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LETTER TO THE EDITOR

Direct observation of pre-critical nuclei in a metastable hard-sphere fluid

M S Elliot, S B Haddon and W C K Poon

Department of Physics and Astronomy, The University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, UK

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Abstract

We imaged at single-particle resolution the birth, life and death of a sub-critical nucleus containing $\sim 10^3$ particles in a crystallizing hard-sphere colloidal fluid at volume fraction $\phi = 0.51$. This gives a lower bound to the critical nuclear size for hard-sphere crystallization at this volume fraction.

1. Introduction

An assembly of hard spheres is, arguably, the simplest model of matter to show a disorder–order, or crystallization, phase transition. The phase behaviour of an assembly of N spheres of radius R occupying a volume V is determined solely by the volume fraction $\phi = \frac{4}{3}\pi R^3 N / V$. Up to $\phi = 0.494$, the stable phase is fluid-like, with no long-range order. At higher volume fractions, configurational ordering into a crystalline lattice gives individual spheres more freedom of movement, albeit in a more or less fixed cage of their nearest neighbours. In the range $0.494 < \phi < 0.545$ the assembly will only partially order, separating into fluid regions at $\phi = 0.494$ and crystalline ones at $\phi = 0.545$, in such a proportion as to conserve the overall volume fraction. For $\phi \geq 0.545$ (up to the maximum volume fraction, at $\phi = \pi/3\sqrt{2} \approx 0.740$, the close-packing limit), the equilibrium state is entirely crystalline.

This picture first emerged in computer simulation [1, 2]. More recently, experiments became possible with the availability of model colloids. Thus, sterically-stabilized polymethylmethacrylate (PMMA) particles suspended in various hydrocarbon liquids behave as almost perfect hard spheres [3, 4]. Experiments using this system have confirmed the pattern of phase behaviour summarized above [5, 6], but have also revealed a number of novel features. For example, while most calculations have assumed a face-centred cubic structure for hard-sphere crystals, i.e. stacking of hexagonal layers in an ABCABC... sequence, light scattering shows that as-formed hard-sphere colloidal crystals have a more-or-less randomly-stacked sequence of hexagonal layers (ABACBA...) [7]. Recent simulations suggest that the equilibrium structure is indeed face-centred cubic [8]. The long-term fate of the metastable random-stacked structures obtained in experiments is an open question [9].

PMMA suspensions have also been used to perform time-resolved light scattering experiments on crystallization *kinetics* [10]. A variety of detailed information, e.g. crystal growth as a function of supersaturation, can be obtained and compared with theory. However,

scattering necessarily involves time- and space-averaging, and can, at best, only give indirect information on local events such as nucleation. Direct information on individual events at the earliest stages of symmetry breaking requires data in real space. Simulation is one way of proceeding [11], although the need for large system size for nucleation studies imposes severe constraints. An alternative is to study model suspensions using the optical microscope, the upper limit of the colloidal length scale being directly resolvable in such an instrument.

The most direct method for observing colloids is *confocal* microscopy, since in principle, individual particle coordinates can be tracked in a bulk sample (e.g. [12]). We have shown earlier, however, that with careful choice of experimental conditions and the use of suitable optics (e.g. phase contrast), conventional (i.e. non-confocal) microscopy can give significant structural information in colloidal crystals [13, 14]. Here we use this technique to study nucleation in a metastable hard-sphere fluid.

2. Experiment

We used 540nm radius PMMA spheres, sterically stabilized with a 10–15 nm coating of chemically-grafted poly-12-hydroxystearic acid, dispersed in a mixture of cycloheptyl bromide (CHPB) and cis-decahydronaphthalene (cis-decalin). The volume fraction of a suspension stock in the coexistence region ($0.494 < \phi < 0.545$) was determined by measuring the relative proportion of fluid and crystal phases [6], and brought to any desired volume fraction by adding or removing solvent. A sample at $\phi = 0.510$ was prepared in a 2 ml glass vial and thoroughly homogenized. A rectangular-section glass capillary tube ($100 \mu\text{m}$ deep \times 2 mm wide), mounted on an ordinary microscope slide, was then filled with colloid by capillary action and sealed with epoxy resin.

The volume fraction (0.51) was chosen to ensure a slow enough rate of nucleation to permit observation of the earliest stages (limited by the ‘dead time’ associated with sample loading) and of isolated nuclei. The exact solvent composition was chosen to optimize two effects simultaneously. First we want to minimize the density difference between particles and solvent and therefore sedimentation, so that we can observe nucleation in the bulk. Secondly, we need to optimize the refractive-index difference between solvent and particles. Values too small or too large lead to no contrast or too much turbidity for bulk imaging respectively [14]. The actual composition, 20:80 of CHPB:cis-decalin by mass, was chosen by trial and error. By measuring the variation in particle concentration with depth in a dilute suspension that had achieved sedimentation equilibrium [14], a value for the sedimentation length $Z_{\text{sed}} = 28 \pm 1 \mu\text{m}$, or nearly 30 particle diameters, was obtained, consistent with the experimental observation that nucleation was not controlled by the bottom wall.

