Available online at www.sciencedirect.com

ScienceDirect

Current Opinion in
Colloid & Interface Science

Oil-coated bubbles in particle suspensions, capillary foams, and related opportunities in colloidal multiphase systems

Sven H. Behrens

Abstract
The interaction of solid particles with fluid interfaces in colloidal multiphase systems can lead to a wide range of fascinating and sometimes useful phenomena. Most of the research in this area has focused on ternary systems with two immiscible fluids and one particle species. After a brief review of some common characteristics, this article discusses recent insights and future opportunities regarding systems that confront particles with multiple types of fluid interfaces, focusing in particular on the interaction of particles with oil-coated bubbles in aqueous media. Relevant examples include the particle-assisted reconfiguration of bubble–droplet morphologies, the separation of hydrophilic particles from aqueous slurries by oily bubble flotation, and the formation of capillary foams, a promising new class of foam materials.

Addresses
School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA, 30332, USA

Corresponding author: Behrens, Sven H. (sven.behrens@chbe.gatech.edu)

Current Opinion in Colloid & Interface Science 2020, **50:**101384

This review comes from a themed issue on **Thin Liquid Films and Foams**

Edited by **Raymond Dagastine** and **Sibani Lisa Biswal**

For a complete overview see the Issue and the Editorial

https://doi.org/10.1016/j.cocis.2020.08.009

Keywords
Bubbles, Foams, Capillary suspensions, Capillary foams, Rheology, Froth flotation.

Introduction: particles and fluid–fluid interfaces

Interest in the behavior of colloidal particles dispersed in a liquid medium goes back to the very roots of colloid science [1]; many of the most fascinating *recent* developments, however, involve systems with at least one additional, immiscible fluid phase and, as a consequence, a fluid–fluid interface for particles to interact with [2–4]. Even the seemingly simple adsorption of an individual particle to a liquid interface still holds open questions and experimental challenges [5]; but it is the effects of fluid interfaces on pairs and ensembles of particles which often give rise to exciting engineering opportunities.

Interface-mediated particle interactions have, for instance, been leveraged for the directed assembly of particles in flat or curved fluid interfaces [6,7], for the reversible bulk assembly of particle clusters via switchable capillary forces [8], the deployment of capillary inks for 3D printing [9], the stabilization of printed, reconfigurable liquid-in-liquid structures [10], the fabrication of bijels for reactive separations [11,12], and to orchestrate the collective motion of active swimmers via interfacial confinement and tension gradients [13,14].

In contrast to colloidal interactions within a bulk fluid, particle interactions mediated or modulated by interfaces tend to be anisotropic, strong, and long-ranged, as exemplified by capillary forces [15] or the electric dipole force between pairs of charged particles at an interface [16]. Add to that the reduction in average particle separation that comes with interfacial assembly and the associated reduction in dimensionality of the particle arrangement, and it is easy to see why multiphase systems with very strong particle coupling can be prepared even from fairly dilute dispersions.

Among all the phenomena known to occur in systems with colloidal particles and fluid–fluid interfaces, the *interfacial adsorption* of particles and *interparticle bridging* are particularly noteworthy because they have far-reaching consequences for the structure and properties of these system and can lead to interesting behavior even in the case of ‘simple’ particles (*i.e.* particles of low complexity, such as inert, spherical particles without patterned surfaces, internal anisotropy, or a particular response to external stimuli).

Interfacial adsorption

Particles with some wettability for each of two interfacing fluids can reduce the system’s free energy by entering into the interface. Calculating the precise value of this energy benefit is complicated by the influence of particle–particle interactions, possibly by line tension, and certainly by any deformation of the interface, which can arise in practice from nonspherical particle shapes, electric charge effects, pinning of the contact line at surface heterogeneities or roughness features, and from external forces acting on the particles. In a first-order approximation that neglects all of these influences, the energy required to remove an adsorbed spherical particle with radius R from the interface is given by the familiar expression

$$|\Delta G| = \pi R^2 \gamma (1 - |\cos\theta|)^2 \tag{1}$$

where γ is the tension of the fluid—fluid interface, and θ is its contact angle with the particle surface. For particles larger than a few nanometers, typical tension values for oil—water or gas—water interfaces, and contact angles not very close to the limits of 0 or 180°, this desorption energy is so large compared with the thermal energy scale kT that adsorption can be considered irreversible in the absence of macroscopic external forces. In coarsening biphasic fluid mixtures, interfacially adsorbed particles therefore remain confined to the interface and impose a kinetic limit to the shrinkage of the interfacial area and thus to the fluid demixing.

Arrested fluid phase separation

This phenomenon is responsible both for the particle-stabilized droplets in Pickering emulsions (or bubbles in Pickering foams) and for the space-spanning particle assemblies in bijels (bicontinuous interfacially jammed emulsion gels) [17,18]. In the case of bijels, the phase separation was originally induced by spinodal demixing, following the idea of a simulation study from 2005 that first predicted bijel formation [19]. Great advances in the preparation of bijels have recently resulted from the realization that solvent transfer—induced phase separation [11,20—22] and even direct mixing [23,24] are viable alternatives to the spinodal route, with fewer limitations regarding the choice of fluids, more robust protocols, and more options to control the characteristic length scale of the two continuous fluid phases separated by the particle-stabilized interface.

Interfacial jamming

One noteworthy difference between the arrested states in bijels and Pickering emulsions is that the particles in bijels are indeed reported to 'interfacially jam' as the acronym suggests, whereas particle jamming *can*, but need not occur in the interface of Pickering emulsion droplets with good long-term stability. Although there is no doubt that interfacial jamming limits droplet coalescence in some systems and can even arrest coalescence in stages of highly nonspherical droplet shapes [25,26], it has also been established that droplets can sometimes remain stable at very sparse coverage [27], and that some particles can alternatively stabilize densely or sparsely covered droplets, depending on solution parameters (pH, ionic strength of the polar phase) that modulate the particles' electrostatics [28—30].

Droplet bridging and gelling

The interaction of two interfaces with sparse particle coverage often results in the formation of a bridging monolayer of particles adsorbed to both interfaces simultaneously [31]. In Pickering emulsions, droplet bridging particles can play a crucial role both in stabilizing the droplets, especially in emulsions with low overall droplet coverage [30,32,33] and in particle-stabilized high internal phase emulsions (HIPEs) [34]. When sufficiently many droplets bind together via bridging particles a space-spanning network (a Pickering emulsion gel) results that shows many rheological features of a classical colloidal gel [35], without the need for any significant particle—particle attraction across the continuous liquid phase or added gelling agents.

Particle-assisted spreading

Another important consequence of the energy benefit associated with particle adsorption to fluid—fluid interfaces is that it can change the spreading behavior of liquids [36]. For instance, an oil drop deposited on a water surface is known to spread spontaneously into an oil film covering the water surface, provided that the free energy cost of the original air—water interface exceeds the combined free energy penalty of the newly created air—oil and oil—water interface. This is the case of a positive oil spreading coefficient

$$S_o = \gamma_{aw} - (\gamma_{ao} + \gamma_{ow}) \tag{2}$$

where γ_{aw}, γ_{ao}, γ_{ow} denote the respective interfacial tensions of the equilibrated fluids. Oil drops with a negative spreading coefficient, by contrast, retain the more compact form of a lens on the water surface; but the adsorption of particles at either or both oil interfaces can shift the interfacial energy balance and induce film spreading [37].

Interparticle bridging

In addition to particle adsorption and the discussed consequences, one more effect involving particles and fluid interfaces is important for the systems discussed in the following sections: the formation of fluid bridges between particles. Liquid bridges between particles in a continuous gas phase are familiar from wet granular materials, and the associated capillary attraction is known to physically bind the bridged solids (think sand castles or the caking that occurs in hygroscopic powders when water condenses in the interstices between neighboring hydrophilic particles). Similar capillary attractions occur in the inverse situation of bubbles nucleating in small gaps between hydrophobic waterborne particles and have been associated with long-range hydrophobic forces [38].

Capillary suspensions

In systems with two liquid phases and particles partially wettable by each of them, liquid interparticle bridges tend to form upon mixing when the volume fraction of one liquid is lower than that of the particles and of the majority liquid phase. Koos and Willenbacher [39] found that even a very small volume of immiscible liquid (well below 1%) added to a stirred particle dispersion or slurry can induce gelation, turning the liquid dispersion into a soft elastic solid. This dramatic effect in arises from interparticle bridges of the minority fluid whose capillary forces keep particles interconnected in a percolating network; it occurs regardless of whether the continuous or the bridging liquid phase wets the particles preferentially, and regardless of which liquid is more polar. Concave pendular bridges between two particles form when the particles are wetted preferentially by the bridging fluid (i.e. with a wetting angle $\theta < 90°$ measured through the fluid bridge; this is referred to as the pendular state). In the opposite case of preferential wetting by the continuous liquid phase ($\theta > 90°$, referred to as the capillary state), the liquid bridges more closely resemble tiny droplets that connect two or several particles [40,41]. Not surprisingly, the bridges in this capillary state have greater volume polydispersity, and the strength of the particle network depends more strongly on processing conditions, with more intensive mixing required for the formation of strong networks with a fine distribution of the bridging liquid, since the capillary network formation now competes with the stabilization of Pickering emulsion droplets [42,43].

Capillary suspensions in the pendular state and in the capillary state, similar to the aforementioned bijels, are examples of the distinct morphologies found in ternary liquid/liquid/particle systems depending on the composition, particle wettability, and processing conditions. A more complete picture of the accessible morphologies has recently emerged thanks to the effort of Velankar et al. [44–46], who have combined insights from capillary suspension and bijel studies with their own work on particle-filled blends of molten polymeric liquids.

All of the phenomena mentioned previously require the presence of one particle phase and two immiscible fluid phases. Fundamental studies on systems with particles and *more* than two fluid phases and thus different types of fluid–fluid interfaces are scarce by comparison (and do not always reveal fundamentally new behavior). The following sections will focus on recently discovered phenomena involving simple particles, a continuous aqueous phase, a water-immiscible liquid (referred to as ‘oil phase’), and air bubbles as a third fluid phase.

