Crystallization of hard-sphere colloids in microgravity

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The structure of, and transitions between, liquids, crystals and glasses have been commonly studied with the hard-sphere model1–6, in which the atoms are modelled as spheres that interact only through an infinite repulsion on contact. Suspensions of uniform colloidal polymer particles are good approximations to hard spheres7–11, and so provide an experimental model system for investigating hard-sphere phases. They display a crystallization transition driven by entropy alone. The particles are much larger than atoms, and the crystals are weakly bound, gravity plays a significant role in the formation and structure of these colloidal crystals. Here we report the results of microgravity experiments performed on the Space Shuttle Columbia to elucidate the effects of gravity on colloidal crystallization. Whereas in normal gravity colloidal crystals grow just above the volume fraction at melting show a mixture of random stacking of hexagonally close-packed planes (r.h.c.p.) and face-centred cubic (f.c.c.) packing if allowed time to settle12, those in microgravity exhibit the r.h.c.p. structure alone, suggesting that the f.c.c. component may be induced by gravity-induced stresses. We also see dendritic growth instabilities that are not evident in normal gravity, presumably because they are disrupted by shear-induced stresses as the crystals settle under gravity. Finally, glassy samples at high volume fraction which fail to crystallize after more than a year on Earth crystallize fully in less than two weeks in microgravity. Clearly gravity masks or alters some of the intrinsic aspects of colloidal crystallization.

The thermodynamic phase diagram for hard spheres as obtained by computer simulations is: \( \phi_{\text{liquid}} < \phi_{\text{freeze}} = 0.494 < \phi_{\text{coast}} < \phi_{\text{melt}} = 0.545 < \phi_{\text{cryst}} < 0.74 \) (refs 1–4), where \( \phi \) is the volume fraction; the simulations also find reduced diffusion and a metastable glass phase for \( \phi > 0.58 \). For typical hard-sphere colloidal systems on Earth the gravitational length \( h \) is about 1–30 \( \mu \text{m} \) (\( mh = kT \)), where \( m \) is the buoyant mass of a particle, \( g \) is the acceleration due to gravity, \( k \) is the Boltzmann’s constant and \( T \) is temperature), below crystallite sizes, and much less than the sample sizes (of the order of centimetres). So it is not clear what effects sedimentation, concentration gradients and gravitational stresses have on the kinetics and thermodynamics of the crystals12.

The particles consist of uniform poly(methylmethacrylate) (PMMA) spheres, 508 or 518 nm in diameter (=\( 2a_0 \)), polydispersity ~5%, with a thin (10-nm) grafted layer of poly(hydroxyesteric acid) to prevent aggregation13. The particles are suspended in an index of refraction (1.51) matching mixture of decalin and tetraclin. Using a stirring bar in the sample cells, the samples were mixed (sheared melted) by the astronauts on day 2 of the flight. The static laser light scattering (wavelength, \( \lambda = 791 \text{ nm} \)) was obtained with a 50-\( \mu \text{m} \) beam focused through a cylindrical sample and lens on a translucent screen and recorded with a video camera. The sample was translated to obtain data from many independent crystallites.

Crystal close packing can be obtained by stacking hexagonal planes of spheres. With a first layer as A, there are two equivalent placements B and C of the second layer above the interstitial sites of the first. If the stacking continues, the f.c.c. lattice is the arrangement ABCABC..., hexagonal close-packed (h.c.p.) is ABABAB..., but any arrangement has the same volume fraction, \( \phi = 0.7404 \). The random arrangement ABACBACBCA... with no repeating sequence.

Figure 1 a, Bragg scattering geometry. A laser beam incident on a cylindrical sample is scattered onto a cylindrical screen. b, Bragg scattering from a sample with \( 2a_0 = 518 \text{ nm} \) and \( \phi = 0.537 \). Note the dominance of streaks rather than spots, indicating Bragg rods and a two-dimensional structure as might be expected for a random hexagonal close-packed (r.h.c.p.) structure. c, d, Computer-generated scattering pattern for f.c.c. (c) and h.c.p. (d) structures.
is r.h.c.p. Simulations indicate that the f.c.c. structure is most stable for $\phi$ near 0.7404. But just above melting, with $\phi = 0.545$, the situation is less clear\textsuperscript{13,14}. Experiments on hard-sphere colloidal crystals in normal gravity find a mixture of r.h.c.p./f.c.c. with more r.h.c.p.\textsuperscript{7,8}.

In Fig. 1b we show a typical CCD (charge-coupled device) image recorded for the laser-Bragg screen (the scattering geometry is shown schematically in Fig. 1a). The unusual and characteristic feature of all of these diffraction patterns is the dominance of Bragg streaks (indicating two-dimensional order) rather than Bragg spots. The streaks result from incoherently stacked two-dimensional ordered sheets as one might expect for the r.h.c.p. structure. In Fig. 1c and d we show typical calculated images for f.c.c. and r.h.c.p.; for our geometry and crystallite size\textsuperscript{15}. Our data is clearly consistent with r.h.c.p. To test for the presence of f.c.c. we digitized the CCD images from many translations of the sample cell and computed the intensity $I$ as a function of scattering wavenumber $q$ (where $q = (2\pi/\lambda) \sin \theta/2$). In Fig. 2 we show $I(\theta)$ (unnormalized by the particle form factor) for the identical sample in the identical apparatus taken the same time after mix-melt in microgravity and normal gravity. The peak at $80^\circ$ in the normal-gravity data is the (2,0,0) f.c.c. Bragg peak, completely absent in the microgravity data. Growth in microgravity yields almost pure r.h.c.p. crystals.

