Gravity-Induced Aging in Glasses of Colloidal Hard Spheres

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(Received 3 February 2004; published 15 July 2004)

The influence of gravity on the long-time behavior of the mean squared displacement in glasses of polydisperse colloidal hard spheres was studied by means of real-space fluorescent recovery after photobleaching. We present, for the first time, a significant influence of gravity on the mean squared displacements of the particles. In particular, we observe that systems which are glasses under gravity (with a gravitational length on the order of tens of micrometers) show anomalous diffusion over several decades in time if the gravitational length is increased by an order of magnitude. No influence of gravity was observed in systems below the glass transition density. We show that this behavior is caused by gravity dramatically accelerating aging in colloidal hard sphere glasses. This behavior explains the observation that colloidal hard sphere systems which are a glass on Earth rapidly crystallize in space.

DOI: 10.1103/PhysRevLett.93.035701 PACS numbers: 64.70.Pf, 05.40.Jc, 82.70.Dd

Hard spheres for which the potential energy is infinite on overlap and (in the absence of fields) zero otherwise freeze upon increasing number density from a fluid into a crystal at a volume fraction, ϕ, of 0.494 [1,2]. In between $\phi = 0.494$ and 0.545, fluid and crystal coexist [3], while, at even higher volume fractions, a single phase (fcc [4]) crystal is thermodynamically stable up to the close packed density corresponding to $\phi = \pi/3\sqrt{2} \approx 0.74$ [5]. Colloids may behave as hard spheres [6]. Besides the thermodynamic freezing transition referred to above, colloidal hard spheres can be brought in a (long-lasting) metastable fluid state by rapid quenching using centrifugation [6]. In the resulting colloidal glass, large-scale particle diffusion and crystallization by homogeneous nucleation stop, implying that crystal nucleation proceeds by large-scale particle diffusion [6,7]. The glass state is reached at a surprisingly small number density of the hard spheres: $\phi \approx 0.57$–0.58, a significantly smaller density than where (monodisperse) hard spheres are jammed at random close packing with $\phi = 0.64$ [8]. It is widely believed that the glass transition of hard spheres corresponds to permanent caging of the particles by their neighbors [7,9]. However, recent computer simulations [10] and experiments under microgravity [11] pose serious doubts on the very existence of a glass transition at $\phi < 0.64$ of monodisperse hard spheres in the absence of a gravity field. These studies show that monodisperse [10] but also (about 5%) polydisperse [11] hard spheres crystallize in the absence of gravity up to volume fractions close to 0.64. In the last study, a system that is a glass on Earth rapidly crystallizes in space after homogenization by mixing.

While microscopic particle movements do not seem to be affected by details of the particle size distribution [12], as far as we are aware, no quantitative studies of the influence of gravity on dynamics in concentrated colloidal suspensions have been reported. In this work we address the question as to what the influence of gravity is on particle mobility (quantified by the mean squared displacement) in glassy systems. For this purpose, we used a polydisperse (7%) system in order to suppress crystallization, at least on experimental time scales. By this construction, crystallization and its consequences (e.g., Ostwald ripening at very long-time scales) will not interfere with the (global) particle dynamics.

We study systems with two different gravitational lengths, order 0.1 mm (referred to as low gravity) and order 10 μm [normal gravity ("normal" refers to the situation for most colloidal model systems, at least for the ones with comparable sizes as studied here)]. The gravitational length is defined by $h = kT/(\frac{4\pi}{3}R^3\Delta\rho g)$, where k is Boltzmann's constant, T is the temperature, R is the particle radius, g is the acceleration due to gravity, and $\Delta\rho$ is the mass density difference between the particles and the solvent. The mass density of the solvent is adjusted so as to vary the gravitational length.

For all experiments, a system of NBD (4-methylaminoethylmethacrylate-7-nitrobenzo-2-oxa-1,3-diazol) labeled polymethylmethacrylate particles were used. The particles are stabilized with poly(12-hydroxystearic acid). The fluorescent dye was incorporated during the polymerization reaction by using the method described in [13]. The average radius of the particles is 295 nm and their polydispersity is 7%. The particles were dispersed in two different mixtures corresponding to the two different gravity conditions referred to above. The first is a density-matched mixture of cis-decalin, tetralin, and carbon tetrachloride with volume ratios 31.5:36.0:32.5, where $\Delta\rho = 0.02$ g/ml, so that $h = 0.2$ mm for $R = 295$ nm. Better matching (smaller $\Delta\rho$) is possible [14], but in that case the particles bleach too quickly for our present purpose. The second solvent we used is a mixture of cis-decalin and tetralin with volume ratios 68:32. In these systems $\Delta\rho = 0.3$ g/ml so that $h = 13$ μm. Note that

microgravity experiments in space correspond to gravitational lengths, h, on the order of meters.

