Metastability and Crystallization in Hard-Sphere Systems

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We present results of large-scale molecular dynamics simulations of hard sphere systems at values of the volume fraction ϕ along the disordered, metastable branch of the phase diagram up to random close-packing ϕ_c. By quantifying the degree of local order, we determine the necessary conditions to obtain a truly random system, enabling us to compute the pressure carefully along the entire metastable branch. Near ϕ_c we show that the pressure scales as $(\phi_c - \phi)^{-\gamma}$, where $\gamma = 1$ and $\phi_c = 0.644 \pm 0.005$. Contrary to previous studies, we find no evidence of a thermodynamic glass transition and find that after long times the system crystallizes for all ϕ above the melting point. [S0031-9007(96)01661-4]

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Random packings of hard spheres have received considerable attention since they serve as a useful model for a number of physical systems, such as simple liquids [1], glasses [2], colloidal dispersions, and particulate composites [3]. The hard-sphere model turns out to approximate well the structure of dense-particle systems with more complicated potentials (e.g., Leonard-Jones interactions) because short-range interparticle repulsion is the major effect in determining the structure.

There is strong numerical evidence for the existence of a first-order disorder/order phase transition in hard sphere systems [4,5]. There are four important branches shown in the phase diagram (Fig. 1), where the pressure p is plotted versus the sphere volume fraction $\phi = 4\pi a^3\rho/3$, with ρ and a being the number density and radius of the spheres, respectively. There is a fluid branch that starts at $\phi = 0$ and continues up to the freezing-point volume fraction, $\phi_f \approx 0.494$. At this point, the phase diagram splits into two parts. One part is a metastable extension of the fluid branch which follows continuously from the previous branch and is conjectured to end at the *random close-packing* state [6], $\phi \approx 0.64$ [7]. The other branch that splits off the freezing point represents the *thermodynamically stable* part of the phase diagram. Both fluid and solid can coexist along the tieline until the melting point $\phi_m \approx 0.545$ is reached. The portion of the curve which continues above the melting point is referred to as the solid or ordered branch, ending at the close-packed fcc crystal volume fraction of $\sqrt{2}\pi/6 = 0.7405$.

There are many difficulties one encounters when simulating hard spheres at densities $\phi > \phi_f$. One cannot melt a crystal at high densities and expect it to spontaneously go into the metastable phase. One must start with a system at a lower density and carefully "compress" the fluid, being cautious not to allow crystallization to occur. Therefore, the system must be evolved in time while still remaining on the disordered metastable branch. There is currently no explicit test for determining whether or not the system is on the metastable branch of the phase diagram. Imprecise methods such as looking for peaks associated with the fcc crystal in the radial distribution function are often used to determine whether the system has left the metastable branch [8,9]. Unfortunately, this method is not sensitive to crystallite formation in very dense amorphous systems. In these "supercooled" systems, small amounts of crystallization can dramatically change the behavior of the system, especially near random close packing.

Previous studies [9–11] have found evidence of a so-called "glass transition" at volume fraction ϕ_g, where $\phi_f \le \phi_g \le \phi_c$. It is an open question as to whether this transition is a true thermodynamic phase transition, or just a continuous change in the dynamic variables caused by the increase in density. If it is a second-order phase transition, as many believe, very precise values of the pressure p must be calculated since one must be able to detect a discontinuity in the first derivative of p as a function of ϕ at $\phi = \phi_g$. This emphasizes even more the necessity

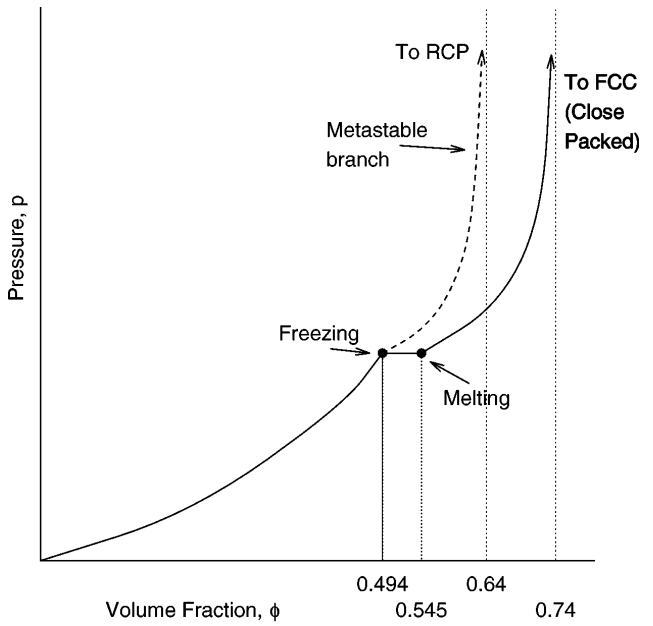

FIG. 1. Phase diagram in the pressure-volume fraction plane for the hard-sphere system.

