ANNUAL REVIEWS

Annual Review of Food Science and Technology

Formation, Structure, and Functionality of Interfacial Layers in Food Emulsions

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Annu. Rev. Food Sci. Technol. 2018. 9:551–87

First published as a Review in Advance on January 18, 2018

The *Annual Review of Food Science and Technology* is online at food.annualreviews.org

https://doi.org/10.1146/annurev-food-030117-012405

Keywords

food emulsions, oil-water interface, emulsifiers, interface structure, interface dynamics

Abstract

Emulsions, i.e., the dispersion of liquid droplets in a nonmiscible liquid phase, are overwhelmingly present in food products. In such systems, both liquid phases (generally, oil and water) are separated by a narrow region, the oil-water interface. Despite the fact that this interface is very thin (in the nanometer range), it represents a large surface area and controls to a great extent the physicochemical stability of emulsions. This review provides an overview of the aspects that govern the composition, structure, and mechanical properties of interfaces in food emulsions, taking into account the complexity of such systems (presence of numerous surface-active molecules, influence of processing steps, and dynamic evolution due to chemical changes). We also review methods that have conventionally, or recently, been used to study liquid-liquid interfaces at various scales. Finally, we focus on the link between interfacial properties and the physical, chemical, and digestive stability of emulsions at different levels and point out trends to control stability via interfacial engineering.

INTRODUCTION

Many food products are emulsions of two immiscible liquid phases (usually oil and water), with one phase dispersed as droplets in the other phase, e.g., oil-in-water (O/W) emulsions (such as milk, salad dressing, and mayonnaise) and water-in-oil (W/O) emulsions (such as butter and margarine). The use of emulsions to bring additional, targeted functionality to foods has been an emerging trend, as emulsions may encapsulate nutrients and nutraceuticals, protect them against chemical degradation, increase their bioavailability, and control their delivery (McClements 2012, McClements et al. 2007).

Because of the small size of the dispersed droplets (approximately 100 nm to 100 μm, i.e., the colloidal scale), emulsions are interface-dominated materials, with an interfacial area between oil and water typically in the m^2 per gram of dispersed material range. This has a number of consequences; for example, a large contact area between immiscible phases leads to a high level of free energy in the systems, which prompts physical instability (Walstra 2003). The composition and structure of the interfacial layer also affect processes that involve both water- and oil-soluble reactants, such as lipid oxidation or lipid digestion (Berton-Carabin et al. 2014, Corstens et al. 2017a, McClements & Decker 2000). It is, therefore, important to control these parameters, but this control is highly challenging.

Emulsifiers (e.g., proteins, phospholipids) that are used to ensure the physical metastability of the system are located at the oil-water interface in food emulsions, and a number of minor components with various surface activity, e.g., antioxidants or free fatty acids, are as well (Heins et al. 2007, Jacobsen et al. 2008, Laguerre et al. 2015, Losada-Barreiro et al. 2013, Waraho et al. 2011). These surface-active components partition between the interface and the other phases of the emulsion, meaning that their interfacial concentration does not reflect their overall concentration (Berton-Carabin et al. 2014). The oil-water interface is not necessarily structurally homogeneous and may have laterally separated domains (Mackie et al. 1999, Wilde 2000). Finally, the interface is a dynamic region, and its composition and structure may change over time through, e.g., interfacial protein polymerization (Monahan et al. 1993), adsorption of lipid oxidation products (Laguerre et al. 2017, Nuchi et al. 2002), or formation of lipolysis products (Golding & Wooster 2010, Leal-Calderon & Cansell 2012, Maldonado-Valderrama et al. 2010).

Initially, we present a number of basic prerequisites related to food emulsions and emulsifiers as well as the physicochemical instability phenomena that such systems are subjected to, from production to the consumer's gastrointestinal tract (GIT). We provide insight into the formation of interfaces in food emulsions, which is mostly about the mechanisms of droplet breakup and emulsifier adsorption in homogenization devices. We discuss the involved timescales, which are typically very short and should be considered when selecting methods for assessment of interface formation and emulsifier adsorption. We then cover the dynamic adsorption behavior of mixtures of emulsifiers and other surface-active species and link it to partitioning behavior. The structure and rheological properties of interfaces in food emulsions are reviewed, highlighting their dynamic evolution due to aging phenomena. Although this aspect has been often overlooked, it needs to become an integral part of the development of stable and functional food emulsions. Analytical methods available to study the composition and structure of interfaces in food emulsions are then reviewed. The design of interfaces with specific functional attributes is discussed as are recent developments in the creation of bioinspired emulsions, e.g., mimicking the natural milk-fat-globule interface in food emulsions.

PREREQUISITES FOR FOOD EMULSIONS

Emulsions: Basic Knowledge and Terminology

Emulsions consist of droplets of one liquid phase dispersed in another immiscible liquid phase, e.g., oil and water (Dickinson 1992a, Leal-Calderon et al. 2007). There are two main types of emulsions: O/W emulsions and W/O emulsions. Because of the molecular incompatibility of each phase, such dispersions tend to undergo phase separation to minimize the contact area between the phases, which results in a change in the free energy of the system (ΔG, J) equal to

$$\Delta G = \gamma \Delta A, \qquad 1.$$

where γ (N/m) is the interfacial tension between oil and water, and ΔA (m^2) is the change in interfacial area in the system. ΔA directly depends on the oil-phase volume fraction and the droplet size. In food emulsions, droplet sizes range from less than 0.1 μm to 100 μm or larger. The interfacial area per unit mass of dispersed phase, or specific surface area (A_{spec}, m^2/g oil), can be calculated as

$$A_{spec} = \frac{3}{r\rho}, \qquad 2.$$

where r is the average oil droplet radius (μm) and ρ is the dispersed phase density (g/ml). The specific surface area in emulsions often reaches several m^2 per g of oil, which promotes phase separation. Rapid phase separation can be avoided via the use of thickeners, which increase the viscosity of the continuous phase and thereby decrease the rate of droplet creaming or sedimentation (McClements 2005). Most food-grade thickening agents, such as xanthan gum, are water-soluble and hence efficient in O/W emulsions (Dickinson 2009). However, the interface also needs to be stabilized, which requires emulsifiers, amphiphilic molecules that tend to adsorb to the oil-water interface and form a protective layer. This causes the interfacial tension to decrease, which facilitates droplet breakup during emulsification (Walstra 2003) and decreases the free energy of the system (Equation 1). The interfacial film can be responsible for repulsive droplet-droplet interactions, which contribute to the emulsion's physical stability. The repulsion can be due to electrostatic interactions (with charged emulsifiers) and/or to steric interactions (due to the overlapping of interfacial molecules from two approaching droplets) (McClements 2005).

Food Emulsifiers

Different types of emulsifiers are used to kinetically stabilize food emulsions (Genot et al. 2013, Hasenhuettl & Hartel 2008). In this section, we briefly present the three main categories: low-molecular-weight emulsifiers (LMWEs), amphiphilic biopolymers, and solid particles.

Low-molecular-weight emulsifiers or surfactants. This category comprises relatively small molecules (molecular weight from approximately 250 g/mol to approximately 1,200 g/mol) that may be synthetic or natural (Kralova & Sjöblom 2009, McClements & Gumus 2016). LMWEs consist of a hydrophilic head (which can be nonionic or charged) and a hydrophobic tail, which is generally constituted by one or more acyl chains. Examples of synthetic food-grade LMWEs include mono- and diglycerides, sucrose esters, derivatives of monoglycerides (e.g., CITREM, a citrate ester), and polyoxyethylene derivatives [e.g., sorbitan esters, such as Tween 20 (polyoxyethylenesorbitan monolaurate)]. Although synthetic LMWEs have been widely used in the food industry, there is increasing interest in natural, biobased alternatives (McClements

& Gumus 2016, McClements et al. 2017), such as phospholipids (often available as lecithins), saponins [e.g., from *Quillaja* (Yang et al. 2013)], and glycolipids [e.g., digalactosyl-diglycerides (Kralova & Sjöblom 2009)], that may be of animal, plant, or microbial origin.

The purity of LMWEs used in food applications is rarely high, and LMWEs may contain unreacted substrates and side products (for synthetic LMWEs) or impurities when extracted from natural sources. For instance, lecithins often contain triacylglycerols and sphingolipids in amounts that exceed 30% (Aboofazeli & Lawrence 1994), and in commercial Tween 20, the fatty acid composition is broad, ranging from capric acid to oleic acid, with only approximately half of the fatty acid composition represented by lauric acid (Berton et al. 2011a).

Amphiphilic biopolymers. This category of emulsion stabilizers comprises different types of water-soluble molecules, mainly proteins and polysaccharides. Proteins tend to adsorb at the oil-water interface, creating a macromolecular film that protects emulsion droplets against physical destabilization, particularly, coalescence (Dickinson 1994). Dairy proteins have been extensively studied, as either their two main fractions (whey proteins and caseins or caseinates) or individual components (e.g., β-lactoglobulin, α-lactalbumin, and β-casein). Depending on their molecular structure and level of molecular organization, dairy proteins have very different behaviors at fluid interfaces. Compact, globular proteins such as β-lactoglobulin form dense and interconnected interfacial films, whereas flexible, disordered proteins such as caseins form thicker yet less dense films (Dickinson 1992b).

Plant proteins have recently gained considerable interest as sustainable alternatives for their animal-based counterparts (Day 2013, Wan et al. 2015). Traditionally, soy proteins have been the focus of attention (Amine et al. 2014, Cui et al. 2014, Fernandez-Avila & Trujillo 2016, Ho et al. 2017, Keerati-u-rai et al. 2011, Kinsella 1979, Shao & Tang 2014, Tang 2017), but potato proteins (Amine et al. 2014, Cheng et al. 2010, Ralet & Guéguen 2000) and proteins from various legume sources such as lentils, peas, and chickpeas (Amine et al. 2014, Geerts et al. 2017, Gumus et al. 2017, Ho et al. 2017, Ladjal Ettoumi et al. 2017) have also become very popular. However, major drawbacks are the relatively low solubility of a number of these plant protein ingredients at low or neutral pH (Carbonaro et al. 1997) and the heavy processing necessary to obtain plant protein isolates.

Some polysaccharides have emulsifying properties because they contain nonpolar groups such as methylated groups or exogenous moieties such as lipids or proteins, which may be bound covalently or noncovalently to the polysaccharide backbone (Dickinson 2009, McClements & Gumus 2016). The most widely used polysaccharide in food emulsions is gum arabic, but modified starches, pectins, and galactomannans (Dickinson 2009, McClements & Gumus 2016, Mikkonen et al. 2016) may also be used.

Colloidal particles. Over the past decade, the use of colloidal particles to stabilize food emulsions has become a popular research topic. These so-called Pickering emulsions have historically been studied with inorganic particles, whereas various naturally occurring particles [e.g., starch granules (Rayner et al. 2012)] as well as manufactured particles from biobased materials [e.g., from proteins (Destribats et al. 2014, Liu & Tang 2014) or lipids (Pawlik et al. 2016, Schröder et al. 2017b)] have become relevant for food applications. For more detail, we refer the interested reader to the following recent reviews: Berton-Carabin & Schroën (2015); Dickinson (2010, 2012); Lam et al. (2014); Rayner et al. (2014); and Tavernier et al. (2016).

Instability Issues in Food Emulsions

Emulsions can destabilize through different mechanisms that are mostly undesired when occurring as a result of physical or chemical effects, but during digestion destabilization is required for food uptake to take place. These three destabilization effects are described in more detail below.

Physical destabilization. Almost all emulsions physically destabilize, which may occur through different phenomena and at various timescales (Leal-Calderon et al. 2007, McClements 2005). Gravitational separation (creaming or sedimentation) results from the density difference between the continuous and dispersed phases and can eventually lead to macroscopic phase separation. Gravitational separation can be slowed down by density matching (e.g., in beverages), decreasing the droplet size, and/or increasing the viscosity of the continuous phase. Both strategies are commonly applied, e.g., in raw milk homogenization and the use of thickening agents (e.g., various gums) in salad dressings.

Droplet flocculation involves aggregation of two or more emulsion droplets to form a floc without the droplets merging. Flocculation can occur if the attractive forces (i.e., van der Waals interactions) between droplets overcome the repulsive forces (i.e., electrostatic and steric repulsion), through bridging at low biopolymer concentration, or because of depletion effects (in the presence of high concentrations of excess emulsifier or thickening agent) (Dickinson 2009, Guzey & McClements 2006). Irrespective of the underlying mechanism, flocculation leads to an increase in effective particle size, which promotes gravitational separation, and in effective dispersed phase fraction because the flocs entrap a fraction of the continuous phase, hence increasing the emulsion's viscosity.

For droplet coalescence to occur, the interfacial film around contacting droplets needs to rupture, leading to the merging of droplets and possibly formation of a layer at the top or bottom of the emulsion, which would constitute a severe appearance defect in most food emulsions. Droplet coalescence leads to a decrease in the total interfacial area, which is thermodynamically favorable (Equation 1). Contrary to flocculation, this phenomenon is irreversible.

Ostwald ripening also leads to increased droplet size, although through different mechanisms and driving forces compared to coalescence. In polydisperse emulsions, small droplets have a larger internal Laplace pressure than do large droplets, which promotes diffusive transfer of the dispersed phase from smaller to larger droplets (Leal-Calderon et al. 2007). Ostwald ripening is often not a considerable problem for food O/W emulsions, as the solubility of triacylglycerols in water is extremely low (McClements 2005), but it can affect foams or emulsions containing flavor or essential oils due to the relatively high water-solubility of these oils.

These destabilization phenomena are connected to the properties of the oil-water interface, although sometimes indirectly. In flocculation, adsorbed molecules may induce electrostatic and/or steric repulsion between droplets, depending on their molecular structure and the environmental conditions (e.g., ionic strength and pH). In the case of coalescence, there is drainage of the continuous phase followed by the creation of a hole in the interfacial layers between the droplets, which can be seen as dilatational deformation (Murray 2011). The mobility of the adsorbed molecules and the viscoelasticity of the interfacial layer can thus affect the coalescence process. Gravitational separation is promoted by flocculation or coalescence through an increased effective droplet size and can also be affected by interfacial mobility (Felderhof 2006). If the droplets are very small (less than 100–200 nm), the interface constitutes a volume fraction that is no longer negligible and can substantially influence droplet density (McClements & Decker 2000). Ostwald ripening is not much influenced by conventional emulsifier-based interfaces that do not affect molecular diffusion, but in Pickering emulsions, the loss of material from the small droplets is arrested by the strong desorption energy of the particles (Ashby & Binks 2000).

Chemical destabilization. Food emulsions are prone to chemical destabilization during processing and storage, mostly through oxidative reactions that degrade polyunsaturated lipids (i.e., lipid oxidation) or labile micronutrients (e.g., vitamins, pigments). Because of the health benefits of polyunsaturated lipids, increasing their amounts in food has become a priority, and thus counteracting lipid oxidation a major challenge. Lipid oxidation is presumably initiated at the surface of the oil droplets, where the labile lipid substrate comes into contact with aqueous prooxidants (e.g., reactive oxygen species and metal ions). Recently, it was proposed that the propagation of the reaction could involve a transport of reactive species and/or intermediate reaction products from the core of an oxidizing oil droplet, through the interface and then the continuous phase to neighboring droplets (Laguerre et al. 2017). Barrier effects of the oil-water interface are hence desirable to prevent the initiation and propagation of the reaction. In that respect, the composition and structure of the oil-water interface are thought to control, at least partly, the rate and extent of lipid oxidation (Berton-Carabin et al. 2014, McClements & Decker 2000, Waraho et al. 2011).

Digestive destabilization. In the human GIT, lipid digestion starts in the stomach but mainly takes place in the small intestine, where the digestion products are also absorbed (Golding & Wooster 2010). Food lipids are mainly triacylglycerols, which are digested by lipases that hydrolyze the ester bonds at the sn-1 and sn-3 positions of the glycerol backbone. Lipases act at the oil-water interface, where the water-soluble lipase and the lipid substrate meet. In humans, the two main types are gastric lipase in the stomach and pancreatic lipase in the small intestine, with the latter needing to be associated with a colipase, which is also secreted by the pancreas. Although most of the lipolysis takes place in the small intestine, prior digestion phases are important, as they affect other emulsion constituents; for example, the low pH and proteolytic activity in the stomach contribute to the physical destabilization of protein-stabilized emulsions (Kenmogne-Domguia et al. 2012).

To ensure optimal lipolysis in the GI tract, several natural mechanisms increase the oil-water interfacial area and prevent inhibition by reaction products. Bile salts and phospholipids, which are highly surface-active components, are secreted in the small intestine to stabilize an existing or newly created oil-water interface and facilitate lipase action (Golding & Wooster 2010, Maldonado-Valderrama et al. 2013, Reis et al. 2009). Bile salts displace emulsifiers from the oil-water interface, starting with competitive adsorption at defects in the interfacial structure. The bile salt domains grow and compress the adsorbed material, and thereby force it to desorb, resulting in an oil-water interface suitable for lipase adsorption and subsequent lipolysis (Corstens et al. 2017a, Golding & Wooster 2010, Maldonado-Valderrama et al. 2013) (**Figure 1**).

FORMATION OF INTERFACES IN FOOD EMULSIONS

Mechanisms of Droplet Breakup and Emulsifier Adsorption

When a continuous liquid phase flows around a liquid droplet, it exerts a shear force on the droplet that may break up if the exerted force is sufficiently large. The ratio of the externally applied stress over the internal, coherent stress is called the Weber number (*We*), which is defined as (Walstra 2003)

$$We = \frac{\sigma_{ext} d}{2\gamma}, \qquad 3.$$

where σ_{ext} is the externally applied stress (Pa) and d is the droplet diameter (m).

