



Food emulsions and foams: Stabilization by particles

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ABSTRACT

Recent advances in the stabilization of emulsions and foams by particles of nanoscale and microscopic dimensions are described. Ongoing research in this highly active field is providing insight into (i) the molecular factors controlling particle wettability and adsorption, (ii) the structural and mechanical properties of particle-laden liquid interfaces, and (iii) the stabilization mechanisms of particle-coated droplets and bubbles. There is much potential for exploiting the emerging knowledge in new food product applications. The preparation of cheap and effective colloidal particles based on food-grade ingredients, especially proteins, is the key technological challenge.

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1. Introduction

Food systems commonly contain particulate material that accumulates at oil–water and air–water interfaces and contributes to the colloidal stabilization of emulsions and foams [1]. The range of particle sizes involved in structuring such systems during and after emulsification and foaming can vary widely from just a few nanometres to tens of micrometres. As applied to emulsion droplets coated by a layer of adsorbed solid particles at the oil–water interface, the mechanism is commonly referred to as Pickering stabilization. Oil-in-water (O/W) or water-in-oil (W/O) emulsions can be produced depending on whether the particles are predominantly hydrophilic or hydrophobic. Important examples of Pickering-type food emulsions are homogenized and reconstituted milks (O/W emulsions stabilized by casein micelles) and margarines and fatty spreads (W/O emulsions stabilized by triglyceride crystals). Examples of edible foams stabilized by particles include whipped dairy cream and dessert toppings stabilized by partially aggregated emulsion droplets [1].

During the past decade there has been increasing interest by physical scientists in the interfacial properties of particles, especially nanoparticles. Some of this progress has been well described in

previous reviews [2–12]. Attention here is directed towards research published during the past 3–4 years. The purpose of this article is to focus on recent developments in (nano)particle stabilization that seem particularly relevant to food emulsions and foams. The perceived relevance may be because the investigators have worked directly with food-grade ingredients, or, alternatively, because the research offers potential strategies or methodologies for developing improved (nano)particle-based systems in food product formulations. This article is mainly concerned with experimental investigations of dispersed systems stabilized by inorganic particles (especially silica nanoparticles), fat crystals, and protein-based nanoparticles. Structures primarily based on supramolecular networks/gels or self-assembled lipids/surfactants are considered to lie outside the scope of the review.

2. Emulsions

According to the conventional explanation for emulsion stabilization by solid particles [1–3], there is an accumulation of particles at the oil–water interface in the form of a densely packed layer. This thick particle layer then prevents droplet flocculation and coalescence by a steric mechanism.

When two particle-coated droplets come close together we can envisage a sort of particle bilayer arrangement as shown schematically in Fig. 1(a). The effectiveness of the physical barrier in inhibiting

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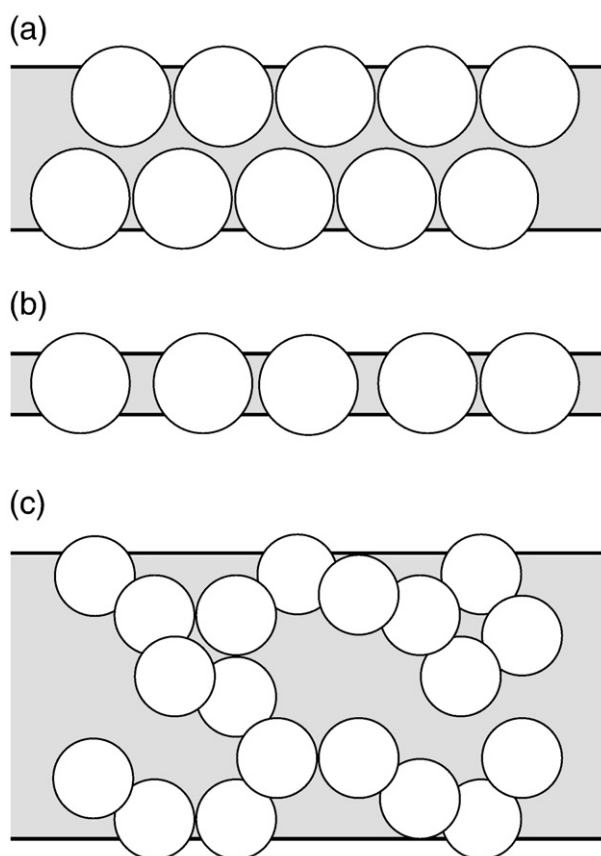


Fig. 1. Schematic representation of alternative stabilizing arrangements of particles in a thin film between closely approaching emulsion droplets: (a) separate closely packed monolayers on the two oil–water interfaces; (b) single dense layer of bridging particles; and (c) low-density network layer of aggregated particles.

coalescence is enhanced by the stability of the thin film of continuous phase between the particle-coated droplets, as determined by the capillary pressure in the film and the surface rheological properties [4]. The magnitude of the steric barrier depends on how difficult it is to remove particles from the interface. The steric barrier is more effective when the particle layer lies predominantly on the outer (convex) side of the dispersed droplets, i.e., when the particles are preferentially wetted by the continuous phase. Particle location at the interface depends on the contact angle θ . For spherical particles of radius r , the free energy of spontaneous desorption (ΔG_D) is proportional to $r^2(1-\cos\theta)^2$. This means that, so long as θ is not too close to 0° (or 180°), the predicted value of ΔG_D for a particle of colloidal size is extremely large compared with the thermal energy (kT); hence the particle is effectively permanently adsorbed. Even a relatively small nanoparticle ($r \sim 5$ – 10 nm), can be regarded as being essentially irreversibly adsorbed, so long as the contact angle is not too far from 90° .

