Nucleation and Growth of Colloidal Crystals

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bcc crystalline colloidal microsphere suspensions are shear melted into the metastable liquid phase. Recrystallization occurs via nucleation and growth of single crystallites at dilute sites. The nearly spherical growing crystals have rough interfaces with a time-independent interface velocity, v. The velocity is found to be consistent with an equation for normal growth with a limiting velocity determined by free-particle diffusion, $v_0 \sim D_0/\xi$, where D_0 is the Stokes diffusion constant of independent noninteracting spheres, and ξ is a length comparable to the particle spacing.

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Aqueous colloidal suspensions of charged polystyrene microspheres provide a new type of system for study of the liquid-solid melting transition. At appropriate particle concentrations, microspheres will order into body-centered cubic (bcc) crystals at room temperature, a result of their strong interaction via a repulsive Coulomb potential screened by H^+ counter ions.[1,2] These equilibrium bcc suspensions can be shear melted by gentle agitation to yield a metastable colloidal liquid phase.[3] In this Letter, we present the first study of the subsequent recrystallization in such a colloidal crystal system.

The experimental apparatus is shown in Fig. 1. Suspensions of sulfonated polystyrene microspheres (Duke Scientific Corporation, catalog No. 5009) of diameter $d = 0.091 \pm 0.0056$ μm were contained in small cylindrical glass vials and were rendered free of ions other than the spheres, H^+, and OH^-, by the addition of ~1 ml of a carefully cleaned and charged strong acid-base mixed-bed ion-exchange resin (Rexyn 101 [H] and Rexyn 201 [OH]).

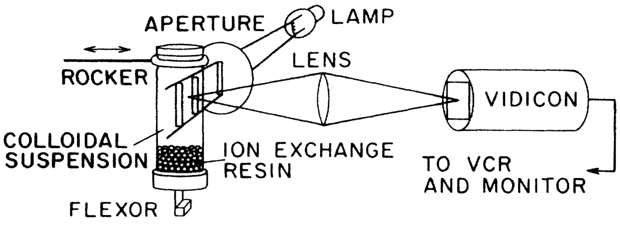

FIG. 1. Experimental setup for our nucleation experiment. White light passes through a slit aperture and illuminates the colloidal suspension. The rocker induces shear melting. The lens, Vidicon, and monitor allow viewing of the growing crystallites in real time and the growth is recorded on a video cassette recorder.

Suspensions were liquid for $n < n_m$ and bcc crystalline in equilibrium over the density range studied ($n_m = 1\ \mu\text{m}^{-3} < n < 3\ \mu\text{m}^{-3}$) as evidenced by a mosaic of bright, wavelength-selective, Bragg reflections of visible light from many single crystallites. The concentration n was measured by powder scattering methods on the crystal phase. A vial to be studied was then held in place by a flexor which allowed an attached rod to rock it as shown in Fig. 1. Gentle agitation (rocking through ~3° at 34 Hz) shear melted the crystals leaving the colloidal liquid phase which is characterized by a diffuse Debye-Scherrer scattered-light ring. This phase is metastable—it does not homogeneously recrystallize. Rather, after some time, individual bcc crystallites nucleate at widely separated locations in the liquid (nucleation site density $N_n \sim 1/\text{mm}^3$ at $n \sim 2n_m$), and grow until they fill the vial. This growth was observed by illumination of the suspension with white light apertured to give scattering from a 2-mm-thick slab of the suspension. Bragg-scattered light from a single growing crystal was collected using a 4× microscope objective (numerical aperture ≈ 0.14) imaged onto a Vidicon, displayed on a video monitor, and recorded on videotape. Once the rocking stopped, the vial was slowly turned about its long axis until a single crystallite rotated into the Bragg condition. Such a growing crystallite is shown in Fig. 2. In these photos, one observes a projection of the crystallite boundary onto the plane perpendicular to the viewing direction.

The growth characteristics were studied as a function of n and were found to be as follows: The outline of a growing crystal is smooth, i.e., not faceted, but is also distinctly nonspherical. The diameter of a growing crystallite was measured as a function of time in four directions which include the smallest and largest apparent dimensions, and then divided by 2 to yield radii

