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PAPER

Can Janus particles give thermodynamically stable Pickering emulsions?

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Emulsions stabilised by solid particles with homogeneous surfaces are thought to be kinetically rather than thermodynamically stable. In the absence of effects due to negative line tension in the contact line around adsorbed particles, the free energy of forming an emulsion droplet coated with a monolayer of adsorbed spherical particles is expected always to be positive, and is dominated by the presence of a fraction of uncovered oil–water interface on the droplet between the particles. It is believed however that particles with well-defined surface areas of different wettability (Janus particles) can be adsorbed considerably more strongly than particles of homogeneous wettability. Here we explore how the greater magnitude of the adsorption free energy of Janus particles can affect the free energy of emulsion formation and show, using a simple approach, that negative free energy changes appear possible. We take into account lateral interactions between adsorbed particles at droplet surfaces arising from electrical, hydration and van der Waals forces.

1. Introduction

It is generally agreed that, in the absence of effects due to line tension, (Pickering) emulsions formed using spherical solid particles with homogeneous wettability, whilst they can be extremely stable in a kinetic sense, are not thermodynamically stable.† This has been shown for example by the pioneering work of Levine and co-workers[1,2] who built on the earlier studies of Menon *et al.*[3–5] The lack of thermodynamic stability arises because bare oil–water interface remains between adsorbed particles at droplet surfaces. It turns out that the positive free energy of forming this bare interface always outweighs the negative contribution arising from particle adsorption. The contribution from particle adsorption can however be increased considerably by using particles with well-defined regions of suitably differing wettability (Janus particles).

As shown previously, in principle the existence of a line tension τ in the solid-liquid–liquid contact line around adsorbed particles can have an effect on particle adsorption and hence emulsion stability, especially in systems with nanoparticles.[6] Negative τ (expansile line) renders the adsorption free energy of a particle more negative, whereas positive τ gives a more positive free energy, and if of sufficient magnitude it can inhibit particle adsorption altogether.

Model systems consisting of monodisperse emulsions, stabilised solely by monodisperse spherical Janus particles and

formed from equal volumes of nonpolar oil (such as an alkane) and water are considered here.

2. Adsorption free energies of isolated Janus particles at the oil–water interface

2.1 Preliminary remarks

The approach used is based on that described in previous work.[6] Particles are supposed to be adsorbed onto drop surfaces from the phase which preferentially wets the particles, and to form hexagonally-packed monolayers on the drops. The liquid volume of a drop is constant and so the drop radius R, measured to the oil–water interface, increases with particle adsorption. The bare oil–water interface between particles is taken to be spherically curved, and the (very small) effect of droplet curvature on the adsorption free energy of the particles can be accounted for. The free energy of formation of an emulsion can be expressed

$$\Delta_{em}G = n_d\Delta_d G = n_d\{A_{ow}\gamma_{ow} + n_p(\Delta_a G - T\Delta_a S)\} \qquad (1)$$

where n_d and n_p are respectively the number of drops in the emulsion and the number of particles adsorbed onto a drop; the free energy of forming a particle-coated drop is denoted $\Delta_d G$. In eqn (1), A_{ow} represents the surface area of a bare, notionally swollen drop (interfacial tension γ_{ow}) but with no particles adsorbed. $\Delta_a G$ is the free energy of adsorption of a particle to the drop surface excluding the entropy change, $\Delta_a S$, due to de-mixing of particles from the phase in which they are initially dispersed. The entropy of dispersion of the droplets in the continuous phase, which in the current context is very small, is ignored.

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† A special case of a thermodynamically stable emulsion involving solid particles is reported by Kraft *et al.* (see *e.g. J. Phys. Chem.*, 2010, **114**, 12257 and earlier papers), but amphiphilic ions derived from hydrolysis of the oil phase used are implicated in the stabilisation.

Below, expressions for the adsorption free energies for a range of spherical Janus particles at the oil–water interface are first reviewed and it is shown by how much the magnitude of the free energies can exceed those for homogeneous particles of the same size. Following this, illustrations are given of how the adsorption of Janus particles can lead to negative free energies of emulsion formation, and it is shown how lateral attractive and repulsive interactions between adsorbed particles modify $\Delta_{em}G$.

When a particle of homogeneous wettability is adsorbed to the oil–water interface, part of the particle is transferred to the less wetting phase. The driving force for the adsorption comes from the removal of oil–water interface, with tension γ_{ow}. Nonetheless, a drop with a close-packed particle monolayer has bare oil–water interface remaining between the particles, the area of which varies with the contact angle of the particle with the oil–water interface (θ_p in Fig. 1). For hexagonally close-packed spheres at a (plane) oil–water interface, with $\theta_p = 90°$, only a fraction 0.906 of the oil–water interface is removed by adsorption; the fraction is less for all other contact angles. Because of this, the free energy of formation of a particle-coated emulsion drop is positive.

Janus particles however can adsorb more strongly at oil–water interfaces than particles with homogeneous wettability.[7–9] For example, an apolar (hydrophobic) cap on a particle with an otherwise polar (hydrophilic) surface‡ renders the already surface active particle amphiphilic in addition. Janus particles can now be prepared with good control over the areas of hydrophilic and hydrophobic parts and their wettabilities.[10]

With reference to Fig. 1, the area of the apolar region of a spherical Janus particle is expressed in terms of the angle α, and its wettability is represented by the contact angle, θ_a (not shown). The latter is the contact angle of the apolar surface with the oil–water interface, as for example when a purely apolar sphere rests at the oil–water interface. Two categories of Janus particles are considered. Depicted in Fig. 1(a) is the case where the contact angle of one or other of the particle surfaces (the polar surface in the example shown) can attain its equilibrium contact angle (θ_p in this case) with the oil–water interface. If the extent of the apolar surface is increased however, such that $\alpha > \theta_p$ as in Fig. 1(b), it is
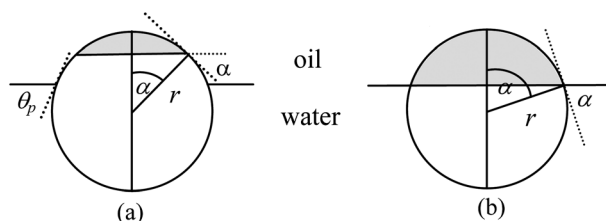
not possible to access the equilibrium contact angle and the particle is located in the oil–water interface at the horizontal circular boundary between the polar and apolar surfaces of the particle.

