

Kinetics of size segregation in quasi-two-dimensional nearly-hard-sphere mixtures

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Time-resolved phase-contrast microscopy has been used to study the dynamics of size segregation in confined binary colloidal suspensions with a size ratio $R_L/R_S \approx 11$ and an approximately hard-sphere potential. The time evolution of the pair-correlation function, the structure factor, the average cluster size, and the total number of large spheres clustered is consistent with entropically driven quasi-two-dimensional "freezing" of the minority component. Clustering is evident as a spinodal-like peak in the low- q structure factor. [S1063-651X(97)07105-5]

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Colloidal suspensions can be useful systems for studying the statistical mechanics of idealized hard-sphere fluids. Recent computational [1–5] and experimental [6–12] efforts have focused on the phase behavior of binary mixtures of disparately sized particles in solution and the so-called *depletion force*. Experimentally, an approximately hard-sphere potential can be achieved by screening out the long-range Coulomb repulsion between particles [8–10]. When the total volume fraction of spheres is sufficiently high, it is well established that these mixtures undergo an entropically driven phase transition in which the particles segregate by size, provided $\alpha = R_L/R_S$ exceeds a threshold value. The dynamics of this instability, which bear a striking resemblance to spinodal decomposition in binary fluid mixtures, remain largely unexplored.

A semiquantitative understanding of this effect is based on the arguments of Asakura and Oosawa [13], and uses the fact that the free energy F of a hard-sphere fluid is purely entropic, depending only on the volume accessible to the center of each sphere. Adding a small amount of volume ΔV to a solution of small spheres reduces F by roughly $k_B T \phi_S (\Delta V/v_S)$, where $v_S = \frac{4}{3}\pi R_S^3$, and ϕ_S is the volume fraction of small particles [8,10]. If $\phi_S > \phi_L$ and $R_L \gg R_S$, the number of small spheres is considerably larger than the number of large spheres, and the former provide the dominant contribution to the entropy. The center of each small particle is excluded from a sphere of radius $R_L + R_S$ around the center of each large particle. When two large spheres come into contact, this excluded volume *decreases* by $\Delta V \approx \frac{3}{2}\alpha v_S$, creating a free-energy well of depth $\Delta_0 \approx \frac{3}{2}k_B T \alpha \phi_S$ known as the *depletion force* [8,10]. The transition can be characterized by a dimensionless parameter $\varepsilon = \Delta_0/k_B T \approx \frac{3}{2}\alpha \phi_S$, and segregation is generally observed when $\varepsilon > 1$ [8,10,11]. A potential well of depth $3k_B T \alpha \phi_S$ also exists between the large spheres and the surface of the cell, leading to distinct surface ordering [8–10] that can be interpreted as a wetting of the bulk crystalline phase [10].

In this paper we use digital video microscopy [14] to study the collective dynamics of entropically driven size seg-

regation in quasi-two-dimensional bidisperse hard-sphere fluids. A similar technique can be used to study Brownian motion of individual spheres in quasi-two-dimensional charge-stabilized suspensions [15]. A uniform depression is slowly etched into a glass slide to a depth $h(2R_L < h < 4R_L)$ and then cleaned thoroughly. After ultrasonic annealing in the bulk, a small amount of the sample is sealed inside the cell with a cover slip using fast-cure epoxy. Over a period of two to three days, phase-contrast microscopic images of a fixed region of the sample are periodically recorded onto Super VHS with a CCD camera. The time-resolved video images are then digitized using frame-grabbing techniques, computer enhanced, and analyzed.

