

Film climbing of particle-laden interfaces

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Abstract

Recent experiments have shown that coalescence of an oil/water/nanoparticle Pickering emulsion contained in a vial induces a nanoparticle-film to climb up the walls of the vial. Here we show that this phenomenon is highly general and can be induced by a variety of particle types, particle sizes ranging from a few nm to a few μm , and different emulsion types. Many of the features of film growth described previously with nm-sized particles are found to remain true even with the far larger particles studied here. Binks et al. [B.P. Binks, J.H. Clint, P.D.I. Fletcher, T.J.G. Lees, P. Taylor, Growth of gold nanoparticle films driven by the coalescence of particle-stabilized emulsion drops, *Langmuir* 22 (2006) 4100–4103] have postulated that the particle films that climb up the walls of a vial are actually comprised of one oil layer and one water layer, with particles adsorbed at the interface between them. We confirm this “sandwich” structure experimentally and also show that such interfacially adsorbed particles can easily exert the very modest surface pressure necessary to sustain the weight of the film. Our experiments highlight the importance of prewetting the walls of the vials; films do not climb unless the walls are prewetted. Finally, while some climbing films are tightly packed particle monolayers, tight packing is not essential; even sparsely populated monolayers can display film climbing.
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1. Introduction

Particles that are partially wetted by two fluids often have a strong tendency to adsorb at the fluid/fluid (liquid/liquid or gas/liquid) interface [1–3]. The energy for desorbing such an interfacially adsorbed particle can be calculated from geometric arguments and is often far larger than the thermal energy kT . Hence particle adsorption is nearly irreversible, i.e. particles can form highly stable monolayers. If such particle monolayers are present on the surface of drops, they can prevent coalescence of drops, and hence lead to stable “Pickering” emulsions. However, if the particle concentration in the monolayer is insufficient, particle-covered drops can still coalesce, and hence stable Pickering emulsions do not result. Under these circumstances a remarkable phenomenon has been noted: as particle-laden drops of an unstable Pickering emulsion coalesce with each other, a film of particles is seen to grow on the walls of the vessel containing the emulsion. This phenomenon was first reported by Mayya and Sastry [4] using emulsions of oil and water with surface-

modified gold nanoparticles adsorbed at the interface. Binks et al. [5] then revisited this same system in greater detail with a slightly different surface chemistry. Both articles [4,5] reported that a violet film of gold nanoparticles could be seen climbing up the walls of the vessel as the emulsion drops coalesced. Very recently, Binks et al. [6] have reported that hydrophobic silica particles and Teflon particles show similar behavior at the air/water interface, and particle films form on the walls of the vessel as air bubbles coalesce.

The physical picture proposed [5] to explain this phenomenon (which will be discussed in greater detail later in Fig. 3) is that as drops coalesce, the total liquid/liquid interfacial area of the emulsion reduces. If particles are adsorbed irreversibly, this decrease in interfacial area corresponds to an increase in interfacial concentration of particles. At some sufficiently high interfacial particle concentration, the large surface pressure of the particles forces the oil/water interface to spread and form a film on the walls of the vessel [5]. As per this proposed mechanism of film formation, the final structure of the film consists of particles sandwiched between layers of water and oil.

Here we further elucidate several aspects of film formation experimentally. First the film formation phenomenon is shown to be much more general than the specific systems discussed

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previously [4–6]; it can occur with a wide variety of particle types and sizes, and even with non-aqueous systems. Furthermore, the film formation process is quite similar for the relatively large particles studied here as compared to the nanoparticles studied previously. Secondly, we image the films across a wide range of magnifications to show that particle loading strongly affects the particle packing and the mobility in the film. Next we directly verify some of the hypotheses about film formation made by Binks et al. [5], and in particular verify that the film indeed has the sandwich structure proposed previously, and that the surface pressure of the particles is sufficient to support the weight of the films. Finally, detailed visualization of film climbing indicates that the process of film formation is more complex on initially dry substrates than on prewetted substrates. Specifically, the growth of the particle film is preceded by the growth of an apparently particle-free film of oil.

2. Materials

Light mineral oil (henceforth referred to as “oil”) was obtained from Fisher and was used as the non-polar phase in all the experiments in this paper. The polar phase was either water (Milli-Q) or ethylene glycol, obtained from Fisher. Octadecyltrichloromethylsilane (OTS), of 97% purity was purchased from Gelest Inc. All chemicals were used as received. Milli-Q water was used in all experiments.

A majority of this study was conducted on iron oxyhydroxide (FeOOH) particles (Fig. 1a) donated by Elementis Pigments Inc. The particles are polydisperse, elongated with an average length of about 0.6 μm , have a density of 4.03 g/cm^3 , and appear yellow in color. Limited experiments were conducted with three

other particle types: carbonyl iron (Fe, ISP Technology), iron oxide (Fe_2O_3 , BASF), and spherical silica (Tokuyama Inc.) to show the generality of film climbing with respect to particle types. The carbonyl iron particles (Fig. 1b), also known as iron pentacarbonyl, are spherical with 2–4 μm diameter, and appear black. The iron oxide particles, which are red in color, appear in SEM images (Fig. 1c) to be micron-scale aggregates of elongated nanoparticles. Some of these aggregates may persist even after ultrasonication during our sample preparation. The spherical silicas are monodisperse, 2.7 μm in diameter, and were rendered hydrophobic by treating with dichlorodimethylsilane (DCDMS). Details of the procedure are provided elsewhere [7,8], but briefly dried silica particles were reacted with DCDMS in anhydrous cyclohexane, centrifuged, washed with cyclohexane and chloroform, and then dried in air at 110 $^\circ\text{C}$.

No surfactants were used in any of this research; all of these particles were active at the oil/water interface without added surfactant.

Most of the imaging was performed with a Canon Digital Rebel SLR camera equipped with a 55 mm focal length lens and a 12 mm extension tube. Higher magnification images of Section 3.2 were collected with Sony CCD video camera equipped with a video-zoom lens (Navitar 6000).