Video microscopy was used to follow the relaxation of the suspension from the metastable fluid state it was in when the tube was filled. Observations were performed on a Zeiss Axioskop FS microscope, using differential interference contrast (DIC or ‘Normaski’) optics and an objective of numerical aperture 1.40. DIC images gradients in refractive index, and gives individual spheres a ‘shaded’ or ‘three dimensional’ appearance, as well as an overall intensity gradient across any image frame [14].

Each image records a $(14 \mu\text{m})^2$ field of view at a position well away from the sides and ends of the capillary. We collected vertical image stacks each of which consisted of 230 images. The fields of view of successive images in a stack were separated by a depth of $0.44 \mu\text{m}$ (close to the depth of field of each individual image), so that the entire depth of the capillary was scanned in each vertical image stack. Each stack of images took a minute or so to collect. This is comparable to the structural relaxation time of the suspension, i.e. the time it takes a particle to diffuse its own diameter.

The first image stack was recorded 14 minutes after the tube was sealed, scans were then taken every 3 minutes, until 65 minutes since sealing; for the next $4\frac{2}{3}$ hours a scanning interval of 12 minutes was used, after which the interval was increased to 3 hours, with the final stack being collected at 17 hours 40 minutes after sealing.

3. Results

Each image in the series of scans was inspected by eye for evidence of crystalline order. Figure 1 shows the results of this survey. There are three distinct regions of crystal. First, a crystallite was visible in the middle of the tube after about 40 minutes; it grew and then receded completely over the next hour or so. Another crystallite appeared shortly after this, about a third of the way up the tube, apparently unconnected with the previous one. At about the same time, a third crystallite grew up from the bottom of the tube. The latter two regions eventually joined and, after about 6 hours from the start of the experiment, the suspension seemed to have reached some sort of steady state, with roughly the bottom third of the tube being crystalline, which is consistent with $\phi = 0.510$. The montage in figure 2 illustrates the highlights of this behaviour: the three regions where crystallization was observed to originate are shown by the images at 48 and 59 μm of the stack at 1.03 hours, the image at 26 μm of the stack at 2.5 hours and the image at 4 μm of the same.

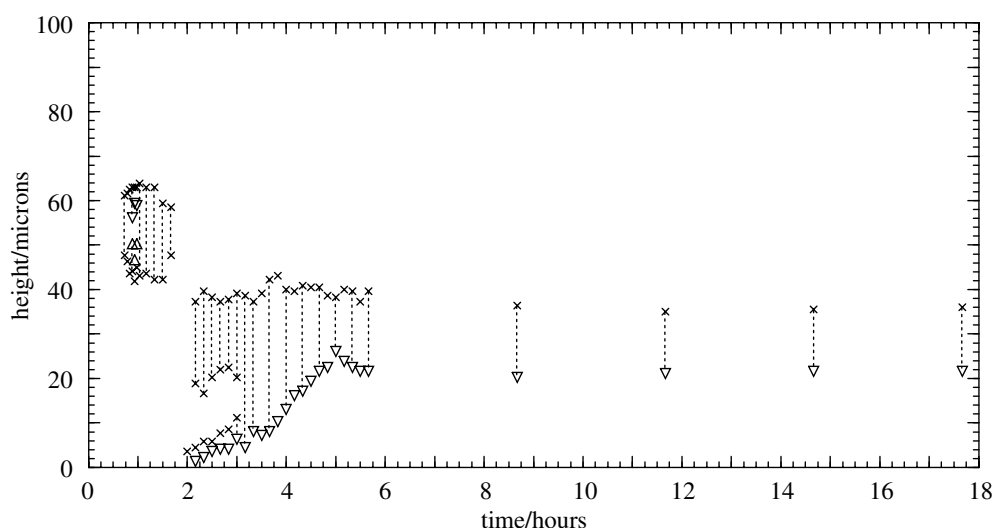


Figure 1. The development of crystalline regions in a 100 μm deep capillary over time since filling with a metastable hare-sphere colloidal fluid at $\phi = 0.51$. The vertical axis represents vertical position within the capillary. Partially crystalline fields of view are shown by a dotted line (outer limit indicated by \times); ∇ and Δ represent the upper and lower bounds of fully crystalline fields of view.

4. Discussion

Of particular interest is the fate of the first crystalline region that appeared, grew and then apparently disappeared. Five explanations are possible: stage drift, diffusion, sedimentation, convection and melting.