As shown in Refs. [15,16] for the first situation, and in [6] for the second, in these solvent mixtures particles behave as hard spheres and are refractive index matched. Some density matching solvents are notorious for causing charge on the particles; see, e.g., [17,18]. However, in the solvent mixture we employed, no indications for the presence of charge have been observed [15,16]. Therefore, the only difference between the low gravity and the normal gravity system is the gravitational length. The volume fractions of the samples were determined relative to random close packing of 7% polydisperse hard spheres [8].

In principle, the self-intermediate scattering function, being the Fourier transform of the mean squared displacement, can be measured by dynamic light scattering (DLS); see, e.g., [19]. However, due to the limited coherence time of lasers, only time scales on the order of hours can be reached by this technique. In order to be able to reach longer time scales, which is necessary for the kind of concentrated systems we are interested in, we applied real-space fluorescent recovery after photobleaching as recently developed by us for colloidal systems and reported in [20]. This method makes use of confocal scanning laser microscopy (CSLM), and allows following particles over time windows that are up to 3 orders of magnitude longer than those reached by DLS.

The method is described in detail in [20], and is only summarized here. Using a CSLM, profiles were bleached in the form of cubes with linear sizes on the order of 10 to 100 particle diameters in the focal plane, and order 10 diameters in thickness. Subsequently the systems were imaged, also by CSLM, by scanning several slices perpendicular to the field of gravity, at different times (from minutes to several weeks). By integrating the fluorescent intensities along the sides of the bleached cubes, intensity profiles were obtained. The decay length of the fluorescent intensity profile, defined by the length where the intensity is half the (normalized) intensity of the unbleached part of the sample, $x_{1/2}$, is related to the mean squared displacement $\langle x^2 \rangle$ by [20]

$$\langle x^2 \rangle \approx 2.20 x_{1/2}^2. \quad (1)$$

All data presented in the subsequent figures are averaged over four to eight cubes per volume fraction, the standard deviation being on the order of 10%. The displacements are in units of the particle radius, and time is in units of the Brownian time $\tau_B = R^2/6D_0 \approx 0.059$ s for our system, where D_0 is the diffusion coefficient at infinite dilution. The size of the particles was chosen small enough so that sufficiently long-time windows are accessible, and large enough so that translation (on average) of the particles over fractions of their sizes can be followed.

In Figs. 1(a) and 1(b) we show the mean squared displacements in samples under the two gravity conditions referred to above: low gravity [Fig. 1(a)] and normal gravity [Fig. 1(b)]. Clearly there is no significant difference between low gravity and normal gravity conditions below volume fractions of 0.55. These suspensions show typical diffusive behavior, characterized by a unit slope in the figures, i.e., $\langle x^2 \rangle \propto \tau$. However, there is a dramatic influence of gravity on samples with higher volume fractions. From Fig. 1(a) it is clear that particles under low gravity move on average over distances on the order of a