Using Equation 3, one can calculate the applied stress needed to make droplets of a given size, provided that the required critical Weber number (We_{cr}) can be estimated. For laminar

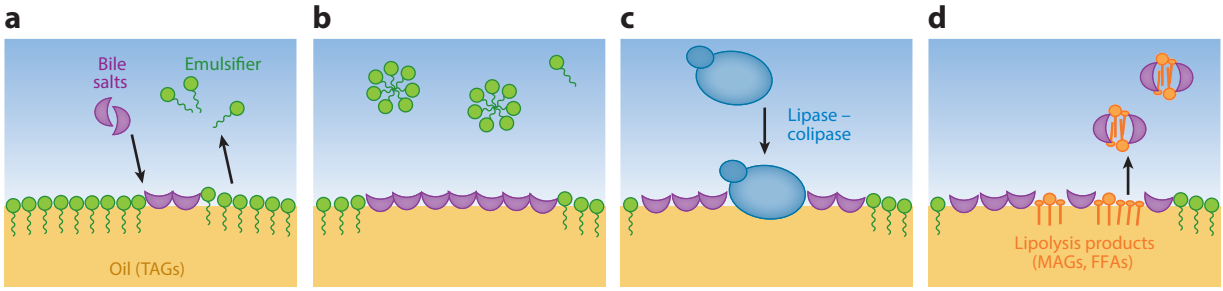

Figure 1

Schematic representation of the steps required for intestinal lipolysis of emulsions. (*a*) Displacement of initially present emulsifiers by bile salts, (*b*) growth of the bile salt domains, (*c*) adsorption of the pancreatic lipase-colipase complex, and (*d*) removal of lipid digestion products from the interface by bile salts via the formation of mixed micelles. Abbreviations: FFAs, free fatty acids; MAGs, monoacylglycerols; TAGs, triacylglycerols.

flow conditions, We_{cr} has been described as a function of the viscosity ratio of the dispersed and continuous phases while assuming constant interfacial tension (Walstra 2003). In turbulent flow conditions, the exact local flow conditions are highly variable, and newly formed droplets collide, which may lead to rapid recoalescence, depending on the extent to which droplets are readily covered by emulsifier molecules (Tcholakova et al. 2008) (**Figure 2**). In practice, it is very difficult to estimate what the actual emulsifier coverage of droplets is during homogenization processes because of the short timescales involved, typically 10^{-4} to 10^{-1} s (Schultz et al. 2004, Walstra 2003).

Adsorption of emulsifiers at the oil-water interface typically occurs in three steps: (*a*) transport toward the subinterface, (*b*) emulsifier adsorption to the interface, and (*c*) possible structural reorganization at the interface; the last step is especially important for proteins (Stang et al. 1994,

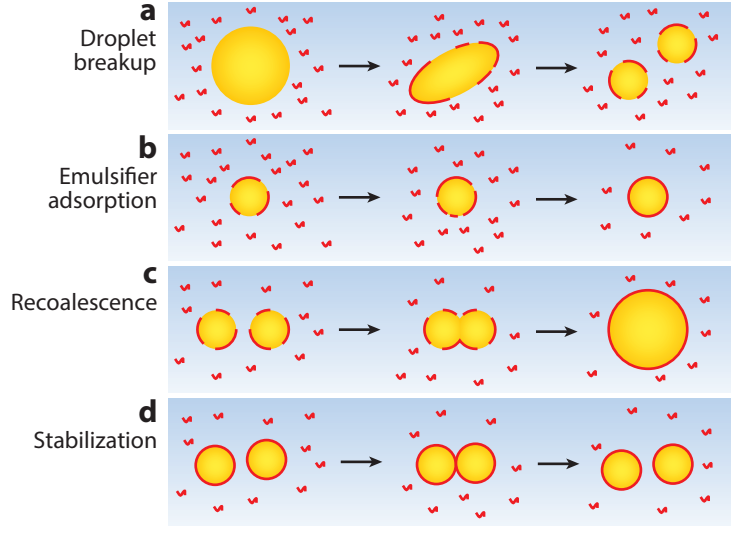

Figure 2

Possible phenomena occurring during emulsification processes, depending on the coverage of emulsion droplets by emulsifiers (*red lines*), going from (*a*) droplet formation to (*b*) emulsifier adsorption as function of time, which can lead to unprotected interfaces that are either (*c*) prone to recoalesce or are (*d*) sufficiently covered interfaces.

Yano 2012, Zhai et al. 2013). Walstra (2003) calculated transport times for complete adsorption (t_{ads}, s) for different emulsifiers, assuming purely diffusion-driven adsorption, using

$$t_{ads} = \frac{\Gamma_\infty^2}{c^2 D}, \quad 4.$$

where Γ_∞ is the final emulsifier surface coverage (mg/m^2), c is the emulsifier concentration in the bulk phase (mg/m^3), and D is the diffusion coefficient (m^2/s). Walstra (2003) found values ranging from a few tens of ms for LMWEs to days for biopolymers. However, in large-scale emulsification processes, intense convection is used to speed up adsorption, with actual adsorption times as short as one microsecond (Walstra 2003).

During the adsorption step, LMWEs and biopolymers (in particular, proteins) behave differently; in proteins, an induction period may be observed during which some molecules adsorb, but interfacial tension is not decreasing (Beverung et al. 1999, Miller et al. 2000). This induction period is due to an initially low number of contact points between protein and fluid interface; for a decrease in interfacial tension, some conformational rearrangements are needed, and this should be taken into account when studying adsorption of proteins (Won et al. 2017).

The adsorption mechanism of colloidal particles (Pickering stabilization) is fundamentally different from that of conventional emulsifiers. Diffusion of such particles is necessarily slower due to their larger size (typically, 50–100 nm to several μm), meaning that active mass transport, or convection, is needed for particles to cross the energy barrier for adsorption, which is due to liquid that has to be removed from the gap separating the approaching particle from the droplet surface (Monteillet et al. 2014, Tcholakova et al. 2008).

Homogenization Methods

Emulsions are often made by mixing the constituent ingredients to obtain a coarse emulsion, which is further refined by passage through an emulsification device (Schroën & Berton-Carabin 2016). In industry, high-pressure homogenizers and rotor-stator systems are commonly used and may require multiple passages depending on the extent of recoalescence. In high-pressure homogenizers, a narrow constriction is used to create a strong (turbulent) shear that may lead to submicron droplets in large-scale equipment (Schuchmann et al. 2013), whereas lab-scale homogenizers operate in the laminar flow regime and therefore hamper the translation of results to large-scale operations. In colloid mills, the velocity difference between rotating and stationary elements creates the shear for droplet breakup (Urban et al. 2006), but the energy density is typically low and making small droplets is difficult. Emulsions can also be produced using other methods, such as membrane emulsification, but these methods are currently unsuitable for most commercial applications (Nakashima & Shimizu 1986, Schröder & Schubert 1999, Vladisavljević & Schubert 2003, Nazir et al. 2010).

In a recent review, Costa et al. (2017) pointed out that homogenization, notably when it involves intense mechanical forces, and the associated increase in the product's temperature can affect the emulsifier molecules (or supramolecular structures). The combined effect of temperature and shear on emulsifiers is often overlooked in emulsion studies. For instance, high pressures can disrupt the tertiary structure of globular proteins, favoring protein unfolding even when the product temperature remains below the protein denaturation temperature, which may lead to protein aggregation. It was also reported that high pressures (typically up to 500 MPa) are able to disrupt the structure of casein micelles, leading to reorganization of casein molecules and formation of aggregates, which could decrease the ability of casein micelles to stabilize emulsions. For Pickering emulsions, some studies reported that the particle size was reduced when subjected

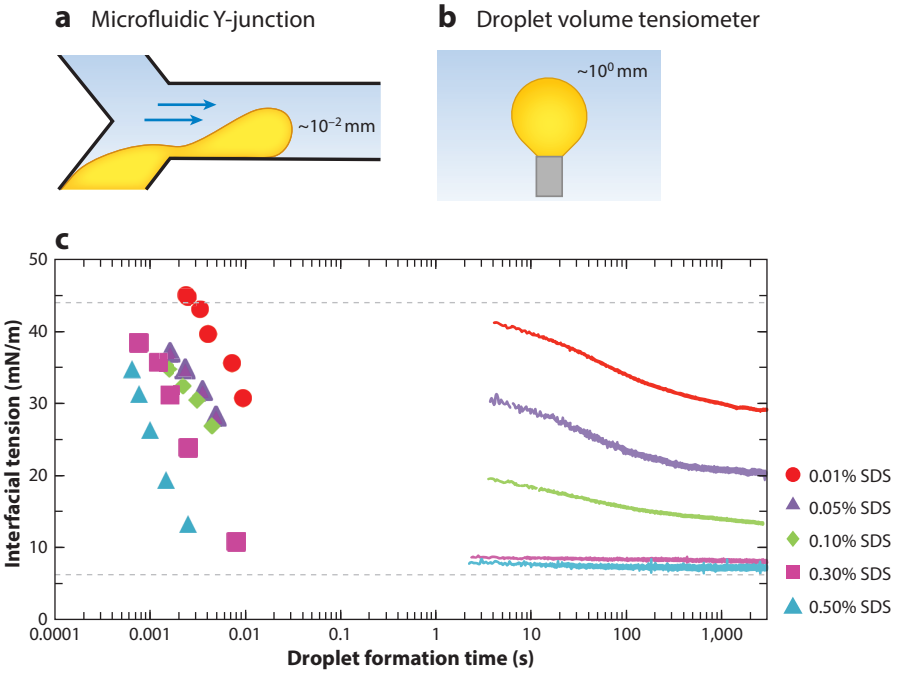

Figure 3

Schematic representation of a (*a*) microfluidic Y-junction and a (*b*) droplet volume tensiometer. (*c*) The interfacial tension at the hexadecane-water interface with various sodium dodecylsulfate (SDS) concentrations in the aqueous phase, as measured with a microfluidic Y-junction (*symbols*) and with a droplet volume tensiometer (*solid lines*). The dotted gray lines represent the equilibrium interfacial tensions between hexadecane and water (*top*) and between hexadecane and a 1% wt SDS solution (*bottom*). Adapted from Muijlwijk et al. (2016a), with permission from Elsevier.

to the emulsification procedure, which could be a result of deaggregation of the colloidal particles (Kurukji et al. 2013, Yusoff & Murray 2011).

Methods to Measure Interface Formation and Emulsifier Adsorption

A number of methods have been developed to measure interfacial tension and thereby emulsifier adsorption at fluid interfaces, e.g., the Wilhelmy plate, the Du Noüy ring, and the spinning drop method (Berry et al. 2015). Among these methods, droplet volume tensiometry, in which a millimetric droplet of one phase is formed at the tip of a needle and immersed in the other phase (**Figure 3*b***) with a different density, is certainly the most widely used (Berry et al. 2015, Miller et al. 1992). The shape of the droplet depends on the balance between gravity and interfacial tension forces; the latter can be determined by analyzing the shape of the droplet. The emulsifier is normally present in one of the phases and starts adsorbing at the fluid interface as soon as the droplet is created, resulting in a change in droplet shape in time.

With the droplet volume tensiometry instruments currently available, the first measurement point is normally obtained after slightly less than one second, and measurements may be conducted for periods of several hours. The timescale for this diffusion-driven process is orders of magnitude longer than typical adsorption times encountered for most emulsifiers in commercial

homogenizers. To probe these conditions, microfluidic devices have been suggested that allow much faster measurements, ranging from 10^{-1} to 10^{2} ms (Muijlwijk et al. 2016a, Steegmans et al. 2009, Wang et al. 2009, Xu et al. 2012). In such systems, emulsion droplets are formed at the junction between two microchannels through which the phases flow (**Figure 3*a***). The droplet size depends on the balance between the shear force exerted by the continuous phase and the interfacial tension; thus, it is possible to determine the interfacial tension at the moment of droplet formation (Muijlwijk et al. 2016a). It is important to note that convection plays an important role in the emulsifier transport to the interface (Alvarez et al. 2012, Muijlwijk et al. 2016b), which is illustrated in **Figure 3*c***. The interfacial tension at the oil-water interface as measured by the microfluidic method (**Figure 3**, left part of the graph) or by droplet volume tensiometry (**Figure 3**, right part of the graph) is plotted as a function of time. The time needed to reach the equilibrium interfacial tension in the microfluidic device is much shorter than in the droplet volume tensiometer as a result of a change in emulsifier transport mechanism to the interface.

Partitioning of Emulsifiers within the Emulsion's Phases

Food emulsions are often formulated with a large excess of emulsifiers compared to the amount needed to cover the oil-water interface (Berton-Carabin et al. 2014). As a consequence, only a small fraction of the emulsifier stabilizes the surface of the oil droplets, and a large fraction remains in the continuous phase, where it can form various colloidal structures such as micelles or aggregates. Different emulsifiers may compete for adsorption at the oil-water interface (Lucassen-Reynders 1994); therefore, the composition of the interface depends on the relative surface activities of the molecules and their adsorption rate and availability (i.e., on their relative concentrations).

The competitive adsorption of proteins and LMWEs has been studied for numerous food systems. For example, Courthaudon and coworkers (Courthaudon et al. 1991a,b,c) studied the competitive adsorption of dairy proteins and LMWEs (e.g., lecithin, Tween 20, oxyethylene glycol ethers). They found that above a certain LMWE-to-protein ratio, water-soluble LMWEs fully dominated the interfacial composition and were able to completely prevent β-casein adsorption. When the surfactant was introduced through the oil phase, some protein material was still present at the droplet surface. More rarely, the formation of an interfacial protein-surfactant complex may take place, as shown for example for β-lactoglobulin and tartaric acid ester (Dickinson & Hong 1994).

The interfacial composition of emulsions made with protein mixtures is mainly determined by kinetic factors, meaning that pure thermodynamic aspects cannot predict the interfacial composition (Dickinson 2011). Substantial work has focused on determining preferential adsorption of dairy proteins; for example, β-lactoglobulin is relatively more present at the emulsion droplet surface than is α-lactalbumin, which could be due to the higher surface hydrophobicity of the former (Dickinson et al. 1989, Schröder et al. 2017a, Ye 2008).

The fact that kinetic factors control to a large extent the composition of adsorbed layers makes it possible to purposely design adsorbed layers by controlling the emulsion formation process. For example, Waninge et al. (2005) made O/W emulsions containing milk proteins and phospholipids and applied different processes while keeping the overall composition identical. They found that proteins dominated the droplet surface when they were present during homogenization, and phospholipids were added posthomogenization, even after several days of equilibration, and vice versa, i.e., phospholipids were predominantly present at the interface when introduced during homogenization, and proteins were added posthomogenization. Jourdain et al. (2009) analyzed the properties of oil-water interfaces made of sodium caseinate and dextran sulfate, either mixed

prior to adsorption, or introduced sequentially. Interfacial shear rheology experiments showed that the mixed system gave much stronger interfacial films compared to the sequentially layered system. This was attributed to more dextran sulfate present at the interface in the mixed system as well as to a greater cross-linking density between both biopolymers.

Dynamic Evolution of Interfaces in Food Emulsions

Following the rapid adsorption of emulsifiers at the oil-water interface during emulsification, many changes in the composition and structure of the formed interfacial layer can occur over periods of time that range from hours to even days. This is mostly the case for large and structurally complex molecules such as proteins. As mentioned above, after adsorption, proteins are often subjected to conformational rearrangements to maximize the favorable interactions and minimize the unfavorable interactions at the oil-water interface, which is also referred to as surface denaturation (McClements 2004). The time needed for such rearrangements depends on the protein structure and, notably, on the involved intramolecular interactions. For example, caseins are largely disorganized and flexible proteins that can rearrange relatively quickly after adsorption at the oil-water interface, whereas globular proteins stabilized by intramolecular covalent and noncovalent bonds, such as β-lactoglobulin, need more time. For globular proteins, surface denaturation leads to exposure of functional nonpolar or sulfhydryl groups, which can serve as a starting point for further interactions with neighboring molecules. It is well known that adsorbed whey proteins (and, in particular, β-lactoglobulin) can establish cross-links at the oil-water interface, leading to the formation of a two-dimensional interfacial network (Dickinson & Matsumura 1991, Monahan et al. 1993). As a result of this reorganization process, changes in interfacial tension can be observed for tens of hours, or even more, which also implies that protein adsorption is a phenomenon that is hardly spontaneously reversible.

