

Metastability and Crystallization in Suspensions of Mixtures of Hard Spheres

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Structural relaxation of metastable fluids and the kinetics of subsequent crystallization are measured by dynamic light scattering and by the growth of the main interlayer reflection in binary mixtures of colloidal polymer particles with hard-sphere-like interactions. The size ratios of the particles lie in the range for which eutectic phase behavior is expected. We find that at a constant volume fraction, close to the melting value of the one-component hard-sphere solid, the addition of up to about 10% by volume of the second component has negligible effect on the particle dynamics in the metastable fluid but significantly retards crystal nucleation and growth. [S0031-9007(97)05123-5]

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In the immediate wake of a quench, achieved either by a fast reduction in temperature in the case of a molecular fluid or by a shear melting process in the case of a suspension, the material finds itself in a state of nonequilibrium. Nucleation studies [1] suggest that there are two stages to the progression from nonequilibrium towards equilibrium. One is a transient stage during which the structure of the material adjusts until it is consistent with the thermodynamic constraints of the quenched state, that is, until a state of metastable equilibrium is attained. The second is a nucleation and growth stage to the stable equilibrium crystal. Interesting questions that arise are, Have these stages similar or disparate time scales, how do these time scales depend on the difference between the components of a binary mixture, and does the time scale of either stage exceed any reasonable experimental time? As is the case for metallic alloys, for example, these issues are inextricably connected to a liquid's propensity to form a glass [2].

Once triggered, nucleation and subsequent crystal growth proceed at rates that are generally too fast to be resolved experimentally. However, crystallization in colloidal suspensions occurs over time scales that are readily accessible. Thus, in addition to their intrinsic importance, suspensions serve as valuable experimental models for exploring general features of crystallization from the melt [3]. In this Letter we address the above questions through measurements of the crystallization kinetics and the particle dynamics of binary mixtures of hard-sphere-like colloidal particles. For the selected size ratios of the spheres (0.83 and 0.73), little or no solubility of one component in the solid of the other is expected [4–6]. Our purpose is to determine the influence of composition on the nucleation kinetics vis-à-vis structural relaxation by gradually increasing the number fraction of the second component. At the same time, we address the apparent inconsistency that, at volume fractions greater than the melting value, computer generated randomly packed configurations of hard spheres are unstable [7], whereas it is possible to create metastable states of randomly packed suspensions of hard spheres which persist for experimentally viable time scales [8].

The colloidal particles used in this work consist of cores of a copolymer of methylmethacrylate and trifluoroethylacrylate [p-(MMA/TFEA)] [9]. To prevent irreversible aggregation, the particles are coated with thin (≈ 10 nm) layers of poly-12-hydroxystearic acid. Particle radii, measured by dynamic light scattering (DLS) and particle core compositions (weight % TFEA), are $R_1 = 380$ nm (24%), $R_2 = 315$ nm (16%), and $R_3 = 520$ nm (16%). The polydispersity of each of the species, also determined by DLS, is about 5%. Compositions of the mixtures and measures of their size disparities or mixing entropies [5], $M(x) = x(1-x)[(R_L - R_S)/(R_L + R_S)]^2$, are shown in Table I (x is the number fraction of the larger particles, and R_L and R_S are the radii of the large and small particles in the mixture, respectively). The 380 nm particles constitute the dominant component, and the compositions were chosen to be well removed from the expected eutectic composition [4–6]. The refractive indices of the particles are sufficiently close to that of the suspending liquid (cis-decalin) that we are able to tune the suspensions' turbidity by varying the temperature. Furthermore, due to the different temperature dependencies of the refractive indices of particle cores, stabilizer shells, and solvent, the shapes of the particle form factors also vary with temperature. An important consequence of this feature coupled with the different core compositions of the species is that, at the temperature (12 °C) and wave vector range where measurements were performed, scattering (per particle) from the dominant component of 380 nm particles is about 10 times greater than scattering from the other particles. The wave vector range encompassed the main structure factor maximum of the colloidal fluid or the main interlayer reflection, in the case of crystallized suspensions.

