Colloidal particles: Surfactants with a difference

Valeria Garbin

Like the more-familiar detergents, tiny particles can help keep emulsions and foams from separating into their component fluids. But their unique properties also enable novel applications.

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If you've ever luxuriated in a bubble bath, you might have wondered how the bubbly foam could last so long—after all, when you shake pure water, the air bubbles you create coalesce rapidly. The bubbles in pure water come together because the system is seeking its lowest-energy state; due to the surface tension of the air–water interface, creating bubbles costs energy. What keeps the foam in a bubble bath from breaking up is surfactant (surface-tension reducing) molecules absorbed onto the bubbles' air–water interfaces. (For details, see the Quick Study by Doug Durian and Srini Raghavan, PHYSICS TODAY, May 2010, page 62.) It is not just in foams that surfactants are used to stabilize—that is, inhibit coalescence; emulsions such as mayonnaise also include surfactants.

Though not as familiar as the detergents in bubble baths, colloidal particles can likewise act as surfactants and stabilize emulsions and foams. Moreover, as with more conventional surfactants, they don't just decrease the surface tension and thus the energy cost of forming interfaces. They can also generate an electrostatic repulsion between bubbles or droplets—as detergents do to help stabilize the bubbles in your bath—or they can simply form a physical barrier between the fluid phases.

Panel a of the figure shows a highly magnified view of a particle-stabilized emulsion. Such emulsions, called Pickering emulsions, are everywhere, as are particle-stabilized foams. Cellulose nanofibers can stabilize emulsions in low-fat foods, and nanoparticles can maintain the integrity of foams and creams in personal-care products. Engineers involved in crude-oil production face the challenge of removing residual water from oil–water emulsions kept intact by clays and sand particles. Metal foams, which are fabricated from high-temperature molten metals, need to be stabilized by solid particles. In addition, particles can have magnetic, optical, or catalytic properties that enable such innovative applications as switchable emulsions that can be destroyed by a magnetic field, responsive films with tunable optical properties, and processes to convert biomass into biofuels.

Those diverse applications present common challenges that are inspiring current research. The obvious one is to ensure that the particles of interest will spontaneously stick to the fluid–fluid interface. We also need to know how long it takes for the particles to cover the interface and how the particles modify the boundary's thermodynamic properties, factors that can affect the performance of a process or product.