Yet, an exception to this is when LMWEs are present or added to emulsions posthomogenization: Adsorbed proteins can then be displaced from the oil-water interface by more surface-active LMWEs (**Figure 4**). Numerous authors have reported such findings, either in real emulsions or

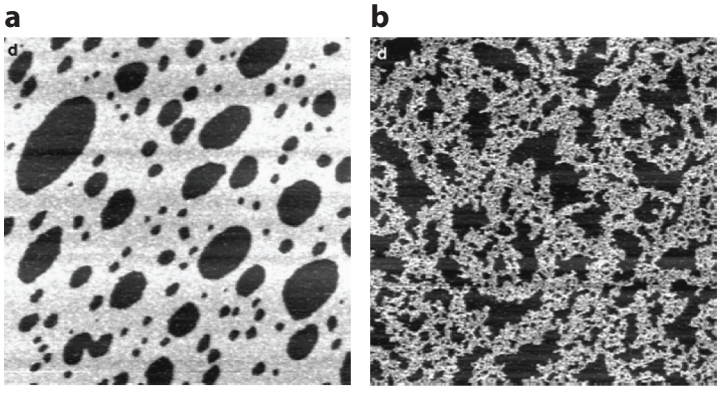

Figure 4

Orogenic displacement of interfacial proteins by low-molecular-weight emulsifiers. Atomic force microscopy image of a Langmuir-Blodgett film (made by loading a Langmuir film formed at the air-water interface onto mica) of (*a*) β-casein or (*b*) β-lactoglobulin partially displaced by Tween 20 (*black domains*). The picture size is 4 μm × 4 μm. Reproduced from Mackie et al. (1999), with permission from Elsevier.

using model interfaces (Chen & Dickinson 1995, Dan et al. 2012, Fang & Dalgleish 1996, Miller et al. 2004, Pugnaloni et al. 2004, Wilde 2000, Wilde et al. 2004). The mechanism through which the competitive displacement of proteins by LMWEs occurs has been termed orogenic displacement (Mackie et al. 2000). Small LMWE domains start forming in the defects of the protein layer and grow over time, compressing the protein layer. Beyond a certain critical surface pressure, the protein layer starts to buckle; while LMWE molecules continue adsorbing, their domains start to merge and parts of the protein layer detach from the interface. Finally, a continuous LMWE phase develops at the interface, leaving just a few disconnected protein areas adsorbed, which may eventually also detach from the interface. Interestingly, the effect of such competitive adsorption on the physical stability of emulsions is not clear; for example, van Aken (2003) found that coalescence in β-lactoglobulin-stabilized emulsions was reduced upon replacement of the interfacial protein by Tween 20, but opposite results had previously been found (Chen et al. 1993), possibly because coalescence was induced under different flow conditions. For aerated O/W emulsion-based systems containing high-melting-point fat (e.g., ice cream, whipped cream), partial replacement of the interfacial proteins by LMWEs is desirable, as it weakens the thick protein layers and allows interpenetration of neighboring oil droplets by fat crystals that protrude outside the droplet surface and hence induce partial coalescence of the droplets. As a result, a three-dimensional network of oil droplets is formed that is responsible for the structural properties and stability (Fredrick et al. 2010, Goff 2008).

Other changes in the composition and structure of the oil-water interface in food emulsions are related to chemical changes in the system and, in particular, the oil phase. It is well known that lipid oxidation products such as hydroperoxides are more polar than the initial triacylglycerols they arise from and tend to accumulate at the oil-water interface (Kittipongpittaya et al. 2012, Nuchi et al. 2002), where they drastically decrease the elasticity of protein layers at the oil-water interface (Berton-Carabin et al. 2016), an effect greatly overlooked in the literature. Similarly, hydrolysis of triacylglycerols (via endogenous lipase, e.g., in raw milk, or by exogenous lipase, e.g., microbial lipase) leads to free fatty acids and monoacylglycerols that are surface-active and may adsorb at the oil-water interface (Wilde & Chu 2011).

STRUCTURAL AND RHEOLOGICAL PROPERTIES OF OIL-WATER INTERFACES

Structure from Molecular to Mesoscopic Scale

It is of great importance to assess the effect of interface structure on emulsion stability, yet in many studies not even the surface load and thickness are investigated. This makes interpretation and comparison of studies very difficult. This section describes various interfacial characteristics related to structural and rheological properties.

Thickness and surface load. The oil-water interface contains concentrated molecular species with dual affinity for oil and for water. The interface is typically a few nanometers thick, e.g., approximately 1 nm for LMWE-stabilized interfaces to 1–15 nm for protein-stabilized interfaces (Atkinson et al. 1995, Dalgleish 1997, Dickinson 2009, Fang & Dalgleish 1993, Singh 2011). The surface load (Γ) varies from less than 1 mg/m^2 for some surfactants to higher than 10 mg/m^2 for biopolymeric emulsifiers (Bos & van Vliet 2001, Walstra 2003). **Table 1** shows typical surface load values in food emulsions and indicates how they depend on emulsion compositional and processing parameters. When combining thickness and surface load, it is possible to estimate emulsifier

Table 1 Examples of emulsion formulations and measured surface loads for different types of emulsifiers: animal-derived proteins, plant-derived proteins, low-molecular-weight emulsifiers, and polysaccharides

Emulsifier type and concentration	Lipid phase and fraction	Aqueous phase	Emulsion procedure	Droplet size (μm)[a]	Surface load (mg/m^2)	Reference
β-LG, 5 g/L	Stripped rapeseed oil, 30 wt%	PIPES buffer 10 mM, pH 6.7	High-pressure homogenizer, 50 bar, 10 min	1.5	1.9	Berton et al. 2011a
		Phosphate buffer 10 mM, pH 3.0		2.2	2.3	
β-casein, 5 g/L		PIPES buffer 10 mM, pH 6.7		1.7	2.8	
BSA, 4 g/L				1.8	1.8	
BSA, 5 g/L	n-Hexadecane, 30 wt%	DI water	Rotor-stator homogenizer, 20,000 rpm, 2 min	10.8	0.8	Rampon et al. 2003c
			High-pressure homogenizer, 70 bar, 12 passes	1.0	1.0	
β-LG, 0.56 wt %	n-Tetradecane, 5 wt%	Phosphate buffer 10 mM, pH 7.0	High-pressure homogenizer (microfluidizer), 300 bar	0.66	1.7	Courthaudon et al. 1991c
β-casein, 0.5 wt %	n-Tetradecane, 20 wt%	Bis-tris propane buffer 20 mM, pH 7.0	High-pressure homogenizer (microfluidizer), 300 bar	0.81	1.8	Courthaudon et al. 1991a
	High-purity soy oil, 20 wt%			0.81	1.1	
β-casein, 0.5 wt %	n-Hexadecane, 20 wt%	Bis-tris propane buffer 20 mM, pH 7.0	High-pressure homogenizer (microfluidizer), 300 bar	1.0	2.6	Courthaudon et al. 1991b
Ovalbumin, 20 g/L	Sunflower oil, 10 wt%	Phosphate buffer 10 mM, pH 7.0	High-pressure homogenizer, 150 bar, 30 passes	2.5	2.5	Delahaije et al. 2013b
β-LG, 5 g/L				0.5	2.5	
WPI, 0.3 wt %	Soybean oil, 20 wt%	Imidazole buffer 20 mM, pH 7.0	Microfluidizer, 0.2 MPa, 10 passes	0.4–0.5	1.5	Hunt & Dalgleish 1994
WPI, 2.5 wt %				0.4–0.5	3.2	
Caseinate, 0.3 wt %				0.4–0.5	1.0	
Caseinate, 2.5 wt %				0.4–0.5	3.2	
WPC, 0.1 wt %	Stripped soybean oil, 28% v/v	DI water + NaCl 0.15 M	Narrow-gap homogenizer, 0.22 to 0.5 MPa	9.5	7.0	Tcholakova et al. 2003
WPC, 1.4 wt %				5.5	1.9	

(*Continued*)

Table 1 (*Continued*)

Emulsifier type and concentration	Lipid phase and fraction	Aqueous phase	Emulsion procedure	Droplet size (um)[a]	Surface load (mg/m^2)	Reference
β-LG, 0.01 wt %	Stripped soybean oil, 30% v/v	DI water + NaCl 0.15 M	Rotor-stator homogenizer, 13,500 rpm, 3 min	48	1.5	Tcholakova et al. 2002
β-LG, 0.1 wt %				36	2.9	
Sodium caseinate, 0.3 wt %	Soybean oil, 30 wt%	DI water, adjusted to pH 7.0	High-pressure homogenizer, 200 bar	0.60	0.5	Ye 2008
Sodium caseinate, 5 wt %				0.50	2.4	
WPC, 0.3 wt %				0.65	0.6	
WPC, 5 wt %				0.50	2.5	
WPI, 15 g/L	Sunflower oil, 10 wt%	DI water, adjusted to pH 3.0	Premix column emulsification device, 3 bar, 5 passes	1.4	6.4	Ladjal Ettoumi et al. 2017
SPI, 4 wt%	Soybean oil, 10 wt%	DI water	Ultra-high-pressure homogenizer, 3,000 bar	0.40 (d_{50})	0.8	Fernandez-Avila & Trujillo 2016
	Soybean oil, 20 wt%		Ultra-high-pressure homogenizer, 150 bar	1.2 (d_{50})	3.4	
SPI, 70 g/L	Sunflower oil, 30% v/v	Tris-HCl buffer, 50 mM, pH 8.0	High-pressure homogenizer, 25 bar	1.1	9.2	Puppo et al. 2008
Soy proteins, 0.3 wt %	Soybean oil, 10 wt%	DI water, adjusted to pH 7.0	Rotor-stator homogenizer, 16,000 rpm, 2 min	7.9	6.9	Cui et al. 2014
Pea protein, 15 g/L	Sunflower oil, 10 wt%	DI water, adjusted to pH 3.0	Premix column emulsification device, 3 bar, 5 passes	1.2	7.5	Ladjal Ettoumi et al. 2017
Chickpea protein, 15 g/L				1.1	5.4	
Lentil protein, 15 g/L				1.7	9.0	
SPI, 2 wt %	Soybean oil, 20% v/v	DI water, adjusted to pH 7.0	High-pressure homogenizer (microfluidizer), 400 bar, 1 pass	1.1 ($d_{4,3}$)	3.8	Shao & Tang 2014
Heated SPI, 2 wt %		DI water, adjusted to pH 7.0 + NaCl, 300 mM		0.9 ($d_{4,3}$)	5.6	
		DI water, adjusted to pH 7.0		0.7 ($d_{4,3}$)	4.2	
Hydrophobized starch, 0.42 g/L	MCTs, 5 wt%	Phosphate buffer 10 mM, pH 6.0	High-pressure homogenizer, 150 bar	5.4	2.0	Nilsson & Bergenståhl 2007
Hydrophobized starch, 1.26 g/L				8.3	10.3	

(*Continued*)

Table 1 (*Continued*)

Emulsifier type and concentration	Lipid phase and fraction	Aqueous phase	Emulsion procedure	Droplet size (um)[a]	Surface load (mg/m^2)	Reference
Spruce galactoglucomannans, 1 wt %	Rapeseed oil, 5 wt%	Citrate buffer 25 mM, pH 4.5	High-pressure homogenizer (microfluidizer), 700 bar, 3 passes	0.39	0.8	Mikkonen et al. 2016
Spruce galactoglucomannans (carboxymethyl derivatives), 1 wt %				0.43	0.4	
Corn fiber gum, 1 wt %				0.31	0.9	
Gum arabic, 1 wt %				1.3	2.5	
Tween 20, 5 g/L	Stripped rapeseed oil, 30 wt%	PIPES buffer 10 mM, pH 6.8	High-pressure homogenizer, 35 bar, 5 min	1.4	2.3	Berton et al. 2011a
Tween 80, 5 g/L		Phosphate buffer 10 mM, pH 3.0		1.6	2.5	
		PIPES buffer 10 mM, pH 6.8		1.7	2.0	
Poloxamer 188, 12.5 wt %	Canola oil, 10 wt%	DI water	High-pressure homogenizer (microfluidizer), 690 bar, 3 passes	0.11	2.9	Malaki Nik et al. 2012
Tween 20, 12.5 wt %				0.11	4.4	
Soy PC, 1 wt % (in the oil phase)	MCTs, 10 wt%	DI water	High-pressure homogenizer, 200 bar, 7 passes	7.0	3.0	Magnusson et al. 2016

[a]Droplet size reported as d_{32}, unless otherwise stated.

Abbreviations: β-LG, β-lactoglobulin; BSA, bovine serum albumin; DI, deionized water; MCTs, medium chain triacylglycerols; PC, phosphatidylcholine; PIPES, piperazine-N,N′-bis(2-ethanesulfonic acid); SPI, soy protein isolate; WPC, whey protein concentrate; WPI, whey protein isolate; wt%, weight percentage.

concentrations at the oil-water interface (e.g., a 5-nm protein layer with 2-mg/m^2 surface load has an interfacial protein concentration of 400 kg/m^3). This implies that at the nanoscale, protein-based interfacial layers behave like gel systems rather than dilute solutions. This, added to the fact that emulsifier molecules located at the interface tend to adopt a certain orientation, implies that interfacial layers can be seen as anisotropic, concentrated films that constitute a separate pseudophase of the emulsion.

Structure of protein-based interfaces. In **Table 1**, substantial differences can be found for the surface load of a given protein, depending on the emulsion formulation parameters and processing conditions. When the total protein concentration in the system is low (protein-poor regime), the surface load corresponds to a protein monolayer and does not depend on protein concentration. In the protein-rich regime, more proteins may adsorb onto the first monolayer, creating denser and/or thicker interfacial structures and possibly multilayers (Gochev et al. 2013, Graham & Phillips 1979, Tcholakova et al. 2003).

The properties of interfacial protein layers can be greatly affected by the continuous phase conditions, such as the pH and ionic strength. A high ionic strength, as well as a pH close to the protein isoelectric point, screens or decreases the net electrostatic charge of the protein. Engelhardt et al. (2013) showed that at a pH near the isoelectric point, β-lactoglobulin formed disordered multilayers with high interfacial dilatational elasticity at the air-water interface. Increasing or decreasing the pH led to a monolayer with repulsive electrostatic interactions among the adsorbed molecules, which decreased the interfacial dilatational elasticity. For flexible β-casein, the thickness of the interfacial film was shown to depend on the effective charge of the hydrophilic, phosphoseryl-rich segment of the protein: Screening the negative charges by increasing the ionic strength makes this segment shrink, accounting for thinning of the adsorbed layer (Dickinson 1998, Horne & Leaver 1995, Leermakers et al. 1996).

Although it is hard to generalize the effect of pH and ionic strength on adsorbed protein layers, the following points seem to be of importance: A low effective charge of the protein (pH close to isoelectric point, high ionic strength) results in fewer repulsive interactions between proteins (or protein segments), which may (*a*) favor the formation of multiple protein layers; (*b*) induce shrinkage of hydrophilic protein segments; and (*c*) favor intermolecular attractive interactions and possibly the formation of an elastic interfacial network.

Lateral heterogeneity of interfaces. When different molecules coexist at the oil-water interface, two-dimensional supramolecular structures can be formed. For instance, lateral phase separation may occur, leading to segregated interfacial domains, a typical example being the formation of patches of proteins and LMWEs (**Figure 4**), although this is a transient situation that eventually leads to total protein displacement from the interface.

Segregated domains of different types of LMWEs have been reported for mixtures of Tween 20 and Span 20 or monolauroyl glycerol on model air-water interfaces (Berton et al. 2012a) as well as of phospholipids and cholesterol in emulsions (Pontani et al. 2013). For protein mixtures, it is not clear whether (or under which conditions) laterally segregated interfacial domains may form. For instance, Mackie et al. (2001) studied mixed films of β-lactoglobulin and β-casein at the air-water interface and found that both proteins coexisted at the interface, with a predominance of β-casein, whereas no structural film heterogeneity was observed by fluorescence microscopy. Conversely, Sengupta & Damodaran (2000) did observe distinct phase-separated bovine-serum-albumin-rich and β-casein-rich regions, coexisting with heterogeneous mixed regions. This was related to the thermodynamic incompatibility of proteins (Razumovsky & Damodaran 1999). It is, however, questionable whether such segregated domains could exist at the surface of emulsion droplets, as the size of the domains on the model surfaces (hundreds of μm) was substantially larger than the typical size of commonly encountered emulsion droplets.

Interfacial Rheology

The complex microstructures observed in oil-water interfaces stabilized by food ingredients affect not only the interfacial tension of the interface, but can also impart a significant resistance against dilatational and shear deformations to those interfaces. For interfaces with an elastic response to deformations, the resistance to dilation is quantified by the surface dilatational modulus E_d, defined as

$$E_d = A\left(\frac{\partial \gamma}{\partial A}\right). \quad 5.$$

In essence, this modulus is the inverse of the isothermal compressibility of the interface and the two-dimensional equivalent of the bulk modulus, *K*. For interfaces with a viscoelastic response to

deformations, the dilatational modulus is a complex parameter, equal to $E_d^* = E_d' + iE_d''$, where E_d' is the dilatational storage modulus, and E_d'' is the dilatational loss modulus. For viscous interfaces, the resistance against dilation is given by the dilatational viscosity, ε_d.

For elastic interfaces, the surface-shear modulus, G_s, represents the resistance of the interface against shear deformations. For viscoelastic interfaces, this is a complex property, equal to $G_s^* = G_s' + iG_s''$, where G_s' is the surface-shear storage modulus, and G_s'' is the surface-shear loss modulus. For viscous interfaces, the relevant property is the surface-shear viscosity, ε_s. Over the past decades, the surface-shear and dilatational properties have been determined for a wide range of air-water and oil-water interfaces stabilized by food ingredients (Sagis 2011).

The parameters we have discussed in this section are all associated with in-plane deformations. Interfaces can also have significant resistances against out-of-plane deformations, such as bending and torsional deformations. For elastic interfaces, the effects of bending are typically captured by introducing the bending rigidities k (mean curvature of the interface), $\bar{k}$ (Gaussian curvature), and C_0 (spontaneous curvature) (Helfrich 1973), and torsion through a surface torsion constant. Dissipative effects can be described by bending and surface torsion viscosities (Aguilar Gutierrez et al. 2017).

