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Letters

Colloidal Crystallization under Time-Averaged Zero Gravity

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Gravitational settling in concentrated colloidal suspensions may be effectively eliminated on a time-averaged basis simply by rotating the samples very slowly in the vertical plane. We describe the application of this procedure to equilibrium studies of the freezing–melting phase transition of essentially hard colloidal spheres.

Introduction

It is now widely accepted that colloidal suspensions show many close analogies with atomic and molecular fluids. For example experiments[1,2] demonstrate that suspensions of near equal-sized sterically stabilized polymeric spheres display the phase equilibria expected for an assembly of hard spheres, probably the simplest of all statistical systems to show a fluid–solid phase transition.[3] At volume fractions, φ, below the freezing concentration $\varphi_f = 0.494$, the suspension is characterized by short-ranged spatial correlations typical of a fluid phase. With increasing concentration, $\varphi > \varphi_f$, the spheres spontaneously rearrange themselves from the (metastable) fluid phase into randomly orientated colloidal crystallites. For $\varphi_f < \varphi < \varphi_m = 0.545$, the melting concentration, the suspension at equilibrium contains coexisting colloidal fluid ($\varphi = \varphi_f$) and crystalline ($\varphi = \varphi_m$) phases, whereas for $\varphi > \varphi_m$ it is fully crystalline. The phase behavior of such "hard-sphere" suspensions has been extensively studied,[4-9] motivated by the opportunities that such model colloidal systems

offer for experimental studies of complex many-body equilibrium and nonequilibrium processes.

Since a colloidal particle is typically 10^3 times larger than an atom, the structural relaxation time in a suspension is of the order of 10^9 times the corresponding atomic quantity. As a consequence colloidal suspensions crystallize over essentially macroscopic time periods (minutes, hours, or even days). Given such slow crystallization rates, sedimentation of the colloidal particles is often significant over the time scale of an experiment. The consequent concentration gradients complicate a quantitative analysis of the colloidal phases[5] and in extreme cases gravitational settling may totally suppress the freezing–melting phase transition.[9,10] Here we report a simple experimental technique which allows conditions of (effectively) zero gravity to be maintained for many months, largely eliminating the effects of sedimentation. First we describe the technique. We then give an example of its application to a two-component suspension where crystallization rates are sufficiently slow such that under normal conditions gravitational settling dominates the phase behavior. The equilibrium properties of this system have been discussed elsewhere,[7] here we give a more complete description of the zero gravity technique which was employed in this earlier work. We show that rapid crystallization in a one-component suspension is almost the same under conditions of either normal or time-averaged zero gravity. Zero gravity conditions are shown to be essential for the observation of the equilibrium phase behavior of multi-component suspensions.

Experimental Section

Time-Averaged Zero Gravity. In order to obtain a reasonable estimate of the equilibrium phase behavior, the rate of gravitational settling must be sufficiently slow compared to crystal

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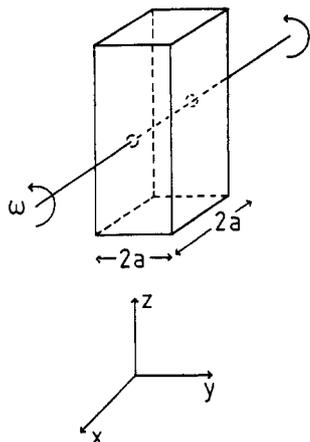(10) Davis, K. E.; Russel, W. B. Adv. Ceramics 1987, 21, 573.

Figure 1. Sample geometry for the time-averaged zero gravity experiments. The square cell of width $2a$ is rotated at an angular frequency ω in the vertical (y,z) plane.

nucleation and growth rates to allow crystallites to form and separate from any coexisting fluid before significant overall sedimentation occurs. Otherwise the colloidal particles are compressed into inhomogeneous amorphous sediments.[9,10] Ideally either microgravity conditions are required or the density of the colloidal particles and the suspension medium must be very closely matched. An alternative and far simpler solution is to rotate the samples very slowly in the vertical plane at an angular frequency ω so that, averaged over one rotation, the mean sedimentation velocity of a particle (relative to the cell walls) is zero. In effect the samples are subjected to conditions of time-averaged zero gravity. The optimum angular frequency ω is determined by a balance between the rate of sedimentation and the magnitude of the rotationally induced shear field within a sample. The angular frequency must be large enough to ensure that concentration and composition gradients at any instant are not significant over the diameter of a crystallite. Yet ω must be sufficiently small so that the rotationally induced shear field does not significantly distort the equilibrium microstructure (see below). Experiments show that an angular frequency of $\omega \sim 7 \times 10^{-5}$ rad s^{-1} (1 revolution per day) is adequate. Samples remain homogeneous and crystallization proceeds throughout the sample volume. At any time the sample can be subjected to "normal" gravity forces, allowing the separation of coexisting fluid and solid phases, simply by stopping the rotation.

