Principles behind Emulsions and Foams

In life, it is often said that opposites attract, but in the kitchen this is not necessarily the case. For example, try to mix oil (or generally speaking, lipids; the following text uses the terms “fat” and “oil” to refer to solid and liquid natural food fats, respectively; the general term “lipid” encompasses both) and water: no amount of mixing or shaking will help you to reach a stable system with oil dispersed in water. In order to understand the fundamental reasons behind this behaviour, we need to consider two things: the electrostatic forces between the individual molecules and the concept of entropy (i.e., the degree of disorder in a system) (Silverstein, 1998).

One characteristic of water molecules is their polarity. Although each molecule is electrically neutral, the electron distribution within the molecule is unbalanced, making the molecule polar. This unbalance arises from the fact that oxygen has a higher electronegativity than hydrogen: the shared electron pairs are more attracted by the oxygen atom than by the hydrogen atoms (McNaught and McNaught, 1997). The oxygen atom thus carries a slight negative charge, and the two hydrogen atoms carry a corresponding positive charge. This is also the reason why water molecules “stick together” at room temperature; the “negative” oxygen attracts the “positive” hydrogen atoms from the neighbouring water molecules.

With most molecules from fat, however, the situation is different, and this has something to do with the structure of the molecules. Generally speaking, natural food fats are made of triacylglycerides (Vilgis, 2011). In oil, such molecules are primarily triacylglycerols, which consist of a glycerine residue attached (esterified) to three fatty acid residues. These fatty acid residues can be of various lengths (number of carbon atoms) and they can either be saturated or unsaturated (single or double bonds between carbon atoms). These long hydrocarbon chains are electrically balanced (unlike water molecules) and are called non-polar.

Thus, upon adding triglycerides into water, the water molecules would have to rearrange (due to their mutual attraction) around the non-polar molecules (Huque, 1989). This process, in turn, would limit the ability of water molecules to move freely, thus resulting in a decrease in entropy in the system (Alger, 1994). However, this decrease in entropy caused by the organized structure around the triacylglycerol molecules is not compensated through any enthalpy gains upon mixing the two substances (Streitwieser et al., 1992). This leads the non-polar molecules to be driven by entropy to “clump” together, which, in turn, again increases the entropy of water within the system. This entropy-driven separation of non-polar and water molecules is also referred to as the hydrophobic effect (“water-fearing”, as opposed to hydrophilic or “water-loving”) (Huque, 1989). Finally, the differences in density between the solvent (water) and the solute (triacylglycerol molecules) cause the lighter substance (fat) to rise to the top.

So, in order to mix water and oil, substances that help in bringing oil and water together (emulsifiers) are needed. There are many different mechanisms by which the emulsifiers work, but this effect is primarily due to the fact that emulsifiers typically consist of a water-soluble (hydrophilic) and a hydrophobic (also referred to as lipophilic) part. When the emulsifier is mixed into an oil–water mixture, the emulsifying molecules tend to move toward the oil–water interface, where the hydrophilic part tends to remain in the water phase and the hydrophobic part tends to stay in the oil phase. When the oil–water system is given mechanical energy (e.g., by whipping), the freshly formed small oil droplets are stabilized by the layer of the emulsifier at the oil–water interface. Emulsions are, however, only metastable and will eventually separate when given enough time.

Depending on the medium in which the emulsifier is more soluble, it can be used to make either water-in-oil emulsions (when the emulsifier is more soluble in/attracted to oil) or oil-in-water emulsions (when the emulsifier is more soluble in/attracted to water) (Ohshima, 2016; Griffin, 1949; Griffin, 1954). This rule (also called “Bancroft’s rule”) does not hold in all cases. There are several factors that can promote or inhibit the efficiency of an emulsifier (e.g., temperature, dissolved salts or presence of proteins). However, as a rule of thumb, it provides a good starting point when preparing emulsions.

Looking at the chemistry and physics behind emulsions, there are several mechanisms that are involved in the process of stabilizing and destabilizing emulsions. Among other things, emulsifiers help in reducing surface tension (and thus the energy) in the water–oil interface (McClements, 2015). Each time an interface is formed in a physical system (e.g., an oil droplet in water), a certain amount of energy is required to form the boundary between the substances. Consequently, large surface
areas require more energy and are, because of this, inherently unstable.

This instability leads to a phenomenon called Ostwald ripening, which takes place in emulsions (Kabalnov et al., 1992). In order to minimize the surface energy in the interface, triacylglycerol molecules migrate from the small oil droplets toward the larger ones, as the energy requirement for forming one large droplet is less than that required to form several small ones. Emulsifiers also limit the fusion of droplets, a phenomenon known as coalescence.

