

## Entropically Driven Surface Phase Separation in Binary Colloidal Mixtures

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We investigate the phase diagram of mixtures of charge stabilized polystyrene spheres of two different sizes in the hard-sphere limit. We observe bulk phase separation into two disordered phases and find a new ordered phase located on the cell walls. The ordered phase occurs at volume fractions as low as 0.2, much less than the value of 0.49 for hard-sphere freezing in monodisperse suspensions, and is qualitatively explained with simple geometric arguments.

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Freezing and crystallization are generally driven by the deep potential minima of chemical and physical bonds that overwhelm the entropic tendency towards disorder. In some cases, however, entropy can actually induce order and cause a liquid to freeze. While this seems counter-intuitive, such entropy-driven freezing transitions have been observed for many years in computer simulations of atoms interacting through a purely repulsive hard-sphere potential [1]. Recently, this freezing transition was observed experimentally in monodisperse, hard-sphere colloidal suspensions [2]. For liquids and suspensions made up of single-size spheres, freezing is observed when the volume fraction  $\phi$  of spheres exceeds approximately 0.49.

In this Letter, we show that for binary mixtures of hard-sphere colloidal particles, entropically driven phase transitions can occur at substantially lower total volume fractions than for monodisperse samples. More importantly, we find that such phase transitions can involve coexistence between two bulk disordered phases (rather than freezing) or coexistence between bulk disordered phases and a *new crystalline phase*, which precipitates on the walls of the sample. We believe this new ordered phase is also entropically driven, and we provide arguments suggesting that phase separation in hard-sphere mixtures should always occur at the sample walls before occurring in the bulk, in agreement with our experimental observations. This entropically driven ordering of particles at the sample walls may be relevant in paints, polydisperse colloids in porous media, and in catalytic systems, which sometimes employ dispersions at reactive surfaces.

Until recently, binary hard-sphere mixtures of all size ratios were expected to be completely miscible in the fluid phase. Calculations of the equation of state and static structure factors within the Percus-Yevick approximation show no phase separation [3]. Recent experiments in colloidal suspensions, however, suggest that hard spheres are sometimes immiscible, although the interpretation of the observations is clouded somewhat by the effects of strong gravitational settling [4,5]. There are also some unambiguous examples of phase separa-

tion in binary systems with softer interparticle potentials, including liquid emulsions [6] and mixtures of colloidal particles with linear polymer molecules [7]. These experiments have nevertheless been modeled as mixtures of hard spheres using an effective potential approach which relies on simple geometric arguments to calculate entropic forces [6,7]. These calculations, however, unrealistically treat the small particles as a noninteracting ideal gas. More recent and rigorous theoretical work [8,9] suggests that phase separation should occur in binary mixtures. Unfortunately, these results are inconclusive either because of uncertainty in the choice of a closure relation [8] or because of the computational effort required to specify where in the phase diagram separation should occur [9].

The effective potential models for structure and phase separation [6,7,10] are based on an argument of Asakura and Oosawa [11] that uses the fact that the free energy in a hard-sphere system is entirely entropic and depends on the volume accessible to the center of each particle. Adding a small volume  $\Delta V$  to an ideal gas of  $N_S$  small particles reduces the free energy,  $F = -kTN_S \ln(V/\lambda^3)$ , by approximately  $kTN_S \Delta V/V$ , where  $\lambda$  is the de Broglie wavelength and  $kT$  is Boltzmann's constant times the temperature. If the volume fractions  $\phi_S$  and  $\phi_L$  of small and large particles are comparable, and the ratio  $a_S/a_L$  of small to large particle diameters is small, there will be many more small particles than large particles. In this limit, the small particles will provide the dominant contribution to the free energy (and entropy) of the system. Since the center of each small particle is excluded from a sphere of diameter  $a_L + a_S$  around each large particle [see Fig. 1(a)], the volume available to each small particle is reduced by the presence of the large particles. However, Asakura and Oosawa [11] pointed out that the total volume available to small particles *increases* when two large particles approach each other so that the spheres of excluded volume overlap [see Figs. 1(a) and 1(b)]. This decreases the free energy of the mixture and produces an effective potential well with a depth of approximately  $(3/2)(a_L/a_S)\phi_S kT$ . Motivated by our observations of a

