

## Fluid-solid transitions on walls in binary hard-sphere mixtures

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**Abstract.** — We present measurements and theory of a fluid-solid phase transition at a hard, flat wall in a two-sized hard-sphere mixture. With particle concentrations well below the level for bulk phase separation, a fluid monolayer (enriched in the larger spheres) forms at the wall. At slightly higher concentrations, the wall fluid freezes into a wall-solid phase which coexists with the bulk fluid. Measurements of large-sphere area fraction *vs.* small-sphere bulk concentration in the fluid and solid phases are in reasonable agreement with the predictions of a model that accounts for entropic excluded-volume effects at a flat wall.

*Introduction.* — Binary hard-sphere mixtures have attracted much attention as useful models for understanding entropic excluded-volume effects [1]. There is mounting experimental [2]-[5] and theoretical [6], [7], [3] evidence that when the size ratio is sufficiently extreme, a binary hard-sphere mixture exhibits fluid-solid phase separation in the bulk. Recent experiments [2], [3] and theory [7] have shown that hard, flat walls induce new behaviour in such systems. In particular, a quasi-two-dimensional fluid of larger spheres forms on the wall at low (bulk) concentrations of small spheres. With increasing small-sphere concentration, this wall fluid freezes, so that a wall-solid phase exists in equilibrium with a bulk fluid phase (see g. 1). Freezing at the wall occurs at concentrations well below the point at which freezing occurs in the bulk. Furthermore, in equilibrium, the wall solid phase is predicted to cover the entire wall, in contrast to bulk freezing, in which two phases can coexist. In this letter, we present measurements of the area fraction of large spheres at a flat wall as a function of the small-sphere concentration in the bulk. These data are compared to the predictions of a mean-field theory [7].

*Theory.* — The equilibrium state of a binary mixture of hard spheres can be described by three parameters: the ratio of the two radii,  $\xi = r_2/r_1$  ( $r_1 > r_2$ ) and the volume fractions of the

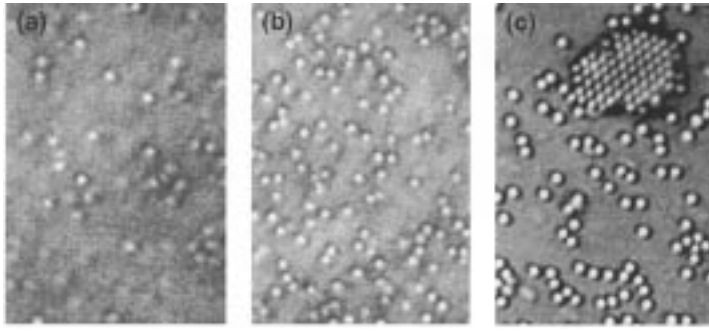


Fig. 1.— Optical micrographs of polystyrene spheres ( $r_1 = 0.413\text{-}\mu\text{m}$ ,  $\phi_1 = 0.02$ ) at a flat, glass wall. (a) With no small spheres, a low area fraction of spheres ( $\eta_1^{\text{wall}}$ ) is seen. The spheres remain in view for much less than a second before disappearing away into the bulk. (b) When small spheres are added ( $r_2 = 0.035\text{-}\mu\text{m}$ ,  $\xi = 0.084$ ,  $\phi_2 = 0.08$ ),  $\eta_1^{\text{wall}}$  increases. The large spheres diffuse along the surface for an average of minutes before escaping to the bulk. The small spheres are invisible. (c) With  $\phi_2 = 0.16$ , a crystallite made of the large spheres can be seen at the surface (after  $\approx 40\text{ h}$ ).

two components,  $\phi_1$  and  $\phi_2$  ( $\phi = N(4\pi r^3)/(3V)$ ,  $N$  = total number of spheres of species;  $V$  = total volume). Rather than repeat the theoretical derivations already outlined in [7] (and detailed in [8]), we summarize here the physics behind the formal statistical mechanics. When the size ratio is extreme ( $\xi \lesssim 0.1$ ), it is reasonably accurate to consider the phase behaviour of the mixture within a “depletion” picture [9], as described in Fig. 2a). Working at fixed chemical potential of the small species (the “semi-grand-canonical” ensemble), Poon and Warren [10] showed that the depletion effect broadens the fluid-crystal bulk coexistence region of the large spheres, which occurs in  $0.494 < \phi_1 < 0.545$  in the absence of small spheres (*i.e.*  $\phi_2 = 0$ ). The resulting bulk phase diagram for  $\xi = 0.15$  is shown in Fig. 2b). At a hard wall, there is also a depletion layer inside of which the centre of a small sphere is excluded, Fig. 2a). The overlap of this wall depletion layer and the depletion layer surrounding a large sphere induces a depletion attraction between the large sphere and the wall [2], [11]. This attraction leads to an enhancement of the density of large spheres considerably beyond the wall enhancement expected for a monodisperse hard-sphere fluid ( $\phi_2 = 0$ ) [12]. Within this layer, the large particles still experience a depletion attraction between themselves, and will freeze at the wall at a much lower total volume fraction than in the monodisperse case ( $\phi_2 = 0$ ) [13]. Poon and Warren calculated the position of the wall-crystallization boundary using an extension of the formalism used for the bulk. There are two adjustable parameters in the theory:  $\lambda$ , parametrising the length of decay of correlations in the pair distribution function of a two-dimensional hard-disk fluid, and  $b$ , the distance perpendicular to the wall over which centres of adsorbed large spheres may move. The predictions of the theory are only weakly sensitive to the values of these two parameters [7], [8]. Here we take  $b = 0.028r_1$ , chosen so that the wall-crystallization transition at  $\phi_2 = 0$  occurs at  $\phi_1 = 0.486$ , the value obtained in computer simulations [13]. The free-energy density of the wall layer of large spheres is given by