Furthermore, differences in density can cause creaming in emulsions (Adams et al., 2007). The emulsified oil droplets remain separate but start floating upwards in the water, thus forming a zone of small oil droplets on top of the water. Ingredients (such as gelatine, starch granules or pectin) and certain preparation methods (such as reducing the water content by boiling or simply whipping), which increase the viscosity of the emulsion, oppose creaming. Also, increasing the number of emulsified droplets in an emulsion can lead to a phenomenon known as jamming, which in turn leads to higher viscosity (Siemens et al., 2010). However, it is also possible to break an emulsified system or even cause it to undergo a phase inversion with the wrong treatment. Making butter by whipping cream is the best example of this. Initially, the cream is a dispersion of oil droplets in water, but continued whipping turns the cream into butter, which is essentially an emulsified system consisting of water droplets in fat. Figure 33.1 shows various types of destabilization mechanisms in emulsions and foams.

**Types of Emulsifiers in Food Emulsions and Foams**

For food applications, a wide range of emulsifiers can be used, depending on the type of food being produced. In food, both natural and synthetic emulsifiers are used. Natural emulsifiers can be divided into three main categories: (1) phospholipids, (2) proteins and polysaccharides and (3) particulate emulsifiers.

Phospholipids have small molecules containing one polar “head” group (phosphate moiety) and a nonpolar “tail” (one or two fatty acid residues). One of the most versatile and widely used phospholipid emulsifiers is lecithin, which can be obtained from egg yolks or from any plant tissues (it is the main material of biological membranes), including soya beans. Lecithin is used in a wide range of culinary applications, such as improving

![FIGURE 33.1 Schematic representation of different processes that lead to destabilization of emulsions and foams.](image-url)
the stability and texture of coffee cream, salad dressings and mayonnaise.

Proteins are polymers whose monomers are amino acids. Many proteins have regions that are alternately hydrophobic and hydrophilic, giving them good emulsification properties. For this reason, alongside their nutritional properties, they are the most widely used emulsifiers in the food industry. Protein-based emulsifiers include egg whites (Drakos and Kiosseoglou, 2006), whey proteins (beta-lactoglobulin) (Hu et al., 2003), milk proteins (caseins) (Dickinson et al., 1998) and gelatine (Olijve et al., 2001) from animal sources.

Polysaccharides are polymers whose monomers (over 100 of them by definition) are saccharides, and they exhibit thickening properties, which aid in enhancing emulsion stability. Examples of polysaccharides include xanthan and gellan gum (extracted from bacterial cultures), carrageenans (extracted from sea weeds), pectins (extracted from fruit peels), natural and modified starches (from grain sources), galactomannans (extracted from seeds of guar beans and konjac) and chitosan (from shells of crustaceans).

Xanthan consists of monomers of β-D-glucopyranosyl glucan as backbone, and its side chains consist of D-mannopyranose and β-D-glucuronic acid. Gellan is a tetrasaccharide, which consists of two residues of D-glucose and one residue each of L-rhamnose and D-glucuronic acid. Carrageenan is a polysaccharide made up of repeating galactose units and 3,6-anhydrogalactose (3,6-AG), both sulfated and non-sulfated; the units are joined by α-1,3 and β-1,4 glycosidic linkages. Starch is made of amylose and amylopectin, of which the monomers are D-glucose. Polysaccharides belonging to the galactomannan family, such as guar gum, etc., consist of monomer units of galactose and mannose. Chitosan is a polysaccharide consisting of sub-units of D-glucosamine and N-acetyl-D-glucosamine.

Particulate or Pickering emulsifiers are a recent addition to the repertoire of food emulsifiers, and include microparticles of materials like starch, microcrystalline cellulose, chitin, cocoa fibres, zein particles (from corn), soy protein particles and flavonoid particles. In recent years, these have been recognized for their roles in stabilizing emulsions and foams in food products. Unlike traditional emulsifying agents, Pickering emulsifiers are much larger (in the size range of a few tens of nanometres to micrometres) and can impart better texture and mouthfeel to food products (Linke and Drusch, 2018). Figure 33.2 shows the microscopic structure of soy oil droplets stabilized by hydrophobic rice starch particles.

Synthetic emulsifiers are artificially made from non-natural sources and include sugar-alcohols like sorbitol, sorbitan monolaurate (Polysorbate 20), sorbitan monostearate (Polysorbate 80), sodium and calcium salts of fatty acids, sucroglycerides, etc. For example, in ice creams, Polysorbate 80 is often added up to 0.5% (v/v) concentration to make the ice cream smoother and easier to handle, as well as increasing its resistance to melting (Goff, 1997). Adding this substance prevents milk proteins from completely coating the fat droplets. This allows them to join in chains and nets, which hold air in the mixture and provide a firmer texture that holds its shape as the ice cream melts.

Emulsions in which the suspended phase is more than 74% in volume are classified as Pickering emulsions. Particulate emulsifiers are added to the bulk emulsion, and stay dispersed even after homogenization, and this is called a Pickering emulsion.

**Examples of Emulsified Systems in Food**

**Milk**

A classic example of food emulsion is milk. As shown in Figure 33.3, the milk fat globules (in the size range 0.1 to 10 μm) are dispersed in water. Fat globules are stabilized by a thin layer (consisting of a mixture of phospholipids and proteins) called the milk fat globule membrane (MFGM). The MFGM consists of about 30% phospholipids (sphingomyelin, phosphatidylcholine and phosphatidylethanolamine) (Lopez and Ménard, 2011), and the remaining fraction consists of glycosylated and non-glycosylated proteins (Kanno, 1990). Additional stability in some cases is provided by micelles of caseins, vital milk proteins. Caseins are found in the form of aggregates called micelles, which are negatively charged at the normal pH of milk, i.e., 6.6 (Sinaga et al., 2017). These charged casein particles repel each other, thus avoiding fat droplet coalescence and stabilizing the milk.