Experimentally it has been observed [13–16] that particle-stabilized emulsion systems can be produced without a full monolayer coverage of particles around the droplets. Therefore, in addition to the classical arrangement of two densely packed monolayers separating adjacent droplets (Fig. 1(a)), we need to consider other possible particle-based structures with the capacity to prevent droplet coalescence. These structures typically involve some aggregation of particles or flocculation of the droplets. For instance, there could be just a single dense layer of bridging particles (see Fig. 1(b)), where each particle is wetted by both dispersed phase regions, but still with the major portion of each particle lying in the aqueous continuous phase [4,15]. As with the particle bilayer arrangement, coalescence stability of the single-layer configuration in Fig. 1(b) is due to a steric

hindrance effect, which prevents significant particle displacement away from or within the bridging layer.

Most particles have fairly uniform surfaces (i.e., they are not amphiphilic). This implies that the surfaces of particle-coated droplets have properties similar to those of the particles themselves. For contact angles favouring strong adsorption at the oil–water interface, this typically means that particles are in a state of weak aggregation. Therefore a third type of interdroplet structural arrangement is commonly encountered in which the droplets are stabilized through the adsorption of aggregated colloidal particles [14,16]. In this case, as illustrated in Fig. 1(c), the steric particle-based barrier is not a simple bilayer (or monolayer); nor is it necessarily densely packed. Rather it consists of a rigid disordered layer/network of particles, adsorbed to the oil–water interface(s), with the whole aggregated structure held together by attractive interparticle forces.

The idealized model involving the stabilization of a Pickering emulsion by a monolayer of uniform spherical particles is rarely realized in practice. Sometimes this is simply because the particles are highly polydisperse. However, even when the primary solid particles are reasonably monodisperse, full dispersion of the monomer particles in the liquid medium is apparently difficult to achieve experimentally, even following high-pressure homogenization or high-intensity ultrasound treatment. This is especially the case for nano-sized particles, where the large surface area (high surface energy) makes complete dispersion from the powder state an unfavourable process thermodynamically. There are numerous reports [3,4,9,11,14,16] of emulsification studies involving silica particles of nominal primary particle size 10–20 nm. But the actual particulate entities involved in stabilizing the Pickering emulsions are not the primary nanoparticles themselves: they are silica aggregates of mean diameter 100–200 nm (based on laser light scattering) and having irregular sizes and shapes (based on electron microscopy). For such polydisperse non-spherical aggregates, the proposition that there is just a single thermodynamic parameter (the three-phase contact angle at the particle surface) determining the character of the interfacial layer structure seems difficult to accept.

Food emulsions are compositionally complex. Their droplets are stabilized to differing extents by proteins, small-molecule surfactants (emulsifiers), and, in certain cases, polysaccharides (hydrocolloids). In terms of the underlying mechanisms of (de)stabilization, there are some similarities and differences between (nano)particles and the other types of emulsifying agents [12,17,18]. When the concentration of emulsifying agent is low, and electrostatic interactions are largely suppressed, the initially formed droplets tend to coalesce fairly rapidly, until their surfaces are protected by a stabilizing layer of particles/molecules. This is usually accompanied by some bridging flocculation due to sharing of adsorbed particles/macromolecules amongst neighbouring droplets. With a high concentration of emulsifying agent under controlled hydrodynamic conditions of emulsification, the resulting droplet size is mainly determined by the interfacial tension. The relevant value of the tension here is the equilibrium value for rapidly adsorbing surfactants, but it is the dynamic tension for slowly adsorbing biopolymers (proteins and hydrocolloids). For (nano)particle emulsifiers (acting alone), the relevant interfacial tension is the (high) value at the bare oil–water interface [12]. This is the primary reason why it is difficult to make particle-stabilized emulsions of small droplet size. Conventional (macro)emulsions are recognized as being metastable, in contrast to microemulsions which are thermodynamically stable (though the formation of thermodynamically stable Pickering emulsions has in fact been reported [19]). Whatever is the character of the emulsifying agent, however, once the emulsion is made, the main factor determining its coalescence stability is the nature of the repulsive interactions between the droplet surfaces. Except at low ionic strength, the primary influence on the range of the interdroplet repulsive interactions is the thickness of the stabilizing layer, as

determined by the relative physical size of the adsorbed species (particles > hydrocolloids > proteins > surfactants) [18].

To produce effective stabilization of O/W emulsions, it has been found that the surface character of hydrophilic silica particles has to be made somewhat hydrophobic. For the purpose of controlling rheological properties, the required surface hydrophobic modification could be achieved by lowering the pH of the aqueous medium (to pH ~2) for nano-sized particles [20] or by adding multivalent cations (La^{3+}) to the medium for larger particles (~200 nm) [21]. Whether the droplet surface is coated by a dense layer of particles or is only sparsely covered can be sensitively influenced by adjusting the pH and/or ionic strength [16]. The strategy of modifying the surface hydrophobicity by adjusting the surface charge density was also implemented [22] by binding potassium hydrogen phthalate to positively charged alumina-coated silica nanoparticles at $3.5 < \text{pH} < 5.5$.

An obvious way to modify the surface hydrophobicity of colloidal particles is through adsorption of low-molecular-weight charged surfactants, e.g., anionic sodium dodecyl sulfate (SDS) or cationic hexadecyltrimethylammonium bromide (CTAB). The balance of interactions in the resulting emulsion system is, however, then potentially more complicated because the surfactant can adsorb at both the liquid interface and the solid particle surface. Hence the attachment strength of the particle to the interface depends on the extent to which the surfactant affects both the interfacial tension and the contact angle. For an O/W emulsion (50 vol.% *n*-dodecane) containing mixtures of nanoparticles and oppositely charged surfactants, Binks et al. [23,24] showed that the most stable coarse droplets were produced under conditions where the amount of adsorbed surfactant was sufficient to optimize the particle wettability and maximize the degree of particle flocculation. For systems based on negatively charged silica particles + cationic CTAB [23] or positively charged alumina-coated silica particles + anionic SDS [24], the most stable emulsions (with respect to creaming and coalescence) were found to possess a gel-like consistency, with microstructural stability enhanced by the presence of particle flocs adsorbed at the oil–water interface. Whether the oil–water interfacial layer has a liquid-like or solid-like character can be sensitively controlled by adjusting the surfactant/particle ratio, as demonstrated by optical scanning tomography on W/O emulsions containing CTAB + silica nanoparticles [25]. In another study involving addition of SDS to Pickering O/W emulsions after emulsification, it was observed [26] that low concentrations of surfactant had no measurable effect on emulsion stability, but at concentrations above the critical micelle concentration there was rapid creaming and flocculation.

