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Abstract
We report new results from our programme of molecular dynamics simulation of hard-sphere systems, focusing on crystallization and glass formation at high concentrations. First we consider a much larger system than hitherto, $N = 86\,400$ equal-sized particles. The results are similar to those obtained with a smaller system, studied previously, showing conventional nucleation and growth of crystals at concentrations near melting and crossing over to a spinodal-like regime at higher concentrations where the free energy barrier to nucleation appears to be negligible. Second, we investigate the dependence on the initial state of the system. We have devised a Monte Carlo 'constrained aging' method to move the particles in such a way that crystallization is discouraged. After a period of such aging, the standard molecular dynamics programme is run. For a system of $N = 3200$, we find that constrained aging encourages caging of the particles and slows crystallization somewhat. Nevertheless, both aged and unaged systems crystallize at volume fraction $\phi = 0.61$ whereas neither system shows full crystallization in the duration of the simulation at $\phi = 0.62$, a concentration still significantly below that of random close packing.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One of Henk Lekkerkerker's longstanding research interests has been phase transitions between disordered and ordered states, particularly those driven by entropy where, paradoxically, the apparently ordered phase has a *higher* entropy than the disordered state from which it grows. In his introduction to a meeting in Amsterdam in 1990 (Lekkerkerker 1991) that he organized jointly with Daan Frenkel and Theo Odijk, Henk eloquently compared and contrasted the freezing transition of hard spheres with the isotropic–nematic transition of liquid crystals. He described how, in both cases, the reduction in entropy associated with the formation of long-range order is offset by the increased 'packing' contribution to the entropy associated with the particles' greater freedom for local motions in the ordered state. Henk's interest in this area, initially just theoretical, motivated his sustained and successful efforts to develop model systems of non-spherical colloidal particles—

rods and plates—his study of which in recent years has led to many important new insights into complex liquid-crystal phase transitions, (e.g. Mourad *et al* (2008)). In this paper, written to celebrate Henk's 65th birthday, we stay with spherical particles where, despite decades of effort, understanding of the entropy-driven crystallization process is still far from complete.

Motivated in part by old experiments on colloidal systems (Pusey and van Megen 1986), we recently started a detailed study by molecular dynamics (MD) of crystallization and glass formation in assemblies of hard spheres. So far we have established that hard-sphere glasses can crystallize, although a quite small spread in particle size, polydispersity less than about 6%, can strongly slow crystallization (Zaccarelli *et al* 2009, Pusey *et al* 2009). At these small polydispersities, the main effect is that size variation stabilizes the fluid phase but destabilizes the solid. We have also found that, at all (small) polydispersities, the crystallization process changes its nature as the concentration of the system is increased

(Zaccarelli *et al* 2009, Pusey *et al* 2009). At relatively low concentrations, near melting, a classic nucleation-and-growth picture applies. Here, transient nuclei form and dissolve by diffusion of the particles. Only if a nucleus happens at random to grow larger than a critical size—determined by an energy barrier representing competition between bulk and interface free energies—does it continue to grow irreversibly to form a stable crystallite (Volmer and Weber 1926, Becker and Doring 1935, Kelton 1991). However, at higher concentrations we found that multiple crystalline nuclei were formed that slowly continued to grow, suggesting that the free energy barrier to nucleation is small or non-existent. Furthermore, the formation of crystal nuclei requires only limited motions of the particles, over distances smaller than the particles' diameter. Thus an important feature of these results is that fully developed diffusion of the particles is not always necessary for crystallization. A high concentration, glassy system, in which particles are largely caged or trapped by their neighbours, can still crystallize. The basic mechanism of this high-concentration nucleation remains to be fully understood, but it appears to involve highly cooperative small-scale motions of groups of particles (Sanz *et al* 2011).

