Thermodynamically Stable Pickering Emulsions

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We show that under appropriate conditions, mixtures of oil, water, and nanoparticles form thermodynamically stable oil-in-water emulsions with monodisperse droplet diameters in the range of 30–150 nm. This observation challenges current wisdom that so-called Pickering emulsions are at most metastable and points to a new class of mesoscopic equilibrium structures. Thermodynamic stability is demonstrated by the spontaneous evolution of binary droplet mixtures towards one intermediate size distribution. Equilibrium interfacial curvature due to an asymmetric charge distribution induced by adsorbed colloids explains the growth of emulsion droplets upon salt addition. Moreover, the existence of a minimal radius of curvature with a concomitant expulsion of excess oil is in close analogy with microemulsions.

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Two categories of oil-in-water emulsions are presently known: transparent microemulsions, having a stable droplet size below 10–20 nm, and all other normal emulsions being turbid due to much larger, unstable oil droplets that spontaneously merge together. Preparation of such normal emulsions (abundant in many food and daily life products) requires prolonged mechanical agitation and emulsifiers to retard the droplet coalescence that eventually demixes the emulsion into separate oil and water phases. In the classical Pickering emulsions [1,2], droplet coalescence is suppressed by adsorption of solid particles at the oil-water interface. The retarded coarsening has always explicitly been attributed [2–9] to a kinetic barrier resulting from the particle adsorption or a viscosity increase of the continuous phase between the droplets. Thus, Pickering emulsification is supposed to be fundamentally different from the spontaneous formation of the thermodynamically stable microemulsions. We have found, however, that a methacrylate oil phase and various types of charged colloids (iron-oxide, silica, and cobalt-ferrite nanoparticles) self-assemble in water to thermodynamically stable, opaque emulsions of monodisperse droplets much larger than in the transparent microemulsions.

This unexpected finding was made in our search for monodisperse magnetic colloidal spheres for studying the statistical physics of magnetic fluids [10–13]. We investigated the functionalization of magnetite nanoparticles [14] with 3-methacyloxypropyl trimethoxysilane (TPM) [15,16], aiming to promote encapsulation of magnetite in the polymerization of polymethylmethacrylate to magnetic polymer colloids. In exploring experiments, TPM, a transparent hydrophobic fluid, was gently stirred with aqueous dark-brown dispersions of magnetite. To our surprise, homogeneous, opaque suspensions [Fig. 1(a)] spontaneously formed that did not demix. Transmission electron microscopy (TEM) images of the suspended particles at first sight [Figs. 1(b)–1(e)] remind one of a traditional Pickering emulsion [1,2], i.e., a dispersed oil (here TPM) kinetically stabilized by solid (here magnetite) particles. We found the occurrence of monodisperse droplets (Fig. 1) rather unexpected for unstable emulsions, even though mechanically stabilized droplets are sometimes quite uniform [6]. However, other observations also threw doubt on purely mechanical stability. TPM, for example, disperses even without any agitation in aqueous magnetite dispersions, whereas formation of thermodynamically unstable emulsions often requires considerable energy input via a high-speed stirrer or a jet homogenizer [17]. Furthermore, mixing the three components—water, TPM, and magnetite fluid—in different order did not affect the final, quite reproducible droplet size. We also noted that sedimentation of emulsions under gravity produced an interface between the settling droplets and the clear supernatant water phase that remained sharp for at least several months, consistent with an unchanging narrow droplet-size distribution.

These observations lead us to the hypothesis that the opaque suspensions as in Fig. 1(a) are actually thermodynamically stable systems, where magnetite and TPM have self-assembled to oil droplets in water, with the nanoparticles inducing an equilibrium curvature of the TPM-water interface. Truly stable droplets with uniform diameters in the range 30–150 nm [Figs. 1(c)–1(e)], it should be noted, are remarkable because, on the one hand, the droplets share thermodynamic stability with the much smaller micro-emulsion droplets (radius up to 10–20 nm [18,19]), but, on the other hand, they scatter enough light for emulsions to be opaque just as the much larger, unstable micron droplets in food products as ice cream, margarine, and mayonnaise. We will now discuss various additional experiments that demonstrate thermodynamic emulsion stability, followed by a possible explanation for the existence of an equilibrium droplet size.