There is ample proof that surface rheological properties affect the formation, stability, and dynamics of emulsions and other soft multiphase materials, such as foams (Bos & van Vliet 2001, Fischer & Erni 2007, Lamorgese et al. 2017, Murray 2002, Sagis 2011). For example, for oil droplets stabilized by proteins, Jones & Middelberg (2003) observed a significant impact of surface rheology on their breakup in a shear field. Dickinson et al. (1988) found a significant effect of surface rheology on the rate of coalescence of protein-stabilized oil droplets at a planar water-oil interface. The deformability and mobility of the interface also affect the creaming rate of droplets (Felderhof 2006, Rehage et al. 2002). Since the deformation and orientation of droplets are affected by surface rheology, the macroscopic rheology of the emulsion, particularly its shear thinning behavior, is also affected (Tadros 1994). These examples illustrate that surface rheology can affect the dynamic behavior of an emulsion on all relevant length scales and that more extensive analysis is needed to link this to emulsion production.

METHODS TO STUDY THE COMPOSITION AND STRUCTURE OF INTERFACES IN FOOD EMULSIONS

Ideally, studies of emulsion systems should be carried out under conditions that are as close as possible to those in the real matrices; however, this is often difficult to achieve because of the opacity of the matrix, the small size of the emulsion droplets, and the interference of other components. Therefore, scientists tend to do measurements at model interfaces, preferably the oil-water interface, even though valuable information can be obtained at the air-water interface. It is important to be cautious when ascribing phenomena observed on model interfaces to behaviors recorded in real emulsions; in such complex systems, evidence needs to be obtained via different measurements to draw strong conclusions.

Direct Measurements in Real Emulsions

The interfacial composition and structure may be approached in real emulsions, either before or after phase separation. The typical techniques used for this are microscopy, spectroscopy, and microfluidics, which we discuss in this section.

Microscopy. Microscopy techniques are very useful in assessing the structure of food emulsions at various scales. Simple optical microscopy is useful to get an overview of the emulsion's structure

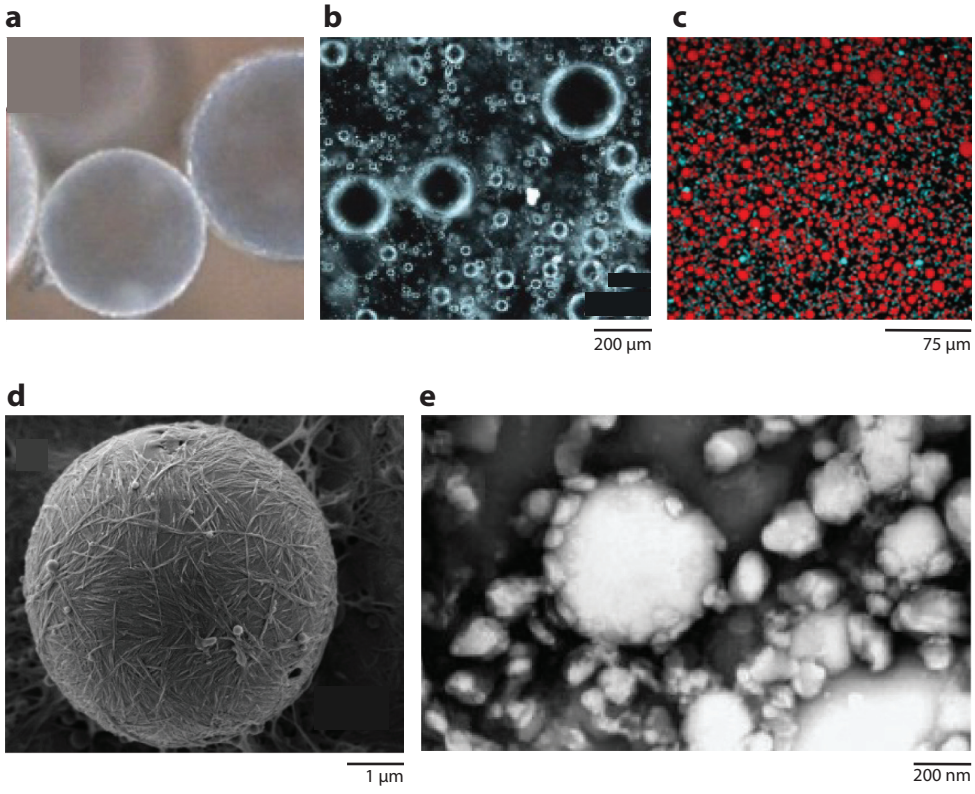

Figure 5

Microscopy images pointing at interfacial composition and structure in emulsions. Polarized light microscopy images of a (*a*) starch granule–stabilized emulsion, with a droplet size of ∼50 µm (Sjöö et al. 2015) and a (*b*) lipid particle–stabilized emulsion (Schröder et al. 2017b). Reproduced with permission from Elsevier and The Royal Society of Chemistry, respectively. (*c*) Confocal laser scanning microscopy image of a walnut oil body suspension (Gallier et al. 2013) (*lipids appear in red*, *proteins in blue*). Reproduced with permission from the American Chemical Society. (*d*) Scanning electron microscopy image of an emulsion droplet stabilized by cellulose nanocrystals (Kalashnikova et al. 2012). Reproduced with permission from the American Chemical Society. (*e*) Transmission electron microscopy image of a lipid particle–stabilized emulsion. Unpublished material courtesy of A. Schröder, Wageningen University.

but does not provide information about the properties of the thin interfacial layer. An exception to this are certain Pickering emulsions made with relatively large particles, which can be seen by optical microscopy (Rayner et al. 2012) or in which the crystalline structure can be made visible by the use of a polarized light filter (Schröder et al. 2017b, Sjöö et al. 2015) (**Figure 5*a*,*b***). Confocal laser scanning microscopy (CLSM) has been widely used to image sections through a three-dimensional opaque material (Dürrenberger et al. 2001). It is often combined with fluorescent dyes that label one or several components of interest, such as proteins and oil (Gallier et al. 2013) (**Figure 5*c***) or two different proteins (Mackie et al. 2001, Sengupta & Damodaran 2000).

Although not yet applied for food systems, super-resolution microscopy has recently emerged as an attractive method to visualize nanostructures covalently labeled with fluorescent tags. For emulsions and liquid-liquid interfaces, the iPAINT (interface point accumulation for imaging in nanoscale topography) technique seems promising, as it enables imaging of interfaces via reversible

adsorption of polymer chains end-functionalized with photo-activatable moieties (Aloi et al. 2016). Although it is always questionable whether dyes are noninvasive, as they may affect the emulsion and interface properties, a recent study pointed out that covalent labeling of β-casein with a fluorescent dye did not affect its interfacial or emulsifying properties (Li et al. 2016).

Compared to optical microscopy, electron microscopy reaches a higher resolution and has been used extensively for studying food structures. Scanning and transmission electron microscopy (SEM/TEM) are both used for emulsions (Kaláb et al. 1995, Klang et al. 2012). SEM is used to study surfaces (Kalashnikova et al. 2012), whereas TEM visualizes the internal structure of the sample (**Figure 5*d*,*e***). The drawback of electron microscopy is the relatively heavy sample preparation needed to measure the sample under vacuum conditions; the samples have to be dried (possibly after freezing) or even replicated with a layer that reproduces their surface.

Spectroscopy techniques. Techniques based on nuclear magnetic resonance (NMR) can be useful to determine the mobility of molecules within different phases of complex multiphase matrices, including the oil-water interface. The relative adsorbed protein mobility in emulsions can be determined by ^{31}P NMR. For example, the mobility of adsorbed caseinate molecules was reduced by the addition of unsaturated monoacylglycerols to the emulsion, which could be interpreted as interfacial entrapment of protein molecules in a dense fat network or cubic phase (Munk et al. 2014b). Electron paramagnetic resonance (EPR) has also proved useful to assess interfacial characteristics such as packing, mobility, and level of molecular organization (Aynié et al. 1992, Berton-Carabin et al. 2013, Le Meste et al. 1991, Munk et al. 2014a). This technique does not directly measure emulsifiers but relies on the use of spin probes (i.e., molecules with a stable unpaired electron) that have an affinity for certain emulsifier molecules and/or the oil-water interface. The obtained spectra give information on the mobility and orientation of the spin probes and the polarity of the environment in which they are located. Although such measurements are simple and do not require preliminary preparation, please note that data treatment and analysis are far from trivial.

Front-surface fluorescence spectroscopy is a technique that is well adapted for noninvasive studies of opaque media, such as emulsions, and has proved useful in studying partitioning of proteins between the interface and the continuous phase. This method is based on the fact that proteins contain tryptophan, which emits fluorescence with variable spectral characteristics depending on its local chemical environment (Granger et al. 2005; Rampon et al. 2001, 2003a,b,c).

Microfluidic techniques. Microfluidic devices can be used to study the formation of emulsion droplets and the adsorption of emulsifiers on very short timescales. They can also be used to study the interfacial properties of emulsion droplets after formation. For example, Krebs et al. (2012) developed a so-called collision chamber in which emulsion droplets collide and coalesce, depending on the flow conditions and the properties of the interfacial layer. This set-up was recently used to study coalescence in protein-stabilized emulsions; interestingly, droplets exhibited good stability to coalescence even at low protein concentrations, provided the time between droplet formation and interaction was sufficient (Muijlwijk et al. 2017). Our group (Krebs et al. 2013) developed a microcentrifuge that can be mounted onto an optical microscope, thus allowing direct observation of emulsion droplets subjected to enhanced gravity conditions (up to 1,000 × g). This enables direct measurement of the thermodynamic stability of emulsions, as expressed by the critical disjoining pressure (Feng et al. 2015, Krebs et al. 2013).

Measurements in Real Emulsions, After Phase Separation

A conventional way to study the composition of the oil-water interface in O/W emulsions is to physically separate the aqueous and creamed phases of the emulsion, followed by analysis of the

components present in both phases (Hunt & Dalgleish 1994). In principle, the surface-active components present in the aqueous phase correspond to the nonadsorbed fraction, whereas those present in the cream phase correspond to the interfacial fraction. However, a number of complications should be pointed out. First, it is assumed that surface-active components present in the creamed phase are adsorbed at the oil-water interface, which is mostly true for hydrophilic emulsifiers such as proteins, but for molecules that are, to some extent, soluble in oil (e.g., phospholipids), it is not possible to distinguish between adsorbed molecules and those present in the core of the oil droplets (Magnusson et al. 2016). Second, the separation step should not disturb emulsifier partitioning within the emulsion, e.g., through droplet coalescence that can easily be checked by measuring the droplet-size distribution in the cream phase. Third, no small oil droplets should remain in the serum phase, but this may be difficult to achieve through centrifugation, and several sequential centrifugation steps, possibly combined with filtration, may be needed. Alternatively, the continuous phase density can be increased by adding a solute such as sucrose (Patton & Huston 1986).

Model Interfaces

Many techniques are available to study the properties of fluid interfaces; where the number of techniques for oil-water interfaces is lower than for air-water interfaces, experiments on the latter can be useful but need to be cautiously interpreted.

Several techniques are available to study dilatational rheological properties of oil-water interfaces. The two most popular techniques are the drop volume tensiometer and the Langmuir trough. For the drop volume tensiometer, the principle and limitations were discussed above in relation to interfacial tension measurements. The dilatational properties of interfacial layers are typically determined by applying sinusoidal area deformations to the oil-water interface of the droplet by pumping fluid in and out of the droplet using a motor-driven syringe. The resulting oscillating surface tension signal is Fourier transformed, and the dilatational storage and loss moduli are determined by the intensity and phase of the first harmonic of the Fourier spectrum. Such an analysis is accurate only at low amplitudes, where the response of the interface is linear. Deformation amplitudes are typically fixed at values between 2% and 10%. Amplitude sweeps, in which the amplitude is varied, and that are standard in the rheology of bulk phases, are still rarely performed in dilatational experiments (Sagis 2011). A typical experiment consists of time sweeps (in which the evolution of the dilatational properties is followed as a function of time) or frequency sweeps (in which the frequencies are typically varied from 0.001 to 0.1 Hz). Experimentation times are in general long (several hours), and properties are typically monitored over several hours (Ravera et al. 2010); in the most-advanced equipment, the liquid constituting the drop (Ferri et al. 2008) or surrounding it (Corstens et al. 2017d) can be exchanged, which allows the interfacial layer to be subjected to variable environmental conditions. Because of the long experimentation time and the slow and small applied deformations, linking dilatational properties to macroscopic emulsion properties is not straightforward.

The Langmuir trough consists of a flat, rectangular trough filled with a subphase (generally, an aqueous phase), at the surface of which the interfacial film is formed, and a Wilhelmy plate that allows for recording the surface pressure. The available surface can be varied by means of one or two movable barriers (**Figure 6*b***). For studying oil-water interfaces, the aqueous subphase is covered by a layer of oil (Murray et al. 2009). The emulsifier is generally spread onto the subphase as a solution, which enables control over the amount of emulsifier present at the interface, but for water-soluble substances, it is also possible to introduce the emulsifier through the subphase and let it adsorb spontaneously. Once the interfacial film is formed and equilibrated, surface pressure

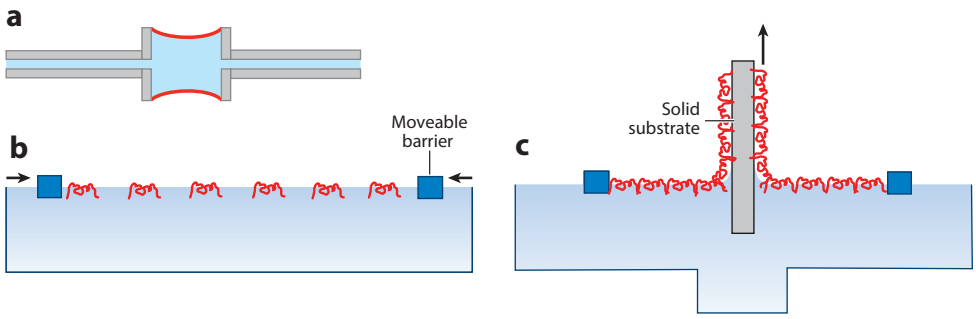

Figure 6

Schematic representation of two model systems to study fluid interfaces. (*a*) A capillary cell for thin films. (*b*) Langmuir trough, possibly equipped with a dipper to prepare (*c*) Langmuir-Blodgett films. The blue phase represents the aqueous phase, and the red line represents the emulsifier molecules or emulsifier-stabilized interfacial layer.

isotherms, i.e., plots of the surface pressure as a function of the available surface area, can be recorded, which can give information about the structural organization and the intermolecular interactions within the layer (Dynarowicz-Latka et al. 2001). Dilatational properties can again be determined by applying sinusoidal deformations to the oil-water interface.

An important advantage of the Langmuir trough is that it may be combined with other techniques to obtain additional information regarding the properties of the interfacial layer, including (*a*) a Brewster angle microscope or an imaging ellipsometer, which gives information regarding the structural organization of the layer (i.e., thickness, structural homogeneity, and presence of cracks, ridges, or segregated domains) (Dynarowicz-Latka et al. 2001); (*b*) a dipper to load the interfacial layer onto a solid substrate (i.e., by the so-called Langmuir-Blodgett technique; **Figure 6*c***), which can be dried and imaged by atomic force microscopy, leading to high-resolution structural information of the film (Bernardini et al. 2013, Gunning et al. 2010); (*c*) a surface potential probe to assess the surface potential of the layer (Dynarowicz-Latka et al. 2001); (*d*) an inverted ultramicroelectrode to measure gas transfer throughout the interface (Toikkanen et al. 2014); (*e*) an infrared reflection absorption spectroscopy tool to obtain insight on the molecular structures at the interface (Audebrand et al. 2013); and (*f*) X-ray- or neutron-scattering measurements to obtain detailed information on the structures present at the interface at different length scales (Dynarowicz-Latka et al. 2001).

There are several techniques to probe surface-shear properties of interfaces, and the most widely used are the biconical disk, double wall ring geometry (DWRG), and the magnetically driven needle rheometer (Sagis & Fischer 2014). The advantage of the first two is that they can be mounted on a stress- or strain-controlled rheometer, which allows for a wide range of tests (steady, oscillatory, step shear, or creep tests). In oscillatory mode, both frequency and strain amplitude sweeps are performed (Sagis & Fischer 2014). The main advantage of the needle rheometer is that it has two orders of magnitude higher sensitivity than the bicone and DWRG, although the flow patterns in the needle rheometer can be far more complex and the extraction of accurate data is nontrivial.

Apart from techniques to study individual oil-water interfaces, there are also techniques to study the behavior of thin liquid films between two air-water interfaces. A thin aqueous film can be formed in a short vertical capillary connected to side capillaries that allow bringing and possibly exchanging liquid inside the film (Wierenga et al. 2009) (**Figure 6*a***). The film is observed

by optical microscopy, and the appearance of the film (dimples, spots, and darker and lighter areas) reveals information about its mesoscopic structure and thickness as a function of time. Most of the work has been conducted at the air-water interface, but, in principle, it should be possible to use this technique at the oil-water interface (Wierenga et al. 2009).

For techniques that can be performed at the oil-water interface, it is common practice to use mineral oils, such as alkanes, that are commercially available with high purity. Conversely, edible oils mostly consist of triacylglycerols and contain substantial amounts of surface-active impurities, which can interfere with the measurements. A good compromise can be to use edible oils stripped of surface-active impurities by means of an adsorbing agent, such as silica or alumina (Berton et al. 2011a).