Milk, when left to stand, separates into a visible fat layer over an aqueous one, in a process called creaming. To avoid creaming, the fat globules in milk are reduced in size by a process called homogenization: the fat globule membrane is ruptured and fat globules are stabilized by casein micelles (Cano-Ruiz and Richter, 1997). Thus, homogenized milk may be considered as a Pickering emulsion.

In contrast to stabilization of milk, in some cases it is necessary to destabilize milk, for example in cheese making. In the manufacture of cheese, acid or rennet is added to milk, reducing the pH or enzymatically hydrolysing a key stabilizing protein in the casein micelle, which destabilizes the casein micelles, resulting in coagulation of fat and protein particles and eventually separation, leading to the formation of cheese. Fermented products such as curd, buttermilk and yoghurt (Bongard, 2009) are also examples of emulsified systems consisting of oil/fat and water. Emulsions in which the suspended phase is more than 74% by
“Plant-Based Emulsions” (Non-Dairy)

Plant-based emulsions are oil-in-water emulsions obtained from nuts, grains, seeds, legumes, and cereals. Plants store oils (i.e., lipids) in the form of droplets (in the size range of ca. 300–350 nm) encapsulated by a layer of phospholipids and proteins (Waschatko et al., 2012). These droplets are called oil bodies or “oleosomes”. Plant-based drinks are generally extracted by blending and then straining soaked grains (barley, rice, oat and wheat), legumes (soy, lupin, pea and ground nuts), nuts (cashew, almond, hazel nut, pistachio, walnut, etc.), seeds (chia, flax, hemp, pumpkin, sesame, sunflower, safflower, etc.), coconut, etc.

Figure 33.4 shows some examples of plant drinks, some of which have been used across cultures around the world for thousands of years. Just as with dairy milk, plant drinks can be used as such or further processed/fermented to products analogous to yoghurt and cheese. Plant-based recipes include horchata (a north African beverage from soaked and sweetened tiger nuts), Indian/Thai chicken curry with coconut milk, tofu-based recipes from soy milk, and wheat milk halwa (a type of dessert from India). Plant drinks have attracted attention in the vegan community worldwide. Apart from being used in food products, plant drinks are also used in a variety of cosmetic and skin care products like skin creams, moisturizer, etc.

Butter and Margarine

Butter is an example of an emulsified system that consists of more than 83% fat, 13% water, about 3% ash and 1% milk proteins (Farmer, 2011). Butter is also a rich source of fat-soluble vitamins like vitamins A, D and E (Delgado-Zamarreño et al., 1995). Butter is made by churning fresh or fermented cream to separate butterfat from buttermilk. In order to make butter, the cream recovered over cow milk is cooled to around 5–7 °C before churning to allow some of the fat to crystallize (Gunstone, 2006). The fat crystals serve as a basis for further crystallization and help to break the milk fat globule membranes during churning (Provost et al., 2016). The milk fat aggregates first into fat particles and later into solid masses.

FIGURE 33.3 Schematic representation of microscopic structure of milk showing fat globules and casein micelles suspended in solution of whey proteins and milk sugars.

FIGURE 33.4 Picture showing (from left to right) oat-based emulsion, coconut-based emulsion, soy-based emulsion and almond-based emulsion.
during churning. The fat mass collected in this process is subsequently kneaded to remove any remaining pockets of butter-milk and to achieve the desired texture. The final texture of butter depends on the size and structure of the fat crystalline network in the butter that is brought about by the kneading process (typically around 14–16 °C) (Fuquay et al., 2011). Butter is available in varieties such as salted butter, spreadable butter, clarified butter, ghee and maitre d’hotel butter. Figure 33.5b also shows a schematic representation of the microscopic structure of butter.

Margarine is another example of an emulsified system consisting of water droplets in a continuous phase of fat, which is used for flavouring, baking and cooking. Margarine was first created by the French chemist Hippolyte Mège-Mouriès in 1869 and was originally made as a cheaper substitute for butter using beef tallow. Today, margarine is made from a variety of oils such as safflower, corn, soy bean and animal fats (Carpenter and Slover, 1973). Just as with butter, margarine consists of about 80% oil, 15–18% water phase and 1–2% salt and other solids. The oil is often hydrogenated to make it less susceptible to oxidation and improve shelf life. The hydrogenated oil and milk (water base) is mixed with lecithins, and the mixture is blended together in an emulsification chamber at 38 °C. This process leads to the formation of an emulsified system consisting of tiny water droplets (0.42–2.7 μm) suspended in a crystalline oil phase (Balinov et al., 1994). Then, the contents are cooled to about 7 °C (in a scraped-surface heat-exchanger called a votator) to a semi-solid state that is further processed and packed.

