysaccharide found in berries, apples, and other fruits. When heated together with sugar, it causes a thickening that is characteristic of jams and jelly gels at low pH.
- *Xanthan gum*—is a polysaccharide secreted by the bacterium *Xanthomonas campestris* responsible for thickening and stabilizing—it is also thermoreversible.

Referring to the physics, the propensity for a gel to form sufficient three-dimensional cross-links depends greatly on the molecular weight of the gelling agent—the lower the weight, the more gel that is needed (Barham et al., 2010).

Take gelatin gels, for example, there is much that can affect the different phases of the product. Firstly, it is the product of the denaturation or disintegration of collagen. Further, the concentration of gelatin seems to affect the melting temperature, i.e., the more concentrated the gel, the higher the melting ranges and vice versa (Cole, 2000). Moreover, other properties like the presence of proteases[9] can also affect the inclination for junctions to form. This is especially so in fruits including pineapple, kiwi, mango, ginger root, papaya, figs, or guava where proteases hinder (by breaking down the protein) rather than aiding the gelling process. The tip in this case is not to use more gelatin but rather to cook the fruits first, effectively denaturing the enzymatic proteins (protease). Also, affecting the gelling rate of gelatin is the pH value of the product to be set. It would seem the lower the pH (more acidic), the longer the gelatin needs to set, and once it does set, it will not be as firm where the pH value is higher (Schrieber and Gareis, 2007).

Other gel-forming agents have found their way into restaurants such as "spherification" whereby flavored alginate solutions are dropped into a solution of calcium creating spheres in the process (El Bulli). Another gel with a higher melting and setting point is agar, which has been used to great effect by Heston Blumenthal in his flaming sorbets (Barham et al., 2010).

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[8] A negatively charged ion.

[9] Protease refers to a group of enzymes whose catalytic function is to hydrolyze (break down) proteins. They are also called proteolytic enzymes or systemic enzymes.

7.2.4.2 Starches

(See also Section 15.2.1)

A different class of gels are those formed by starches. These not only occur when food is being cooked but also can be made inside the kitchen too. Starch granules are the main storage form of carbohydrates in plants; they are polysaccharides assembled from the simple sugar glucose and can contain anywhere from five hundred to several hundred thousand glucose molecules. Starch has many industrial applications although more importantly for us it is also an additive in foods. Chemically, vegetable starches are composed of two different molecules, amylose (20%–30%) and amylopectin (70%–80%), although the plants also incorporate some proteins within their starch.[10] Starch molecules are broken down by enzymes known as amylases, and the digestibility of a given starch is influenced by its physical form. In plants, starch is present in microscopic granules.[11] Cooking starch-containing items results in gelatinization (not to be confused with gelation, which is the process of setting something in a jellylike substance). When starch gelatinizes, its molecules hydrate, and the starch granules begin to swell. This enhances the enzymatic breakdown of the starch itself. Cold water will not greatly affect the amylose or amylopectin in a starch granule, but hot water will. Furthermore, by adding heat, the starch granules in ordered crystalline layers start to melt (>60°C/140). This disordering and opening up of the structure allow amylose molecules (quite water-soluble) to soak up the water while the branched amylopectin less so. As the starch molecules significantly overlap with one another, so they do not fully dissolve; instead, they form a soft gel. In general, starch granules can absorb (depending on variety) a considerable amount of water without losing their integrity. It is this swelling and subsequent absorption of water that provides the thickening effect of starches used in the kitchen. By way of example, potato starch granules can absorb liquids and swell up to 100 times their original volume (Barham et al., 2010). Indeed, the thickening of soups and sauces by ingredients such as flour, arrowroot, tapioca starch, or corn starch is an example of the gelatinization of starch granules into their optimal swollen state. These can serve to thicken soups and sauces as mentioned, or upon cooling, they can leave a suspension in a gel-like state, for example, a traditional “blancmange.”

Of note, here is the problem of overcooking. By overcooking the starch, it can have disastrous effects on the soup or sauce as the granules disintegrate; they release amylopectin and amylose into the sauce with the resultant thinning of the product.

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[10] Importantly, different plants (and different varieties of the same plant) incorporate widely differing amounts of protein in their starch granules.

[11] A typical granule of starch may be a few micrometers across.

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