

Two distinct time scales in the dynamics of a dense hard-sphere liquid

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The dynamic behavior of a dense hard-sphere liquid is studied by numerically integrating a set of Langevin equations that incorporate a free energy functional of the Ramakrishnan-Yussouff form. At relatively low densities, the system remains, during the time scale of our simulation, in the neighborhood of the metastable local minimum of the free energy that represents a uniform liquid. At higher densities, the system is found to fluctuate near the uniform liquid minimum for a characteristic period of time before making a transition to an inhomogeneous minimum of the free energy. The time that the system spends in the vicinity of the liquid minimum before making a transition to another one defines a new time scale of the dynamics. This time scale is found to decrease sharply as the density is increased above a characteristic value. Implications of these observations on the interpretation of experimental and numerical data on the dynamics of supercooled liquids are discussed.

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I. INTRODUCTION

The dynamic behavior of dense supercooled liquids has been the subject of extensive experimental, theoretical, and numerical studies [1,2] over several decades. However, the present understanding of some of the observed phenomena remains far from complete. In recent years, considerable progress has been achieved through the development of mode coupling (MC) theories [3] of the dynamics of dense liquids. MC theories provide a detailed and qualitatively correct description of the observed dynamics [4] in a temperature range that covers the first few decades of the growth of the characteristic relaxation time τ of so-called "fragile" liquids [2] in the supercooled regime. In conventional MC theories [5,6], τ is predicted to exhibit a power-law divergence at an *ideal glass transition temperature* T_c .

Experimental and numerical results for the first few decades of the growth of τ are consistent with this prediction. Numerical studies of the long-time dynamics of simple one-component liquids at temperatures close to or lower than T_c are difficult because nucleation [7] of the crystalline solid takes place if the simulation is continued for a long time at such temperatures. In laboratory experiments, on the other hand, many liquids can be maintained in the supercooled state for long periods of time at temperatures which are substantially lower than the temperature T_c obtained from power-law fits to experimental data at higher temperatures. Such experiments

show that the predictions of conventional MC theories do not provide a correct description of the actual dynamic behavior for temperatures close to or lower than T_c . The system is very much in the liquid state at this temperature (relaxation times are typically of the order of 10^{-8} s and viscosities are of the order of 10^2 P at T_c) and the growth of τ as the temperature is lowered further is described reasonably well by the Vogel-Fulcher law [8]. Thus a temperature that is slightly higher than the T_c obtained from power-law fits to the data for higher temperatures may be called a crossover temperature, which separates two distinct regimes of the dynamic behavior of fragile liquids. These two regimes are characterized by different temperature dependences of the relaxation times.

A number of other experiments [9,10] also suggest the existence of a crossover between two qualitatively different dynamical regimes at a temperature close to T_c . Recent versions of MC theories [11–13] have established the existence of cutoff mechanisms which eliminate the divergence at T_c predicted earlier. However, these calculations do not lead to definite predictions about the behavior to be expected for temperatures lower than T_c . It is generally believed that "activated processes" play an important role in the dynamics at these temperatures. However, the nature of these "activated processes" has not been elucidated so far. There have been several attempts [14–16] to describe the behavior observed at temperatures lower than T_c in terms of a *thermodynamic glass transition* which would take place at a temperature T_g lower than T_c if thermodynamic equilibrium could be maintained all the way down to this temperature. However, a calculation that establishes the existence of such a transition in a physically realistic system is not yet available.

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We address here some of the questions mentioned above by means of a numerical simulation of the dynamics of a dense hard-sphere liquid. Our simulation involves explicit numerical integration of the dynamics of the fluid as described by a set of Langevin equations [17,18] in which information about the equilibrium structure of the liquid is incorporated in the form of a mean field free energy functional of the Ramakrishnan-Yussouff form [19]. This free energy functional is known [20,21] to possess, at sufficiently high densities, many “glassy” local minima in addition to the ones representing the uniform liquid and crystalline solid states. The dynamics of this system at relatively low values of the density within the “supercooled” regime was simulated in an earlier study [17,18]. It was found there that at such densities the system remains confined to the neighborhood of the liquid minimum of the mean field free energy during the time scale of our simulation. This time scale was much longer than the relaxation times associated with the decay of small-amplitude density fluctuations near the liquid minimum. The nature of the growth of the longest relaxation time with increasing density and the form of the decay of density correlation functions in time were found to be in qualitative agreement with the predictions of MC theories.

