

Metastability and Depletion-Driven Aggregation

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Depletion-driven self-assembly in binary colloidal mixtures is studied via the time evolution of the cluster-size distribution and structure factor as the mixtures equilibrate after shear melting. The data suggest a two-stage crystallization process governed by an initial collapse into an amorphous metastable state, the growth kinetics of which are interpreted within the context of reversible aggregation and early-stage phase separation. [S0031-9007(98)07565-6]

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The segregation of a binary fluid and the crystallization of a simple liquid are familiar examples of first order phase transitions [1,2]. In mixtures whose components interact through excluded volume, these two phenomena can be driven simultaneously via a *depletion force* [3–5]. The phase-ordering dynamics of such systems have just begun to be investigated, and the underlying physics may have relevance to such things as the crystallization of globular proteins and nematic ordering of rodlike particles in the presence of a nonadsorbing polymer [6,7]. Beyond their broad commercial significance, colloidal suspensions serve as useful models for a variety of condensed matter systems, from crystals [8,9] and glasses [10] to critical fluids [11] and fractal networks [12]. In this Letter, video microscopy is used to study depletion driven self-assembly in confined binary suspensions of nearly hard-sphere colloids. The results suggest that crystallization in these mixtures is a two-stage process governed by an initial collapse into an amorphous metastable state, and the kinetics of cluster formation are interpreted within the context of both reversible colloidal aggregation and entropically driven phase separation.

The mixtures consist of monodisperse polystyrene spheres of diameter $2R_L = 2.9 \mu\text{m}$ and $2R_S = 213 \text{ nm}$ (stabilized with a charged polymer surfactant) in aqueous suspensions containing enough salt (0.01 M) to screen the electrostatic repulsion to short range. The large-sphere volume fraction is fixed at $\phi_L = 0.025$ for small-sphere volume fractions $0 \leq \phi_S \leq 0.4$. Rapid gravitational settling of the large spheres restricts their motion to a plane [13], leading to two-dimensional trajectories in the bulk free-energy landscape. This facilitates tracking of the large spheres and has potential relevance to microscale lithography and lubrication. A shell of excluded volume around each large sphere means that when two come into contact the effective value of ϕ_S decreases, lowering the entropic free energy by an amount Δ [3]. If $\Delta/k_B T$ is big enough, the large spheres aggregate into clusters. For the geometry in question, a close-packed triangular lattice yields the greatest reduction in excluded volume, and hence the greatest decrease in free energy. Phase separation

was observed only for $\phi_S \geq 0.20$, in agreement with the bulk phase diagram of a comparable system [4]. The value of ϕ_L is below the percolation threshold, and slightly lower values yield smaller clusters, while slightly higher values yield clusters that are percolated over the field of view.

The sample cell is an epoxy-sealed microscope slide and cover slip with $15 \mu\text{m}$ thermocouple wire as spacer. All measurements were carried out at $(22 \pm 0.5)^\circ\text{C}$. Digital video micrographs were collected with both $10\times$ and $40\times$ objectives to obtain coarse and fine grained images of the evolving structure. The latter yields just over 10^3 large-sphere centers per video frame, and data from 15 frames were averaged together for a typical measurement. This was accomplished by recording the relaxation after repeated shear melting, where the shear flow was introduced by gently compressing the cover slip of the sample cell. Frames taken with the $40\times$ objective were digitized and computer analyzed to obtain the planar coordinates of the large-sphere centers ($\pm 100 \text{ nm}$). Frames taken with the $10\times$ objective were Fourier analyzed, averaged together, azimuthally averaged, and then divided by the analogous quantity for $\phi_S = 0$, which constitutes dividing out the large-sphere form factor.