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of being able to precisely tell when the system is in the metastable state, the crystalline state, or somewhere in between.

The intent of this Letter is to carefully study the metastable branch and answer the questions posed above. Specifically we will employ a quantitative measure of the local order to probe for signs of crystallization, and show that $g(r)$ is not sensitive to crystallite formation. Using this local-order measure, we will carefully calculate the pressure as a function of ϕ along the metastable branch, i.e., $\phi_f \leq \phi < \phi_c$, and determine whether there exists a thermodynamic glass transition. Finally, we carry out an asymptotic study of how the pressure in the system diverges near random close-packing and compare it to previous works. In what follows we describe briefly our new results; further details are given elsewhere [12].

Most techniques that are used to create random dense hard-sphere (RDHS) systems create nonequilibrium systems. However, we are interested in an equilibrium RDHS system which, along the metastable branch ($\phi_f \leq \phi \leq \phi_c$), will generally have significantly different properties than the nonequilibrium systems. In theory, it is a simple matter to equilibrate RDHS systems using simple molecular dynamics (MD) or Monte Carlo (MC) techniques, but in practice this is very difficult. The process of going from the initial nonequilibrium RDHS system to the equilibrium RDHS system is *fundamental* to the study of RDHS systems. This has generally not been noted by previous studies.

The question of equilibration is a subtle one because there are two phenomena which occur simultaneously during the equilibration process for the range $\phi_f \leq \phi \leq \phi_c$. The first is that of the system moving from the nonequilibrium state to a final equilibrium state. However, at the same time, the RDHS system is crystallizing. This is due to the fact that the equilibrium RDHS system is metastable, and further evolution of the system moves the system toward the stable branch of the dense hard-sphere system which is the crystalline branch for densities above the melting-point volume fraction ϕ_m (see Fig. 1). The time scale for the nonequilibrium to metastable equilibrium transition τ_m is generally much shorter than the time scale related to the transition from the metastable to the stable ordered branch, τ_c, i.e., $\tau_c \gg \tau_m$. However, τ_c and τ_m can be similar in some cases, and vary depending on the density and nature of the initial nonequilibrium system.

Accordingly, it is important that the systems be carefully monitored during the equilibration process. The most important property of the system is the pressure which is trivially related to the contact value of the radial distribution function (RDF) $g(\sigma)$ by the relation $p/\rho k_B T = 1 + 4\phi g(\sigma)$ [1], where ρ is the number density and T is the absolute temperature. Initially, p or $g(\sigma)$ is usually much higher in the nonequilibrium configurations created by most algorithms which involve a "quenching" procedure, so there is a steady, exponential-like decay of the p as the system settles into the equilibrium state. As the system begins to crystallize, the p drops further. This drop in p is not as smooth as that due to the equilibration process. It is sometimes characterized by sharp drops, especially at densities close to RCP, caused by the sudden crystallization of parts of the system.

Previous studies have attempted to determine the onset of crystallization by studying the radial distribution function [9]. The quantity $\rho 4\pi r^2 dr g(r)$ gives the average number of particle centers in a shell of thickness dr at a radial distance of r from the center of a particle. Effectively, the RDF distribution function measures the extent to which the position of the particle centers deviates from that of an uncorrelated ideal gas. As crystallization begins to occur, a very small peak begins to appear for values of r which correspond to the next nearest neighbor in the fcc lattice. For a close-packed system, this occurs at $r/\sigma = \sqrt{2}$, but for the small crystallites that appear in the random system it occurs at approximately $r/\sigma \approx 1.5$ [13]. Previous investigators assumed that there was no crystallization if the peak was not seen. This method is very unsatisfying since the lack of its appearance does not necessarily mean that crystallization is not occurring, and it is difficult to determine exactly when this peak appears.