Rotationally Induced Shear Field. Figure 1 shows the experimental geometry. The square-section cell, of width $2a$, is rotated about an axis normal to one of the large faces. In a completely filled cell, rotationally induced shear effects should be negligible. However the presence of even a small air bubble will result in a rapid time-dependent shear field near positions of instability, i.e. when the cell is horizontal. To avoid this instability the cell was typically half-filled with the colloidal suspension. In such a case, for small rotation rates such that $a(\rho\omega/\eta)^{1/2} \ll 1$ where η is the suspension's viscosity and ρ is its density, the velocity field is quasi-stationary.[11] The velocity profile, relative to the cell and normalized by the cell half-width a, is approximately[12]

$$\bar{V}(x,y) = -\hat{z}\frac{\omega}{N}\left\{\frac{y}{2}(1 - |y|) - \sum_{m=0}^{\infty}\frac{4}{(2m + 1)^3\pi^3}\frac{\cosh(2m + 1)\pi x \sin(2m + 1)\pi y}{\cosh(2m + 1)\pi}\right\} \quad (1)$$

where x, y, and z are Cartesian coordinates (in units of a) with the origin at the cell center, $\hat{z}$ is a unit vector in the $+z$ direction and the normalizing constant N is defined such that

$$\int\int_0^{+1}\bar{V}(x,y)\, dx\, dy = -\hat{z}\omega \quad (2)$$

The corresponding rate of strain is

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(12) A similar expression, for the related problem of fluid flow in a rectangular cross-section capillary, is quoted by Hamilton, J. D.; Stevens, T. J. *J. Colloid Interface Sci.* **1967**, *25*, 519.
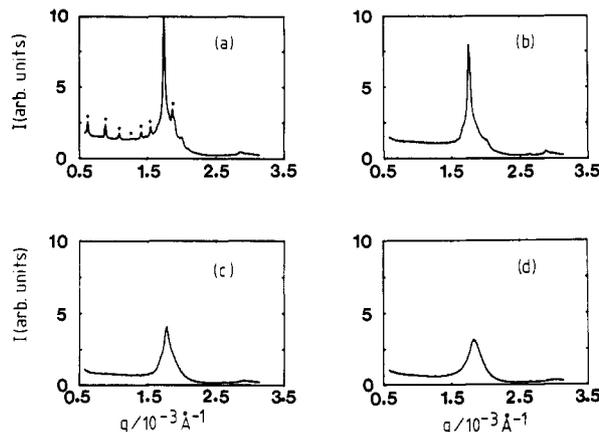

Figure 2. Scattering from a binary colloidal mixture of PMMA spheres of diameters 670 nm (species A) and 407 nm (species B). The suspension of total volume fraction $\varphi = 0.566$ and composition AB$_{32}$, had stood undisturbed for 33 days. The sample was inhomogeneous and parts a–d show the vertical variation in the measured intensity from a 1-mm horizontal stripe at heights of (a) 24.6 mm, (b) 23.6 mm, (c) 15 mm, and (d) 10 mm from the cell base. While parts a, b, and c show scattering characteristic of crystalline phases, part d shows an amorphous phase. The strong reflection at $q \sim 1.7 \times 10^{-3}$ Å^{-1} in parts a–c arises from the (001) reflection, indexed on a hexagonal basis, of an irregularly stacked close-packed crystal of small spheres.[6] The less intense (110) reflection from this structure is also apparent at $q \sim 2.9 \times 10^{-3}$ Å^{-1}. The progression of low angle reflections in part a, marked by asterisks, results from the binary alloy AB$_{13}$.

$$\dot{\gamma} = \frac{1}{2}\left[\left(\frac{\partial\bar{V}}{\partial x}\right)^2 + \left(\frac{\partial\bar{V}}{\partial y}\right)^2\right]^{1/2}$$

Typically, with $a = 5$ mm and $\omega = 7 \times 10^{-5}$ rad s^{-1}, the maximum strain rate is calculated from eq 1 as 3×10^{-4} s^{-1}.