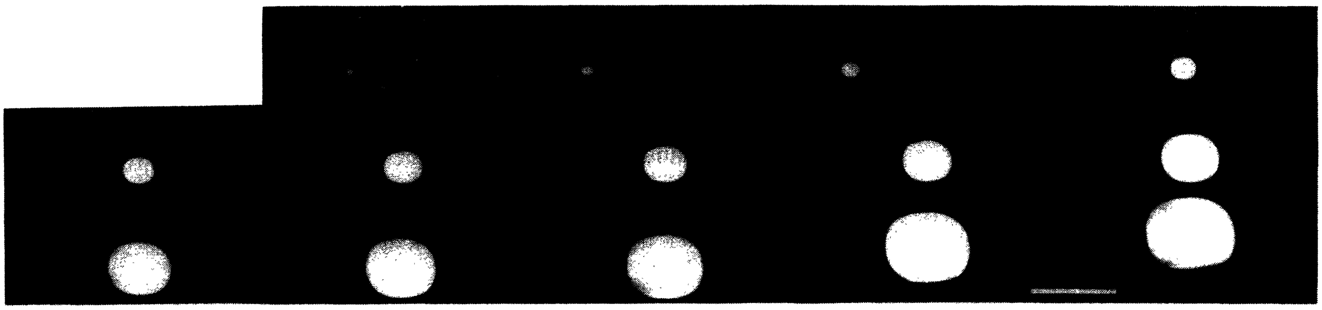

FIG. 2. A single bcc colloidal crystal growing in a metastable liquid phase. Two seconds separate each frame and the first frame occurs eight seconds after the cessation of rocking. The bar in the lower right-hand corner corresponds to a length of 1 mm. The flattening of the bottom edge of the crystal in the last frame corresponds not to the formation of a facet, but rather it is the limit of growth in this direction as it has intersected with another crystal domain not in the Bragg condition. The crystal will continue to grow in the other directions until similar intersections occur.

$r(t)$. A plot of these data, such as those in Fig. 3, shows a linear relationship for each direction. Therefore the slope of a linear fit is the growth rate, v, which is the velocity of the crystal-liquid interface. These rates were averaged to give a mean growth rate for a given crystallite. Since the crystallites which could be studied contained many unit cells ($r > 30$ μm), it would appear that linear growth is the asymptotic behavior at large r. At small dimensions ($r < 30$ μm) crystallites exhibited velocities less than the constant asymptotic rate, a possible consequence of the nucleation barrier due to surface-tension effects. However, precise characterization of small crystallites requires apparatus improvements and is currently being carried out. The nucleation site density and its dependence on n has also been studied and found to increase significantly with increasing n. These results will be reported in a later publication.

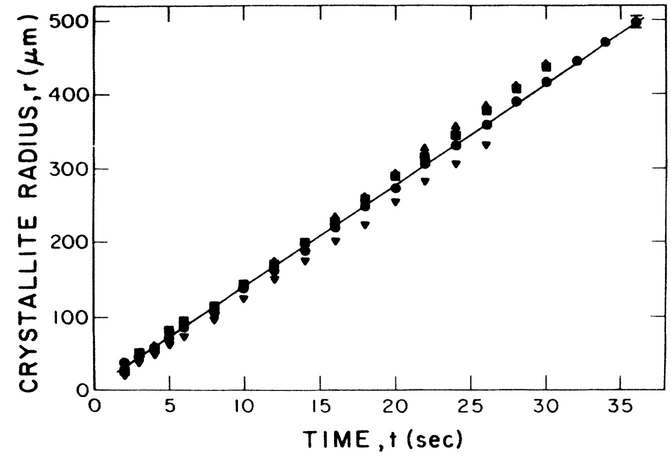

FIG. 3. The four measured radii of the colloidal crystal shown in Fig. 2. Rocking ceased at $t \sim -6$ sec. The growth rate v is deduced from an average of the slopes. The displayed linear fit is for the circles. The fits for the other points are similarly good.

Three qualitative inferences can be made immediately. First, the dilute nucleation (less than one crystallite per 10^9 particles for $n_m < n < 2n_m$), symptomatic of a first-order phase transition, implies that the shearing has produced a metastable liquid phase, i.e., the two states are separated by a significant energy barrier. Alternatively, a highly defected crystal structure could have resulted. Such a structure, however, would lose its defects in a spatially homogeneous way—the crystals would appear everywhere, as opposed to at dilute nucleation sites. Second, the shape of a growing crystallite shows that the crystal-liquid interface is above the roughening transition both in equilibrium and under all observed growing conditions. Geometrical analysis indicates that the growth is fastest along the crystallite [111] axes. Third, the crystal growth for this system is isothermal because of the low number density of colloidal particles combined with the 1-cal/cc heat capacity of the water. The latent heat per unit volume is $l \sim k_B T n$ providing a temperature rise $\sim 10^{-9}$ °C for the crystallization of the aqueous suspension.

