

Crystallization in Glassy Suspensions of Colloidal Hard Spheres

Willem K. Kegel†

Van't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, Utrecht University,
Padualaan 8, 3584 CH Utrecht, The Netherlands

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Crystallization in suspensions of colloidal hard spheres with a volume fraction of 0.631 ± 0.004 , and a polydispersity of less than 3%, is studied experimentally. The mass density of the solvent is almost equal to that of the particles. Normal (1g-like) gravity conditions are simulated by centrifugation. It is shown that there is a limiting density of the quenched hard-sphere fluid, close or equal to the random close-packed density (with a volume fraction of 0.644 ± 0.005), above which crystallization is no longer observed. The results rule out the possibility that gravitational stress in quenched colloidal hard-sphere fluids, with volume fractions lower than the one corresponding to random close packing of spheres, irreversibly induces a packing geometry in which crystallization is suppressed.

1. Introduction

A system of hard spheres subject to thermal agitation is probably the simplest model of interacting atoms. Computer simulation reveals that this model exhibits a freezing transition^{1,2} with coexisting volume fractions of 0.494 ("freezing" volume fraction) and 0.545 ("melting" volume fraction).³ Under appropriate conditions, sterically stabilized colloidal suspensions behave to a good approximation as hard spheres.⁴ In these suspensions, the particles are stabilized by a layer of polymers attached to their surface and are dispersed in a solvent with the same refractive index as the particles so as to minimize van der Waals attraction. In this experimental system of hard spheres, not only was the freezing transition verified but another type of transition was found as well: a glass transition at a volume fraction of approximately 0.58.⁴ Above this glass transition, homogeneous nucleation of crystals was no longer observed, and at the same time large-scale particle diffusion stops, as deduced from the saturation of the autocorrelation function of particle concentration fluctuations.⁵ Heterogeneously nucleated crystals were found to grow into plate-shaped crystals, however, indicating that the "glass" state is not thermodynamically stable but is a result of the concentrated homogeneous fluid not being able to explore crystalline configurations. To access these crystalline configurations apparently requires large-scale diffusion. Evidence for a glass transition in hard-sphere systems has also been found by computer simulation by, e.g., Speedy.⁶ In this work, among other things, indications were found that the (reproducible) equation of state of the metastable hard-sphere fluid contains a discontinuity, indicating an underlying thermodynamic transition. These results are disputed in ref 7, where it is found that hard-sphere systems, larger than the ones studied in ref 6, always crystallize up to volume fractions of at least 0.63–0.64

(not more accurately specified by the authors), which is close to the value of random close packing which is found to be 0.644 ± 0.005 . Even more recently, a system of colloidal hard spheres with a volume fraction of 0.619 was studied in a space shuttle.⁸ In this system crystals were formed in microgravity within 3.6 days. Back on earth, the lower part of the sample was shear-melted by mixing, and the crystalline region above it was observed to slowly grow into this mix-melted region. After a month this growth stopped, and the melted region showed no signs of nucleation.

The questions that remain are (1) if a density of the quenched hard-sphere fluid exists above which crystallization ceases, even without gravity, and (2) how the presence of gravity inhibits crystallization in concentrated colloidal hard spheres. These questions are addressed by studying a system of colloidal hard spheres, as close as possible to the random close-packed density but such that they can still be made initially homogeneous by mixing. The particles are dispersed in a mixture of solvents with approximately equal mass density as the particles, and "gravity" is varied by centrifugation.

2. Experimental Section

The colloidal system, poly(methyl methacrylate) (PMMA), stabilized by the covalently surface linked stabilizer poly(12-hydroxystearic acid) (PHS), was prepared according to the procedure described in ref 9 and 10. The diameter of the particles (in the solvent mixture described below) is $1.03 \mu\text{m}$, and the polydispersity, estimated from light scattering and electron microscopy, is smaller than 3%. Such a small polydispersity is only possible for relatively large particles. The particles were dispersed in a solvent mixture of (almost) equal refractive index and mass density as the particles *cis*-decalin, tetralin, and carbon tetrachloride with mass fractions of 0.0493, 0.3756, and 0.5751, respectively. The refractive index of this mixture is 1.5030, and the mass density is 1.2381 g/cm^3 , being significantly larger than the density of the PMMA particles in hydrocarbons such as dodecane, where it is found to be 1.18 g/cm^3 . This difference is due to the fact that the particles were found to swell significantly in the mixture, i.e., a factor of 1.28 in diameter relative to the situation in dodecane, as determined by static light scattering

† E-mail: W.K.Kegel@chem.uu.nl.