The kinetics are studied via the cluster-size distribution, $n_k(t)$, and the structure factor, $S(q, t)$, of the large spheres. The pair-correlation function $g(r)$ exhibits a nearest-neighbor peak at $2R_L$, the width of which yields a clustering criterion [14]. The distribution $n_k(t)$ gives the probability of finding a cluster of size k at time t subject to the constraint $\sum_k k n_k = 1$ imposed by particle conservation, where the largest clusters observed were $100 < k < 500$. The structure factor has peaks at fixed $q > 1 \mu\text{m}^{-1}$ whose intensities increase with time, and a peak at $q_{\text{max}}(t) < 1 \mu\text{m}^{-1}$ that moves toward lower q and increases in intensity with time. Examples of $n_k(t)$ and $S(q, t)$ are shown in Figs. 1 and 2 along with images of the domain structure. The viscosity of the host suspension increases with ϕ_S , and it is convenient to define the reduced time t/τ where $\tau = 2d\Delta t R_L^2 / \langle |\Delta \mathbf{r}|^2 \rangle$. In this expression, $\langle |\Delta \mathbf{r}|^2 \rangle$ is an ensemble average of

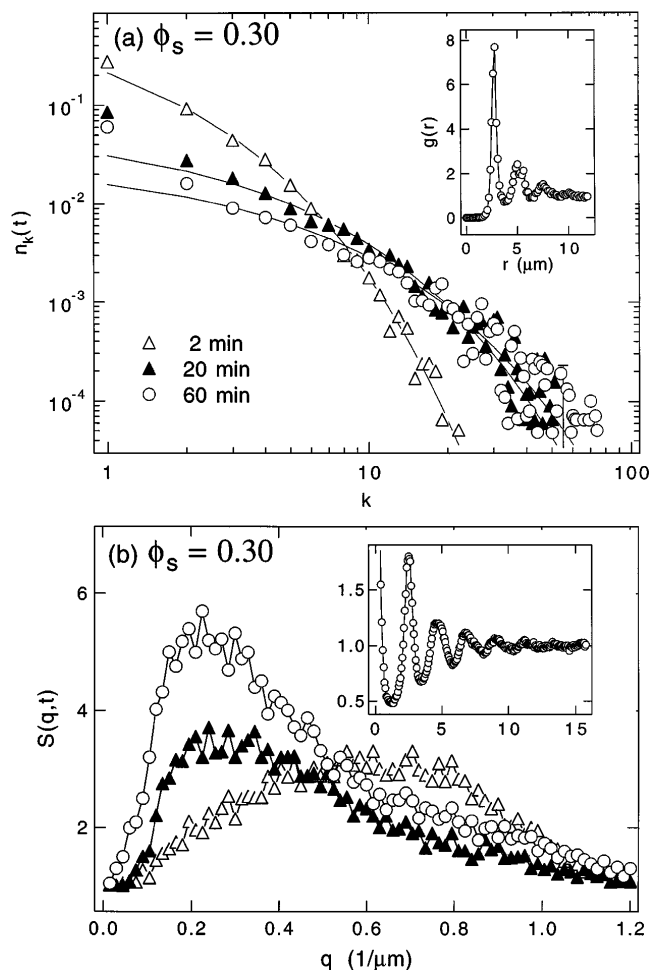


FIG. 1. (a) $n_k(t)$ and (b) $S(q,t)$ for $\phi_S = 0.30$ during the first hour of phase separation, where the markers correspond to the times after shear melting shown in the top figure. The inset in (a) shows $g(r)$ at $t = 60$ min, and the large- k fits of $n_k(t)$ are as described in the text. The lower figure shows the time evolution of the low- q peak in $S(q,t)$, and the inset shows the higher order structure at $t = 60$ min.

the mean-square displacement of isolated large spheres during $\Delta t = 60$ s and $d = 2$. This yields $\tau = 2.4, 3.15, 3.6,$ and 6.4 min for $\phi_S = 0.20, 0.25, 0.30,$ and 0.40 , respectively.