$$f = f_{\text{ideal}}(b) + f_{2\text{D}} + f_{\text{depletion}}(\lambda). \quad (1)$$

The first term denotes the free-energy density of an ideal gas confined to a layer of thickness  $b$ ; the middle term is the non-ideal contribution from a two-dimensional system of hard *discs* (fluid or crystal), parametrised from simulations; the last term accounts for big-sphere-big-sphere and big-sphere-wall depletion attractions (the former interaction within the wall layer

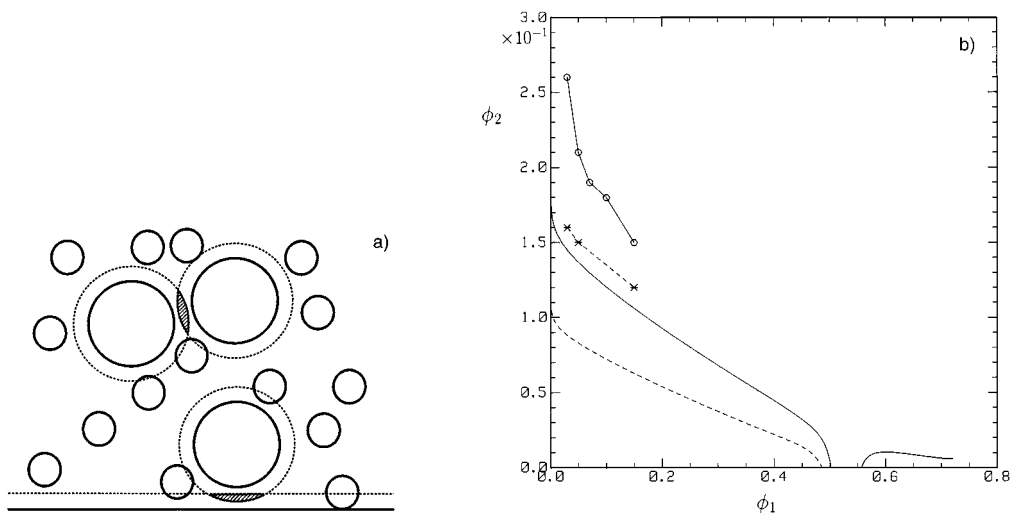


Fig. 2. — a) The depletion effect. Continuous lines represent the large and small hard spheres and a hard wall. Dotted lines delineate the depletion zones inside of which the centre of a small sphere is excluded. Hatched areas represent overlapping depletion zones. The increase in volume accessible to the small spheres due to such overlapping depletion zones leads to an increase in their entropy, hence an attraction between large spheres and between a large sphere and the wall. b) The predicted phase boundaries in the  $(\phi_1, \phi_2)$ -plane for size ratio  $\xi = 0.15$ . Below the lowest boundary (dashed), we have bulk and wall fluids. On the lowest boundary there is wall crystal-fluid coexistence. Immediately above the lowest boundary we find wall crystals and bulk fluid. Above the continuous line, there is bulk crystal-fluid coexistence. The dashed line with asterisks and the continuous line with circles represent the experimental wall crystallization and bulk phase separation boundaries obtained by Dinsmore *et al.* [3].

giving rise to the  $\lambda$  dependence). The surface phase diagram calculated by minimising this free energy for  $\xi = 0.15$  is shown in g. 2b). Below the wall crystallization boundary, the adsorbed layer of large spheres is predicted to be a fluid state. Across the boundary, the large spheres at the wall freeze into a (single-layer) two-dimensional triangular arrangement with an abrupt change in density [8]. The large-sphere wall-area fraction for the case of  $\xi = 0.14$  is shown in g. 3a). The area fraction  $\eta_1^{\text{wall}} = N_1 \pi r_1^2 / (\text{wall-area})$ . The small spheres are assumed to be a disordered fluid throughout.