In the present study, we have considered higher densities and monitored the time evolution of the system over longer times. In particular, we have addressed the following question: under what conditions and over what time scales does the system make a transition from the neighborhood of the uniform liquid minimum to one of the many other inhomogeneous minima of the free energy? In our simulations, the system is started off in a state which is close to the liquid minimum and its evolution in time is followed by integrating the equations of motion forward in time. As explained in more detail in Sec. II, at regular intervals along the simulated time evolution of the system we use a deterministic free energy minimization procedure [20,21] to locate the free energy minimum that lies closest in phase space to the state of the system at the current point on its trajectory. This allows us to monitor the free energy minima near which the system fluctuates at different points along its trajectory.

For a hard-sphere system, the density rather than the temperature is the relevant control variable: one must consider increased densities rather than lower temperatures. At relatively low densities ($n^* \leq 0.95$, where the dimensionless density parameter n^* is defined as $n^* \equiv \rho_0 \sigma^3$, with ρ_0 being the average number density of the system and σ the hard-sphere diameter), we find that the system remains in the vicinity of the liquid minimum during the very long time scale of our simulation. A qualitatively different behavior is found at higher densities ($n^* \geq 0.96$). At these densities, we find that after spending an initial period of time (which decreases as the density is increased) near the liquid minimum, the system makes a transition to one of the inhomogeneous minima of the free energy. These inhomogeneous minima are characterized by a strong clumping of the local density at a small number of points.

We have found a convenient way to define, as discussed

in Sec. II, a characteristic time $\tau'(n^*)$ to describe the time scale associated with the transition of the system from the uniform liquid minimum to one of the nonuniform minima of the free energy. This transition is signaled in our simulation by a zero crossing of the excess free energy, defined as the difference between the current value of the free energy and its value at the uniform liquid minimum. The time $\tau'(n^*)$ is found to increase sharply as n^* approaches the value $n^* \approx 0.95$ from above. It exceeds the longest time scale of our simulation for $n^* \leq 0.954$. The dependence of τ' on the density is the main result of our simulation.

The time scales that describe the relaxation of small-amplitude density fluctuations near the liquid minimum were calculated in our previous simulation [17,18] for $n^* \leq 0.93$. The dependence of τ , the longest one of these time scales, on the density in this regime was found to be well described by the Vogel-Fulcher law (and also by a power law at lower densities). We find that the time scale τ' calculated in the present simulation becomes shorter than the extrapolated value of τ as the density is increased above $n^* \approx 0.98$. These results imply the existence of a *crossover density* n_x^* in the range $0.95 < n_x^* < 0.96$ at which the time scale τ' apparently diverges or at least becomes orders of magnitude larger than the time scales accessible in our simulation. For densities lower than n_x^* , a system prepared in a state close to the liquid minimum remains in its vicinity over the time scale of observation, so that a description of its dynamics in terms of small fluctuations about the uniform liquid minimum is adequate. For values of n^* higher than n_x^* , the inhomogeneous local minima of the free energy have to be taken into account in a proper description of the dynamics.

The model and methods used in our simulation are not adequate for dealing with the strong density inhomogeneities present near the nonuniform minima of the free energy. For this reason, we have not been able to simulate the long-time dynamics of the system at densities higher than n_x^* . However, we have carried out a detailed investigation of the nature of the density distribution at the free energy minima to which the system makes transitions at densities higher than n_x^* . These minima are found to exhibit some of the characteristics of very disordered fcc crystals, but certain characteristic features expected for random close packing also appear to be present. For a system of finite size, a sufficiently defective crystal is effectively indistinguishable from a glass. If these configurations are identified as crystalline states with defects, then τ' would be essentially the same as the homogeneous nucleation time of the crystalline solid. The dynamics of homogeneous nucleation of the crystalline solid in a supercooled liquid has been studied extensively by molecular dynamics (MD) simulations [7]. Our calculation differs from these MD simulations in one important aspect. The onset of homogeneous nucleation is detected in MD simulations by looking for its signature in measured thermodynamic quantities. These signatures may be difficult to detect in some cases. In contrast, since we deal with a free energy functional which exhibits a well-defined local minimum representing the uniform liquid state, any

transition away from it can be monitored directly in our simulation. An interpretation of our observations as transitions to an imperfect crystalline state as the density is increased above a characteristic value would be in qualitative agreement with the results of MD simulations [22] of the hard-sphere system.