**Spreads, Dips, Dressings and Sauces**

Spreads, dips, dressings and sauces are also emulsified systems of an oil phase suspended in a water phase. In the case of spreads and dips, the proportion of the oil/fat, i.e., the suspended phase, is very high compared with the suspension medium, i.e., the watery base. Such emulsified systems with a very high percentage (>74% by volume) of oil phase are called HIPEs (Pulko and Krajnc, 2012). Hummus is a good example of a spread/dip and is made from a mixture of chickpea (*Cicer arietinum*) puree, tahini (paste from ground sesame seeds), lemon juice (*Citrus limon*), olive oil (*Olea europaea*), cumin (*Cuminum cyminum*) and salt (Figure 33.6).

In this mixture, chickpea puree acts as the water base, and proteins present in the tahini (sesame proteins) act as emulsifier that stabilizes it (Al-Mahasneh et al., 2017).

Hollandaise is an example of a sauce, which contains egg yolks, pepper, lemon juice, butter and salt. For the sauce, the egg yolk is mixed with water (or wine, vinegar or lemon juice), and mixed while heating. This allows the proteins present in egg yolk to denature partially and coagulate to allow the formation of a foam while mixing (Hopia et al., 2013). The melted butter is added subsequently into the mixture, which is then emulsified (together with the lipids from the egg yolk) by the proteins and lecithin from the egg yolk. The resulting sauce is a combination of an (oil-in-water) emulsion, a foam and a suspension, as it contains melted fat droplets, air bubbles and protein aggregates from the egg (This, 2016; Rognsa et al., 2014). The final texture of the sauce, in turn, depends on the amount of air incorporated into the sauce and the size of the fat droplets (Hopia et al., 2013; Rognsa et al., 2014).
Sausages

Sausages, such as German frankfurter, Austrian wiener, hot dogs, mortadella, bologna, liver sausages and pâté, are also examples of emulsified dispersions of fat in water together with particulates of meat. The manufacturing process of sausages involves the preparation of an emulsified mixture of finely chopped or minced meat in water together with seasonings, salts and, where necessary, binders or extenders (Belitz et al., 2004). The exact composition of ingredients depends on the type of sausage being produced. Initially, the (muscle and fat) tissue is comminuted (i.e., chopped, flaked, ground and/or minced) to the desired degree (Toldra, 2010; Varnam et al., 1995). The final texture of the sausages is determined by the duration and the method of comminution (Belitz et al., 2004). This process generates a lot of heat, however, due to friction between the sausage batter and the blades (heating the contact surface up to 80 °C) and can increase the temperature of the meat mixture by 10–20 °C during the first 15 minutes of processing (Toldra, 2010; Pearson and Gillett, 2012). To minimize cooking losses and achieve optimum stability for the emulsified system, the comminution temperatures should be kept below 18 °C (Belitz et al., 2004; Essien, 2003; Zayas, 2012). This is achieved by using ice or iced water. When meat is cut into fine particles, the muscle fibres and connective tissue are broken into pieces and mixed with fat droplets and particles of fatty tissue. During the processing, the fat partially melts and leads to the formation of an emulsion system with the proteins present in the system (Belitz et al., 2004). The different types of protein contribute to different degrees to the formation of a monomolecular layer (ca. 130 nm in thickness) around the fat globules (in decreasing order of importance: myosin, actomyosin, sarcoplasmic proteins and actin) (Belitz et al., 2004). The fat droplets (together with water) in the mixture are thus suspended in a matrix of (salt-soluble) proteins, leading to a thick paste, which is an emulsified suspension (Figure 33.7) (Zayas, 2012).

To further improve the texture and mouthfeel, other components such as water binders and emulsifying agents are added to the mixture. Finally, a mixture of spices, salt and sodium nitrite is added, which also helps in curing the meat. Depending on the type of sausage being produced, the sausage batter may be loaded into casings and sold raw (e.g., bratwurst and breakfast sausages) or smoked (e.g., kielbasa), fermented (e.g., sucuk), cooked (e.g., liver sausage, blood sausage) or dried (e.g., salamis and cervelats) (Belitz et al., 2004; Pearson and Gillett, 2012).

Anise-Flavoured Liquors and Spirits (Microemulsions)

A special type of emulsion called a microemulsion occurs when a highly hydrophobic oil (e.g., anethole in anise-flavoured drinks) dissolved in a water–ethanol solution (as, for example, in ouzo) is diluted with water. In this case, a spontaneous oil-in-water emulsion is formed, the mixture turning from being clear to opalescent (cloudy) (Carteau et al., 2008). This is commonly called the “ouzo effect” (also “pastis effect”), or “louche”, or “spontaneous emulsification” (Lopez-Montilla et al., 2002). Microemulsions form spontaneously and are highly stable even without any surfactant.