Lecithin, a zwitterionic surfactant, is one of the most important emulsifiers routinely used in food applications. The long-term stability of fine O/W emulsions (10 vol.% triglyceride oil) prepared with silica nanoparticles + soybean lecithin (or oleylamine) was investigated by Eskandar et al. [27]. These authors reported that a synergistic improvement in coalescence stability was evident only when the nanoparticles were initially added to the oil phase. Under such circumstances, the free energy of particle adsorption estimated from measurements of interfacial tension and contact angles could be successfully correlated with the long-term stability.

Also of particular relevance to food applications are Pickering emulsion systems containing non-ionic surfactants. The creaming and coalescence stability of O/W emulsions (20 vol.% vegetable oil) prepared with a mixture of hydrophilic silica particles (primary particle size ~12 nm, aggregate size ~150 nm) and food-grade emulsifier monoolein (HLB = 3.8) was recently investigated as a function of pH and system composition [28]. In the absence of silica particles, the emulsions prepared with monoolein as sole emulsifier were highly unstable, exhibiting complete phase separation at pH = 2 after a couple of hours. With the mixed emulsifier system, the concentrations of both monoolein and silica particles were found to affect the emulsion droplet size, up to some threshold concentrations beyond which the droplet size

was apparently limited by the emulsification process. Under optimized conditions, the mixed emulsifier system was found to produce rather coarse emulsions, which were highly unstable to creaming, but possessed long-term stability against coalescence. A two-stage synergistic mechanism was proposed [28] to explain the coalescence stability. It was assumed that the function of the small-molecule surfactant was to delay coalescence and to induce droplet break-up during emulsification, via its rapid adsorption and lowering of the interfacial tension. This short-term interfacial stabilization by the monoolein allows time for the silica particles to assemble at the oil–water interface and thereby provide the long-term storage stability.

One way of avoiding having to add any small-molecule surfactant to modify the particle wettability is to stabilize an emulsion by heteroaggregation of a binary mixture of oppositely charged nanoparticles. Binks et al. [29] used this technique to make coarse gel-like O/W emulsions. They found that only those particle mixtures giving rise to flocculated aqueous dispersions were of low enough net charge and sufficiently hydrophobic to adsorb around oil droplets and confer stability. Another strategy is to use solid particles that are themselves amphiphilic – so-called 'Janus particles' (after the two-faced Roman god of doorways). These non-uniform particles are characterized by two different hemispherical or surface regions, one polar and the other non-polar, with two different contact angles. Janus particles have considerable advantages for use in emulsion stabilization and nanotechnology, but they are more difficult to make than conventional (nano)particles [5].

The effect of particle shape on the coalescence stability of Pickering emulsions has been investigated recently by Madivala et al. [30]. For both O/W and W/O emulsions, the authors observed a strong dependence of emulsion stability on the particle aspect ratio in the range from 1 to 9. It appears that sufficiently long particles are effective emulsifying agents when spherical or less elongated particles of similar wettability cannot produce a stable emulsion. The behaviour was rationalized [30] in terms of the effect of particle aspect ratio on surface coverage and shape-induced attractive capillary interactions, as reflected in measurements of the interfacial shear rheology at the planar oil–water interface.

Oil-continuous emulsions can be stabilized by wax particles, both natural (e.g., beeswax) and synthetic (polyethylene-based). Rousseau and Hodge have reported [31,32] that paraffin wax crystals can enhance the coalescence stability of W/O emulsions made with an oil-soluble surfactant as the primary emulsifying agent. The stabilization mechanism involves wax particle adsorption and the formation of a particle network in the continuous oil phase which immobilizes coarse water droplets thereby preventing sedimentation. Emulsion properties were found to be dependent on whether the wax crystals were present in the oil phase prior to emulsification at ambient temperature, or whether they were formed *in situ* by rapid cooling following high-temperature emulsification [31,32]. Using the latter procedure, the crystals were smaller and the resulting emulsions were more stable. In a separate study, Binks and Rocher [33] investigated the application of various types of commercial wax particles in the stabilization of W/O emulsions (50 vol.% squalene). While these formulations contained no added surfactant, it would appear that the adsorption of surface-active molecules from the melted wax made a substantial contribution to emulsion stability, over and above the stability contributed by the wax particles themselves.

Dispersed fat crystals are the essential structural components of edible fatty spreads [1]. After crystallization from the partially saturated oil phase, the triglyceride crystals interact and aggregate to form a three-dimensional network which provides long-term stability to the dispersed water droplets and a solid-like textural character to the food product [34]. Triglyceride crystals adsorbing at the oil–water interface contribute to W/O emulsion stability by the Pickering mechanism. The association of the fat crystals with the interface increases the surface viscoelasticity, especially when the

adsorbed crystals are flocculated. Addition of small-molecule emulsifiers influences the fat crystal morphology, the strength of the crystal–crystal interactions, and the wetting properties of the crystals at the oil–water interface [1]. When the interparticle interactions are net attractive, and the particle concentration is sufficient to form a gel-like network with a finite yield stress, the destabilizing processes of sedimentation and flocculation are inhibited completely. Heating above 30 °C causes a loss of droplet stability; the rate-limiting step for coalescence is the melting of the Pickering crystals around the dispersed aqueous droplets [35]. In a concentrated O/W emulsion containing interfacial fat crystals, thermal processing can lead to gelation of the system due to partial coalescence or a jamming mechanism [36].