The system we studied is based on that investigated by Kaplan *et al.* [8] and Dinsmore, Yodh, and Pine [9,10]. Charge-stabilized polystyrene microspheres were suspended in aqueous 0.01-M NaCl solutions. We chose $R_S = 0.249 \pm 0.005 \mu\text{m}$ and $R_L = 2.8 \pm 0.05 \mu\text{m}$, with $\alpha = 11.24 \pm 0.44$. These sizes are roughly five times larger than any previously considered [16], and offer ease of viewing of the large spheres, which are comparable in size to a typical biological cell. Rapid gravitational settling of the large spheres ensures a single monolayer, with particle conservation applying in the two-dimensional (2D) plane of the glass surface. Bulk solutions were prepared with $\phi_S^0 = 0.275$ and $\phi_L^0 = 0.0318$. The low-shear solution viscosity ($T = 24^\circ\text{C}$) was measured against a glycerol-water standard to be $\eta = (2.1 \pm 0.1) \times 10^{-2}$ P. Actual volume fractions for confined samples differed only slightly from ϕ_S^0 and ϕ_L^0 . No evidence of irreversible flocculation of the small particles was observed in the bulk or under the microscope.

Figure 1 shows enhanced micrographs ($h = 10 \mu\text{m}$) at (a) $t = 35$ min and of the same region at (b) $t = 2465$ min. Clustering of the large spheres with time is clearly evident. We also prepared monodisperse samples having the same ϕ_L but with no small spheres present. In one, a solution of 0.26 weight fraction glycerol in water was used to match the bidisperse viscosity, and the NaCl concentration was reduced to 0.008 M to account for the slight change in dielectric constant, thus ensuring that the screening length remains the same. The other was an aqueous suspension with 0.01-M

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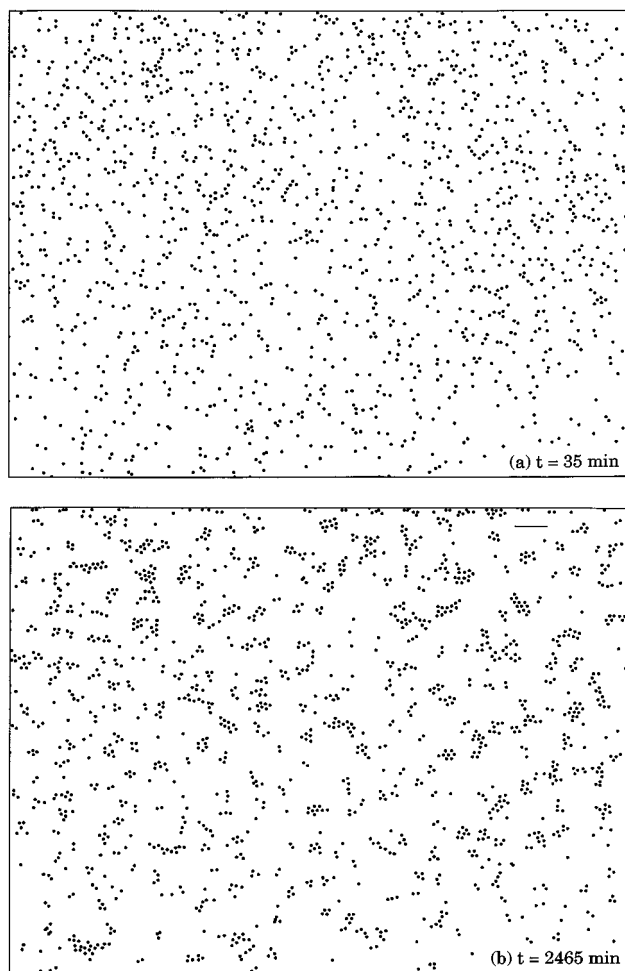


FIG. 1. Micrographs of a binary mixture at $t = 35$ min (a) and the same region at $t = 2465$ min (b). The scale bar is $50 \mu\text{m}$. Dots whose centers lie within the mean particle diameter represent a slight degree of clumping in the z (out of the page) direction.

NaCl. Although some relatively weak structure was present in the controls, it was unspectacular compared to that observed in the binary mixtures. In addition, the spheres in the control samples were virtually static at late time, suggesting that the small spheres provide a dynamic coupling between the solvent and the large spheres.