However, an alternative interpretation in which the minima to which the system makes transitions for $n^* > n_g^*$ are identified to represent glassy states is also compatible with our data. Even if this interpretation is not appropriate for the hard-sphere liquid, it is likely to be so in other so-called good glass-forming liquids for which the time scale for nucleation of the crystalline solid can be very long. As discussed in Sec. III, the results of our simulation suggest an explanation of the experimentally observed crossover in the dynamic behavior of such liquids near the ideal glass transition temperature of MC theories in terms of a transition to glassy minima of the appropriate free energy functional.

The remaining part of this paper is organized as follows. Section II contains a brief description of the Langevin equations considered in this work, the numerical method used for integrating them forward in time, and a detailed description of the results obtained from these simulations. In Sec. III, we summarize the main conclusions drawn from this study, compare our results with those obtained from MD simulations of the dynamics of dense hard-sphere liquids, and discuss the implications of our observations on the interpretation of experimental and numerical data on the dynamics of supercooled liquids.

II. MODEL, METHODS, AND RESULTS

As we have mentioned in the preceding section, we study in this paper a Langevin equation model for the dynamics of a hard-sphere liquid. It is precisely the same as the model studied in Ref. [18]. We will therefore give here only an outline and will refer the reader to Ref. [18] for details.

We introduce first the statics, which in this case takes on particular importance. The equilibrium properties of the system are described by a free energy functional of the two fields in the problem: the number density field $\rho(\mathbf{r}, t)$ and the current density field $\mathbf{g}(\mathbf{r}, t)$. This free energy functional is the sum of two terms

$$F_{\text{tot}}[\rho, \mathbf{g}] = (m_0/2) \int d\mathbf{r} \frac{|\mathbf{g}(\mathbf{r})|^2}{\rho_0} + F[\rho], \quad (1)$$

where m_0 is the mass of a hard-sphere particle and $F[\rho]$ is of the Ramakrishnan-Yussouff [19] (RY) form

$$F[\rho] = F_0[\rho_0] + T \int d\mathbf{r} \{ \rho(\mathbf{r}) \ln[\rho(\mathbf{r})/\rho_0] - \delta\rho(\mathbf{r}) \} - \frac{T}{2} \int d\mathbf{r} \int d\mathbf{r}' C(|\mathbf{r} - \mathbf{r}'|) \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}'). \quad (2)$$

In Eq. (2) F_0 is the free energy of the uniform liquid of density ρ_0 which is equal to the average density

studied, T is the temperature (the Boltzmann constant is set to unity), $\delta\rho(\mathbf{r}) \equiv \rho(\mathbf{r}) - \rho_0$ is the deviation of the local density from its average value, and $C(|\mathbf{r} - \mathbf{r}'|)$ is the Ornstein-Zernike direct correlation function of the liquid of density ρ_0 . If one expands the logarithm in Eq. (2) to second order in the density fluctuations, one obtains after standard manipulations the usual expression relating the direct correlation function to the static structure factor $S(\mathbf{q})$. For $C(r)$ we use the standard Percus-Yevick form [23] for hard spheres.