The important relationship between the wettability of food colloid particles and the type of particle-stabilized emulsion produced has been demonstrated experimentally by Paunov et al. [37]. In this work the contact angles were determined by a novel gel trapping technique [38,39]. This involved spreading the particles at the oil–water (or air–water) interface, and then gelling the aqueous sub-phase with a non-adsorbing hydrocolloid (gellan gum) to fix the particles in their original positions at the liquid interface. Subsequent moulding of the gel surface with a curable silicone elastomer (PMDS) allowed the replica to be imaged by SEM, so determining the particle locations with respect to the original liquid interface. The use of this semi-quantitative technique was demonstrated [37] for three kinds of contrasting particles: triglyceride crystals (10–30 µm), calcium carbonate particles coated with stearic acid (1–10 µm), soy protein aggregates (1–30 µm). The fat crystals gave large contact angles at the oil–water interface ($\theta \sim 120^\circ$); W/O emulsions were stabilized preferentially for all volume fractions of oil (*n*-decane). The coated calcium carbonate particles were of intermediate wettability ($\theta \sim 90^\circ$); they gave O/W emulsions at low oil volume fractions (<50 vol.%); but these inverted to W/O emulsions at high oil content. The soy protein particles were predominantly hydrophilic; they produced O/W emulsions at all volume fractions.

In addition to the various particulate systems mentioned above, Pickering emulsions can also be stabilized by many other kinds of particles – polystyrene latices [40], clay platelets [41,42], microfibrillated cellulose [43], cyclodextrin–alkane precipitates [44] and microgels [45–47]. The study of soft microgel particles is of particular technical interest because of their potential applications as stimuli-responsive stabilizers, i.e., particles whose effectiveness is sensitive to environmental variables such as pH and temperature. For instance, in a study of coarse O/W emulsions stabilized by cross-linked poly(*N*-isopropylacrylamide)-*co*-methacrylic acid microgel particles (~500 nm), it was reported [47] that the emulsions could be broken by pH reduction and by heating well above the volume phase transition temperature. The responsiveness of these microgels was found to be sensitive also to the polarity of the dispersed oil phase. Based on complementary interfacial dilatational rheology measurements, Brugger et al. [47] demonstrated a correlation between the viscoelasticity of the interfacial microgel layer and the emulsion stability. The transition from highly elastic to less elastic interface at pH ~5 could be explained in terms of a predominant contribution of the charged methacrylic acid groups to the elasticity of the layer.

In general, when solid particles adsorb at a liquid–liquid interface at a high packing fraction, there is a loss of interfacial mobility. This phenomenon is known as ‘interfacial jamming’ [48]. The process of jamming can arrest interfacial tension-driven morphological coarsening, leading to the stabilization of individual droplets of highly non-spherical shapes [49,50]. This phenomenon has led to the concept of a new type of soft matter called ‘bijels’ (bicontinuous interfacially jammed emulsion gels) [48,51,52]. A bijel is prepared from a bicontinuous morphology into which are introduced some adsorbing particles. The interfacial tension drives structural coarsening, and there is a gradual reduction in the total interfacial area. During this process the

bicontinuous morphology is abruptly stabilized by jamming once a certain surface concentration of particles has been reached. Analogous to the interfacial jamming in conventional O/W and W/O emulsion systems, evidence for the same phenomenon has also been recently found [53] in a bicontinuous water-in-water (W/W) emulsion based on a phase-separating aqueous solution of gelatin + starch. In this mixture of thermodynamically incompatible biopolymers, as the microstructure develops via spinodal decomposition, the added colloidal particles (polystyrene latex ~300 nm) were observed to adsorb at the newly formed liquid–liquid interface. Fig. 2 shows images of the phase-separated system (gelatin/starch/sugars/water/latex) held at 40 °C for (a) 16 min and (b) 16 h. Regions completely depleted of the colloidal particles appear black in these images. We have observed [53] that the particles are predominantly concentrated at the liquid–liquid interface and in the regions of gelatin-rich phase. In the early stages of observation (Fig. 2(a)) the phase boundaries appear fairly smooth, as