Direct measurements of diffusion constants for isolated spheres confined between glass plates are described elsewhere [15,17]. By following the centers of several large spheres through a displacement $\Delta\mathbf{r}$ over an interval of time $\Delta t = 1800$ s, we measure the characteristic diffusion time $\tau_L = 4R_L^2 \Delta t / \langle |\Delta\mathbf{r}|^2 \rangle \approx 680$ s (11.33 min) for the mixture shown in Fig. 1. From consecutive images, the total number of large spheres clustered [$N(t)$] and the average large-sphere cluster size [$n(t)$] can be determined (Fig. 2). The behavior was reproduced several times. The criterion used for clustering of adjacent large spheres was that their centers fell within roughly $(2.8)R_L$. The lines in Fig. 2 represent the power-law fits (excluding the first point for n and the first two for N) $n(t) = At^\beta$ and $N(t) = Bt^{\beta'}$, with $\beta \approx \beta' = 0.12 \pm 0.03$. The insets show the fractional deviation. With the exception of the two earliest times, the number of clus-

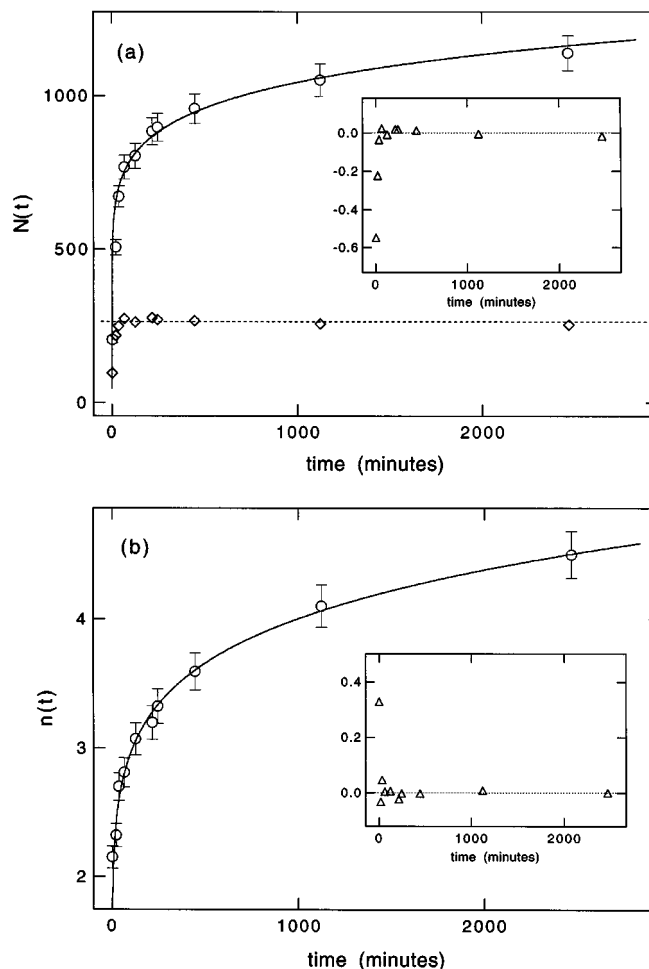


FIG. 2. (a) Total number of large spheres clustered [$N(t)$] and (b) average cluster size of the large spheres [$n(t)$] as a function of time for the binary mixture shown in Fig. 1. The solid lines are power-law fits of the data, and the insets show the fractional deviation between data and fit. The number of clusters as a function of time is shown in (a) as open diamonds.

ters (N/n) is relatively constant, as shown in Fig. 2(a). The positions of the larger clusters change little with time, while their exact structure continues to evolve. A fraction were observed to grow smaller with time, indicating the reversible nature of the attraction.