Whereas fluid and solid phases can coexist in the bulk, we expect from the theory a *sharp transition* between wall-fluid and wall-solid phases. The bulk in a colloidal experiment is effectively a constant-particle-number system, where it is possible to observe *coexisting* fluid and solid phases. The wall layer, however, freely exchanges spheres with the bulk, so that the chemical potentials of the two species are held constant. The bulk acts like a particle reservoir; as soon as the wall-solid chemical potentials fall below the wall-fluid chemical potentials, the entire surface should be covered with the solid phase.

*Experiments.* — Charge-stabilized polystyrene spheres dispersed in approximately 0.01-molar NaCl in a density-matching mixture of  $\text{H}_2\text{O}/\text{D}_2\text{O}$  were used. At this salt concentration the Coulombic repulsion between particles is screened to short distances ( $\approx 5$  nm), so that they behave effectively as hard spheres. The negatively-charged glass surface acts like a hard wall [14]. The observed behaviour [2], [3] for  $2r_1 = 0.460 \mu\text{m}$ ,  $2r_2 = 0.069 \mu\text{m}$  ( $\xi = 0.15$ ) is shown in g. 2b). At low concentrations of small spheres ( $\phi_2$ ), samples remained single-phase

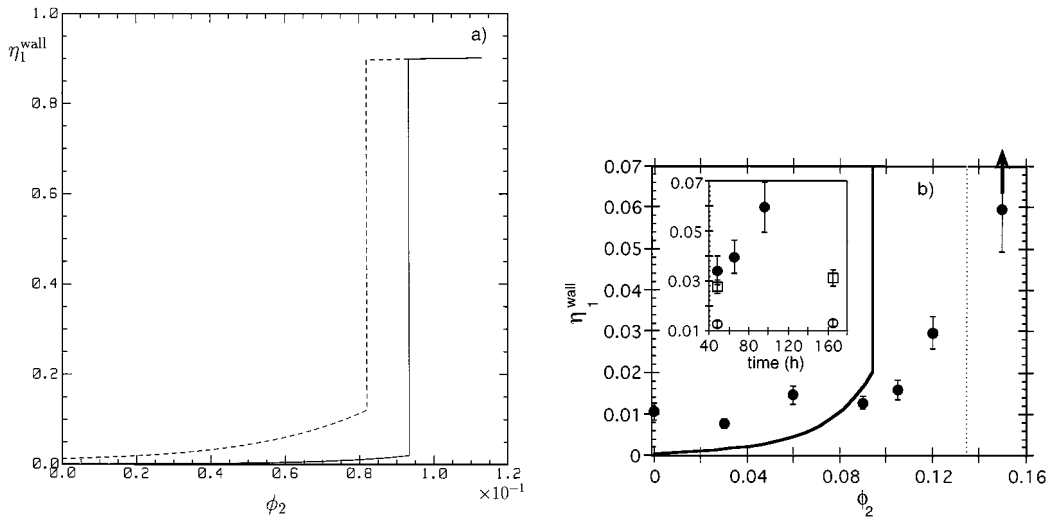


Fig. 3. — The area fraction of large spheres ( $\eta_1^{\text{wall}}$ ) at the wall as the bulk density of small spheres ( $\phi_2$ ) is increased past the wall fluid-crystal transition point, for a size ratio of  $\xi = 0.14$ . The bulk density of large spheres is fixed at  $\phi_1 = 0.03$  for all parts of this figure. a) Theoretical prediction, for wall layer thickness  $b = 0.028r_1$  (full line) and  $0.43r_1$  (dashed line). b) Comparison of theory ( $b = 0.028r_1$ ) and experiment. The bulk is fluid for each sample. Inset:  $\eta_1^{\text{wall}}$  as function of time; open circles ( $\phi_2 = 0.09$ ), squares ( $\phi_2 = 0.12$ ) and filled circles ( $\phi_2 = 0.15$ ). In the last sample,  $\eta_1^{\text{wall}}$  continued to increase over time.

colloidal fluids in the bulk. The concentration of large spheres was enhanced, however, at the wall (compare g. 1 a) and b)). Within this wall-fluid phase, individual large spheres diffused along the wall (in roughly two dimensions) for an average of up to several minutes before “escaping” to the bulk fluid phase. At intermediate concentrations of small spheres ( $\phi_2 \approx 0.15$ ), iridescent spots were observed growing on the walls of the sample container. Optical microscopy revealed crystallites of large spheres with domains of triangular-ordered large-sphere planes aligned parallel to the wall, (g. 1 c)). The large-sphere lattice is permeated by a disordered fluid of small spheres which can pass through the interstices of the lattice. At higher  $\phi_2$  ( $\gtrsim 0.20$ ), bulk phase separation occurred, giving rise to sediments with ordered arrangements of large spheres which were observed under the optical microscope. At the highest  $\phi_2$ , amorphous sediments were formed in the bulk (see [3] for a detailed discussion).