3. Results

3.1. The film-climbing experiment, mechanism, and its generality

We will first note some qualitative features regarding film growth in the case of FeOOH particles, and specifically point out similarities with previous research on the much smaller gold nanoparticles [4,5]. The basic film growth procedure, denoted the “shake-and-stand” procedure, consisted of shaking together all the ingredients in a vial for a few seconds, and then allowing the vial to stand upright under quiescent conditions. A typical recipe was as follows: an aqueous suspension of 0.07 wt% particles was prepared and sonicated for 5 min. Two millilitre of this suspension, and 2 ml of oil was added to an 8 ml glass vial; this corresponds to a particle loading of 1.4 mg for the 4 ml of total liquid. The vial was shaken by hand for a few seconds. This shaking gave the particles an opportunity to adsorb at the oil/water interface, and particle-covered drops were evident after shaking (Fig. 2a); the fact that the drops rise to the top indicates that the drops are oil and the emulsion is of the oil-in-water type. At this particle loading, these particle-covered oil drops were not stable and started coalescing, and a film of particles was found to climb upwards along the walls of the vial (Fig. 2b). Henceforth in this paper, we will use the term “film climbing” rather than “film growth” or “film formation” used previously. The particle film continued climbing (Fig. 2c and d), generally reaching all the way up to the top of the vial (Fig. 2e).

As noted by Binks et al. [5] film climbing is directly associated with coalescence of the drops; once coalescence stops, film climbing stops as well. From visual observation of the top surface of the emulsion, we can describe the film growth procedure in greater detail than previously [4,5]. In particular, unlike

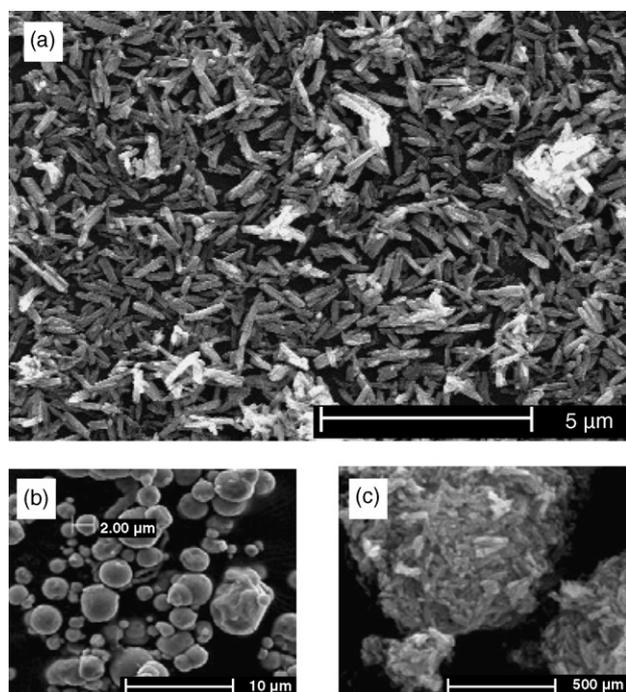


Fig. 1. SEM images of the three types of particles used in the experiment. (a) Iron oxyhydroxide FeOOH, (b) a carbonyl iron (Fe), and (c) iron oxide (Fe_2O_3).

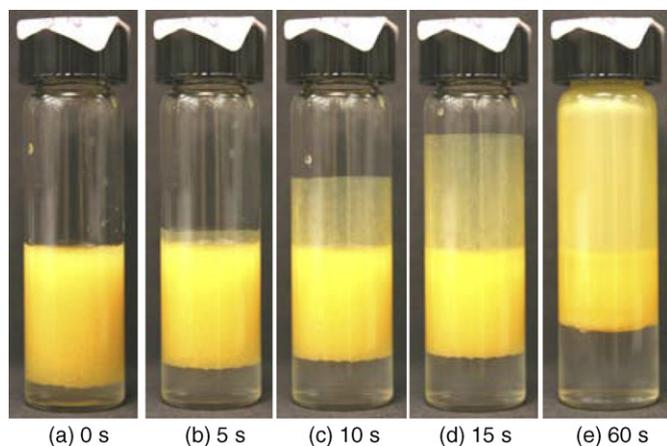


Fig. 2. Sequence of film climbing for FeOOH particles. The time after stopping the shaking of the vial is noted below each image. The change in color intensity from (d) to (e) is attributable to an increase in interfacial concentration of particles in the film with increasing coalescence. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

Mayya and Sastry [4], film climbing does not start immediately after the emulsion has “settled down after the shaking process” [4]. In the as-shaken vial, all of the oil is emulsified, and hence the top surface of the liquid is the air/water interface as shown in Fig. 3a. Initial coalescence causes a lens of oil to form at the top surface of the emulsion (Fig. 3b), but this initial coalescence is not accompanied by film climbing. With additional coalescence, the lens increases in extent until the entire cross-section of the vial is spanned by a continuous oil/water interface (Fig. 3c). Subsequent coalescence of drops with the continuous oil/water interface induces film climbing. Indeed, the advancing front of the climbing film occasionally appears to “jump” upward due to the coalescence of an especially large drop. The mechanistic explanation suggested previously is that as coalescence deposits particles at the continuous oil/water interface, it raises the particle concentration locally. The corresponding spreading pressure (i.e. Marangoni stress) pushes the oil/water

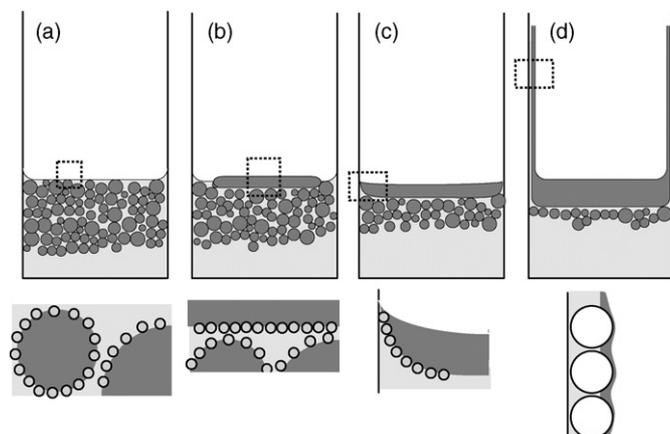


Fig. 3. Schematic of film climbing process. (a) Emulsion after shaking: particles are adsorbed at the interface, (b) drops coalesce and form an oil lens, (c) the lens grows to span the cross-section of the bottle, and (d) particles force the film to climb upwards. In (a)–(d), the region of each dotted rectangle is shown in magnified form below each figure.

interface up the walls of the vial. Consistent with this physical picture, coalescence of drops with each other (rather than with the continuous oil/water interface) did not contribute to film climbing. In summary, while experimental observations of film climbing of the FeOOH particles are broadly in agreement with the physical picture proposed by Binks et al. [5], Fig. 3 gives a more refined picture of the initial stages of film climbing, in particular stressing that film climbing does not start until a lens of oil completely covers the top surface of the vial. (Previous publications are not explicit on this point, but the schematic in Binks et al. [5] suggests that the top surface of their emulsion is the air/oil interface even at the earliest time of observation after shaking the vial.) Finally, we note that Goedel and co-workers [9,10] have described the phenomenon of “particle-assisted wetting” in which interfacially active particles induce the spreading of one liquid on the surface of another immiscible liquid. The film-climbing phenomenon may be regarded as a variation of particle-assisted wetting in which particles assist a liquid/liquid interface to spread on a solid substrate.