In this paper, limiting consideration to equal-sized (monodisperse) hard spheres, we extend our earlier work in two directions. First, in order to investigate possible system-size dependence and to obtain better statistical averaging, we consider much larger systems, $N = 86\,400$ particles as opposed to 2000 previously. Broadly speaking the results are similar, but we present the data in a different, perhaps clearer, way. We show that the root-mean-square displacement of the particles, measured from the beginning of the simulation to the beginning of crystallization, is many particle radii at lower concentrations but saturates at about one radius at high concentrations. Second, returning to smaller systems, we investigate how the results of the simulations depend on the preparation of the initial states. We compress a low concentration fluid system to the desired final high concentration using a Monte Carlo method that actively suppresses crystallization. Then, before the molecular dynamics simulation is started, the system may be run for a further time at fixed concentration using the same, crystallization-suppressing, Monte Carlo method. We call this process 'constrained aging'. There are clear differences between the behaviours of systems prepared with and without active suppression of crystallization; there is also a significant dependence on the period of constrained aging. Nevertheless, these results confirm our earlier finding that glassy states of hard spheres can, in many cases, crystallize. However, we also found that, using the method just described, it is possible to prepare long-lived glassy states of equal-sized hard spheres at concentrations significantly below that of random close packing.

2. Methods

2.1. Molecular dynamics simulations; definition of crystalline particles

We have described the details of our molecular dynamics (MD) simulations elsewhere (Zaccarelli *et al* 2009, Pusey

et al 2009) so we only give a brief summary here. The simulations are performed in an NVT ensemble with periodic boundary conditions, using an event-driven algorithm for particles interacting via hard potentials. We quote length in units of σ, the particle diameter. Time is measured in units of $\sigma (m/k_{\mathrm{B}}T)^{1/2}$, roughly the time taken by a free particle to move one diameter; here m is the particle mass, k_{B} the Boltzmann constant and T the temperature. The volume (or packing) fraction is given by $\phi \equiv \pi N \sigma^3 / 6V$, where N is the number of particles and V the system's volume, and pressure p is reported below in units of $k_{\mathrm{B}}T/\sigma^3$. The mean-square displacement of the particles is calculated from

$$\left\langle \Delta r^2 (t) \right\rangle = \frac{1}{N} \sum_{i=1}^{N} |r_i (t) - r_i (0)|^2, \qquad (1)$$

where $r_i(t)$ is the position of particle i at time t. Unless otherwise stated below, the zero of time in this expression represents the start of the MD experiment (after any prior aging done with the constrained Monte Carlo algorithm).

The degree of crystallinity $X(t)$ of a system is defined as the number of particles in solid-like environments ('crystalline particles') at time t divided by the total number of particles. Following Steinhardt *et al* (1983), van Duijneveldt and Frenkel (1992) and ten Wolde *et al* (1996), crystalline particles are identified via the rotationally invariant bond order parameter d_6. This procedure labels particles as crystalline according to the extent to which the coordination of a particle with its nearest neighbours resembles that of a close-packed solid lattice. Nearest neighbours are identified using the cut-off independent criterion of van Meel and Frenkel (2010). In the current work, particles i and j are said to be 'connected' if $d_6(i, j) \geqslant 0.7$. A particle is labelled as crystalline if it is connected with at least six of its neighbours.

2.2. Preparation of the initial states; constrained aging

For the large system (section 3.1), a glassy configuration is generated by first rapidly compressing a small system (400 or 3200 particles) to a high packing fraction, $\phi \approx 0.64$. This process is repeated until we find a system in which less than 1% of the particles are crystalline. This configuration is then replicated periodically in space to give a large system with $N = 86\,400$ which is isotropically expanded to the desired concentration before starting the MD run. We checked that, beyond a very short initial transient, there was no remnant in the MD runs of the periodicity resulting from the replication procedure.

For the smaller systems ($N = 3200$) discussed in section 3.2, we start from a configuration equilibrated at low packing fraction (around $\phi = 0.50$). Then, we run an NpT Monte Carlo procedure (e.g. Frenkel and Smit (1996)) at high pressure ($p = 200$) in such a way that the density increases rapidly. To avoid crystallization during compression we accept or reject trajectories of ten Monte Carlo cycles according to the Metropolis criterion applied to the potential $k(N_s/N)^2/2k_{\mathrm{B}}T$, where N_s is the total number of crystalline particles and k is set to 1.5×10^6. When the desired packing
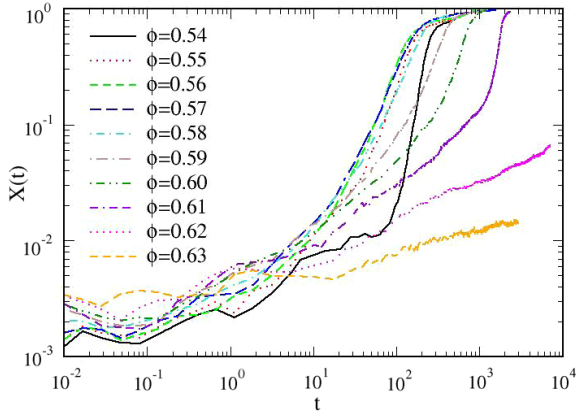
Figure 1. Growth of crystallinity $X(t)$ in a system of 86 400 hard spheres at the concentrations indicated.

