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Small solid particles and liquid lenses at fluid/fluid interfaces

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Abstract The behaviour of small solid particles and liquid droplets at fluid interfaces is of wide interest, in part because of the roles they play in the stability of foams and emulsions. Here we focus on solid particles at liquid interfaces, both singly and in highly structured monolayers. We briefly mention small oil lenses on water in connection with the determination of line tension, τ. Particles are surface-active in the sense that they often adhere quite strongly to liquid surfaces, although of course they are not usually amphiphilic. The three-phase contact line around a particle at an interface is associated with an excess free energy resulting in a tendency of the line to contract (positive τ, which is a 1D analogue of surface tension) or to expand (negative τ). Positive line tension acts so as to push the contact angle of a particle with the fluid interface further away from 90°, i.e. to force the particle towards the more "wetting" of the two bulk phases. It also leads to activation barriers to entry and departure of particles from an interface. The behaviour of particle monolayers at octane/water interfaces is also discussed . It is found that, for monodisperse spherical polystyrene particles containing ionisable sulphate groups at the surface, highly ordered monolayers are formed. This appears to result from very long range electrostatic repulsion mediated through the oil phase. Surface pressure–surface area isotherms are discussed for particle monolayers and it is shown, using light microscopy, that at monolayer "collapse" particles are not expelled from the monolayers but rather the monolayer folds, remaining intact. This has an important bearing on methods, involving the use of the Langmuir trough, for the experimental determination of contact angles and line tensions in particulate systems.

Key words Line tension · Liquid lenses · Particles at interfaces · Particle monolayer structure · Wettability

Introduction

Our interest in the behaviour of small solid particles and liquid droplets at interfaces stems from the effects which they have on the stability of foams and emulsions [1, 2]. For particles and/or droplets to affect the stability of foams and emulsions, they must first enter a fluid/fluid interface. For example, for hydrophobic particles to be effective aqueous foam breakers, the particles must be able to enter the liquid/vapour interface of the foam films. It is believed that the films are ultimately ruptured by the particles bridging the films, which then de-wet the particles [3]. Pickering emulsions [4] are emulsions which contain droplets stabilised by close-packed layers of particles taken up at the droplet oil/water interfaces.

Entry of a droplet or particle into an interface may be prevented either because the process is not thermodynamically feasible or because a metastable thin liquid film exists between the particle or droplet and the fluid interface (Fig. 1a) [5]. The stability of particles and droplets (in the shape of lenses) in liquid interfaces is determined by the relative values of the surface tensions and areas of the various interfaces present. In addition to the interfaces, there also exists a three-phase contact line around a lens or particle in a fluid/fluid interface (Fig. 1b, c). The contact line is associated with a line tension, i.e. an excess free energy per unit length, which can be positive (contractile) or negative (tending to expand) (unlike interfacial tension, which is always positive) [6]. Line tension, which is a 1D analogue of interfacial tension, has received renewed interest recently. The magnitude of the theoretical values is small, of the order of 10^{-12} N [6]. On the other hand, experimental values have varied widely, from close to theoretical estimates to as high as 10^{-6} N and even greater [7]. At the high end of positive values, the existence of line tension could drastically affect the entry and wettability of even quite large particles and droplets or lenses at interfaces [8–10].

In this paper we describe some of our work on single particles and lenses at interfaces, including the estimation and measurement of line tensions, as well as the behaviour of monolayers of monodisperse spherical polystyrene latex particles at oil/water interfaces. In connection with the latter, our interest has centred on the structure of the monolayers as they are compressed and the mode of "collapse" of the monolayers at high applied surface pressures. The nature of the collapse process has an important bearing on proposed methods which utilise the Langmuir trough for the determination of contact angles of spherical particles with liquid surfaces [11–13] and line tensions of the solid/liquid/fluid contact lines around the particles [14].

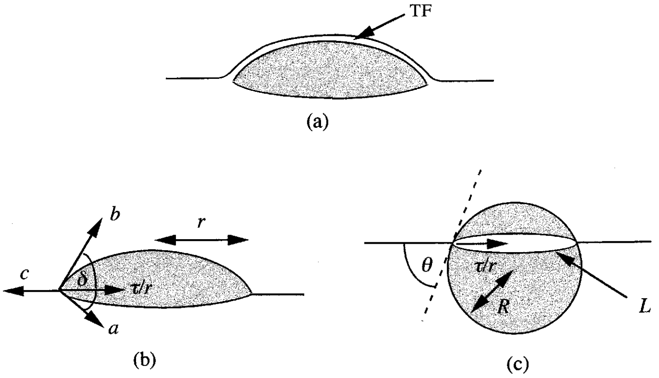

Fig. 1 **a** A lens at a liquid/vapour interface with a metastable thin film (*TF*) separating lens and vapour phase. **b** A lens at a fluid/fluid interface. *a*, *b* and *c* are interfacial tensions and the *arrows* denote the direction of action of the forces. τ is the line tension and *r* is the radius of the three-phase contact line. The lens angle is denoted as δ. **c** A spherical particle, radius *R*, resting in a fluid/fluid interface. *L* is the three-phase contact line, radius *r*, and θ is the contact angle (measured into the lower phase which is usually an aqueous phase) of the particle with the fluid interface