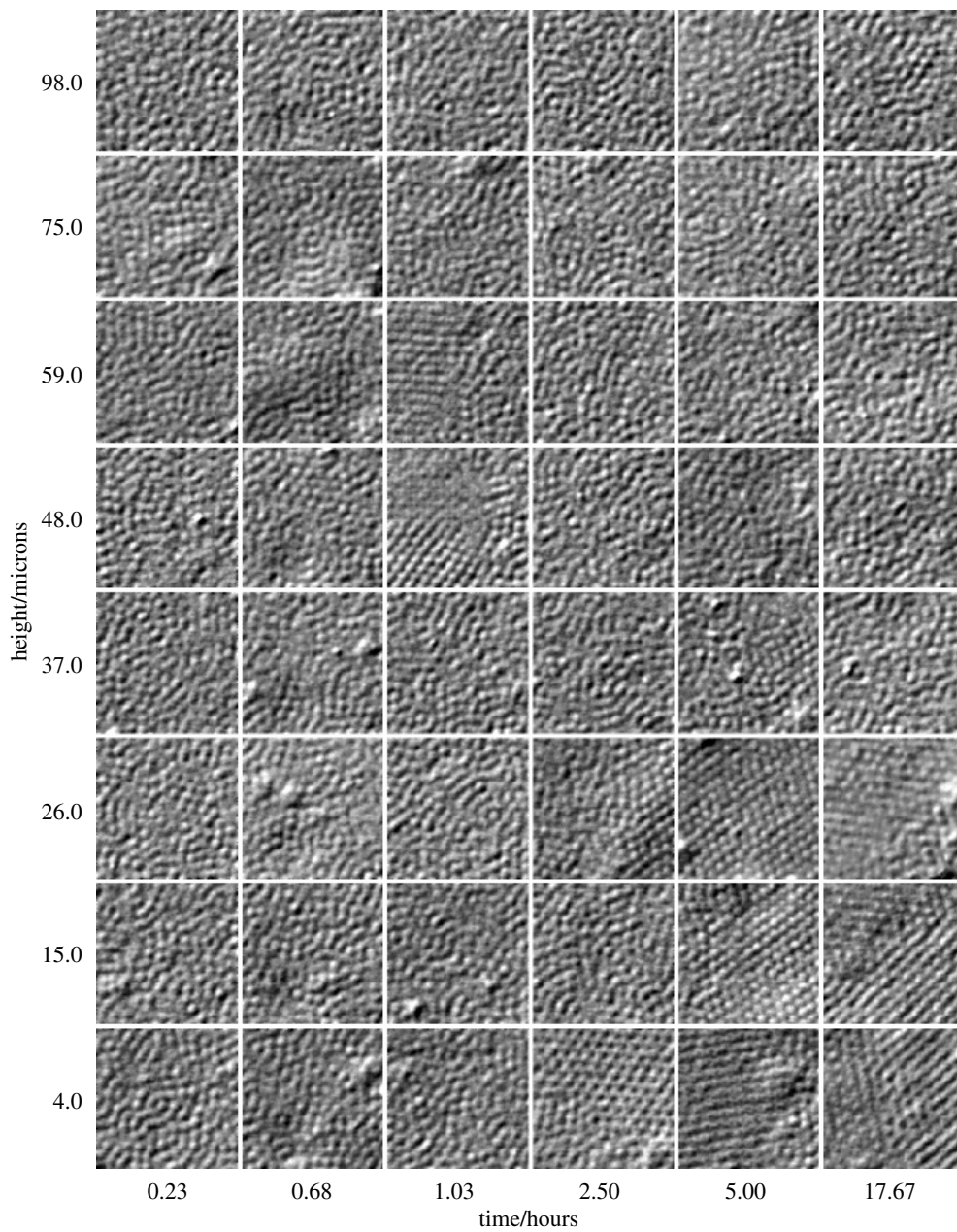


Figure 2. Images of a density-matched suspension at $\phi = 0.510$, showing the appearance of the suspension at heights $z = 4, 15, 26, 37, 48, 59, 75$ and $98 \mu\text{m}$ above the bottom of the $100 \mu\text{m}$ deep capillary tube, at times of 14, 41, 62, 150, 300 and 1060 minutes after being left to equilibrate. Each image records a $(14 \mu\text{m})^2$ field of view.

Stage drift causing movement of the sample relative to the objective can be ruled out, as movements $O(10^0) \mu\text{m}$ are the maximum recorded over similar time scales and conditions. Our field of view is $O(10^1) \mu\text{m}$. Diffusion is also unlikely. The time for a crystallite of size

$L \sim 20 \mu\text{m}$ to diffuse its own spatial extent is of the order of $L^3\eta/6\pi k_B T \sim O(10^5)\text{s}$ using the results of Meeker *et al* [15] for the suspension viscosity η . The crystallite does not disappear by sedimentation: the upper and lower bounds of this region, figure 1, show no evidence for any general vertical drift. Convection has never been observed, except during the filling of capillary tubes and at the edges of drying out suspensions. Moreover, a time-lapsed recording over half an hour played back at high speed showed no such drift in a similar suspension.