Suspensions of the individual particle types show the disorder-order (freezing-melting) transition expected for the hard-sphere system. In this regard, these suspensions have the same characteristics as those, with cores consisting of pure polymethylmethacrylate (PMMA), studied extensively in previous work [10], where it has also been shown that these suspensions crystallize into structures comprising randomly stacked, close-packed layers

TABLE I. Suspension properties: the symbol used to denote each sample shown in the figures, the volume percent and radius of the second (minority) species (the radius of the majority species is 380 nm), the number fraction x of the larger particles, the size disparity M of the mixture, the crystallization time τ_c , and the power-law exponent μ of the crystallization process. See text for details.

Symbol	Volume % (Radius)	x	$M [\times 10^{-4}]$	$\log_{10}[\tau_c] (\pm 0.02)$	$\mu (\pm 0.2)$
Diamond	...	1	0	3.69	2.5
Square	2 (315 nm)	0.965	3.2	3.87	2.3
Circle	5 (315 nm)	0.915	7.0	4.27	2.9
Triangle	10 (315 nm)	0.836	11.1	4.88	4.1
Star	2 (520 nm)	0.008	13.9	4.05	2.3
Cross	10 (520 nm)	0.042	39.3

of particles [11]. Accordingly, sample volume fractions ϕ are expressed in effective hard-sphere terms relative to the freezing value ($\phi_f = 0.494$) for a system of perfectly identical hard spheres [12].

All suspensions studied have the same volume fraction, $\phi = 0.55$, which is just above the melting value (0.545) of the one-component hard-sphere solid [12]. This value is chosen because in these colloidal systems it is where the fastest crystallization rates are observed [3]. The procedure by which the samples are prepared to a desired volume fraction has been described previously [8,10]. Shear melting of the suspensions is achieved by tumbling them on a rotary mixer for several hours, after which DLS and crystal growth studies were commenced.

Figure 1 shows intermediate scattering functions, $f(q', \tau)$, measured on colloidal fluids by DLS at the wave vector given by $q'R_1 = 3.2$. Here, as in all of the figures, time is expressed in units of the Brownian characteristic time $\tau_b = R_1^2/D_0$ ($= 1.11$ s), where D_0 is the free particle diffusion coefficient of the 380 nm particles in cis-decalin at 12 °C. The position of the main maximum of the static structure factor of the one-component fluid is $q_m R_1 = 3.45$. For the mixtures, given the relatively high contrast of the particles of radius $R_1 = 380$ nm at the wave vector q' , $f(q', \tau)$ represents a good approximation to the partial intermediate scattering function of the species of radius R_1 . We explain the slower relaxation, seen at intermediate times in the mixtures, as follows. An increase in the free volume of the 380 nm particles occurs when small numbers of them are replaced by an equal volume of (invisible) particles of radius R_2 or R_3 . This affects both the (partial) structure factor $S(q)$ and the hydrodynamic factor $H(q)$ of the 380 nm particles and, in turn, alters the rate of relaxation of concentration fluctuations of wave vector q' [since $D(q) = H(q)/S(q)$ and $F(q, \tau \rightarrow 0) \sim \exp[-D(q)q^2\tau]$ [13]. One sees from the inset in Fig. 1 that when the influence of this change to the short-time diffusion coefficient is removed, by expressing the results in the form $\ln[f(q', \tau)]/D(q')$, the data essentially coincide. Accordingly, we conclude that the small composition changes explored here have negligible influence on structural relaxation. In addition, as seen from Fig. 1, we can ascribe the same characteristic relaxation time τ_s given by $\log_{10}(\tau_s) \approx 2$ in all cases.