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and scaling on the freezing concentration. This swelling process takes 2–3 days, after which the particle size is constant as measured over several weeks using light scattering and confocal microscopy. Because of this swelling, the solvent composition that corresponds to a minimum in the buoyant mass of the particles had to be determined by iteratively measuring the sedimentation velocity of the particles (using centrifugation) and adding one of two stock solutions of equal refractive index but different mass density. With this procedure, the density difference between particles and solvent was estimated to be of order 10^{-4} g/cm³, as deduced from the sedimentation rate of the diluted particles in a sample with a somewhat mismatched refractive index. This density difference corresponds to a gravitational length $h = kT/m_b g$ of order millimeters. In this equation, kT is the thermal energy, m_b the buoyant mass of a particle, and g the acceleration due to gravity. “Conventional” solvents for these particles, such as mixtures of decalin and tetralin, have densities of approximately 0.3 g/cm³ smaller than the particles. For the particles of the size used here, this corresponds to h of order micrometers. Systems under microgravity, on the other hand, as in ref 8, have h of order meters. So, the system studied here is just between these two extremes. Note that the gravitational length h is inversely proportional to the density difference between the colloids and the solvent but inversely proportional to the cube of the size of the particles, i.e., $m_b = \pi D^3 \Delta \rho / 6$, with D the particle diameter and $\Delta \rho$ the mass density difference between colloids and solvent. So, one could achieve a similar gravitational length by using conventional solvents and colloids smaller than approximately 100 nm in diameter. With these small particles, even true microgravity conditions (h of order meters) can be reached using the solvent mixture as described above. However, such small particles are significantly more polydisperse than large ones, with usually more than 5% polydispersity. With these large polydispersities, the crystal nucleation rate is very slow. This is a practical reason for using large particles. A more fundamental one is that polydispersity may influence the location and maybe even the existence of a “glass transition”. This will be discussed later.

It was verified that the system behaves as hard spheres by several observations. The most important is that the position of the first peak of the pair correlation function in a system of similar particles with a fluorescent core, as determined by confocal scanning laser microscopy, does not depend on the volume fraction. The range of volume fractions over which the pair correlation function was measured is 0.45–0.64. This observation indicates that there is no significant soft repulsive part in the interaction potential. The possibility of an attractive contribution was excluded by measuring the value of the second virial coefficient using light scattering of similar, but smaller, dilute particles. This value equals the one for hard spheres. Another indication of hard-sphere behavior is that it was found that the crystal volume in the coexistence region between colloidal fluid and crystal grows linearly with the (dry) mass fraction of colloid in the sample, and once the freezing volume fraction is set at 0.494, the melting fraction follows at 0.543 ± 0.011 , in good agreement (albeit with a large uncertainty) with the value of 0.545, as determined using Monte Carlo computer simulation of hard spheres.³

The samples were prepared by (ultra)centrifugation of a stock suspension and subsequent removal of (most part of) the clear supernatant. The particles were redispersed by slowly tumbling the samples for 1 week. This procedure leads to homogeneous samples, as was verified by adding a small amount of (fluorescent) tracer particles (of approximately the same size) before tumbling and inspecting the samples, after tumbling, by light microscopy. The tracer particles were indeed distributed homogeneously through the sample. The volume fraction of the samples is 0.631 ± 0.004 , as determined from the dry mass fraction of the colloids, after scaling at the freezing volume fraction. For the system studied here, this is the highest volume fraction that could be handled. Higher volume fractions were found to have such a large viscosity that they could not be homogenized in a reasonable time.