The observed dependence of v on particle concentration is shown in Fig. 4. The growth rate increases rapidly from $v = 0$, at the colloidal-liquid-colloidal crystal melting concentration n_m, to slowly increasing values which saturate at $v \sim 20$ μm/sec at large n. Since the interface is above the roughening transition one might expect normal growth[4] which was first proposed by Wilson[5] and Frenkel,[6] for which the interface velocity has the form

$$v = v_0 \{ 1 - \exp(-\Delta\mu / k_B T) \}. \quad (1)$$

Here v_0 has units of velocity and is related to kinetic behavior at the crystal surface and is multiplied by a statistical sticking factor determined by $\Delta\mu / k_B T$, the ratio of the chemical potential difference between the

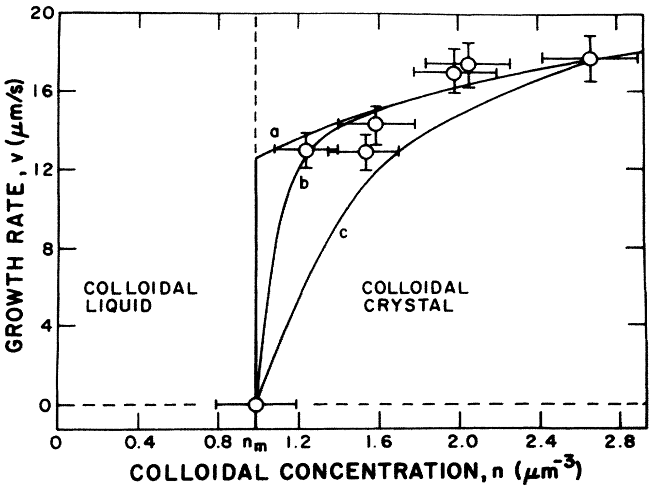

FIG. 4. Measured growth rate v as a function of the concentration n. Suspensions were in the colloidal liquid phase for $n \lesssim n_m = 1.0$ per μm^3. Also shown are three plots, a, b, and c, of the form of the growth equation (2) with $A = 0.68$ and $B = 1\times 10^{-11}$, 3×10^{-13}, and 1×10^{-13} erg, respectively. These three curves are shown to indicate the qualitative dependence of v from Eq. (2) on the parameter B which determines the ratio of $\Delta\mu$, the liquid-crystal chemical potential difference, to $n - n_m$, the concentration difference. The parameters A and B for curve b are from a two-parameter nonlinear least-squares fit which yields $A = 0.68$, implying $\xi = 0.78 d_{\rm nn}$, where $d_{\rm nn}$ is the nearest-neighbor distance in a bcc lattice and $B = 3\times 10^{-13}$ erg, yielding $\Delta\mu = 8 k_{\rm B} T$ at $n = 2 n_m$.

liquid and crystal states to the thermal energy, $k_{\rm B}T$. For $\Delta\mu / k_{\rm B} T$ large, v saturates at v_0, suggesting that this form might fit the data.

To make this comparison, it is necessary to consider the possible physical interpretation of the coefficient v_0 and its dependence on n. In a recent computer simulation of the growth from the melt of the (111) surface of argon, Broughton, Gilmer, and Jackson[7] found interface velocities given by Eq. (1) when v_0 is nearly the free-particle (streaming) thermal velocity. In this case, under saturation conditions $v \approx v_0$ and the crystal is growing as fast as it possibly can—i.e., particle arrivals are limited by their thermal velocities. The equivalent quantity in our situation would be $v_0 = 4D_0/\xi$, where $D_0 = k_{\rm B}T/3\pi\eta d$ is the Stokes diffusion coefficient for a single particle in the aqueous suspending medium (viscosity η), and ξ is comparable to the interparticle spacing. v_0 is the mean velocity for a particle freely diffusing in a plane over the distance ξ. The calculation of v_0 for our conditions shows that, in fact, $v_0 \approx 20$ μm/sec, suggesting that crystal growth saturating at the free diffusion limit is the correct physical picture. To obtain a quantitative comparison we set $\xi = A n^{-1/3}$, where A is a fitting constant, to obtain $v_0 = 4 D_0 n^{1/3}/A$, with D_0 set equal to 4.38×10^{-8} cm^2/sec, the free-diffusion value value for our case of a 0.091-μm-diam paraticle in water at room temperature. Next, we need to know the dependence of $\Delta\mu$ on concentration, for which we make the simplest assumption that $\Delta\mu$ increases linearly with $n - n_m$: $\Delta\mu = B[(n - n_m)/n_m]$, where B is a constant. The growth equation then becomes

$$v = 4D_0 \frac{n^{1/3}}{A}\left\{1 - \exp\left[-\frac{B}{k_{\rm B}T}\left(\frac{n - n_m}{n_m}\right)\right]\right\}. \qquad (2)$$