The aggregation is reversible and phase separating mixtures initially reach a state of cluster/single-particle coexistence. The amorphous clusters lead to a liquidlike structure factor (Fig. 2) with a nearest-neighbor peak at $q_0 \approx 2.5 \mu\text{m}^{-1} \approx 2\pi/\sqrt{3}R_L$, while $n_k(t)$ can be described by $n_k(t) = n_0(t) \exp[-\alpha(t)k^\nu]$ at large k with $\nu \approx 0.6$ for all ϕ_S [Fig. 1(a)]. After an intermediate period of metastability, the aggregates start to collapse into an ordered solid, which is evident as an increase in the intensity of the principal Bragg peak and a splitting of the second order peak (Fig. 2). Fragmentation becomes less common and $n_k(t)$ becomes weighted toward larger k as the crystalline domains coarsen. The two-step se-

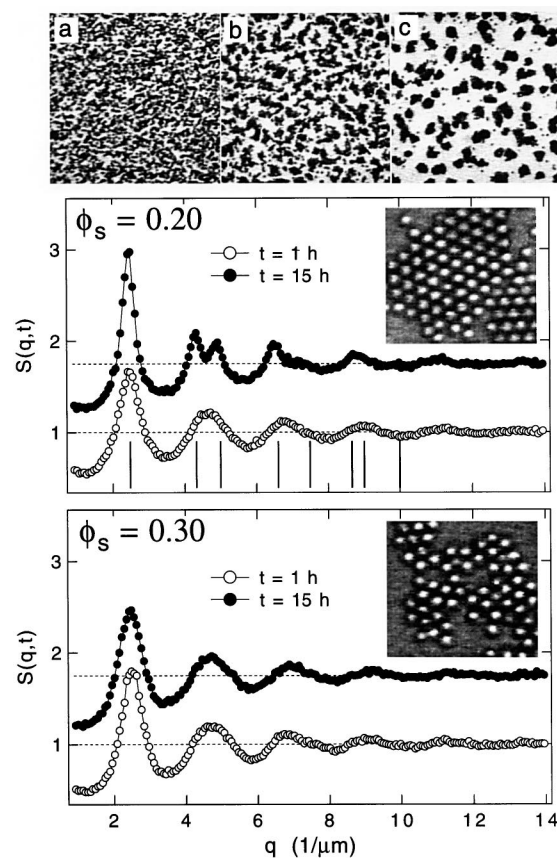


FIG. 2. Coarse grained structure for $\phi_S = 0.25$ at (a) 2 min, (b) 60 min, and (c) 20 h after shear melting. The width of each micrograph is $350 \mu\text{m}$. The lower figures show the higher-order structure in $S(q,t)$ at late times for $\phi_S = 0.20$ and 0.30 . The insets show micrographs of the typical packing morphology at $t = 15$ h, where the width of each micrograph is $30 \mu\text{m}$. The vertical bars show the first eight Bragg peaks for a two-dimensional close-packed crystal with $2R_L = 2.9 \mu\text{m}$. The curves for $t = 15$ h have been offset by 0.75 for clarity.

quence from shear-melted fluid to crystallites is shown in Fig. 2. Clusters of the amorphous phase contain localized regions of close packing but are globally disordered and open [15], while clusters of the ordered phase are uniform and compact. The above observations suggest that freezing in these mixtures is a two-stage process governed by an initial collapse into an amorphous metastable state. This is somewhat similar to a “hidden” gas-liquid binodal in colloid/polymer mixtures [5–7] and is readily seen by following the time evolution of $S(q_0, t)$ [Fig. 3(a)], where mixtures with $\phi_S < 0.3$ reach an initial plateau before starting to order. Crystallization becomes suppressed for $\phi_S \geq 0.3$, suggesting that the system becomes trapped in the amorphous phase.

Confinement of the large spheres slows the growth process considerably, which permits a novel glimpse into the earliest stages of segregation in a binary mixture. One possible theoretical approach starts from the