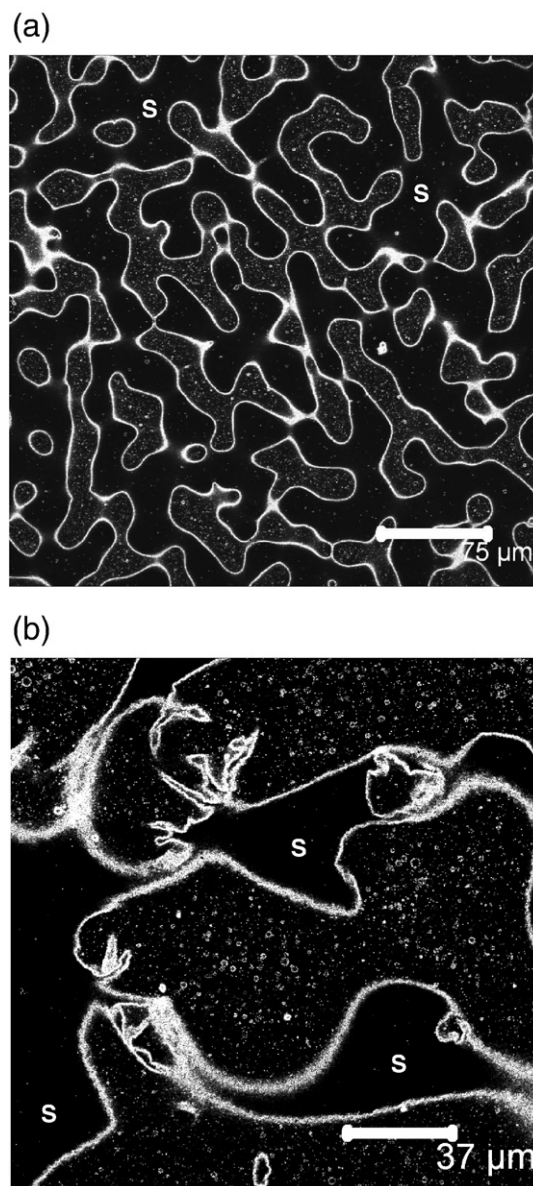


Fig. 2. Confocal microscopy images of the structure of a phase-separated mixture of gelatin (7 wt.%) + oxidized starch (4 wt.%) in an aqueous medium (25.5 wt% sucrose, 31.4 wt% glucose syrup, pH = 5.2) containing polystyrene latex particles ($d_{32} = 313$ nm, 0.7 wt.%). The sample was quenched from 90 to 1 °C, held at 1 °C for 10 min, heated to 40 °C at 6 °C min⁻¹, and observed at 40 °C after (a) 16 min and (b) 16 h. Dark regions are depleted of particles. Starch-rich domains are identified by the symbol S. (Reproduced from Firoozmand et al. [53] with permission.)

found in the absence of particles. But with increased particle concentration and ageing time (Fig. 2(b)), the extent of wrinkling of the particle-laden liquid–liquid interface becomes very pronounced. The developing morphological behaviour was interpreted [53] as being indicative of an interfacial region that is substantially elastic (solid-like) in character.

In emulsions prepared as encapsulation vehicles for delivery of drugs or nutrients, one may ask how the release rate of the encapsulant is affected by the presence of a solid particle layer at the oil–water interface, as opposed to, say, a surfactant-based stabilizing layer. Experiments designed to answer this question were recently designed by Chevalier et al. [54,55] for the cases of the topical delivery of a hydrophilic compound (caffeine) from W/O emulsions and a lipophilic compound (retinol) from O/W emulsions. Comparison was made between Pickering emulsions (50 vol.% oil) stabilized by silica particles and the equivalent surfactant-stabilized emulsions of similar average droplet size ($\sim 10\ \mu\text{m}$ for W/O, $\sim 3\ \mu\text{m}$ for O/W). The authors found that caffeine absorption by the skin was substantially faster from silica particle-stabilized W/O emulsions than from surfactant-stabilized W/O emulsions [54], and also that retinol penetrated further into the skin when delivered from Pickering O/W emulsions than from polysorbate-based O/W emulsions [55]. In addition to differences in diffusive permeation rates through the differing structures of the two kinds of layers, it was postulated that the rigidity of the multilayer silica shell around the droplets was an additional factor influencing the stability and breakdown of the emulsions during the topical administration.

With continuing advances in computer hardware and software, the structural and kinetic properties of systems containing nanoparticles at interfaces are now accessible to numerical modelling on the atomistic scale. Lane et al. [56] have used a molecular dynamics (MD) simulation to determine the hydrodynamic drag on two approaching soft nanoparticles in a bulk solvent, and on a single nanoparticle approaching a plane surface. Each soft nanoparticles consisted of a rigid amorphous silica core (5 nm diameter) onto which short poly (oxyethylene) oligomers were grafted. The authors found [56] that the simulated particle–particle and particle–surface forces were purely repulsive, without the oscillations normally characteristic of uncoated hard spheres.

Computer simulation of the structuring of a nanoparticle monolayer at a fluid interface was first demonstrated using the technique of Brownian dynamics [57]. Subsequently, using molecular dynamics, Luo et al. [58] have simulated the behaviour of small hydrocarbon-like nanoparticles (1.2 nm diameter) at the water–trichloroethylene interface, followed by a recent pioneering investigation [59] of the competitive adsorption and cooperative interactions in adsorbing mixtures of nanoparticles + anionic surfactant molecules (SDS). During this simulation, clusters of nanoparticle–surfactant complex were observed to diffuse towards the oil–water interface to form the

mixed adsorbed layer. Uncharged nanoparticles were found to coexist with the adsorbed surfactant at low SDS concentrations, but these were competitively displaced from the interface at high surfactant concentrations. Competitive displacement was not observed, however, in the equivalent MD simulations involving charged nanoparticles. Fig. 3 shows a snapshot of the simulated structure of the mixed layer of SDS + nanoparticles [59]. The hydrophobic tails of the SDS molecules are seen to be attracted to the adsorbed nanoparticles and also to the bulk oil phase. A general conclusion drawn from these simulations was that the interfacial tension and interfacial thickness were significantly influenced by the presence of the charged surfactants, but not by the presence of the (very small) nanoparticles.

3. Foams

The stabilization of bubbles and foams by particles has been receiving great attention from researchers in recent years [2,7–10]. A strong motivation for this activity is the general recognition that long-term stability is much more difficult to achieve for aerated systems than it is for emulsions. Hence the incorporation of colloidal particles as a possible way of enhancing foam stability is a matter of great technological and commercial significance. This is especially important for food systems because the presence of an aerated structure provides the essential textural characteristics of highly popular foods such as ice-cream [60]. Furthermore, the incorporation of gas bubbles as a full or partial replacement for dispersed fat particles can play a useful role in the development of healthier products.

The inherent instability of foam arises from the high free energy of the gas–liquid interface. This constitutes the thermodynamic driving force for reducing the total interfacial area through the combined processes of bubble coalescence and disproportionation (Ostwald ripening). Thin films in polyhedral foams are very much greater in size than those in concentrated emulsions, and so the probability of film rupture is higher. Also bubbles are typically larger and less dense than oil droplets, and so gravity creaming is much faster for dispersions of gas bubbles than for the corresponding O/W emulsions. Even more important, however, is the fact that the appreciable solubility of the gas in the aqueous phase of a foam leads to a steady diffusive mass transport between bubbles of different sizes under the influence of local Laplace pressure gradients. Unless bubbles are embedded in a solid matrix, as in ice-cream [60], or surrounded by a rigid shell-like adsorbed layer, this relentless process of disproportionation inevitably leads to the loss of all but the largest bubbles in the system [2,7].