fraction is reached during compression ($\phi = 0.59$, 0.60, 0.61 or 0.62) the configuration is saved and used as an input for a 'constrained aging' run. In these runs the system is aged in a Monte Carlo simulation at constant volume; crystallization is avoided in the same way as in the compression. In this case, the constant k is tuned during the run to get 20%–25% of the ten-cycle trajectories accepted. The particle displacement is also tuned to get an average acceptance of trial displacements of 35–45%. During the constrained aging simulation we save a configuration every time the overall pressure drops by a few per cent. Finally, we use the configurations resulting from these constrained aging runs as starting configurations for unconstrained molecular dynamics runs described above. Typically we find that the constrained aging process provides systems with initial crystallinity $X(0)$ less than 0.01 (see figure 3). We have also verified that, during constrained aging, the value of the bond order parameter d_6, averaged over all the particles, remains well below the threshold for identifying crystalline particles, set at $d_6 = 0.7$, implying amorphous structures. For $\phi = 0.59$ and 0.60 d_6 rises slightly during aging to about 0.32, whereas for $\phi = 0.61$ and 0.62 it saturates at about 0.28.

3. Results and discussion

3.1. Large system

Figure 1 shows the growth of crystallinity $X(t)$ as a function of time and volume fraction for a system of 86 400 equal-sized hard spheres at various volume fractions ϕ. The sample at volume fraction $\phi = 0.63$ does not crystallize significantly over the time of the simulation. At $\phi = 0.62$, the crystallinity $X(t)$ grows slowly, but has only reached ~ 0.07 by the end of the simulation. Full crystallization occurs increasingly rapidly as the concentration is reduced from $\phi = 0.61$ to 0.59. In this regime of concentration, a relatively slow initial growth is followed by much faster growth once the crystallinity reaches $X(t) = 0.15$–0.20. For $0.58 \geqslant \phi \geqslant 0.55$ there is not such a marked switch between slower and more rapid growth. At $\phi = 0.54$, the overall process slows again; however, once there is significant crystallization, $X(t) \sim 0.01$, the subsequent
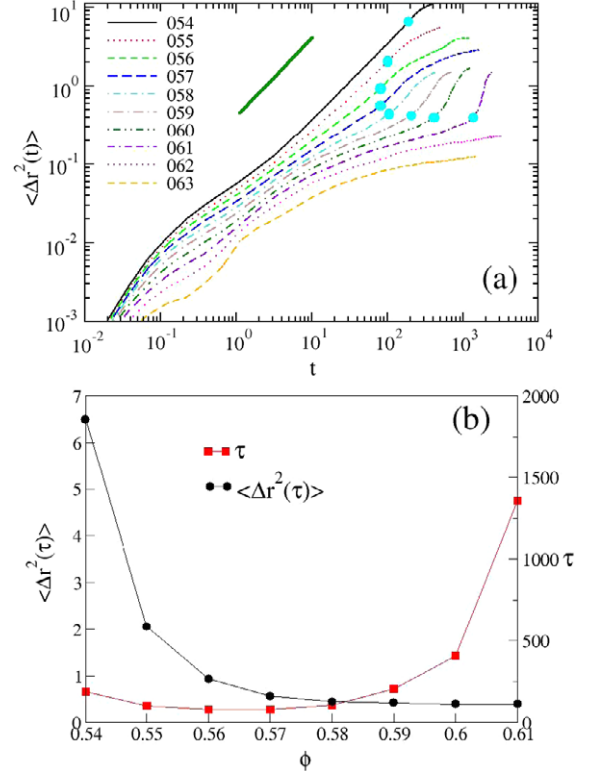