Crystallization was measured by following the growth of the orientationally averaged reflection associated with the formation of close-packed layers of particles. The fraction of crystal $X(\tau)$ present in the scattering volume is calculated from the area under this reflection. The spectrometer used and the procedure by which this peak was isolated from the total intensity scattered from crystal plus fluid, during solidification, were described previously [3].

Figure 2 shows the evolution of $X(\tau)$ (in arbitrary units) for suspensions of different composition. In all cases, a sharp increase in $X(\tau)$, attributed to nucleation and growth [3], crosses over to a stage, attributed predominantly to coarsening, where $X(\tau)$ increases much more slowly. The important feature, as far as the present discussion is concerned, is the significant slowing of the crystallization process that occurs as the fraction of the second component is increased. This suggests discrimination of the species during solidification by either the formation of a

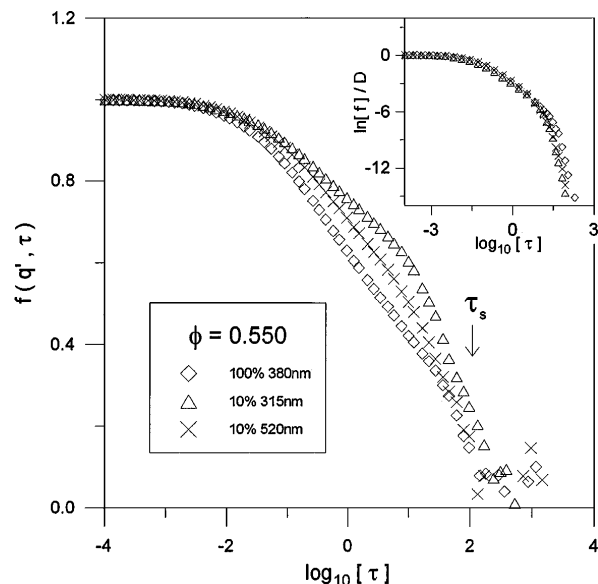


FIG. 1. Intermediate scattering functions $f(q', \tau)$ versus the logarithm of dimensionless time, at an effective hard-sphere volume fraction of $\phi = 0.550$ for three compositions (by volume) indicated. Inset shows $\ln[f(q', \tau)]/D(q')$ where $D(q')$ is the short-time q -dependent diffusion coefficient obtained from the initial decay of the intermediate scattering function $f(q', \tau)$.

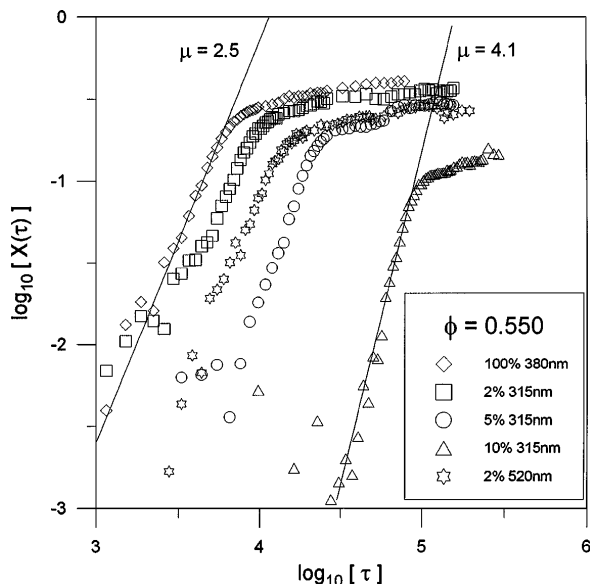


FIG. 2. Logarithm of the amount of crystal $X(\tau)$ versus the logarithm of dimensionless time for the compositions (by volume) indicated. Straight lines, with slopes $\mu = 2.5$ and $\mu = 4.1$, are fits to the steepest sections of the data.

compositionally ordered solid or partitioning of the species. We exclude the first of these options by our observation that the positions of the interlayer and higher order reflections [14] are invariant to temperature. Recall that the relative weightings of the scattering powers of particles of different species are quite sensitive to temperature. While at 12 °C the 315 nm particles are effectively invisible relative to the 380 nm particles; at 18 °C the different sized particles have comparable scattering powers for wave vectors around the main interlayer reflection. Accordingly, we conclude that the crystal phase is formed largely, if not entirely, by the dominant component of 380 nm particles. Crystallization times τ_c , characterized by the time where $dX(\tau)/d\tau$ is a maximum, and power-law exponents, obtained as illustrated in Fig. 2, are given as a function of composition in Table I.