The underlying physical principles are depicted in Figure 33.8 as a simplified system of three components, with ethanol being the emulsifier (with a hydrophobic hydrocarbon tail and a hydrophilic OH group). The (yellow) oily odorant molecules in ouzo surround themselves with ethanol molecules (red dots) and are thus dispersed in the continuous water phase (blue dots). However, ethanol is not a particularly strong emulsifier (with a partition coefficient of around −1.0 to −1.5) due to its short hydrophobic tail of only two carbon atoms (Leo et al., 1971; Vilgis, 2011). Thus, the ethanol molecules are only loosely bound to the oil–water interface and retain much of their freedom to diffuse and move around in the solution. A thermodynamic equilibrium is thus formed between the states of being bound to the oil–water interface and being diffused in the water. This equilibrium can then, in turn, be disturbed by adding water into the drink. The ethanol molecules diffuse within a larger volume of water, thus reducing the number of available alcohol molecules near the anethole molecules. This causes the anethole molecules to come together to “share” the available ethanol molecules with each other. This process continues with the addition of water until the anethole droplets become large enough to scatter light, which
causes the solution to become turbid. The droplet size of such emulsions ranges from 300 nm to about 2.4 μm and can change with composition and time (Grillo, 2003).

Pastis (France), aquavit (Scandinavia), arak (Persia and the Middle East), sambuca (Italy), aguardiente (Columbia), anis (Spain), ouzo (Greece), absinthe (Europe), mastik (Balkans), raki (Turkey) and xtabentun (Mexico) are a few examples of liquors that form microemulsions when served with water. These liquors generally contain essential oils extracted into alcohol from a range of spices (like wormwood, anise and fennel), herbs (like peppermint, coriander, hyssop, etc.) and botanicals (like roots, barks, flowers and seeds). This effect is also demonstrated in Figure 33.9: it is apparent that a small amount of water is enough to disturb the delicate balance in the drink and to cause it to turn cloudy.

Beverages
Beverages such as fruit/vegetable juices and milk-based beverages like chocolate milk, milkshakes and several types of coffee-based beverages fall into the category of emulsified suspensions (a suspension and also an emulsion). A simple example such as fruit juice contains crushed fruit pulp suspended in water. To this base, several different flavouring oils such as citrus peel (Citrus sinensis), lemon (Citrus limon), lavender (Lavandula angustifolia), peppermint (Mentha piperita), thyme (Thymus vulgaris), cinnamon (Cinnamomum verum), tea tree (Melaleuca alternifolia), rose wood (Dalbergia nigra), etc. are added to improve the flavour of the juice. Further, polysaccharides such as xanthan (Mirhosseini et al., 2008), carrageenan or pectin (Ibarz et al., 1996) may be added to improve the mouthfeel and flow properties, stability and shelf life of the final product.

Another class of beverages are milk based, such as fruit milkshakes, chocolate milks and coffee-milk-based beverages. In all these beverages, milk forms the water base of the beverage, and most of the flavouring compounds, such as carotenoids, polyphenols and essential oils, are emulsified into fine droplets suspended in this water phase (Voilley and Etiévant, 1995). The fat component of the milk is also suspended in this complex mixture, thus forming an oil-in-water emulsion. Many of the final properties of these beverages, like texture, mouthfeel, flavour release, stability and shelf life, depend on droplet size distribution, viscosity and interactions between different components in the mixture.

Foams in Food Systems
Foams in food systems are typically dispersions of gas bubbles in a liquid, which at first sight resemble emulsions. Instead of fat molecules (or triacylglycerols, to be exact), the dispersed phase in foams consists of a gas (e.g., air or carbon dioxide), and the dispersion medium is typically a liquid. However, incorporating air into a liquid without any additional stabilizers typically results in
only in short-lived bubbles. More stable culinary foams are thus created with proteins, fats or surfactants (abbreviation from “surface active agent”) (Myhrvold et al., 2011). Different types of foams are stabilized by different underlying mechanisms. For example, a foam made with egg white is a typical foam stabilized by proteins. In this case, the protein molecules are partially denatured by whipping and subsequently coat the surface of the air bubbles. In this process, the denatured proteins rearrange at the water–gas interface in such a way that the hydrophobic segments of the protein stick to the gas phase while the hydrophilic parts remain in the water phase (Kijowski, 1995; Brown, 2018). In this way, the proteins form a thin film around the air bubbles, thus stabilizing the foam.

Whipping cream, on the other hand, is stabilized with semi-solid fat crystals (Hasenhuettl and Hartel, 2008). Dairy triacylglycerides have melting points between −40 °C and +40 °C, so that at room temperature, whipping cream contains both solid fat crystals and melted fat (Chandan, 2011; Marshall et al., 2012). Through whipping, the triacylglycerol molecules (in crystals and in liquid droplets) move to the edges of the gas bubbles, where they form a thin membrane around them, stabilizing the foam. Thus, as the triacylglycerol molecules have to be present both as solid crystals and in melted form in order to make whipped cream, the temperature of the cream should not be too high. According to the current consensus, the best whipped cream is achieved by using chilled/refrigerated whipping cream at around 5–10 °C (Hasenhuettl and Hartel, 2008; Ihara et al., 2010; Myhrvold et al., 2011; Provost et al., 2016; Brown, 2018).