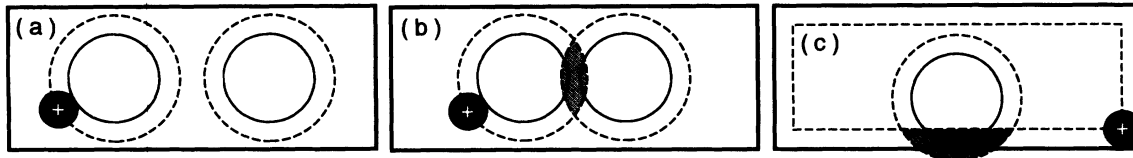


FIG. 1. The free energy of an ideal gas of  $N_S$  small particles is  $-kTN_S \ln V/\lambda^3$ , where  $V$  is the volume accessible to the center of each small particle. (a) That volume does not include a sphere around each large particle with a diameter equal to the sum of the large and small particle diameters. (b) When large particles approach each other, some of the excluded volume overlaps, effectively making a small increase in the volume available to the small particles. This decreases the free energy by approximately  $kTN_S(\Delta V/V)$ . (c) The same effect occurs as a large particle approaches a wall, but  $\Delta V$  is approximately twice as large.

new surface phase, we apply the same geometric argument to large particles near a flat wall [Fig. 1(c)]. To our surprise, we find that the potential of a large particle near a wall is nearly *twice* as deep as the potential between two large balls [12] when  $a_S/a_L \ll 1$ . A large particle caught in this entropic well, which has a depth of approximately  $3(a_L/a_S)\phi_S kT$ , will be confined to lie with its surface within one small ball diameter of the wall, thus making an effectively two-dimensional fluid of large particles.

In our experiments, we investigated the phase diagram of nearly hard-sphere binary colloidal suspensions for nine different diameter ratios and for a large number of volume fractions of large and small spheres. Our approach is straightforward. We mixed commercially prepared polystyrene particles of various sizes and observed them visually over the course of several days. These systems are charge stabilized with a screening length of roughly 4 nm and total volume fractions generally less than 0.30. The salt concentration was 0.01M to 0.02M. The samples are good, though imperfect models of hard-sphere systems. The mixtures were placed in 1-mm-thick cuvettes and observed over the course of several hours. In some of our samples, we monitored the diffuse transmission of a laser beam through the samples as a function of time in order to detect changes in bulk structure [13]. We found, however, that the final states were readily visible by eye, making real-time monitoring of the diffuse transmission unnecessary. We observed four final states: (1) a single homogeneous disordered phase, (2) coexistence between two disordered bulk phases, (3) coexistence between a disordered bulk phase and a crystalline phase localized on the sample walls, and (4) coexistence between two disordered bulk phases and a surface crystalline phase. *Bulk* crystallization, characterized by Bragg scattering from an extended volume of the sample *not* restricted to a thin layer near the walls, was not observed. In samples in which phase separation occurred, the different phases were often visible by eye within 12 h, and almost always within 48 h. None of these separated states was observed in monodisperse samples at similar total volume fractions.

The homogeneous systems (state 1) exhibited no change discernible by direct visual observation or by diffusing-wave spectroscopy [14,15] over a period of at

least two weeks.

Bulk separation into two disordered phases (observed in states 2 and 4) was characterized by the sample separating into upper and lower layers which differed in optical opacity. The two layers were separated by a sharp boundary. These layers could usually be seen under ambient light, but were occasionally detectable only when the cell was illuminated from behind with white light. The optical contrast between phases arises primarily because of the difference in the concentration of the large 460-nm-diam spheres in the two phases; the large spheres have a very large optical cross section compared to the small 65-nm-diam spheres [16].

The crystalline surface phase (observed in states 3 and 4) was characterized by the presence of Bragg scattering from discrete areas on the surface. Under an optical microscope, these areas appear as polycrystalline faceted regions exhibiting different colors, with facets as large as a few millimeters across (see Fig. 2). The colors arise from Bragg scattering from the crystallite; different colors most likely indicate different crystalline orientations with respect to container walls. The structure of these crystals has not been determined. While the thickness of the crystallites is difficult to ascertain *in situ*, crystallites scraped from the wall, dried, and observed with an electron microscope were less than 5 large sphere diameters thick. Diffusing-wave spectroscopy was used to qualita-



FIG. 2. Surface crystallites as viewed under an optical microscope.