The approach here is a macroscopic one, and may well be inappropriate for systems with nanoparticles, say with radius of the order of 10 nm. Cheung and Bon,[11] using Monte Carlo simulations, show that nanoparticles have considerable orientational freedom at a fluid interface. Further, the presence of capillary waves broadens the particle-interface interaction significantly beyond the particle radius. For larger Janus particles however, with radius $\geq$ 100 nm say, it is reasonable to suppose that particles will be oriented at oil–water interfaces with each of the two surfaces on a particle being (mainly) in contact with the more wetting of the two liquid phases,[12] as illustrated in Fig. 1. No account is taken of effects that may arise as a consequence of surface roughness of the particles.[13]

In all the examples that follow, unless otherwise mentioned, the systems contain spherical particles with radius $r = 100$ nm adsorbing to the oil–water interface with tension $\gamma_{ow} = 0.05$ N m^{-1}, similar to that for interfaces between alkanes and water.

2.2 Particles exhibiting an equilibrium contact angle with the oil–water interface

Expressions for the free energies of adsorption, and of transfer of particles between oil and water phases, are readily obtained from the areas of solid surfaces transferred between liquid phases, and the difference between the final and initial solid-liquid interfacial tensions. The latter are related to contact angles and the oil–water interfacial tension *via* Young's equation. When the free energy of emulsion formation is considered later, it is supposed that the emulsion is made from oil and water with the particles originally dispersed in the more wetting phase, so that $\Delta_{em}G$ is expressed relative to the lower of the two free energy states. For this reason free energies of adsorption of particles from the more wetting phase are considered below.§

The free energy of adsorption of a Janus particle to the oil–water interface from the more wetting liquid phase is given by[7,8,11]

$$\frac{\Delta_a G}{2\pi r^2 \gamma_{ow}} = (1 \pm \cos\alpha)(\cos\theta_a - \cos\theta_p) - 0.5(1 \pm \cos\theta_x)^2 \quad (2)$$

For adsorption from water with $\alpha < 90°$ (*i.e.* for $\Delta_a^{w\to ow}G$) the signs in the first and third brackets are both negative and θ_x is θ_p. When $\alpha > 90°$ and adsorption is from oil, the signs in the two brackets are both positive and θ_x is θ_a. The convention is followed throughout that contact angles are always taken across the *aqueous* phase. Suppose that θ_a (θ_p) is held constant as θ_p (θ_a) is increased. At some stage, when $\theta_x = \theta_{x,t}$, the preferred phase for the particles flips from water (oil) to oil (water), and then adsorption of the particles from the oil (water) phase is considered. The expression for the free energy of adsorption after transfer of particles from one liquid phase to the other is

Fig. 1 (a) A polar Janus particle with an apolar cap (shaded). An equilibrium contact, θ_p, of the polar region is attained with the oil–water interface. (b) The extent of the apolar cap is larger such that $\alpha > \theta_p$ and no equilibrium contact angle with the oil–water interface is possible. The particle is pinned in the oil–water interface at the boundary between the polar and apolar regions.

‡ A polar surface is taken to be one for which $\theta_p < 90°$ and an apolar surface one for which $\theta_a > 90°$. A "cap" is the region of spherical surface with area less than that of a hemisphere.

§ For systems with equal volumes of oil and water and homogeneous particles it is often (but not always) found that, for example, for $\theta < 90°$ oil-in-water emulsions are formed, *i.e.* particles are adsorbed from the continuous rather than the droplet phase of the favoured emulsion. It is this case that is considered in the paper.

$$\frac{\Delta_a G}{\pi r^2 \gamma_{ow}} = -(1 \pm \cos\theta_x)^2 \qquad (3)$$

The positive sign in the bracket is to be taken with $\theta_x = \theta_p$ and the expression is then for adsorption from oil, *i.e.* for $\Delta_a^{o \to ow} G$. For adsorption from water after transfer from oil, the sign brackets is negative and $\theta_x = \theta_a$.

The contact angle $\theta_{p,t}$ or $\theta_{a,t}$ can be obtained from the expression for the free energy of transfer of a particle from one liquid phase to the other, $\Delta_t G$:

$$\frac{\Delta_t G}{2\pi r^2 \gamma_{ow}} = \pm(1 - \cos\alpha)\cos\theta_a \pm (1 + \cos\alpha)\cos\theta_p \qquad (4)$$

The positive signs in front of the brackets in eqn (4) refer to transfer from water to oil as θ_p is increased, and the negative signs are for transfer from oil to water as θ_a is decreased. When $\theta_x = \theta_{x,t}$, $\Delta_t G = 0$ so that from eqn (2)

$$\cos\theta_{p,t} = \cos\theta_a\left(\frac{\cos\alpha - 1}{\cos\alpha + 1}\right); \cos\theta_{a,t} = \cos\theta_p\left(\frac{\cos\alpha + 1}{\cos\alpha - 1}\right) \qquad (5)$$

It is clear from Fig. 1 that, for example, for the polar surface of a particle to remain in contact with the oil–water interface θ_p must exceed α. Since only adsorption from the preferred phase is of interest here, calculations using eqn (2) are restricted to the range of angles $\alpha < \theta_p < \theta_{p,t}$ for $\alpha < 90°$, and to the range $\theta_{a,t} < \theta_a < \alpha$ for $\alpha > 90°$.

When the free energy of transfer of a particle between liquids is zero and $\theta_x = \theta_{x,t}$, $\Delta_a G$ is obviously the same for adsorption of a particle from water and from oil. Jiang and Granick[14] define the quantity $\Delta_a^{o \to ow} G / \Delta_a^{w \to ow} G$, which they term the Janus balance, J. As pointed out by them, and as is seen below, the magnitude of the free energy of adsorption is maximum when $\theta_x = \theta_{x,t}$ and $J = 1$.