Figure 2. (a) Mean-square displacements, $\langle \Delta r^2(t) \rangle$, corresponding to the crystal growth data of figure 1. The points indicate the times, at each concentration, when the crystallinity reaches $X(t) = 0.20$. Note that at $\phi = 0.54$ and 0.55 well-defined diffusive regions, $\langle \Delta r^2(t) \rangle \propto t$ (the thick line has a gradient of one), are observed at long times, whereas at higher concentration significant crystallization occurs while the motion is still sub-diffusive. (b) Dependence on concentration of the time τ (squares, right axis) and mean-square displacement $\langle \Delta r^2(\tau) \rangle$ (circles, left axis) at which the crystallinity reaches 0.20; taken from the points in (a).

growth is fast. Interestingly the growth curves for the four samples $0.58 \geqslant \phi \geqslant 0.55$ appear almost identical.

In order to investigate this last point, we show in figure 2(a) the mean-square displacements (MSDs) of the particles corresponding to the crystal growth data of figure 1. Also shown on these curves are the points at which the crystallinity reaches 0.20. From these points we plot in figure 2(b) the 'crystallization time' τ, the time to reach $X(t) = 0.20$, and the value of MSD at that time. First we see from figure 2(a) that, not surprisingly, the dynamics slow down—the particles move less in a given time—as the concentration increases. At $\phi = 0.54$, the MSD initially increases like t^2, reflecting ballistic free flight of the particles before colliding with their neighbours. At longer times, after many collisions, a clear linear dependence on t is seen, corresponding to fully developed diffusion. The crystallinity reaches 0.20 when the MSD $\langle \Delta r^2(t) \rangle \approx 6.5$, implying a root-mean-square displacement of about 2.5 particle diameters. As we have discussed earlier (Pusey *et al* 2009), the crystallization process at this relatively low concentration ($\phi = 0.54$) is well described by a classic nucleation-and-growth picture.

At $\phi = 0.55$, the long-time diffusive regime of the MSD is barely evident and at higher concentrations the motion is still
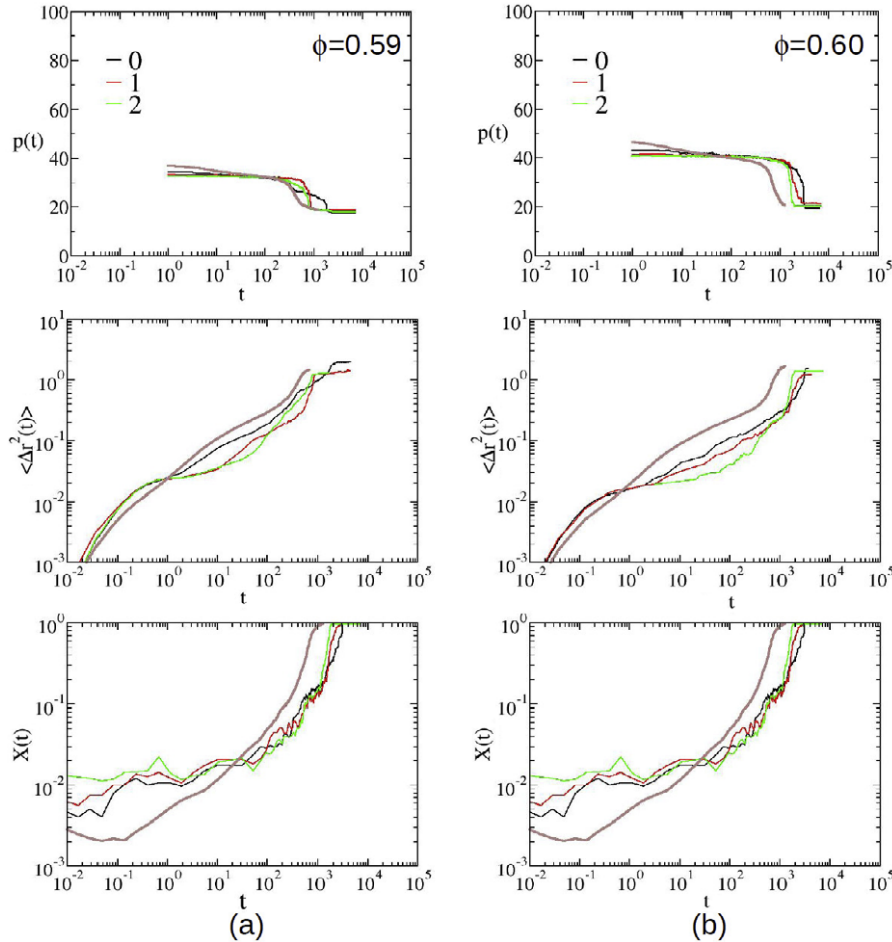
Figure 3. Pressure $p(t)$, mean-square displacement $\langle \Delta r^2(t) \rangle$ and crystallinity $X(t)$ for 3200 hard spheres at concentrations $\phi = 0.59$, 0.60, 0.61 and 0.62 ((a)–(d)). The systems were prepared by a Monte Carlo process in which crystallization was suppressed. They were then either run immediately with the MD programme (curves labelled 0) or were subjected to increasingly long periods of 'constrained aging' (see text) before starting the MD runs (curves 1, 2 and, in the case of $\phi = 0.61$, 3). The thick (brown) curves show the equivalent data for the large unaged system described in section 3.1 (thus the results for the crystallinity and mean-square displacement are taken from figures 1 and 2(a) respectively).