Oil-coated bubbles in aqueous particle dispersions

Wetting in three-fluid systems

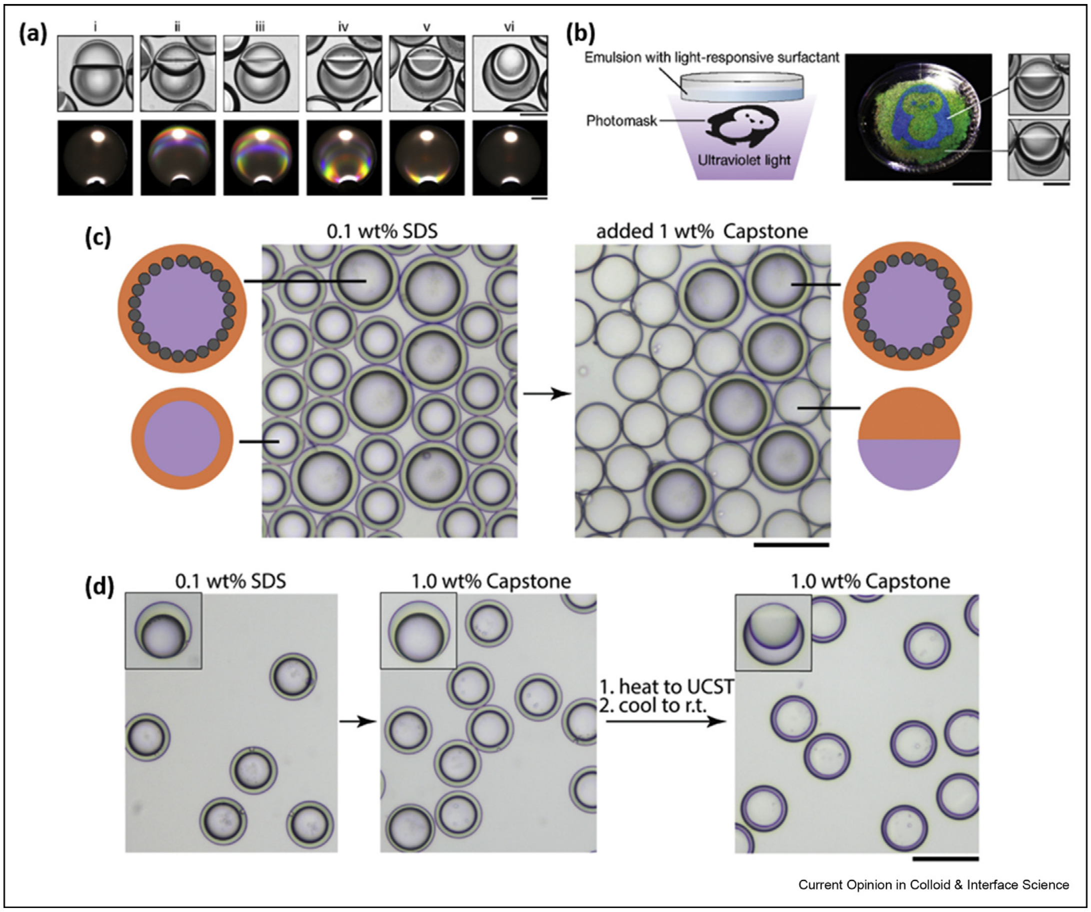
Equilibrium configurations of two fluid drops in a fluid medium have mostly been studied using three mutually immiscible liquids and gained renewed attention because of the advances in the microfluidic production of multiple emulsions over the past two decades [47–49]. The encounter of two liquid drops in a liquid medium can produce three qualitatively different outcomes, depending on the interfacial tensions γ_{ij} associated with the three possible liquid pairings, or the respective spreading coefficients S_j of each phase, where $S_j = \gamma_{ik} - (\gamma_{ij} + \gamma_{jk})$, in a generalization of Eq. (2), is the spreading coefficient of liquid j at the interface of liquids i and k. It is easy to see that at most one of the three phases can have a positive spreading coefficient. If the continuous liquid phase does, the two drops will remain separated in this medium; if one of the drops has a positive spreading coefficient, it will spread around the other drop and fully engulf it. Finally, if all three spreading coefficients are negative, the drops will *partially* wet each other, where two drops with *similar* spreading coefficient form a Janus drop, *i.e.* a ‘two-faced’ composite structure with a low-curvature internal interface and similar portions of its two liquid components facing outward, whereas a droplet with significantly higher (less negative) spreading coefficient partially engulfs the other [47,50].

Because surfactants reduce the tension of the interface to which they adsorb, they can be used to change the balance of interfacial tensions and, by extension, the spreading coefficients and the resulting wetting configuration. Doing so with stimulus-responsive surfactants even permits the in situ reconfiguration of complex emulsion droplets, as demonstrated in an impressive study by Zarzar et al. [51], who used composite droplets of a hydrocarbon (H) and fluorocarbon (F) oil in water (W) to demonstrate the controlled and fully reversible reconfiguration between F/H/W double emulsion droplets, inverted (H/F/W) droplets, and the intermediate states of H–F Janus droplets and partial engulfment of one oil by the other. Recent follow-up work has used this droplet shape control for a number of fascinating optical applications, including reconfigurable liquid microlenses [52], lenses that can quantitatively sense and visualize enzyme activity [53], and iridescent lenses with tunable structural coloration (Figure 1a and b) [54].

Particle effects on wetting configurations

A very recent follow-up study has looked at the effect of particles at the oil–oil interface of these H–F composite droplets [55]. It finds that F/H/W double emulsion droplets known to reconfigure into Janus droplets upon addition of a fluorosurfactant cannot do so when their F/H interface is stabilized by (modified silica) particles of appropriate wettability (Figure 1c). In that case, the only identified pathway to droplet reconfiguration involves the temporary removal of the F/H interface by raising the temperature to a point, where the two oils become miscible (Figure 1d).

Figure 1



Iridescence of biphasic oil droplets depending on the curvature of the oil–oil interface (**a–b**). Reprinted with permission from a study by Goodling et al [54]. Copyright 2019 Springer Nature. Alteration of the internal interfacial curvature in heptane–perfluorohexane biphasic droplets causing a change in the iridescence (a, top row). Scale bar, 50 μm. The bottom row shows photographs of the iridescence pattern as viewed from $\theta = 0°$ with an illumination angle of $\theta = 35°$. Scale bar, 1 cm. A light-responsive surfactant was added to allow photopatterning of the emulsion shape, and hence, reflected color in a Petri dish (b, scale bar, 2 cm). Images on the right show a side view of the droplet shapes giving rise to the blue and green colors (scale bar, 50 μm). Particles inhibit surfactant-induced morphology change in O/O/W emulsion droplets, but droplets can be triggered to change morphology upon heating (**c–d**). Adapted with permission from a study by Cheon et al [55]. Copyright 2020 American Chemical Society. Double emulsion droplets of polyfluorooctane (PFO)/hexane/water containing modified silica particles at 1 wt/vol % (larger diameter droplets) were mixed with PFO/hexane/water droplets without particles (smaller droplets) in 0.1 wt % sodium dodecyl sulfate (SDS) (c). Upon adding the fluorosurfactant Capstone, only the droplets without particles reconfigured to Janus morphology. The transmission optical micrographs are 'top view' images, and the Janus droplets orient with their oil–oil interface parallel to the substrate, which is why the interface is not visible. Double emulsion droplets of PFO/hexane/water with 1 wt/vol % particles did not change shape as the surfactant was switched from SDS to Capstone (c and d) but did reconfigure upon heating to the upper critical solution temperature (about 34–37 °C) and subsequent cooling (d). In the final droplet morphology with particles after heating, the PFO phase almost fully engulfed the hexane. Inset images are side views of exemplary droplets from each sample, taken by gently shaking the emulsion to roll the droplets on their side. Scale bars are 100 μm.

Particles as wetting modifiers

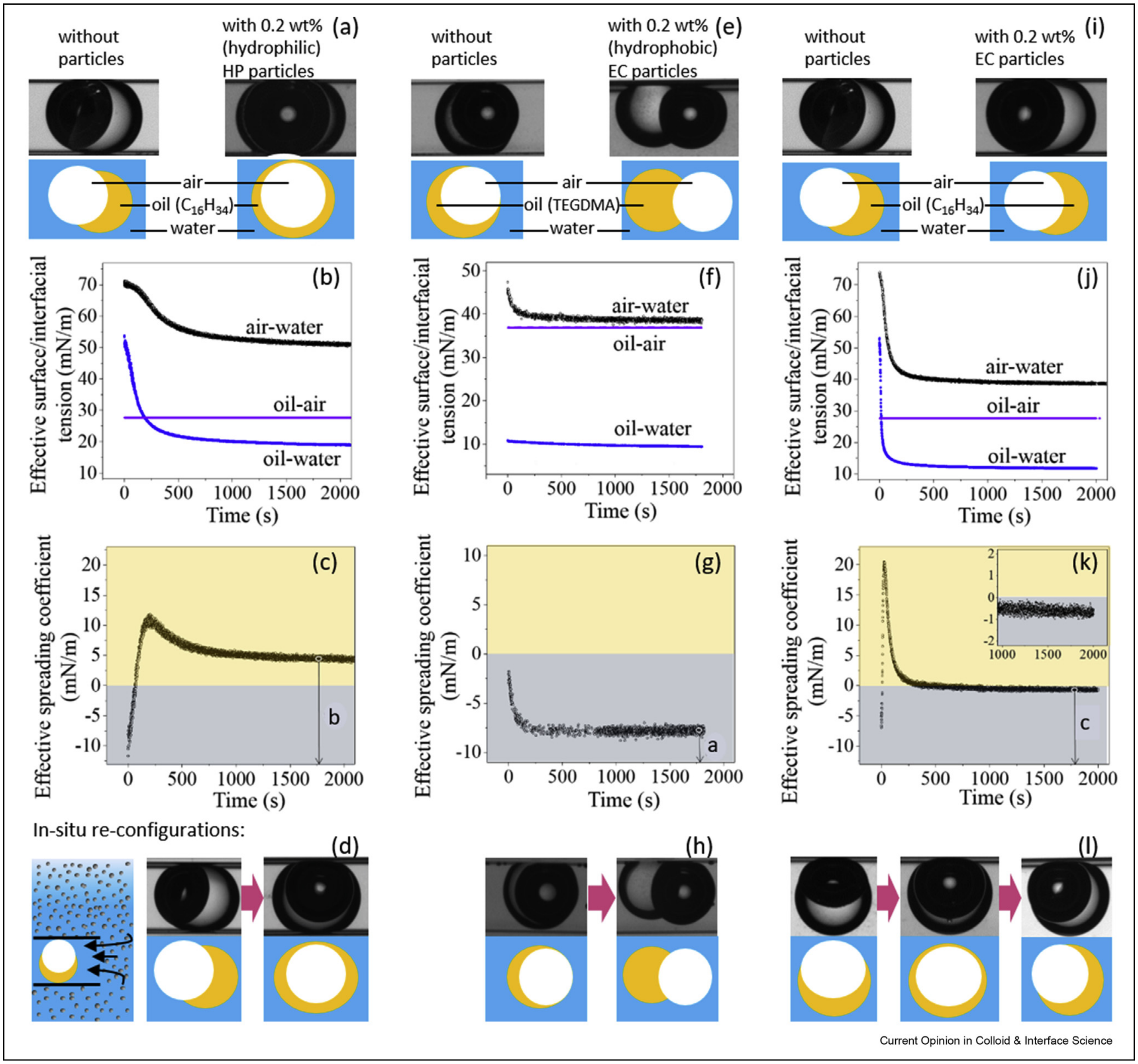
The observation that particles can inhibit droplet reconfiguration should NOT lead to the conclusion that particles always do so, or that they cannot be used to trigger reconfiguration. Contrary to a widespread misconception, all strongly adsorbing particles (not only Janus particles), effectively lower the interfacial tension. The resulting tension γ' can be expressed, at the same level of approximation as Eq. (1), by

$$\gamma' = \gamma\left[1 - \phi(1 - \cos\theta)^2\right] \tag{3}$$

where γ is the interfacial tension in the absence of particles, ϕ is the interfacial coverage (area fraction of the adsorbed particles in the interface), and θ the particle contact angle [56]. For moderate to high coverage and near-neutral particle wetting ($\theta \approx 90°$), the associated surface pressure $\Pi = \gamma - \gamma'$, which promotes the expansion of the covered interface, can be substantial. Particles can therefore be used to induce reconfigurations, as demonstrated in a study of droplet–bubble configurations in water [57].