Experimental

Materials

In the study of particle monolayers at the oil/water interface, octane was used as the oil. It was 99% pure as supplied (Aldrich, UK) and was passed three times through chromatographic alumina to remove polar impurities before use. Dodecane (99% from Aldrich), from which lenses were formed on water in the determination of the line tension, was treated in the same way as octane. Dodecanol, added to dodecane to reduce the oil/water interfacial tension in the lens work, was 99% pure from Aldrich and was used as received. The surfactants employed in the particle monolayer work were sodium dodecyl sulphate (Lancaster, UK) and decyl β-D glucopyranoside (decyl β-glucoside from Sigma, UK). They were both 99% pure samples and were used as received, as was sodium chloride (an AnalaR sample).

Particle monolayers were formed from monodisperse polystyrene particles of 2.6-μm diameter, supplied by Interfacial Dynamics (USA) as a surfactant-free aqueous dispersion. They were spread using propan-2-ol (AnalaR from BDH) as the spreading solvent. The particles, which had sulphate groups on the surface, carried a surface charge in water of 7.7 μC cm^{-2}, corresponding to one sulphate group in 2 nm^{2}.

The water was purified by passing it through an Elga UHQ II unit fitted with a UV irradiation unit and with cartridges for ion exchange, reverse osmosis, organic adsorption and ultramicrofiltration. The surface chemical purity of the water was determined by measurement of its surface tension, which was consistently 72.8 ± 0.1 mN m^{-1} at 293 K.

The Langmuir film balance and its use

A computer-controlled Teflon mini Langmuir trough (model 601M, Nima Technology, UK), which could readily be housed on a microscope stage, was used to compress and expand the particle monolayers. The apparatus was modified for use with oil/water interfaces by fitting a stainless steel lining as shown in Fig. 2. In this way the oil/water interface was pinned where the sharp upper edge of the lining meets the Teflon edge. The moving barriers were also constructed of stainless steel. Several compression/expansion cycles could be carried out without a significant loss of spread particles. Surface pressures (Π) were obtained using a filter paper Wilhelmy plate which was aligned either perpendicular to or

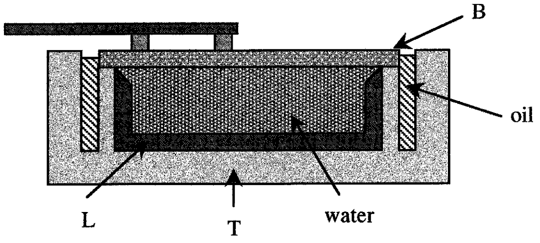

Fig. 2 End-on view of the mini Langmuir trough which could be housed on a microscope stage to view particle monolayers at the oil/water interface during lateral compression. The trough (*T*) is constructed from Teflon and is fitted with a steel lining (*L*). The aqueous phase is contained in the steel lining and the oil phase covers the aqueous phase and also fills the channel around the edge of the trough. The barriers (*B*) are constructed of steel

parallel to the trough barriers (see later). All experiments were carried out at room temperature, which was around 293 K.

A Nikon Optiphot 2 microscope, fitted with a JVC TK 1381 digital colour charge-coupled-device camera, was used to obtain images of oil lenses on water and of particle monolayers during compression.

Results and discussion

Background to attachment of solid particles to fluid interfaces

If a solid particle (radius R) is, say, hydrophobic, it might be supposed that it would, in a system of hydrocarbon and water, prefer to reside totally in the oil phase; however, particles (hydrophobic or hydrophilic) are usually strongly attached to oil/water interfaces. Figure 3 represents two fluid phases, α and β, and a spherical particle (s) initially totally in phase α, being adsorbed at the α/β interface. All the interfaces have interfacial tensions, γ, associated with them, and the three-phase contact line ($\alpha/\beta/s$) around the adsorbed particle has a line tension, τ [9]. Upon uptake of the particle by the interface, the area A_2 of the s/α interface is lost, being replaced by an equal area of the s/β interface. Importantly, the area A_3 of the planar α/β interface is lost, and an $\alpha/\beta/s$ contact line of length l is created.

The likely effect of the contact line on the wettability of the particle at the interface is unclear since the magnitude of the line tension and indeed its sign are usually unknown. If a theoretical estimate of τ (around 10^{-12}–10^{-11} N [6]) is assumed then formation of the contact line will usually have negligible influence on the contact angle, θ (Fig. 1). Much higher experimental values of the solid/liquid/vapour line tension, of the order of 10^{-6} N, have, however, been reported and such (positive) values could have very marked effects on θ [9]. We note that positive line tension tends to force the particle further into the more wetting phase, i.e. to push θ further away from 90°; conversely negative (expansile) line tension brings the contact angle closer to 90°.

