LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 1998 issue.

NOTES

Is there a glass transition for dense hard-sphere systems?

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The precise nature of the glass transition in fluids is still an unresolved question, despite the fact that many real liquids have been known for many years to form glasses upon cooling. As a matter of fact, many continue to dispute the notion that it corresponds to a truly thermodynamic phase transition, while others have not agreed as yet to whether it is a first or a second order phase transition. On the theoretical side, the situation is no better. In the case of hard-sphere fluids, some recent investigations[1,2] have concluded that a glass transition exists at a packing fraction intermediate between that of the freezing point[3] ($\eta_f \simeq 0.497$) and the one of random close-packing[4] ($\eta_{RCP} \simeq 0.644$). Such a prediction has been given some support through experiments with colloidal hard spheres,[5,6] which relatively easily form glasses and have the same thermodynamic equilibrium phases as atomic hard spheres. Nevertheless, new comprehensive data obtained via large-scale molecular dynamics and Monte Carlo simulations, as well as a careful assessment of previous simulation results of systems of dense hard spheres at packing fractions, including the metastable fluid branch from η_f to η_{RCP} by Rintoul and Torquato,[7] led them to conclude that there was no evidence of a thermodynamic phase transition. Among other things, these data provided accurate numbers for the contact values of the radial distribution function of the hard-sphere system in the metastable branch, which were in turn found to be in good agreement with analytical predictions from an earlier theory by Torquato.[8] In this note, our aim is to reexamine the simulation results from a different perspective. According to our reasoning, the presence of a transition from a metastable fluid state to an amorphous (glassy) state at a particular packing fraction η_g (specified later on) is wholly compatible with the simulation data.

In a previous paper[9] we considered the structure of hard-sphere metastable fluids using a rational-function approximation (RFA) method[10] to analytically derive the radial distribution function. A key feature of the method is that it provides a fluid structure thermodynamically consistent with a given equation of state. When the equation of state of the hard-sphere fluid is the accurate and recently derived Padé (4.3) (which is constructed from the knowledge of the first eight virial coefficients[11,12] and whose explicit expression will be omitted but may be found in the former two references), the method leads to a threshold density beyond which no meaningful fluid structure can be derived. This corresponds to a packing fraction which we called $\eta_g = 0.5604$. It should be noted that the Padé (4.3) equation of state only presents a pole at a density near the crystalline close-packing value $\eta_0 \simeq 0.7405$, well above the threshold value. By assuming that the pressure p is continuous at η_g while it exhibits a change in slope on going from the fluid phase to the glass,[1] we also proposed within the same method an equation of state for the glass of the form

$$\frac{p}{\rho k_B T} = \frac{A}{1 - \eta/\eta_{RCP}}, \quad (\eta \geqslant \eta_g). \tag{1}$$

where k_B is the Boltzmann constant, T is the absolute temperature, ρ is the number density, and $\eta = (\pi/6)\rho\sigma^3$ is the packing fraction, σ being the hard-sphere diameter. In this equation. A and η_{RCP} were obtained in a self-consistent way as $A = 2.765$ and $\eta_{RCP} = 0.6448$. Since the equation of state of the hard-sphere system may be written in terms of the contact value of the radial distribution function $g(\sigma^+)$ as

$$\frac{p}{\rho k_B T} = 1 + 4\eta g(\sigma^+), \tag{2}$$

the values of $g(\sigma^+)$ in the range $0 \leqslant \eta \leqslant \eta_{RCP}$ may be obtained by comparing Eq. (2) with the Padé (4.3) if $\eta \in [0, \eta_g]$ and with Eq. (1) if $\eta \in [\eta_g, \eta_{RCP}]$, respectively. The stable fluid branch is known to be adequately described by the Padé (4,3).[12] For our purposes, the most interesting region is the one beyond the freezing point. In Fig. 1 we have plotted $1/g(\sigma^+)$ vs. η in the interval $\eta_f \leqslant \eta \leqslant \eta_{RCP}$ using the values derived with the aforementioned procedure, as well as those from the equation of state proposed by Torquato[8] (which will not be written down either), together with the simulation data.[7] The improvement of the agreement with the simulation results obtained with our values, as compared to the ones predicted by Torquato's theory, is clearly manifest in the figure.