An illustration of how free energies of adsorption vary with θ_p (for $\alpha < 90°$) and θ_a ($\alpha > 90°$) is given in Fig. 2. In Fig. 2a

adsorption free energies, calculated using eqn (2), are shown as a function of θ_p for the adsorption from water of polar particles with apolar caps ($\alpha < 90°$), for various values of α as indicated. The full line with positive slope on the right of the diagram, passing through $\theta_{p,t}$ for the various values of α, represents the (common) adsorption free energy of the particles from oil after transfer, calculated using eqn (3). In Fig. 2b similar results are given for apolar particles with polar caps ($\alpha > 90°$) adsorbed from oil for various α. For the values of parameters chosen (see figure legend), Fig. 2b is the mirror image of Fig. 2a

Minimum free energy of adsorption. It is clear from Fig. 2 that the introduction of an apolar (polar) cap onto a polar (apolar) particle increases the magnitude of the free energy of adsorption. The minimum of a curve of, say, free energy of adsorption *versus* θ_p for a given α and θ_a (as in Fig. 2a) corresponds, as seen, to the condition where the distribution of particles is equal between oil and water phases and $\theta_p = \theta_{p,t}$. As α is increased, α and $\theta_{p,t}$ mutually approach and the absolute minimum in adsorption free energy for a given value of θ_a, $\Delta_a^{w \to ow} G_m$, corresponds to $\alpha = \theta_{p,t}$ and these parameters are denoted α_m and $\theta_{p,tm}$. The relationship between $\alpha_m (= \theta_{p,tm})$ and θ_a can, by reference to eqn (5), be seen to be

$$\cos\theta_a = \cos\alpha_m\left(\frac{\cos\alpha_m + 1}{\cos\alpha_m - 1}\right) \qquad (6)$$

and noting eqn (2), $\Delta_a^{w \to ow} G_m$ is given by

$$\frac{\Delta_a^{w \to ow} G_m}{2\pi r^2 \gamma_{ow}} = (1 - \cos\alpha_m)(\cos\theta_a - \cos\alpha_m) - 0.5(1 - \cos\alpha_m)^2 \qquad (7)$$

To obtain α_m as a function of θ_a, the required root of eqn (6) is

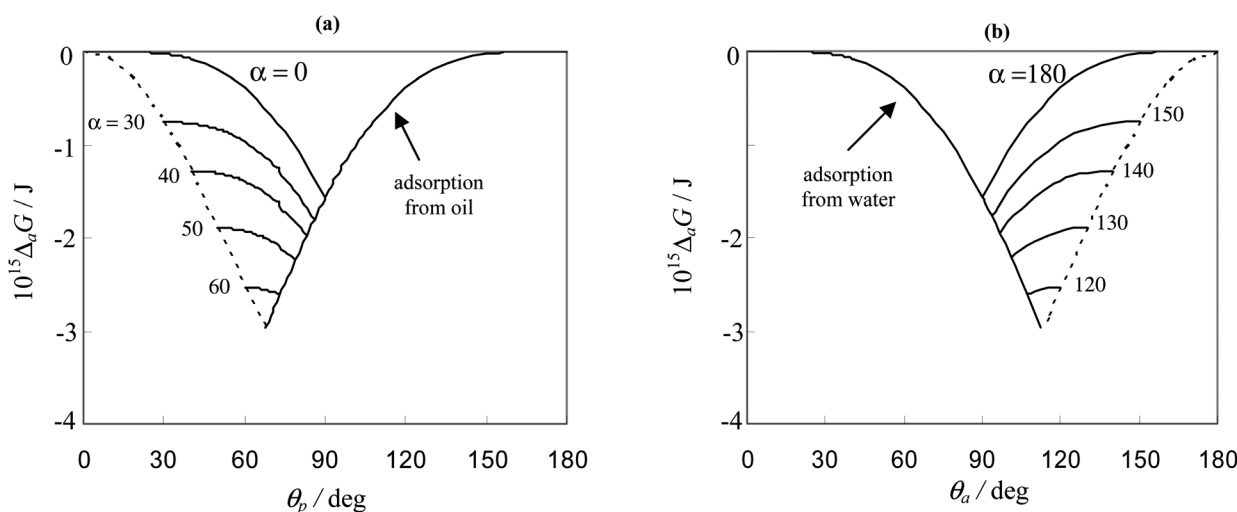$$2\cos\alpha_m = (\cos\theta_a - 1) + \{(1 - \cos\theta_a)^2 - 4\cos\theta_a\}^{0.5} \qquad (8)$$

(a)

(b)

Fig. 2 Free energies of adsorption as a function of θ_p or θ_a of isolated spherical Janus particles, radius 100 nm, at the oil–water interface with $\gamma_{ow} = 50$ mN m^{-1}. (a) Adsorption from water of polar particles with an apolar cap ($\theta_a = 150°$) whose size is defined by the angle α as indicated on the curves. The curves are truncated at α as indicated by the dotted line on the left. The full curve with positive slope is for the adsorption of the particles from oil for $\theta_p > \theta_{p,t}$ (see text). (b) Adsorption from oil of apolar particles with a polar cap ($\theta_p = 30°$). The curves are truncated at α as indicated by the dotted line on the right. The full curve with negative slope is for the adsorption of the particles from water for $\theta_a < \theta_{a,t}$.
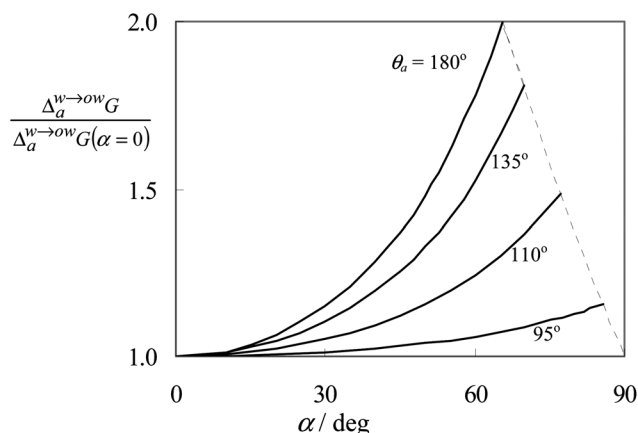
Fig. 3 Minimum free energies of adsorption, relative to that at $\alpha = 0°$, as a function of α. Each curve is for a given value of θ_a as indicated and is truncated at $\alpha = \alpha_m = \theta_{p,t\,m}$, where the free energy is $\Delta_a^{w\rightarrow ow}G_m$ (shown by the dashed line). Assumed values are $r = 100$ nm and $\gamma_{ow} = 50$ mN m^{-1}.