Simulation and Modeling

For computer modeling of interfacial dynamics, there are currently a number of frameworks available, either based on the Gibbs dividing surface model or the diffuse interface model (Lamorgese et al. 2017). The former considers the interface to be a two-dimensional object and assigns excess properties to that surface. The latter assumes the interface to be a region of finite thickness in which all fields (for example, mass density or energy density) vary rapidly but continuously from their value in one bulk phase to their value in the other. The diffuse interface model has found widespread application in modeling coalescence and droplet breakup/pinch-off as well as the early stages of phase-separation in immiscible systems (Lamorgese et al. 2017). For modeling interfacial rheology, the Gibbs dividing model has predominantly been used (Lamorgese et al. 2017, Sagis 2011).

Compared to bulk phase rheology, modeling of interfacial rheology is still in its infancy, which especially holds for dilatational rheology. Given the complexity of the matter, it is not surprising that in most studies no model is used (Sagis 2011). If a model is used, it is often too simple (e.g., a Kelvin model) to describe the nonlinear dynamics often observed in interfaces with a complex microstructure. The most often used model to describe surface shear is the phenomenological linear Maxwell model with some variations (the multimode Maxwell model, the Jeffreys model, or the Burgers model) (Sagis 2011), and it has to a lesser extent been used for dilatational data. For the relaxation behavior of interfaces after step-shear or step-dilatational deformations, either multiple exponential or stretched exponential models were used (Sagis 2011).

In recent years, a growing number of studies have focused on the large deformation regime, which is more relevant for food emulsions, predominantly using large amplitude oscillatory shear or large amplitude oscillatory dilatation analyzed using Lissajous-Bowditch curves (Sagis & Fischer 2014). Nonlinear surface rheological models to analyze such curves are scarce, and the best candidates for this task would be structural models in which the stress response of the interface is linked explicitly to some locally averaged structural parameters of the interfacial microstructure (for example, a local second-order polymer segment orientation or particle orientation tensor). Although such models are commonly used for describing complex bulk phases (Larson 1999), such as polymer melts or solutions, concentrated dispersions, or liquid crystalline phases, they are not yet widely available for complex interfaces. Recently, Luo et al. (2014, 2015) developed a structural model for the surface stress tensor of an interface stabilized by hard ellipsoidal particles (i.e., a Pickering stabilized interface) in terms of the second moment of the particle orientation distribution. The model was developed within the GENERIC nonequilibrium thermodynamic framework (Öttinger 2005, Sagis & Öttinger 2013), with material parameters determined by Monte Carlo and nonequilibrium molecular dynamics simulations. In principle, with this type of approach, it is also possible to construct models for even more complex interfaces than observed in food emulsions.

FUNCTIONALITY AND FUNCTIONALIZATION OF INTERFACES IN FOOD EMULSIONS

To Achieve Better Physical Stability

As detailed earlier, the interfacial properties control to a large extent the physical stability of food emulsions. A variety of physically stable food products can be made by using a good match between the emulsifiers, the environmental conditions, and the interactions with nonadsorbed species. Advanced interfacial design is not always necessary, but a few special cases are worth mentioning. For example, Zeeb et al. (2011) found that enzymatic cross-linking of interfacial gelatin-pectin mixed layers improved the freeze-thaw and creaming stability of emulsions compared to single-component or non-cross-linked layers, which they attributed to the formation of a highly elastic and resistant interfacial layer. Delahaije et al. (2013a,b; 2014) studied the effect of glycation and succinylation of proteins on emulsion stabilization and found that both modifications improved stability to salt-induced flocculation. Glycation leads to steric interactions between droplets, whereas succinylation induces protein unfolding and thus facilitates protein adsorption during emulsification.

A recent breakthrough regarding the design of highly physically stable food emulsions relates to the use of particles instead of conventional emulsifiers to adsorb at the oil-water interface. As discussed above, these so-called Pickering emulsions can have excellent physical stability because of the strong desorption energy of the adsorbed colloidal particles, which prevents coalescence and Ostwald ripening.

To Achieve Better Chemical Protection of the Oil Phase

Efficient strategies to counteract lipid oxidation in emulsions are an important topic in the food field. Ideally one would like to increase the level of unsaturated lipids, which are interesting for their health benefits to avoid the use of synthetic additives (such as synthetic antioxidants) that may be needed to protect these oils that are prone to oxidation. As lipid oxidation in O/W emulsions is initiated at the droplet surface, the interfacial properties have been postulated to largely contribute to the initiation and propagation of the reaction (Berton-Carabin et al. 2014). In model systems, emulsions stabilized by anionic surfactants are generally more prone to oxidation compared to emulsions stabilized by nonionic or cationic surfactants (Mancuso et al. 1999, Mei et al. 1998). This effect could be due to the ability of a positively charged interface to repel metal cations (which are strong prooxidants, even at trace concentrations), whereas a negatively charged interface would attract them, therefore bringing them in contact with the lipid substrate. However, this trend is far from generic; in particular, in protein-stabilized emulsions, no correlation was found between surface charge and oxidative stability (Berton et al. 2011b, Hu et al. 2003, Villiere et al. 2005), which may be due to differences in the amino acid composition between proteins and hence to different free-radical-scavenging and metal-chelating activities. Proteins adsorbed at the oil-water interface have been shown to undergo early and extensive oxidative degradations in oxidizing emulsions (Berton et al. 2012b, Salminen et al. 2009), which could make them active intermediates in the reaction pathways. Finally, nonadsorbed proteins can also act as antioxidants, which complicates the interpretation of droplet charge effects.

The thickness and density of the oil-water interfacial layer have often been mentioned as important factors regarding the barrier properties against lipid oxidation. Compared to emulsions stabilized by other proteins, casein-stabilized emulsions generally have better oxidative stability, which may be due to their ability to provide high interfacial coverage and form thick interfacial layers (Hu et al. 2003, Nielsen et al. 2013). Increasing the interfacial thickness can also be achieved by

consecutive deposition of several layers of oppositely charged polymers onto oil droplets through the so-called layer-by-layer technique, which has generally been associated with a better oxidative stability of emulsions (Chen et al. 2011, Lesmes et al. 2010). Recently, Salminen et al. (2013, 2017) showed that lipid oxidation in O/W emulsions could be reduced via the formation of a solid fat shell at the surface of the oil droplets, which was achieved by combining a small fraction of high-melting-point fat in the oil phase and a surfactant able to template fat crystallization.

A promising interface-based strategy to counteract lipid oxidation in emulsions is the localization of antioxidants at the oil-water interface, where they can optimally exert their activity. A large amount of work has been conducted to make natural antioxidants amphiphilic via enzymatic or chemical modification, which has proved to be an efficient strategy (Laguerre et al. 2013, 2015). It also seems possible to physically or chemically trap antioxidants within complex interfacial structures, such as biopolymer multilayers (Lomova et al. 2010, Pan & Nitin 2015).

Effects Due to Chemical Alterations of Emulsifiers

Although lipid oxidation has long been recognized as a major issue for the stability of food emulsions, oxidation reactions pertaining to other components may also be of importance, even though less work has been conducted on such aspects. Protein oxidation can occur during the production or storage of the protein ingredient (Fenaille et al. 2005) or concomitantly with lipid oxidation once the emulsion is formed (Berton et al. 2012b, Leaver et al. 1999, Rampon et al. 2001, Salminen et al. 2009), resulting in a broad range of chemical and structural modifications (e.g., fragmentation, aggregation, side-chain modifications) (Lund et al. 2011). It is well known that oxidation decreases protein digestibility (Obando et al. 2015, Sante-Lhoutellier et al. 2007), but less information is available regarding the consequences on the functional properties of proteins, and, in particular, their ability to physically stabilize oil-water interfaces. A few studies (Kong et al. 2013, Liu et al. 2015) have found that limited levels of protein oxidation promote emulsifying efficiency, whereas higher protein oxidation levels prevent the formation of physically stable emulsions. These authors hypothesized that moderate protein oxidation partially unfolds proteins, thereby promoting protein adsorption at the oil-water interface during homogenization, whereas extensive protein oxidation leads to substantial loss in protein solubility. Recently, we investigated the influence of protein oxidation on the adsorption kinetics and interfacial rheology of the formed oil-water interfacial layers (Berton-Carabin et al. 2016). We found that protein oxidation led to a decrease in interfacial elasticity compared to nonoxidized samples, which we attribute to the formation of a broad range of proteinaceous species, including peptides and aggregates, that cannot form an interconnected network. Accordingly, emulsions stabilized with such oxidized proteins were more prone to coalescence than emulsions stabilized with the nonoxidized material (Muijlwijk et al. 2017). Very recently, we observed that Langmuir-Blodgett protein films made at the air-water interface presented a more heterogeneous structure, with aggregates when the proteins had been oxidized, compared to films made with nonoxidized proteins, as visualized by atomic force microscopy (**Figure 7**; E. Hinderink, H. van den Broek, K. Schroën, L. Sagis, C. Berton-Carabin, unpublished data). This illustrates that protein oxidation can have a major influence on the structure of protein-based interfacial films and thus, potentially, on their functional properties.

LMWEs may also be subjected to chemical modifications and, in particular, oxidation. For example, the polyoxyethylene chains of sorbitan esters such as Tween 20 can undergo autooxidation, resulting in hydroperoxide formation, side-chain cleavage, and eventually formation of short-chain acids (Kerwin 2008). Nuchi et al. (2001) showed that increasing the level of Tween 20 hydroperoxides in Tween 20–stabilized emulsions decreased the oxidative stability of the oil phase. Another study by Pan et al. (2013) showed that free-radical permeation across the surface of lecithin-stabilized oil droplets occurred more quickly with previously oxidized lecithin than

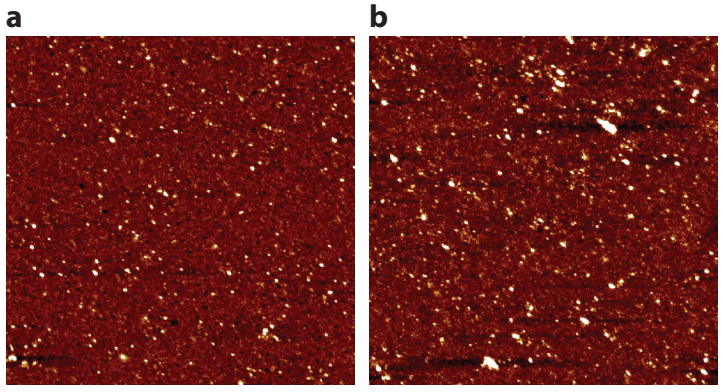

Figure 7

Atomic force microscopy images of dried Langmuir-Blodgett films prepared at the air-water interface with (*a*) nonoxidized or (*b*) oxidized pea protein isolate. The loading of the films onto mica was conducted at a surface pressure of 15–20 mN/m. Protein oxidation was conducted for 3 h in aqueous solution with a metal-catalyzed oxidation system, as described in Berton-Carabin et al. (2016). In panel *b*, more and larger aggregates are visible in the film, suggesting structural heterogeneity. The dimensions of the image are 2 μm × 2 μm. The overall layer height is approximately 4 nm, with black representing the lower areas and white the higher ones. The images are part of ongoing research and obtained by E. Hinderink and H. van den Broek, Wageningen University.

with fresh lecithin. Yet, in general, the chemical degradation status of food emulsifiers is very rarely considered when studying their interfacial properties or physicochemical stability of the corresponding emulsions.

To Achieve Controlled Fate in the Gastrointestinal Tract

In the past few years, there has been increasing interest in controlling the digestive fate of multiphase food systems, such as food emulsions: On the one hand, facilitating the digestion and bioavailability of health-promoting compounds is often desired, and on the other hand, it can be interesting to delay or prevent digestion of certain macronutrients, such as lipids, to prolong satiety signals, which could be a basis for weight-management strategies (Corstens et al. 2017a). An extensive review on how the digestion of lipophilic components can be controlled by the properties of the oil-water interfaces is outside the scope of this review, but we provide a few recent examples and suggestions for further reading; a number of reviews on these topics are available (Corstens et al. 2017a; McClements & Li 2010; McClements et al. 2008a,b; Singh et al. 2009).

Some differences were observed between the rate and extent of lipolysis in emulsions stabilized by various emulsifiers (Chu et al. 2009, Couëdelo et al. 2015, Mun et al. 2007). Yet these trends often failed to be generalized or were not confirmed when switching from in vitro systems to in vivo trials (McClements & Li 2010; McClements et al. 2008a,b). This may be due to the fact that experimental conditions can largely vary from one study to another as well as to the fact that major changes in the interfacial composition occur before the oil droplets reach the small intestine, i.e., the place where most of the lipolysis occurs.

Attempts have also been made at constructing advanced interfacial structures to reduce lipolysis, for example, through biopolymer multilayers. Although the addition of extra interfacial layers sometimes seemed promising in that respect (Mun et al. 2006), here again the potential of such systems remains limited because of possible destabilization in digestive conditions (Corstens et al.

2017c,d). It may thus be concluded that preventing lipolysis in emulsions through interfacial design is extremely challenging, especially for real food applications, because of the harsh and variable conditions encountered in vivo. A promising alternative could, however, be the entrapment of emulsion droplets within hydrogels, which in turn can control diffusion of the lipase and other molecules involved in the digestion process to the lipid substrate (Corstens et al. 2017b, Sarkar et al. 2015, Zhang et al. 2014).

Recent Trend: Bioinspired Emulsions

Among the trends that have recently emerged in the field of food emulsions, a remarkable one pertains to the development of emulsions with an interfacial structure that mimics that of emulsions occurring in nature, i.e., oil bodies (in plants) and milk-fat globules (in mammals) (Gallier et al. 2017). In both cases, the involved interfaces have complex structures and compositions, which are directly related to their biological production pathways in vivo: Oil bodies are covered by a monolayer of phospholipids and embedded proteins, mostly from the oleosin family, and milk-fat globules are covered by a trilayer of phospholipids with specific proteins and cholesterol (**Figure 8*a*,*b***).

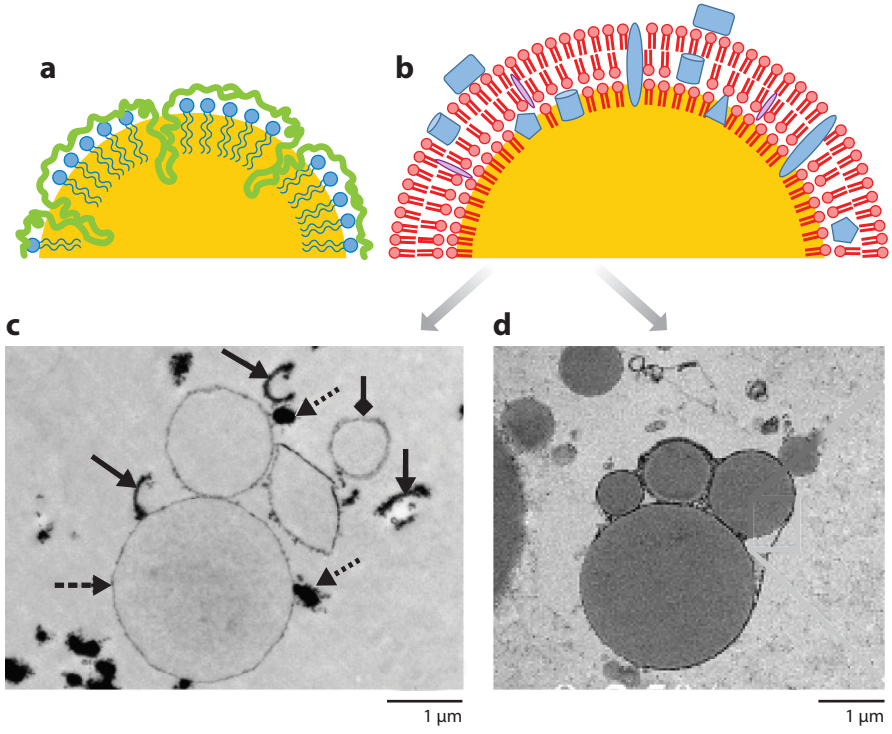

Figure 8

Schematic representation of natural emulsions and their interfacial structure. (*a*) Oil bodies and (*b*) milk-fat globules. (*c*) Transmission electron microscopy (TEM) images of manufactured emulsions with interfacial design inspired by the milk-fat-globule membrane, including a bovine milk phospholipid source (Gallier et al. 2015). (*d*) Modified posthomogenization to add an external phospholipid layer onto lactoferrin-stabilized droplets (Livney et al. 2017). In panel *c*, dotted arrows point to interfacial casein micelles, dashed arrows point to small interfacial protein aggregates, and solid arrows point to milk-fat-globule membrane fragments. Both TEM images (Gallier et al. 2015, Livney et al. 2017) are reproduced with permission from Elsevier.

Recently, some attempts have been made to reproduce, or have been inspired by, the milk-fat-globule membrane in food emulsions. It is thought that the natural membrane can bring short- and long-term health benefits to sensitive populations such as infants (Bourlieu et al. 2015, Oosting et al. 2014). The adopted strategies have been diverse, from incorporating a bovine milk phospholipid source (Gallier et al. 2015) or milk-fat-globule membrane fragments (Lopez et al. 2017) when making the emulsion to posthomogenization modification of emulsion droplets, e.g., through electrostatic adsorption of an external phospholipid layer (Livney et al. 2017) (**Figure 8*d***). Obviously, the higher the complexity of the interface engineering strategy, the more difficult it is to bring them to the level of industrial production. Alternatively, e.g., oil bodies as they occur in nature could be harvested by mild recovery (Nikiforidis et al. 2014).