In Fig. 3 we show photographs of a sample in liquid–solid coexistence. On the left is the pre-flight photograph where the denser crystal phase settled below the liquid phase. On the right the same sample is shown after mix-melting and 3.6 days of crystallization in microgravity. The microgravity crystals are larger and exhibit dendritic arms (see inset) previously undetected and un presumed. (Dendrites have been reported for charged colloids near a surface\textsuperscript{16}.) The red and green colours indicate single crystals with different Bragg peaks which scatter visible white light with different colours in the same direction.

Should we expect dendrites? Ackerson and Schatzel\textsuperscript{17,18} explored the nucleation and growth of hard-sphere crystals experimentally and theoretically. Their model includes dynamics and kinetics...
particular to colloidal crystals. Our linear stability analysis of their equations indicates a dendritic instability at $\sim 1 r_c$ (the critical nucleus $r_c \approx 3 \mu m$ for our system at $\phi = 0.504$) similar to the instability at $\sim 7r_c$ in molecular systems.

As a crystallite grows, its mass increases and in gravity it sinks faster. The viscous stresses applied to the crystallite (radius $R$) surfaces support its buoyant mass, $M$, and induce internal stresses of the order of $Mg/4\pi R^2$. When these stresses exceed the yield stress of the crystal, the crystal breaks. For a crystalline solid the yield stress, $\sigma_{y,cr}$ is given approximately by $\beta G$, where $G$ is the shear modulus and typically $\beta \approx 10^{-1}$ to $10^{-2}$. Taking $M \approx (4\pi/3)R^3\sigma_{y,cr}$, $G \approx \chi kT\rho_0$, $\Delta \phi = \phi_{\text{nuke}} - \phi_{\text{nuke}} = 0.05$ and $\sigma_0 = 0.25 \mu m$ we have $R_{\text{crit}} \approx \chi kT/(2\pi\sigma_{y,cr}) \approx 20H$, where $H$ is the gravitational length ($\approx 30 \mu m$ for our samples) $\chi \approx \phi$ (ref. 21), and $\rho$ is the buoyant density of the particles. A sinking spherical particle can only grow to $\sim 600 \mu m$. Dendritic arms are sheared off much more readily. Sedimentation also sets up a flow field which can alter the diffusion field. For our samples, convection from sedimenting crystallites of radius $R$ is faster than diffusion over the distance $R$ when $R \geq \tau$ several times $\tau_0$, which may alter the growth mechanism.

The ‘glass’ sample that we studied had $\sigma_0 = 508nm$, $\phi = 0.619$, well into the glassy regime observed in other ground-based systems. After mix-melting in normal gravity, the sample was allowed to sit undisturbed for a period of more than a year and never crystallized. The sample was mix-melted in microgravity and to our surprise began nucleation within 3.6 days. By the last experimental day of the shuttle flight the astronauts remarked on the centimeter sized crystals that had formed and filled the cell. This sample survived re-entry and sat in its fully crystalline state in our laboratory for 6 months. We then used the stirring bat in the sample cell to mix-melt the bottom half of the sample. For a month the crystalline region slowly grew into the disordered region and then essentially stopped. Figure 4 shows this sample two months after the bottom half was mix-melted. The glass region not in contact with the crystal has shown no evidence of nucleation. We therefore conclude that, at $\phi > 0.58$, the nucleation and growth of the crystals are greatly hindered in a gravitational field. This may result from the geometry of random packings realized with and without applied stresses (for example, random close packing is $\phi = 0.64$, random loose packing, for systems under shear or gravity, is less well defined but is found to be $\phi \sim 0.58$; ref. 25).

We note that neither dendritic growth nor growth under sedimentation represent the slow quasi-equilibrium process that would assure an equilibrium crystal structure. The r.h.c.p. structure may be the equilibrium structure, but it may also result from non-equilibrium growth. The fact that f.c.c. packing was not found in microgravity but on crystalline samples brought back to normal gravity growth. The fact that f.c.c. packing was not found in normal gravity samples indicates a dendritic instability at $\phi \approx 0.504$, similar to the instability at $\sim 7 r_c$ in molecular systems.

Sensors such as electrodes and optical fibre devices, optrodes, can be used to determine steep concentration gradients of chemical species in aquatic microenvironments, such as in the pore waters of surface sediments and microbial mats, but are limited to a restricted range of determinands. The highest-resolution measurements of trace-metal concentrations in pore waters, at about 1.25 mm, have been provided by a recently developed thin-film gel technique, but the resultant metal distributions suggest that sub-millimetre-scale gradients need to be determined if the fluxes and cycling of the metals are to be fully quantified and understood. Here we report the development of this thin-film gel technique to measure Zn, Mn, Fe and As fluxes and concentrations at a resolution of 100 $\mu m$, and demonstrate the utility of the method in situ within the surface microenvironment and overlying microbial mat of a stream. Vertical profiles through the mat and sediments, and horizontal two-dimensional mapping just below the sediment–water interface, reveal the contrasting gradients, fluxes and remobilization niches of the four metal species at a sub-millimetre scale. The microbial mat appears to be an important regulator of the cycling of these metals. This technique has the potential to be extended to other chemical species and applied to other microenvironments with steep concentration gradients, such as redox boundaries, plant roots, animal burrows and sites of precipitation/dissolution in soils and sediments. Microbial mats are laterally compressed ecosystems that support