In Fig. 3 minimum adsorption free energies are presented as a function of α for various θ_a (in the range 90° to 180°). The energies are given relative to the minimum free energy for $\alpha = 0°$, *i.e.* that for a homogeneous particle with $\theta = 90°$, which is $-\pi r^2 \gamma_{ow}$; the larger the ratio the more negative the adsorption free energy of the Janus particle. Each of the curves in the figure is truncated at α_m corresponding to a given θ_a, and the dashed line passes through the lowest minimum adsorption free energies, $\Delta_a^{w\rightarrow o}G_m$ for the various θ_a. For $\theta_a = 180°$, α_m is 65.53°, and interestingly the free energy of adsorption for $\alpha = \alpha_m$ is twice that for $\alpha = 0°$. That is, for a system with given particle size and oil–water interfacial tension, the largest possible magnitude of the adsorption free energy is that for $\theta_a = 180°$ and $\theta_p = \theta_{p,tm} = \alpha_m$, given by eqn (6) and (8). The right hand side of eqn (7) is -1 for $\theta_a = 180°$ as can be seen by introducing α_m obtained by use of eqn (6).

Results can be obtained similarly for apolar particles with polar caps and are the mirror image around 90° of those in Fig. 3. The minimum of minima of adsorption free energies in this case is given when $\theta_p = 0°$, for $\alpha_m = 114.47°$.

2.3 Particles without an equilibrium contact angle with the oil–water interface

If an equilibrium contact angle cannot be attained it is supposed that a Janus particle rests in the oil–water interface with the boundary between its polar and apolar regions coplanar with the interface, as illustrated in Fig. 1(b). In this case, the free energies of adsorption of a particle from water and from oil respectively, are given by

$$\frac{\Delta_a^{w\rightarrow ow}G}{\pi r^2 \gamma_{ow}} = -\left[2(\cos\alpha - 1)\cos\theta_a + \left(1 - \cos^2\alpha\right)\right] \quad (9)$$

$$\frac{\Delta_a^{o\rightarrow ow}G}{\pi r^2 \gamma_{ow}} = -\left[2(1 + \cos\alpha)\cos\theta_p + \left(1 - \cos^2\alpha\right)\right] \quad (10)$$

As an example, in what follows adsorption from water is considered using eqn (9). The limits of θ_a between which the particle (i) has no equilibrium contact angle with the oil–water

interface and (ii) transfers to oil are (i) α and (ii) $\theta_{a,t}$ given by eqn (5). Some illustrations are given in Fig. 4 of the way in which the adsorption free energy varies with θ_a; results are expressed relative to the free energy of adsorption of a homogeneous particle of the same size with a contact angle of 90° ($-\pi r^2 \gamma_{ow}$), which as mentioned is the maximum magnitude of the adsorption free energy for a homogeneous particle.

The two full curves in Fig. 4 are for particles with $\theta_p = 30°$; the lower of the curves is for $\alpha = 80°$, and the particles do not transfer to oil below $\theta_a = 180°$. The upper full curve is for particles with $\alpha = 100°$, for which oil becomes the more wetting phase when $\theta_a = 127.5°$. The dashed curve is given for $\alpha = 90°$ and $\theta_p = 0$, and as seen the magnitude of the adsorption free energy reaches its maximum of three times that for adsorption of a homogeneous particle with $\theta = 90°$. This is also readily appreciated by inspection of eqn (9).

A Janus particle pinned at the oil–water interface, although unable to access an equilibrium contact angle, is nonetheless trapped in an energy minimum. Suppose a vertical force F is applied to an adsorbed Janus particle with $\alpha = 90°$. If the contact line slips around the particle either apolar surface will be submerged in water or polar surface in oil (hatched area in Fig. 5a). The free energy change $\Delta\uparrow G$ for an upward displacement (causing an increase in angle ϕ from 90°) is given by

$$\Delta\uparrow G = -\pi r^2 \gamma_{ow}\cos\phi[2\cos\theta_p - \cos\phi] \quad (11)$$

For a Janus particle with $r = 100$ nm and $\theta_p = 45°$ at an interface with $\gamma_{ow} = 0.05$ N m^{-1}, the change in free energy accompanying a change in ϕ from say 90 to 95° is about $5 \times 10^4\ kT$.

If the contact line rather than slipping, remains pinned to the oil–water interface a vertical force is required to create a meniscus as illustrated in Fig. 5b. Neglecting buoyancy effects for such small particles, the (capillary) force F required to form the meniscus is

$$F = 2\pi r \gamma_{ow}\cos\psi \quad (12)$$

The curvature of the meniscus in Fig. 5b is greatly exaggerated; the capillary length in systems of interest is about 4 mm. For a sphere with radius 100 nm at a fluid interface with tension 0.05 N m^{-1}, the meniscus height h for $\psi = 85°$ can be shown[15] to
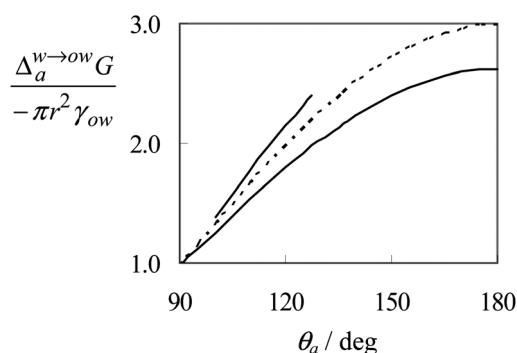