Confocal microscopy on a fluorescent oil phase [20] shows that without magnetite particles, TPM coalesces in quiescent water to large polydisperse spheres, precisely the coarsening expected for normal unstable emulsions. However, upon addition of magnetite dispersion, the coarsening stops and actually reverses: TPM blobs gradually...
shrink and disappear as oil disperses to uniform droplets (further details on confocal experiments are given in Ref. [20]). A crucial test pro or contra thermodynamic emulsion stability is the time dependence of the size distribution after blending two emulsions to a binary mixture of large and small emulsion droplets. If the emulsions are unstable, the interfacial Gibbs energy by definition exceeds that of a nondispersed bulk, so the droplet surface area will spontaneously decrease in time by coalescence or Ostwald ripening. Consequently, the average droplet size will grow beyond that of the large droplets in the initial mixture. If, on the contrary, the binary mixture evolves towards a stable size distribution with an average dictated by the overall amounts of TPM and magnetite, this distribution should be intermediate to the initial distributions of the starting binary mixture. Figure 2 demonstrates that the binary emulsions follow the second scenario: On a time scale of minutes, the two Gaussian parent distributions $A$ and $B$ of Fig. 2 merge into one intermediate Gaussian size distribution $C$. The latter is indeed the equilibrium state, because the same distribution is formed in a separate emulsion prepared in one step from mixing TPM and magnetite fluid in the same total amounts as in the binary mixture.

The stabilizing action of nanoparticles is not at all restricted to magnetite: We found that also (laboratory-made) cobalt-ferrite [21] and commercially available silica nanoparticles (Ludox, DuPont, average diameter 25 nm) may induce spontaneous emulsification of TPM in water [20].

We will now discuss a possible explanation for the existence of the thermodynamically stable droplet size. First, we address particle adsorption at the TPM-water interface, focusing on magnetite particles as an exemplary case. A solid particle may be trapped at an oil-water interface in a deep energy well when the particle is wetted by both oil and water [9]. Since we cannot directly assess wettability of magnetite nanoparticles, we have measured contact angles of TPM and water on a polished, cut surface of a macroscopic magnetite mineral [20]. It turns out that the mineral is indeed wetted by both liquids, though with a clear preference for TPM, which almost completely wets a magnetite surface whereas water shows a measurable con-
tact angle $\theta = 34^\circ \pm 4$. These results indicate that the colloids prefer oil over water. Assuming that reduction of the oil-water interface is the main driving force for adsorption, the adsorption free energy of a sphere with radius $R_m$ on an oil-water interface with interfacial tension $\gamma$ is [9]

$$-\pi r^2 \gamma = -\pi R_m^2 (1 - z^2) \gamma = -\pi R_m^2 (1 - \cos^2 \theta) \gamma,$$  

where $r$ is the radius of the plane of adsorption, located at a distance $zR$ ($-1 < z < 1$) from the sphere center. Spinning-drop measurements [20] yield $\gamma = 8 mN/m = 1.9kT/nm^2$ for the water-TPM interface, corresponding for $z = 0$ to an adsorption energy of about $6R_m^2kT$ ($R_m$ in nanometers). Radii of magnetite particles are typically in the range $R_m = 2–6$ nm yielding adsorption energies in the range $20–200kT$. Thus, the whole magnetite size distribution should strongly adsorb on TPM droplets, as is indeed the case: TEM images (Figs. 1 and 2,) never show free nanoparticles, in neither the case of emulsions stabilized by silica [20] nor cobalt-ferrite colloids.

We note here that, as shown in Ref. [22], the work to create the interface contains positive, quadratic terms in the colloid size, but these can be offset, at least in principle, by a negative contribution linear in the particle size, which contains the line tension. That may lead to a net negative free energy of creating the interface, which could occur for the small particles studied here, as the (positive) quadratic terms always dominate for a large colloid size. This line tension argument could explain why we never observed stable emulsions for colloids with a much larger radius than the nanoparticles in this study.