Because of the high tension associated with (clean) gas–water interfaces, a bubble's encounter with an oil drop in water can yield only two stable configurations (at least in the absence of surfactants): either complete or partial engulfment of the bubble by the oil, depending on the sign of the oil spreading coefficient (Eq. (2)). Particles preferentially adsorbing at the oil–water interface were found to trigger the transition from partial to full bubble engulfment (Figure 2a–d) in perfect analogy with the particle-assisted spreading of oil at planar water surfaces [37], whereas particles with a preference for the air–water interface were seen to promote dewetting of the bubbles by the oil (Figure 2e–h).

Figure 2



Current Opinion in Colloid & Interface Science

Particle-induced bubble wetting and dewetting, adapted from a study by Zhang et al. [57] with permission from John Wiley and Sons. Bubble engulfment by hexadecane in an aqueous dispersion of hypromellose phthalate (HP) particles in the aqueous phase (**a**); interfacial tensiometry indicates particle adsorption at both water interfaces with a larger tension drop at the oil–water interface (**b**), which results in the effective oil spreading coefficient becoming positive as particle adsorption proceeds (**c**); the same reconfiguration is observed in situ upon particle addition (**d**). Bubble dewetting by triethyleneglycol dimethacrylate (TEGDMA) due to the presence of ethyl cellulose (EC) particles (**e**), for which interfacial tensiometry confirms preferential adsorption at the air–water interface (**f**) and an ensuing drop in the oil spreading coefficient (**g**), further corroborated by in situ dewetting upon particle addition (**h**). Partial bubble engulfment by hexadecane is observed in the absence of particles and in presence of EC particles (**i**), which adsorb to both the oil–water and air–water interface (**j**), in a way that makes the oil spreading coefficient transiently become positive (**k**). The corresponding in situ reconfiguration upon particle addition shows transient bubble engulfment (**l**).

Particle-induced changes of droplet-bubble configuration can also produce interesting reentrant behavior [57] that may have no analogy in surfactant-induced reconfiguration: ethyl cellulose particles adsorbing both to the air—water interface and to a hexadecane—water interface were found to change the engulfment of an air bubble by hexadecane from partial to complete and then back to partial as particle adsorption proceeded. This happened reproducibly and independently of the droplet/bubble orientation with respect to the tube orifice through which the particles were delivered. It suggests that particles first adsorb at the oil-water interface and take longer to enter and expand the air—water interface. Measurements of the particles' adsorption kinetics at an air bubble and at a hexadecane droplet in water with a pending drop tensiometer confirmed that particle adsorption at the air—water interface proceeds a bit more slowly (Figure 2j) and shows that, as a result, the oil spreading coefficient jumps from negative to positive values and then drops back to negative (Figure 2k) in agreement with the observed reentrant wetting effect (Figure 2l).

The delay in adsorption at the air—water interface compared with the oil—water interface suggests kinetic adsorption barriers of different height at the two interfaces. The particles of this study are negatively charged, as are typically both air—water and oil—water interfaces in the relevant pH window (likely due to adsorbed acidic trace impurities [58,59]). An electrostatic barrier, caused by repulsive double layer and image charge forces [60] between particles and both types of interfaces, is therefore expected. More importantly, van der Waals interactions cause an attraction of (most) solids to oil—water interfaces [61], but a repulsion from air—water interfaces [62], the present particles being no exception. Hence the air—water interface plausibly presents a higher barrier to particle adsorption than the oil-water interface. It should be mentioned though, that such barrier differences are notoriously difficult to probe by tensiometry and may not fully explain the observed differences in adsorption kinetics, since one should expect the particle adsorption from a quiescent liquid to weakly curved interfaces to be diffusion-limited [63,64].

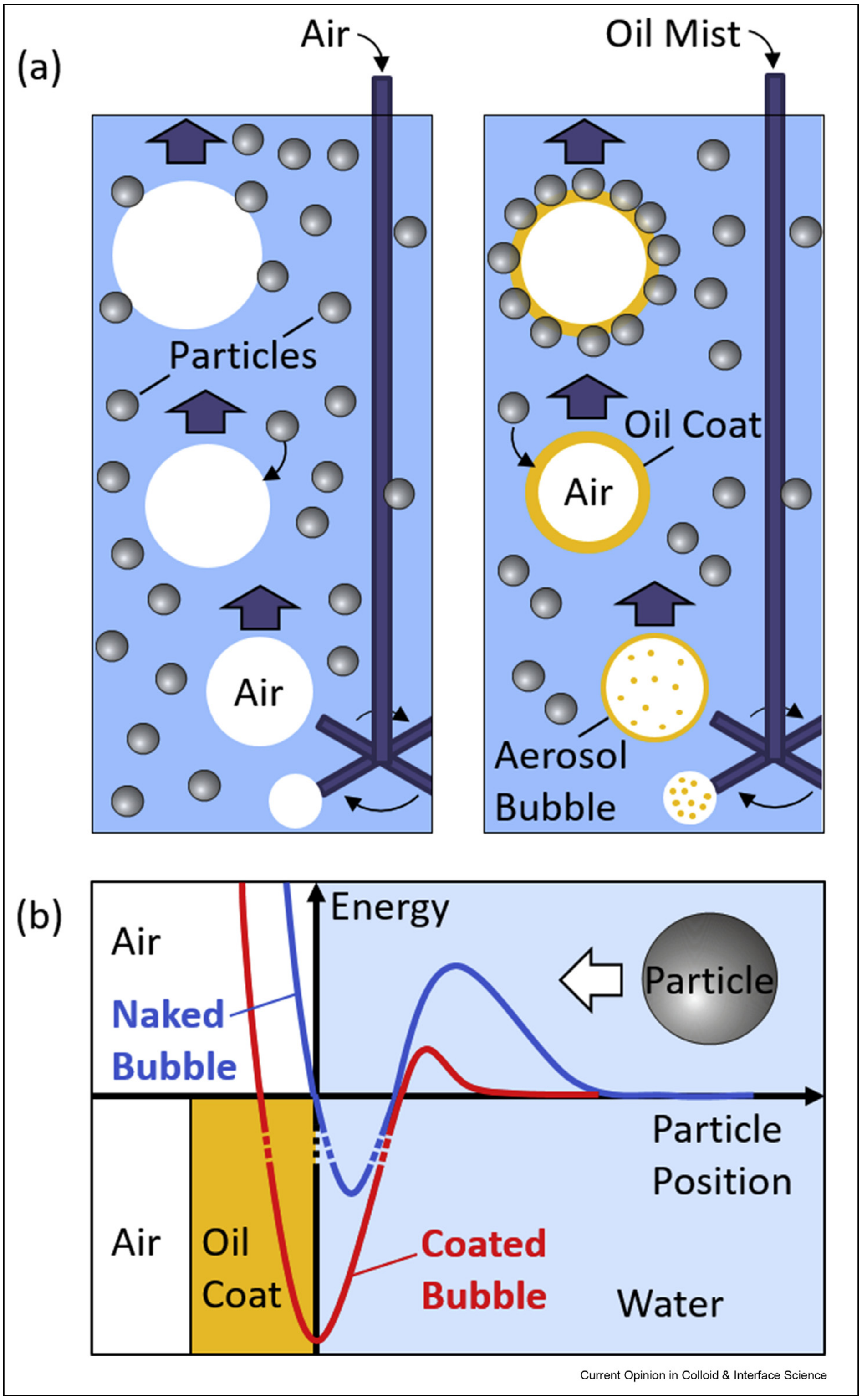
Particle adsorption to bare bubbles and oil-coated bubbles

We have already seen that particles in aqueous dispersion can help spread a coat of oil around an air bubble, and, because neutral wetting at the oil—water interface is optimal for this, it is easy to understand that less polar oils are most easily spread by less hydrophilic particles and more polar oils by more hydrophilic ones. Given that *every* oil has a higher dielectric constant than air, and considering that water-dispersible particles tend to be at least somewhat hydrophilic, it is also easy to appreciate that the affinity of water-borne particles to bubbles can typically be improved by *some* type of oily bubble coating. This may prove useful in the formulation of microbubbles for biomedical applications, where both lipid coated bubbles and protein or nanoparticle decorated bubbles play an important role, *e.g.* as contrast agents [65]. It is especially relevant in the context of froth flotation, a technology that uses macroscopic bubbles at large industrial scales for the separation of particulates from liquid (often aqueous) dispersions and slurries, for example, in mining operations, wastewater treatment, or paper recycling [66]. The technique relies on the adsorption of sufficiently hydrophobic particles to rising air bubbles, which then combine in a froth at the surface of the liquid column and are readily skimmed off. When the targeted particles are too hydrophilic to adsorb strongly to the bubble surface, particle hydrophobizing agents referred to as 'collectors' are commonly added to the system, but they raise costs and can lead to undesired side effects.

An interesting alternative is to effectively render the bubbles less hydrophobic by applying an oil coat to them, for instance, by using a fine oil mist instead of pure air in the bubble preparation (Figure 3a). The oil quickly deposits at the air—water interface and forms a bubble coat, which can also be used as a vehicle for small amounts of oil-soluble amphiphiles that further optimize particle wetting at the oil—water interface [67] and render the separation process more selective [68] without the need to add large amounts of collectors to the bulk liquid. This strategy known as 'reactive oily bubble flotation' has been explored for the recovery of minerals [69] and low rank (hydrophilic) coals [70,71].

In the context of flotation deinking, a step commonly used in paper recycling, an early study published in 1998 already found that oil-coated bubbles performed better than ordinary bubbles in the removal of hydrophilic flexographic ink particles [72], but the idea of oily bubble flotation did not gain traction in the deinking field. Since then, we have witnessed a shift in high volume printing away from offset printing (with hydrophobic ink particles) toward inkjet printing, which uses water-based inks with hydrophilic particles. Because of their low affinity for (uncoated) bubbles, these 'greener' inks ironically lead to reduced deinkability and thus lower paper recyclability via the established processes [73]. It therefore seems timely to reconsider flotation deinking with oil-coated bubbles. We just completed a study (submitted for publication after the present opinion piece) on the removal of inkjet ink from pulped newsprint paper by flotation deinking that demonstrates significant benefits of an oily bubble coat according to a number of standard performance metrics, including the ISO brightness and effective residual ink concentration of the recycled paper and the fiber loss during deinking.