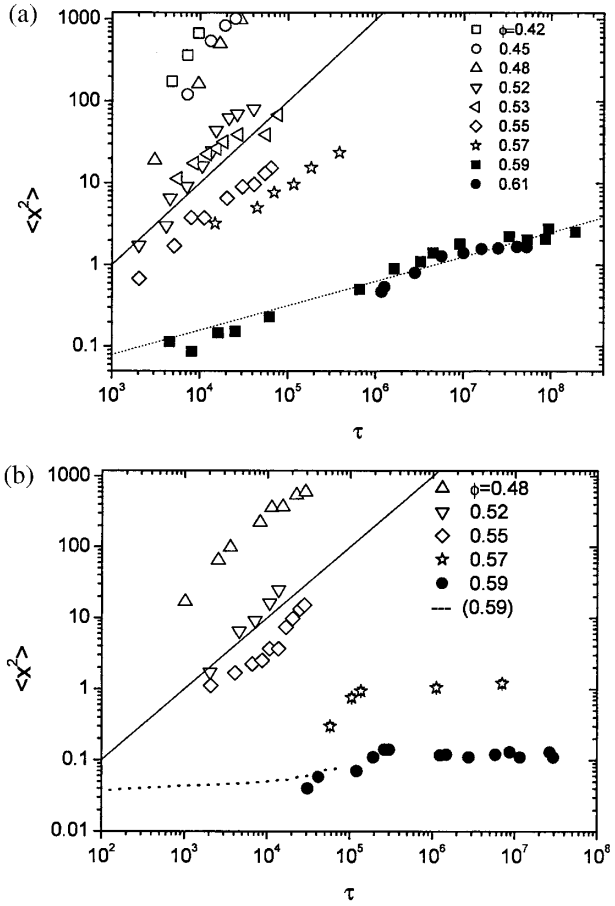

FIG. 1. Mean squared displacements $\langle x^2 \rangle$ [as defined by Eq. (1) in the text] in units of the squared particle radius versus time, τ, in units of Brownian time τ_B (for a definition see text). (a) Particles under low gravity (in a density matched solvent). The solid line with unit slope has been drawn to indicate diffusive behavior. The dotted line is given by $\langle x^2 \rangle = 0.012\tau^{0.3}$. The volume fractions of the systems are indicated. Empty symbols correspond to volume fractions below the glass transition volume fraction of 0.58, and filled symbols are for the volume fractions above the glass transition. Note that the apparent superdiffusive behavior of the data for $\phi < 0.48$ is not significant: the data are statistically compatible with simple diffusive behavior. (b) As in (a) but now for systems under normal gravity. Here the dotted line is for data from van Megen [19], to be compared to our data for a volume fraction of 0.59.

particle diameter in 10^7–10^8 Brownian time units, and they seem to obey a power law given by $\langle x^2\rangle \propto \tau^{0.3}$ over more than five decades in time; we will get back to that later. In contrast, particles under normal gravity move only over distances that are an order of magnitude smaller. They reach a plateau region after roughly 10^4–10^5 Brownian time units and thus remain a true "glass" within our experimental time window. In the same Fig. 1(b) we have plotted DLS data from van Megen [19]; these data clearly are consistent with ours under normal gravity conditions. Our results indicate a strong influence of gravity on particle displacements; preliminary indications of this have been reported in [20]. This is surprising, as the gravitational length in our system, even under normal gravity (where $h = 13\ \mu$m), equals many particle diameters. Thus it must be that gravity couples to movements involving many particles, such as shear inhomogeneities [7] or dynamical heterogeneities [16,21]. We now address the question as to what the influence of gravity is on the aging behavior of colloidal glasses. Earlier studies indicate that glassy systems of colloidal hard spheres under gravity age [19]; i.e., the function $\langle x^2\rangle(\tau)$ depends on the waiting time. The waiting time is defined as the time (after homogenization) the suspension is left undisturbed before starting the experiments.

We measured the mean squared displacements after several waiting times, t_w. In Fig. 2 the results for a system under normal gravity and with a volume fraction of 0.59 are presented. $t_w = 0$ corresponds to starting the measurements immediately after the sample was prepared. The other data in the figure correspond to waiting times of 1 to 5 days, as indicated. It can be seen in Fig. 2 that in a window of 5 days there is some slowing down of particle movements upon increasing waiting time. These observations are comparable to those reported in Ref. [19], and might well be caused by sedimentation of the particles.

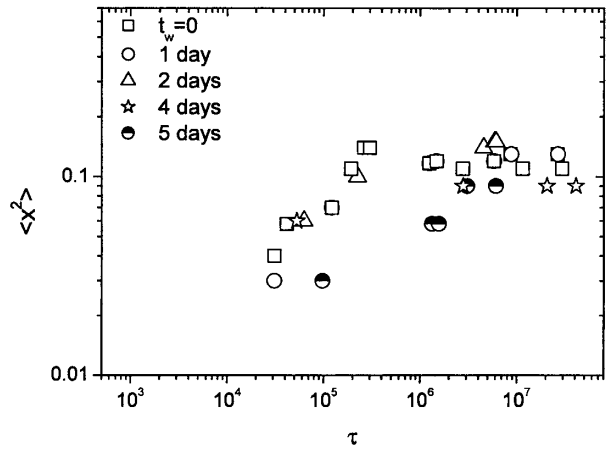

FIG. 2. Mean squared displacement of a system under normal gravity after several waiting times, t_w as indicated. The volume fraction of the colloids is 0.59.