The film-climbing phenomenon is robust, and occurs even if the above preparation procedure is not followed exactly. For example, while Fig. 2a started with a good dispersion of particles in the aqueous phase, this was not essential. The same phenomenon could be seen if dry particles are added to a vial already containing oil and water, or if particles are first dispersed in oil and then shaken with water. Film climbing can be repeated numerous times in the same vial. However, if the vial (with a climbed film) is allowed to stand for several days, or if the vial is left open (allowing water to evaporate), the particles adhere strongly to the walls of the vial and cannot be dislodged by shaking the vial.

All of the above observations are broadly true for several other particle types studied in our lab. Fig. 4a shows a film of μm -sized carbonyl iron particles induced by coalescence of an oil-in-water emulsion; in this system, film climbing proceeded essentially identically to Fig. 2. Fig. 4b shows a film of iron oxide Fe_2O_3 particles formed from coalescence of an oil-in-water emulsion.

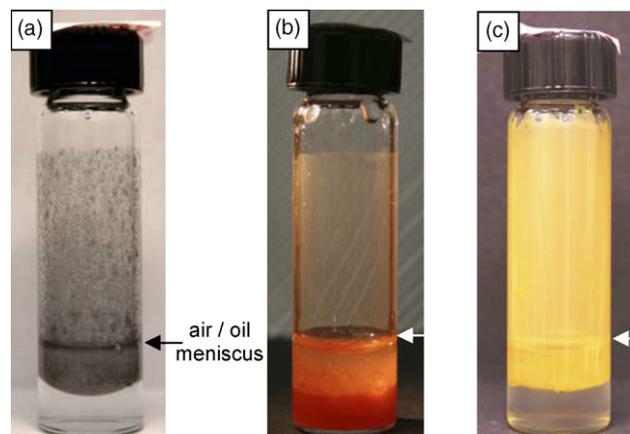


Fig. 4. Climbed films of (a) carbonyl iron particles at oil/water interface, (b) Fe_2O_3 particles at oil/water interface, and (c) FeOOH particles at oil/ethylene glycol interface. Arrows show the position of each air/oil meniscus. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article).

A minor difference in this case is that the aqueous phase in the lower part of the vial appeared bright red even after film climbing, suggesting that most of the particles were still suspended in water. The film climbing was therefore driven by only the fraction of the particles that adsorbed at the oil/water interface. Fig. 4c shows a FeOOH climbing film formed from coalescence of an oil-in-ethylene glycol emulsion—to our knowledge, the first example of film climbing in a non-aqueous system. The film climbed much more slowly in this case, typically taking a few minutes to reach the top of the vial. We believe that this is because the higher viscosity of ethylene glycol (vs. water) retards both coalescence as well as film climbing. Finally, we have also seen film climbing induced by coalescence of a water-in-oil emulsion containing 2.7 μm diameter silica particles. Since the particles were rendered hydrophobic (see Section 2), the initial emulsion was of the water-in-oil type as evidenced by the fact that the drops sank after the vial was shaken. Therefore the coalescing water drops were located far below the top surface (i.e. air/oil interface), and hence film growth began far below the top surface of the emulsion. This is different from all the previous cases in which the coalescing drops [4,5] or bubbles [6], were present near the topmost air/fluid interface. These colloidal silica particles are not significantly colored, therefore the corresponding films (not shown) are more difficult to see than those shown in Fig. 4.

To summarize, combining the results of this research with those of previous publications, it appears that film climbing can occur under a wide variety of circumstances. The possible particle types include gold nanoparticles [4,5], fumed silica [6], Teflon fluoropolymer [6], and FeOOH, Fe_2O_3 , Fe, and colloidal silica (present research). The particles include a variety of surface chemistries and sizes ranging from <20 nm for the gold nanoparticles, to well over a micron for the Fe particles and the spherical hydrophobic silica particles. Film climbing can be induced in a variety of fluid pairs: by coalescence of air bubbles in water [6], oil drops in water (this research and [4,5]), water drops in oil (this research), or oil drops in ethylene glycol (this research). Thus we conclude that the film climbing behavior, and the corresponding qualitative features, are very general. We propose that any system in which (1) particles adsorb at a fluid/fluid interface but (2) do not stop coalescence, can grow films on the walls of the vessel.

The remainder of this paper describes more detailed experiments on one specific system, viz. the oil/water emulsions with FeOOH particles. These particles were chosen because the corresponding films are bright yellow, and hence are easy to image. Furthermore, the particles themselves are sufficiently large that they can be imaged adequately by environmental SEM. Section 3.2 considers the effect of varying the particle loading on the film climbing process. Sections 3.3 and 3.4 verify the two key hypotheses [5] underlying the physical picture of Fig. 3, viz. (1) that film climbing occurs because of the spreading pressure of the interfacially adsorbed particles, and (2) that the final structure of the film consists of the particles sandwiched between layers of oil and water. Finally Section 3.5 examines the effect of the wettability of the walls on film climbing.

3.2. Effect of particle loading

The particle loading was found to affect the color and mobility of the films, and this will be discussed here. In the following, the particle loading is quoted as the mass of particles added to the vial, keeping the oil and water phase volumes fixed at 2 ml each (same as Fig. 2). The particle loading, denoted by m , was varied from 1.4 mg to 0.014 mg. Films generated from the shake-and-stand procedure were imaged in at three different magnifications.