Figure 3



Current Opinion in Colloid & Interface Science

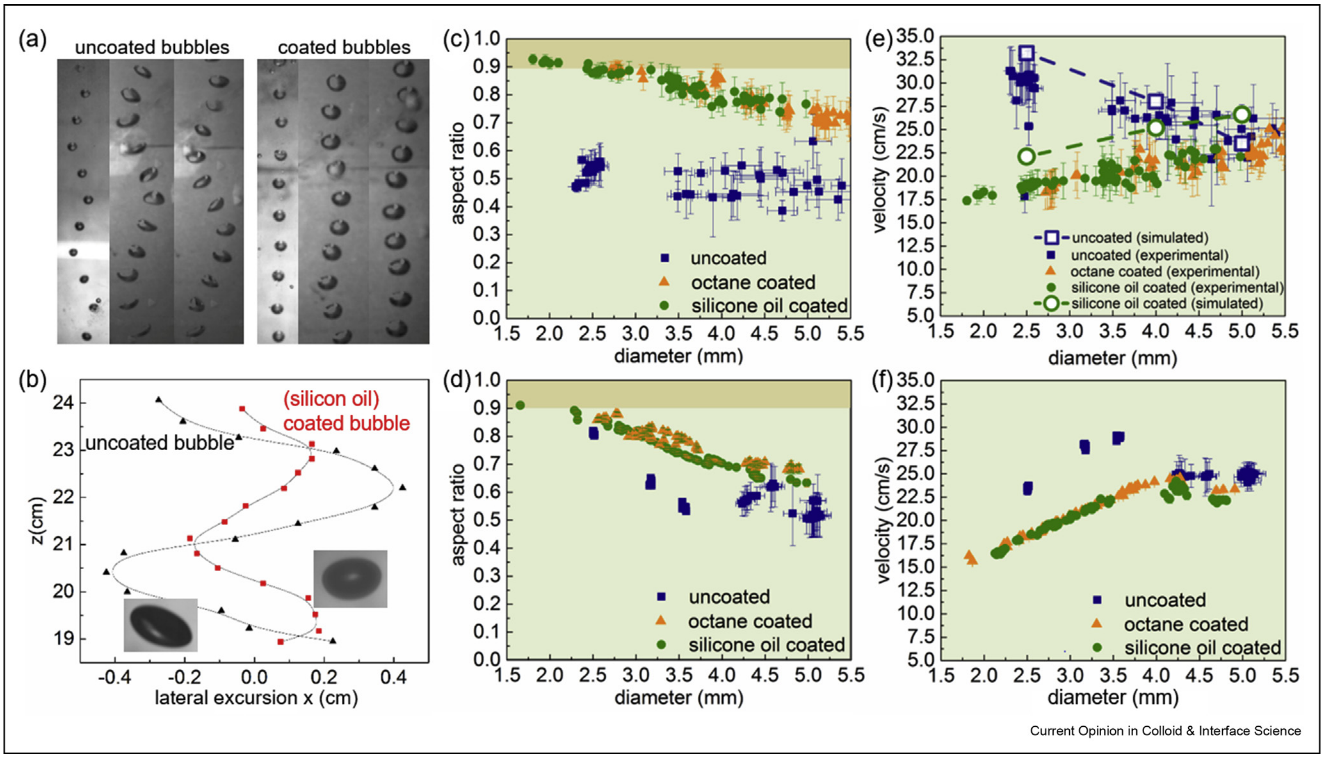
Standard bubble flotation versus oily bubble flotation of hydrophilic particles (**a**); schematic of a particle's interaction with a naked versus an oil-coated bubble (**b**).

In addition to providing more favorable wetting conditions for particles attached to the bubble surface (stronger attachment energy), the presence of the oil coat is known to significantly decrease the so-called induction time τ_i, *i.e.* the time required for the rupture of the aqueous film initially separating particles from the bubble interface after they have been brought in close contact with a bubble [71]. This time depends sensitively on the height of the kinetic barrier, and obviously needs to be shorter than the contact time τ_c (residence time of particles in close proximity to the surface) for particle attachment to the bubbles to occur and flotation separation to succeed. Figure 3b shows a qualitative sketch of the energy landscape experienced by a particle at a bubble surface, with the presence of an oily bubble coat lowering both the energy well and the energy barrier and thus providing both a *thermodynamic* and a *kinetic* benefit.

Further benefits, related to *fluid dynamics* and therefore not captured in Figure 3b, were suggested by a recent study that compared the trajectory, velocity, and shape fluctuations of individual rising bubbles with and without an oil coat, but of comparable overall size (Figure 4) [74]. The presence of an oil coat was found to suppress bubble deformations; coated bubbles thus retain a more spherical shape than their 'naked' counterparts. The coated bubbles also rise in a straighter, less tortuous trajectory, which is not surprising, because it is known from ordinary bubbles that the shape stability and path stability of rising bubbles strongly correlate [75,76]. Despite their shorter trajectory, the coated bubbles were found to rise more slowly, primarily because their oil component raised the overall bubble density. Generally speaking, the differences observed between oil-coated and uncoated bubbles are reminiscent of the differences reported between bubbles in clean water and in contaminated water [77], (as may be rationalized by noting that an oil coat resembles adsorbed contaminants in reducing mobility at the water interface and thus increasing bubble drag). Similarly, the higher sphericity, slower rise, and straighter trajectory of oil-coated bubbles is also known from uncoated, but smaller bubbles [78].

For froth flotation, the slower and less jiggly bubble motion of oil-coated bubbles implies that particles in close proximity to a bubble will spend more time there; and so the oil coat helps meet the requirement $\tau_i < \tau_c$ both by reducing the induction time [71] *and* by raising the contact time. Moreover, the suppression of bubble shape fluctuations means a steadier interface of more

Figure 4



Current Opinion in Colloid & Interface Science

Influence of an oily bubble coat on bubble dynamics, adapted from a study by Wang et al. [74] with permission from The Royal Society of Chemistry. Rising bubbles with and without a coat of silicone oil (**a**), (average bubble diameters are 2.5, 4.0 and 5.0 mm); measured trajectories of a naked and coated 4 mm bubble (**b**); average bubble aspect ratio (ratio of minor to major axis length) for coated and uncoated bubbles rising in water (**c**) and in 40% sugar solution with a viscosity of 5.8 cP (**d**); upward velocity of rising coated and uncoated bubbles in water (**e**) and in 40% sugar solution (**f**).

nearly constant area; thus the oil coat not only strengthens the attachment of adsorbed particles, but also dampens any interface perturbation that could lead to the detachment of weakly bound particles [79].

The combined thermodynamic, kinetic and hydrodynamic consequences of an oily bubble coat for particle–bubble attachment could prove useful for separation tasks not traditionally addressed by froth flotation, including specialty separations and protein purification.

Capillary foams

Simultaneous dispersion of a solid, liquid, and gas phase in water

Attempts to disperse both air and liquid oil in an aqueous particle suspension can yield dramatically different outcomes depending on the mixing ratios, particle wettability and mixing intensity. If particles are too hydrophilic to stabilize the oil droplets, or if electrostatic repulsion from the interfaces prevent their adsorption [60], mixtures tend to separate rapidly. Similarly, particles hydrophobic enough to stabilize bubbles in Pickering foams, often prove unable to do so in the presence of oil because of the well known antifoaming properties of oils [80,81]. Some particles of sufficient affinity for both air–water and oil–water interfaces have been shown to stabilize mixtures of bubbles and emulsion droplets, referred to as emulsion foams or foamulsions [82,83]. (Emulsion foams can also be stabilized by surfactants instead of particles, but the surfactant-stabilized systems tend to have shorter lifetimes [84]). Good long-term stability of emulsion foams appears to be correlated with the use of gel-forming particles, and the temperature dependence of particle gelation can render the foams' stability thermoresponsive [83,85]. In a recent study, emulsion foams with 5–60% of oil were stabilized by fibrils of glycyrrhizic acid and shown to collapse when the temperature was raised above the gel–sol transition temperature of the fibrils, either through external heating or, in systems with incorporated carbon black particles, through irradiation by UV light [85].

An entirely different type of foam can be stabilized by the synergistic action of particles and a very small amount of oil. Oil volume fractions of as little as 0.1% and no more than a few percent, added to an aqueous suspension of particles with near-neutral wetting for the oil-water interface, can lead, upon frothing, to the formation of a stable capillary foam [86–89]. The characteristic structure of this kind of foam, whose discovery was first reported in 2014 [86], is shown in Figure 5a–e. Bubbles tend to be coated by a film of oil, which is spread and stabilized by particles adsorbed at the film interface. The coated bubbles (Figure 5f) are further incorporated in the gel network of a capillary suspension (Figure 5g) formed by oil-bridged particles in the continuous aqueous bulk. More generally, a capillary foam may be defined as a foam formed in a continuous liquid and stabilized synergistically by solid particles and a small amount of an immiscible secondary liquid that mediates capillary interactions.

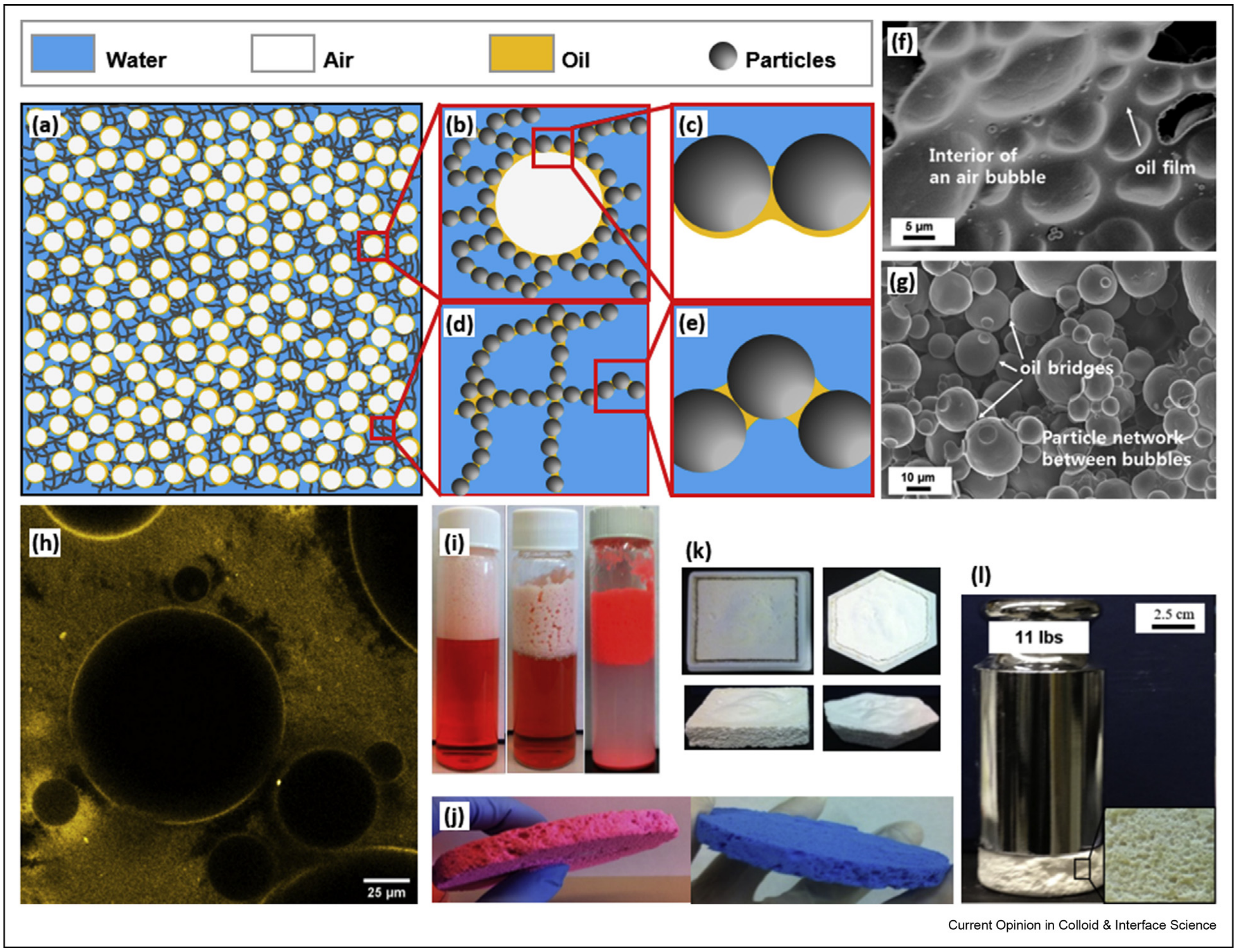
Cooperative behavior of particles and oil in capillary foams

The formation of the particle gel is necessary to immobilize the bubbles and was in fact found to precede the bubble entrapment during foam formation [88]. Yet, it is not a sufficient condition for foam stability: hydrophobized silica particles preferentially wetted by oil with a large contact angle ($\theta > 130°$) at the oil–water interface were found to interconnect via pendular oil bridges, but this particle–oil combination did not stabilize an aqueous foam [86]. Similarly, the effective oil spreading coefficient, accounting for the interfacial energy reduction by adsorbed particles, was estimated to be positive for all investigated systems that produced stable capillary foams, but the tendency to engulf bubbles in a composite coat of oil and particles does not by itself guarantee that stable foams can form [86]. Clearly, capillary foams are not just capillary suspensions with simple gas inclusions, nor are they simply o/w-Pickering emulsions with gas-filled emulsion droplets.