It could be reasonably argued that this agreement may be coincidental. However, we are persuaded that such is not the case. The argument goes as follows. First of all, the simula-
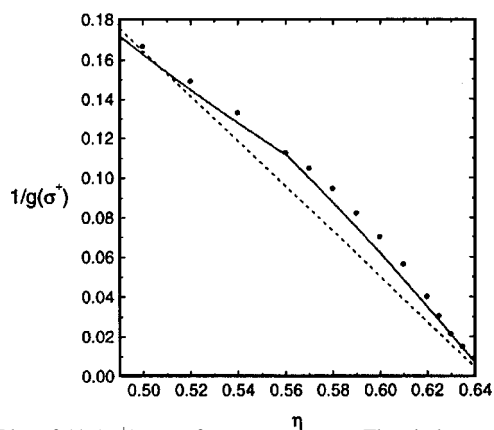
FIG. 1. Plot of $1/g(\sigma^+)$ vs η for $\eta_f \lesssim \eta \lesssim \eta_{RCP}$. The circles represent the simulation data from Rintoul and Torquato (Ref. 7) the broken line represents the theoretical curve from Torquato (Ref. 8), and the continuous line the theoretical curve corresponding to this work.

tion data are totally consistent with the presence in the equation of state of a simple pole at $\eta = \eta_{RCP}$. None of the accurate and thoroughly used equations of state for the fluid phase [including the Padé (4,3) and the popular Carnahan–Starling (CS) equation[13]] presents such a feature. In fact, one can easily check that the CS equation of state is very accurate even in part of the metastable fluid branch up to $\eta \simeq 0.54$, after which it goes totally wrong. This suggests that at some packing fraction intermediate between η_f and η_{RCP} the system must cease to be a fluid and go into an amorphous phase whose equation of state is different from that of the fluid and has a simple pole at η_{RCP}. What our method provides is precisely the possibility that a threshold packing fraction η_g (greater than η_f) exists, beyond which no fluid phase description is physically acceptable. It also gives the criteria to determine η_g and η_{RCP}. It should be stressed that as discussed in Ref. 9, neither the Padé (4,3) equation of state for the fluid phase nor the free-volume form given by Eq. (1) for the amorphous phase are crucial for such a result, although they have the right properties and lead to the values $\eta_g = 0.5604$ and $\eta_{RCP} = 0.6448$ in a self-consistent way. As further support for the validity of our approach (and hence for the existence of the glass transition), the following evidence can be given. In a totally independent development, Zhou and Stell[14] have analytically derived an approximate (thermodynamically consistent) cavity function $y(r)$ for a hard-sphere fluid in which the only input is the equation of state. Of course the cavity function and the radial distribution function should have the same values at contact for a given η, and the same applies to the contact values of the first few derivatives. We have checked that for any prescribed η, the contact value of the first derivative is identical in both approaches, namely the one coming from the RFA method for $g(r)$ and the one arising from the cavity function $y(r)$ due to Zhou and Stell. Additionally, the packing fraction dependence in the contact values of the second and third derivatives is qualitatively also the same, the numerical differences being, of course, ascribed to the approximate nature of both the cavity function and the radial distribution function. In particular, if the Padé (4,3) equation of state is used, we have

confirmed that the contact value of the first derivative of the cavity function diverges to minus infinity as $\eta \to \eta_g$, which we claimed to be the signature for the glass transition in Ref. 9.

The most serious difficulty with the conclusions drawn from our development is tied to the fact that, in principle, it is not rigorous to extrapolate the fluid equation of state into the metastable branch.[15] This is indeed a questionable assumption in view of the fact that in order for the hard-sphere system to exist as a metastable fluid, external constraints must be applied to avoid crystallization above the freezing density. While the rather good accuracy of the Padé (4,3) (or the CS) equation with respect to the simulation data already suggests that in this case the extrapolation (although rigorously questionable) seems not to be inappropriate, it must be remarked that the support for the existence of the glass transition within the RFA method is independent of such an extrapolation. Any reasonable equation of state for the metastable fluid gives rise to a certain density η_g, beyond which the RFA method ceases to yield an acceptable physical structure for a fluid phase. For instance, the equation of state proposed by Alexanian and Bose[1,16] gives $\eta_g \simeq 0.551$.

In conclusion, in this paper we have provided evidence that the recent simulation data for the contact value of the radial distribution function of a dense hard-sphere system are consistent with the existence of a threshold packing fraction η_g ($\eta_f < \eta_g < \eta_{RCP}$) separating a fluid phase and an amorphous (glassy) phase. In our view, this suggests the likelihood of a glass transition in a hard-sphere system. Nevertheless, due to the scarcity of the simulation data in the region around $\eta = 0.56$, it would be premature to give a definite answer to the question posed in the title of this paper on the basis of this evidence. Yet, our expectation is that the present results serve as a motivation to perform more simulations in the vicinity of η_g.

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