Numerous experimental studies [61,62,63,64,65,66,67,68,69,70,71–76] have demonstrated that the formation of a close-packed particle layer at the gas–liquid interface generates a sort of ‘colloidal armour’ that can inhibit, or even stop altogether, the destabilizing processes of bubble coalescence and coarsening. It has been established [61–63,66,72] that individual particle-stabilized bubbles can remain

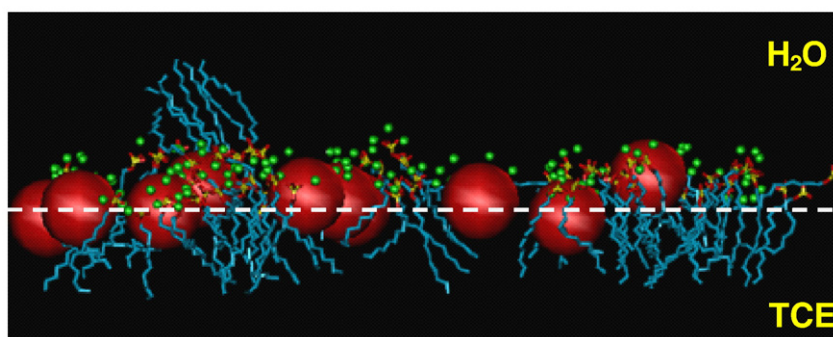


Fig. 3. Structure of adsorbed layer of negatively charged nanoparticles + anionic surfactant molecules (SDS) at the water–trichloroethylene (TCE) interface from molecular dynamics simulation. Nanoparticles are represented as red spheres, and hydrophobic tails of SDS molecules are represented as blue chains. Sodium ions are in green. (Reproduced from Luo et al. [59] with permission.)

stable against disproportionation for days or weeks, as compared with the equivalent protein-stabilized bubbles which typically collapse within an hour or so [63,72]. The formal condition that a bubble is stable against coarsening is the Gibbs stability criterion, $E > \gamma/2$, where E is the surface dilatational elasticity and γ is the surface tension [74]. As with Pickering emulsions, the effectiveness of particle binding to the interface is controlled by the contact angle [61,62,64,65]. Using a novel dispersion method in ethanol/water, Binks and Horozov [64] have made highly stable foams using silica nanoparticles of high hydrophobicity in the absence of any added surfactant. For the routine stabilization of aqueous foams, an appropriate degree of hydrophobic particle character can be achieved in various ways, including the binding of amphiphilic molecules to the surface of hydrophilic inorganic particles [70–72]. As with Pickering emulsions, the effectiveness of the particle-coated interface seems to be reinforced under conditions of particle aggregation. There is evidence in some systems [61–63,75,76] for the stabilization structure involving the formation of a weak gel-like particle network throughout the aqueous phase, including the associated particles of the ‘colloidal armour’. By analogy with the more well-established phase inversion of Pickering emulsions [17], the inversion of an aqueous foam into a water-in-air powder (‘dry water’) could be achieved [67] by progressively increasing the particle hydrophobicity at constant air/water ratio, or by changing the air/water ratio at fixed particle wettability.

The underlying physical mechanism for the stabilization of armoured bubbles by monodispersed spherical particles has been confirmed by computer simulation [77]. As the simulated bubble shrinks, depending on its radius R relative to the particle radius r , it takes up a shape that is either faceted ($r/R \sim 0.1$) or crumpled ($r/R \ll 0.1$). At the same time, the surface energy and Laplace pressure decrease until a local energy minimum is reached. The metastable equilibrium state is characterized by a mainly saddle-shaped gas–liquid interface having zero mean curvature and therefore a vanishing Laplace pressure [77]. An additional factor affecting foaming behaviour when the particle concentration is very high is the structuring of the particles in the bulk aqueous medium; this phenomenon was also recently demonstrated by computer simulation [78].

Foam assembly involves a high degree of synergism involving structural building blocks on length scales spanning several orders of magnitude (macroscopic/microscopic/nanoscale/molecular). Fig. 4 is a set of images reproduced from the work of Gonzenbach et al. [70]

showing the hierarchical features of a foam stabilized by a mixture of silica particles + surfactant molecules. On the macroscopic scale, this high-volume foam had a creamy white appearance (Fig. 4(a)); it possessed a yield stress, and so the material could support its own weight under gravity, rather like a dollop of whipped dairy cream. Confocal microscopy images show that the bubble sizes were in the range of 10–50 μm (Fig. 4(b)), and that each bubble was stabilized by a dense layer of colloidal particles ($\sim 1 \mu\text{m}$ diameter) (Fig. 4(c)). The surface hydrophobicity and optimum wettability of the stabilizing particles were controlled by adsorption of amphiphilic molecules of hexylamine (Fig. 4(d)).

The relationship between protein molecular structure and protein foaming behaviour is complex [79]. One contributory factor is the state of aggregation of the protein. The presence of colloidal particles of protein is commonly observed in microscopic images of food protein foam systems, e.g., aerated egg albumen [80]. One may ask therefore whether the particle character of a food protein ingredient plays any major role in controlling the foaming properties. It has been tentatively suggested [1,2] that the well-known functionality of ovalbumin in aerated foods could be associated with its tendency to form coagulated protein networks and surface-active stabilizing particles [81]. In contrast to ovalbumin, another protein from egg white, lysozyme, is a poor foaming agent in its native state; but dry heating (at 80 °C) has been shown by Desfougères et al. [82] to improve substantially its foaming properties, as well as to induce protein aggregation. According to these authors, the presence of aggregates *per se* is not essential for the improvement of the foaming properties of lysozyme. Rather it is that the conditions (and consequently the interactions) that favour aggregation are also the ones that favour the formation of stable foams [82]. In the case of the milk protein β -lactoglobulin, depending on the conditions, the presence of soluble or insoluble aggregates has been reported to have a positive influence on foam stability [83–85]. Taking all this evidence as a whole, there seems to be a general tendency for incipient loss of protein solubility to enhance interfacial viscoelastic properties and therefore to enhance foam stability [2,79]. But in some instances, at least, the presence of aggregated protein particles (e.g., by whipping or heating) may be an indirect consequence of this loss of solubility rather than the direct cause of the improved foam stability.