Despite the aforementioned caveats, many oil–particle pairings are suitable for stabilizing capillary foams, and the protocols for foam production are rather robust and forgiving. Particles successfully employed in capillary foams range in size from tens of nanometers to tens of microns, and include inorganic particles such as modified silica or aluminum oxide (Figure 5h), particles from synthetic polymers such as polyethylene (Figure 5f, g and i) or polyvinyl chloride (Figure 5j–l), cellulosic particles, and protein particles (whey protein particles, not yet published). Importantly, particles too hydrophilic to stabilize the air–water interface of Pickering foams can still be very suitable for stabilizing the oil–water interface of coated bubbles and for making capillary foams with a shelf life on the order of months or years. Therefore, the simple addition of a small amount of oil can be an economical and time-saving alternative to the surface modification of particles for foam stabilization.

The compatibilizing effect of the oil can be taken even further. A recent study by Dunstan et al. [90] on capillary suspensions showed that the particle-bridging oil phase can also provide a way to modify particle wettability in situ: in the reported case, hydrophilic calcium carbonate particles dispersed in either water or glycerol as the polar medium were shown to form strong capillary suspension gels with oil bridges of peppermint oil or isopropyl myristate – but only if the particles were hydrophobized, either by pretreatment with oleic acid,

Figure 5



Current Opinion in Colloid & Interface Science

Capillary foam schematic (**a**–**e**), adapted with permission from a study by Zhang et al. [88]. Copyright 2017 American Chemical Society; SEM images of a solidified bubble coat (**f**) and particle network (**g**) reproduced from a study by Zhang et al. [86] with permission from John Wiley and Sons; confocal image of a capillary foam prepared with 93 nm modified silica particles and heptane (**h**) adapted with permission from a study by Essenmacher [89]. Copyright 2018. The fluorescently labeled oil is seen as a diffuse yellow cloud in the network of oil-bridged particles and as a bright yellow ring in the oil film coating the bubbles. Comparison of colored liquid foams (**i**), (left to right: surfactant-stabilized foam and Pickering foam with dyed aqueous phase, and a capillary foam with dyed oil phase). Dry capillary foam pads with dyed, polymerized oil phase (**j**); mold-cast (**k**) and load-bearing (**l**) dry capillary foams. Figure 5(i–l) adapted with permission from a study by Zhang et al. [87]. Copyright 2015 American Chemical Society.

or in situ through at least a small amount of oleic added to the oil phase. This principle of in situ particle modification through an oil-soluble wetting agent, already familiar from the ‘reactive oily bubble flotation’ [69,91] described before, should be applicable in capillary foams, too.

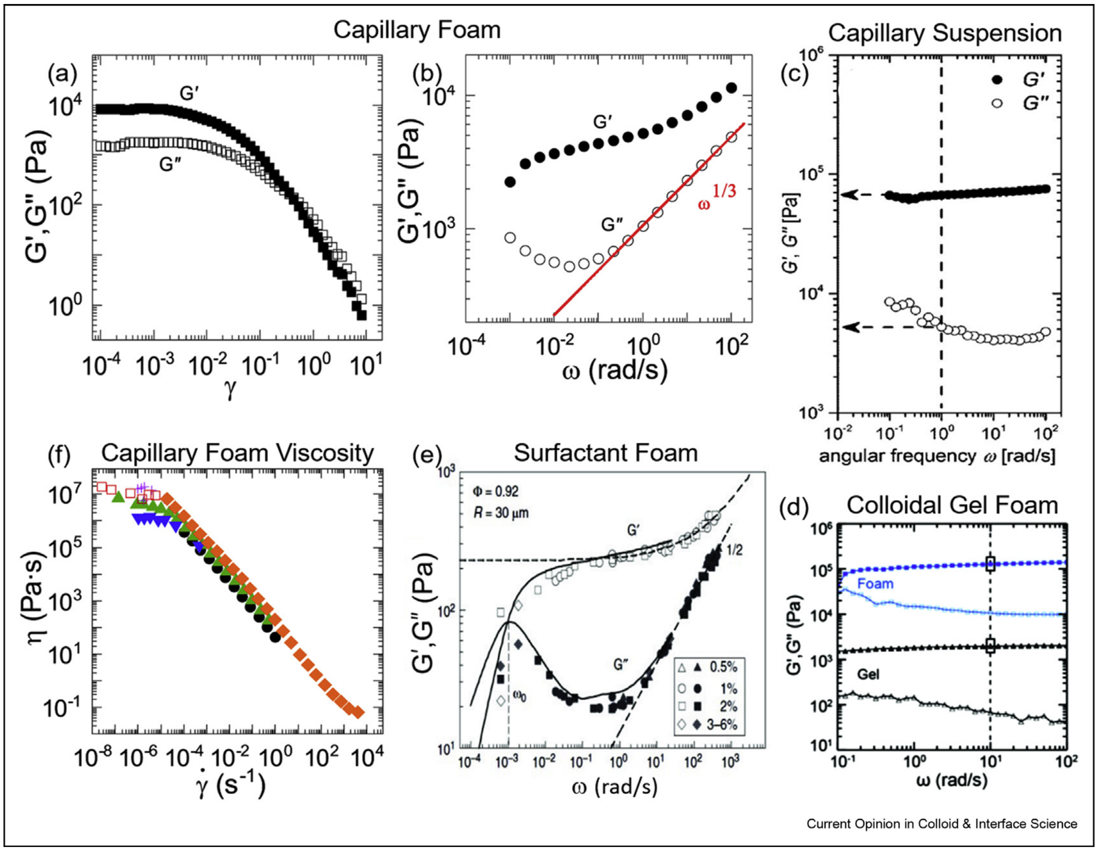
Solid capillary foams

The presence of an oil phase in these aqueous foams also offers opportunities for the preparation of solid foams. Many capillary foams with nonvolatile oil components will survive gentle drying, but the resulting dry foams tend to be mechanically unstable. More robust solid foams can be obtained if the oil phase is solidified prior to drying. Using the photopolymerizable trimethylolpropane trimethacrylate as the oil phase and UV-curing it before drying has been shown to yield very stable, albeit somewhat brittle, lightweight porous solids with large pores defined by the original bubbles, and smaller pores corresponding to the mesh size of the bubble-embedding particle gel (Figure 5k–l) [87]. These capillary foams can be mold cast and support loads far above their own weight; the use of polydimethylsiloxane or other elastomers as the oil phase or an oil phase component further allows us to make rubbery (nonbrittle) solid foams. Preliminary results of ongoing research suggest that oils like coconut oil or shea butter, that are solid at room temperature but liquid at slightly elevated processing temperatures, can be used for capillary foam mousses with promise for low fat foods or skin care products depending on the type of particles used. Common strategies to grow solid polymer layers at oil—water interfaces, such as interfacial precipitation or interfacial polymerization (of oil-soluble and water-soluble reactants, as in the case of polyurethane or polyurea) have not yet been applied to capillary foams but likely provide further options for tuning chemical and mechanical properties of the solid foams. Potential uses of solid capillary foams for lightweight packaging, thermal or acoustic insulation, shock absorption or filtration are easily conceivable. More sophisticated applications such as foam-based tissue scaffolding [92,93] or foam solutions to heat transport and thermal energy storage [94,95] may also benefit from the unique structure and multiscale porosity of solid capillary foams but would require more specialized oil and particle components and/or functionalizations. While the work still needed to tune foam properties for any particular application should not be underestimated, requirements of biocompatibility or biodegradability certainly present no principal roadblock for capillary foams. Finally, it has been shown that dyes added to the oil phase allow for both solid and liquid capillary foams with an intense and uniform coloration throughout the material (Figure 5i and j) [87], which is notoriously difficult to achieve in traditional water-based foams [96]. It also suggests that capillary foams may be useful for formulating other oil-soluble active ingredients, especially when low concentrations and precise dosing are desired.

Rheology of capillary foams

A recent rheological study investigated the viscoelastic behavior of wet capillary foams [97]. Result of oscillatory shear experiments are shown in Figure 6 and compared to literature results on related systems. The strain sweep (for an angular frequency of ω = 1 rad/s; Figure 6a) shows a linear regime in which the storage modulus G’ exceeds the loss modulus G”, indicating that the capillary foam behaves like an elastic solid at low strains. Larger strains disrupt the foam’s network structure, and at a strain $\gamma \approx 0.5$ a transition from solid-

Figure 6



Current Opinion in Colloid & Interface Science

Capillary foam rheology, adapted from a study by Okesanjo et al. [97] with permission from The Royal Society of Chemistry. Storage and loss modulus of capillary foams in a strain sweep (**a**), and a frequency sweep (**b**), for comparison with frequency sweep for a capillary suspension (**c**), (adapted with permission from a study by Bossler et al. [42]), for a colloidal gel foam (**d**), (adapted with permission from a study by Muth and Lewis [99]. Copyright 2017 American Chemical Society), and for a surfactant-stabilized foam (**e**), (adapted from a study by Gopal and Durian [102] with permission) (**f**) Viscosity versus strain rate. Blue inverted triangles and violet crosses (repeats) are obtained from controlled stress experiments on a parallel plate (PP) setup; green triangles (PP), black circles (repeats on PP), and orange diamonds (Couette cell) are obtained from controlled strain rate experiments; open red squares are obtained from creep experiment on a PP setup.

like to liquid-like behavior is observed. A frequency sweep (at $\gamma = 0.001$, within in the linear regime) shows a rather pronounced frequency dependence of both moduli (Figure 6b). This is remarkable because gelled systems typically display only a very weak frequency dependence of the storage modulus; and capillary suspensions are no exception [40,98], as seen in the example of Figure 6c from a study by Bossler et al. [42]. Clearly, the presence of the bubbles has an important effect on the foam rheology. One might expect that the viscoelastic response of capillary foams should more closely resemble that of other gelled systems containing particle-stabilized bubbles. Some colloidal gel foams prepared from aqueous suspensions of hydrophobized alumina particles would seem to be an especially close relative of capillary foams because they, too, contain a gelled network of attractively interacting particles that immobilizes particle-covered bubbles, at similar bubble volume fractions as found in capillary foams (20—60%), albeit without involving an oil phase [99]. Such gel foams have proven useful for direct foam writing of architected porous ceramics [100,101], and their rheological properties have been studied, too [99]. As shown in Figure 6d [99], however, the presence of bubbles in these gels does *not* lead to the frequency dependence observed in capillary foams (Figure 6b).