Steinhardt, Nelson, and Ronchetti [14] have proposed a more quantitative measure of local order in the system that is often used in studies of crystallization. First, one must define a set of bonds connecting neighboring spheres in the system. One then assigns the value

$$Q_{lm}(\mathbf{r}) \equiv Y_{lm}(\boldsymbol{\theta}(\mathbf{r}), \boldsymbol{\phi}(\mathbf{r})) \tag{1}$$

to each bond oriented in a direction $\mathbf{r}$, where the Y_{lm} are the spherical harmonics. These values are then averaged over all bonds to get

$$\overline{Q}_{lm} \equiv \langle Q_{lm}(\mathbf{r}) \rangle \, . \tag{2}$$

The quantity $\overline{Q}_{lm}$, for a specific l and m, is dependent on the coordinate system, but an invariant quantity Q_l can be obtained in the following manner:

$$Q_l \equiv \left(\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |\overline{Q}_{lm}|^2 \right)^{1/2} \tag{3}$$

We are specifically interested in Q_6, as it will approach 0 for a completely disordered system and will have a nonzero value in the presence of any sort of crystallization. For our simulations, we have chosen bonds to be defined between spheres separated by a distance r, where $\sigma \leq r \leq 1.5\sigma$.

The initial random dense hard-sphere (RDHS) systems were created using the technique described by Clarke and Wiley [15]. The systems were equilibrated using standard hard-sphere molecular dynamics [16]. The time scale used in the figures is arbitrary, but is scaled in such a way that it was equivalent for systems of any number of particles. One primary advantage of using the MD equilibration over the MC technique is that the pressure could be measured directly via the virial or by extrapolating $g(r)$ to the contact value ($r = \sigma$). Unless

otherwise specified, the number of spheres used for each simulation was 2000. This is significantly larger than many previous simulations which usually started with 500 or 864 spheres.

To illustrate the utility of Q_6 as an appropriate signature of the local order in the system, we have plotted the scaled order parameter Q_6 vs t and the corresponding contact value $g(\sigma)$ vs t at $\phi = 0.58$ (Fig. 2) for a *small time interval in our simulations.* Here, Q_6 is multiplied by the square root of the number of bonds so that value of Q_6 for a finite spatially uncorrelated system is ≈ 1 (see Ref. [12] for details). This volume fraction was specifically chosen because it is close to the point at which many studies have noticed a discontinuity in the first derivative of the pressure as a function of volume fraction, i.e., a glass transition. The time does not start at 0, as we are trying to demonstrate the slow crystallization of an equilibrium random system, and not the equilibration of a nonequilibrium system. The contact value shows a steady drop, while the order parameter Q_6 shows a steady rise above its completely random value of approximately 1.0. As Q_6 approaches 2.0, there is significant disorder in the system, and the contact value is significantly changed from its value when Q_6 was closer to 1.0. This gives clear evidence that *the system is forming crystallites, even for the small interval shown.* However, the RDF showed no signs of a peak for r/σ around 1.4–1.5. For times much greater than those shown in Fig. 2, the system eventually crystallizes [12], as discussed below. We have found that once the value of Q_6 (scaled by the square root of the number of bonds) rises above a value of ≈ 1.5, there is significant crystallization, and it can no longer be considered to lie on the metastable branch.

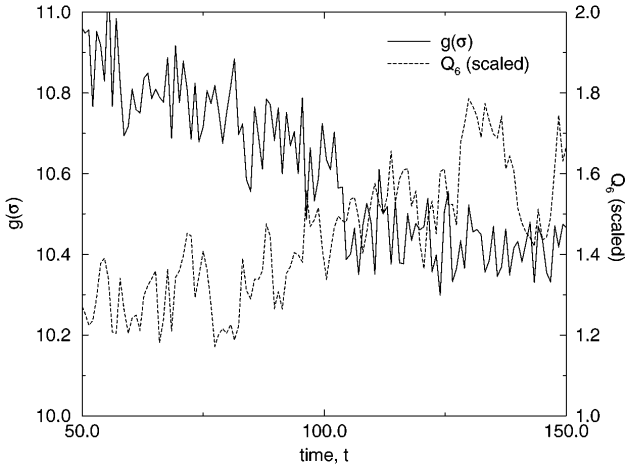

FIG. 2. Plot of the contact value of the RDF $g(\sigma)$ (solid line) and the scaled value of Q_6 as a function of time for a random hard sphere system at $\phi = 0.58$. The scale for $g(\sigma)$ is shown on the left while the scale for Q_6 is on the right. As Q_6 decreases with time, $g(\sigma)$ decreases. Note that at very large times ($t \approx 10^3$–10^4 on this time scale), the system eventually crystallizes [12].