Fig. 4 Free energies of adsorption of Janus particles from water relative to the free energy of adsorption of a homogeneous particle with $\theta = 90°$. Lower full curve is for $\alpha = 80°$ and $\theta_p = 30°$, and upper full curve is for $\alpha = 100°$ and $\theta_p = 30°$. The dashed curve is for $\alpha = 90°$ and $\theta_p = 0°$.
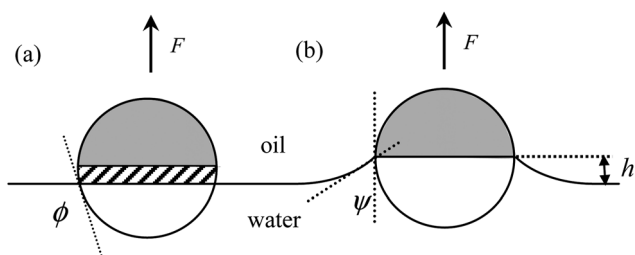
Fig. 5 An upward force F is applied to a Janus particle (with $\alpha = 90°$) at an oil–water interface. (a) The contact line slips around the particle and the hatched area of polar surface is transferred from water to oil, giving an increase in ϕ above 90°. (b) The contact line is pinned to the oil–water interface and the meniscus around the particle is formed as illustrated.

be about 100 nm. The work of lifting the adsorbed particle through this height is of the order of $3 \times 10^4 kT$.

In summary, the magnitude of the free energies of adsorption of Janus particles can be considerably greater than for homogeneous particles of the same size and at the same interface. The greatest free energy of adsorption of a homogeneous particle (which is for $\theta = 90°$) is $-\pi r^2 \gamma_{ow}$. On the other hand the maximum free energy of adsorption of a Janus particle which exhibits an equilibrium contact angle with the oil–water interface is $-2\pi r^2 \gamma_{ow}$. For Janus particles that consist of 2 hemispheres of different wettability, the maximum possible free energy of adsorption is $-3\pi r^2 \gamma_{ow}$.

3. Stabilisation of emulsions by particles

3.1 Free energies of emulsion formation

When the free energies of adsorption of particles are introduced into calculations of $\Delta_{em}G$ using eqn (1)[6] results such as those presented in Fig. 6 for the formation of 1 m³ monodisperse emulsion with equal volumes fractions ϕ (=0.5) of oil and water
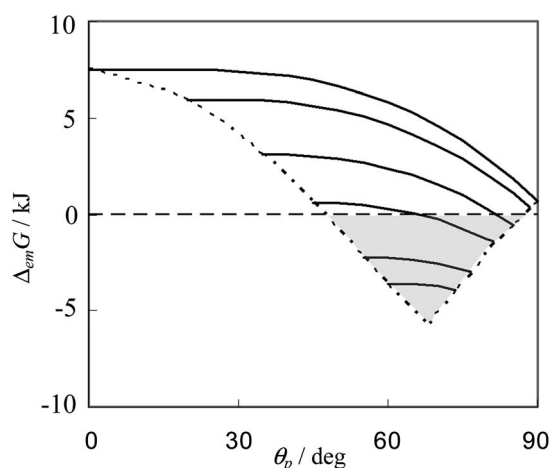

Fig. 6 Free energy of formation of 1 m³ (with $\phi_o, \phi_w = 0.5$) monodisperse Pickering emulsions (drop radius $R = 10$ μm), stabilised by Janus particles, as a function of θ_p. Values assumed are $\gamma_{ow} = 50$ mN m⁻¹, $r = 100$ nm and $\theta_a = 150°$. The curves are for, from top, $\alpha = 0, 20°, 35°, 45°, 55°$ and 60° and are truncated at α at low angles and at $\theta_{p,t}$ at high angles, as indicated by the dashed lines.

are obtained. In this example the particles are polar with apolar caps and have equilibrium contact angles with the oil–water interface, θ_p. They are adsorbed from water to the droplet interfaces and the emulsions are expected to be oil-in-water type,[6] although this does not emerge from the present treatment. The (un-swollen) drop radius R has been taken as 10 μm, and the particle radius is 100 nm.[¶] Curves are given for a range of α and, for the reasons discussed are truncated at $\theta_p = \alpha$ at low angles and at $\theta_{p,t}$ at high angles. Values of other relevant parameters are given in the figure legend. Importantly, negative values of $\Delta_{em}G$ are evident over a range of α and θ_p (shaded area in the figure). Also presented in Fig. 7 are results for emulsions formed with polar Janus particles that have apolar caps of a fixed size ($\alpha = 60°$) and a range of wettabilities (θ_a). For the regime represented all $\Delta_{em}G$ values are negative.

Similar calculations can be made for emulsions stabilised by apolar particles with polar caps, and again negative values of $\Delta_{em}G$ can result. For example, if θ_p is set at 30°, θ_a is varied (from 90° to 180°) and α values which are the complements of those represented in Fig. 6 are assumed, the free energy diagram obtained is the mirror image of that in Fig. 6.

Since the free energy of emulsion formation arises as the relatively small difference between the free energy of forming bare droplet interface and the free energy of particle adsorption, the design of Janus particles can be expected to be an important factor in the stability of Pickering emulsions. As seen, the maximum adsorption free energy of a Janus particle can be up to three times greater than that for a homogeneous particle of the same size. For example, if we exclude lateral interactions between adsorbed particles (see below) and $\Delta_a S$ (eqn (1)), the free energy of forming an emulsion with homogeneous particles with $\theta = 90°$
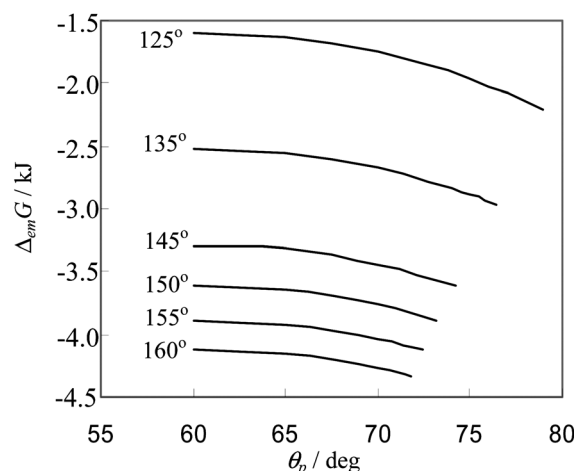

Fig. 7 Free energy of formation of 1 m³ ($\phi_o, \phi_w = 0.5$) monodisperse Pickering emulsions (drop radius $R = 10$ μm) stabilised by Janus particles, as a function of θ_p. Values assumed are $\gamma_{ow} = 50$ mN m⁻¹, $r = 100$ nm and $\alpha = 60°$. The curves, which are for the values of θ_a indicated, start at 60° (=α) and are truncated at $\theta_{p,t}$.