Instead, a much closer qualitative resemblance to the frequency-dependent elastic and viscous response of capillary foams can be found in classical aqueous foams, *i.e.* concentrated dispersions of bubbles in a particle-free surfactant solution, as shown in Figure 6e [102]. It should be noted that the elasticity in those systems is associated with an increase in the air—water interfacial area due to the distortion of jammed bubbles and therefore can be observed only for bubble volume fractions above the random close packing (rcp) limit of ~64%, whereas the elastic response shown in Figure 6a and b reflects the behavior of capillary foams with bubble volume fractions roughly half of the rcp threshold.

A recent study by Mikhailovskaya et al. [103] on surfactant stabilized foams with high gas volume fraction and a slowly gelling particle dispersion in the continuous phase finds that the storage modulus of the gel foam can be expressed as a simple superposition of contributions from the nongelled foam and the elastic gel matrix when the elastocapillary number $Ca = G_0/(\gamma/R)$ exceeds unity (where G_0 is the shear modulus of the continuous phase, γ the surface tension, and R the bubble radius). Counterintuitively, a larger relative contribution of the gel matrix ($\sim 1/Ca$) is found for smaller values of Ca. Given the high bubble volume fraction of these foams and the confinement of particles to a small amount of liquid in the interstices (Plateau borders) between facetted bubbles, insights into the rheology of these systems may be of limited value to understanding capillary foams, whose spheroidal bubbles are mechanically coupled, not by direct bubble—bubble contact, but through the particle network in a surrounding liquid bulk that takes up much of the foam volume.

For now, it remains unclear how exactly the viscoelastic effects of the gel network and of the bubble coatings in capillary foams conspire to yield the observed foam rheology. The qualitative resemblance of Figure 6b for a capillary foam and Figure 6e for a classical foam may suggest that bubble deformations (mediated and coupled by the particle gel) play a bigger role to capillary foam rheology than the viscoelastic properties of the particle gel itself. Moreover, the observed scaling of G', G" at high frequencies with G" $\propto \omega^{\nu}$ and $\nu < 1/2$ may point to a prominent influence of bubble rigidity. High interfacial rigidity has previously been linked to similar anomalous scaling in surfactant stabilized foams with cosurfactants of low water solubility [104]. In capillary foams, the coat of oil and particles covering the bubbles likely accounts for very rigid bubble surfaces that are firmly incorporated into the external gel network, thus guaranteeing a strong coupling of bulk and interfacial rheology.

Figure 6f shows the shear thinning behavior of capillary foams, inferred from a variety of different experiments. Notably, the viscosity far exceeds the viscosity of water over the entire (12 orders of magnitude) range of strain rates probed. If this behavior, observed for capillary foams with large particles, extends to capillary foams with particles in the nanometer size range, then such foams could be very useful as displacing fluids in oil recovery. Foam flooding has long been explored as a way to mitigate conformance problems, *i.e.* inefficiencies resulting from nonuniformity of the flood front, such as viscous fingering, gravity override due to vertical gradients in the density and mobility of the displacing fluid, and channeling through high permeability zones and paths in heterogeneous or fractured reservoirs [105,106]. For improved performance, the goal is to reduce the mobility k_r/η of the displacing fluid relative to that of the oil, where k_r is the relative permeability and η the viscosity of the respective fluid [107]. Aqueous foams in general offer the advantage of having a higher viscosity than either its water or gas phase alone, and for capillary foams the difference is particularly large. Moreover, particle-stabilized foams are known to be more stable than surfactant stabilized foams at the temperature and pressure conditions encountered in oil recovery [108], but poor foam stability upon contact with oils often remains a challenge [109]. Capillary foams, on the other hand, show high stability in contact with oil, which is not surprising, given the stabilizing role that oil plays as an ingredient in these foams. Similar arguments can be made for the possible benefits of capillary foams in hydraulic fracturing or in soil remediation, but judging the potential for any of these applications will first require careful studies of foam flow in model porous media. For surfactant stabilized foams, such studies have revealed a continual loss of foam bubbles due to either bubble coalescence (promoted by film drainage, capillary suction, and mechanical stresses) or diffusion coarsening, and shown that such foam degradation can be offset by the in situ generation of new lamella through a variety of mechanisms (referred to, suggestively, as 'snap-off', 'lamella division', 'leave behind', and bubble 'pinch-off') [110]. It remains to be seen how the oil-coated bubbles and oil-bridged particles in capillary foams respond to flow in extreme confinement and what options for the flow-induced regeneration of the foam structure may exist.

Conclusions and outlook

In this article, I have tried to substantiate the claim that colloidal multiphase systems containing at least one particulate species and different types of fluid interfaces present great opportunities, both for fundamental research, and for materials and process innovation. In doing so, I have focused deliberately on the case of oil-coated droplets interacting with 'simple particles' in particle-assisted droplet reconfiguration, oily bubble flotation, or within capillary foams. These scenarios involving quaternary air/oil/particles/water systems are still relatively simple and not hard to manipulate, but, as discussed throughout the paper, they already have a widespread and largely unexplored application potential in areas such as medicine, water management, paper recycling, food processing, oil recovery, and many more. Possible expansions of the presented considerations include the concept of a 'capillary emulsion', obtained in a thought experiment by replacing the dispersed gas phase in a capillary foam with a third immiscible liquid, such as a halogenated oil. While no such system has been reported yet, it should in principle be possible to realize and could have very useful properties: a dried capillary emulsion with dispersed droplets of a phase-change material, enclosed in a coat and particle network formed by a heat conducting solidified bridging phase, would for instance seem like a good candidate for thermal management applications. Obviously, one can go further and increase the system complexity, *e.g.* by including multiple particle species, by adding a fourth fluid phase, or by replacing the 'simple' particles with stimulus-responsive particles for controlled foam breaking, or with a particle species that drives structure formation all by itself, such as patchy or active particles, whose inherent tendency to self-assembly would now compete with the kind of structure formation observed in simple capillary foams … The possibilities seem endless.

Declaration of competing interest

The author declares that he is unaware of any competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

Acknowledgements

The work in this article was made possible with the financial support from the National Science Foundation (CBET-1706475). Helpful discussions with Omotola Okesanjo, Xiaotang Du, Songcheng Wang, Carson Meredith, and Joelle Frechette are gratefully acknowledged.

References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest
** of outstanding interest

1. Russel WB, Saville DA, Schowalter WR: *Colloidal dispersions*. Cambridge: Cambridge University Press; 1989.

2. Binks BP: **Colloidal particles at a range of fluid-fluid interfaces**. *Langmuir* 2017, **33**:6947–6963.

3. Dasgupta S, Auth T, Gompper G: **Nano- and microparticles at fluid and biological interfaces**. *J Phys-Condens Matter* 2017, **29**:373003.1–373003.41.

4. Maestro A, Santini E, Guzman E: **Physico-chemical foundations of particle-laden fluid interfaces**. *Eur Phys J E* 2018, **41**: 97.1–97.21.

5. Ballard N, Law AD, Bon SAF: **Colloidal particles at fluid interfaces: behaviour of isolated particles**. *Soft Matter* 2019, **15**: 1186–1199.

6. Liu IB, Sharifi-Mood N, Stebe KJ: **Capillary assembly of colloids: interactions on planar and curved interfaces**. In Sachdev S, Marchetti MC. *Annual review of condensed matter physics*, vol. 9; 2018:283–305. Annual Reviews: Palo Alto.

7. Maestro A: **Tailoring the interfacial assembly of colloidal particles by engineering the mechanical properties of the interface**. *Curr Opin Colloid Interface Sci* 2019, **39**:232–250.

8. Bharti B, Rutkowski D, Han K, Kumar AU, Hall CK, Velev OD: **Capillary bridging as a tool for assembling discrete clusters of patchy particles**. *J Am Chem Soc* 2016, **138**:14948–14953.

9. Roh S, Parekh DP, Bharti B, Stoyanov SD, Velev OD: **3D Printing by multiphase silicone/water capillary inks**. *Adv Mater* 2017, **29**:1701554.1–1701554.7.

10. * Forth J, Liu XB, Hasnain J, Toor A, Miszta K, Shi SW, Geissler PL, Emrick T, Helms BA, Russell TP: **Reconfigurable printed liquids**. *Adv Mater* 2018, **30**:1707603.1–1707603.7.

The authors use carboxylic acid functionalized nanoparticles to stabilize intricate aqueous filament structures printed into an aminopropyl terminated oil. Nanoparticles jammed at the interface render the printed liquid-in-liquid constructs responsive to chemical cues and amenable to repeated reconfiguration.

11. * Di Vitantonio G, Wang T, Haase MF, Stebe KJ, Lee D: **Robust bijels for reactive separation via silica-reinforced nanoparticle layers**. *ACS Nano* 2019, **13**:26–31.

The authors demonstrate a base catalyzed ester hydrolysis in a silica reinforced bijel formed by solvent transfer-induced phase separation (STRIPS). Maintaing the bijel integrity during reagent flow and under the harsh conditions of the chemical reaction is a major milestone toward the practical use of bijels for reactive separations.

12. Cha S, Lim HG, Haase MF, Stebe KJ, Jung GY, Lee D: **Bicontinuous interfacially jammed emulsion gels (bijels) as media for enabling enzymatic reactive separation of a highly water insoluble substrate**. *Sci Rep* 2019, **9**:6363.1–6363.6.

13. Fei WJ, Gu Y, Bishop KJM: **Active colloidal particles at fluid-fluid interfaces**. *Curr Opin Colloid Interface Sci* 2017, **32**:57–68.

14. Chen TQ, Kondepudi DK, Dixon JA, Rusling JF: **Particle flock motion at air-water interface driven by interfacial free energy foraging**. *Langmuir* 2019, **35**:11066–11070.

15. Danov KD, Kralchevsky PA: **Capillary forces between particles at a liquid interface: general theoretical approach and**

interactions between capillary multipoles. *Adv Colloid Interface Sci* 2010, **154**:91–103.

16. Masschaele K, Park BJ, Furst EM, Fransaer J, Vermant J: **Finite ion-size effects dominate the interaction between charged colloidal particles at an oil-water interface**. *Phys Rev Lett* 2010, **105**. 048303.1-048303.4.

17. Herzig EM, White KA, Schofield AB, Poon WCK, Clegg PS: **Bicontinuous emulsions stabilized solely by colloidal particles**. *Nat Mater* 2007, **6**:966–971.

18. Cates ME, Clegg PS: **Bijels: a new class of soft materials**. *Soft Matter* 2008, **4**:2132–2138.

19. Stratford K, Adhikari R, Pagonabarraga I, Desplat JC, Cates ME: **Colloidal jamming at interfaces: a route to fluid-bicontinuous gels**. *Science* 2005, **309**:2198–2201.

20. Haase MF, Stebe KJ, Lee D: **Continuous fabrication of hierarchical and asymmetric bijel microparticles, fibers, and membranes by solvent transfer-induced phase separation (STRIPS)**. *Adv Mater* 2015, **27**:7065–7071.