SUMMARY AND FUTURE DIRECTIONS

The oil-water interface is crucial to food emulsions, as it controls to a large extent their physicochemical stability. It is challenging to design interfaces with controllable composition and structure, as surface-active species partitions between the different available phases and possibly compete for adsorption. Most food emulsions are not in thermodynamic equilibrium; hence, the interfacial properties are dependent on the processing conditions and steps as well as the dynamic evolution of the systems. It is therefore essential to characterize the composition and structure of interfaces at relevant time and length scales (**Figure 9**).

It is important to further develop methods that enable probing the interfacial phenomena occurring during emulsion droplet formation, i.e., at the timescale of submilliseconds to

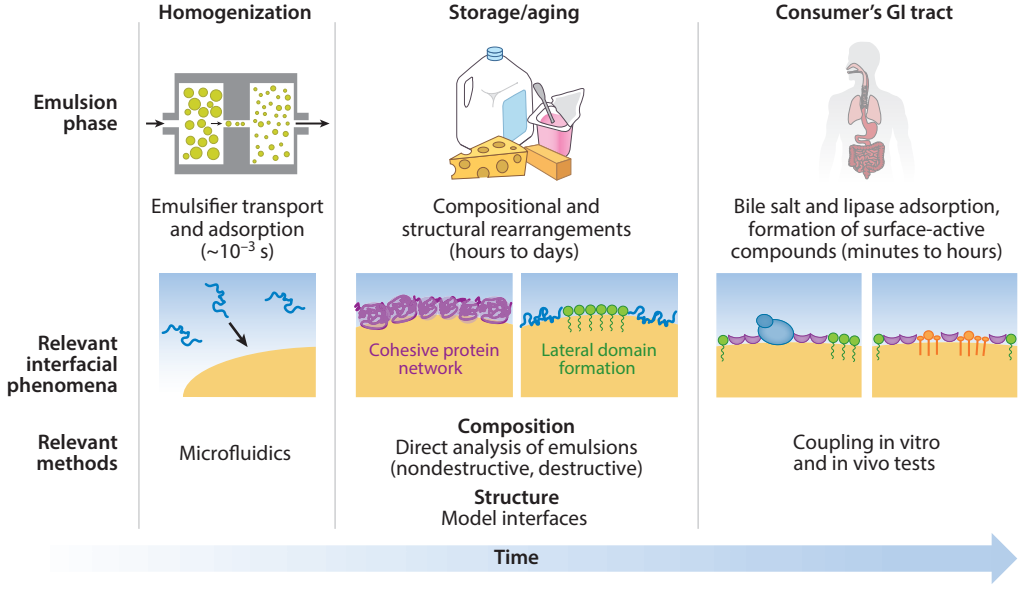

Figure 9

From the production of food emulsions until their end-use. The major interfacial phenomena involved and the relevant timescales and characterization methods in a schematic overview. During production, effects take place within a very short timescale, and microfluidic devices are ultimately suited to probe these effects. During storage and aging, the rheological properties of the interfacial layers are more prominent, whereas during digestion complex interfacial behavior occurs that ideally can be charted by combining in vitro and in vivo observations. Abbreviation: GI, gastrointestinal.

milliseconds. For this, microfluidic-based methods have recently proved useful in model systems, which now need to be extended to a broad range of emulsions.

The composition of the oil-water interface in emulsions can fairly easily be determined by nondestructive or destructive methods. When the composition is known, the supramolecular structures formed by the interfacial components, as well as the mechanical properties of the formed layers, should be determined. For this, model interfaces are often used, with the assumption that the observed phenomena are representative of the situation in real emulsions. A combination of different techniques and length scales is recommended to obtain unambiguous information; for this, the newest developments in modeling can be instrumental. Another aspect that is worth pointing out is the fact that the chemical state of the emulsifiers used to make emulsions is often overlooked, in spite of the fact that it can substantially affect the interfacial properties and the subsequent emulsion stability. Ultimately, when food emulsions are subjected to digestive conditions, it has proved difficult to structure the oil-water interface to obtain controlled gastrointestinal fate. This illustrates that in this case food emulsions also need to be structured beyond the interfacial scale.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

LITERATURE CITED

Aboofazeli R, Lawrence MJ. 1994. Investigations into the formation and characterization of phospholipid microemulsions. II. Pseudo-ternary phase diagrams of systems containing water-lecithin-isopropyl myristate and alcohol: influence of purity of lecithin. *Int. J. Pharm.* 106:51–61

Aguilar Gutierrez OF, Herrera Valencia EE, Rey AD. 2017. Generalized Boussinesq-Scriven surface fluid model with curvature dissipation for liquid surfaces and membranes. *J. Colloid Interface Sci.* 503:103–14

Aloi A, Vilanova N, Albertazzi L, Voets IK. 2016. iPAINT: a general approach tailored to image the topology of interfaces with nanometer resolution. *Nanoscale* 8:8712–16

Alvarez NJ, Walker LM, Anna SL. 2012. A criterion to assess the impact of confined volumes on surfactant transport to liquid-fluid interfaces. *Soft Matter* 8:8917–25

Amine C, Dreher J, Helgason T, Tadros T. 2014. Investigation of emulsifying properties and emulsion stability of plant and milk proteins using interfacial tension and interfacial elasticity. *Food Hydrocoll.* 39:180–86

Ashby NP, Binks BP. 2000. Pickering emulsions stabilised by Laponite clay particles. *Phys. Chem. Chem. Phys.* 2:5640–46

Atkinson PJ, Dickinson E, Horne DS, Richardson RM. 1995. Neutron reflectivity of adsorbed β-casein and β-lactoglobulin at the air/water interface. *J. Chem. Soc. Faraday Trans.* 91(17):2847–54

Audebrand M, Ropers M-H, Riaublanc A. 2013. Disappearance of intermolecular β-sheets upon adsorption of β-lactoglobulin aggregates at the oil-water interfaces of emulsions. *Food Hydrocoll.* 33(2):178–85

Aynié S, Le Meste M, Colas B, Lorient D. 1992. Interactions between lipids and milk proteins in emulsion. *J. Food Sci.* 57(4):883–91

Bernardini C, Stoyanov SD, Arnaudov LN, Cohen Stuart MA. 2013. Colloids in Flatland: a perspective on 2D phase-separated systems, characterisation methods, and lineactant design. *Chem. Soc. Rev.* 42:2100–29

Berry JD, Neeson MJ, Dagastine RR, Chan DYC, Tabor RF. 2015. Measurement of surface and interfacial tension using pendant drop tensiometry. *J. Colloid Interface Sci.* 454:226–37

Berton C, Genot C, Guibert D, Ropers M-H. 2012a. Effect of lateral heterogeneity in mixed surfactant-stabilized interfaces on the oxidation of unsaturated lipids in oil-in-water emulsions. *J. Colloid Interface Sci.* 377(1):244–50

Berton C, Genot C, Ropers M-H. 2011a. Quantification of unadsorbed protein and surfactant emulsifiers in oil-in-water emulsions. *J. Colloid Interface Sci.* 354(2):739–48

Berton C, Ropers M-H, Guibert D, Solé V, Genot C. 2012b. Modifications of interfacial proteins in oil-in-water emulsions prior to and during lipid oxidation. *J. Agric. Food Chem.* 60(35):8659–71
Berton C, Ropers M-H, Viau M, Genot C. 2011b. Contribution of the interfacial layer to the protection of emulsified lipids against oxidation. *J. Agric. Food Chem.* 59(9):5052–61
Berton-Carabin CC, Coupland JN, Elias RJ. 2013. Effect of the lipophilicity of model ingredients on their location and reactivity in emulsions and solid lipid nanoparticles. *Colloids Surf. A* 431:9–17
Berton-Carabin CC, Ropers M-H, Genot C. 2014. Lipid oxidation in oil-in-water emulsions: Involvement of the interfacial layer. *Compr. Rev. Food Sci. Food Saf.* 13:945–77
Berton-Carabin CC, Schröder A, Rovalino Cordova A, Schroën K, Sagis LMC. 2016. Protein and lipid oxidation affect the viscoelasticity of whey protein layers at the oil-water interface. *Eur. J. Lipid Sci. Technol.* 118:1630–43
Berton-Carabin CC, Schroën K. 2015. Pickering emulsions for food applications: background, trends and challenges. *Annu. Rev. Food Sci. Technol.* 6:263–97
Beverung CJ, Radke CJ, Blanch HW. 1999. Protein adsorption at the oil/water interface: characterization of adsorption kinetics by dynamic interfacial tension measurements. *Biophys. Chem.* 81(1):59–80
Bos MA, van Vliet T. 2001. Interfacial rheological properties of adsorbed protein layers and surfactants: a review. *Adv. Colloid Interface Sci.* 91:437–71
Bourlieu C, Bouzerzour K, Ferret-Bernard S, Le Bourgot C, Chever S, et al. 2015. Infant formula interface and fat source impact on neonatal digestion and gut microbiota. *Eur. J. Lipid Sci. Technol.* 117(10):1500–12
Carbonaro M, Cappelloni M, Nicoli S, Lucarini M, Carnovale E. 1997. Solubility-digestibility relationship of legume proteins. *J. Agric. Food Chem.* 45(9):3387–94
Chen B, Li H, Ding Y, Rao J. 2011. Improvement of physicochemical stabilities of emulsions containing oil droplets coated by non-globular protein-beet pectin complex membranes. *Food Res. Int.* 44(5):1468–75
Chen J, Dickinson E. 1995. Protein/surfactant interfacial interactions. Part 3. Competitive adsorption of protein + surfactant in emulsions. *Colloids Surf. A* 101:77–85
Chen J, Dickinson E, Iveson G. 1993. Interfacial interactions, competitive adsorption and emulsion stability. *Food Struct.* 12(2):1
Cheng Y, Xiong YL, Chen J. 2010. Antioxidant and emulsifying properties of potato protein hydrolysate in soybean oil-in-water emulsions. *Food Chem.* 120(1):101–8
Chu B-S, Rich GT, Ridout MJ, Faulks RM, Wickham MSJ, Wilde PJ. 2009. Modulating pancreatic lipase activity with galactolipids: effects of emulsion interfacial composition. *Langmuir* 25(16):9352–60
Corstens MN, Berton-Carabin CC, De Vries R, Troost FJ, Masclee AAM, Schroën K. 2017a. Food-grade micro-encapsulation systems that may induce satiety via delayed lipolysis: a review. *Crit. Rev. Food Sci. Nutr.* 57(10):2218–44
Corstens MN, Berton-Carabin CC, Elichiry-Ortiz PT, Hol K, Troost FJ, et al. 2017b. Emulsion-alginate beads designed to control in vitro intestinal lipolysis: towards appetite control. *J. Funct. Foods.* 34:319–28
Corstens MN, Berton-Carabin CC, Kester A, Fokkink R, van den Broek JM, et al. 2017c. Destabilization of multilayered interfaces in digestive conditions limits their ability to prevent lipolysis in emulsions. *Food Struct.* 12:54–63
Corstens MN, Osorio Caltenco LA, de Vries R, Schroën K, Berton-Carabin CC. 2017d. Interfacial behaviour of biopolymer multilayers: influence of in vitro digestive conditions. *Colloids Surf. B* 153:199–207
Costa ALR, Gomes A, de Andrade CCP, Cunha RL. 2017. Emulsifier functionality and process engineering: progress and challenges. *Food Hydrocoll.* 68:69–80
Couëdelo L, Amara S, Lecomte M, Meugnier E, Monteil J, et al. 2015. Impact of various emulsifiers on ALA bioavailability and chylomicron synthesis through changes in gastrointestinal lipolysis. *Food Funct.* 1726–35
Courthaudon JL, Dickinson E, Christie WW. 1991a. Competitive adsorption of lecithin and b-casein in oil in water emulsions. *J. Agric. Food Chem.* 39:1365–68
Courthaudon JL, Dickinson E, Dalgleish DG. 1991b. Competitive adsorption of beta-casein and nonionic surfactants in oil-in-water emulsions. *J. Colloid Interface Sci.* 145(2):390–95
Courthaudon JL, Dickinson E, Matsumura Y, Clark DC. 1991c. Competitive adsorption of β-lactoglobulin + Tween 20 at the oil-water interface. *Colloids Surf.* 56:293–300

Cui Z, Chen Y, Kong X, Zhang C, Hua Y. 2014. Emulsifying properties and oil/water (O/W) interface adsorption behavior of heated soy proteins: effects of heating concentration, homogenizer rotating speed, and salt addition level. *J. Agric. Food Chem.* 62:1634–42

Dalgleish DG. 1997. Adsorption of proteins and the stability of emulsions. *Trends Food Sci. Technol.* 8:1–6

Dan A, Kotsmar C, Ferri JK, Javadi A, Karbaschi M, et al. 2012. Mixed protein-surfactant adsorption layers formed in a sequential and simultaneous way at water-air and water-oil interfaces. *Soft Matter* 8(22):6057–65

Day L. 2013. Proteins from land plants: potential resources for human nutrition and food security. *Trends Food Sci. Technol.* 32:25–42

Delahaije RJBM, Gruppen H, van Nieuwenhuijzen NH, Giuseppin MLF, Wierenga PA. 2013a. Effect of glycation on the flocculation behavior of protein-stabilized oil-in-water emulsions. *Langmuir*. 29(49):15201–8

Delahaije RJBM, Wierenga PA, Giuseppin MLF, Gruppen H. 2014. Improved emulsion stability by succinylation of patatin is caused by partial unfolding rather than charge effects. *J. Colloid Interface Sci.* 430:69–77

Delahaije RJBM, Wierenga PA, van Nieuwenhuijzen NH, Giuseppin MLF, Gruppen H. 2013b. Protein concentration and protein-exposed hydrophobicity as dominant parameters determining the flocculation of protein-stabilized oil-in-water emulsions. *Langmuir* 29(37):11567–74

Destribats M, Rouvet M, Gehin-Delval C, Schmitt C, Binks BP. 2014. Emulsions stabilised by whey protein microgel particles: towards food-grade Pickering emulsions. *Soft Matter* 10:6941–54

Dickinson E. 1992a. *An Introduction to Food Colloids*. Oxford: Oxford Univ. Press

Dickinson E. 1992b. Structure and composition of adsorbed protein layers and the relationship to emulsion stability. *J. Chem. Soc. Faraday Trans.* 88(20):2973–83

Dickinson E. 1994. Protein-stabilized emulsions. *J. Food Eng.* 22:59–74

Dickinson E. 1998. Proteins at interfaces and in emulsions. Stability, rheology and interactions. *J. Chem. Soc. Faraday Trans.* 94(12):1657–69

Dickinson E. 2009. Hydrocolloids as emulsifiers and emulsion stabilizers. *Food Hydrocoll.* 23(6):1473–82

Dickinson E. 2010. Food emulsions and foams: stabilization by particles. *Curr. Opin. Colloid Interface Sci.* 15(1–2):40–49

Dickinson E. 2011. Mixed biopolymers at interfaces: competitive adsorption and multilayer structures. *Food Hydrocoll.* 25(8):1966–83

Dickinson E. 2012. Use of nanoparticles and microparticles in the formation and stabilization of food emulsions. *Trends Food Sci. Technol.* 24(1):4–12

Dickinson E, Hong ST. 1994. Surface coverage of β-lactoglobulin at the oil-water interface: influence of protein heat-treatment and various emulsifiers. *J. Agric. Food Chem.* 42:1602–6

Dickinson E, Matsumura Y. 1991. Time-dependent polymerization of β-lactoglobulin through disulphide bonds at the oil-water interface in emulsions. *Int. J. Biol. Macromol.* 13(1):26–30

Dickinson E, Murray BS, Stainsby G. 1988. Coalescence stability of emulsion-sized droplets at a planar oil-water interface and the relationship to protein film surface rheology. *J. Chem. Soc. Faraday Trans. 1.* 84(3):871–83

Dickinson E, Rolfe SE, Dalgleish DG. 1989. Competitive adsorption in oil-in-water emulsions containing α-lactalbumin and β-lactoglobulin. *Food Hydrocoll.* 3:193–203

Dürrenberger MB, Handschin S, Conde-Petit B, Escher F. 2001. Visualization of food structure by confocal laser scanning microscopy (CLSM). *LWT Food Science Technol.* 34:11–17

Dynarowicz-Latka P, Dhanabalan A, Oliveira ON. 2001. Modern physicochemical research on Langmuir monolayers. *Adv. Colloid Interface Sci.* 91:221–93

Engelhardt K, Lexis M, Gochev G, Konnerth C, Miller R, et al. 2013. pH effects on the molecular structure of β-lactoglobulin modified air-water interfaces and its impact on foam rheology. *Langmuir* 29:11646–55

Fang Y, Dalgleish DG. 1993. Casein adsorption on the surfaces of oil-in-water emulsions modified by lecithin. *Colloids Surf. B* 1:357–64

Fang Y, Dalgleish DG. 1996. Competitive adsorption between dioleoylphosphatidylcholine and sodium caseinate on oil–water interfaces. *J. Agric. Food Chem.* 44:59–64

Felderhof BU. 2006. Effect of surface elasticity on the motion of a droplet in a viscous fluid. *J. Chem. Phys.* 125:124904

Fenaille F, Parisod V, Tabet JC, Guy PA. 2005. Carbonylation of milk powder proteins as a consequence of processing conditions. *Proteomics* 5(12):3097–104

Feng H, Ershov D, Krebs T, Schroen K, Cohen Stuart MA, et al. 2015. Manipulating and quantifying temperature-triggered coalescence with microcentrifugation. *Lab Chip* 15:188–94

Fernandez-Avila C, Trujillo AJ. 2016. Ultra-high pressure homogenization improves oxidative stability and interfacial properties of soy protein isolate-stabilized emulsions. *Food Chem*. 209:104–13

Ferri JK, Gorevski N, Kotsmar C, Leser ME, Miller R. 2008. Desorption kinetics of surfactants at fluid interfaces by novel coaxial capillary pendant drop experiments. *Colloids Surf. A* 319:13–20

Fischer P, Erni P. 2007. Emulsion drops in external flow fields - The role of liquid interfaces. *Curr. Opin. Colloid Interface Sci.* 12:196–205

Fredrick E, Walstra P, Dewettinck K. 2010. Factors governing partial coalescence in oil-in-water emulsions. *Adv. Colloid Interface Sci.* 153(1–2):30–42

Gallier S, Acton D, Garg M, Singh H. 2017. Natural and processed milk and oil body emulsions: bioavailability, bioaccessibility and functionality. *Food Struct*. 13:13–23

Gallier S, Tate H, Singh H. 2013. In vitro gastric and intestinal digestion of a walnut oil body dispersion. *J. Agric. Food Chem.* 61(2):410–17

Gallier S, Vocking K, Post JA, Van De Heijning B, Acton D, et al. 2015. A novel infant milk formula concept: mimicking the human milk fat globule structure. *Colloids Surf. B* 136:329–39

Geerts MEJ, Mienis E, Nikiforidis CV, van der Padt A, van der Goot AJ. 2017. Mildly refined fractions of yellow peas show rich behaviour in thickened oil-in-water emulsions. *Innov. Food Sci. Emerg. Technol.* 41:251–58

Genot C, Kabri T, Meynier A. 2013. Stabilisation of omega-3 oils and enriched foods using emulsifiers. In *Food Enrichment with Omega-3 Fatty Acids*, ed. C Jacobsen, NS Nielsen, AF Horn, AD Sorensen, pp. 150–93. Cambridge: Woodhead Publ.

