

Particle film growth driven by foam bubble coalescence†

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Water films stabilised by hydrophobic particles are found to spread rapidly up the inner walls of a glass vessel containing water and hydrophobic particles when it is shaken; shaking produces unstable particle-stabilised foam bubbles whose coalescence with the air/water interface drives film growth up the inner walls of the container.

The adsorption of particles at liquid interfaces can be very strong if the contact angle between the interface and the nanoparticle surface is not too far from 90°. For particles with diameters larger than about 10 nm, the energy of adsorption is commonly orders of magnitude larger than the thermal energy and so particle adsorption is irreversible. This strong adsorption finds application in the use of particles to stabilize emulsions² and foams³ and is also of interest as a basis for methods to manipulate and assemble nanoparticles into various structures such as 2D films on solids^{4–6} and 3D porous solids.⁷

In 1999, Mayya and Sastry⁴ reported a technique for the spontaneous growth of colloidal nanoparticle superlattice films onto a glass surface from an aqueous dispersion. They took an aqueous dispersion of 13 nm diameter gold particles capped with 4-carboxythiophenol and added an immiscible layer of toluene containing a low concentration of octadecylamine. After vigorous shaking for 30 s and “once the biphasic solution settled down after the shaking process”, a violet coloured film of gold particles rapidly climbed the inner wall of the container starting from the oil/water interface. They were able to immerse a pre-wetted glass slide in the oil/water interface causing the films to grow up the slide so that they could then remove and characterize the gold nanoparticle films. Further work on the mechanism of this process by Binks *et al.*⁶ showed that the growth of the particle stabilised film was driven by coalescence of particle-stabilised emulsion drops with the oil/water interface between the bulk oil and water phases. Because the particles are irreversibly adsorbed, the reduction in emulsion drop interfacial area has to be offset by a corresponding expansion in the film area by growth up the inner walls of the vessel. Similar film growth has also been observed in systems containing silver nanoparticles stabilised by sodium oleate in water/toluene mixtures.⁵ All of the systems showing this type of film growth have involved oil/water systems and have included a surface active agent which is thought to adsorb at both the oil/water and particle surfaces (octadecylamine in the case of refs. 4

and 6 and sodium oleate in ref. 5). In this study we show that rapid film growth can occur in much simpler systems consisting of water and particles alone in the absence of both oil and surfactant.⁸

Two types of particle were used. The first were silica nanoparticles supplied by Wacker-Chemie and have an average primary particle diameter of 10–30 nm but are fused together into so-called “primary aggregates” which are generally non-spherical with sizes in the range 100–500 nm. The particle hydrophobicity was varied by covalently bonding their surfaces with either dichlorodimethylsilane (DCDMS) or poly(dimethylsiloxane) (PDMS) to different extents. The surface hydrophobicity was characterised in terms of the percentage of unreacted SiOH groups remaining at the surface with 100% SiOH (untreated particles) being the most hydrophilic and 20% SiOH being the most hydrophobic particles used here. We also used poly(tetrafluoroethylene) (PTFE) particles (Zonyl[®]MP1400 made by DuPont and supplied by E&E Ltd, UK) with a primary aggregate diameter of 7–12 μm and a specific surface area of 3 m² g⁻¹. Water, purified by reverse osmosis and passage through a Milli-Q reagent water system, had a resistivity of >18 MΩ cm. All experiments were made at room temperature of 20 °C.

Films for microscopy were produced in a home-built cell which had a well of dimensions 13 × 63 × 3 mm. Following addition of water and particles, a standard microscope slide was placed on top of the well to seal it. Shaking of the cell produced a particle film on the slide which could then be removed, dried and imaged. Optical micrographs were recorded using a Nikon Labophot transmission microscope. Scanning electron micrographs were taken using a Zeiss EVO 60 SEM instrument with a voltage of 22 kV and a probe current of 20 pA. Samples for SEM were coated with an Au/Pd (mass ratio 82 : 18) film of 1.5 nm thickness and attached to the sample mount using a conductive silver solution. SEM images were recorded with the samples tilted 40° from horizontal. The contact angles of water drops on solid surfaces in air were measured using a Krüss DSA10 drop shape analyser.

The film growth phenomenon can be summarised as follows (see video included as ESI† and Fig. 1).

A small mass, typically 0.01 g, of hydrophobic particles is placed on the surface of 10 ml of water in a measuring cylinder (28 mm inner diameter by 200 mm height). Vigorous hand shaking for 20 s or so produces a few ml of unstable foam bubbles. When shaking is stopped, coalescence of the foam bubbles with the air/water surface causes a water film stabilised by the silica particles to climb rapidly up the inner glass walls of the measuring cylinder, typically within a second or so. If the system is re-shaken, the film is lost and foam bubbles are re-formed which, when shaking stops, again coalesce causing the film to re-climb the walls.