As can be seen in Figs. 3(a) and 3(b), the situation is completely different for the glassy systems under low gravity; the systems gradually move over smaller and smaller distances the longer the waiting time. After $t_w =$ 12–17 days, the mean squared displacements in the systems under low gravity are comparable to those for the systems under normal gravity conditions, but with $t_w = 0$. These observations indicate that gravity significantly accelerates aging in colloidal glasses: low gravity systems reach the state of normal gravity systems only after many (order 10^7 in this case) Brownian time units following homogenization of the system. The observations in Fig. 2 imply that at very long times, say, $\tau > 10^7$, $\langle x^2\rangle$ should reach a plateau even for $t_w = 0$. The data for $\phi > 0.57$ in Fig. 1(a) [and $t_w = 0$ in Figs. 3(a) and 3(b)] are not inconsistent with that. However, we simply do not have sufficient data available beyond $\tau = 10^7$ to be able to unambiguously determine the functional form of $\langle x^2\rangle(\tau)$. We therefore rescaled the data for $t_w > 0$ in Fig. 3(a) to $t_w = 0$. In rescaling, the new values of τ are given by $\tau^* = (\tau + t_w)$ and the new values of $\langle x^2\rangle$ by $\langle x^2\rangle^*(\tau^*) = [\langle x^2\rangle(t_w = 0, \tau(t_w = 0)) + \langle x^2\rangle(t_w, \tau(t_w))]$.

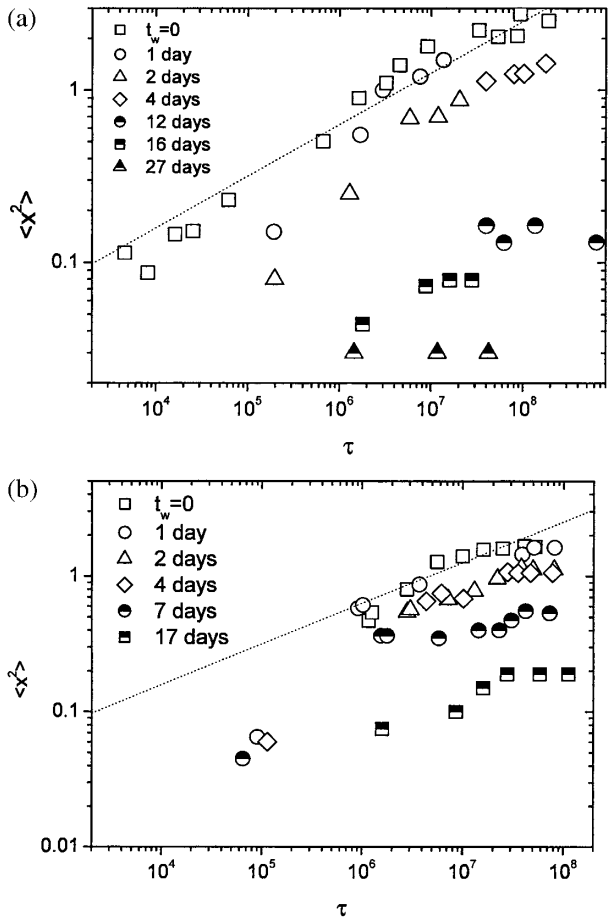

FIG. 3. As Fig. 2, but now under low gravity. The volume fractions are (a) 0.59 and (b) 0.61. The dotted lines are given by $\langle x^2\rangle = 0.012\tau^{0.3}$.

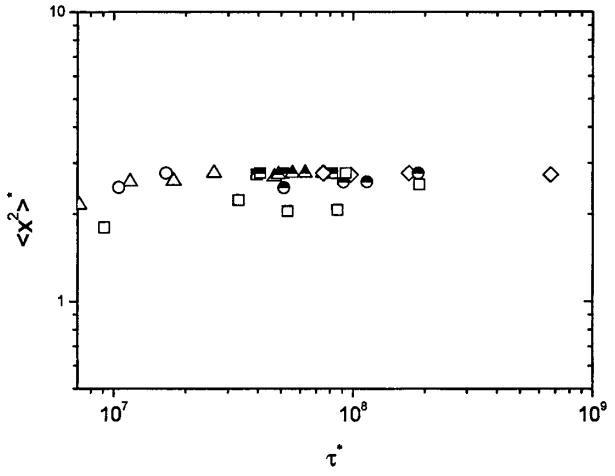

FIG. 4. Rescaled values of the mean squared displacements from Fig. 3(a). In rescaling, the new values of τ are given by $\tau^* = (\tau + t_w)$ and the new values of $\langle x^2 \rangle$ by $\langle x^2 \rangle^*(\tau^*) = [\langle x^2 \rangle(t_w = 0, \tau(t_w = 0)) + \langle x^2 \rangle(t_w, \tau(t_w))]$; see text.