A hole in the surface

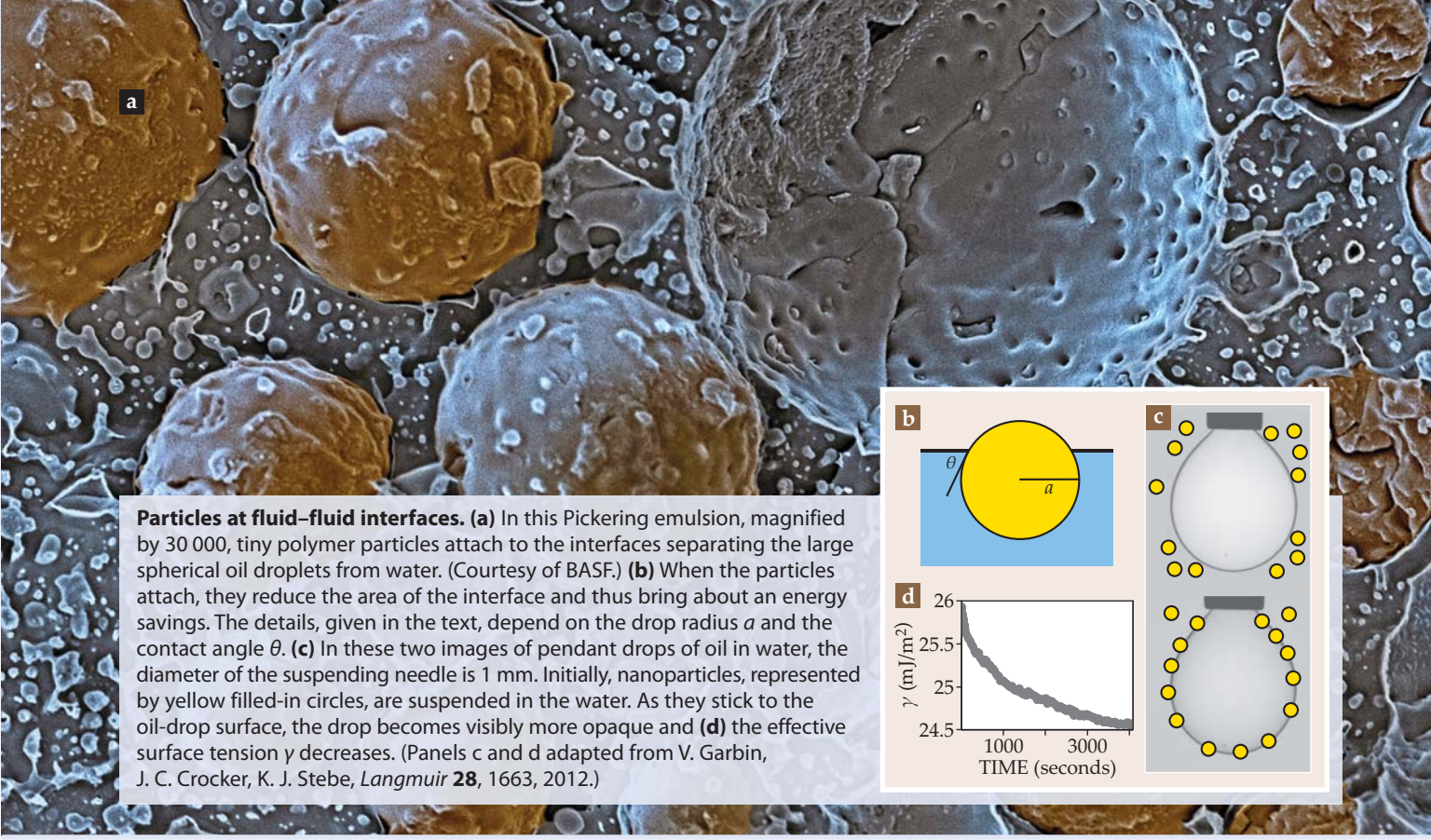
Typical surfactants are asymmetric molecules. One side is hydrophilic—likes to be in water—because its energy is reduced in an aqueous environment. The other, hydrophobic side prefers to be in air or oil. They therefore stick to fluid–fluid interfaces because they pay an energy penalty for finding themselves in the "wrong" fluid phase. A solid particle will stick to an interface even if it doesn't have sides with different properties. The reason is shown in panel b of the figure: The particle makes a hole in the fluid–fluid interface and reduces the contact area of the two fluids. Since the energy price of producing the interface is the surface tension γ_0 times the area, the hole reduces the energy cost. The size of the hole depends on how the particle straddles the interface, which may be parameterized by the contact angle θ.

In greater detail, the energy savings ΔE realized by inserting a particle of radius a into the interface may be expressed as $\Delta E = \pi a^2 \gamma_0 (1 \pm \cos\theta)^2$, where the sign depends on which fluid originally contained the particle. For a particle with a radius as small as 2 nm at an oil–water interface (for which $\gamma_0 \approx 30$ mJ/m^2), the energy savings can be up to 100 times the thermal energy $k_B T$. Therefore, unless the particles are extraordinarily tiny or θ is very close to 0° or 180°, thermal fluctuations at room temperature will not desorb the particles from the interface and back into the bulk fluid: Monolayers at fluid–fluid interfaces are robustly stable.

The contact angle is determined by Young's law, which involves not only the surface tension γ_0 between the two fluids meeting at the interface but also the surface tensions γ_{1s} and γ_{2s} between the solid particle and the two fluids: $\cos\theta = (\gamma_{1s} - \gamma_{2s})/\gamma_0$. For there to be particle absorption, the right-hand term must have a magnitude of less than one, so that the contact angle exists. Satisfying that bound may require a balancing of the surface tensions between the three media, which can be achieved by manipulating the surface properties of the particles—for example, by chemically modifying them so that they are more hydrophilic or hydrophobic. Furthermore, by engineering $\gamma_{1s} \approx \gamma_{2s}$, one can arrange for θ to be near 90°, the angle for which the energy payoff for particle sticking is greatest.