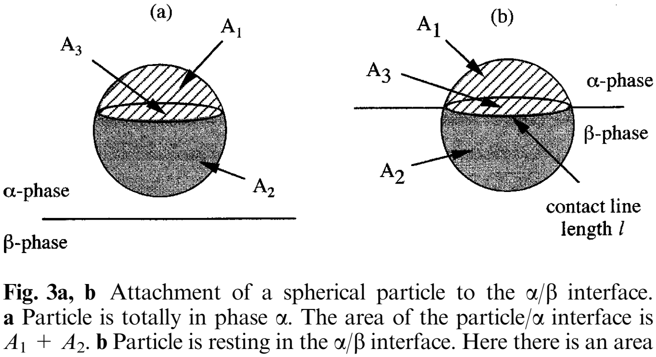

Fig. 3a, b Attachment of a spherical particle to the α/β interface. **a** Particle is totally in phase α. The area of the particle/α interface is $A_1 + A_2$. **b** Particle is resting in the α/β interface. Here there is an area A_2 of the particle/β interface and an area A_1 of the particle/α interface. A plane area A_3 of the α/β interface is lost and a contact line (length l) between α, β and the particle is formed

It is simple to show that the free-energy change, ΔG, accompanying "adsorption" of a spherical particle of radius R from the more "wetting" phase to the α/β interface is [9]

$$\Delta G = -\pi R^2 \gamma_{\alpha/\beta}\left[(1 \pm \cos\theta)^2 - \frac{2\bar{\tau}}{\sin\theta}(1 \pm \cos\theta)\right] , \qquad (1)$$

where the reduced line tension $\bar{\tau} = \tau/\gamma_{\alpha\beta}R$ and $\gamma_{\alpha\beta}$ is the α/β interfacial tension. The positive sign in the cosine terms in Eq. (1) applies for $\theta > 90°$ and the negative sign applies for $\theta < 90°$. Equation (1) indicates that when the line tension is negligible, spherical particles at equilibrium in the interface are most strongly attached for $\theta = 90°$. This arises since in this condition the largest area of the α/β interface (πR^2) is lost on particle adsorption. In systems where the effects of (positive) τ are important, the particle has a stable configuration in the interface when $\Delta G < 0$ [9], i.e. when (for the case of $\theta < 90°$)

$$\frac{2\bar{\tau}}{\sin\theta} < (1 - \cos\theta) \ . \qquad (2)$$

Thus the condition where

$$\bar{\tau} = 0.5 \sin\theta(1 - \cos\theta) \qquad (3)$$

represents a wetting transition, at which the free energy of a system with a particle in the interface is the same as that when the particle is in the (more wetting) bulk phase. We designate the reduced line tension for this situation as $\bar{\tau}_c$. It transpires that for $\bar{\tau} > \bar{\tau}_c$ and up to a value $\bar{\tau}_m$, metastable conditions exist for the particle in the interface. Above $\bar{\tau}_m$, however, no stable condition is possible. The conditions of metastability imply that (for positive line tension) there can be activation barriers for entry and removal of a particle from the interface [9].

Since $\bar{\tau} = \tau/\gamma R$, and noting Eq. (1), it is clear that the smaller the particle the larger the effect of line tension on particle wettability (θ) and on the stability at the interface. For example, for a system in which θ is 70° in the absence of the effect of line tension (i.e. for suitably large R) and for $\gamma = 25$ mN m^{-1} (as for an alkane on a fluorinated surface), it can be shown that for $\tau = 10^{-6}$ N, spherical particles of diameters less than about 0.2 mm should have no stable configuration at the liquid interface [9, 10]. This means that such particles cannot be incorporated into the surface of, say, a large drop of the liquid. We have shown experimentally [9] that fluorinated glass spheres down to diameters of about 10–20 μm can be picked up by a drop of dodecane, and it was concluded that τ in this system must be less than around 10^{-8} N.

The measurement of line tension is not simple and relatively few good measurements have appeared in the literature. Ducncan et al. [15] have determined solid/

liquid/vapour line tensions by observing the variation of the contact angle with the contact line radius (in the millimetre range) for liquid drops resting on smooth solid surfaces. The values reported have been high, around 10^{-6} N and upwards. We have also sought to measure line tensions, but in order to avoid potential problems associated with surface roughness and heterogeneity we have turned to liquid/liquid/vapour systems where necessarily all surfaces are molecularly smooth. Again, for such systems some experimental results have been high (and negative, -1.3×10^{-6} N) [16] and another result (for octane lenses on 3 and 5 mol dm^{-3} NaCl in air) is much smaller and positive (between about 10^{-10} and 10^{-9} N) [17].

Before discussing the measurement of liquid/liquid/vapour line tensions we note that we have proposed a method for the determination of solid/liquid/vapour line tensions which involves the observation of capillary condensation, either in a packed bed of monodisperse spheres or in the surface force apparatus (SFA) [18, 19]. Consider as an example capillary condensation in the SFA, which is used to determine directly the forces between molecularly smooth (coated) mica surfaces [20]. Crossed mica cylinders are employed, giving a configuration which is locally effectively equivalent to that of a sphere close to (or in contact with) a flat surface. Condensation occurs as shown in Fig. 4 and involves the formation of two three-phase contact lines of radius r. We have shown how, inter alia, for a relative vapour pressure of 0.95, r varies with the separation, H, (see Fig. 4) for a series of values of line tension (in the range 0–100 nN). It is shown how the limit of stability (minimum r) of a liquid bridge as H is increased depends on the line tension. To give an idea of the effect of τ on condensation, for a liquid with a surface tension of 25 mN m^{-1} and a contact angle with mica in the absence of line tension effects of 45°, the value of H at the stability limit is about 60 nm (with $r = 4$ μm). For a line tension of 100 nN H is reduced to around 28 nm, at which $r = 16$ μm [19]. We have also discussed the effects of surface forces on capillary condensation [18].