TABLE I. Systems studied: systems in which phase separation was observed in at least one sample are denoted by S (surface phase separation) or B (bulk separation). All lengths in are in nanometers. Almost all samples were at total volume fractions below 0.30.

$a_S$	$a_L$	$a_L/a_S$	Phase separation	Number of particles
137	460	3.4	...	4
65	299	4.6	...	6
102	605	5.9	...	1
65	460	7.1	S,B	many
102	825	8.1	S,B	5
65	605	9.3	S,B	3
65	625	9.6	S	5
65	825	12.7	S,B	10
65	945	14.5	S,B	4

tively examine the dynamics of the surface phase *in situ*. In contrast to correlation functions obtained from the noncrystalline regions, the diffusing-wave spectroscopy autocorrelation functions of light scattered from crystallites never decayed to zero. This indicates that the motion of the scattering particles is confined by the crystal lattice [15].

We believe that the surface crystals form because of a combination of factors: the enhanced concentration of large balls along the wall is caused by the large entropic well near the wall described earlier, and the crystals arise because of entropic attraction between large spheres in the surface layer. Once nucleated, the 2D crystallite may seed additional crystalline layers extending a short distance into the bulk. However, significant work is needed to establish the detailed structure of the surface phase and its growth into the bulk.

There are three axes in the phase diagram for these systems: the ratio of particle diameters  $a_S/a_L$  and the volume fractions of each species  $\phi_L$  and  $\phi_S$ . A number of diameter ratios were investigated (Table I); one system (460/65 nm) has been explored in detail. Phase separation was not observed in samples with both a diameter ratio less than 7 and total volume fraction less than 0.3. These results are in qualitative agreement with the recent theory of Biben and Hansen [8] which predicts that phase separation occurs for particle diameter ratios  $a_L/a_S \gtrsim 5$ . We found that the surface phase (Fig. 3) always separates at *lower* volume fractions than the bulk, consistent with the relatively stronger attraction of large particles to the wall in our simple model. At the highest volume fractions, above the upper line in Fig. 3, the dynamics of phase separation was very slow, taking more than 5 days, suggesting that the samples may have been in a glassy state or that they may not have reached thermodynamic equilibrium.

In samples above the upper line in Fig. 3 the solid grown on the cell walls consisted of small white spots, which did not display Bragg scattering. Monodisperse hard-sphere systems also display wetting by an ordered phase, but the wetting occurs at concentrations very near

the bulk freezing transition [17], in sharp contrast to the binary system.

It is useful to compare our results with those of a similar experiment, reported recently by van Duijneveldt, Heinen, and Lekkerkerker (DHL) [4], in which binary mixtures of polymer-stabilized silica spheres in cyclohexane were studied. In the DHL experiment, bulk phase separation was observed similar to the bulk separation we observe. However, no surface crystalline phase was reported. In contrast to the system studied by DHL, the polystyrene system we use exhibits much slower particle settling, more optical scattering, and a somewhat less ideally hard-sphere interaction potential. The details of the DHL experiment explain why the surface phase may not have been observed. First, the rate at which the surface phase separation proceeds in our experiments is slow compared to the settling times in the DHL experiments but fast compared to the monodisperse settling time in this experiment. The density of polystyrene, 1.05 g/ml, is much closer to that of our solvent, water, than the densities of the silica spheres, 1.81 and 1.51 g/ml, are to the density of cyclohexane, 0.78 g/ml. Since the settling rate of particles is proportional to the buoyancy, which is the difference in mass between a particle and an equal volume of solvent, settling proceeds much faster in the DHL system than in ours where the buoyancy is 20 times smaller. As a consequence, settling times in the silica system are a few hours, which is comparable to the time required for phase separation, while the settling times of the polystyrene system are significantly slower (i.e., days), which allows the slow dynamics of phase separation to proceed. The optical scattering power of individual spheres is also much higher since the index mismatch for polystyrene in water  $n_{\text{particle}}/n_{\text{solvent}}$  is 1.59/1.32 rather than 1.46/1.43. The silica/cyclohexane system is generally prized for its weak scattering, which allows the use of single scattering optical techniques at high volume fractions. For surface sensitivity, strong scattering is desirable.