Why does the TPM-water interface adopt a particular equilibrium curvature? Kralchevsky et al. [8] predict that solid particles produce an interfacial bending moment only when they adsorb as a close-packed layer. Since the magnetite particles do not closely pack (see Fig. 1), it appears that the colloids per se do not induce preferred curvature. However, we must also pay heed to asymmetrically distributed electrical charges on both sides of the oil-water interface. On the water side, a higher concentration of surface charges will be present, tending to bend the interface around the oil phase. In other words, asymmetric double layers are forced to overlap owing to the strong colloid adsorption, and the resulting osmotic bending stress will be spontaneously released by surface curvature, which increases the interfacial distance between adsorbed colloids. Even if this increase is modest, its effect will be substantial if the double-layer repulsion between adsorbed colloids varies steeply with their separation distance. In addition, ions from nonoverlapping double-layer parts also contribute to the bending moment, because they also gain entropy as ion clouds expand due to curvature. These effects are well known in microemulsions with charged surfactants [18].

Several observations clearly confirm the essential role of counterions in the preferred curvature in our emulsions. If adsorbed colloids indeed repel each other via hemispherical double layers, the addition of salt should reduce the occupied area per colloid and, consequently, increase the emulsion droplet radius. Figure 3(a) shows that the addition of NaCl increases the turbidity of an emulsion, manifesting according to dynamic light scattering [Fig. 3(a)] indeed spontaneous growth of monodisperse droplets towards a larger equilibrium size. A second consequence of hemispherical double-layer repulsions is that growth of oil droplets to accommodate added TPM is limited: Reduction of the interfacial curvature builds up osmotic bending
stress until further uptake of added oil is prohibited, leading to expulsion of excess oil. We indeed find clear evidence for this scenario, as further explained in the legend of Fig. 3(b). A third observation confirming the important role of counterions is that lowering the pH to near-neutral values destroys emulsion stability, presumably because the charge density on the colloids is becoming too low to produce a significant osmotic bending stress. With respect to the salt effect in Fig. 3, we note an interesting analogy with microemulsions [18] for which the average droplet radius \( R \) depends on the salt concentration \( c \) via \( (1/R) = A - B ln c, \) with \( A \) a constant, and \( B = kT/\pi Q K, \) where \( Q \) denotes the Bjerrum length in water (0.72 nm at \( T = 298 \) K). It is assumed here [18] that the bending elastic modulus \( K \) is much larger than the thermal energy \( kT \). Also, for our stable Pickering emulsion, the droplet radius increases with salt concentration \( (R = 50 \text{ nm for } c = 5 \text{ mM}, R = 97 \text{ nm for } c = 10 \text{ mM}) \). Moreover, these data correspond to a bending modulus of about \( K \approx 33kT \), which clearly implies an oil-water interface that is stiff on the emulsion length scale, just as in the case of microemulsions.

The thermodynamic size control of our particle-stabilized emulsions is an important advantage for their applications. Magnetite-TPM emulsions, for example, can be employed as templates for monodisperse magnetic latex spheres, which are difficult to synthesize otherwise [23]. Further, the methacrylate groups in TPM allow polymerization (by light or initiator) of droplets to solid spheres of the same size that remain in stable suspension. This enables us to quantify particle growth [Figs. 1(c)–1(e) and 3(b)] and size distributions (Fig. 2), circumventing the usual problems, such as the fixation of emulsions for the electron microscope [2] in the analysis of droplets that are too small for imaging by light microscopy.

In conclusion, we have demonstrated the spontaneous self-assembly of nanoparticles, oil, and water to truly stable emulsions with a uniform droplet size intermediate between microemulsions and the unstable normal macroemulsions. Clear evidence for thermodynamic stability is provided by the reproducibility of droplet sizes, the time evolution of the size distribution in a binary droplet mixture, and the spontaneous oil dispersal observed \emph{in situ} via confocal microscopy and dynamic light scattering. Equilibrium curvature plays a key role in our emulsions and appears to derive from the preference of counterions for one side of the interface, as confirmed by the peculiar salt effect on droplet growth, and the existence of a minimal curvature with expulsion of excess oil. In view of the high energy input in the usual mechanical emulsion preparation, it is clearly of interest to extend the search for other stable combinations of oil and nanoparticles. Our observation of spontaneous emulsification for three types of nanoparticles (magnetite, silica, and cobalt ferrite) warrants the expectation that many more exceptions may exist to the conventional distinction between stable microemulsions and unstable normal emulsions.

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