Equation (2) is shown plotted along with $v(n)$ data in Fig. 4, for $A = 1.36$ and $B = 1\times 10^{-11}$, 3×10^{-13}, and 1×10^{-13} erg (curves a, b, and c, respectively). The best two-parameter nonlinear least-squares fit, shown in curve b, gives $\xi = 1.36 n^{-1/3} = 0.78 d_{\rm nn}$ where $d_{\rm nn}$ is the bcc nearest-neighbor distance and $\Delta\mu \sim 8 k_{\rm B} T$ for $n \approx 2 n_m = 2$ μm^{-3}.

This quantitative result, namely that $\xi = 0.78 d_{\rm nn}$, confirms the qualitative observation made above that the free-diffusion value of the growth velocity obtained as $\Delta\mu$ is increased is governed by τ, the time required for the free diffusion of a sphere over a distance ξ comparable to the nearest-neighbor distance. An entire lattice plane is added to the crystal every τ. The similarity of this result to that of Broughton, Gilmer, and Jackson,[7] noted above, is striking. These authors carried out a molecular-dynamics computer simulation of the growth of the [111] face of a bcc crystal of a Lennard-Jones solid from the melt. Their results showed a saturation velocity in the normal-growth model that was much larger than that calculated from particle self-diffusion in the melt, the mechanism that might be expected to apply. Rather they found v_0 to be essentially the thermal (Maxwellian) velocity, that is, a layer of particles could find their positions in the crystal in the time it took a single particle to move thermally the nearest-neighbor distance. In our colloidal system of microspheres in water, individual "free" spheres between interactions with one another execute Brownian motion in contrast to the Maxwellian streaming between interactions of "free" Lennard-Jones particles in the simulation. Hence carrying the results of the simulation over to the colloidal system would have, under saturation conditions, a layer of particles added in the time necessary for free diffusion of a particle in the water over the nearest-neighbor distance. This is just what we find. Note that employing D_s, the microsphere self-diffusion coefficient in the liquid, would produce a saturation velocity an order of magnitude too small, since $D_0 \sim 10 D_s$,[8] D_s being controlled by particle-particle interactions.

Our observations that the interface is rough and that the limiting growth is controlled by single-particle adsorption suggest a structure for the growing interface in which locally the interfaces are one particle thick—the surface is stepped, presenting a variety of single-crystal adsorption sites. In this picture, any interface diffuseness would come from the fluctuations in the position of this locally "sharp" interface.

To conclude, our principal findings are that the shearing produces a metastable colloidal liquid which then undergoes a first-order liquid-crystal phase transition, that under the growth conditions studied here the liquid-crystal interface is rough, and that the limiting growth velocity is determined by free-particle diffusion as opposed to any collective diffusion process. This work was supported by National Science Foundation Grants No. DMR 8512071 to one of us (N.A.C.), and No. DMR 8500704 to another (B.J.A.). One of us (N.A.C.) was supported in part by a J. A. Guggenheim Foundation Fellowship.

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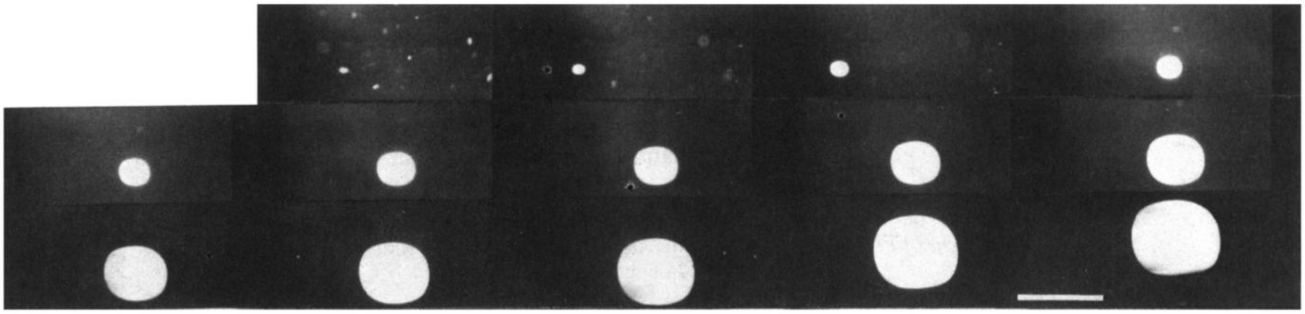

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