The density of the wall layer (fluid or crystal) in samples which remained single-phase fluids in the bulk was measured by video microscopy. Repeatable results independent of sample orientation were obtained. The wall area fraction,  $\eta_1^{\text{wall}}$ , of large spheres with centres lying within a distance of  $r_1$  and  $r_1 + t$  of the wall was measured by counting:  $\eta_1^{\text{wall}} = N_1 \pi r_1^2 / A$ , where  $N_1$  is the number of large spheres observed in an area  $A$  ( $N_1 \approx 10000 - 20000$ ). The depth of field of the microscope objective and the image-processing algorithm determined  $t$ , an estimate of which can be obtained by assuming that when  $\phi_2 = 0$ , there is no enhancement of large-sphere concentration at the wall, so that  $N_1 = 3At\phi_1 / (4\pi r_1^3)$ . Thus,  $\eta_1^{\text{wall}}(\phi_2 = 0) = (3/4)\phi_1(t/r_1)$ . In this way, we estimate that  $t = 130 \text{ nm} = 0.43r_1$ . Results for a system with  $2r_1 = 0.605 \mu\text{m}$ ,  $2r_2 = 0.083 \mu\text{m}$  at  $\phi_1 = 0.03$  are shown in g. 3 b) as a function of  $\phi_2$ . All samples with  $\phi_2 \leq 0.12$  remained in the wall-fluid phase, with no crystallites even after 3 weeks. In the samples with  $\phi_2 = 0.15$ , wall-crystallites became visible after one week and continued to increase in size for several weeks, until the samples were discarded. We measured  $\eta_1^{\text{wall}}$  as

a function of time, before the wall crystallites appear, for several samples (fig. 3, inset). In samples which remained fluid at the wall ( $\phi_2 \leq 0.12$ ),  $\eta_1^{\text{wall}}$  did not change between 50 and 170 hours after mixing, indicating full equilibration. At  $\phi_2 = 0.15$  (above the wall-freezing point), however, we found that the area fraction was still rapidly increasing with time even before crystallites had appeared. The crystallites, which appeared after one week, continued to grow (in area and in thickness) for up to several weeks, indicating that these mixtures had not reached equilibrium. The last data point on fig. 3b) therefore represents a lower bound for  $\eta_1^{\text{wall}}$ .

*Comparison and conclusions.*— The experimental measurements of  $\eta_1^{\text{wall}}$  confirm the presence of an equilibrium wall-fluid phase, enriched in large spheres, as predicted by the theory. With  $\phi_2 > 0.1$ ,  $\eta_1^{\text{wall}}$  was noticeably larger than in the monodisperse mixture ( $\phi_2 = 0.$ ), fig. 1. With  $\phi_2 \geq 0.15$ , the wall-solid phase appears. The theory and experiment agree reasonably well with regard to the relative positions of the wall and bulk crystallization boundaries, fig. 2b). The predicted positions are, however, too low. The statistical-mechanical model used in [7] employs a mean-field approximation which is reasonably accurate for monodisperse mixtures of hard spheres and *non-interacting* small particles (polymers in a theta solvent). The effect of a slight non-ideality in the small species has been investigated [10]. The differing values of the wall-layer thickness parameter,  $b$ , may, at first sight, be another source of discrepancy; however, the theory is insensitive to large variations in  $b$ , fig. 3a).

Perhaps the most serious source of discrepancy between experiment and theory is kinetic effects. The data points in fig. 3b) were all taken before the system had reached equilibrium. The  $\eta_1^{\text{wall}}$  values were measured before wall crystallites appeared. When they first appeared, the wall crystallites typically did not cover the entire surface, but continued to grow for as long as the samples were observed (months). During this time, the surface state was in fact one of (non-equilibrium) fluid-crystal coexistence. Moreover, such coexistence was observed over a range of volume fractions. (Dinsmore *et al.* [3] discuss these effects in detail.) It is probable that if one could wait long enough before taking measurements, there would be closer agreement with the equilibrium statistical-mechanical prediction of  $\eta_1^{\text{wall}}$ .

Finally, the observed wall crystals had many layers of large spheres (up to  $\approx 10^2$ ) which formed first on the surface and then grew into the bulk. Possibly the appearance of a single ordered layer (accompanied by a large density jump) can be seen as the first step in a sequence of layering transitions [15], of which only the initial stage is treated by the theory in ref. [7]. Consideration of such layering (or similar, roughening) effects may explain why large, thick and faceted crystallites formed at lower  $\phi_2$  and small, thin and rough crystallites (1-2 layers) formed at higher  $\phi_2$ , well above the wall phase transition point [3].

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