21. Haase MF, Jeon H, Hough N, Kim JH, Stebe KJ, Lee D: **Multifunctional nanocomposite hollow fiber membranes by solvent transfer induced phase separation**. *Nat Commun* 2017, **8**: 1234.1–1234.7.

22. Boakye-Ansah S, Schwenger MS, Haase MF: **Designing bijels formed by solvent transfer induced phase separation with functional nanoparticles**. *Soft Matter* 2019, **15**: 3379–3388.

23. Cai DY, Clegg PS, Li T, Rumble KA, Tavacoli JW: **Bijels formed by direct mixing**. *Soft Matter* 2017, **13**:4824–4829.

24. Huang CL, Forth J, Wang WY, Hong KL, Smith GS, Helms BA, Russell TP: **Bicontinuous structured liquids with sub-micrometre domains using nanoparticle surfactants**. *Nat Nanotechnol* 2017, **12**:1060–1063.

25. Studart AR, Shum HC, Weitz DA: **Arrested coalescence of particle-coated droplets into nonspherical supracolloidal structures**. *J Phys Chem B* 2009, **113**:3914–3919.

26. Pawar AB, Caggioni M, Ergun R, Hartel RW, Spicer PT: **Arrested coalescence in Pickering emulsions**. *Soft Matter* 2011, **7**: 7710–7716.

27. Vignati E, Piazza R, Lockhart TP: **Pickering emulsions: interfacial tension, colloidal layer morphology, and trapped-particle motion**. *Langmuir* 2003, **19**:6650–6656.

28. Ngai T, Auweter H, Behrens SH: **Environmental responsiveness of microgel particles and particle-stabilized emulsions**. *Macromolecules* 2006, **39**:8171–8177.

29. Gautier F, Destribats M, Perrier-Cornet R, Dechézelles J-F, Giermanska J, Héroguez V, Ravaine S, Leal-Calderon F, Schmitt V: **Pickering emulsions with stimulable particles: from highly- to weakly-covered interfaces**. *Phys Chem Chem Phys* 2007, **9**:6455–6462.

30. Destribats M, Gineste S, Laurichesse E, Tanner H, Leal-Calderon F, Heroguez V, Schmitt V: **Pickering emulsions: what are the main parameters determining the emulsion type and interfacial properties?** *Langmuir* 2014, **30**:9313–9326.

31. Stancik EJ, Fuller GG: **Connect the drops: using solids as adhesives for liquids**. *Langmuir* 2004, **20**:4805–4808.

32. Horozov TS, Binks BP: **Particle-stabilized emulsions: a bilayer or a bridging monolayer?** *Angew Chem Int Ed* 2006, **45**: 773–776.

33. Bizmark N, Ioannidis MA: **Nanoparticle-stabilised emulsions: droplet armouring vs. droplet bridging**. *Soft Matter* 2018, **14**: 6404–6408.

34. Kaganyuk M, Mohraz A: **Impact of particle size on droplet coalescence in solid-stabilized high internal phase emulsions**. *Langmuir* 2019, **35**:12807–12816.

35. Lee MN, Chan HK, Mohraz A: **Characteristics of Pickering emulsion gels formed by droplet bridging**. *Langmuir* 2012, **28**: 3085–3091.

36. Xu H, Goedel WA: **Particle-assisted wetting**. *Langmuir* 2003, **19**:4950–4952.

37. Ding AL, Goedel WA: **Experimental investigation of particle-assisted wetting**. *J Am Chem Soc* 2006, **128**:4930–4931.

38. Christenson HK, Claesson PM: **Direct measurements of the force between hydrophobic surfaces in water**. *Adv Colloid Interface Sci* 2001, **91**:391–436.

39. Koos E, Willenbacher N: **Capillary forces in foam rheology**.
** *Science* 2011, **18**:897–900.

The first study observing and explaining the gelation of colloidal suspensions upon addition of a small amount of an immiscible secondary liquid. Particle bridging by the secondary liquid is identified as the reason for the formation of highly elastic particle networks in either the "pendular" or the "capillary" state, depending on whether particles are wetted preferentially by the liquid bridges or by the continuous liquid phase.

40. Bossler F, Koos E: **Structure of particle networks in capillary suspensions with wetting and nonwetting fluids**. *Langmuir* 2016, **32**:1489–1501.

41. Danov KD, Georgiev MT, Kralchevsky PA, Radulova GM, Gurkov TD, Stoyanov SD, Pelan EG: **Hardening of particle/oil/water suspensions due to capillary bridges: experimental yield stress and theoretical interpretation**. *Adv Colloid Interface Sci* 2018, **251**:80–96.

42. Bossler F, Weyrauch L, Schmidt R, Koos E: **Influence of mixing conditions on the rheological properties and structure of capillary suspensions**. *Colloids Surf A Physicochem Eng Asp* 2017, **518**:85–97.

43. Hauf K, Koos E: **Structure of capillary suspensions and their versatile applications in the creation of smart materials**. *MRS Commun* 2018, **8**:332–342.

44. Velankar SS: **A non-equilibrium state diagram for liquid/fluid/**
* **particle mixtures**. *Soft Matter* 2015, **11**:8393–8403.

The structures observable in ternary mixtures of particles and two immiscible fluids are charted by the author in a threedimensional diagram parametrized by the different compositions and relative particle wettability.

45. Yang JY, Roell D, Echavarria M, Velankar SS: **A microstructure-composition map of a ternary liquid/liquid/particle system with partially-wetting particles**. *Soft Matter* 2017, **13**: 8579–8589.

46. Amoabeng D, Tempalski A, Young BA, Binks BP, Velankar SS: **Fumed silica induces co-continuity across a wide composition range in immiscible polymer blends**. *Polymer* 2020, **186**: 121831.1–121831.10.

47. Pannacci N, Bruus H, Bartolo D, Etchart I, Lockhart T, Hennequin Y, Willaime H, Tabeling P: **Equilibrium and nonequilibrium states in microfluidic double emulsions**. *Phys Rev Lett* 2008, **101**:164502.1–164502.4.

48. Shah RK, Shum HC, Rowat AC, Lee D, Agresti JJ, Utada AS, Chu LY, Kim JW, Fernandez-Nieves A, Martinez CJ, Weitz DA: **Designer emulsions using microfluidics**. *Mater Today* 2008, **11**:18–27.

49. Lee H, Choi CH, Abbaspourrad A, Wesner C, Caggioni M, Zhu TT, Nawar S, Weitz DA: **Fluorocarbon oil reinforced triple emulsion drops**. *Adv Mater* 2016, **28**:8425–8430.

50. Torza S, Mason SG: **3-Phase interactions in shear and electrical fields**. *J Colloid Interface Sci* 1970, **33**:67–83.

51. Zarzar LD, Sresht V, Sletten EM, Kalow JA, Blankschtein D,
** Swager TM: **Dynamically reconfigurable complex emulsions via tunable interfacial tensions**. *Nature* 2015, **518**:520–524.

This article reports the first dynamic reconfiguration of droplet morphologies in complex three-and four-phase emulsions and demonstrates reversible droplet reconfigurations via pH- or light-responsive surfactants.

52. Nagelberg S, Zarzar LD, Nicolas N, Subramanian K, Kalow JA, Sresht V, Blankschtein D, Barbastathis G, Kreysing M, Swager TM, Kolle M: **Reconfigurable and responsive droplet-based compound micro-lenses**. *Nat Commun* 2017, **8**: 14673.1–14673.9.

53. Zarzar LD, Kalow JA, He XP, Walish JJ, Swager TM: **Optical visualization and quantification of enzyme activity using dynamic droplet lenses**. *Proc Natl Acad Sci USA* 2017, **114**: 3821–3825.
 *
Enzyme activity is quantified and visualized by using enzyme-responsive surfactants to alter the configuration and lensing properties of three-phase emulsion droplets.

54. Goodling AE, Nagelberg S, Kaehr B, Meredith CH, Cheon SI, Saunders AP, Kolle M, Zarzar LD: **Colouration by total internal reflection and interference at microscale concave interfaces**. *Nature* 2019, **566**:523–527.
 *
Reconfigurable three-phase emulsion droplets are used to generate iridescent structural color through a previously unrecognized mechanism.

55. Cheon SI, Batista Capaverde Silva L, Ditzler R, Zarzar LD: **Particle stabilization of oil–fluorocarbon interfaces and effects on multiphase oil-in-water complex emulsion morphology and reconfigurability**. *Langmuir* 2020, https://doi.org/10.1021/acs.langmuir.9b03830 (ASAP).
 *
The authors show that the reconfiguration of o/o/w emulsion droplets by appropriate surfactants can be suppressed by particles adsorbed at the o/o interface. The droplets only relax into a thermodynamically favored new configuration, when the interface is temporarily removed by thermally driving the oils out of the miscibility gap.

56. Zhang Y, Wang S, Zhou J, Zhao R, Benz G, Tcheimou S, Meredith JC, Behrens SH: **Interfacial activity of nonamphiphilic particles in fluid–fluid interfaces**. *Langmuir* 2017, **33**: 4511–4519.

57. Zhang Y, Shitta A, Meredith JC, Behrens SH: **Bubble meets droplet: particle-assisted reconfiguration of wetting morphologies in colloidal multiphase systems**. *Small* 2016, **12**: 3309–3319.
 *
This study shows that particles can induce bubble-droplet reconfigurations from partial to complete bubble engulfment or vice versa depending on which interface the particles adsorb to preferentially. An instance of transient bubble engulfment by the oil is also observed, consistent with particle adsorption to both the air–water and oil-water interface, but with different adsorption kinetics.

58. Uematsu Y, Bonthuis DJ, Netz RR: **Impurity effects at hydrophobic surfaces**. *Curr Opin Electrochem* 2019, **13**:166–173.

59. Roger K, Cabane B: **Why are hydrophobic/water interfaces negatively charged?** *Angew Chem Int Ed* 2012, **51**:5625–5628.

60. Wang H, Singh V, Behrens SH: **Image charge effects on the formation of Pickering Emulsions**. *J Phys Chem Lett* 2012, **3**: 2986–2990.

61. Israelachvili JN: *Intermolecular and surface forces*. 3 ed. Amsterdam: Elsevier; 2011.

62. Tabor RF, Manica R, Chan DYC, Grieser F, Dagastine RR: **Repulsive van der Waals forces in soft matter: why bubbles do not stick to walls**. *Phys Rev Lett* 2011, **106**. 064501.1-064501.4.
 *
The authors use atomic force microscopy for the first direct measurement of repulsive van der Waals forces between bubbles and solids across water.

63. Alvarez NJ, Walker LM, Anna SL: **Diffusion-limited adsorption to a spherical geometry: the impact of curvature and competitive time scales**. *Phys Rev E* 2010, **82**. 011604.1-011604.8.

64. Hua XQ, Frechette J, Bevan MA: **Nanoparticle adsorption dynamics at fluid interfaces**. *Soft Matter* 2018, **14**:3818–3828.
 *
The authors use dynamic interfacial tension measurements to follow the adsorption of nanoparticles to oil-water interfaces and show that the adsorption kinetics is well described for low and moderate coverage by the Ward-Tordai model for diffusion-limited surfactant adsorption, combined with a Frumkin isotherm and a surface equation of state that accounts for the effect of particle wetting on interfacial tension. The model is further extended to cover the competitive adsorption of surfactant-particle mixtures.