Dodecane/water/vapour line tension

With reference to Fig. 1b, for a lens of oil resting on an aqueous subphase the lens angle, δ depends on the various interfacial tensions, on the magnitude and sign of the line tension and on the contact line (lens) radius r [21, 22]. It is readily shown that [21]

$$a \cos\left(\frac{b\delta}{a+b}\right) + b \cos\left(\frac{a\delta}{a+b}\right) = c - \frac{\tau}{r} , \tag{4}$$

where a, b and c are the various interfacial tensions indicated in Fig. 1b.

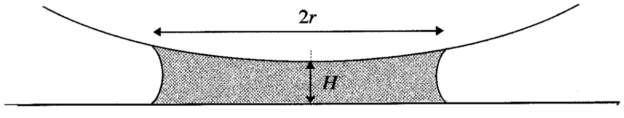

Fig. 4 Surface force apparatus configuration of crossed cylinders, which is locally equivalent to a sphere close to a flat surface. The closest separation is H and vapour condenses in the gap. To a good approximation the two solid/liquid/vapour contact lines each have radius r

We have studied systems of small lenses (r in the range 10–150 μm) of a very dilute solution of dodecanol in dodecane resting on a water subphase (see also Ref. 21). The lens angles observed were less than 2° and were measured interferometrically. For such small lenses the water surface remains effectively planar up to the contact line. We show the microscopic images of a collection of lenses obtained using a reflectance objective in Fig. 5. The fringes were fitted to a theoretical model as described elsewhere [21] in order to obtain both the lens angle and radius. An intensity–radius profile and the theoretical fit are shown in Fig. 6. In this way radii could be obtained to within 0.1 μm and δ could be obtained to within 0.01°.

A set of lens angle–lens radius data is shown in Fig. 7a; the same data set is plotted according to Eq. (4) in Fig. 7b. The variation in δ is very small, about 0.2° for a change in lens radius of around 130 μm. The line tension is found from the slope of the linear plot in Fig. 7b, and for this system $\tau = 1.6 \times 10^{-11}$ N. Thus, as in the case of the solid polystyrene latex particles in liquid/vapour interfaces, we find no evidence for very large values of line tension although they may of course exist in other systems. It is worth remarking that wetting transitions exist for lenses in liquid surfaces just as for particles [23]. For example, for a lens of pure dodecane,

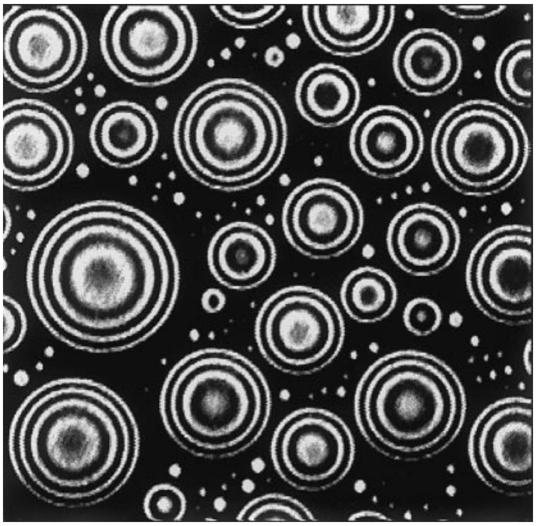

Fig. 5 Images of lenses of dodecane (containing 2 mM dodecanol) on water showing interference fringes; the lens angles δ (see Fig. 1b) are approximately 2°

volume 1 μm^3, on water the (hypothetical) critical value of the line tension above which a stable lens could not exist is 14.2 nN; metastable lenses are possible for τ between this value and 21.4 nN. Above 21.4 nN no stable configuration exists for the lenses which would completely dewet the water surface.

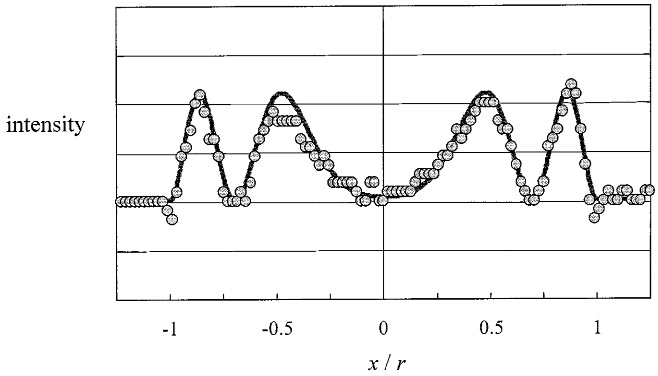

Fig. 6 An intensity versus lens radius profile. The *points* are the experimental data and the *solid line* is the best fit obtained from theory by adjusting the lens radius and the lens angle