The volume fraction of a close-packed crystal ϕ_c is related to the position q_c of the main interlayer reflection through $\phi_c = \frac{2(q_c R)^3}{9\sqrt{3}\pi^2}$, where R is the radius of the particles in the crystal phase. Thus, from the time dependence of the position of the interlayer peak, we obtain the average volume fraction in the crystal phase $\phi_c(\tau)$ [3] shown in Fig. 3. One can see that at all times $\phi_c(\tau)$ exceeds the volume fraction, $\phi = 0.55$, of the initial metastable fluid. The monotonic decrease in $\phi_c(\tau)$ has been attributed to the reduction in the volume fraction of the fluid, and concomitantly its osmotic pressure, during the growth of the crystal phase in which the particles are packed more efficiently than in the fluid [3]. However, due to slow coarsening, a process impeded by the polydispersity of the “single species” suspension and size disparity of the mixtures, the equilibrium crystal volume fraction has not been reached at the termination (four days) of the measurements.

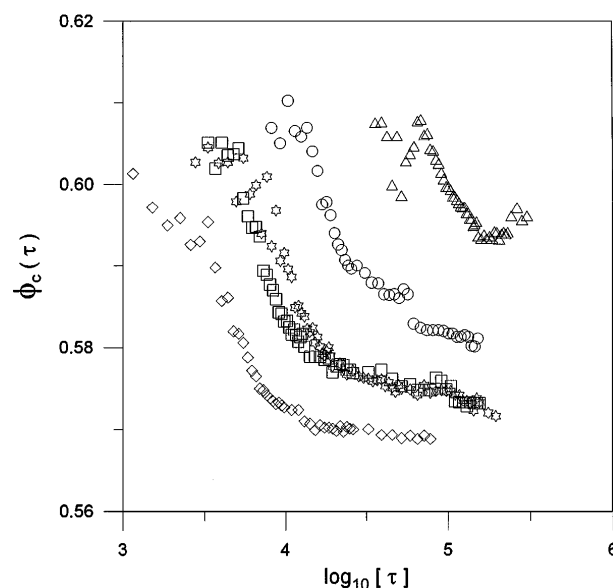


FIG. 3. Average volume fraction $\phi_c(\tau)$ of the crystal phase versus logarithm of dimensionless time. Symbols corresponding to composition are the same as in Fig. 2.

Interestingly, upon the addition of a second “invisible” component (of 315 or 520 nm particles), the interlayer reflection that develops upon the solidification of the fluid moves to higher wave vectors. The corresponding increase in the volume fraction of the crystal phase (Fig. 3), seen with increasing disparity of the mixture, is compatible with the elevation of the freezing/melting volume fractions expected for these hard-sphere mixtures [4]. Presumably, due to the close proximity of the composition-volume fraction space explored here to the melting line, we were unable to distinguish coexisting phases even after several weeks. However, results at lower volume fractions (in the coexistence region) are similar to those presented in Figs. 1–3 and will be presented in a future publication.