A similar behavior is seen at other values of ϕ above the freezing point ϕ_f. The implication is that there is a constant rearrangement occurring in these systems which is driving the pressure down. The effect is seen in the RDF only after significant rearrangement has taken place.

By monitoring the local-order measure Q_6, we are able to identify the metastable state and compute the contact value of the RDF (or pressure) along the entire metastable branch. The data in Fig. 3 are calculated from the virial using MD methods. The curve shows a steady increase, but does not show a discontinuity in the first derivative as would be expected from a second-order phase transition.

The argument for the existence of the glass transition in simulations of hard spheres is usually based on the fact that when the system is brought to a dense state by quickly expanding the spheres (or "quenching"), it does not crystallize for long periods of equilibration. It is then supposed that the system is locked into the amorphous state and cannot reach the crystalline state. After performing many such equilibrations, we have found that this effect is primarily due to *system size*. By performing equilibrations between melting ϕ_m and random close-packing ϕ_c, we have found that if one waits for long enough times (typically 10^7–10^8 collisions in some cases), the systems will eventually equilibrate and crystallize. We emphasize that crystallization occurred even for systems very close to ϕ_c ($\phi \approx 0.63$–0.64). We have encountered many smaller systems that do not crystallize, but most of these had at most 500 particles. Once the system size was on the order of 2000–5000 particles, crystallization usually occurred at shorter time scales.

Interestingly, recent Shuttle experiments of hard-sphere colloidal dispersions carried out in microgravity showed a very similar crystallization behavior for volume fractions between $\phi_m = 0.545$ and $\phi = 0.62$ [17]. These systems consisted of approximately 2×10^{13} PMMA spheres of diameter 0.518 μm, which supports our point that finite-size effects keep smaller systems from crystallizing. (Of

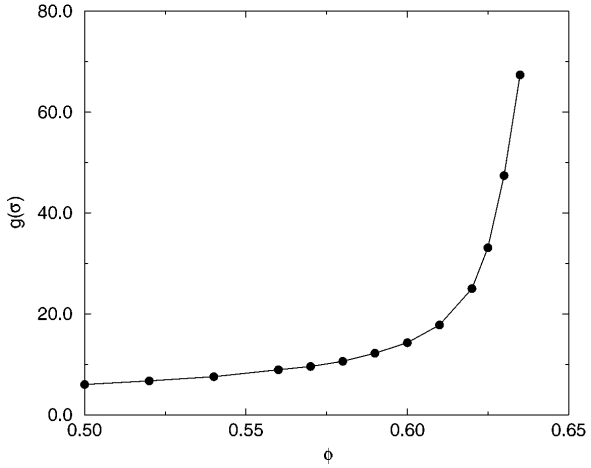

FIG. 3. Plot of simulation data for the equilibrium contact value of dense random hard-sphere systems.

course, hydrodynamic effects in the Shuttle experiment are ignored in our simulations, albeit under the absence of gravity.) Similar experiments done under normal surface gravity indicate that crystallization does not occur for RDHS systems that have densities which are roughly between ϕ_m and ϕ_c.

It is also possible to see why previous simulations were perhaps able to see a change in the first derivative of p as a function of density for values of ϕ close to where they thought a second-order phase transition existed. We first note that at a volume fraction of $\phi \approx 0.59$, the time required for metastable equilibrium τ_m was greater than that of the time required for crystallization τ_c. The value of p in this case had to be determined by looking at times at which crystallization had not yet occurred and extrapolating those values for long times, assuming an exponential decay to a final value. We believe that the fact that the crystallization time scale is so short in this case is the main cause for a belief that there is a "transition" near this volume fraction. The pressure calculated at this volume fraction in most simulations contains significant crystallization and therefore the value of p is too low. Even if the pressure is measured carefully within the region around $\phi = 0.59$, the errors associated with the pressure measurement are really still too large to say conclusively that a transition does exist since the second derivative is also increasing rapidly along with the first derivative.