The overall mechanism (Fig. 1) is similar to particle emulsion systems described in the introduction. Shaking the initial

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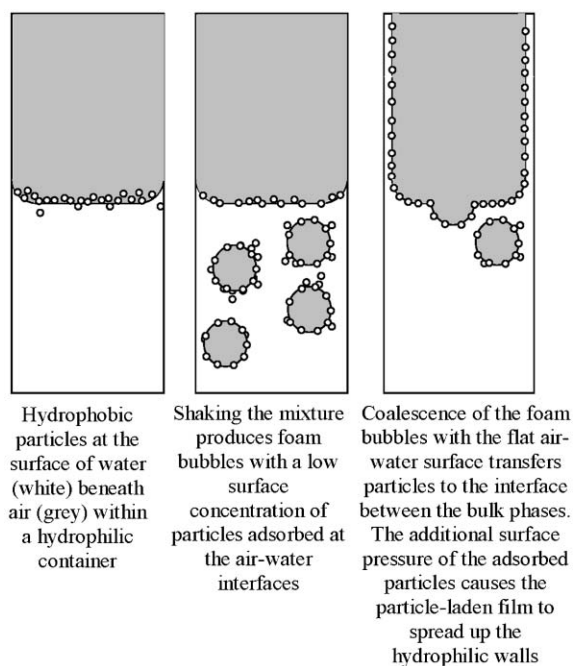


Fig. 1 Mechanism of particle-stabilised foam bubble collapse driving film growth.

two-phase mixture forms foam bubbles. The foam bubbles are unstable with respect to coalescence with the flat air/water interface, presumably because the adsorption of silica particles at the curved and flat air/water surfaces is too low to prevent coalescence. However, the particles at low concentration in the surface are likely to be adsorbed irreversibly with an adsorption energy greatly in excess of thermal energy. In this situation, bubble coalescence reduces the total air/water surface area, increases the surface concentration of adsorbed particles and hence increases their surface pressure in the air/water interface separating the bulk phases. This increased surface pressure drives the film climbing up the vessel walls. Bubble coalescence will stop when the surface concentration of adsorbed particles is sufficient to stabilize the surfaces against coalescence, a feature which has many similarities with the phenomenon of limited coalescence observed in emulsions stabilized solely by particles.⁹ Film growth will stop when the surface pressure of the adsorbed particles has reduced below a critical level as a result of the area expansion. Within this mechanism, we would expect that the process of bubble loss with film growth and the reverse process of bubble formation with film loss would be repeatedly reversible by shaking, as is observed experimentally.

According to the mechanism of Fig. 1, film growth should be directed *up* the vessel walls when the contact angle of water with the vessel wall is less than 90° but should go *down* the walls when the contact angle is greater than 90° . To confirm this, DCDMS silica nanoparticles with 20% SiOH were shaken with water in a vessel with water contact angle of greater than 90° (hydrophobised using 1 wt% octadecyltrichlorosilane in toluene for 60 min at room temperature under nitrogen). Slight film movement downwards was observed but the resultant glass-air/water film was unstable.

For DCDMS silica nanoparticles with 20% SiOH, repeating a process of a single shake of the vessel followed by allowing the film to climb the walls leads to a progressive increase in the film height

with number of shakes. The film height reached increases approximately linearly with number of shakes and reaches the top of the vessel used (200 mm) after 57 shakes. Fig. 2 shows the effect of particle amount on the film height and growth rate. For systems with low particle mass, the film is fairly transparent and uniform and shows very rapid growth. At higher particle mass, the film growth is slowed and the film is seen to carry large visible particle aggregates with it. For Fig. 2–3, the error bars shown were estimated from repeat measurements.

Fig. 3 shows the effect of changing the hydrophobicity of silica nanoparticles on the height of film produced under the standard conditions described in the figure legend. Maximally hydrophilic particles (100% SiOH) showed no film growth, presumably because particle attachment to the surface is too weak in this case. Making the particles more hydrophobic by treating the surfaces with DCDMS or PDMS leads to a strong increase in film growth, presumably because the attachment strength of the particles to the air/water surface is increased. It is noticeable that the longer chain hydrophobic PDMS group is more effective than the shorter chain DCDMS at low surface densities (corresponding to high % SiOH) when the longer chain is likely to fill a larger surface area. The two plots converge at high surface density (corresponding to low % SiOH) when chain crowding is expected to shrink the area occupied by the longer chain.

Fig. 4 shows optical and SEM images of 20% SiOH silica nanoparticle films deposited using the film cell. The mass ratio of silica to water (0.01 : 0.5) is high relative to the systems described in

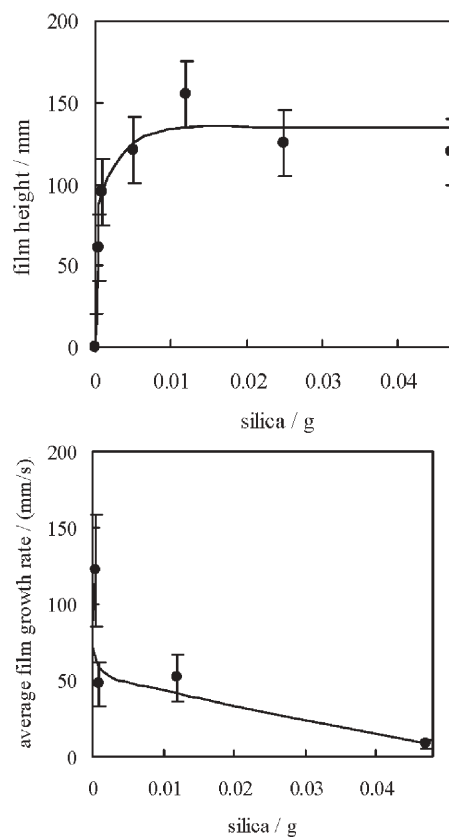


Fig. 2 Film height (upper plot) and average film growth rate (lower plot) vs. mass of silica DCDMS particles (20% SiOH). The water volume was 10 ml and shaking time was 20 s.