Finally, foams can be formed using emulsifiers, such as lecithin from egg yolk. The underlying physics in this case are similar to those described earlier in the context of emulsions: the emulsifier molecules arrange themselves at the gas–liquid interface in such a way that the hydrophobic part of the emulsifier remains in the gas and the hydrophilic in the water phase (Vega et al., 2012).
Emulsions: Emulsified Systems in Food

Culinary foams, just like emulsions, are inherently not stable and collapse over time (with the exception of solid foams such as bread). The mechanisms of foam decay are similar to those of emulsion instability and phase separation (Hasenhuettl and Hartel, 2008; Bamforth et al., 2011). To name some, the walls between bubbles can burst (causing the bubbles to merge), leading to foam coalescence. As gasses are (to varying degree depending on the gas and pressure) soluble in water, the gas molecules can dissolve into the water phase and escape the bubbles. This process takes place between bubbles with different Laplace pressures, which leads the bubbles to diffuse from areas of high Laplace pressure (small bubbles) into areas of lower Laplace pressure (large bubbles). For example, the Laplace pressure of an air bubble (at 25 °C) in water with a diameter of 1000 μm is around 300 Pa (Weaire and Hutzler, 2001). Halving the diameter (500 μm) leads the pressure to increase to almost 600 Pa, and a bubble of only 100 μm has a Laplace pressure of almost 3 kPa. This behaviour of gas molecules diffusing from smaller to larger bubbles is called disproportionation (the foam “version” of Ostwald ripening). Finally, as a foam consists of a dispersed gas phase separated by a thin membrane from the continuous water phase, the water slowly drains away from between the bubbles, a phenomenon called film drainage.

Beer Foams

The beer head is one of the first characteristics we tend to notice when we receive our drink. Too much of it, and we feel cheated out of our beer; too little of it, and the beer appears flat and stale.

Not surprisingly, scientific research has also established that the quality of the beer foam is perceived as one of the most (if not even the most) important signs of overall quality in a served beer (Bamforth, 2000). Apart from the perceived quality, however, beer foam also fulfills several other important functions. To name some, the foam dampens the oscillations of the liquid when the glass is carried (about 10% in comparison to a headless beer) (Narziß et al., 2017). It also serves as a barrier, slowing down the escape of gas out of the beer; the bitter flavour of hops tends to concentrate in it, and many aroma compounds also tend to concentrate in the foam (Bamforth, 2016). Lastly, the foam also contributes to the mouthfeel of the beer, and in part to the characteristic CO₂ tingle (Langstaff and Lewis, 1993a; Langstaff and Lewis, 1993b).

A lot of research effort has been put into understanding the life of beer foam. There are several substances that contribute to (or reduce) foam quantity and quality (such as proteins, polyphenols, alpha acids, oligo-/polysaccharides and metal ions, to name some) (Bamforth et al., 2011). Essentially, however, beer foam is a type of foam stabilized by proteins, originating mainly from the malts (Asano and Hashimoto, 1976, 1980; Bamforth, 1985). A further important factor increasing the stability of the beer foam is the so called iso-alpha-acids contributed by the hops. The iso-alpha-acids molecules are surface-active and contribute to the head stability by cross-linking foam proteins. An example of an alpha acid is humulone, also called alpha-lupulic acid ((6S)-3,5,6-trihydroxy-2-(3-methylbutanoyl)-4,6-bis(3-methylbut-2-en-1-yl)cyclohexa-2,4-dien-1-one). Together, these two components lay the foundations for a stable beer foam. Further components such as polyphenols and melanoidins similarly support the foam stability (Bamforth, 1998; Bamforth et al., 2011; Lewis and Lewis, 2003). Finally, substances that increase the beer viscosity (polysaccharides such as β-glucans, consisting of six-sided D-glucose monomers) and pentosans ([[(2R,3R,4S,5R)-2-hydroxy-5-[(2S,3R,4S,5R)-5-hydroxy-3,4-disulfooxyoxan-2-yl] oxy-3-sulfooxyoxan-4-yl] hydrogen sulphate) originating from the malts) slow down the rise of the gas bubbles in the beer, giving them more time to collect foam-promoting substances on their way up (Bamforth et al., 2011). However, research until now has not been able to show unambiguously that increased viscosity increases the foam stability by reducing foam drainage. Fats and detergents, on the other hand, inhibit foam formation and destabilize existing foams, which is why dirty drinking glasses tend to make themselves noticeable (Langstaff and Lewis, 1993a; Dickie et al., 2001; Bamforth et al., 2011). Apart from the main players in beer foam stability (proteins and iso-alpha-acids), factors such as alcohol content, pH, polyphenols and gas type influence the foam quality in beer. Both ethanol and polyphenols have been shown to be foam-promoting or foam-inhibiting depending on the exact circumstances (Sarker et al., 1995; Brierley et al., 1996; Bamforth, 1998; Evans et al., 1999, 2002; Fisher et al., 1999; Lewis and Lewis, 2003). Ethanol generally lowers the surface tension in beer foam, and thus, it could be expected that high ethanol content would promote foam stability (weak correlation between ethanol content and improved foam stability has been established in some studies (Bamforth, 1998). However, it has also been observed that a high ethanol content possibly disturbs the interactions between proteins and iso-alpha-acids and thus destabilizes the foam (akin to lipids).