A unique class of proteins, possessing remarkable interfacial and foam stabilizing properties, are known as ‘hydrophobins’ [86,87]. These are small proteins of highly stable native structure produced by

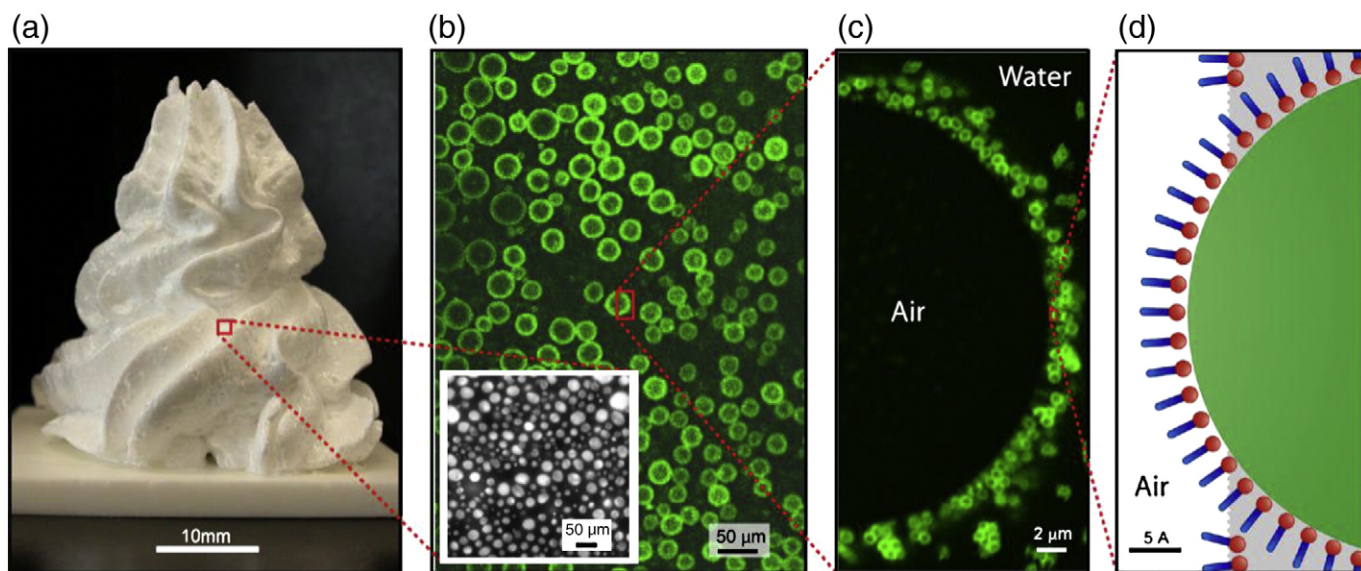


Fig. 4. Representation of the structure of a high-volume particle-stabilized foam on various length scales: (a) macroscopic, (b) low-resolution microscopic, (c) high-resolution microscopic, and (d) nanoscale/molecular. The confocal images in (b) and (c) were obtained following dilution of the concentrated foam (inset in (b)) containing fluorescently labelled silica particles with hexylamine as the surfactant. (Reproduced from Gonzenbach et al. [70] with permission.)

filamentous fungi. They tend to self-associate into small aggregates in aqueous media. The soluble type II hydrophobins are more surface-active than all the major food proteins (including β -casein), and they have a strong tendency to self-assemble at the air–water interface to form highly viscoelastic layers [87]. Values of the surface shear viscoelasticity have been found to be much higher than those of other proteins investigated. Also, unlike other food proteins, it appears that the hydrophobin adsorbed layer can fully prevent bubble shrinkage due to disproportionation: hydrophobin-based foams have been prepared which remain stable for months or even years [88,89]. A striking structural feature of the hydrophobin molecule is that it is rigid like a small solid particle; it is also amphiphilic, having a hydrophobic patch on one side of the molecule. A simple representation of an individual hydrophobin molecule might therefore be rather like a nanosized Janus particle. In fact, some useful analogies have been drawn [90] between the interfacial behaviour of hydrophobin and the stabilization of interfaces by self-assembled Janus particles.

Despite the considerable potential benefits of adsorbed particles as stabilizing structural units in aerated systems, it is important to recognize that the presence of even a small quantity of lipid-based particulate material in a polyhedral foam can be detrimental to stability [1]. For a hydrophobic particle large enough to touch both surfaces of the thin liquid film between a pair of bubbles, the Laplace pressure in the film adjacent to the extraneous particle may become positive. This induces liquid flow away from the particle, causing liquid to break contact with the particle, leading to film rupture. Another type of contaminating particle is one that spreads its contents at the air–water interface. The nearby film liquid is made to move in the same direction as the spreading particulate material, which induces a local thinning of the film, so enhancing the probability of rupture [1]. Both of these mechanisms are involved in the destabilization of aqueous food foams by fatty particles.

High density arrangements of particles can provide long-term stability to aerated systems even in the absence of particle adsorption, especially if the closely packed particles (e.g., sugar granules) form a continuous network structure [91]. In foods, an important class of particle-stabilized system is the whipped dairy-based emulsion in which gas cells are stabilized by a network of partly coalesced fat globules. Destabilization of the O/W emulsion can be sensitively affected by shearing conditions [92], the presence of emulsifiers [93,94], and the crystallization state of the fat [34,94]. During the whipping of natural cream (fat content ~ 35 wt.%), the partially crystalline fat globules adhere to bubble surfaces, and subsequently they become clumped together by a process of surface-mediated partial coalescence [95]. This process continues until a three-dimensional network of clumped fat globules is built up, which holds and stabilizes the incorporated bubbles, and consequently provides the desired texture and mechanical strength (yield stress) to the final whipped cream (typical gas-to-liquid volume ratio $\sim 120\%$).