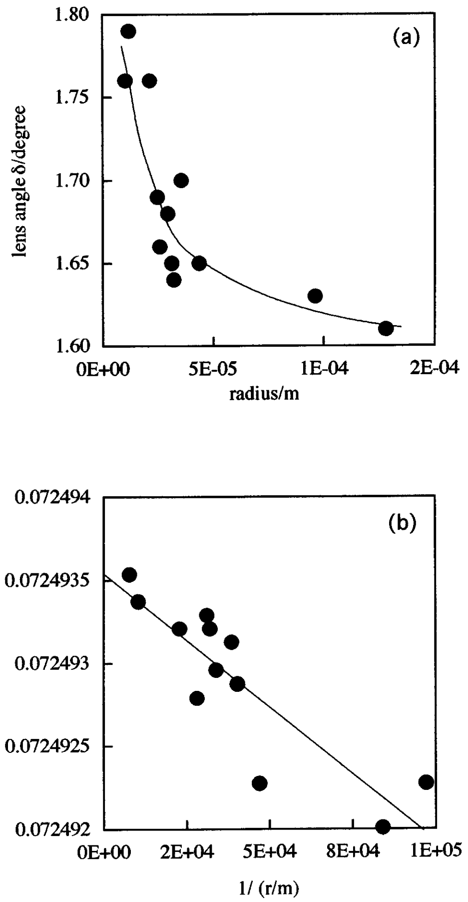

Fig. 7 **a** Lens angle, δ, as a function of the lens (contact line) radius *r*. **b** Linear plot according to Eq. (4)

Particle monolayers at oil/water interfaces

We have already mentioned aspects of the behaviour of single spherical particles at fluid interfaces. Here we extend the discussion to include the behaviour of particle monolayers at fluid interfaces, mainly the octane/water interface. Part of the motivation for this work has been to gain information about the mode of collapse of particle monolayers at high surface pressures, applied on a Langmuir trough. We have previously proposed methods for the determination of contact angles and line tensions [11, 14] in which it has been supposed (without direct evidence) that particles are expelled from the monolayers at "collapse". A typical surface pressure (Π)–monolayer area (A) isotherm for a particle monolayer at an oil/water interface is depicted in Fig. 8. The "knee" on the curve occurs at the "collapse" pressure, Π_C. The particles used in our work have a diameter of 2.6 μm so the monolayers can be observed microscopically during compression on a mini Langmuir trough (see Experimental) located on the stage of a reflectance microscope.

In addition to collapse behaviour we also investigated monolayer structuring resulting from lateral interparticle forces. The particle surfaces contain ionisable sulphate groups as discussed earlier.

Structure of particle monolayers

When octane is layered onto a particle monolayer spread at the air/water surface, what was originally a fairly

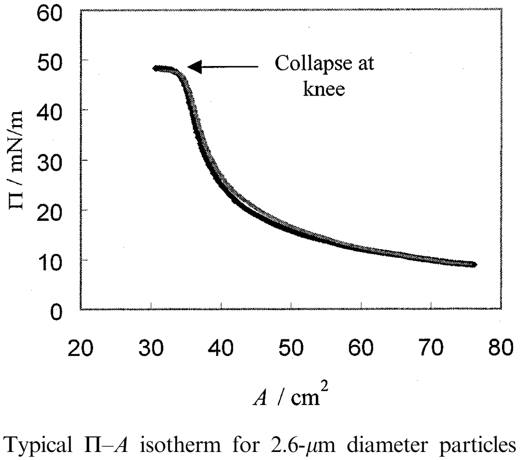

Fig. 8 Typical Π–A isotherm for 2.6-μm diameter particles at the octane/water interface (*upper curve*). The surface pressure at the knee is the collapse pressure, Π_C. The *lower curve* is for a monolayer at an octane/0.1 mol dm^{-3} NaCl solution interface. It is seen that the isotherm is effectively unchanged by the high concentration of NaCl

disordered monolayer becomes, quite remarkably, a highly ordered hexagonal array (2D colloidal crystal) at the oil/water interface. Even in the presence of 100 mM NaCl in the aqueous phase, when there is considerable aggregation at the air/solution interface, the monolayer at the octane solution interface retains a fairly high degree of order (Fig. 9). There are obviously strong long-range repulsive forces operating at the oil/water interface over several microns which are absent at the air/water surface.

For the octane/water interface the Π–A isotherm is virtually unchanged by the addition of 100 mM NaCl to the aqueous phase (Fig. 8). Furthermore the structure of the monolayer remains relatively unaffected. We conclude from this that the long-range repulsion acts through the oil phase, since the presence of inorganic electrolyte is expected to shield electrostatic repulsion in the aqueous phase. It has been mentioned that 100 mM NaCl causes aggregation of monolayers at the air/water surface (Fig. 9a). We will show in detail elsewhere that the observed repulsion could originate from a small amount of charge at the oil/particle interface. Such charge could easily arise as a result of the presence of trapped or hydration water between particle and oil. The surface charge required to account for the observed long- range repulsion (through the oil phase) is around 1% of the total possible charge (number of sulphate groups) on the particle surface.