Gochev G, Retzlaff I, Aksenenko EV, Fainerman VB, Miller R. 2013. Adsorption isotherm and equation of state for β-lactoglobulin layers at the air/water surface. *Colloids Surf. A* 422:33–38

Goff HD. 2008. 65 years of ice cream science. *Int. Dairy J.* 18(7):754–58

Golding M, Wooster TJ. 2010. The influence of emulsion structure and stability on lipid digestion. *Curr. Opin. Colloid Interface Sci.* 15(1–2):90–101

Graham DE, Phillips MC. 1979. Proteins at liquid interfaces. III. Molecular structures of adsorbed films. *J. Colloid Interface Sci.* 70(3):427–39

Granger C, Barey P, Toutain J, Cansell M. 2005. Direct quantification of protein partitioning in oil-in-water emulsion by front-face fluorescence: avoiding the need for centrifugation. *Colloids Surf. B* 43(3–4):158–62

Gumus CE, Decker EA, McClements DJ. 2017. Formation and stability of w-3 oil emulsion-based delivery systems using plant proteins as emulsifiers: lentil, pea, and faba bean proteins. *Food Biophys*. 12(2):186–97

Gunning AP, Kirby AR, Parker ML, Cross KL, Morris VJ. 2010. Utilizing atomic force microscopy in food research. *Food Technol*. 64:32–37

Guzey D, McClements DJ. 2006. Formation, stability and properties of multilayer emulsions for application in the food industry. *Adv. Colloid Interface Sci.* 128–130:227–48

Hasenhuettl GL, Hartel RW. 2008. *Food Emulsifiers and Their Applications*. New York: Springer

Heins A, McPhail DB, Sokolowski T, Stöckmann H, Schwarz K. 2007. The location of phenolic antioxidants and radicals at interfaces determines their activity. *Lipids* 42(6):573–82

Helfrich W. 1973. Elastic properties of lipid bilayers: theory and possible experiments. *Z. Naturforsch*. 28:693–703

Ho KKHY, Schroën K, San Martín-González MFS, Berton-Carabin CC. 2017. Physicochemical stability of lycopene-loaded emulsions stabilized by plant or dairy proteins. *Food Struct*. 12:34–42

Horne DS, Leaver J. 1995. Milk proteins on surfaces. *Food Hydrocoll*. 9(2):91–95

Hu M, McClements DJ, Decker EA. 2003. Lipid oxidation in corn oil-in-water emulsions stabilized by casein, whey protein isolate, and soy protein isolate. *J. Agric. Food Chem.* 51(6):1696–700

Hunt JA, Dalgleish DG. 1994. Adsorption behaviour of whey protein isolate and caseinate in soya oil-in-water emulsions. *Food Hydrocoll*. 8(2):175–87

Jacobsen C, Let MB, Nielsen NS, Meyer AS. 2008. Antioxidant strategies for preventing oxidative flavour deterioration of foods enriched with n-3 polyunsaturated lipids: a comparative evaluation. *Trends Food Sci. Technol.* 19(2):76–93

Jones DB, Middelberg APJ. 2003. Interfacial protein networks and their impact on droplet breakup. *AIChE J.* 49(6):1533–41

Jourdain LS, Schmitt C, Leser ME, Murray BS, Dickinson E. 2009. Mixed layers of sodium caseinate + dextran sulfate: influence of order of addition to oil-water interface. *Langmuir*. 25(17):10026–37

Kaláb M, Allan-Wojtas P, Miller SS. 1995. Microscopy and other imaging techniques in food structure analysis. *Trends Food Sci. Technol.* 6:177–86

Kalashnikova I, Bizot H, Cathala B, Capron I. 2012. Modulation of cellulose nanocrystals amphiphilic properties to stabilize oil/water interface. *Biomacromolecules* 13(1):7471–79

Keerati-u-rai M, Wang Z, Corredig M. 2011. Adsorption of soy protein isolate in oil-in-water emulsions: difference between native and spray dried isolate. *J. Am. Oil Chem. Soc.* 88(10):1593–602

Kenmogne-Domguia HB, Meynier A, Viau M, Llamas G, Genot C. 2012. Gastric conditions control both the evolution of the organization of protein-stabilized emulsions and the kinetic of lipolysis during in vitro digestion. *Food Funct*. 3(12):1302–9

Kerwin BA. 2008. Polysorbates 20 and 80 used in the formulation of protein biotherapeutics: structure and degradation pathways. *J. Pharm. Sci.* 97(8):2924–35

Kinsella JE. 1979. Functional properties of soy proteins. *J. Am. Oil Chem. Soc.* 56(3):242–58

Kittipongpittaya K, Chen B, Panya A, McClements DJ, Decker EA. 2012. Prooxidant activity of polar lipid oxidation products in bulk oil and oil-in-water emulsion. *J. Am. Oil Chem. Soc.* 89(12):2187–94

Klang V, Matsko NB, Valenta C, Hofer F. 2012. Electron microscopy of nanoemulsions: an essential tool for characterisation and stability assessment. *Micron* 43(2–3):85–103

Kong B, Xiong YL, Cui X, Zhao X. 2013. Hydroxyl radical-stressed whey protein isolate: functional and rheological properties. *Food Bioprocess Technol*. 6(1):169–76

Kralova I, Sjöblom J. 2009. Surfactants used in food industry: a review. *J. Dispers. Sci. Technol.* 30(9):1363–83

Krebs T, Ershov D, Schroen CGPH, Boom RM. 2013. Coalescence and compression in centrifuged emulsions studied with in situ optical microscopy. *Soft Matter* 9:4026–35

Krebs T, Schroen K, Boom R. 2012. A microfluidic method to study demulsification kinetics. *Lab Chip* 12(6):1060–70

Kurukji D, Pichot R, Spyropoulos F, Norton IT. 2013. Interfacial behaviour of sodium stearoyllactylate (SSL) as an oil-in-water pickering emulsion stabiliser. *J. Colloid Interface Sci.* 409:88–97

Ladjal Ettoumi Y, Berton-Carabin C, Chibane M, Schroën K. 2017. Legume protein isolates for stable acidic emulsions prepared by premix membrane emulsification. *Food Biophys*. 12(1):119–28

Laguerre M, Bayrasy C, Lecomte J, Chabi B, Andrew E, et al. 2013. How to boost antioxidants by lipophilization? *Biochimie* 95:20–26

Laguerre M, Bayrasy C, Panya A, Weiss J, McClements DJ, et al. 2015. What makes good antioxidants in lipid-based systems? The next theories beyond the polar paradox. *Crit. Rev. Food Sci. Nutr.* 55(2):183–201

Laguerre M, Bily A, Roller M, Birtic S. 2017. Mass transport phenomena in lipid oxidation and antioxidation. *Annu. Rev. Food Sci. Technol.* 8:391–411

Lam S, Velikov KP, Velev OD. 2014. Pickering stabilization of foams and emulsions with particles of biological origin. *Curr. Opin. Colloid Interface Sci.* 19(5):490–500

Lamorgese A, Mauri R, Sagis LMC. 2017. Modeling soft interface dominated systems: a comparison of phase field and Gibbs dividing surface models. *Phys. Rep.* 675:1–54

Larson RG. 1999. *The Structure and Rheology of Complex Fluids*. New York: Oxford Univ. Press

Leal-Calderon F, Cansell M. 2012. The design of emulsions and their fate in the body following enteral and parenteral routes. *Soft Matter* 8(40):10213–25

Leal-Calderon F, Schmitt V, Bibette J. 2007. *Emulsion Science*: *Basic Principles*. New York: Springer

Leaver J, Law A, Brechany E. 1999. Covalent modification of emulsified beta-casein resulting from lipid peroxidation. *J. Colloid Interface Sci.* 210(1):207–14

Leermakers FAM, Atkinson PJ, Dickinson E, Horne DS. 1996. Self-consistent-field modeling of adsorbed β-casein: effects of pH and ionic strength on surface coverage and density profile. *J. Colloid Interface Sci.* 178:681–93

Le Meste M, Closs B, Courthaudon JL, Colas B. 1991. Interactions between milk proteins and lipids: A mobility study. In *Interactions of Food Proteins*, ed. RA Barford, N Parris, pp. 137–47. Washington, DC: ACS

Lesmes U, Sandra S, Decker EA, McClements DJ. 2010. Impact of surface deposition of lactoferrin on physical and chemical stability of omega-3 rich lipid droplets stabilised by caseinate. *Food Chem*. 123(1):99–106

Li M, Auty MAE, O'Mahony JA, Kelly AL, Brodkorb A. 2016. Covalent labelling of β-casein and its effect on the microstructure and physico-chemical properties of emulsions stabilised by β-casein and whey protein isolate. *Food Hydrocoll*. 61:504–13

Liu F, Tang C-H. 2014. Emulsifying properties of soy protein nanoparticles: Influence of the protein concentration and/or emulsification process. *J. Agric. Food Chem*. 62:2644–54

Liu Q, Lu Y, Han J, Chen Q, Kong B. 2015. Structure-modification by moderate oxidation in hydroxyl radical-generating systems promote the emulsifying properties of soy protein isolate. *Food Struct*. 6:21–28

Livney YD, Ruimy E, Ye AM, Zhu X, Singh H. 2017. A milkfat globule membrane-inspired approach for encapsulation of emulsion oil droplets. *Food Hydrocoll*. 65:121–29

Lomova MV, Sukhorukov GB, Antipina MN. 2010. Antioxidant coating of micronsize droplets for prevention of lipid peroxidation in oil-in-water emulsion. *ACS Appl. Mater. Interfaces* 2(12):3669–76

Lopez C, Cauty C, Rousseau F, Blot M, Margolis A, Famelart M-H. 2017. Lipid droplets coated with milk fat globule membrane fragments: microstructure and functional properties as a function of pH. *Food Res. Int.* 91:26–37

Losada-Barreiro S, Bravo-Díaz C, Paiva-Martins F, Romsted LS. 2013. Maxima in antioxidant distributions and efficiencies with increasing hydrophobicity of gallic acid and its alkyl esters. The pseudophase model interpretation of the "cutoff effect." *J. Agric. Food Chem.* 61:6533–43

Lucassen-Reynders EH. 1994. Competitive adsorption of emulsifiers. 1. Theory for adsorption of small and large molecules. *Colloids Surf. A* 91:79–88

Lund MN, Heinonen M, Baron CP, Estévez M. 2011. Protein oxidation in muscle foods: a review. *Mol. Nutr. Food Res.* 55(1):83–95

Luo AM, Sagis LMC, Ilg P. 2014. The Landau free energy of hard ellipses obtained from microscopic simulations. *J. Chem. Phys.* 140:124901

Luo AM, Sagis LMC, Öttinger HC, De Michele C, Ilg P. 2015. Modelling the rheology of anisotropic particles adsorbed on a two-dimensional fluid interface. *Soft Matter* 11:4383–95

Mackie A, Gunning A, Wilde P, Morris V. 1999. Orogenic displacement of protein from the air/water interface by competitive adsorption. *J. Colloid Interface Sci.* 210:157–66

Mackie AR, Gunning AP, Ridout MJ, Wilde PJ, Morris VJ. 2001. Orogenic displacement in mixed β-lactoglobulin/β-casein films at the air/water interface. *Langmuir* 17:6593–98

Mackie AR, Gunning AP, Wilde PJ, Morris VJ. 2000. Orogenic displacement of protein from the oil/water interface. *Langmuir* 16:2242–47

Magnusson E, Nilsson L, Bergenståhl B. 2016. Effect of the dispersed state of phospholipids on emulsification. Part 1. Phosphatidylcholine. *Colloids Surf. A* 506:794–803

Malaki Nik A, Langmaid S, Wright AJ. 2012. Nonionic surfactant and interfacial structure impact crystallinity and stability of β-carotene loaded lipid nanodispersions. *J. Agric. Food Chem.* 60(16):4126–35

Maldonado-Valderrama J, Gunning AP, Wilde PJ, Morris VJ. 2010. In vitro gastric digestion of interfacial protein structures: visualisation by AFM. *Soft Matter* 6(19):4908–15

Maldonado-Valderrama J, Holgado Terriza JA, Torcello-Gómez A, Cabrerizo-Vílchez MA. 2013. In vitro digestion of interfacial protein structures. *Soft Matter* 9(4):1043–53

Mancuso JR, McClements DJ, Decker EA. 1999. The effects of surfactant type, pH, and chelators on the oxidation of salmon oil-in-water emulsions. *J. Agric. Food Chem.* 47(10):4112–16

McClements DJ. 2004. Protein-stabilized emulsions. *Curr. Opin. Colloid Interface Sci.* 9(5):305–13

McClements DJ. 2005. *Food Emulsions: Principles, Practices and Techniques*. Boca Raton: CRC Press

McClements DJ. 2012. Advances in fabrication of emulsions with enhanced functionality using structural design principles. *Curr. Opin. Colloid Interface Sci.* 17(5):235–45

McClements DJ, Bai L, Chung C. 2017. Recent advances in the utilization of natural emulsifiers to form and stabilize emulsions. *Annu. Rev. Food Sci. Technol.* 8:205–36

McClements DJ, Decker EA. 2000. Lipid oxidation in oil-in-water emulsions: impact of molecular environment on chemical reactions in heterogeneous food systems. *J. Food Sci.* 65(8):1270–82
McClements DJ, Decker EA, Park Y. 2008a. Controlling lipid bioavailability through physicochemical and structural approaches. *Crit. Rev. Food Sci. Nutr.* 49(1):48–67
McClements DJ, Decker EA, Park Y, Weiss J. 2008b. Designing food structure to control stability, digestion, release and absorption of lipophilic food components. *Food Biophys.* 3:219–28
McClements DJ, Decker EA, Weiss J. 2007. Emulsion-based delivery systems for lipophilic bioactive components. *J. Food Sci.* 72(8):R109–24
McClements DJ, Gumus CE. 2016. Natural emulsifiers—biosurfactants, phospholipids, biopolymers, and colloidal particles: molecular and physicochemical basis of functional performance. *Adv. Colloid Interface Sci.* 234:3–26
McClements DJ, Li Y. 2010. Structured emulsion-based delivery systems: controlling the digestion and release of lipophilic food components. *Adv. Colloid Interface Sci.* 159(2):213–28
Mei L, McClements DJ, Wu J, Decker EA. 1998. Iron-catalyzed lipid oxidation in emulsion as affected by surfactant, pH and NaCl. *Food Chem.* 61(3):307–12
Mikkonen KS, Xu C, Berton-Carabin C, Schroën K. 2016. Spruce galactoglucomannans in rapeseed oil-in-water emulsions: efficient stabilization performance and structural partitioning. *Food Hydrocoll.* 52:615–24
Miller R, Fainerman VB, Leser ME, Michel M. 2004. Kinetics of adsorption of proteins and surfactants. *Curr. Opin. Colloid Interface Sci.* 9:350–56
Miller R, Fainerman VB, Makievski AV, Krägel J, Grigoriev DO, et al. 2000. Dynamics of protein and mixed protein/surfactant adsorption layers at the water/fluid interface. *Adv. Colloid Interface Sci.* 86(1–2):39–82
Miller R, Hofmann A, Hartmann R, Schano KH, Halbig A. 1992. Measuring dynamic surface and interfacial tensions. *Adv. Mater.* 4(5):470
Monahan FJ, McClements DJ, Kinsella JE. 1993. Polymerization of whey proteins in whey protein-stabilized emulsions. *J. Agric. Food Chem.* 41:1826–29
Monteillet H, Workamp M, Appel J, Kleijn M, Leermakers FAM, Sprakel J. 2014. Ultrastrong anchoring yet barrier-free adsorption of composite microgels at liquid interfaces. *Adv. Mater. Interfaces* 1300121:1–9
Muijlwijk K, Colijn I, Harsono H, Krebs T, Berton-Carabin C, Schroën K. 2017. Coalescence of protein-stabilised emulsions studied with microfluidics. *Food Hydrocoll.* 70:96–104
Muijlwijk K, Hinderink E, Ershov D, Berton-Carabin C, Schroën K. 2016a. Interfacial tension measured at high expansion rates and within milliseconds using microfluidics. *J. Colloid Interface Sci.* 470:71–79
Muijlwijk K, Huang W, Vuist J, Berton-Carabin C, Schroën K. 2016b. Convective mass transport dominates surfactant adsorption in a microfluidic Y-junction. *Soft Matter* 12:9025–29
Mun S, Decker EA, McClements DJ. 2007. Influence of emulsifier type on in vitro digestibility of lipid droplets by pancreatic lipase. *Food Res. Int.* 40(6):770–81
Mun S, Decker EA, Park Y, Weiss J, McClements DJ. 2006. Influence of interfacial composition on in vitro digestibility of emulsified lipids: potential mechanism for chitosan's ability to inhibit fat digestion. *Food Biophys.* 1(1):21–29
Munk MB, Erichsen HR, Andersen ML. 2014a. The effects of low-molecular-weight emulsifiers in O/W-emulsions on microviscosity of non-solidified oil in fat globules and the mobility of emulsifiers at the globule surfaces. *J. Colloid Interface Sci.* 419:134–41
Munk MB, Larsen FH, Van Den Berg FWJ, Knudsen JC, Andersen ML. 2014b. Competitive displacement of sodium caseinate by low-molecular-weight emulsifiers and the effects on emulsion texture and rheology. *Langmuir* 30:8687–96
Murray BS. 2002. Interfacial rheology of food emulsifiers and proteins. *Curr. Opin. Colloid Interface Sci.* 7:426–31
Murray BS. 2011. Rheological properties of protein films. *Curr. Opin. Colloid Interface Sci.* 16(1):27–35
Murray BS, Xu R, Dickinson E. 2009. Brewster angle microscopy of adsorbed protein films at air-water and oil-water interfaces after compression, expansion and heat processing. *Food Hydrocoll.* 23:1190–97
Nakashima T, Shimizu M. 1986. Porous glass from calcium alumino boro-silicate glass. *Ceram. Jpn.* 21:408
Nazir A, Schroën K, Boom R. 2010. Premix emulsification: a review. *J. Membr. Sci.* 362(1–2):1–11
Nielsen NS, Horn AF, Jacobsen C. 2013. Effect of emulsifier type, pH and iron on oxidative stability of 5% fish oil-in-water emulsions. *Eur. J. Lipid Sci. Technol.* 115(8):874–89