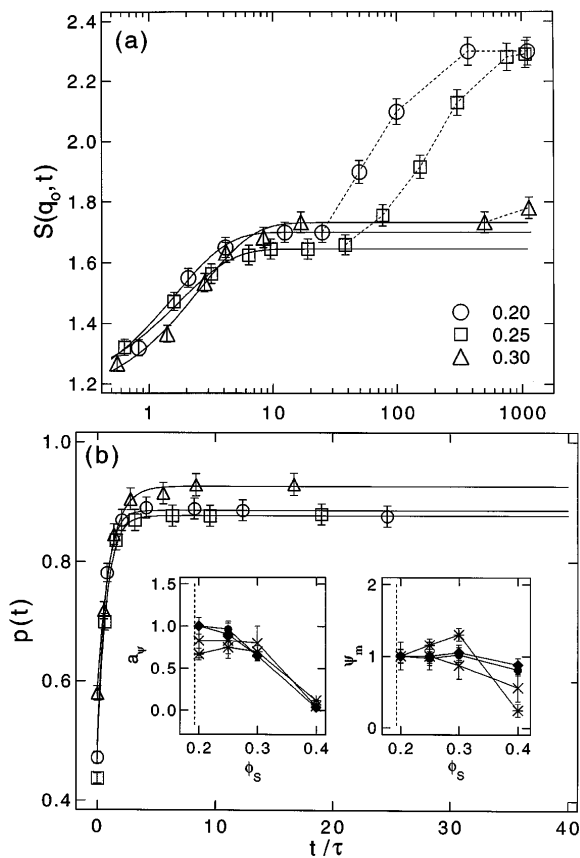


FIG. 3. (a) Time evolution of $S(q_0, t)$, where the fits up to the first plateau are as described in the text. (b) Time evolution of $p(t)$, where the fits are as described in the text. The left inset shows $a_\psi(\phi_S)$ and the right inset shows $\psi_m(\phi_S)$ for $\psi = S(q_0, t)$ (circles), $p(t)$ (diamonds), $s(t)$ (stars), and $R(t)$ (crosses), where the data have been divided by a constant (0.6, 1.44, 0.147, and 0.248 for a_ψ and 1.7, 0.89, 25, and 32 μm for ψ_m) to achieve a common vertical scale. The dashed line is the coexistence threshold.

Smoluchowski equation [2]

$$\dot{n}_k = \frac{1}{2} \sum_{i=1}^{k-1} (K_{i,k-i} n_i n_{k-i} - F_{i,k-i} n_k) - \sum_j (K_{kj} n_k n_j - F_{kj} n_{k+j}), \quad (1)$$

where K_{ij} and F_{ij} are coagulation and fragmentation kernels, respectively. If the first plateau in Fig. 3(a) is viewed as a steady state of Eq. (1), then moments will relax to metastable values after shear melting. Sorensen *et al.* [16] have shown that the mean cluster size

$$s(t) = \sum_k k^2 n_k(t)$$

relaxes exponentially, and one can argue that $R(t) = 2\pi/q_{\text{max}}(t)$ and the fraction of particles in clusters, $p(t) = \sum_{k>1} k n_k(t)$, relax exponentially as well [17]. $S(q, t)$ can

also be expressed as a moment [2], and $s(t)$, $p(t)$, $R(t)$, and $S(q_0, t)$ all relax according to $\delta\psi(t) = \delta\psi_0 \exp(-a_\psi t/\tau)$, where $\delta\psi(t) = \psi_m - \psi(t)$ is the displacement of the moment from its metastable value. Fits of $S(q_0, t)$ and $p(t)$ are shown in Fig. 3 with $a_\psi(\phi_S)$ and $\psi_m(\phi_S)$. The decrease in a_ψ with increasing ϕ_S suggests increasing energetic barriers to aggregation which would be consistent with nonideal behavior [18].

Figure 4 shows a plot of $s^2 n_k(t)$ as a function of $x = k/s$, where the distributions have been truncated at $k = 20$ to eliminate scatter in $n_k(t)$ at large k . The data suggest the scaling relation [16,19] $s^2 n_k(t) = G(k/s)$, where $s(t)$ varies from around 2 at $t = 0$ to around 30 in the first plateau. The fits in Fig. 4 are $G(x) \sim x^{-1.53}$ for $x \rightarrow 0$ and $G(x) \sim \exp(-3.5x^{0.6})$ for $x \rightarrow \infty$. A power law for $x \rightarrow 0$ is reminiscent of reaction-limited aggregation [20], which might simply reflect the fact that the particles do not necessarily bond upon first contact when the aggregation is reversible. An exponential decay has been suggested for large x [21]; however, the data suggest that a stretched exponential decay gives a better description in the present case [22].