[¶] The surface of a drop with un-swollen radius of 10 μm contains of the order of 3.6×10^4 close-packed particles with radius 100 nm. The radius of the particle-coated drop up to the oil–water interface is about 10.03 μm for $\theta_p = 70°$.

is +0.7 kJ (Fig. 6). Using Janus particle with $\alpha = 65.53°$ and $\theta_a = 180°$ (see Fig. 3), $\Delta_{em}G$ is now -5.9 kJ. If particles with $\alpha = 90°$ are employed, the greatest magnitude of $\Delta_{em}G$ attainable is -12.9 kJ for $\theta_a = 180°$ and $\theta_p = 0$.

3.2 Effect of lateral interactions between adsorbed particles

It is likely that particles of interest will carry some surface charge and will mutually repel neighbouring adsorbed particles. For a number of systems the repulsion is mediated mainly through the oil phase,[16] and it is this that gives rise to the highly ordered particle monolayers at oil–water interfaces observed experimentally.[16,17] The electrical repulsion will be partly offset by attractive interactions arising from lateral van der Waals forces.

The average electrical energy of repulsion, U_{elec}, per particle in a hexagonally packed monolayer of spherical particles is given by[6]

$$U_{elec} = \frac{q^2}{2\pi\varepsilon_o\varepsilon_r}\left[\frac{1}{L} - \frac{1}{\sqrt{L^2+16\varsigma^2}} + \frac{1}{L}\ln\left\{\frac{1+\sqrt{1+16\varsigma^2/L^2}}{2}\right\}\right] \tag{13}$$

The interaction through oil is long range, and eqn (13) takes into account many body interactions, as well as the presence of image charges in the water at the interface. The charge at the particle-oil interface is taken to be a point charge q a distance $\varsigma = r(3 + \cos\theta)/2$ from the lowest part of the particle-water interface as illustrated in Fig. 8. The particle is supposed to have a low relative permittivity ε_r, similar to that of the oil; ε_r is about 2–3 for polystyrene and 3–4 for silica, similar to that for alkanes of about 2. In eqn (13), L is the separation between centres of neighbouring particles in the monolayer and is equal to $2r$ in a close-packed monolayer. Interaction energies of all kinds (see below) must be added to $\Delta_a G$ to give the net free energy of particle adsorption into the monolayer. In considering the electrical repulsion, no distinction is made between hydrophobic and hydrophilic surfaces of particles in contact with the oil.

To calculate U_{elec} physically realistic values of q, which is the product of the area of particle surface in contact with oil and the surface charge density σ at the solid-oil interface, are needed. For hydrophobised silica surfaces in alkane Horozov et al.[17] report low values of σ in the range 1–80 μC m^{-2}; here the upper limit of 80 μC m^{-2} is taken, and the effects of a much higher value of 800 μC m^{-2} are also considered. To illustrate how the presence of surface charge can influence $\Delta_{em}G$ the adsorption, from water, of polar particles having an apolar cap with $\alpha = 60°$ and

$\theta_a = 150°$, is considered. This is one of the systems represented in Fig. 6 and 7. For $\sigma = 80$ μC m^{-2} the magnitude of $\Delta_a^{w\to ow}G$ is between 10^3 and 10^4 times greater than that of U_{elec}, and the charge has a negligible effect on the free energy of emulsion formation. For $\sigma = 800$ μC m^{-2} however, the electrical energy is increased by a factor 10^2 (since $U_{elec} \propto q^2$) and U_{elec} ranges from about 1.5 to 3% of $\Delta_a^{w\to ow}G$. The way in which this influences $\Delta_{em}G$ is illustrated in Fig. 9. The effect is significant, rendering $\Delta_{em}G$ less negative by about 5% for $\theta_p = 60°$ and by about 10% for $\theta_p = 74°$; importantly however $\Delta_{em}G$ remains negative.

Estimates of the magnitudes of attractive van der Waals interactions between adsorbed particles can be made using the expression for *two* like particles given by Levine et al.:[1]

$$U_{vdW}(D) = -\frac{A_w}{24D}\left[1 + \frac{r\cos\theta_p}{\sqrt{Dr+r^2\cos^2\theta_p}}\right]$$
$$-\frac{A_o}{24D}\left[1 - \frac{r\cos\theta_p}{\sqrt{Dr+r^2\cos^2\theta_p}}\right] \tag{14}$$

Here, A_w and A_o are the Hamaker constants for the interaction of a pair of particles across water and oil respectively. The closest separation between particle surfaces, D, is $(L - 2r)$, where L is the separation of centres of the two particles. To calculate $U_{vdW}(D)$ using eqn (14) a non-zero value of D must be assumed. Since close-packed particle layers are being considered, D is arbitrarily set at the very small value of 0.1 nm. Taking values of Hamaker constants $A_w = 0.8 \times 10^{-21}$ J and $A_o = 0.2 \times 10^{-21}$ J (appropriate for the interaction of silica particles across water and octane respectively) the energy of attraction per particle is about $-80kT$ over the range of θ_p from 60 to 74°. This can be compared with the repulsive electrical energy between particles with $\sigma = 80$ μC m^{-2} of between $+100$ kT and $+200$ kT over the same range of θ_p and so both in the context of emulsion formation can be considered to be negligible.

