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Bridging interaction between a water drop stabilised by solid particles and a planar oil/water interface

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We demonstrate that the particle mediated interaction between a pendant water drop, covered by a latex particle monolayer, and a planar decane/water interface leads to bridging, analogous to flocculation in solid-stabilised emulsions. The results also provide information about the particle contact angle at the oil/water interface.

Solid particles can adsorb strongly to both liquid/vapour and liquid/liquid interfaces, and, depending on their hydrophobicity, can be excellent stabilisers of both foams and emulsions,[1,2] enhancing the kinetic stability of air bubbles to disproportionation[3] and oil and water drops to coalescence.[4] Recently, super-long range interaction between charged polystyrene (PS) latex[5] and silica[6] particles, adsorbed at planar air/water and oil/water interfaces have been described, which is believed to be due to Coulombic repulsion of residual surface charges through the air (oil) phase.[5] Paunov *et al.*[7] demonstrated that the adsorption of charged solid particles at liquid surfaces is regulated by the surface charge accumulation at the liquid interface. Emulsions stabilised solely by silica nanoparticles can be either oil-in-water (o/w) or water-in-oil (w/o) depending on the inherent wettability of the particles, the oil-to-water volume ratio and the type of oil phase used.[1,2,8] Polystyrene latex particles with surface sulfate groups only stabilise w/o emulsions,[8,9] whereas similar particles with pH-responsive cationic amino surface groups only stabilise o/w emulsions.[10]

Despite the importance of the interactions in solid-stabilised emulsions, very little experimental work has been reported investigating the phenomena occurring as two liquid surfaces are brought into contact in the presence of adsorbed particles. Velikov *et al.*[11] looked at the dynamics of thinning of plane parallel foam films (air/water/air) stabilised by a cationic surfactant in the presence of negatively charged PS latex particles initially in bulk. Due to the coupling between the surfactant headgroups and the particles, such particles become partially hydrophobic *in situ* and a layer of particles simultaneously adsorbs at the two film surfaces, thus forming a bridging monolayer of hexagonal ordering over large distances.

Here, we study the interaction between a single large water drop coated with particles in an oil phase as it approaches and contacts a planar oil/water interface devoid of particles. The sketch of the system is presented in Fig. 1. This configuration mimics that between two large emulsion drops in the early stages of emulsification. We demonstrate that drops stabilised by a latex particle monolayer exhibit a strong adhesion to a planar oil/water interface (Fig. 1(b)) due to bridging of the two liquid surfaces by the particles. We conducted a series of experiments in which the pendant drop was detached from the bottom liquid surface. We discuss the possibility of calculating the contact angle the particles make with the oil/water interface from the shape of the meniscus formed on contact, for the possible case of reversible bridging.

Single pendant drops of an aqueous suspension of monodisperse sulfate PS latex particles, 9.6 μm in diameter (from IDC), were produced in *n*-decane (from Sigma) by using a Krüss DSA-10 Drop Shape Analysis system with syringe needles ranging from 0.5 to 1.5 mm in diameter. Decane was purified by passing through chromatographic alumina. The concentration of NaCl in the latex suspension was adjusted to 1 mM to facilitate particle adsorption at the decane/water interface. A particle monolayer was formed on the surface of the water droplets in decane by multiple infusion and withdrawal of the aqueous suspension with a syringe (see Figs. 1(a) and 2(a)). The latter corresponds to multiple expansion and contraction of the latex particle monolayer at the droplet surface, which allows additional particles from the suspension to be adsorbed and accommodated within the monolayer. A pendant water drop covered by a dense monolayer of latex particles is shown in Fig. 2(a). Further withdrawal of liquid with the syringe causes a collapse of the monolayer (Fig. 2(b)) which results in an asymmetric shape of the pendant drop.

In Fig. 3 we present a series of images of a pendant water drop with a complete monolayer of latex particles approaching a planar decane/water interface which leads to irreversible bridging of the two liquid surfaces by the particle monolayer. Once adhered to the bottom surface, it was impossible to completely detach the pendant drop without breaking it up with the formation of a small "satellite" water droplet on the planar liquid surface, which was also stable

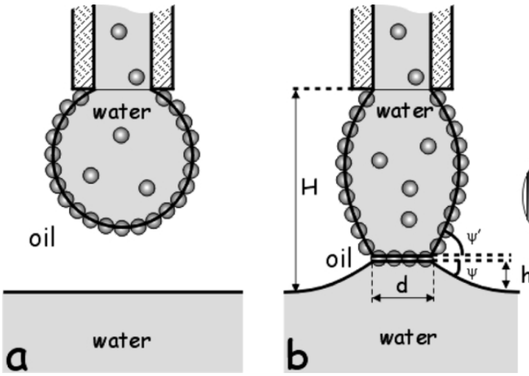

Fig. 1 (a) A pendant water drop, stabilised by a monolayer of solid particles, in oil. The drop is formed by multiple expansion and contraction of an aqueous suspension of latex particles into an oil (decane) phase. (b) The pendant drop (attached to a capillary) is approached to a flat oil/water surface where the two oil/water interfaces are bridged by the latex particles. *H* is the distance between the flat surface and the capillary tip, *d* is the diameter of the w/o/w liquid film, ψ and ψ' are the liquid meniscus slope angles and *h* is the height of the film with respect to the planar oil/water interface.