Tension via shape analysis

Adsorbed particles effectively reduce the surface tension relative to γ_0, the value for a clean interface. But if you could squeeze into the spaces between adsorbed particles and look at the fluid–fluid interface on the microscopic scale, you'd see the surface tension is unchanged. The effective reduction at the macroscopic scale arises because the adsorbed particles generate a two-dimensional pressure Π that opposes the tendency of surface tension to make surfaces contract and minimize their area. At macroscopic scales, the effective surface tension γ of



Particles at fluid–fluid interfaces. (a) In this Pickering emulsion, magnified by 30 000, tiny polymer particles attach to the interfaces separating the large spherical oil droplets from water. (Courtesy of BASF.) **(b)** When the particles attach, they reduce the area of the interface and thus bring about an energy savings. The details, given in the text, depend on the drop radius a and the contact angle θ. **(c)** In these two images of pendant drops of oil in water, the diameter of the suspending needle is 1 mm. Initially, nanoparticles, represented by yellow filled-in circles, are suspended in the water. As they stick to the oil-drop surface, the drop becomes visibly more opaque and **(d)** the effective surface tension γ decreases. (Panels c and d adapted from V. Garbin, J. C. Crocker, K. J. Stebe, *Langmuir* **28**, 1663, 2012.)

a particle-laden interface is $\gamma = \gamma_0 - \Pi$. Ultimately, the surface pressure Π is due to entropy and interparticle repulsion.

The effective surface tension can be measured with the classical methods of interface science. One approach is based on macroscopic force balance, including surface tension forces, and one specific realization of that approach is called drop-shape analysis. All that is required is an image of a drop of liquid as it hangs from a needle placed in another fluid; panel c of the figure shows two examples.

The shape of a pendant drop is determined by the balance between the downward pull of gravity and the upward pull of the surface tension that tends to restore the spherical shape of the drop. That balance is described by a nondimensional number, the Bond number $Bo = \Delta\rho g L^2/\gamma$. Here, $\Delta\rho$ is the density difference between the two fluids, g is the acceleration due to gravity, and L is a characteristic length scale, in this case, the size of the drop. If Bo is too large, gravity prevails and the drop detaches from the needle. If it's too small, surface tension prevails, the drop remains spherical, and drop-shape analysis doesn't work. Therefore the size of the drop must be compatible with an intermediate value of Bo for which both gravitational and surface-tension forces are relevant.

The equilibrium shape of the drop is governed by the fundamental equation of capillarity, the Young–Laplace equation $\Delta p = 2\gamma/R$, which relates the pressure change Δp across a curved interface to the effective surface tension and radius of curvature R. Given an image of the drop, one can extract the drop's contour, determine R as a function of the height h above the drop apex, and calculate the pressure change via $\Delta p = \Delta\rho g h$. The final steps are to solve the Young–Laplace equation numerically, fit the solution to the measured contour, and extract the effective surface tension.

Where do we go from here?

A clean fluid–fluid interface is not immediately covered by particles. Instead, the particles progressively latch on to the surface until they reach maximum coverage. As they do, Π increases and γ decreases. With the drop-shape analysis described above, one can track the temporal evolution of γ as particles are absorbed at the interface; panel d of the figure shows a representative measurement.

The seemingly simple measurements of how γ evolves provide important information on bulk transport mechanisms and the effectiveness of particles in stabilizing interfaces. Researchers have come up with clever experimental designs for exploring the two competing time scales of particle transport: diffusion rates and the kinetic rates at which particles attach to an interface. For instance, they can intentionally enhance convection to access kinetic rates. Such experiments provide data vital for, among other things, the fabrication of dispersants to clean up oil spills. Control over the rate at which particles populate an interface is central to the development of responsive films that self-assemble from suspension in response to chemical stimuli and essential to the design of novel materials that we may one day find in solar cells, sensors, and other devices. Interfacial nanoparticles are being used as catalysts, but to optimize that application we'll need to learn both how to promote particle adsorption and how to control desorption so as to recover the catalyzing particles. There are near-term benefits, too: The knowledge gained by studying particles at fluid–fluid interfaces is helping manufacturers produce their goods at less cost to the consumer and environment.

Additional resources

▶ R. G. Larson, *The Structure and Rheology of Complex Fluids*, Oxford U. Press, New York (1999).

▶ B. P. Binks, "Particles as surfactants—similarities and differences," *Curr. Opin. Colloid Interface Sci.* **7**, 21 (2002).

▶ F. Bashforth, J. C. Adams, *An Attempt to Test the Theories of Capillary Action by Comparing the Theoretical and Measured Forms of Drops of Fluid*, Cambridge U. Press, Cambridge, UK (1883), online at http://archive.org/details/cu31924012328385. ■