As seen, for systems in which α is approximately 90° the oil-water interface can be pinned at the (possibly rather diffuse) region between the two hemispheres of a Janus particle so that neither of the two equilibrium contact angles are attained. Following e.g. Lucassen[18] and Stamou et al.,[19] Park et al.[20] propose that the contact line around the particle is undulating,
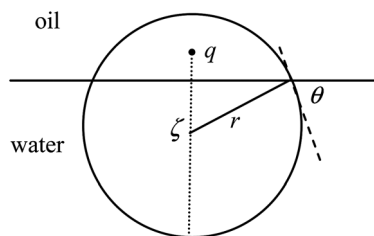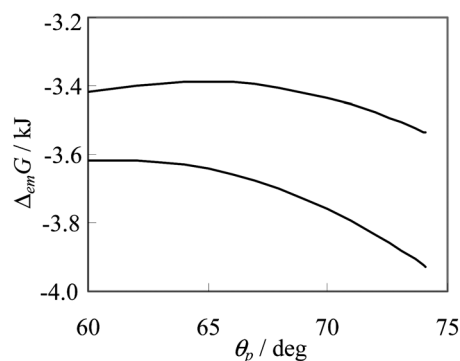

Fig. 8 A spherical particle with low relative permittivity resting at an oil–water interface. The charge on the particle is represented as a point charge q at a distance ς from the lowest part of the particle-water interface.

Fig. 9 Variation of $\Delta_{em}G$ with θ_p for the formation of 1 m^3 emulsion from equal volumes of oil and water with $\alpha = 60°$ and $\theta_a = 150°$. Other parameters are as given in the legend to Fig. 7. The lower curve is for $\sigma = 0$ and the upper curve for $\sigma = 800$ μC m^{-2}.

and this gives rise to an (observed and measured) attraction between particles resulting from capillary forces.

3.3 Effect of surface coverage on the free energy of interface formation

As seen, the free energy of formation of emulsions stabilised by hexagonally close-packed Janus particles can be negative when relatively small long-range lateral electrical repulsion between adsorbed particles is present. However, it is likely that in a nearly close-packed particle monolayer lateral repulsion considerably greater than the electrical repulsion considered, exits. This could possibly arise from short range solvation (hydration) forces or solid elastic forces.[1] The repulsive energy, U_{hyd}, between *two* spherical particles due to hydration forces can be represented by (see *e.g.* ref. 21):

$$U_{hyd} = \pi r P_o \lambda^2 \exp(-D/\lambda) \qquad (15)$$

in which λ is a decay length, P_o a hydration force constant and D the closest separation of particle surfaces. From experimental data, λ ranges from 0.2 to 1.1 nm and P_o (for hydrophilic surfaces) is in the range 10^6 to 5×10^8 N m^{-2}.

It has been observed experimentally that, if the supply of particles is not too large during the formation of a Pickering emulsion, the emulsion drop size distribution is determined by the particle concentration, and effectively all the particles are adsorbed.[22] It may be that, depending in part on the nature and range of the short range repulsive forces, close-packing of particles will not be attained.

It is convenient in what follows to consider the free energies associated with the formation of *unit area* of plane particle-coated oil–water interface. If the (in the context) small contributions from surface curvature, van der Waals interactions and $\Delta_a S$ (see eqn (1)) are ignored, the free energy $\Delta_u G$ of forming unit area of particle-coated oil–water interface, which is proportional to $\Delta_{em} G$, is given by

$$\Delta_u G = \gamma_{ow} + \left(\Delta_a G + U_{elec} + U_{hyd}/2\right)\big/\left(2r'^2\sqrt{3}\right)$$
$$= \gamma_{ow} + \Delta_u G_a + \Delta_u G_{elec} + \Delta_u G_{hyd} \qquad (16)$$

where

$$r' = L/2 = \sqrt{\left(1/x n_{cp} 2\sqrt{3}\right)} = r/\sqrt{x} \qquad (17)$$

The number of particles per unit area at hexagonal close-packing, n_{cp}, is $1/(2r^2\sqrt{3})$, and the fractional surface coverage x is the ratio of the number of particles in unit area to n_{cp}. Some values of $\Delta_u G$ are shown in Fig. 10 as a function of surface coverage, together with the components ($\gamma_{ow} + \Delta_u G_a$), $\Delta_u G_{elec}$ and $\Delta_u G_{hyd}$.

The hydration contribution has been calculated using $\lambda = 1.1$ nm and $P_o = 5 \times 10^8$ N m^{-2}. For $\theta_p = 60°$ for example, only 75% of the particle surface is immersed in the aqueous phase and so as a crude approximation $\Delta_u G_{hyd}$ used in the Figure is 0.75 that given by use of eqn (15). The largest contributors to $\Delta_u G$ are γ_{ow} (positive) and $\Delta_u G_a$ (negative). In the range of x from 0.9 to 1, D varies from about 11nm to zero and in this interval the electrical contribution to $\Delta_u G$ barely changes. On the other hand, the very short range
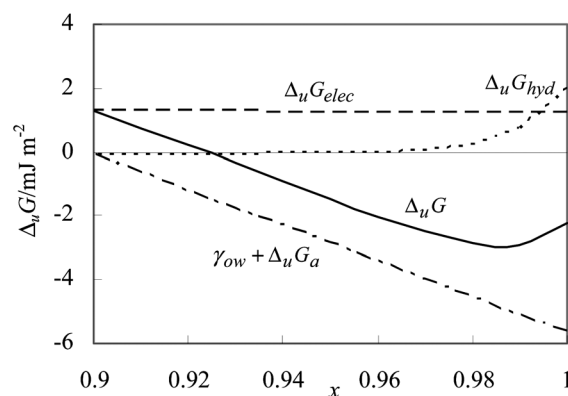

Fig. 10 Free energy of forming unit area of particle covered oil–water interface, $\Delta_u G$, as a function of fractional surface coverage x (full line). Dashed curves are for the components of $\Delta_u G$ as indicated. Parameters assumed are: $r = 100$ nm, $\gamma_{ow} = 50$ mN m^{-1}, $\alpha = 50°$, $\theta_a = 150°$, $\theta_p = 60°$ and $\sigma = 800$ μC m^{-2}. Parameters used in the calculation of $\Delta_u G_{hyd}$ are (see text) $\lambda = 1.1$ nm and $P_o = 5 \times 10^8$ N m^{-2}.

hydration force results in $\Delta_u G_{hyd}$ of virtually zero until x ≈ 0.96, which then rises exponentially with x (D). Using the parameters given in the legend to Fig. 10, the total free energy of forming unit area of interface exhibits a minimum of approximately -3 mJ m^{-2} at around $x = 0.99$, and is zero for x ∼ 0.923 (see below).