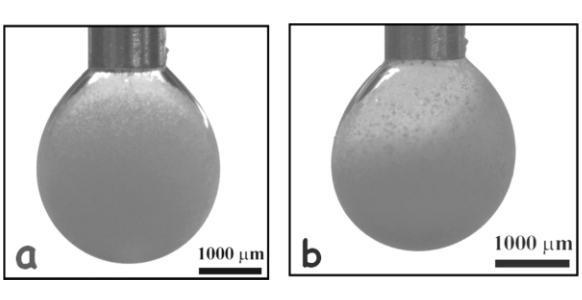

Fig. 2 Optical micrograph of a pendant drop of water in decane, stabilised by a monolayer of PS latex particles. (a) The particle monolayer on the drop surface is incomplete. (b) The particle monolayer is collapsing above the point of close-packing as liquid is withdrawn from the capillary and the drop area is reduced. The droplet shape gets skewed as the particle monolayer collapse progresses.

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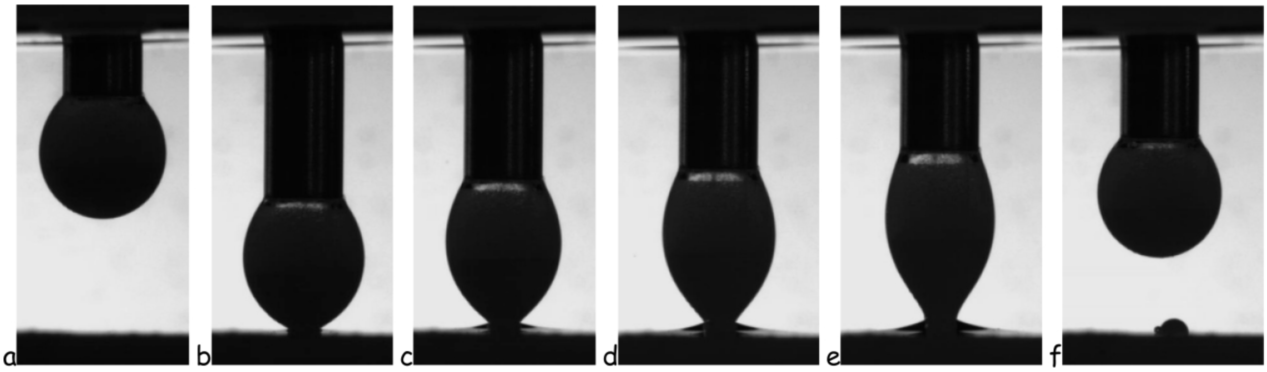

Fig. 3 Optical micrographs of a pendant water drop, stabilised by a monolayer of 9.6 μm sulfate PS latex particles in decane, approaching a flat decane/water interface. The pendant drop (image (a)) adheres to the flat decane/water interface (image (b)) and gradual pulling up of the capillary cannot detach the particle monolayer from the bottom decane/water interface (images (c)–(e)). The upper meniscus develops instability and the droplet breaks up (image (f)) leaving a small satellite water drop (stabilised by latex particles) on the decane/water interface (capillary diameter is 1.504 mm).

against coalescence with the lower phase (water). Table 1 summarises the geometrical parameters of the bridged drop in Fig. 3 as a function of the vertical position H of the capillary tip. One sees that the upper meniscus slope angle ψ' is much larger than the lower meniscus slope angle ψ which is an indication that the drop develops a capillary instability well before that of the lower meniscus. In this particular case this happens as the particles bridging the two liquid surfaces (Figs. 3(c)–(e)) detach from one of the w/o/w film interfaces. Note that the diameter d of the contact line of the bridging particle monolayer (w/o/w film) does not change within the experimental error during the pulling of the drop from the planar liquid interface. The latter seems to be due to the close packing of particles within the bridging monolayer and to the apparent stability of the two surfaces of the film against the pulling force.