We mention in passing an interesting observation which relates to our earlier discussion of the strength of attachment of single particles to fluid interfaces and the greater strength of mutual lateral repulsion of particles at oil/water interfaces than at air/water surfaces. If very small air bubbles are formed at the oil/water interface it is observed that the polystyrene particles adhere to the bubbles. From the disposition of the particles around a bubble it is apparent that particles are mutually repulsive. We show in Fig. 10 images of particles attached to air bubbles at the octane/water interface. The particles are obviously closer together around the bubbles than in the surrounding planar oil/water interface. This means that the adsorption free energy

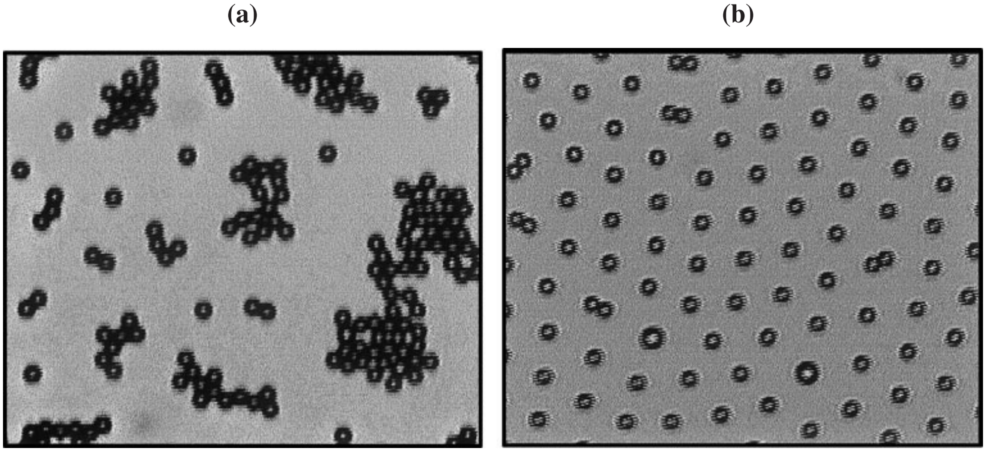

Fig. 9 Monolayers of 2.6- μm diameter particles **a** at the air/100 mmol dm^{-3} NaCl interface and **b** after layering on octane

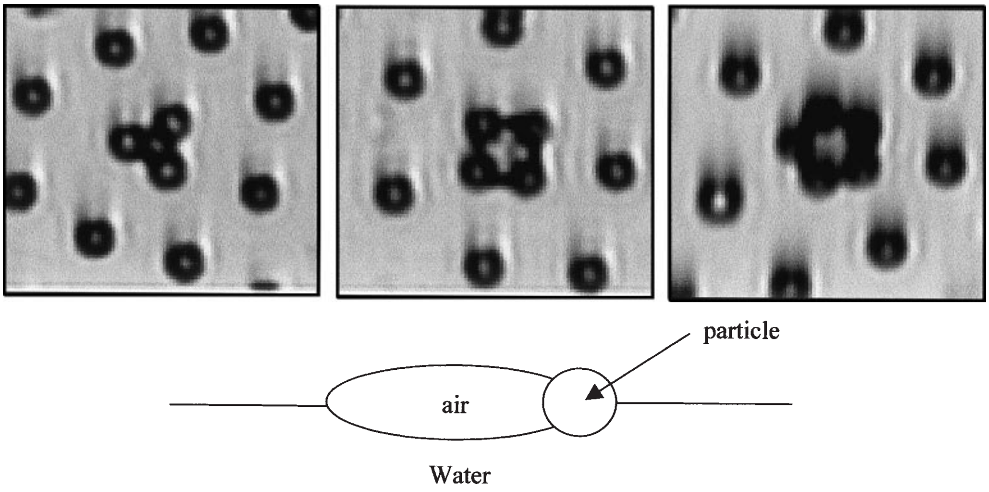

Fig. 10 Particles attached to air bubbles introduced at the octane/water interface. From the positions assumed, the particles at the bubble surfaces are clearly repulsive, but are much closer together than the particles in the neighbouring oil/water interface. In a sense the particles are adsorbed at two interfaces simultaneously, the oil/water and the air/water surfaces

for a single particle is greater around the bubble than at the oil/water interface and/or the lateral repulsion between particles is reduced at the bubble surface. The configuration of particles around the bubble is expected to be rather complex because the particle is partially "adsorbed" at three different interfaces: the oil/air and air/water surfaces and the oil/water interface. The energy of attachment to a given interface can be calculated from Eq. 1 from a knowledge of the contact angle, θ, and the interfacial tension (ignoring the small effects of line tension). Although we know θ at the oil/water and air/water interfaces we do not know it for the oil/air interface.

Compression and collapse of particle monolayers

As discussed, the polystyrene particles studied are mutually very repulsive at the octane/water interface. It is seen in Fig. 11a that even at large separation between particle surfaces (when the surface pressure is low) a highly structured monolayer is created, with hexagonal packing. As the monolayer is compressed on the Langmuir trough, the monolayer structure becomes distorted to give a rhombohedral array (Fig. 11b), presumably because the compression is anisotropic. Further compression beyond collapse (see the isotherm in Fig. 8) leads first to a gentle folding of the monolayer, and then at greater compression, the monolayer becomes corrugated (Fig. 11c, d). Importantly, we do not observe expulsion of particles from the monolayer, either singly or as aggregates.