Here, the quantity $\tau(t_w)$ refers to the time passed after waiting time t_w. The result is shown in Fig. 4. This figure unambiguously shows a plateau of $\langle x^2 \rangle$ for $\tau > 10^7$ Brownian time units. We therefore conclude that the power law behavior we observed (see also Ref. [20]) corresponds to transient behavior in the systems studied here. It is an interesting open question whether the plateau as in Fig. 4 will ever be reached in even weaker gravity fields, such as microgravity.

It is tempting to speculate that relaxation of shear inhomogeneities, which will always form upon preparing colloidal systems with high volume fractions, is responsible for the dramatic influence of gravity on the aging behavior that we observe. If it is, then, in principle, the behavior of the systems should depend on the way they are prepared (that is, homogenized). So far we have no indications for that being the case, but the situation is under study.

Independent of the mechanism causing the aging behavior, our results qualitatively explain why it is that systems that are glasses on earth rapidly crystallize in space, as observed in [11]. In order for crystals to form, it is expected that the time to form crystal nuclei [say, roughly, 1/(nucleation rate)] should be within the time window that particles move over distances on the order of their own diameter. In that case a significant number of particle cages will have broken down, enabling particles to rearrange and form crystal nuclei. These nuclei, of course, do not form in our polydisperse model system. Particle movements on the order of their size can be accomplished under low gravity (and apparently microgravity [11]), but not under normal gravity, as clearly shown by comparing Figs. 1(a) and 1(b).

To summarize, we showed, for the first time, the quantitative influence of gravity on particle mobility in glassy colloidal systems. Gravity dramatically accelerates aging in glassy systems, thereby reducing the time window in which crystal nucleation may proceed, which lowers the glass transition density. We feel that the important question that remains is by what precise mechanism gravity couples to (collective?) particle movements.

We thank Bill van Megen for kindly providing his data, and Dirk Aarts and Roel Dullens for comments on the manuscript.

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[1] W. W. Wood and J. D. Jacobsen, J. Chem. Phys. **27**, 1207 (1957).
[2] B. J. Alder and T. E. Wainwright, J. Chem. Phys. **27**, 1208 (1957).
[3] W. G. Hoover and F. H. Ree, J. Chem. Phys. **49**, 3609 (1968).
[4] P. G. Bolhuis, D. Frenkel, S.-C. Mau, and D. A. Huse, Nature (London) **388**, 235 (1997).
[5] T. C. Hales, P. Sarnak, and M. C. Pugh, Proc. Natl. Acad. Sci. U.S.A. **97**, 12 963 (2000).
[6] P. N. Pusey and W. van Megen, Nature (London) **320**, 340 (1986).
[7] W. van Megen and S. M. Underwood, Nature (London) **362**, 616 (1993).
[8] W. Schaertl and H. Sillescu, J. Stat. Phys. **77**, 1007 (1994).
[9] W. Gotze and L. Sjogren, Phys. Rev. A **43**, 5442 (1991).
[10] M. D. Rintoul and S. Torquato, Phys. Rev. Lett. **77**, 4198 (1996).
[11] J. Zhu, M. Li, R. Rogers, W. Meyer, R. H. Ottewill, Crew-Shuttle-Columbia, W. B. Russel, and P. M. Chaikin, Nature (London) **387**, 883 (1997).
[12] S. I. Henderson, T. C. Mortensen, S. M. Underwood, and W. van Megen, Physica (Amsterdam) **233A**, 102 (1996).
[13] G. Bosma, C. Pathmamanoharan, E. H. A. de Hoog, W. K. Kegel, A. van Blaaderen, and H. N. W. Lekkerkerker, J. Colloid Interface Sci. **245**, 292 (2002).
[14] W. K. Kegel, Langmuir **16**, 939 (2000).
[15] E. H. A. de Hoog, W. K. Kegel, A. van Blaaderen, and H. N. W. Lekkerkerker, Phys. Rev. E **64**, 021407 (2001).
[16] W. K. Kegel and A. van Blaaderen, Science **287**, 290 (2000).
[17] A. Yethiraj and A. van Blaaderen, Nature (London) **421**, 513 (2003).
[18] U. Gasser, E. R. Weeks, A. Schofield, P. N. Pusey, and D. A. Weitz, Science **292**, 258 (2001).
[19] W. van Megen, T. C. Mortensen, S. R. Williams, and J. Müller, Phys. Rev. E **58**, 6073 (1998).
[20] N. Simeonova and W. K. Kegel, Faraday Discuss. **123**, 27 (2003).
[21] E. R. Weeks, J. C. Crocker, A. C. Levitt, A. Schofield, and D. A. Weitz, Science **287**, 627 (2000).