It is convenient to introduce appropriate dimensionless variables at this point. As in Ref. [18], we take the computational lattice constant h as the unit of length, which is later related to the hard-sphere diameter σ . For the unit of time we take

$$t_0 = h/c, \quad (3)$$

where c is the speed of sound

$$c^2 = \frac{1}{m_0 \rho_0 \kappa}. \quad (4)$$

The compressibility κ is related to $S(\mathbf{q})$ by $T\rho_0\kappa = S(q=0)$. The time t_0 is [18] of order of the characteristic phonon time for wave vectors of order $1/\sigma$ and it is related to the Enskog collision time t_E by

$$t_E^{-1} = 4\pi^{1/2} n^* g(\sigma) K^{1/2} (h/\sigma) t_0^{-1}, \quad (5)$$

where $n^* \equiv \rho_0 \sigma^3$, $g(\sigma)$ is the pair-correlation function at contact for hard spheres [24], and

$$K = \frac{T}{m_0 c^2}. \quad (6)$$

If one then introduces the dimensionless variables

$$\mathbf{x} = \mathbf{r}/h, \quad (7)$$

$$n = \rho h^3, \quad (8)$$

$$\mathbf{j} = \mathbf{g} h^3 / c, \quad (9)$$

then one has, for the free energy in units of $m_0 c^2$,

$$F[n, \mathbf{j}] = (1/2) \int d\mathbf{x} |\mathbf{j}(\mathbf{x})|^2 / n_0 + F[n], \quad (10)$$

where

$$F[n] = F_0[n_0] + K \int d\mathbf{x} \{ n(\mathbf{x}) \ln[n(\mathbf{x})/n_0] - \delta n(\mathbf{x}) \} - \frac{K}{2} \int d\mathbf{x} \int d\mathbf{x}' C(|\mathbf{x} - \mathbf{x}'|) \delta n(\mathbf{x}) \delta n(\mathbf{x}'). \quad (11)$$

The quantity K defined in Eq. (6) is a function of the density only.

We proceed now with the dynamics. The Langevin equations are derived in the standard way [18,11,25] by taking $n(\mathbf{x}, t)$ (note that henceforward t is the dimensionless time) and $\mathbf{j}(\mathbf{x}, t)$ to be the slow hydrodynamic variables, then computing the required Poisson brackets

with the functional derivatives of the free energy defined in Eqs. (10) and (11), and finally adding the appropriate dissipative terms. The equations thus obtained for the dynamics of our model are

$$\frac{\partial n(\mathbf{x}, t)}{\partial t} + (1/n_0)\nabla \cdot (n\mathbf{j}) = 0, \quad (12)$$

$$\begin{aligned} \frac{\partial j_i}{\partial t} = & -n\nabla_i \frac{\delta F}{\delta n} - (1/n_0) \sum_j \nabla_j (j_i j_j) \\ & - (1/n_0) \sum_j j_j \nabla_i j_j + (1/n_0)\eta \nabla^2 j_i + \Theta_i(\mathbf{x}, t), \end{aligned} \quad (13)$$

where η is the dimensionless shear viscosity which can [18] be expressed in terms of the density. The noise fields $\Theta(\mathbf{x}, t)$ satisfy the second fluctuation dissipation theorem

$$\langle \Theta_i(\mathbf{x}, t)\Theta_j(\mathbf{x}', t') \rangle = -2K\lambda\eta n_0 \delta_{i,j} \nabla^2 \delta(\mathbf{x} - \mathbf{x}') \delta(t - t') \quad (14)$$

and the quantity λ is a dimensionless measure of the strength of the equilibrium fluctuations.

The details of the derivation of these dynamical equations and a thorough discussion of the assumptions that go into the model [including the form of the first term in Eq. (10)] are given in Ref. [18]. We emphasize that we use here not only the same model as in Ref. [18], but also the same values of the parameters in the problem which, in addition to the average dimensionless density n^* , are only h/σ and λ . In particular, the value of h/σ ($h/\sigma = 1/4.6$) is chosen so that the wave number at the first peak of the static structure factor $S(\mathbf{q})$ of the liquid lies in the middle part of the first Brillouin zone of the computational lattice. We also use the same numerical methods and the same cubic lattice with N^3 sites and $N = 15$ to integrate the equations of motion, Eqs. (12) and (13), and to generate the noise fields in Eq. (14). Thus the results obtained here are directly comparable with those in Ref. [18].