3. Results

One of the homogenized samples, further referred to as sample I, was put at rest, while another, sample II, was centrifuged for 120 h at a speed creating a gravitational length in the system of approximately $10 \mu\text{m}$, corresponding to “normal” gravity conditions on earth in colloidal systems, and subsequently put at rest as well. The samples were visually inspected from time to time for the formation of crystals, which are unambiguously detected by their Bragg reflection of visible light. In sample I, after 48 h, very small crystals, on the order of 0.1 mm in size, became visible at the dispersion/air interface, but after 4 days, many more crystallites were observed that were distributed homogeneously throughout the sample. These crystals slowly grew in time. In sample II, a large density of crystals was formed at the dispersion/air interface during centrifugation, but some were nucleated seemingly homogeneously in the upper part of the sample as well. After being put at rest, the crystals in the upper part slowly grew downward for several months, but then the process virtually stopped and the lower part of the sample remained amorphous for a year. The volume fractions of the particles in the lower and upper parts of the sample (II) were found to be 0.635 and 0.627, respectively, with an uncertainty of approximately 0.006. These values were determined in a sample with a larger volume than the one depicted in Figure 1, immediately after centrifugation. Although this difference is not significant, it was found that the viscosity of the lower part of the sample was remarkably higher than the one in the upper part, so that it can qualitatively be concluded that the volume fraction in the lower part in sample II is higher than 0.631 ± 0.004 . A third sample, sample III, was centrifuged for a time chosen significantly shorter than the time to form crystals in the undisturbed sample (I), 24 h, at the same speed. Immediately after centrifugation only a few crystallites were observed at the air–dispersion interface in this sample. After being put at rest, it showed the same behavior as the one that had not been centrifuged. The different procedures and observations are summarized in Table 1.

Samples I and II, more than a year after they had been put at rest, are shown in Figure 1. Crystallites in the upper part of these samples, particularly in sample I, are significantly smaller than the ones in the lower part of sample I. This is due to breaking and partly shear melting of the crystallites closest to the dispersion–air interface, because the colloidal fluid (very slowly) drains down at the walls of the container after tumbling.

4. Discussion and Conclusions

To summarize, crystallization throughout the sample is observed in systems with a very small density difference between colloids and solvent and with a volume fraction as high as 0.631. When normal gravity conditions are “switched on” by centrifugation, lasting longer than the time to form crystals in an undisturbed sample, it is found that only the upper part of the sample crystallizes. Centrifugation over a shorter time again leads to homogeneously distributed crystals in the sample. These observations indicate that, at high volume fractions, crystallization is prohibited in a centrifugal field, even when the strength of this field is as low as the one under normal gravity conditions in colloidal systems. Because of centrifugation, the volume fraction of the spheres in the lower part of sample II is higher than the volume fraction in sample I and must also be higher than the one in (the lower part of) sample III, because the last mentioned

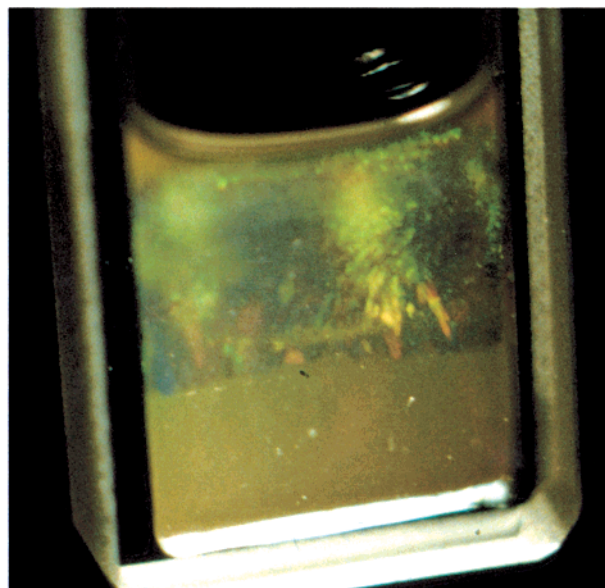
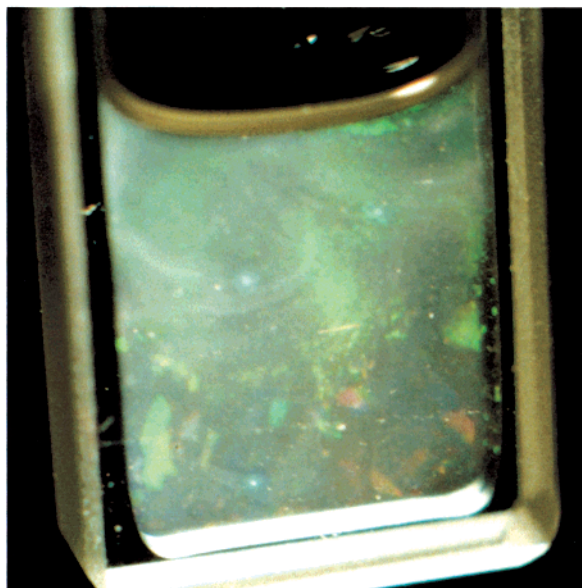