sub-diffusive, $\langle \Delta r^2(t) \rangle \propto t^\mu$ with $\mu < 1$, at the crystallization time when $X(t)$ reaches 0.20. For $\phi = 0.55, 0.56, 0.57$ and 0.58, this crystallization time is almost independent of concentration even though the dynamics slow significantly with increasing concentration. This is consistent with the observation, made above, that the full $X(t)$ versus t curves for these states more or less superimpose (figure 1). However, it appears that this data collapse simply reflects an accidental cancellation between the effects of a thermodynamic driving force (the supersaturation) that increases with concentration and the slowing dynamics, rather than signifying some more fundamental property (see also Pusey *et al* (2009)).

It is interesting that at higher concentrations still, $\phi = 0.59, 0.60$ and 0.61, the MSD at which $X(t) = 0.2$ virtually saturates at $\langle \Delta r^2(t) \rangle \approx 0.4$, implying a root-mean-square particle displacement of slightly more than one particle radius (figure 2(b)). However, over this small increase of concentration, the time τ taken to crystallize increases strongly. An implication of these findings is that, at high concentrations, crystallization requires just a small rearrangement of particle

positions, and that the main effect of increasing concentration is to increase the time needed for this rearrangement.

The results for the concentration dependence of the crystallization time shown in figure 2(b) agree quite well with those found in our earlier, smaller, simulations (Pusey *et al* 2009, figure 5(a)), with the exception of the point at $\phi = 0.54$. As we argued in Pusey *et al* (2009), at that relatively low concentration, the density of nuclei is small; then a small simulation box contains, on average, less than one nucleus, so that one has to wait for a long time for one to appear. Our present result for the nucleation rate at $\phi = 0.54$ agrees well with the recent work of Filion *et al* (2010) (table II) who calculated hard-sphere nucleation times by several simulation methods and provided a detailed comparison with other calculations and experiments.