65. Upadhyay A, Dalvi SV: **Microbubble formulations: synthesis, stability, modeling and biomedical applications**. *Ultrasound Med Biol* 2019, **45**:301–343.

66. Furstenau MC, Jameson GJ, Yoon R-H: *Froth flotation: a century of innovation*. Littleton, CO: SME; 2007.

67. Zhou F, Wang LX, Xu ZH, Ruan YY, Chi R: **A study on novel reactive oily bubble technology enhanced collophane flotation**. *Int J Miner Process* 2017, **169**:85–90.

68. Zhou F, Wang LX, Xu ZH, Liu QX, Chi R: **Reactive oily bubble technology for flotation of apatite, dolomite and quartz**. *Int J Miner Process* 2015, **134**:74–81.

69. Zhou F, Wang L, Xu Z, Ruan Y, Zhang Z, Chi R: **Role of reactive oily bubble in apatite flotation**. *Colloids Surf A Physicochem Eng Asp* 2017, **513**:11–19.

70. Chen SJ, Li LL, Qu JZ, Liu QZ, Tang LF, Tao XX, Fan HD: **Oily bubble flotation technology combining modeling and optimization of parameters for enhancement of flotation of low-flame coal**. *Powder Technol* 2018, **335**:171–185.

71. Wang SW, Tao XX: **Comparison of flotation performances of low rank coal in air and oily bubble processes**. *Powder Technol* 2017, **320**:37–42.

72. Maiolo J, Pelton R: **Aerosol-enhanced flotation - a possible approach to improved flotation deinking**. *J Pulp Pap Sci* 1998, **24**:324–328.

73. Ben YX, Dorris G: **Is deinkability of inkjet prints an issue?** *Tappi J* 2011, **10**:17–27.

74. Wang SC, Zhang Y, Meredith JC, Behrens SH, Tripathi MK, Sahu KC: **The dynamics of rising oil-coated bubbles: experiments and simulations**. *Soft Matter* 2018, **14**: 2724–2734.
 *
Bubbles with an oil coat are shown to rise more slowly, follow a straighter trajectory, and maintain a more compact shape than similarly sized uncoated bubbles. These qualitative features were also captured in three-dimensional bubble rise simulations treating the coated bubbles as a single phase with effective density, viscosity, and interfacial tension with the surrounding water.

75. Tripathi MK, Sahu KC, Govindarajan R: **Dynamics of an initially spherical bubble rising in quiescent liquid**. *Nat Commun* 2015, **6**:6268.1–6268.9.

76. Clift R, Grace JR, Weber ME: *Bubbles, drops, and particles*. Mineola, NY: Dover; 2013.

77. Alves SS, Orvalho SP, Vasconcelos JMT: **Effect of bubble contamination on rise velocity and mass transfer**. *Chem Eng Sci* 2005, **60**:1–9.

78. Wu M, Gharib M: **Experimental studies on the shape and path of small air bubbles rising in clean water**. *Phys Fluids* 2002, **14**:L49–L52.

79. Garbin V: **Collapse mechanisms and extreme deformation of particle-laden interfaces**. *Curr Opin Colloid Interface Sci* 2019, **39**:202–211.

80. Miller CA: **Antifoaming in aqueous foams**. *Curr Opin Colloid Interface Sci* 2008, **13**:177–182.

81. Denkov ND: **Mechanisms of foam destruction by oil-based antifoams**. *Langmuir* 2004, **20**:9463–9505.

82. Wege HA, Kim S, Paunov VN, Zhong QX, Velev OD: **Long-term stabilization of foams and emulsions with in-situ formed microparticles from hydrophobic cellulose**. *Langmuir* 2008, **24**:9245–9253.

83. Patel AR, Drost E, Blijdenstein TBJ, Velikov KP: **Stable and temperature-responsive surfactant-free foamulsions with high oil-volume fraction**. *ChemPhysChem* 2012, **13**: 3777–3781.

84. Salonen A, Lhermerout R, Rio E, Langevin D, Saint-Jalmes A: **Dual gas and oil dispersions in water: production and stability of foamulsion**. *Soft Matter* 2012, **8**:699–706.

85. Wan ZL, Sun YE, Ma LL, Zhou FB, Guo J, Hu SQ, Yang XQ: **Long-lived and thermoresponsive emulsion foams stabilized by self-assembled saponin nanofibrils and fibrillar network**. *Langmuir* 2018, **34**:3971–3980.

86. Zhang Y, Wu J, Wang H, Meredith JC, Behrens SH: **Stabilization of liquid foams through the synergistic action of particles and an immiscible liquid**. *Angew Chem Int Ed* 2014, **53**: 13385–13389.
 * *

This article reports the discovery of capillary foams. Particles too hydrophilic to stabilize Pickering foams are seen to enable the preparation of ultrastable surfactant-free foams when combined with a small amount of oil. The particle assisted spreading of oil around the bubbles and a network of oil-bridged particles connecting the bubbles are identified as characteristic features of capillary foams.

87. * Zhang Y, Allen MC, Zhao R, Deheyn DD, Behrens SH, Meredith JC: **Capillary foams: stabilization and functionalization of porous liquids and solids**. *Langmuir* 2015, **31**: 2669–2676.

Different preparation routes are found to yield the same capillary foam structure. Some potential foam applications are illustrated by preparing mold-cast and load bearing porous solids, as well as wet and dry foams with intense colors impossible to achieve in traditional foams.

88. Zhang Y, Wang S, Zhou J, Benz G, Tcheimou S, Zhao R, Behrens SH, Meredith JC: **Capillary foams: formation stages and effects of system parameters**. *Ind Eng Chem Res* 2017, **56**:9533–9540.

89. Essenmacher SD: *Particle affinity for oil-water interfaces and selective adsorption*. M.S. Thesis. Georgia Institute of Technology; 2018. https://smartech.gatech.edu/handle/1853/60242.

90. * Dunstan TS, Das AAK, Starck P, Stoyanov SD, Paunov VN: **Capillary structured suspensions from in situ hydrophobized calcium carbonate particles suspended in a polar liquid media**. *Langmuir* 2018, **34**:442–452.

The authors report on the first capillary suspensions with in-situ hydrophobized particles. Oleic acid is used to raise the affinity of water-borne hydophilic calcium carbonate particles for different oils thereby enabling the gelation of aqueous suspensions via particle bridging by the oil. The requisite hydrophobization can be achieved either by pretreating the particles ex-situ or by simply incorporating some oleic acid in the oil phase.

91. Liu J, Mak T, Zhou Z, Xu Z: **Fundamental study of reactive oily-bubble flotation**. *Miner Eng* 2002, **15**:667–676.

92. Wubneh A, Tsekoura EK, Ayranci C, Uludag H: **Current state of fabrication technologies and materials for bone tissue engineering**. *Acta Biomater* 2018, **80**:1–30.

93. Perez RA, Mestres G: **Role of pore size and morphology in musculo-skeletal tissue regeneration**. *Mater Sci Eng C-Mater Biol Appl* 2016, **61**:922–939.

94. Huang XB, Chen X, Li A, Atinafu D, Gao HY, Dong WJ, Wang G: **Shape-stabilized phase change materials based on porous supports for thermal energy storage applications**. *Chem Eng J* 2019, **356**:641–661.

95. Zhang P, Xiao X, Ma ZW: **A review of the composite phase change materials: fabrication, characterization, mathematical modeling and application to performance enhancement**. *Appl Energy* 2016, **165**:472–510.

96. Kim S, Barraza H, Velev OD: **Intense and selective coloration of foams stabilized with functionalized particles**. *J Mater Chem* 2009, **19**:7043–7049.

97. * Okesanjo O, Tennenbaum M, Fernandez-Nieves A, Meredith JC, Behrens SH: **Rheology of capillary foams**. *Soft Matter* 2020, **16**: 6725–6732.

This is the first study of capillary foam rheology. It reveals a flow behavior reminiscent of colloidal gels, but a frequency dependence of the viscoelastic shear moduli in the linear regime more akin to that of surfactant stabilized liquid foams with much higher gas volume fraction.

98. Mohraz A: **Interfacial routes to colloidal gelation**. *Curr Opin Colloid Interface Sci* 2016, **25**:89–97.

99. * Muth JT, Lewis JA: **Microstructure and elastic properties of colloidal gel foams**. *Langmuir* 2017, **33**:6869–6877.

A rheological study of colloidal gel foams in which particle decorated bubbles are embedded in a network of mutually attractive colloidal particles. The presence of the foam bubbles in the gel is seen to increase the elastic shear modulus roughly linearly with increasing specific interfacial area.

100. Minas C, Carnelli D, Tervoort E, Studart AR: **3D printing of emulsions and foams into hierarchical porous ceramics**. *Adv Mater* 2016, **28**:9993–9999.

101. Muth JT, Dixon PG, Woish L, Gibson LJ, Lewis JA: **Architected cellular ceramics with tailored stiffness via direct foam writing**. *Proc Natl Acad Sci USA* 2017, **114**:1832–1837.

102. Gopal AD, Durian DJ: **Relaxing in foam**. *Phys Rev Lett* 2003, **91**: 4.

103. Mikhailovskaya A, Trappe V, Salonen A: **Colloidal gelation, a means to study elasto-capillarity effects in foam**. *Soft Matter* 2020, **16**:2249–2255.

104. Costa S, Hohler R, Cohen-Addad S: **The coupling between foam viscoelasticity and interfacial rheology**. *Soft Matter* 2013, **9**:1100–1112.

105. Schramm LL. In *Foams: fundamentals and applications in the petroleum industry*, vol. 242. American Chemical Society; 1994.

106. Rossen WR: **Foams in enhanced oil recovery**. In *Foams - theory, measurement, and applications*. Edited by Prud'homme RK, Khan SA, New York: Marcel Dekker Inc.; 1996: 413–464.

107. Conn CA, Ma K, Hirasaki GJ, Biswal SL: **Visualizing oil displacement with foam in a microfluidic device with permeability contrast**. *Lab Chip* 2014, **14**:3968–3977.

108. Yekeen N, Manan MA, Idris AK, Padmanabhan E, Junin R, Samin AM, Gbadamosi AO, Oguamah I: **A comprehensive review of experimental studies of nanoparticles-stabilized foam for enhanced oil recovery**. *J Petrol Sci Eng* 2018, **164**: 43–74.

109. Farajzadeh R, Andrianov A, Krastev R, Hirasaki GJ, Rossen WR: **Foam-oil interaction in porous media: implications for foam assisted enhanced oil recovery**. *Adv Colloid Interface Sci* 2012, **183**:1–13.

110. * Xiao S, Zeng Y, Vavra ED, He P, Puerto M, Hirasaki GJ, Biswal SL: **Destabilization, propagation, and generation of surfactant-stabilized foam during crude oil displacement in heterogeneous model porous media**. *Langmuir* 2018, **34**: 739–749.

Three zones are identified by the authors in experiments involving the displacement of crude oil from model porous media via surfactant-stabilized foam: a displacement zone where the foam coalesces upon initial contact with the oil, a transition zone where the solid surface is altered from oil-wet to water-wet, and a foam bank zone where foam is generated within the porous media through several mechanisms.