Figure 1. Left: System of colloidal hard spheres of volume fraction 0.631 ± 0.004 in a solvent mixture with (almost) equal refractive index and mass density, sample I (see text), approximately 1 year after homogenization. Right: Same system, approximately 1 year after being centrifuged for 120 h immediately after homogenization, sample II in the text. The width of the containers is 1 cm, and their thicknesses are 0.5 cm.

Table 1. Summary of the Different Sample Treatments, and Observations

sample	centrifuged at 10^3g , $h \approx 10 \mu\text{m}$ (h)	observation of crystals
I	0	whole sample (see Figure 1)
II	120	upper part of the sample (see Figure 1)
III	24	whole sample

sample has been centrifuged over a significantly shorter time than sample II. Because no crystallization was observed in the lower part of sample II over a period of a year, these observations suggest that in the systems studied here there is a limiting volume fraction above which crystallization ceases, at least on a human time scale. This volume fraction must be larger than 0.631 and thus is close or equal to the random close-packed density, with a volume fraction of approximately 0.64. Hard spheres that were quenched to this high a volume fraction indeed showed no indication of crystalline order.¹¹

Crystallization may be suppressed in the centrifuged sample, I, for roughly two reasons. First, crystalline fluctuations may be suppressed in an (even very slowly) sedimenting sample by a dynamic mechanism. Second, as suggested in ref 8, the geometry of random packings with and without applied stresses¹² may be responsible for this observation. In the latter case, the geometry induced by centrifugation (in which the long-time self-diffusion constant should be zero) may be either reversible (it changes when centrifugation stops) or irreversible (it remains in the same state when centrifugation stops). The observation that crystallization occurs after centrifugation has stopped (in sample III) rules out the "irreversible scenario" of the second possibility, at least at volume fractions that are lower than the one corresponding to

random close packing. The important question that remains is if packings can be identified that are present under normal gravity but not under low gravity and vice versa. This question may hopefully be answered by further work using confocal microscopy and an appropriate model system.

The observations in the sample used in the space shuttle experiment,⁸ as described in the Introduction, are consistent with the results on the even more concentrated sample studied here, and so are the findings of a 'glass transition in refs 4 and 5, i.e., a volume fraction (of about 0.58) above which homogeneous crystallization was no longer observed. In these studies, it was found that crystals were formed in the upper parts of the samples that slowly grew into the amorphous lower part, just as what is found here. Similar behavior was found using slightly charged silica particles with 320 nm diameter and a polydispersity of 6%.¹³ The gravitational length in these systems is of comparable magnitude to the one in the systems studied here under centrifugation, but the particles are smaller and the polydispersity is larger. It has been shown that the crystallization rate dramatically slows down when polydispersity is increased (see refs 14 and 15), although no systematic experimental studies have been carried out so far. Indeed, besides gravity, other subtle effects such as the shape of the size distribution of the colloidal particles¹⁴ or the detailed form of the interparticle potential may significantly alter rare events such as crystallization in dense colloidal fluids, and thereby the location or even existence of a glass transition.

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