For the formation of a monodisperse emulsion (1 m^3 with equal volumes of oil and water) with a fixed number of particles, reduction in fractional coverage by particles is brought about by forming a greater number of smaller droplets. The number of particles which will give hexagonally close packed layers on the drops with (un-swollen) radius $R = 10$ μm is 4.39018×10^{18}. The emulsion free energy $\Delta_{em} G$ is the product of the total emulsion surface area and $\Delta_u G$. Taking the same values for the various parameters as used in Fig. 10 the free energies of emulsion formation have been calculated and are shown as a function of R in Fig. 11. A minimum in $\Delta_{em} G$ is observed for $R = 9.86$ μm.
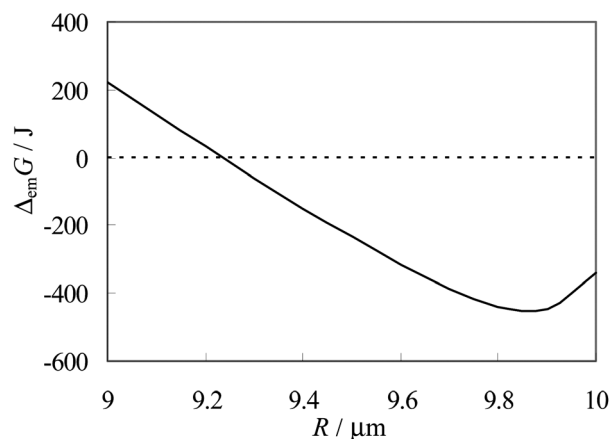

Fig. 11 Free energy of formation of 1 m^3 emulsion, with equal volumes of oil and water, as a function of un-swollen drop radius R. The number of particles, radius 100 nm, is fixed at 4.39018×10^{18}. Values taken for the other parameters are: $\gamma_{ow} = 50$ mN m^{-1}, $\alpha = 50°$, $\theta_a = 150°$, $\theta_p = 60°$, $\sigma = 800$ μC m^{-2}, $\lambda = 1.1$ nm and $P_o = 5 \times 10^8$ N m^{-2}.

Unlike the adsorption of surfactant molecules, particle adsorption is irreversible because the adsorption free energy is so large relative to kT. So, although $\Delta_{em}G$ can pass through a minimum with respect to drop size (surface coverage by particles), it may be that the coverage corresponding to minimum energy is not attained in practice.

Interactions between droplets in an emulsion have not been considered here. Such interactions are of course of great significance and contribute to the overall free energy of emulsion formation. The normal DLVO forces can be expected to be present, with electrical repulsion opposing flocculation and van der Waals attraction favouring adhesion of droplets. Flocculation can lead to instability towards creaming or sedimentation. The aim of the present work however has been to show that the free energy of formation of an emulsion drop coated by Janus particles can be negative.

Finally it is noted that the surface coverage of a plane particle monolayer at an oil–water interface can be readily varied on a Langmuir trough.[23] By analogy with the commonly employed treatment of surfactant systems one can write

$$\gamma_{eff} = \gamma_{ow} - \pi \tag{18}$$

where the effective interfacial tension, γ_{eff} is equivalent to $\Delta_u G$, and π is the surface pressure of the film. As seen, the surface pressure is the lowering of interfacial tension resulting from adsorption of the particle monolayer. It has been found experimentally that monolayer "collapse", consisting of monolayer folding, occurs when the magnitude of the applied surface pressure, π_{app}, becomes equal to that of the interfacial tension of the particle-free interface, γ_{ow} i.e. when γ_{eff} is zero. Noting eqn (18), and that $\gamma_{eff} \equiv \Delta_u G$

$$\pi = -\pi_{app} = -(\Delta_u G_a + \Delta_u G_{elec} + \Delta_u G_{hyd}) \tag{19}$$

and so, at monolayer collapse

$$\gamma_{ow} + \Delta_u G_a = -(\Delta_u G_{elec} + \Delta_u G_{hyd}) \tag{20}$$

which in the system represented in Fig. 10 occurs as seen for $x \sim 0.923$. Compression of particle layers around emulsion droplets could conceivably occur as a result of droplet coalescence, and the frequently observed existence of oddly shaped droplets may well indicate that the effective tension of the droplet is close to zero.

Conclusions

The major contributions to the free energy of formation of particle-coated oil–water interfaces (and emulsion droplets) arise from (i) the creation of bare oil–water interface and (ii) the adsorption of particles to the interface; thus $\Delta_u G$ ($\Delta_{em}G$) is the relatively small difference between two large quantities. For systems with homogeneously-wetted particles the free energy of formation of bare oil–water interface always dominates and the free energy of forming the particle-coated interface is always positive. For systems with Janus particles however, the magnitude of the adsorption free energy can be considerably increased and the free energy of forming particle-coated interfaces can become negative when the surface coverage by particles is sufficiently high. It has been shown that suitable Janus particles can have a maximum adsorption free energy with 3 times the maximum magnitude of that for a homogeneous particle of the same size. Adsorbed particles in concentrated monolayers interact laterally. It is found that long range electrical repulsion (through the oil phase) can have a significant effect on the free energy of emulsion formation whereas van der Waals attraction appears to be negligible. In almost close-packed particle layers it is proposed that hydration forces can become important and in principle give rise to a minimum in the free energy of interface (and emulsion) formation as a function of surface coverage by particles.

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