The images in the top row of Fig. 5 were taken with a digital SLR camera. Fig. 5a shows that at the highest loading of $m = 1.4$ mg (identical to Fig. 2, but after full coalescence had occurred), the film is bright yellow. Interestingly, the bottom portion of the film (i.e. the oil/water meniscus) appears wrinkled and buckled. Such a buckled monolayer has been shown to occur when the particle monolayer is tightly crowded [11,12]. With decreasing m , the color intensity of the films decreased (Fig. 5a–d). At the lowest loading of $m = 0.014$ mg (Fig. 5a), the very faint color of the film made visualization of the fully climbed monolayer difficult, however, the climbing front could still be imaged while the film was still advancing up the walls of the vial. The decrease in color intensity with particle loading is likely attributable to a decrease in the interfacial concentration of particles in the film.

To verify this, the shake-and-stand experiments were repeated but imaging was conducted with a CCD-video camera equipped with a video-zoom lens. At this higher magnification, the decrease in interfacial concentration in the film with decreasing particle loading is clearly apparent (Fig. 5e–h). At the highest loading of $m = 1.4$ mg (Fig. 5e), the film appears featureless, characteristic of a tightly packed layer of particles with little intensity contrast. With decreasing particle loading, some contrast in the form of dark spots appears, and at $m = 0.35$ mg (Fig. 5g), the film has several holes in which no particles are visible. At the lowest loading of $m = 0.014$ mg loading (Fig. 5h), the film is comprised of sparse white specks (presumed to be either individual particles or small particle clusters), with large areas of the film appearing to be particle free.

Finally, we sought to image the structure of the films at the resolution of single particles. Standard SEM is not suitable for this purpose because while it is easy to evaporate all the water from the films, it is not possible to evaporate all the mineral oil. Even traces of oil are sufficient to compromise the high vacuum of a SEM chamber. Therefore we imaged films using environmental scanning electron microscopy (E-SEM), which permits imaging under modest vacuum levels at which evaporation of mineral oil is not a concern.

The shake-and-stand procedure was repeated in vials scored on the outside with a diamond cutter, and the vials were allowed to stand for 2 days to allow the films to drain. The oil and water in the vials was then withdrawn with a pipette. We sought to characterize the structure of the as-climbed film, and hence it was important to verify that the structure was preserved prior to electron microscopy. Therefore, during the entire 2 days of standing and the subsequent pipette withdrawal, the films were

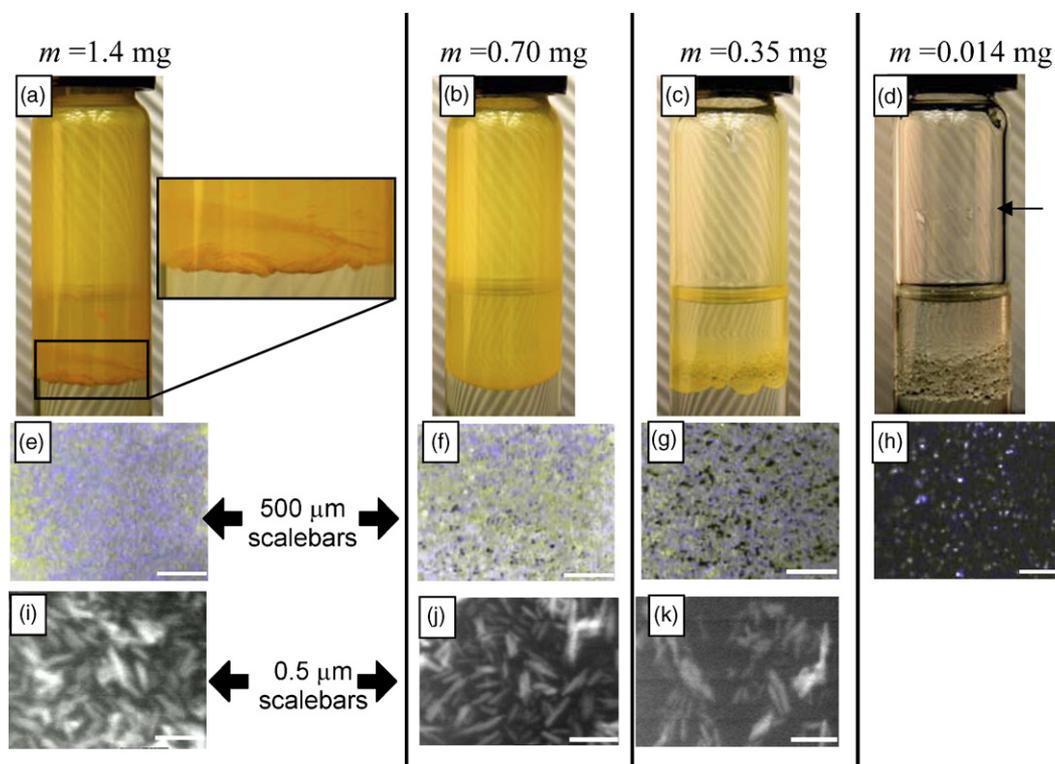


Fig. 5. Film structure at the particle loadings listed above each column of images. (a)–(d) Macroscopic images with a SLR camera. Images (a)–(c) are fully climbed films, whereas (d) was captured during climbing (see text). The upper edge of the climbing film is indicated by the arrow in (d). The inset to (a) is a magnified view of the buckled/wrinkled film. (e)–(h) Optical images of the climbed film with a zoom-lens. Regions with particles appear white. (i)–(k) E-SEM images, with particles appearing white. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article).

imaged with the video-zoom lens. Such imaging showed that at $m = 0.014$ mg, the film structure was not preserved when withdrawing oil and water with a pipette, and hence this sample was not studied further. At the higher particle loadings however, the films were immobile (see below) and did not appear to undergo any changes during the standing or the withdrawal. Therefore these films were deemed suitable for subsequent imaging; these vials were broken along the scores, and fragments of the glass walls were examined by E-SEM at a voltage of 28 kV, 8 mm working distance, and a vacuum of 3 Torr. E-SEM does not require samples to be coated with a conductive layer of metal, hence we believe that these images (Fig. 5i–k) are truly representative of the structure of the as-climbed films. These images confirm that $m = 1.4$ mg corresponds to a tightly packed film, and that films grown from lower particle loadings do have particle-free regions. Indeed, Fig. 5k indicates that at $m = 0.35$ mg, the film is far from close packed.