As mentioned, we have previously proposed methods for the determination of particle contact angles (θ in Fig. 1) [11] and line tensions [14] based on the assumption that particles are expelled from a monolayer at collapse. On that basis it has been supposed that the collapse pressure can be equated with the energy required to remove particles, in unit area, out of the monolayer into the more "wetting" phase. The proposed method for the measurement of θ has subsequently been used by others [12, 13]. On the basis of our present findings, however, the methods must be considered to be suspect. It may be that the mode of monolayer collapse is dependent on the size and nature of the particles. Nonetheless, in situ observation of the mode of collapse

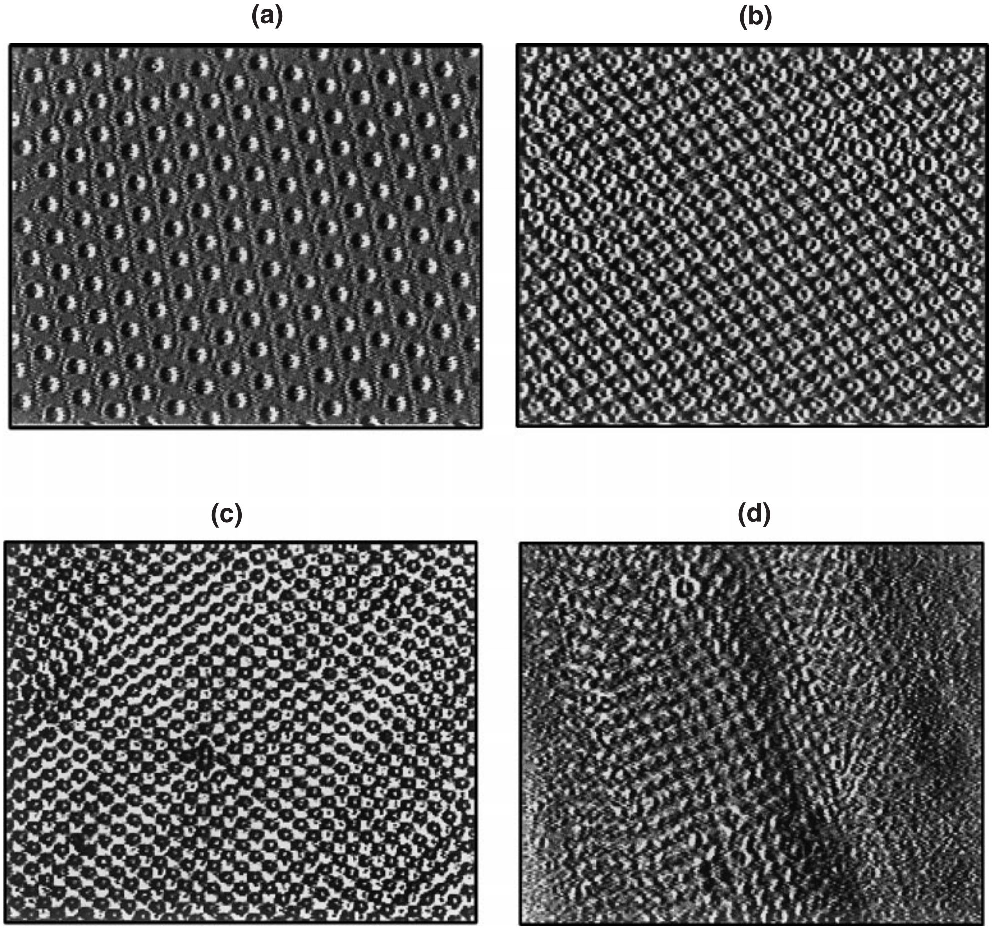

Fig. 11a–d Images of monolayers of polystyrene particles (2.6 μm diameter) at the octane/water interface in a Langmuir trough. **a** Hexagonal packing at a very low surface pressure, close to zero. **b** Rhombohedral packing just below the collapse pressure (see Fig. 8). **c** Gentle folding just above the collapse pressure. **d** Corrugated monolayer well above the collapse pressure. Note that particles are not expelled from the monolayer, either singly or as aggregates

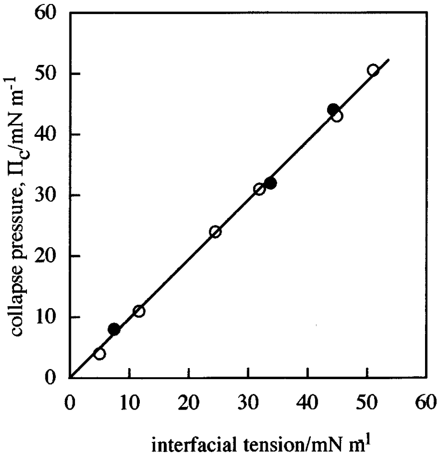

Fig. 12 Collapse pressures of monolayers of 2.6-μm diameter polystyrene spheres at the octane/water interface in the presence of sodium dodecyl sulphate (*filled symbols*) and decyl β-glucoside (*open symbols*)

of monolayers of submicroscopic particles, such as those likely to be used in the determination of line tension for example, is likely to prove difficult.