Figure 3 shows the pair-correlation function $g(r)$ calculated from the digital 2D array of the large-sphere centers. Clustering is evident as a dramatic nearest-neighbor peak at $r/D_L \approx 1.25$, with minor peaks in (c) at $r/D_L \approx 2.45$ and 3.6 . Figure 4 shows the structure factor $S(q)$ calculated from the same data, with a nearest-neighbor peak at $qD_L/2\pi \approx 0.8$. These peak positions are fixed, while the intensities increase with time. The inset of Fig. 3(c) shows the time dependence of both nearest-neighbor-peak intensities. Multiplying by a constant scales both data sets onto $n(t)$ and $N(t)$, as might be expected in a first approximation. The growth of large clusters is evident as a *spinodal-like* peak in $S(q)$ for $q < \pi/D_L$, as shown in the inset of Fig. 4(c). Based on the packing density implied by Fig. 3(c), the position of the late-time peak in $S(q)$ corresponds to cluster dimensions span-

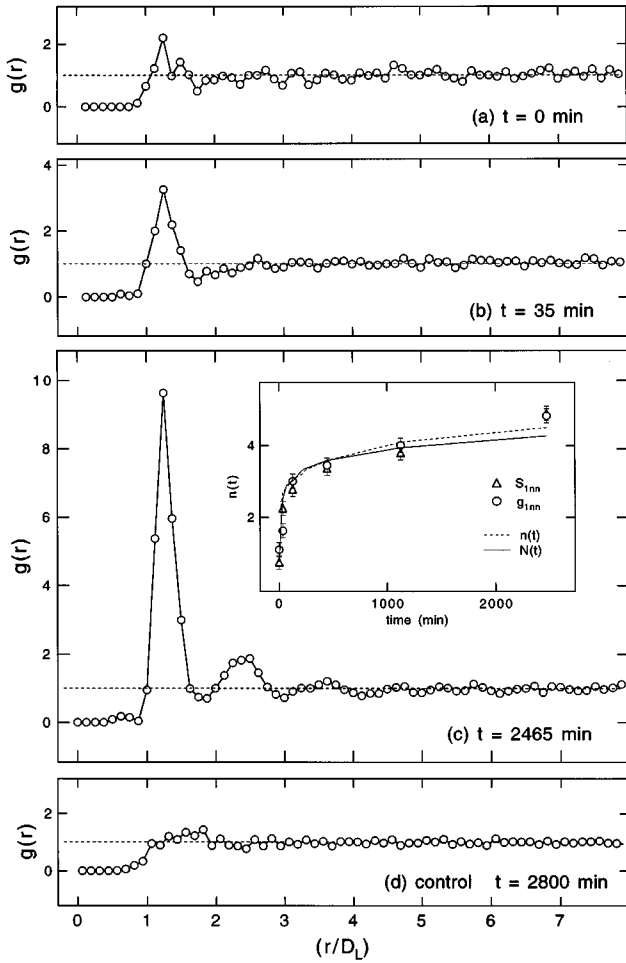


FIG. 3. Pair-correlation functions $g(r)$ as a function of r/D_L , where D_L is the large sphere diameter. Data shown are for a bidisperse sample at (a) $t=0$, (b) $t=35$ min, and (c) $t=2465$ min, and (d) a control sample at $t=2800$ min. The inset to (c) shows the time dependence of nearest-neighbor peaks in $g(r)$ (circles) and $S(q)$ (triangles) scaled on to $n(t)$ (dashed line) and $N(t)$ (solid line).

ning 9–10 large spheres, consistent with Fig. 1(b). Figures 3(d) and 4(d) show the late-time structure observed in the controls.