Much insight can be gained by comparing the area required to accommodate all the particles at the interface, A_{particle} , with the area of the climbed films, A_{film} . To make this comparison, we assume that each particle is a cuboid of dimensions $L \times w \times w = 0.6 \mu\text{m} \times 0.12 \mu\text{m} \times 0.12 \mu\text{m}$ as estimated from Fig. 1a. Then assuming that particles lie flat on the interface, and that all particles are adsorbed on the interface, a simple geometric calculation yields the area required for the interfacially adsorbed particles. These numbers are listed as a function of particle loading in Table 1. The vial diameter (13.5 mm) and the typical height of the climbed films (about 20 mm) yields the total interfacial area, A_{film} , after film climbing is complete; this number is noted in the third column of Table 1.

A comparison of these numbers allows a simple interpretation of the images of Fig. 5. At the lowest particle loading, $A_{\text{film}} \gg A_{\text{particles}}$, and hence the monolayer is only sparsely populated by particles, as indeed evident in Fig. 5h. At $m = 0.35$ mg

Table 1
A comparison of area required by interfacially adsorbed particles with area of films

Loading, m (mg)	Interfacial area of particles, $m/(\rho w)$ ^a (mm ²)	Total area of climbed film, $\pi R^2 + 2\pi R h$ ^b (mm ²)	Remarks
0.014	29	143 + 848 = 991	Sparse particles in film
0.35	725		Some particle-free regions
0.7	1450		
1.4	2900		Close packed with buckling

^a This assumes that the particles have dimensions of $L \times w \times w$ (see text), that all particles are at the interface, and that they are tightly packed. ρ is the particle density, 4.03 g/cm³.

^b Here the vial diameter is $2R = 13.5$ mm, and the film height is assumed to be $h = 20$ mm.

and $m = 0.7$ mg, $A_{\text{film}} \approx A_{\text{particles}}$, consistent with films with a high – but still incomplete – particle coverage (Fig. 5f, g, j, and k). Finally, at 1.4 mg the $A_{\text{film}} \ll A_{\text{particles}}$ and hence the film area is not sufficient to accommodate all the particles even if they are tightly packed, thus causing the film to buckle (Fig. 5a).

Particle loading was also found to dramatically affect the mobility of particles within the film. This was clearly visible in observations of climbing films at the high magnification of the video-zoom lens. At $m = 1.4$ mg, the film climbed like a rigid “sheet”, the advancing edge of the climbing film was straight and horizontal, and different parts of the film climbed at exactly the same speed with no relative motion within the film. At lower loadings, individual particles or particle clusters had substantial mobility, the advancing edge was jagged, and at any instant, different regions of the film had different upward climbing velocities. Finally, at the lowest loading of $m = 0.014$ mg, the film remained highly mobile even after climbing: even after 2 days of standing the vial, the white specks evident in Fig. 5e could be set in motion by disturbing the vial even slightly. These changes in film mobility with particle loading will become evident in another context in Section 3.3 in this paper.

Finally, Binks et al. [5] have speculated that in some cases, their gold nanoparticles films may consist of multiple layers. We have seen no evidence of multilayer formation in our experiments, and our E-SEM images seem to suggest that the films are monolayers. Yet, the FeOOH films at high concentration can readily fold, wrinkle and buckle as seen in the inset to Fig. 5a. These wrinkles and folds relax and reform upon tilting the vial to disturb the monolayer; it is therefore conceivable that such an ability to form folds may permit multilayer formation in some cases.

3.3. Direct verification of the film structure

As mentioned at the end of Section 3.1, one essential feature of the physical model of film climbing [5] is that the final film

structure is comprised of a layer of particles between films of water and oil. To verify this directly, we contacted the surface of the film, first with a drop of oil and then with a drop of water using the experimental assembly illustrated in Fig. 6a. A Hamilton microsyringe with a 28 gauge needle (0.36 mm, also the dimension of the scalebars in images of Fig. 6), was attached to a micrometer-translation stage. It was then placed with its tip close to the inner wall of a freshly shaken vial. After film climbing was complete and the particles in the monolayer had stopped moving, the microsyringe was translated towards the film until the drop of liquid (oil or water) at the tip of the syringe contacted the monolayer. This experiment was conducted at two different particle loadings: $m = 0.35$ mg (same as Fig. 5c), and $m = 1.4$ mg (same as Fig. 5a). The results are provided as movie files (OilTouch0_35mgFilm.avi, WaterTouch0_35mgFilm.avi, OilTouch1_4mgFilm.avi, and WaterTouch1_4mgFilm.avi) and some frames extracted from these movies are shown in Fig. 6.

At both particle loadings, upon contacting the monolayer with the oil drop (Fig. 6b and d), the oil drained away without disrupting the monolayer. Furthermore, the movie OilTouch0_35mgFilm.avi ($m = 0.35$ mg) shows that immediately after coalescence, the oil spreads radially outwards with no sharp meniscus visible. These observations strongly indicate that the top surface of the monolayer is a film of oil.

In contrast, upon contacting the films with a water drop, the water did not spread evenly on the surface of the film confirming that the top surface of the film is not water. Instead Fig. 6c and e show that the water drop coalesced with the film, but left a hole in the monolayer. This indicates that the water drop coalesced not with the top surface of the film, but with an underlying layer of water. Certainly, such coalescence with an underlying water layer cannot occur without disrupting the particles in the monolayer. In summary, these experiments provide strong support for Fig. 3d, viz. that the final film is comprised of a particle monolayer sandwiched between layers of oil and water [5].