In order to investigate the reversibility of the bulk

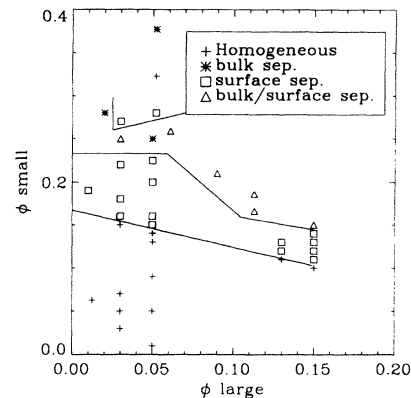


FIG. 3. Phase diagram of 460/65 nm system. The dynamics of separation were very slow in the upper region, suggesting the existence of a glassy state.

phase separation that we observed, we stirred samples by tumbling and placing them in an ultrasonic bath. Their behavior repeated exactly; even when monitoring the intensity of transmitted light through the sample, the same time dependence was observed to within a few percent.

The fluid-solid transition is also reversible. Crystallites, which can be removed from the surface by vigorous shaking, grow back when the shaking stops. To check for irreversible flocculation, we diluted the suspension surrounding the crystals and watched under a microscope; the crystallites dissolved in less than a minute, demonstrating convincingly that no irreversible flocculation had occurred. The surface crystalline phase was observed for several values of  $a_S/a_L$  (see Table I) and in cells made from different materials, including glass, quartz, and polystyrene. The surface crystalline phase was observed on both flat and round cells walls; the radius of curvature of the wall was large compared to the size of the individual crystallites. The surface phase is robust.

The system we use consists of electrically charged polystyrene spheres, which are highly screened by small ions in solution. Because of the high degree of screening, we expect the interaction between spheres to be well approximated by a hard-sphere potential [18]. A common approach for ascertaining how closely the interparticle potential approximates a hard-sphere potential is to find the volume fraction at which a monodisperse suspension of particles crystallizes [2]. By comparing this to 0.49, the known volume fraction for the hard-sphere freezing transition, the effective hard-sphere size of the spheres can be determined. A sensitive measurement of this volume fraction is obtained from 0.205  $\mu\text{m}$  particles, in which crystallization is observed at  $\phi = 0.44$ . This result indicates that the effective radius of the particles is less than 4 nm larger than the physical radius [19].

We have observed phase separation in an essentially hard-sphere system. In addition to bulk phase separation, we find a striking, new ordered phase located on the cell walls (Fig. 2), which is observed at volume fractions as low as 0.2, substantially less than the value of 0.49 for the hard-sphere freezing transition in monodisperse suspensions. These phase transitions can be understood as entropically driven transitions which arise from a small-sphere mediated *entropic* attractive interaction between large spheres. Several questions about the surface phase remain unaddressed. These include its structure and composition, details of the growth kinetics, and the equilibrium two-dimensional, fluidlike surface phase, which probably exists below the phase separation line in Fig. 3.