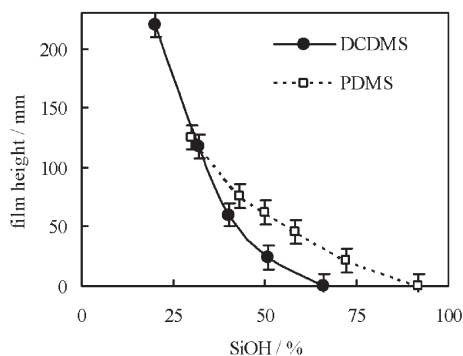


Fig. 3 Variation of film height with particle hydrophobicity (expressed as % SiOH) for DCDMS and PDMS treated silica nanoparticles. For each experiment, 0.01 g particles was shaken for 20 s with 10 ml of water in a 28 mm (inner diameter) \times 200 mm (height) measuring cylinder. Particles with % SiOH <25% produced films which filled the available height, *i.e.* 200 mm.

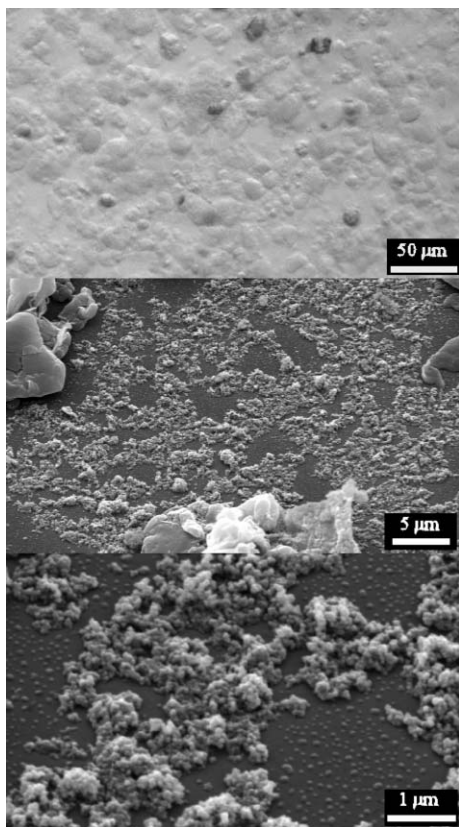


Fig. 4 Optical (top) and scanning electron microscope (middle and lower) images of films formed by shaking 0.01 g of 20% SiOH DCDMS silica particles with 0.5 ml of water for 30 s in the film cell.

Fig. 2 and so films with an excess of silica particles are expected. The micrographs show features in three distinct size regimes. The largest features are 5–10 μm and probably correspond to large agglomerates of silica. At an intermediate size range, there is a fairly random patchwork of connected silica aggregates on a length scale of about 0.2 μm . These features may correspond to silica which remains airborne during the shaking/film formation but which subsequently sediments onto the film. Finally, there are film

Table 1 Comparison of advancing contact angles for a water drop in air on smooth surfaces and particle films

System	Advancing contact angle/ $^{\circ}$
Hydrophobised smooth glass	95
Film of 20% DCDMS SiOH silica particles	170
Smooth PTFE tape	144
Film of PTFE particles on glass	159

regions comprising separated circular spots of 100 nm approximate diameter. These film regions appear to underlie the other regions and are thought to correspond to particles adsorbed in the grown film surfaces following water evaporation from the film. Consistent with the separation of these silica spots, it is known that hydrophobic particles (monodisperse silica of 3 μm diameter hydrophobised using DCDMS) adsorbed at the air/water surface show strong repulsion over very long ranges of the order of 10 μm .¹⁰

Most of the results described here refer to hydrophobised silica nanoparticles. However, we have also observed similar patterns of film climbing behaviour for several different types of hydrophobic particles in water including PTFE particles and monodisperse spherical silica particles (0.6 μm diameter) coated with DCDMS. The microscopic appearance of PTFE particle films shows features on three length scales which are very similar to those seen in Fig. 4 for silica. Overall, the phenomena seen here appear to be reasonably general and not dependent on particular particle size, type or polydispersity.

Finally, it is well known that roughness can enhance the hydrophobicity of surfaces as probed by the contact angle of a water droplet placed on the surface. The effect is exemplified in nature by the Lotus and other plant leaf surfaces which have roughness covering multiple length scales,¹¹ as noted for the films of Fig. 4. With this background in mind, we determined the water droplet contact angles shown in Table 1 where it can be seen that the roughness of the particle films produced here enhances the surface hydrophobicity relative to the corresponding smooth surface.

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