Pusey *et al* (2009) also discussed the dependence on concentration of the ratio of the crystallization time τ to the time τ_d taken by a particle to diffuse one diameter, i.e. $\langle \Delta r^2(\tau_d) \rangle = 1$ (see figure 5(c) of Pusey *et al* (2009)). At low concentrations we found $\tau/\tau_d \gg 1$, implying that a typical particle diffuses several diameters before crystallization
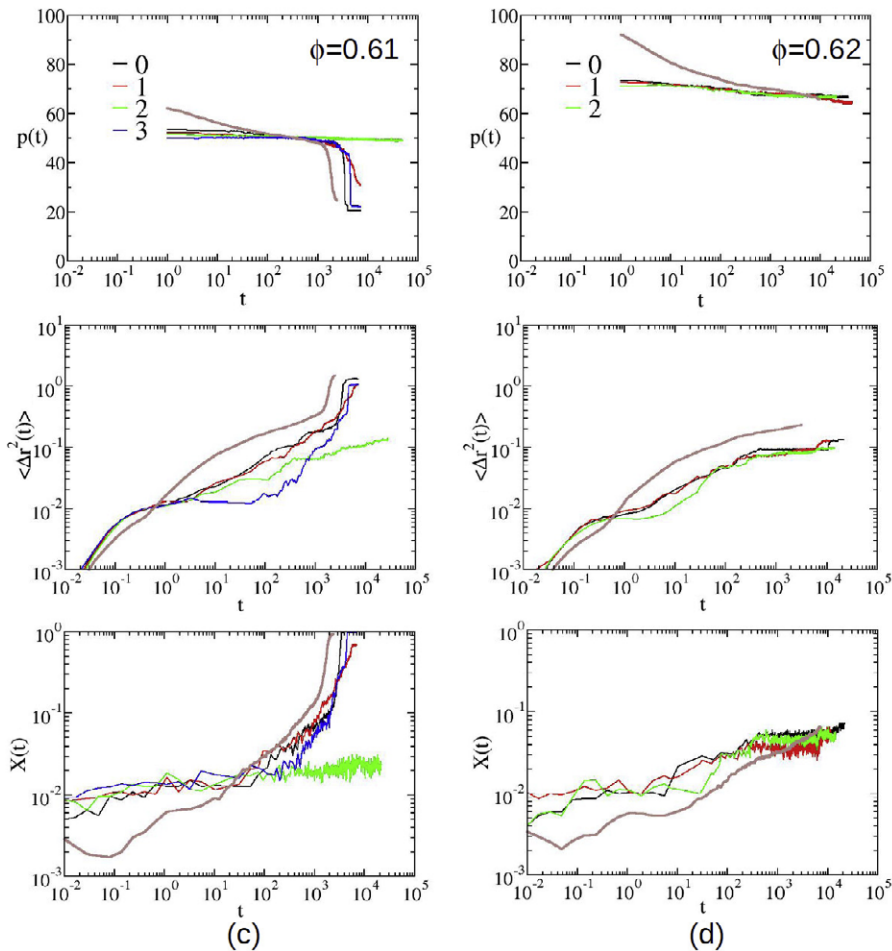
Figure 3. (Continued.)

takes place, and corresponding to the points at $\phi = 0.54$ and 0.55 in figure 2(b), where $\langle \Delta r^2(\tau) \rangle > 1$. However, at higher concentrations, we found $\tau/\tau_{\rm d} \leqslant 1$, corresponding to the saturation of MSD at $\langle \Delta r^2(\tau) \rangle \approx 0.4$ in figure 2(b). Plotting $\langle \Delta r^2(\tau) \rangle$ against concentration, as in figure 2(b), is probably the better way to present these findings because of the difficulty in estimating τ_d when, at high concentrations, the particles do not achieve fully developed diffusion before crystallizing.

Note that the MSDs of figure 2(a) are measured from times $t = 0$ representing the initial configuration of the MD runs (equation (1)), and are therefore not directly comparable with those shown in figure 2 of Zaccarelli *et al* (2009). The latter are for polydisperse systems at concentrations below that of the glass transition, and exclude displacements during an initial transient pressure decay towards a stationary state. It is not possible to do the same here because crystallization in the monodisperse case is much more rapid and can occur before this transient is complete. There is accordingly no contradiction with the view taken in Pusey *et al* (2009) that the primary effect of polydispersity is to inhibit crystallization without otherwise changing the dynamics seen in the glass. Our current results nonetheless confirm that crystallization can occur, within the glass, under conditions where the root-mean-square displacement is significantly smaller than one particle diameter. However, unlike the results of Zaccarelli *et al* (2009),

none of the MSDs in figure 2(a) shows a clear 'glassy plateau' which would imply strong trapping or caging of the particles. These observations motivate a closer look at the effects on crystallization of the preparation of the initial state.

3.2. Effects of the initial state and aging

We return now to a smaller system, 3200 particles, where the initial state for the molecular dynamics runs is prepared by the Monte Carlo compression process described in section 2.2 in which crystallization is actively suppressed. The MD data run can start immediately after the final concentration is reached, or the system can be subjected to further constrained aging by continuing the Monte Carlo process, still with suppression of crystallization, at the fixed final concentration.