The magnitude of the shear-flow-induced distortion of the suspension microstructure may be estimated from the Péclet number, Pe $= \dot{\gamma}\tau_R$, where τ_R is the structural relaxation time. For Pe $\ll 1$, Brownian forces dominate shear forces so that the microstructure under shear is essentially the equilibrium distribution. The local rearrangement time for spheres in a concentrated one-component suspension is relatively long, being $\tau_R \sim R^2/6D_L$, where R is the hard sphere radius and D_L the corresponding (long time) self-diffusion constant. In a suspension of near uniformly sized hard spheres, experiments[13,14] indicate, at freezing, $D_L/D_0 \sim 0.02$, where D_0 is the diffusion constant of an isolated particle. So with $R \leq 300$ nm, the maximum Péclet number is approximately 6×10^{-4}, and shear effects should be negligible. Even in a multicomponent suspension where relaxation times may be up to 50 times longer,[7] the maximum Péclet number is still much smaller than unity.

Results and Discussion

Slow Crystal Nucleation and Growth. In systems where the rate of crystal nucleation and growth is slower than the rate of sedimentation, the behavior, observed on standing, is highly nonequilibrium. Figure 2 shows the complex sequence of phases that are formed under normal gravity ($\omega = 0$) following differential sedimentation in a binary colloidal suspension, mixed initially by shaking. The suspension consisted of a mixture of poly(methyl methacrylate) spheres, stabilized by grafted poly(12-hydroxystearic acid), of diameter 670 nm (species A) and spheres of diameter 407 nm (species B), corresponding to a diameter ratio of 0.61, suspended in a near refractive-index-matched liquid medium of cis-decalin and carbon disulfide. The overall suspension volume fraction was $\varphi = \varphi_A + \varphi_B = 0.566$ and the two components were mixed in the ratio AB$_{32}$. The equilibrium phase behavior of suspensions of this type, under time-averaged zero gravity,

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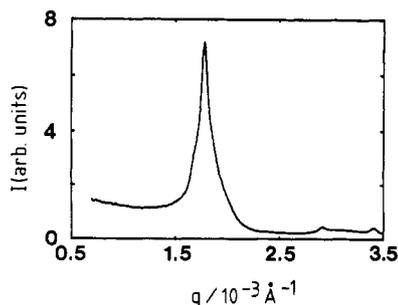
Figure 3. Crystallization under time-averaged zero gravity. The sample depicted in Figure 2 was rapidly tumbled to form a metastable fluid phase and then left to crystallize under time-averaged zero gravity. Crystallization occurred homogeneously, at random sites, within the sample. The rotation was stopped after 138 days at which point there was no sign of gravitational settling. The scattered intensity shows the characteristic powder diffraction pattern of an irregularly stacked crystal of small spheres.[6]

Figure 4. Phase diagrams for suspensions obtained under normal gravity (circles) and zero gravity (squares). The solid and dashed lines show the result of a linear regression fit to the coexistence region data for conditions of normal and zero gravity, respectively. To account for the stabilizing layer and possible swelling by the solvent, the measured freezing core volume fraction φ_c should be scaled to coincide with the theoretical[3] hard sphere freezing point ($\varphi = 0.494$). In the present case this amounts to a radius increment of ~ 10 nm, in reasonable agreement with previous studies and the expected length of an extended poly(12-hydroxystearic) acid chain.[7]