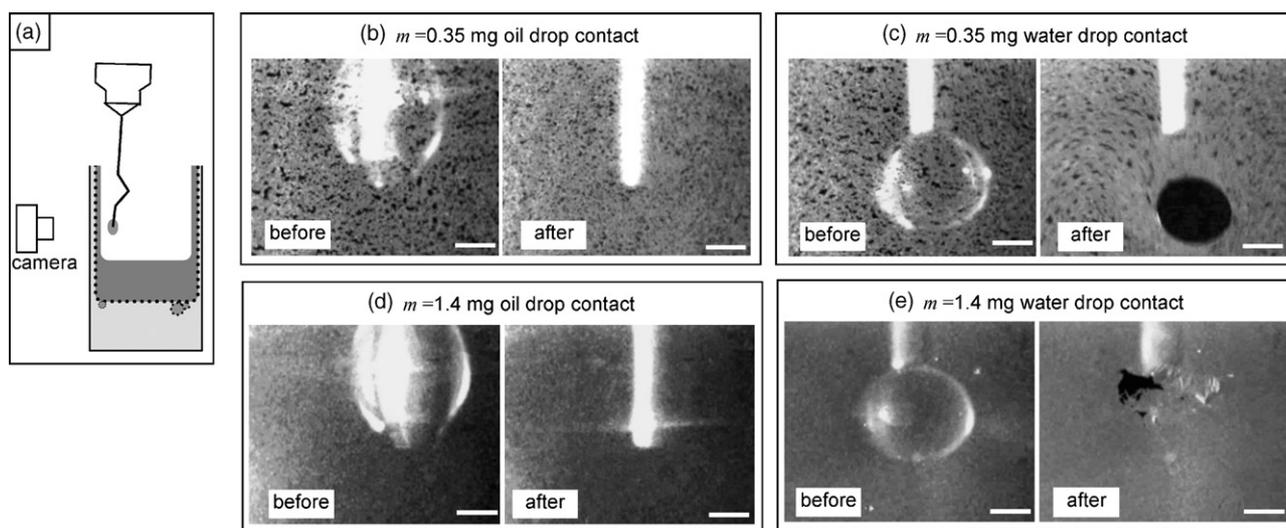


Fig. 6. (a) Schematic of contacting climbed films with drops of oil or water. The film is contacted with an oil drop in (b) and (d) and with a water drop in (c) and (e). In each pair of images, the left image is before drop contact, and the right image is after drop contact. The scale bar in each image is 0.36 mm, and the needle would appear to be the same diameter if it were in sharp focus. The oil wets the outer surface of stainless steel needle, whereas a water drop remains pendant, hence oil and water drops appear to be of different shapes. The entire drop-contact experiments are available as movies in the supplemental material.

The movies also illustrate the dramatic difference in the mobility of the monolayers with changing particle loading mentioned at the end of Section 3.2. At $m=0.35$ mg, upon contacting an oil or water drop, a large area of the monolayer becomes mobile and different parts of the monolayer move readily with respect to each other (see movies *OilTouch0.35mgFilm.avi* and *WaterTouch0.35mgFilm.avi*). In contrast, at $m=1.4$ mg, coalescence affected the monolayer only locally (*OilTouch1.4mgFilm.avi* and *WaterTouch1.4mgFilm.avi*). Moreover, the hole created in the $m=1.4$ mg film (Fig. 6e) is jagged with some wrinkles in the surrounding area, indicative of a jammed and completely immobile monolayer.

3.4. Spreading pressure due to particle adsorption

As mentioned in Section 3.1, the postulated mechanism for film climbing is that as coalescence deposits particles at the continuous oil/water interface, the local increase in particle concentration causes a surface pressure (or spreading pressure), which in turn drives film growth. It is therefore crucial to establish that these particles can exert a surface pressure *at all*, and if so, verify that the pressure is sufficient to explain film climbing.

Surface pressure can be measured using a pendant drop apparatus, but for these experiments, the shake-and-stand procedure of adsorbing particles at the interface is not suitable. Hence we devised an alternative procedure. A 0.07 wt% particle/water suspension was charged into the syringe of the pendant drop apparatus (Krüss DSA100) and a drop of this suspension was injected into the oil phase held in a glass cuvette. This pendant drop was imaged and the interfacial tension obtained from drop shape analysis. At short times, the interfacial tension was found to be close to that of oil/water (~ 62 mN/m). With time, as the particles adsorbed at the oil/water interface by sedimentation or

by Brownian motion, the interfacial tension reduced to about 25% of its original value (Fig. 7). The final value of 15.5 mN/m at 19 h is not an equilibrium value and the interfacial tension was still reducing gradually. It is noteworthy that the Laplace-Young equation fits the shape of pendant drop throughout the experiment, suggesting that the interfacial tension remained uniform over the surface of the drop as particles adsorbed. The results of Fig. 7 demonstrate that adsorbed particles can exert substantial surface pressures. Non-interacting “hard” particles at modest interfacial concentrations can only exert relatively small surface pressures (roughly $RT \times$ interfacial concentration), thus the substantial surface pressures of Fig. 7 are likely attributable to repulsion between interfacially adsorbed particles [13–15].

It is of immediate interest to test if the magnitude of surface pressure found here (about 40 mN/m) is sufficient to support a film with the structure of Fig. 3d. We write a simple force balance at equilibrium for the situation of Fig. 3d

$$\frac{d\pi}{dz} = (t_o\rho_o + t_w\rho_w + m_p)g = t_{\text{total}}\rho_{\text{ave}}g \quad (1)$$

where t_o and t_w are the thicknesses of the oil and water layer, respectively, ρ_o and ρ_w are their densities, m_p the mass of particles per unit area of the film, π the surface pressure, and z is the distance coordinate along the vertical direction. The quantity in the parenthesis has been defined as $t_{\text{total}}\rho_{\text{ave}}$, which is the mass per unit area of the film. The above equation essentially states that at equilibrium, the weight of the film must be balanced by a gradient in the surface pressure (i.e. the Marangoni stress) exerted by the particles. Integrating the above equation over the height of the film (or equivalently, performing a force balance over the entire height, h , of the film) obtains

$$\pi(h) - \pi(0) = \int_0^h t_{\text{total}}\rho_{\text{ave}}g dz, \quad (2)$$

i.e. the weight of the entire film is balanced by a difference in spreading pressure at the bottom versus at the top. We first note that *at equilibrium*, the film cannot be significantly thicker than the particle size; any excess oil or water would drain down with time. Accordingly, an order of magnitude estimate of the weight of the film may be obtained by simply assuming that the total thickness of the film (water layer, particles, and oil) is equal to the size of the particles (about $0.6 \mu\text{m}$ in their largest dimension), the mean density of the film is 2000 kg/m^3 , and the film height is typically at least 20 mm in our experiments. Substituting these numbers obtains $\pi(h) - \pi(0) = 0.2 \text{ mN/m}$. Thus, only a small difference in surface pressure (and presumably a small difference in particle concentration) is sufficient to support the weight of the film at equilibrium.