Figures 3(a)–(d) show the results of these simulations for the (high) concentrations ϕ = 0.59, 0.60, 0.61 and 0.62. We plot the pressure $p(t)$, crystallinity $X(t)$ and mean-square displacement $\langle \Delta r^2(t) \rangle$ as functions of time t. Curves 0 correspond to systems for which the MD runs were started immediately after preparation whereas curves 1, 2, 3 correspond to increasingly long periods of constrained aging. Also shown as thick lines in figure 3 are the corresponding results for the large system, discussed in section 3.1, prepared without active suppression of crystallization. We notice

immediately that, while the pressure for the large system shows an initial steady decrease at all concentrations, the pressure for the smaller system, both unaged and aged, is much flatter, implying a more stationary state before crystallization begins. We also see that, in general, the rapid increase in crystallinity after $X(t)$ reaches 0.10–0.20 is signalled also by a rapid drop in pressure and a fast increase in the MSD.

At all concentrations shown there are noticeable effects of the aging process in the smaller system. First, the pressure at the start of the MD runs drops consistently and significantly with increased aging, suggesting the development of more efficient packing of the particles in the aged amorphous states. The subsequent behaviour of the systems is, however, quite varied. At $\phi = 0.59$, the unaged system (curve 0) starts to crystallize first, but then shows a slower approach to full crystallization. The pressure of the most aged system (curve 2) remains almost constant for some time, but in the end it is (just) the fastest to crystallize. At $\phi = 0.60$, again the aged systems crystallize fastest. The simulations at $\phi = 0.61$ show intriguing results. Now the unaged system (curve 0) crystallizes fastest. Surprisingly, the aged system represented by curve 2 does not crystallize ($X(t) < 0.03$) in the duration of the simulation. However, further aging does lead to crystallization (curve 3). This erratic dependence on aging time of the system's behaviour suggests that, even at these high concentrations where particle motions are limited, there is a stochastic element to the crystallization process. We discuss this point in more detail in a forthcoming paper (Sanz *et al* 2011). Further intriguing results are found at $\phi = 0.62$. Here aging has relatively little effect. The crystallization initially grows slowly but then saturates at about 0.05.

We now look more closely at the mean-square displacements. We note that the MSDs for the large unaged system (thick lines) are significantly different from those for the smaller system. First, at short times $t < 1$, the displacements are smaller, implying that, after their ballistic initial motion, the particles feel the effect of collisions with their neighbours sooner. However, at intermediate times $1 < t < 1000$, the displacements in the large system are larger, reflecting, as noted above (section 3.1), relatively weak caging of the particles by their neighbours.

By contrast, the particles in the smaller system show more freedom at short times, but the distinct development of a plateau in the MSD, starting at $t \approx 0.5$, implies stronger caging. Furthermore, at all concentrations, increasing the period of constrained aging leads to a more extended plateau. Strikingly, for the most aged system at $\phi = 0.61$ the MSD is nearly flat over two decades in time before crystallization starts.

In summary, actively suppressing crystallization while preparing the initial state leads to a glassier system as judged by the form of the MSD. Further constrained aging of the system enhances this glassiness in a manner similar to that seen in the conventional aging of non-crystallizing polydisperse systems (e.g. Zaccarelli *et al* (2009)). Nevertheless, qualitatively, the systems prepared in this way show the same crystallization behaviour as the larger system discussed in section 3.1. Thus, up to and including $\phi = 0.61$, both systems

crystallize, but, at $\phi = 0.62$, only partial crystallization is seen, $X(t) < 0.10$, in the duration of the simulation. The crystallization times are significantly longer for the small system, implying a dependence on the initial state, though, without further investigation, we cannot rule out a direct effect of system size itself.

4. Further discussion and conclusions

There has been longstanding debate about whether assemblies of hard spheres do, or do not, show a glass transition. Early experiments on colloids found a dramatic slowing down of particle dynamics at concentration $\phi \approx 0.58$ as well as a marked change in the appearance of the crystals formed (Pusey and van Megen 1986, 1987, van Megen and Underwood 1993, 1994). These observations were interpreted as indications of a glass transition. Nevertheless, these colloidal systems were observed to crystallize, both on Earth (Pusey and van Megen 1986) and in microgravity (Zhu *et al* 1997, Cheng *et al* 2001), at concentrations higher than that of the apparent glass transition. Also, the early computer simulations of Rintoul and Torquato (1996) on equal-sized hard spheres found crystallization at concentrations approaching (but still below) random close packing, $\phi_{RCP} \approx 0.64$ (see e.g. Parisi and Zamponi (2010), Hermes and Dijkstra (2010) and Jiao *et al* (2011) for further discussion of random close packing).