The above results provide the following picture of equilibration of a quenched fluid. We assume that any unstable structures, induced during the quench [15], melt or dissipate without a significant thermodynamic barrier and that such dissipation is affected by the same large-scale diffusive particle motions as those that drive structural relaxation in the metastable fluid, i.e., the time scale of the transient that takes the fluid from the quenched nonequilibrium state to metastable equilibrium is given by the structural relaxation time τ_c . Figure 1 suggests that such structural relaxation is largely unaffected by the composition of the binary mixture, at least over the range of compositions studied. However, crystal nucleation and growth are strongly influenced by composition (Fig. 2). In fact, in all cases the crystallization times are sufficiently long relative to the structural relaxation time [$\log_{10}(\tau_s) \approx 2$] to render the metastable fluid states experimentally viable, i.e., they persist long enough to allow reproducible measurements of their structural and dynamical properties.

Given that the particle dynamics is largely unaffected by the inclusion of a second species, the accompanying

retardation of the crystallization rate can, in terms of classical nucleation theory, therefore be attributed mainly to an increase in nucleation barrier: The entropy of mixing (the "size disparity" of Table I) in competition with the packing entropy causes an increase in the volume fraction of crystal nuclei (Fig. 3). Macroscopically, this is manifested by an elevation of the volume fraction at freezing [4] (analogous to a depression of the freezing temperature in the case of molecular systems [5,6]) as the composition of the mixture departs from the extremities of a eutectic phase diagram.

If one assumes that the amount of crystal during the nucleation and growth stage can be expressed by [16] $X(t) \sim t^\mu \sim L^3(t)N(t)$, where L and N are, respectively, the average linear crystal dimension and number of crystals, and if, in the absence of other evidence, one also assumes that the nucleation rate is constant ($N \sim t$), then $L \sim t^{(\mu-1)/3}$. Then from the values of μ , shown in Table I, it follows that crystal growth in the suspension of the 380 nm particles alone is diffusion limited ($L \sim t^{1/2}$) and becomes interface limited ($L \sim t$) as the fraction of smaller particles in the suspension is increased. This change in the nature of the growth process may be explained by the reduction in the rate at which particles are incorporated in the crystal due to the increased demixing at the solid-fluid interface that occurs when the fraction of the second component is increased. According to the model of Ackerson and Schätzel [17], a reduction in growth velocity incurs a reduced reliance on material transport (i.e., the conserved order parameter) leading to interface limited growth. Analogously, the growth of atomic crystals may be transport or interface limited, depending on whether the incorporation rate is faster or slower than the (latent) heat flux.

Note the crystallization of the suspension of 380 nm particles alone is still about 100 times slower than the structural relaxation time (Figs. 1 and 2). Given the strong influence of composition on crystallization times, attributed here to fractionation in binary mixtures, and the difference in compositions of coexisting solid and fluid phases, seen in computer simulations of polydisperse hard-sphere systems with symmetrical particle size distributions [18], it is not inconceivable that a polydispersity of 5%, possessed by our single species suspensions, could cause a significant retardation of the crystallization process relative to that of a system of identical hard spheres. Thus, there is no evidence in this work that contradicts the recent conclusion [7] that, for a system of identical hard spheres above the melting volume fraction, the time to progress from the quenched nonequilibrium state to metastable equilibrium is comparable to the nucleation time. While the diffusive motions of near micrometer-sized particles are many orders of magnitude slower than atoms, the existence of long-lived metastable fluid and glass states observed in suspensions of hard sphere [8] could possibly be largely, if not entirely, due to the retarding influence

of polydispersity on the crystallization process. However, in this context we point out again that the results of Fig. 1 indicate that small levels of polydispersity have a negligible effect on the particle dynamics.

From a study of the particle dynamics in the metastable fluid phases and the crystallization kinetics of binary mixtures of hard-sphere colloidal particles, we conclude that (i) the addition of small amounts of a second component, at constant volume fraction, in a mixture of hard-sphere colloids significantly retards crystal nucleation and growth but has negligible influence on the particle dynamics; (ii) the retardation of crystallization is accompanied by a change from diffusion limited to interface limited growth; (iii) polydispersity in colloidal suspensions can be exploited to control the lifetime of metastable fluid states and facilitate vitrification without appreciable effect on the structural relaxation processes.

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