The most likely explanation would therefore seem to be that the crystalline region has melted. What we have observed is then a pre-critical nucleus. The second crystallite observed after 2 hours between 20–40 μm from the bottom of the capillary, figure 1, has a similar spatial extent. We may therefore expect it to have melted by circa 3 hours. By this stage, however, a third crystallite was growing from the bottom of the capillary. It was probably nucleated because of the enhanced particle density near the bottom wall was due to sedimentation (although the bulk density remained unaffected). These two crystallites ‘met’ at just over 3 hours and merged.

The procedure for analysing colloidal crystal structures using image stacks from conventional microscopy has been described in detail before [14]. Here we quote the results of such an analysis of the pre-critical nucleus described above. It shows that the pre-critical nucleus is not grossly anisotropic in overall shape. Internally, the crystallite consists of planes of hexagonally-arranged particles (albeit with many defects). Viewing the three-dimensional reconstruction at 90° to the direction of stacking and comparing to models [13, 14] show that the stacking is face-centred cubic with a single stacking fault (i.e. ... ABCABABC ...). Recent simulations [8, 11] suggest that the most probable *equilibrium* structure for small hard-sphere crystallites is random stacked. This does not, however, rule out individual more-or-less face-centred cubic nuclei (cf the critical nucleus in figure 3 of [11]).

Measuring the interparticle spacing allows us to estimate the average volume fraction of the pre-critical nucleus to be $\phi_n \sim 0.5$. This value is surprisingly low—the natural assumption is that the crystallite should be at the melting density, $\phi_m = 0.545$. Similar measurements on colloidal crystals in stable coexistence with colloidal fluid did give $\phi \sim 0.55$, so that the low value measured for ϕ_n is not due to systematic errors. Our measurement is not necessarily inconsistent with light-scattering observations that crystallites are denser than the metastable fluid [10]—these experiments probe an ‘average’ growing crystallite while our observations pertain to a single pre-critical nucleus that ultimately melted. In fact, one recent calculation [16] suggests that critical nuclei may well have $\phi < \phi_m$, even though the physical origin of this effect remains unclear. We note that our observed ϕ_n is close to the density of the surrounding metastable fluid. This may suggest that nucleation is a two-stepped process—ordering into a lattice takes place first, followed by densification (*not* observed in our pre-critical nuclei, which melted). Density-functional theory of freezing in a Lennard–Jones system may support this possibility. Shen and Oxtoby [17] plotted the free energy as a function of crystallinity and density at one temperature. Moving away from the metastable liquid in a direction of constant density but increasing crystallinity encounters a significantly lower energy barrier than fluctuations in an orthogonal direction (constant, i.e. zero, crystallinity but increasing density).

Treating the observed pre-critical nucleus as a sphere, its radius reached at least 10 μm . In classical nucleation theory, the free-energy ΔG required to form a nucleus of N particles is given by $\Delta G = A\gamma + N\Delta\mu$, where A is the surface area of the nucleus, γ the surface energy per unit area and $\Delta\mu$ the chemical potential difference. This suggests a critical nucleus size $R_c = -\frac{8\pi\gamma R^3}{3\phi_n\Delta\mu}$ for which ΔG is a maximum, R being the particle radius and ϕ_n the volume fraction of the nucleus. Using literature expressions for $\Delta\mu$ and γ [18], we obtain $R_c^{\text{calc}} \sim 7 \mu\text{m}$. Given the significant uncertainties involved in this estimate, it supports

our suggestion that the crystallite that disappeared from view was a pre-critical nucleus, and $R_c^{\text{expt}} \sim 10 \mu\text{m}$ provides a lower bound for the critical nuclear size at this volume fraction. The recent simulations of Auer and Frenkel [11] do not include volume fractions low enough for direct comparison with our experiments; nevertheless our lower bound of $N_c > 1000$ particles in the critical nucleus at $\phi = 0.510$ is not inconsistent with their finding that $N_c \sim 250$ at $\phi = 0.5207$.

5. Conclusion

We have observed the birth, life and death of a pre-critical nucleus in a metastable hard-sphere colloid at volume fraction $\phi = 0.510$ using conventional optical microscopy. This pre-critical nucleus is face-centred cubic with a single stacking fault. It provides a lower bound of 1000 particles in the critical nucleus at this volume fraction. This study shows the potential of direct observation for studying local phenomena such as nucleation in model colloids. Similar observations have recently been made using confocal microscopy [19].

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