Nikiforidis CV, Matsakidou A, Kiosseoglou V. 2014. Composition, properties and potential food applications of natural emulsions and cream materials based on oil bodies. *RSC Adv.* 4:25067–78
Nilsson L, Bergenståhl B. 2007. Emulsification and adsorption properties of hydrophobically modified potato and barley starch. *J. Agric. Food Chem.* 55(4):1469–74
Nuchi CD, Hernandez P, McClements DJ, Decker EA. 2002. Ability of lipid hydroperoxides to partition into surfactant micelles and alter lipid oxidation rates in emulsions. *J. Agric. Food Chem.* 50(19):5445–49
Nuchi CD, McClements DJ, Decker EA. 2001. Impact of Tween 20 hydroperoxides and iron on the oxidation of methyl linoleate and salmon oil dispersions. *J. Agric. Food Chem.* 49(11):4912–16
Obando M, Papastergiadis A, Li S, De Meulenaer B. 2015. Impact of lipid and protein co-oxidation on digestibility of dairy proteins in oil-in-water (O/W) emulsions. *J. Agric. Food Chem.* 63:9820–30
Oosting A, van Vlies N, Kegler D, Schipper L, Abrahamse-Berkeveld M, et al. 2014. Effect of dietary lipid structure in early postnatal life on mouse adipose tissue development and function in adulthood. *Br. J. Nutr.* 111:215–26
Öttinger HC. 2005. *Beyond Equilibrium Thermodynamics*. Hoboken, NJ: Wiley
Pan Y, Nitin N. 2015. Effect of layer-by-layer coatings and localization of antioxidant on oxidative stability of a model encapsulated bioactive compound in oil-in-water emulsions. *Colloids Surfaces B* 135:472–80
Pan Y, Tikekar RV, Nitin N. 2013. Effect of antioxidant properties of lecithin emulsifier on oxidative stability of encapsulated bioactive compounds. *Int. J. Pharm.* 450(1–2):129–37
Patton S, Huston GE. 1986. A method for isolation of milk fat globules. *Lipids* 21(2):170–74
Pawlik A, Kurukji D, Norton I, Spyropoulos F. 2016. Food-grade Pickering emulsions stabilised with solid lipid particles. *Food Funct.* 7:2712–21
Pontani L-L, Haase MF, Raczkowska I, Brujic J. 2013. Immiscible lipids control the morphology of patchy emulsions. *Soft Matter* 9:7150–57
Pugnaloni LA, Dickinson E, Ettelaie R, Mackie AR, Wilde PJ. 2004. Competitive adsorption of proteins and low-molecular-weight surfactants: computer simulation and microscopic imaging. *Adv. Colloid Interface Sci.* 107:27–49
Puppo MC, Beaumal V, Chapleau N, Speroni F, de Lamballerie M, et al. 2008. Physicochemical and rheological properties of soybean protein emulsions processed with a combined temperature/high-pressure treatment. *Food Hydrocoll.* 22:1079–89
Ralet M-C, Guéguen J. 2000. Fractionation of potato proteins: Solubility, thermal coagulation and emulsifying properties. *LWT Food Sci. Technol.* 33:380–87
Rampon V, Genot C, Riaublanc A, Anton M, Axelos MA V, McClements DJ. 2003a. Front-face fluorescence spectroscopy study of globular proteins in emulsions: displacement of BSA by a nonionic surfactant. *J. Agric. Food Chem.* 51:2482–89
Rampon V, Genot C, Riaublanc A, Anton M, Axelos MA V, McClements DJ. 2003b. Front-face fluorescence spectroscopy study of globular proteins in emulsions: influence of droplet flocculation. *J. Agric. Food Chem.* 51(9):2490–95
Rampon V, Lethuaut L, Mouhous-Riou N, Genot C. 2001. Interface characterization and aging of bovine serum albumin stabilized oil-in-water emulsions as revealed by front-surface fluorescence. *J. Agric. Food Chem.* 49(8):4046–51
Rampon V, Riaublanc A, Anton M, Genot C, McClements DJ. 2003c. Evidence that homogenization of BSA-stabilized hexadecane-in-water emulsions induces structure modification of the nonadsorbed protein. *J. Agric. Food Chem.* 51(20):5900–5
Ravera F, Loglio G, Kovalchuk VI. 2010. Interfacial dilational rheology by oscillating bubble/drop methods. *Curr. Opin. Colloid Interface Sci.* 15(4):217–28
Rayner M, Marku D, Eriksson M, Sjöö M, Dejmek P, Wahlgren M. 2014. Biomass-based particles for the formulation of Pickering type emulsions in food and topical applications. *Colloids Surf. A* 458:48–62
Rayner M, Sjöö M, Timgren A, Dejmek P. 2012. Quinoa starch granules as stabilizing particles for production of Pickering emulsions. *Faraday Discuss.* 158:139–55
Razumovsky L, Damodaran S. 1999. Thermodynamic incompatibility of proteins at the air-water interface? *Colloids Surf. B* 13:251–61
Rehage H, Husmann M, Walter A. 2002. From two-dimensional model networks to microcapsules. *Rheol. Acta* 41(4):292–306

Reis P, Holmberg K, Watzke H, Leser ME, Miller R. 2009. Lipases at interfaces: a review. *Adv. Colloid Interface Sci.* 147–148:237–50

Sagis LMC. 2011. Dynamic properties of interfaces in soft matter: experiments and theory. *Rev. Mod. Phys.* 83(4):1367–1403

Sagis LMC, Fischer P. 2014. Nonlinear rheology of complex fluid-fluid interfaces. *Curr. Opin. Colloid Interface Sci.* 19(6):520–29

Sagis LMC, Öttinger HC. 2013. Dynamics of multiphase systems with complex microstructure. I. Development of the governing equations through nonequilibrium thermodynamics. *Phys. Rev. E.* 88(2):22149

Salminen H, Heinonen M, Decker EA. 2009. Antioxidant effects of berry phenolics incorporated in oil-in-water emulsions with continuous phase β-lactoglobulin. *J. Am. Oil Chem. Soc.* 87(4):419–28

Salminen H, Helgason T, Kristinsson B, Kristbergsson K, Weiss J. 2013. Formation of solid shell nanoparticles with liquid ω-3 fatty acid core. *Food Chem.* 141(3):2934–43

Salminen H, Helgason T, Kristinsson B, Kristbergsson K, Weiss J. 2017. Tuning of shell thickness of solid lipid particles impacts the chemical stability of encapsulated w-3 fish oil. *J. Colloid Interface Sci.* 490:207–16

Sante-Lhoutellier V, Aubry L, Gatellier P. 2007. Effect of oxidation on in vitro digestibility of skeletal muscle myofibrillar proteins. *J. Agric. Food Chem.* 55(13):5343–48

Sarkar A, Juan JM, Kolodziejczyk E, Acquistapace S, Donato-Capel L, Wooster TJ. 2015. Impact of protein gel porosity on the digestion of lipid emulsions. *J. Agric. Food Chem.* 63:8829–37

Schröder A, Berton-Carabin C, Venema P, Cornacchia L. 2017a. Interfacial properties of whey protein and whey protein hydrolysates and their influence on O/W emulsion stability. *Food Hydrocoll.* 73:129–40

Schröder A, Sprakel J, Schroën K, Berton-Carabin CC. 2017b. Tailored microstructure of colloidal lipid particles for Pickering emulsions with tunable properties. *Soft Matter* 13:3190–98

Schröder V, Schubert H. 1999. Production of emulsions using microporous, ceramic membranes. *Colloids Surf. A* 152:103–9

Schroën K, Berton-Carabin CC. 2016. Emulsification: established and future technologies. In *Production, Handling and Characterization of Particulate Materials*, Vol. 25, ed. HG Merkus, GMH Meesters, pp. 257–89. Cham, Switz.: Springer Int. Publ.

Schuchmann HP, Köhler K, Azad Emin M, Schubert H. 2013. Food process engineering research and innovation in a fast changing world: paradigms/case studies. In *Advances in Food Process Engineering Research and Applications*, ed. S Yanniotis, pp. 41–59. New York: Springer

Schultz S, Wagner G, Urban K, Ulrich J. 2004. High-pressure homogenization as a process for emulsion formation. *Chem. Eng. Technol.* 27(4):361–68

Sengupta T, Damodaran S. 2000. Incompatibility and phase separation in a bovine serum albumin/beta-casein/water ternary film at the air-water interface. *J. Colloid Interface Sci.* 229:21–28

Shao Y, Tang C-H. 2014. Characteristics and oxidative stability of soy protein-stabilized oil-in-water emulsions: influence of ionic strength and heat pretreatment. *Food Hydrocoll.* 37:149–58

Singh H. 2011. Aspects of milk-protein-stabilised emulsions. *Food Hydrocoll.* 25(8):1938–44

Singh H, Ye A, Horne D. 2009. Structuring food emulsions in the gastrointestinal tract to modify lipid digestion. *Prog. Lipid Res.* 48(2):92–100

Sjöö M, Emek SC, Hall T, Rayner M, Wahlgren M. 2015. Barrier properties of heat treated starch Pickering emulsions. *J. Colloid Interface Sci.* 450:182–88

Stang M, Karbstein H, Schubert H. 1994. Adsorption kinetics of emulsifiers at oil-water interfaces and their effect on mechanical emulsification. *Chem. Eng. Process.* 33:307–11

Steegmans MLJ, Warmerdam A, Schroën KGPH, Boom RM. 2009. Dynamic interfacial tension measurements with microfluidic Y-junctions. *Langmuir* 25(17):9751–58

Tadros TF. 1994. Fundamental principles of emulsion rheology and their applications. *Colloids Surf. A* 91:39–55

Tang C-H. 2017. Emulsifying properties of soy proteins: a critical review with emphasis on the role of conformational flexibility. *Crit. Rev. Food Sci. Nutr.* 57(12):2636–79

Tavernier I, Wijaya W, Van der Meeren P, Dewettinck K, Patel AR. 2016. Food-grade particles for emulsion stabilization. *Trends Food Sci. Technol.* 50:159–74

Tcholakova S, Denkov ND, Ivanov IB, Campbell B. 2002. Coalescence in beta-lactoglobulin-stabilized emulsions: effects of protein adsorption and drop size. *Langmuir* 18:8960–71

Tcholakova S, Denkov ND, Lips A. 2008. Comparison of solid particles, globular proteins and surfactants as emulsifiers. *Phys. Chem. Chem. Phys.* 10(12):1608–27

Tcholakova S, Denkov ND, Sidzhakova D, Ivanov IB, Campbell B. 2003. Interrelation between drop size and protein adsorption at various emulsification conditions. *Langmuir* 19(14):5640–49

Toikkanen O, Lähteenmäki M, Moisio T, Forssell P, Partanen R, Murtomäki L. 2014. Study of oxygen transfer across milk proteins at an air-water interface with scanning electrochemical microscopy. *J. Agric. Food Chem.* 62(10):2284–88

Urban K, Wagner G, Schaffner D, Röglin D, Ulrich J. 2006. Rotor-stator and disc systems for emulsification processes. *Chem. Eng. Technol.* 29:24–31

van Aken GA. 2003. Competitive adsorption of protein and surfactants in highly concentrated emulsions: effect on coalescence mechanisms. *Colloids Surf. A* 213(2–3):209–19

Villiere A, Viau M, Bronnec I, Moreau N, Genot C. 2005. Oxidative stability of bovine serum albumin- and sodium caseinate-stabilized emulsions depends on metal availability. *J. Agric. Food Chem.* 53(5):1514–20

Vladisavljević GT, Schubert H. 2003. Preparation of emulsions with a narrow particle size distribution using microporous α-alumina membranes. *J. Dispers. Sci. Technol.* 24(6):811–19

Walstra PW. 2003. *Physical Chemistry of Foods*. New York: Marcel Dekker

Wan Z-L, Guo J, Yang X-Q. 2015. Plant protein-based delivery systems for bioactive ingredients in foods. *Food Funct.* 6:2876–89

Wang K, Lu YC, Xu JH, Luo GS. 2009. Determination of dynamic interfacial tension and its effect on droplet formation in the T-shaped microdispersion process. *Langmuir* 25:2153–58

Waninge R, Walstra P, Bastiaans J, Nieuwenhuijse H, Nylander T, et al. 2005. Competitive adsorption between beta-casein or beta-lactoglobulin and model milk membrane lipids at oil-water interfaces. *J. Agric. Food Chem.* 53:716–24

Waraho T, McClements DJ, Decker EA. 2011. Mechanisms of lipid oxidation in food dispersions. *Trends Food Sci. Technol.* 22(1):3–13

Wierenga PA, Basheva ES, Denkov ND. 2009. Modified capillary cell for foam film studies allowing exchange of the film-forming liquid. *Langmuir* 25(11):6035–39

Wilde P, Mackie A, Husband F, Gunning P, Morris V. 2004. Proteins and emulsifiers at liquid interfaces. *Adv. Colloid Interface Sci.* 108–109:63–71

Wilde PJ. 2000. Interfaces: their role in foam and emulsion behaviour. *Curr. Opin. Colloid Interface Sci.* 5:176–81

Wilde PJ, Chu BS. 2011. Interfacial & colloidal aspects of lipid digestion. *Adv. Colloid Interface Sci.* 165:14–22

Won JY, Gochev G, Ulaganathan V, Krägel J, Aksenenko EV, et al. 2017. Mixed adsorption mechanism for the kinetics of BLG interfacial layer formation at the solution/tetradecane interface. *Colloids Surf. A* 519:146–52

Xu JH, Dong PF, Zhao H, Tostado CP, Luo GS. 2012. The dynamic effects of surfactants on droplet formation in coaxial microfluidic devices. *Langmuir* 28:9250–58

Yang Y, Leser ME, Sher AA, McClements DJ. 2013. Formation and stability of emulsions using a natural small molecule surfactant: Quillaja saponin (Q-Naturale). *Food Hydrocoll.* 30:589–96

Yano YF. 2012. Kinetics of protein unfolding at interfaces. *J. Phys. Condens. Matter* 24:1–16

Ye A. 2008. Interfacial composition and stability of emulsions made with mixtures of commercial sodium caseinate and whey protein concentrate. *Food Chem.* 110(4):946–52

Yusoff A, Murray BS. 2011. Modified starch granules as particle-stabilizers of oil-in-water emulsions. *Food Hydrocoll.* 25(1):42–55

Zeeb B, Fischer L, Weiss J. 2011. Cross-linking of interfacial layers affects the salt and temperature stability of multilayered emulsions consisting of fish gelatin and sugar beet pectin. *J. Agric. Food Chem.* 59(19):10546–55

Zhai JLI, Day L, Aguilar MI, Wooster TJ. 2013. Protein folding at emulsion oil/water interfaces. *Curr. Opin. Colloid Interface Sci.* 18:257–71

Zhang Z, Decker EA, McClements DJ. 2014. Encapsulation, protection, and release of polyunsaturated lipids using biopolymer-based hydrogel particles. *Food Res. Int.* 64:520–26