The growth rate of the solid phase will be the product of a kinetic coefficient and a thermodynamic driving force. The values of α and ϕ_S used in this experiment are such that the depth of the free-energy well is significantly larger than the thermal energy ($\epsilon \approx 4.5 \pm 0.2$). When this is the case, there is evidence that the late-time solid phase is glassy [10,11,18]. The kinetics fall naturally into an early-stage regime ($t < \tau$) and a late-stage regime ($t > \tau$), where τ is a characteristic time of order τ_L . In the early stage the number of clusters increases quickly with time. The kinetic coefficient is determined by the mobility of a single large sphere, and the driving force is determined by ϵ . This regime corresponds to the earliest data points in Fig. 2 ($t < 30$ min $\approx 3\tau_L$) where the growth rate is constant.

In the late-stage regime the kinetic coefficient is limited by the mobility along the wall, which decreases as the clusters grow. The number of clusters thus levels off, and $n(t)$ becomes proportional to $N(t)$. The driving force also de-

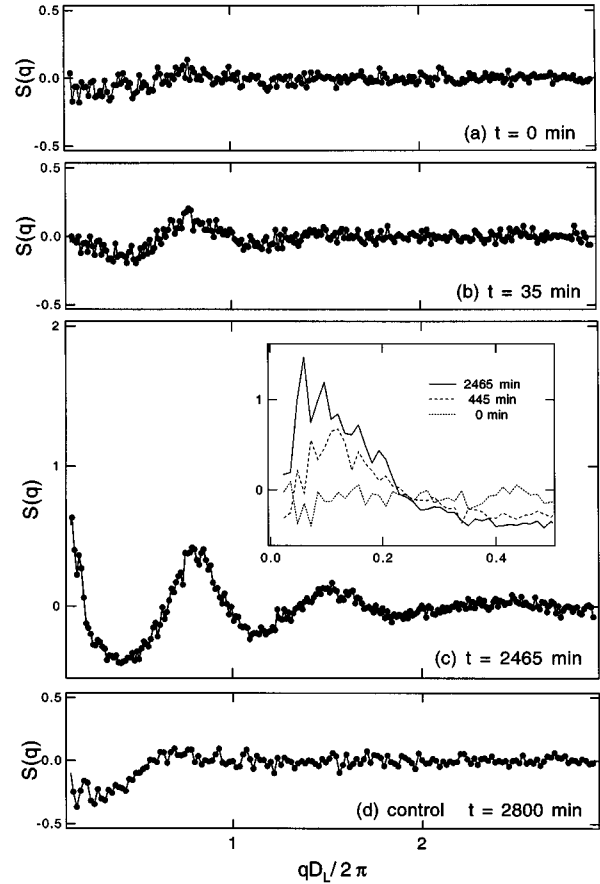


FIG. 4. Structure factor $S(q)$ as a function of $qD_L/2\pi$ for a binary mixture at (a) $t=0$, (b) $t=35$ min, and (c) $t=2465$ min, and (d) a control at $t=2800$ min. The inset to (c) shows the time evolution of the spinodal-like peak at low q , reflecting the growth of clusters spanning several large-sphere dimensions.

creases as N approaches its equilibrium value. Our results suggest that the growth can be described by a power law in this regime. The total area fraction of large spheres in Fig. 1 is ≈ 0.08 , and at $t=2465$ min the fraction of large spheres in “solid” is 0.77. For the geometry in question, a triangular close-packed lattice yields the smallest free energy for an *ideal* hard-sphere mixture. The appearance of the first-nearest-neighbor peak at $r=(1.25)D_L$ implies that the structures are not close packed. At $t=2465$ min the area fractions of solid and fluid phases (Fig. 1) are 0.88 and 0.015, respectively, corresponding to volume fractions of roughly 0.59 and 0.01. Although some clusters in Fig. 1(b) show crystalline order, a significant number do not. Because ϵ is large, clusters may have a tendency to retain their original configuration rather than reorient into a lower free-energy one, which might explain the presence of fractal-like structures [18]. It is important to note that the kinetics reported here are unique to the confined geometry. In comparable bulk systems, the solid phase forms a gel-like sediment [10], while here it forms a quasi-two-dimensional glassy phase of isolated clusters.

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