Since the pendant drop experiment measured surface pressures of over 40 mN/m, we conclude that the particles can easily develop the surface pressure necessary to support the weight of the film at equilibrium. In fact, the above analysis suggests that the measured surface pressure may be able to sustain an equilibrium film height of at least 2 m. Indeed, Binks et al. [5] were able to demonstrate films of the order of 1 m in height with gold nanoparticles, although the procedure was more complex than the simple shake-and-stand procedure followed here.

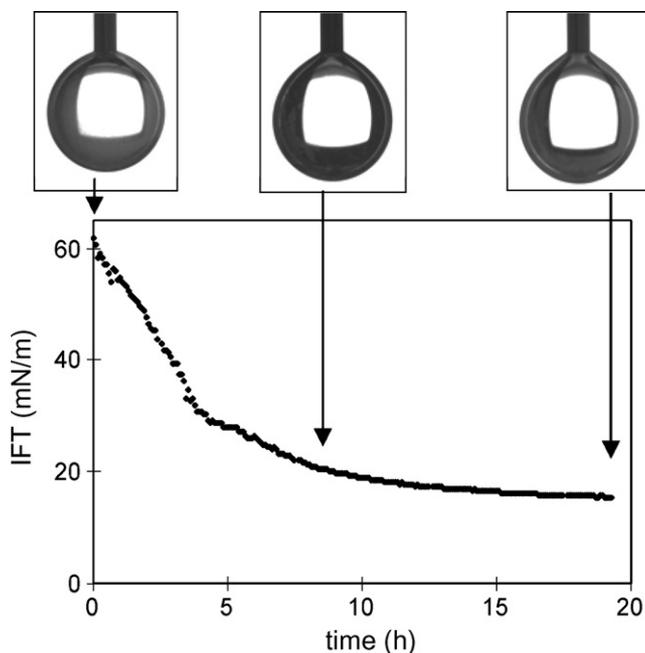


Fig. 7. Interfacial tension (IFT) vs. time, and corresponding pendant drop shapes at $t=0$, $t=8.33$ h, and $t=18.6$ h.

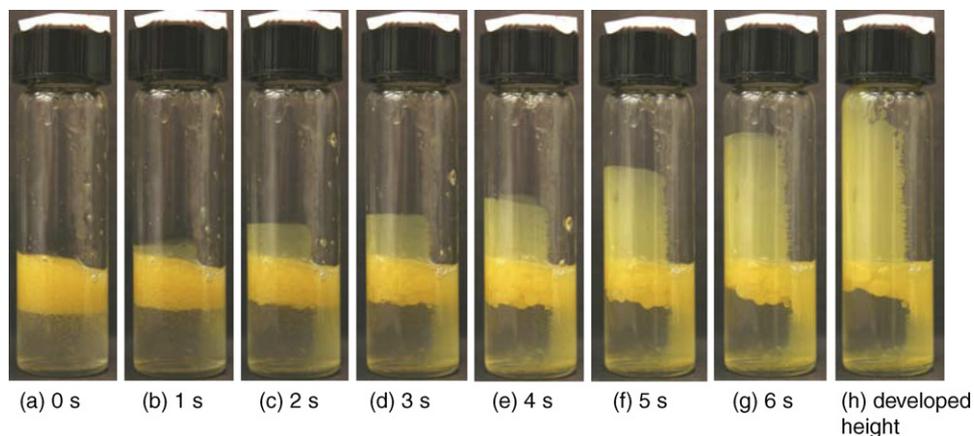


Fig. 8. Effect of hydrophobicity of the walls of the bottle. The time after stopping the shaking of the vial is noted below each image. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

3.5. Effect of wettability of walls

For gold nanoparticles, the wettability of the walls was shown to play a significant role in the film climbing process. Binks et al. [5] showed that if the glass/water/oil contact angle (as measured through the water) was less than 90° , i.e. the glass was relatively hydrophilic, the film climbed upwards. For hydrophobic glass surfaces with contact angle exceeding 90° , the film growth was

directed downwards. We sought to verify that the same is true for the much larger FeOOH particles considered here.

A glass vial was laid on its side and 0.5 ml of a 0.005 M solution of OTS in hexane was added using a pipet. After 2 min, the solution was withdrawn with a pipet, the vial rinsed with pure hexane, and finally with water. The vial was kept in the same horizontal position throughout this procedure. The net result of this procedure was to cause a vertical strip of the vial to become