Polyphenols, on the other hand, are assumed to slightly promote foam stability in the same way as iso-alpha-acids do (cross-linking proteins in the foam) (Lewis and Lewis, 2003; Bamforth, 1998; Sarker et al., 1995). However, polyphenols are also generally associated with the precipitation of foam-promoting proteins in different stages of the brewing process (and leading to haze formation later in the finished product) (Lewis and Serbia, 1984; Barth, 2013; Bamforth, 2016).

The pH of beer has been observed to correlate with foam stability (Melm et al., 1995; Bamforth and Kanauchi, 2003). The reason for this is assumed to be the amphiphilic nature of proteins and iso-alpha-acids, which means that a variation in pH results in a change in charge in these substances. Thus, a lower pH could lead to a greater dissociation of the proteins and iso-alpha-acids, which would in turn promote their migration to the beer–gas interface. The change in charge is also expected to aid their interaction.

Lastly, beer is typically carbonated either using carbon dioxide or nitrogen, as demonstrated in Figure 33.12. Guinness is typically nitrogenized, whereas in other types of beer (such as wheat beer), carbon dioxide is used. The advantage of using nitrogen in beer when compared with CO₂ arises mainly from the substantially lower solubility of nitrogen in beer (about 100 times less than CO₂) and from the fact that it is pH neutral (Bamforth et al., 2011). Due to the lower solubility of nitrogen, higher gas pressures can be used to dispense beer through narrower openings to produce a great number of small bubbles (Carroll, 1979; Barth,
The foam stability is, in turn, enhanced by the lower partial pressures between the inner bubble and the atmosphere when using nitrogen. Thus, by the time the foam on a wheat beer is long gone, the foam on a Guinness remains practically unchanged.

**Ice Creams**

Ice creams, when considering their physics and chemistry, are surprisingly complex systems. A wide range of frozen desserts fall under the category of “ice cream”. Dairy ice creams (dairy ingredients, sugar and flavours), gelato (Italian custard-based ice cream) and sorbet (fruit-based ice cream that contains no fat and no milk) are a few popular varieties (Clarke, 2015). They are complex emulsified systems consisting of air (about 30–50% of the volume), ice crystals (up to 40%), fat crystals (5–10%) and an aqueous phase consisting of sugar, milk proteins and flavouring components (Merkus and Meesters, 2013).

The proteins play a role in stabilizing fat globules and air bubbles in the ice cream. At the same time, some emulsifiers are added to ice cream mixtures to displace some of the proteins adsorbed to the fat interfaces (Marshall et al., 2003). This not only allows the fat droplets to partially coalesce and entrap air bubbles (similar to the mechanism in whipped cream) but is also very important for the right texture and to slow the meltdown (Cropper et al., 2013). Any remaining proteins that are not adsorbed to the interfaces remain dissolved in the unfrozen water phase and increase its viscosity (El-Zeini, 2016). Finally, yet importantly, the proteins also influence the flavours of the ice cream. As the milk protein content of the ice cream increases, there is a corresponding decrease in flavour intensity due to binding interactions of flavour molecules with proteins (Hansen, 1996).

The term “sugar” in ice cream manufacturing covers several different kinds of sugar compounds, including such sugars as D-glucose, D-fructose, sucrose and sugar alcohols (Ozdemir et al., 2008). Apart from sugar giving the ice cream its sweetness, the softness and the viscosity of the ice cream can be modified by varying the sugar content and the composition of the added sugar mix (Clarke, 2015). Generally speaking, a higher sugar content leads to fewer ice crystals in ice cream, thus making it softer (Vega et al., 2012). Addition of sugar molecules causes a depression in the freezing point of water in ice cream. This slows down the crystallization process and thus leads to the formation of fewer ice crystals. The same effect can also be attained without increasing the sweetness of the ice cream by using different kinds of sugars.

The fat in ice cream also plays several roles. As already mentioned, the fat helps to stabilize the foam part of the ice cream, but it is also responsible for the creamy texture, and any fat-soluble flavour molecules are dissolved in it. The fat also influences the mouldability (Goff, 1997; Goff, 2008) of the ice cream and helps it to retain its shape when it is melting. Butterfat, cream and vegetable oils are commonly used in both industrial and homemade ice creams as fat sources.

Water makes up about 60–72% of ice cream’s weight (Clarke, 2015). Not all of this is frozen into crystals; 15–27% remains liquid and contains dissolved sugars and proteins. Smaller ice crystals are preferred over large ones, as they give a softer texture, unlike larger crystals, which lead to a coarser, gritty texture. The problem, however, is the propensity of the ice crystals for recrystallization, which causes the small ice crystals to merge into larger ones over time. This is also one of the major factors limiting ice cream’s shelf life. In order to slow this down, it is necessary to use stabilizers (usually polysaccharides such as locust bean gum or carrageenans). Apart from limiting ice crystal growth, stabilizers also help to achieve a smooth texture, reduce or slow down lactose crystal growth, and increase the ice cream’s resistance against meltdown.