Our understanding of the physics of the drop detachment is the following. The critical meniscus slope angle, $\psi = \psi^*$, calculated from the drop profile in Fig. 3(e) corresponds to the maximum pulling force on the particle film before instability occurs. The bridging film would detach only if the maximal pulling force (equal to the reduced weight of the bottom meniscus), F_g, exceeds the maximum force NF_p that the bridging monolayer of particles can withstand, *i.e.* $F_g = NF_p$. Here $F_p = 2\pi\gamma R\cos^2(\theta/2)$, where γ is the oil/water interfacial tension, R and θ are the particle radius and three-phase contact angle (measured through water), respectively, and $N = \pi d/2R$ is the number of particles in the periphery of the bridging film. Note that the maximum pulling force F_g can be calculated from the geometrical parameters of the drop profile, $F_g = \pi\gamma d\sin\psi^* + \frac{1}{4}\pi d^2\Delta\rho g h^*$, where $\Delta\rho = \rho_{\text{water}} - \rho_{\text{oil}}$ and g is the gravity acceleration. Then, two cases are possible: (i) If $F_g < NF_p$, then the upper meniscus breaks before detachment of the bridging particle monolayer; (ii) If $F_g \geq NF_p$, the bridging film will detach from the planar liquid surface before the upper meniscus develops instability. From the latter equation one can estimate for what value of the particle contact angle θ the droplet would detach and when it would break before detachment. Using the values of the parameters from Table 1 for the critical drop (Fig. 3(e)) we estimate that $\theta \approx$ 140°. This allows the contact angle of the bridging particles to be determined by measuring the geometrical parameters (ψ, h and d) of the 'critical drop'. If however, the breaking of the drop occurs before detachment of the bridging monolayer we cannot determine the value of the particle contact angle from the maximum pulling force. On the other hand, θ in this case should be larger than 90° since this is the condition for the particles to 'bridge' the two liquid surfaces. This is evidence that the sulfate latex particles, although negatively charged and dispersed in water, are significantly hydrophobic and are wetted preferentially by the oil (decane) phase.[12] The latter is also reflected in the fact that sulfate latex particles stabilise only water-in-oil emulsions.[8,9]

Table 1 Table of capillary-to-interface separation distance (H), meniscus slope angles (ψ', ψ), meniscus contact diameter (d) and the height of the film (h). Fig. 3(e) corresponds to the critical values

Fig.	H/μm	ψ'/°	ψ/°	d/μm	h/μm
3(a)	4518	–	–	–	–
3(b)	2639	32.6	2.35	590	145
3(c)	2976	44.65	14.45	602	253
3(d)	3217	51.15	15.62	602	289
3(e)	3566	71.5	21.8	590	349
3(f)	3795	–	–	–	–

In summary, we have designed a novel method for studying the interaction between liquid surfaces bridged by solid particles which allows information about the particle wettability of the particle monolayer on the surface of the liquid drop to be obtained by measurement of macroscopic parameters of the liquid menuscus. We present direct proof that the contact angle of the sulfate latex particles at the decane/water interface is larger than 90° which is a neccesary condition for bridging of the two liquid surfaces. In a follow up paper we will discuss how the surface pressure of the particle monolayer can be determined.

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Notes and references

1 B. P. Binks, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 21.
2 B. P. Binks and S. O. Lumsdon, *Langmuir*, 2000, **16**, 8622.
3 Z. Du, M. P. Bilbao-Montoya, B. P. Binks, E. Dickinson, R. Ettelaie and B. S. Murray, *Langmuir*, 2003, **19**, 3106.
4 S. Arditty, C. P. Whitby, B. P. Binks, V. Schmitt and F. Leal-Calderon, *Eur. Phys. J. E*, 2003, **11**, 273.
5 R. Aveyard, J. H. Clint, D. Nees and V. N. Paunov, *Langmuir*, 2000, **16**, 1969; E. J. Stancik, M. J. O. Widenbrant, A. T. Laschitsch, J. Vermant and G. G. Fuller, *Langmuir*, 2002, **18**, 4372.
6 F. Ghezzi, J. C. Earnshaw, M. Finnis and M. McCluney, *J. Colloid Interface Sci.*, 2001, **238**, 433; G. Tolnai, F. Csempesz, M. Kabai-Faix, E. Kalman, Zs. Keresztes, A. L. Kovacs, J. J. Ramsden and Z. Hórvölgyi, *Langmuir*, 2001, **17**, 2683.
7 V. N. Paunov, B. P. Binks and N. P. Ashby, *Langmuir*, 2002, **8**, 6946.
8 E. Vignati, R. Piazza and T. P. Lockhart, *Langmuir*, 2003, **19**, 6650.
9 B. P. Binks and S. O. Lumsdon, *Langmuir*, 2001, **17**, 4540.
10 J. I. Amalvy, S. P. Armes, B. P. Binks, J. A. Rodrigues and G-F. Unali, *Chem. Commun.*, 2003, 1826.
11 K. P. Velikov, F. Durst and O. D. Velev, *Langmuir*, 1998, **14**, 1148.
12 V. N. Paunov, *Langmuir*, 2003, **19**, 7970.
13 E. J. Stancik, M. Kouhkan and G. G. Fuller, *Langmuir*, 2004, DOI: 10.1021/1a0356093.