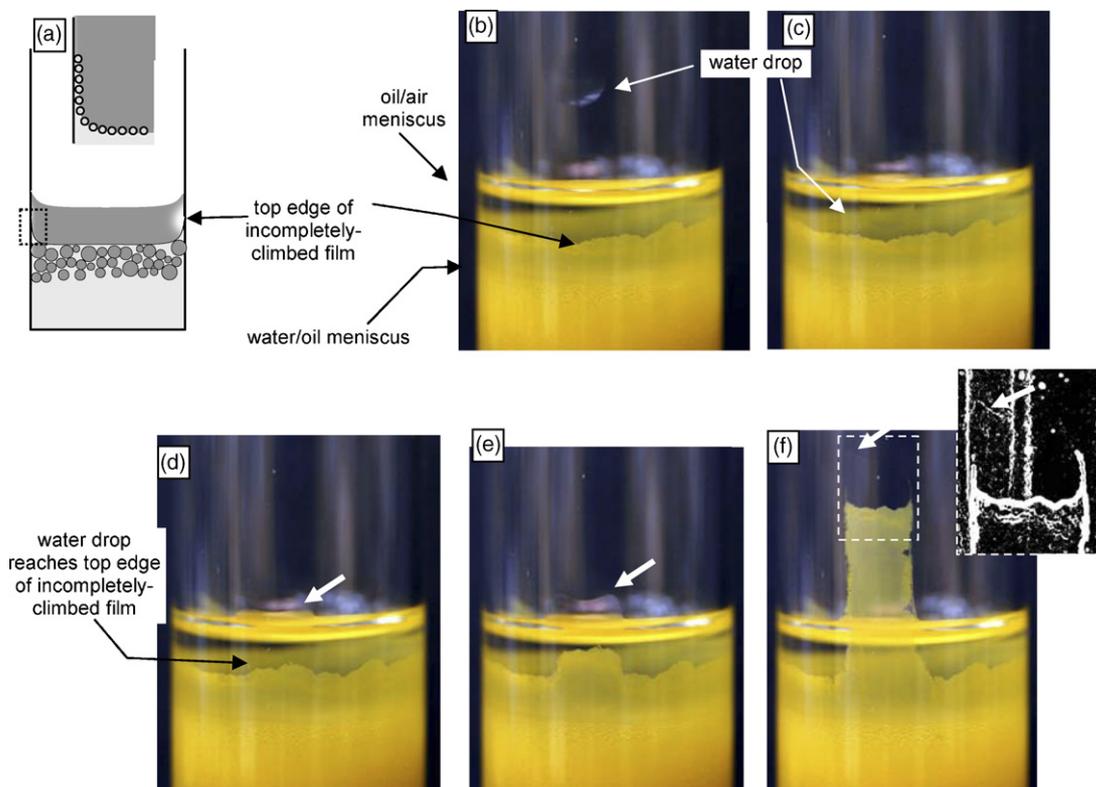


Fig. 9. Effect of prewetting of the walls. (a) Schematic picture and (b) experimental image of a shaken emulsion transferred to a dry vial. The inset to (a), which is a magnified view of the dotted rectangle, shows that a film of particles does form on the wall, but does not climb very high; the top edge of this “incompletely climbed film” is marked in (a) and (b). A water drop was rolled down the wall of the vial as seen in (b); (c) the water drop has entered oil phase, but not yet reached the top edge of the existing particle film; (d)–(f) the water drop reaches the existing particle film, which then climbs up the track left by the water drop. An oil front climbs ahead of the particles; the upper edge of this oil front is identified by the white arrows in (d)–(f). In (f), the oil front is faint, but clearer in the inset which shows a portion of the image subjected to an edge detection algorithm. A movie of this process, UpperAndLowerFront.avi, in another experimental run is available in the supplemental material. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

hydrophobic. The shake-and-stand procedure was then repeated in this vial. As shown in Fig. 8, whereas the film climbed upwards over most of the vial surface, in the hydrophobic portion, the particle film climbed downwards, consistent with Binks et al. [5] Indeed, the downward film grew more readily (its growth appears complete at 1 s), presumably because downward film growth is aided by gravity.

Mayya and Sastry [4] have also noted that gold nanoparticle film formation was considerably faster if the glass surface was prewetted, and once again it is of interest to compare the behavior of the larger FeOOH particles. In the standard procedure of Section 3.1, the glass surfaces are, of course, already wetted during the shaking. To test the effect of prewetting, the oil/water/particle mixture was shaken in one vial, and then carefully transferred into another vial with a pipet. Two cases were contrasted. If the emulsion was transferred into a vial which had been previously rinsed with pure water, coalescence and film climbing occurred unimpeded, similar to Fig. 2. In contrast, if the emulsion was transferred into a dry vial, the oil drops were found to coalesce, but only incomplete film growth was evident. The final state corresponded to Fig. 9a and b: a film of particles reached a few mm above the oil/water meniscus, but never climbed above the oil/air meniscus. In summary, unlike for gold nanoparticles [4], for the FeOOH particles considered here, prewetting does not merely accelerate film formation, but is an *essential* condition for film formation: without prewetting, films do not climb at all.

What is the reason for incomplete film climbing on dry glass? We speculate that film climbing is frustrated by the contact angle hysteresis at the glass/water/oil contact line, i.e. the particles at the oil/water interface in Fig. 9a and b still exert a significant surface pressure, but this pressure is insufficient to advance the oil/water contact line on the dry glass surface. To verify that such a “frustrated” particle monolayer is still capable of film climbing, a water drop was rolled down the inner wall of the glass vial (this drop is visible on the wall of the vial in Fig. 9b). As soon as the drop reached the top edge of the incompletely climbed film (Fig. 9c), a particle film climbed up the track left by the water drop (Fig. 9c–e). This confirms that the incompletely climbed monolayer is capable of film climbing, provided a prewetted wall is made available.

The most remarkable aspect of Fig. 9 is that as soon as the water drop rolling down the wall reached the top edge of the incompletely climbed film, a *second* climbing front was visible far above the advancing particle film. This upper climbing front, whose motion is more clearly visible in the movie “UpperAndLowerFront.avi” supplied as supporting material, appears to be initiated at the *oil/air* interface, i.e. the climbing particles are preceded by a film of oil alone. At longer times, it becomes increasingly difficult to image the upper front, yet, Fig. 9f as well as the movie “UpperAndLowerFront.avi” suggest that it remains a few mm ahead of the climbing particles for much of the climbing process. We are uncertain about the origin of this oil front but present the following hypothesis: as soon as the water drop reaches the top edge of the particle-laden oil/water interface, the particle monolayer starts climbing

at a high velocity. The corresponding bulk flow in the film of water induces an upward motion over the entire oil/water interface—even in parts of the interface not yet covered with particles.

4. Summary and conclusions

We have studied an unusual film-climbing phenomenon in which coalescence of an unstable Pickering emulsion contained in a vial induces a particle-film to climb on the walls of the vial. While this phenomenon has been described previously with nanoparticles at the oil/water or air/water interface, we show that it is very general: film climbing can be induced by particles of a variety of types, and sizes ranging from a few nm to a few μm , can be induced in non-aqueous systems, and can be induced by coalescence of either oil-in-water or water-in-oil emulsions. Furthermore, many of the features of film climbing documented previously for nm-sized particles are found remain valid even when particles are far larger. Accordingly, we postulate that any emulsion in which (1) particles adsorb irreversibly at the interface, but (2) do not stop coalescence, will show film growth on the walls of the vessel containing the emulsion.

The mechanism proposed by Binks et al. [5] is that since particles cannot desorb from the interface, coalescence raises the interfacial concentration of the particles. The corresponding rise in surface pressure induces a monolayer of particles to push the oil/water interface up the walls of the vial. We have verified some key aspects of this postulated mechanism in one specific emulsion system composed of oil, water, and FeOOH particles. In particular, by contacting the films with drops of oil or water, we confirm that the films do indeed have a three-layer structure of particles sandwiched between layers of oil and water. A simple force-balance suggests that at equilibrium, a very modest surface pressure is sufficient to sustain the weight of the film. Pendant drop experiments show that particle adsorption at the oil/water interface can easily induce the surface pressures necessary to explain film climbing. Images of the films across a large range of magnifications show that tight packing is not a necessary condition for film growth; some films are very sparsely populated with particles. Finally, our experiments show that films do not grow on “dry” walls; prewetting is a necessary condition for film growth.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.colsurfa.2007.08.018.

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