Making a short leap from the fundamental physics to manufacturing ice cream, there are different possibilities for how to make the ice cream after mixing the ingredients. Factory-produced ice cream is typically homogenized, pasteurized and aged before further processing (Batt and Tortorello, 2014), but for home use, these steps are skipped. In the food industry, the freezing is quite
often done with devices called scraped surface heat exchangers, which in their simplest form consist of a cylindrical container with a double wall and a rotating dasher in the middle. The working principle is quite similar to that of a refrigerator; a liquefied gas (typically liquid ammonia) flows through the double wall of the cylinder and cools the container (down to around −30 °C) as it evaporates. The dasher in the middle scrapes the frozen ice cream off the walls of the vessel while beating and aerating it simultaneously. After initial freezing, the ice cream is hardened at around −30 to −45 °C in a freezer with cold air. Alternatively, the ice cream can also be processed via low-temperature extrusion, whereby the ice cream is sent through a cylindrical container with refrigerated walls and a screw extruder. This method offers several advantages in comparison to the first method, such as higher shear stress with lower shear rate, lower processing temperatures, and the formation of smaller ice crystals and air bubbles.

The basic principles of ice cream manufacturing stay the same for homemade ice cream. The easiest way to do this is by using an ice cream maker, which works in the same way as the scraped surface heat exchangers used in professional manufacturing. One of the major differences in this case is the freezing temperature (around −20 °C), which is reached by using salted ice water (or an eutectic mixture of ice and salt, to be precise). Alternatively, the ice cream mixture can be whisked at regular intervals while freezing (e.g., once every hour for two or three times) to break the ice crystals. In this way, however, the consistency of the ice cream won’t necessarily be as good as by using an ice cream maker.

Pacojet Ice Cream

One possible way of making ice cream in professional gastronomy is by using Pacojet. In this equipment, the ice cream mixture is frozen overnight and the frozen mixture is “blended” (or “pacotized”) the following day. We conducted our own experiments on different flavour combinations in this way. The basic recipe used in our simple experiments consisted essentially of the main flavour component (e.g., mango juice, red wine, tea-flavoured milk or plant-based drink), an emulsifier (e.g., egg yolk or pure lecithin), fat (e.g., olive oil or butter), and sugar. The following are four examples for recipes we used (Figure 33.13).

Mango-mint-olive oil ice cream

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mango juice</td>
<td>440 g</td>
<td></td>
</tr>
<tr>
<td>Olive oil</td>
<td>60 g</td>
<td></td>
</tr>
<tr>
<td>Caster sugar</td>
<td>100 g</td>
<td></td>
</tr>
<tr>
<td>Handful of mint</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Glühwein ice cream

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glühwein / mulled wine</td>
<td>220 g</td>
<td></td>
</tr>
<tr>
<td>Berry juice (mixed berries, e.g., black currants, raspberries)</td>
<td>220 g</td>
<td></td>
</tr>
<tr>
<td>Melted butter</td>
<td>60 g</td>
<td></td>
</tr>
<tr>
<td>Caster sugar</td>
<td>100 g</td>
<td></td>
</tr>
<tr>
<td>Egg yolk</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Earl Grey ice cream

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full-fat milk</td>
<td>300 g</td>
<td></td>
</tr>
<tr>
<td>Whipping cream</td>
<td>200 g</td>
<td></td>
</tr>
<tr>
<td>Earl Grey tea</td>
<td>3 bags</td>
<td></td>
</tr>
<tr>
<td>Sugar</td>
<td>100 g</td>
<td></td>
</tr>
<tr>
<td>Egg yolk</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Blueberry-oat ice cream

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oat milk</td>
<td>400 g</td>
<td></td>
</tr>
<tr>
<td>Melted butter</td>
<td>60 g</td>
<td></td>
</tr>
<tr>
<td>Blueberries (frozen)</td>
<td>300 g</td>
<td></td>
</tr>
<tr>
<td>Oats</td>
<td>60 g</td>
<td></td>
</tr>
<tr>
<td>Sugar</td>
<td>100 g</td>
<td></td>
</tr>
<tr>
<td>Egg yolk</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

For the recipe with Earl Grey, the milk–cream mixture was warmed up and the tea bags soaked in it for about 10 minutes. Otherwise, the ingredients were simply mixed together/blended and frozen overnight. The frozen mixture was pacotized the following day and served immediately. For better consistency, the pacotized ice cream can be stored in a freezer for about an hour before serving. The ingredients and amounts can easily be varied for different flavour combinations and consistencies. As quite often, the only limit is your imagination!

Conclusion

This chapter is intended to give a rough overview on the topic of emulsified systems and foams in the context of food systems. Emulsified systems play a big role in the food industry, but they can also be found in the cosmetic, pharmaceutical and chemical industries, to name a few. Among foods, there is a great variety of emulsified systems ranging from beverages to solid food. As both emulsified systems and foams are fundamentally metastable, it is important to understand the physical principles underlying this instability. This allows one to improve the shelf life, flavour, aroma retention, texture and many other aspects of food products. Understanding these principles will also help with home cooking,
whether saving a failing mayonnaise or appreciating why chilled whipping cream is better suited for whipping than warm.

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