Finally we report some findings on the influence of the addition of surfactant to systems of interest and its effect on the collapse pressure, Π_c. We note firstly that surfactant has little effect on the contact angle. This is not unusual for hydrophobic solids [1]; however, both the Π–A isotherms and Π_c are strongly dependent on the presence of surfactant and on its concentration. We find, for a range of surfactants and surfactant concentration, that Π_c is, within experimental error, equal to the interfacial tension, γ, of the octane/water interface in the absence of particles. This is exemplified in Fig. 12 for systems with sodium dodecyl sulphate and decyl β-glucoside. The correspondence holds for γ from over 50 mN m^{-1} down to the lowest tension investigated, about 4 mN m^{-1}. The surface pressure exerted by the mutually repulsive particles tends to cause expansion of the monolayer-covered surface, whereas the oil/water tension of the interface between the particles tends to cause contraction. At collapse the two opposing effects become equal. Clearly, the energy required to force particles closer together at and beyond collapse is greater than that required to fold the monolayer at constant monolayer area.

Conclusions

The wetting of an isolated spherical particle at a fluid interface, usually discussed in terms of the contact angle which the particle makes with the interface, is determined jointly by the values of the various interfacial tensions and the (line) tension in the three-phase contact line. Positive (contractile) line tension tends to force the particle towards the more "wetting" bulk phase. There is a wetting transition at which the contact angle becomes discontinuously zero or 180°. Line tensions obtained theoretically are usually of the order of 10^{-12}–10^{-11} N, but some experimental values are very much higher, around 10^{-6} N and upwards. Such large positive line tensions would be expected to have a drastic effect on the wetting of small particles at interfaces. Behaviour of lenses at interfaces is expected to parallel that of particles in many ways, although of course the lenses are deformable. We report an experimentally obtained value of the line tension for dodecane lenses on water of 1.6×10^{-11} N.

Surface pressure–surface area isotherms for particle monolayers can be obtained on a Langmuir trough in much the same way as for insoluble molecules. We have observed particle monolayers at octane/water interfaces microscopically during compression on a trough. There are very long-range repulsive forces between the polystyrene particles that give rise to highly organised monolayers. It appears that the repulsion, which is not strongly affected by electrolyte, is mediated through the oil phase. At high applied surface pressures the monolayers "collapse", but it is found that, contrary to what has often been assumed, particles are not ejected from a monolayer but rather the monolayer retains its integrity and folds. This finding has an important bearing on the validity of methods that have been proposed for the determination of contact angles and line tensions.

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References

1. Aveyard R, Cooper P, Fletcher PDI, Rutherford CE (1993) Langmuir 9:604
2. Aveyard R, Clint JH (1995) J Chem Soc Faraday Trans 891:2681
3. Garrett PR (1993) In: Garrett PR (ed) Defoaming. Surfactant Science Series, vol 45. Dekker, New York, pp 1–117
4. Menon VB, Wasan DT (1988) Sep Sci Technol 23:2131
5. Bergeron V, Fagan ME, Radke CJ (1993) Langmuir 9:1704
6. Rowlinson JS, Widom B (1984) Molecular theory of capillarity. Oxford Science Publications, Oxford
7. Drehlich J (1996) Colloids Surf A 116:43
8. Mingins J, Scheludko A (1979) J Chem Soc Faraday Trans I 75:1
9. Aveyard R, Clint JH (1996) J Chem Soc Faraday Trans I 92:85

10. Aveyard R, Beake BD, Clint JH (1996) J Chem Soc Faraday Trans 92:4271
11. (a) Clint JH, Taylor SE (1992) Colloids Surf A 65:61; (b) Clint JH, Quirke N (1993) Colloids Surf A 78:277
12. Aveyard R, Binks BP, Fletcher PDI, Rutherford CE (1994) Colloids Surf A 83:89
13. Mate M, Fendler JH, Ramsden JJ, Szalma J, Horvolgyi Z (1998) Langmuir 14:6501
14. Aveyard R, Clint JH (1995) J Chem Soc Faraday Trans 91:175
15. Duncan D, Li D, Gaydos J, Neumann AW (1995) J Colloid Interface Sci 169:256
16. Chen P, Susnar SS, Amirfazli A, Mak C, Neumann AW (1997) Langmuir 13:3035
17. Dussaud A, Vignes-Adler M (1997) Langmuir 13:581
18. Aveyard R, Clint JH, Paunov VN, Nees D (1999) Phys Chem Chem Phys 1:155
19. Aveyard R, Clint JH (1997) J Chem Soc Faraday Trans 93:4409
20. Israelachvili JN (1992) Intermolecular and surface forces. Academic Press, London
21. Aveyard R, Clint JH, Nees D, Paunov VN (1999) Colloids Surf A 146:95
22. Pujado PR, Scriven LE (1972) J Colloid Interface Science 40:82
23. Aveyard R, Clint JH (1997) J Chem Soc Faraday Trans 93:1397