Another perhaps more fundamental approach is a description in terms of a fluid/fluid phase separation into coexisting large-sphere-rich and large-sphere-poor phases as a precursor to the formation of isolated crystallites. Such a treatment would be more intimately linked to the thermodynamic (entropic) nature of the clustering phenomenon, and the peak in $S(q, t)$ at $q_{\text{max}}(t)$ would correspond to the usual spinodal-like evolution at low q . Because of the presence of the wall, however, the cluster growth would be kinetically “pinned” in the regime corresponding to the first plateau in Fig. 3(a), the process being analogous to

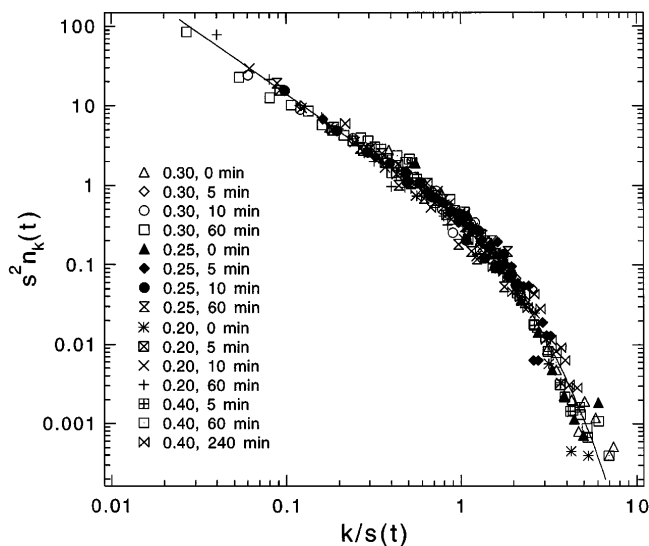


FIG. 4. A scaling plot of $s^2 n_k(t)$ vs $x = k/s(t)$ in the regime of amorphous growth, where the distributions have been truncated at $k = 20$ to eliminate scatter at large k ; the asymptotic fits are as described in the text.

the transient freezing of isolated clusters at low temperatures in dynamic percolation transitions induced by phase separation as discussed by Hayward *et al.* [23]. Provided the shear-melted state is not too far removed from the transient state ($\delta\psi/\psi_m < 1$) and the large-sphere confinement is not too severe, an exponential relaxation would be a reasonable leading order approximation. The coefficient $a_\psi(\phi_S)$ would be related to the strength of the thermodynamic driving force, the nonzero value at the phase boundary [Fig. 3(b)] being consistent with a first-order phase transition.

In conclusion, depletion-driven crystallization in confined nearly hard-sphere mixtures is observed to occur via an initial collapse into an amorphous metastable state, the growth kinetics of which exhibit a scaling of the cluster-size distribution of the form $s^2 n_k(t) = G(k/s)$, where $s(t)$ is the average cluster size. Changes in the kinetics with quench depth (ϕ_S) appear to be contained entirely in the moment $s(t)$, while the form of the scaling curve appears to be independent of quench depth. More theoretical work is needed to further elucidate the details of the process and perhaps establish a link between the two seemingly different interpretations.

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- [14] The clustering criterion is set as an input parameter in the computer code that tabulates n_k from the large-sphere centers and was chosen as the distance at which $g(r)$ decays to 0.75 of its nearest-neighbor value. Slight deviations from this did not alter the results, and the same criterion was used for all ϕ_S . Distributions from different frames corresponding to the same time were normalized and then averaged together.
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- [22] Starting from Eq. (1) with $K_{ki} \sim k^y$ in the $k \rightarrow \infty$ limit (where $y = 1 - 1/D$, with D as defined in [15]) one can assume detailed balance and argue [E.K. Hobbie (unpublished)] that $G(x) \sim \exp(-cx^\nu)$ for large x , where $\nu = 1/D \approx 0.6$.
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