Using this data, we can study the behavior of $g(\sigma)$ as $\phi \rightarrow \phi_c$. There is strong numerical evidence that $g(\sigma)$ diverges as $(\phi_c - \phi)^{-\alpha}$ as $\phi \rightarrow \phi_c$. By fitting the our data for $\phi \geq 0.60$ on a log-log plot, we found that $\alpha \approx 1$, within the errors of our simulation. An extrapolation to $g(\sigma)^{-1} = \infty$ gives a value of 0.644 ± 0.005 for ϕ_c.

Our results for ϕ_c and α are somewhat similar to previous numerical results, but do clear up some discrepancies between them. Tobochnik and Chapin [18] studied the behavior of $g(\sigma)$ for ϕ near ϕ_c and arrived at the values $\alpha = 1$ and $\phi_c = 0.69$. Their value of ϕ_c is much larger than the results given by most other simulations of $\phi_c \approx 0.64$, due in part to the small system sizes ($<$500 spheres) and because $g(\sigma)$ is more difficult to establish in MC simulations. Song *et al.* [19] also attempted to evaluate α and ϕ_c, using data from Alder and Wainwright [16], and Erpenbeck and Wood [20]. They obtained a value of $\phi_c = 0.6435$ and a value of $\alpha = 0.76 \pm 0.02$. This value of ϕ_c is much more in line with previous estimates as well as our estimate. The error associated with their estimate of α did not seem to be derived in a systematic way, and it was probably much too small.

We can also use these very precise results to check the analytical predictions of Torquato [6] of $g(\sigma)$ for $\phi_c \leq \phi \leq \phi_c$. The theoretical prediction has the correct asymptotic behavior of $(\phi_c - \phi)^{-1}$ as well as the correct value of $g(\phi_f)$ built into it, and is therefore very accurate for most values of $g(\sigma)$ in this range. There is a slight deviation from prediction for values which are in-between ϕ_f and ϕ_c, however [12].

We have established a quantitative means of testing for local order in a system of dense hard spheres. By using this technique, we are not only able to establish when the system is truly random, but have also shown that previous methods of looking for the next-nearest-neighbor peak in the RDF are not precise enough. Using this technique, we have measured precise values of the contact value $g(\sigma)$ for the hard sphere system on the metastable branch for values $\phi_m \leq \phi < \phi_c$. With these new accurate results, we see no evidence of a second-order phase transition in the vicinity of the so-called "glass transition". We also find that $g(\sigma)$ diverges near RCP as $(\phi_c - \phi)^{-1}$, where $\phi_c = 0.644$. We do not see any indication of a fractal exponent, as indicated by earlier studies.

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[1] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).
[2] R. Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983).
[3] S. Torquato and F. Lado, Phys. Rev. B **33**, 6428 (1986).
[4] W. G. Hoover and F. H. Ree, J. Chem. Phys. **49**, 3609 (1968).
[5] H. Reiss and A. D. Hammerich, J. Phys. Chem. **90**, 6252 (1986).
[6] S. Torquato, Phys. Rev. E **51**, 3170 (1995); Phys. Rev. Lett. **74**, 2156 (1995).
[7] J. G. Berryman, Phys. Rev. A **27**, 1053 (1983).
[8] W. S. Jodrey and E. M. Tory, Powder Technol. **30**, 111 (1981).
[9] R. J. Speedy, J. Chem. Phys. **100**, 6684 (1994).
[10] J. Yeo, Phys. Rev. E **52**, 853 (1995).
[11] A. van Blaaderen and P. Wiltzius, Science **270**, 1177 (1995).
[12] M. D. Rintoul and S. Torquato, J. Chem. Phys. (to be published).
[13] This is due to the fact that the spheres are not necessarily touching, but are just locally arranged in the crystalline configuration.
[14] P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. B **28**, 784 (1983).
[15] A. S. Clarke and J. D. Wiley, Phys. Rev. B **35**, 7350 (1987).
[16] B. J. Alder and T. E. Wainwright, J. Chem. Phys. **33**, 1439 (1960).
[17] J. Zhu, M. Li, W. B. Russel, P. M. Chaikin, R. Rogers,and W. Meyers (to be published).
[18] J. Tobochnik and P. M. Chapin, J. Chem. Phys. **88**, 5824 (1988).
[19] Y. Song, R. M. Stratt, and E. A. Mason, J. Chem. Phys. **88**, 1126 (1988).
[20] J. J. Erpenbeck and W. W. Wood, J. Stat. Phys. **35**, 321 (1984).