Acid-induced aggregation of protein-coated emulsion droplets in the vicinity of the air–water interface has been shown [96] to have a substantial positive influence on the coalescence stability of individual gas bubbles subjected to a sudden pressure drop. This stabilizing effect was observed to be closely correlated with corresponding changes in the pH-dependent surface shear rheology. However, the same study also showed [96] that the influence of pH and aggregated emulsion droplets on bubble disproportionation rate and surface dilatational properties was much less significant. In a separate project involving emulsified systems of moderately high oil content (30 vol.%), it was found [97–99] that aerated cream-like foams could be stabilized in the complete absence of partial coalescence by whipping a caseinate-stabilized emulsion under pH-lowering conditions which induced the emulsion droplets to become aggregated at the bubble surfaces. Moreover, it was subsequently demonstrated [100] that rheological behaviour similar to that of traditional whipped cream (overrun 120%) could be achieved in

such an acidified aerated system through the incorporation of a suitable oil-soluble emulsifier (LACTEM) in conjunction with a sufficiently high proportion of fully solid-like emulsion droplets.

4. Conclusions and outlook

The past few years have seen enormous growth in the amount of fundamental and applied research relating to particle-stabilized emulsions and foams. Some of the newly discovered enthusiasm for this subject is undoubtedly attributable to a desire amongst some researchers to join the potentially lucrative bandwagon of nanoparticle research which exists now across the whole breadth of the scientific community. A cynical observer with a long memory could therefore be forgiven for thinking that the novelty of some recently published work is really little more than a 'rediscovery' of traditional colloid science knowledge long forgotten or neglected. Whilst recognizing that this analysis does contain an element of truth, it is clear to this reviewer that a considerable amount of genuinely original and exciting information has been obtained recently for particle-based colloidal systems using a variety of modern instrumental methods, supported by powerful insight from modelling and computer simulation.

The proportion of this research that is directly applicable to foods is necessarily small. Nevertheless, it appears that the special properties of particle-laden interfaces do have much to offer in developing the science of food structuring [101,102] and in formulating novel structures for improved health and wellness [103–109]. A key challenge for the industry is to produce nanoparticles and microparticles that are both effective and also acceptable for use in food products on the commercial scale. Within the voluminous literature on nanoparticles, it is apparent that there are still relatively few studies involving food-grade ingredients. There is certainly increasing interest in bionanoparticle systems, although some kinds of systems studied so far, such as virus particles [110,111], would seem to be unsuitable for food applications.

Natural biopolymer structural assemblies are obviously attractive as (nano)particle building blocks. Polysaccharides such as starch and cellulose represent a readily accessible and inexpensive source of particulate material for potential food use. And, indeed, after appropriate hydrophobic modification, these materials can be highly effective in the stabilization of emulsions and foams [112,113]. However, protein-based particles probably have greater flexibility as stabilizing agents due to their natural amphiphilicity and surface activity, as well as their potential as multifunctional nanoscale delivery vehicles for nutraceuticals [114]. The most intensively investigated of all the natural colloidal particles is the casein micelle [115]. As the main stabilizing entity of homogenized and recombined milk, the casein aggregate can properly be considered as the prototype structure for building milk protein-based nanoparticles — reassembled from a mixture of sodium caseinate and calcium salts [116], or modified from the native micellar form by internal enzymatic cross-linking [117]. Also possessing favourable attributes for stabilizing emulsions and foams are whey proteins (and other globular food proteins); it is now well recognized that, depending on the conditions, individual whey proteins can self-assemble into various kinds of assorted colloidal aggregates, including fibrils [118,119] and nanotubes [120]. There are also reports of more exotic bionanoparticle emulsifiers, such as ferritin, a 24-subunit iron storage protein composed of a hollow shell-like structure (with inner and outer diameters of 7 and 12 nm, respectively) [121]. Other novel possibilities with specific functionalities could emerge from the design of nanoparticle–protein conjugates [122].

Finally, in the opinion of this reviewer, one of most promising ways of making nanoscale structures for stabilization of food colloids is through the exploitation of associative protein–polysaccharide interactions [18,123–125]. In considering the mechanistic and structural consequences of protein–polysaccharide interactions in aqueous media, there is a subtle overlap between effects of interactions on

the macromolecular scale and those on the colloidal scale. The molecular forces involved may be physical (electrostatic, hydrogen bonding, and hydrophobic) and/or covalent (transglutaminase-catalysed cross-linking, Maillard reaction, etc.). Different kinds of stable composite nanoparticles have been prepared by Singh et al. from mixtures of sodium caseinate + gum arabic, based on the alternative mechanisms of electrostatic complexation [126] or enzymatic conjugation [127]. An important benefit of complexing casein with a charged polysaccharide is the maintenance of solubility and functionality under acidic pH conditions [128,129]. Schmitt et al. have reported directly on the interfacial and foaming properties of β -lactoglobulin-acacia gum complexes [130]. The authors demonstrated that the electrostatic complexes formed a thick hydrated network at the bubble surface which was more effective than the pure protein in preventing destabilization due to disproportionation. In another example, aggregates of heat-denatured globular protein (e.g. β -lactoglobulin) have been stabilized by adsorbing charged polysaccharide (e.g. pectin) onto the protein aggregate surface, thereby producing so-called core-shell bionanoparticles [131]. For purposes of encapsulation, there is considerable activity in preparing nanogels and core-shell nanoparticles from mixtures of proteins with the cationic polysaccharide chitosan [132,133]. Some of these protein-polysaccharide complexes may have application in the stabilization of food emulsions and foams.

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