A problem in interpreting such observations is that, at these high concentrations, amorphous states of hard spheres are unstable towards further crystallization once any significant amount of crystal has formed. This initial crystal can be compressed to concentrations approaching ordered close packing, $\phi_{CP} \approx 0.74$, thus creating free volume in the system which facilitates further crystallization. This phenomenon is almost certainly responsible for the fast, late-time, crystal growth seen in figure 1 at $\phi = 0.59$, 0.60 and 0.61 (see also section 3.1). Thus a crucial question is whether the high concentration crystallization observed, both in colloid experiments and in simulations, results from some residual crystal in the samples arising, in some way, from their preparation. Indeed van Megen and Underwood (1993) suggested that the shear-melting process by which apparently amorphous colloid samples were prepared could in fact leave small shear-aligned nuclei on which crystal could grow. In the case of simulations there is always the possibility that some crystal could be formed during compression of the system to the high concentration.

The work reported in this paper goes some way towards clarifying the dependence of subsequent behaviour of hard-sphere systems on the preparation of the initial state. We have used a Monte Carlo method, in which a term in the potential actively discourages crystallization, both to compress the system and to perform subsequent constrained aging. As discussed in section 3.2, systems prepared in this way show qualitatively similar crystallization behaviour to those prepared without active suppression of crystallization. However, crystallization is slowed and systems subjected to constrained aging show more pronounced glass-like behaviour, in terms of the structure of the mean-square displacement, before the

onset of crystallization. In this connection, the behaviour at $\phi = 0.61$, figure 3(c), shows strong sensitivity to the nature of the initial state. The unaged system, curves 1, crystallizes; the partially aged system, curves 2, does not crystallize fully in the duration of the simulation; however further aging, curves 3, leads again to crystallization. In this last case, the MSD shows a nearly flat plateau for two decades of time, implying strong caging of the particles, before rather suddenly increasing. In the end, the most aged system crystallizes almost as rapidly as the unaged one.

These observations support our earlier claim (Zaccarelli *et al* 2009) that the nucleation of crystals at concentrations above the apparent ideal glass transition, $\phi_G \approx 0.58$, is an intrinsic property of systems of equal-sized hard spheres and not the result of residual crystal in the initial state. As discussed in section 3.1, the results of figure 2(a) show that, up to $\phi \approx 0.56$, nuclei develop by diffusion of the particles via a standard nucleation-and-growth process. However, at $\phi \geqslant 0.58$, particles need move only a distance of about one radius to initiate crystallization. This appears to be the process that has been called spinodal nucleation, where the free energy barrier to forming a nucleus is small compared to, or at least comparable with, the thermal energy (for further discussion of spinodal nucleation see Trudu *et al* (2006) and Wang *et al* (2007) in the context of Lennard-Jones systems, Ni *et al* (2010) who investigate the crystallization of hard rods, and Cavagna (2009) for a more general review). Note that plotting the data in the form of figure 2(a) suggests just two regimes of nucleation–nucleation and growth at the lower concentrations and spinodal nucleation at high concentration—rather than the three suggested by Pusey *et al* (2009). Understanding the mechanisms underlying the high-concentration nucleation is a major focus of ongoing work which we report on elsewhere (Sanz *et al* 2011).

An important initial motivation for our series of simulations was to try to understand the marked change in the appearance of the crystals in the colloid experiments—from many small compact crystallites to much larger irregular ones—that was observed on crossing the apparent glass transition at $\phi_G \approx 0.58$ (Pusey and van Megen 1986, van Megen and Underwood 1993). The simulations reported here on equal-sized spheres do not show such an effect: there is only a relatively small, smooth, increase in crystallite size around this concentration. The colloidal particles were polydisperse with a relative standard deviation in size of about 5%. Thus, a possibility that remains to be investigated is that even this relatively small degree of polydispersity has a large effect on the crystallization mechanisms at these high concentrations.

Finally, we repeat one notable feature of our findings. At concentrations $\phi = 0.62$ and 0.63, high concentrations but significantly below that of random close packing, we do not observe complete crystallization, suggesting that it *is* possible to prepare long-lived glassy states of equal-sized hard spheres.

Acknowledgments

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