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- [1] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 1991), 2nd ed.
- [2] P. N. Pusey and W. van Meegen, *Nature (London)* **320**, 340 (1986).
- [3] J. L. Lebowitz, *Phys. Rev.* **133**, A895 (1964).
- [4] J. S. van Duijneveldt, A. W. Heinen, and H. N. W. Lekkerkerker, *Europhys. Lett.* **21**, 369 (1993).
- [5] S. Sanyal, N. Easwar, S. Ramaswamy, and A. K. Sood, *Europhys. Lett.* **18**, 107 (1992).
- [6] J. Bibette, D. Roux, and F. Nallet, *Phys. Rev. Lett.* **65**, 2470 (1990); J. Bibette, D. Roux, and B. Pouligny, *J. Phys. II (France)* **2**, 401 (1992).
- [7] A. P. Gast, W. B. Russel, and C. K. Hall, *J. Colloid Interface Sci.* **109**, 161 (1986); **96**, 251 (1983).
- [8] T. Biben and J. P. Hansen, *Phys. Rev. Lett.* **66**, 2215 (1991).
- [9] D. Frenkel and A. A. Louis, *Phys. Rev. Lett.* **68**, 3363 (1992).
- [10] P. Bartlett and R. H. Ottewill, *Langmuir* **8**, 1919 (1992).
- [11] S. Asakura and Oosawa, *J. Polym. Sci.* **32**, 183 (1958).
- [12] Note that  $\Delta V$  was incorrectly typed in Eq. (2) of Ref. [11]. The overlapping volume between two spheres of radius  $(a_L + a_S)/2$  separated by  $a_L < a < a_L + a_S$  is  $(\pi/6)(a_L + a_S - a)^2(a_L + a_S + a/2)$ , and between a sphere of radius  $R$  whose center is  $a_L/2 < a < a_L/2 + a_S$  away from a wall the overlapping volume is  $(\pi/3)(a_L + a_S/2 - a)^2(a_L/2 + a_S + a)$ . This argument sets no lower limit on the size of small particles.
- [13] S. Fraden and G. Maret, *Phys. Rev. Lett.* **65**, 512 (1990); P. D. Kaplan, A. G. Yodh, and D. J. Pine, *Phys. Rev. Lett.* **68**, 393 (1992).
- [14] D. J. Pine, D. A. Weitz, J. X. Zhu, and E. Herbolzheimer, *J. Phys. (Paris)* **51**, 2101 (1990); P. D. Kaplan, M. H. Kao, A. G. Yodh, and D. J. Pine, *Appl. Opt.* **32**, 3828 (1993).
- [15] A. Meller and J. Stavans, *Phys. Rev. Lett.* **68**, 3646 (1992).
- [16] The scattering cross section for green light is 2500 times larger for a single 460 nm polystyrene sphere than a 65 nm one. At equal volume fractions, the larger number of small particles reduces this imbalance, but the total cross section is still 7 times larger for 460 nm particles.
- [17] D. J. Courtemanche and F. van Swol, *Phys. Rev. Lett.* **69**, 2078 (1992).
- [18] This is in contrast to similar phenomena observed in systems with long range repulsion by S. Hachisu, A. Kose, Y. Kobayashi, and K. Takano, *J. Colloid Interface Sci.* **55**, 499 (1976).
- [19] The interparticle potential falls exponentially with distance due to screened Coulomb repulsion and algebraically due to van der Waals attraction. Accurate estimates of either potential are difficult to obtain, especially in the highly screened limit. We have observed that increasing the ion concentration from 0.01M to 0.02M has a small effect on the location of the homogeneous-surface phase line, while increasing the ion concentration to 0.05M causes irreversible flocculation in several days. The secondary minimum in the combined potential, however, is generally believed to be much less than  $kT$ , while the entropic attraction between large particles and the cell walls is several  $kT$ .

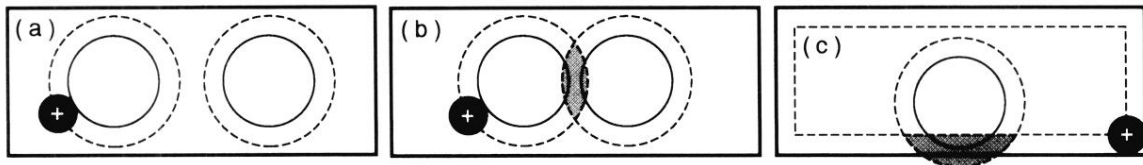


FIG. 1. The free energy of an ideal gas of  $N_S$  small particles is  $-kTN_S \ln V/\lambda^3$ , where  $V$  is the volume accessible to the center of each small particle. (a) That volume does not include a sphere around each large particle with a diameter equal to the sum of the large and small particle diameters. (b) When large particles approach each other, some of the excluded volume overlaps, effectively making a small increase in the volume available to the small particles. This decreases the free energy by approximately  $kTN_S(\Delta V/V)$ . (c) The same effect occurs as a large particle approaches a wall, but  $\Delta V$  is approximately twice as large.

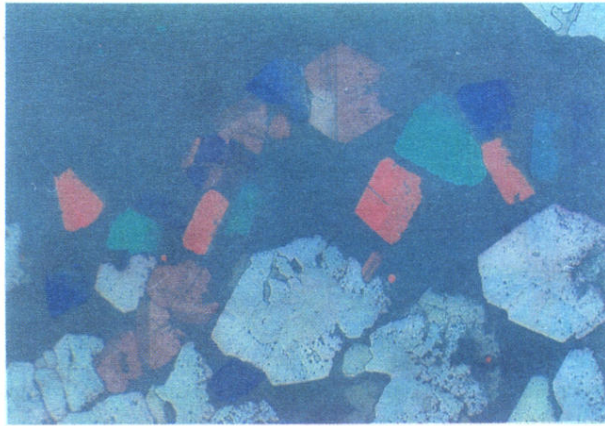


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