is described below (see also ref 7). First we concentrate on the nonequilibrium structures that are formed after gravitational settling. Figure 2 shows the q dependence ($q = (4\pi n/\lambda) \sin (\vartheta/2)$, where ϑ is the scattering angle, n the suspension refractive index, and λ the laser wavelength) of the light scattered by a 1 mm thick horizontal stripe at various heights in the suspension, after standing for 33 days. In the top 1 mm of crystal (24.6 mm from the cell base) the scattered intensity, Figure 2a, contains features characteristic of an irregularly stacked close-packed crystal of small spheres (species B), for example the (001) Bragg reflection[6] at $q \sim 1.7 \times 10^{-3}$ Å^{-1}, together with a sequence of low angle reflections, labeled by asterisks in Figure 2a, which arise[15] from the ordered alloy structure AB_{13}. The observation of AB_{13} is intriguing since equilibrium studies[15] of the same system have shown that AB_{13} structures are formed only in suspensions with compositions between AB_{10} and AB_{16}. One millimeter lower down in the sample (see Figure 2b) there is no sign of the AB_{13} reflections. The scattered intensity is now consistent with a single crystalline phase of small spheres with the large spheres in amorphous structures. Figure 2c shows that the suspension is still crystalline about 15 mm from the cell base; however diffraction broadening of the main Bragg reflection (cf. Figure 2b) indicates that the crystallite size becomes very small toward the base of the cell. At a height of 10 mm above the base of the cell, the scattered intensity, Figure 2d, has no sharp Bragg diffraction peaks, suggesting an amorphous structure. Comparison of the positions of the most intense peaks in Figure 2a–c shows that the crystal density increases with increasing depth within the sample.

By contrast Figure 3 shows the scattered intensity measured, for the same sample as Figure 2, after slow tumbling ($\omega \sim 7 \times 10^{-5}$ rad s^{-1}) for 138 days and standing ($\omega = 0$) for 40 h. The scattered intensity is now the same, within experimental error, at all positions within the suspension. The measured scattered intensity is consistent with a crystalline phase of small spheres with the remaining, relatively small number of, large spheres in amorphous structures. As discussed in detail elsewhere,[7] the amorphous structures formed during slow tumbling reflect the dynamics of the suspension and not the influence of a gravitational field. The absence of concentration gradients and of totally amorphous sediments at the base of the cell, both of which are characteristic of colloidal settling under gravity,[8–10] indicates that slow tumbling has largely eliminated the effects of sedimentation. In addition the observation that the suspension is largely crystalline illustrates that the rotational-induced shear field cannot
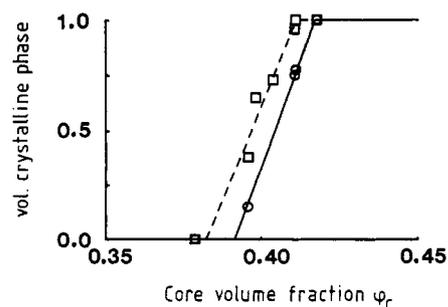
be significant, since colloidal crystals are readily melted by large shearing forces.[6]

Rapid Crystal Nucleation and Growth. In one-component suspensions of PMMA particles the crystallization rate normally exceeds the rate of gravitational settling. Hence a reasonably accurate estimate of the equilibrium phase behavior can be obtained under conditions of normal gravity.[2] We have demonstrated that essentially the same phase diagram is obtained under time-averaged zero gravity so, as the arguments above indicate, the shear-induced distortion of the suspension microstructure is minimal. Figure 4 shows the phase diagrams determined for a suspension of poly(methyl methacrylate) spheres of diameter 262 nm and polydispersity [(standard deviation of particle size distribution)/mean] of ~ 0.08. The squares of Figure 4 show the results of time-averaged zero gravity measurements in which the samples, after an initial shaking, were slow tumbled for 3 days during which period crystallization occurred. Standing for 66 h effected a gravitational separation of the coexisting crystal and fluid phases. The corresponding static measurements are shown as the circles in Figure 4. Here the samples were simply left standing for 74 h during which time both crystallization and phase separation occurred. The slight disagreement between the two measurements probably reflects the neglect of the compaction of the initially formed crystalline phase which occurs in the untumbled samples.[5]

Conclusions

We have described a simple technique which allows colloidal phase transitions to be followed under conditions of effectively zero gravity. In colloidal suspensions, especially multicomponent systems, crystallization may be sufficiently slow so that, without the present procedure, gravitational settling dominates the phase behavior resulting in dense, inhomogeneous sediments. Under time-averaged zero gravity, suspensions remain homogeneous with crystallization proceeding throughout the sample volume. The present procedure, which we consider essential for an equilibrium study of multicomponent suspensions, allows time-averaged zero gravity conditions to be maintained for many months. Finally we note that in light-scattering studies of aggregating colloids, Lin et al.[16] previously used the related procedure of inverting the sample cell between measurements to reduce the effect of gravitational settling.

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