The dynamics of this system at densities $n^* \leq 0.93$ was extensively studied in Refs. [17,18]. We review now some of the results which are relevant for the present work. In the density range mentioned above, we found that, after an initial transient behavior that depended somewhat on the initial conditions (results reported in Refs. [17,18] and here are for initial conditions where the density is uniform and the currents vanish), the system became stationary in that the time-dependent density-density correlation function (or its spatial Fourier transform, the dynamic structure factor) $S(\mathbf{r} - \mathbf{r}', t_1, t_1 + t) \equiv \langle \delta n(\mathbf{r}, t_1)\delta n(\mathbf{r}', t_1 + t) \rangle$ became independent of t_1 , except for random fluctuations. The mean field free energy of the system as calculated from Eq. (11) also became stationary, fluctuating around the liquid value. It was then possible to calculate the equilibrium dynamic structure factor $S(\mathbf{q}, t)$. The decay of these density correlations took a simple exponential form at low densities, but for densities higher than $n^* = 0.83$ (the density at which

the RY free energy exhibits [20] a crystallization transition) we obtained, for wave vector values near the peaks of the static structure factor, decay behavior in qualitative agreement with that predicted by MC theories. At a given density, the largest characteristic decay time (that is, at the most slowly decaying wave vector), which we denote here by τ , was found to obey a Vogel-Fulcher law [8] which takes the following form when the density, rather than the temperature, is the externally controlled variable:

$$\tau(n^*) = Ae^{B/(v-v_c)}, \quad (15)$$

where $v \equiv 1/n^*$ and $v_c \approx 0.81$, corresponding to a density $n_c^* \approx 1.23$. The values of τ as given from Eq. (15) and with the parameter values found in Ref. [18] are plotted in Fig. 1 extrapolated to the higher density range studied in this paper.

As the density is increased beyond $n^* = 0.93$ in the present work, there is a qualitative change. Instead of locally equilibrating after a relatively brief transient, we find that the system does not seem to reach a steady state, but rather that the mean field free energy drifts slowly. As the density is increased further, it becomes clear that the mean field free energy is slowly drifting to a value below that of the liquid minimum, that is, the quantity δF defined as [see Eq. (11)]

$$\delta F \equiv F[n] - F_0[n_0] \quad (16)$$

becomes negative. If the numerical computation is carried out much beyond this point, large density fluctuations begin to occur. Thus we see that the system is crossing over to an inhomogeneous state characterized by strong density inhomogeneities. These reflect, of course, the incipient formation of a solid.

It is not possible to follow the further evolution of the system through the dynamical equations. First, the time scales involved become extremely long. Second, the presence of large scale density fluctuations introduces numerical instabilities in the solution, which reflect the fact that the basic assumptions of the fluid dynamical model no longer apply when the fluctuations are so large and the system no longer liquidlike. Therefore, a different strategy is needed to extract the information on the charac-

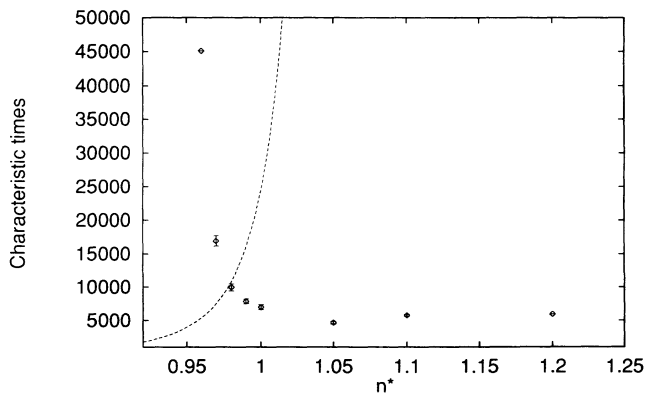


FIG. 1. The characteristic times τ (dashed curve) and τ' (symbols) defined in the text as a function of density.

teristic time, which we call τ' , for this crossover.

The strategy that we employ is the following. We use uniform boundary conditions and numerically integrate the dynamic equations (12) and (13). We monitor several quantities as a function of time, namely, the equal time current correlations, the maximum local density, and the mean field free energy δF [see Eq. (16)]. After an initial transient, we find that the current correlations settle at their equilibrium value as given by the equipartition theorem. The maximum local density and the mean field free energy vary very slowly. The former increases with time, while δF , which after the initial transient is a small positive quantity, shows a slow tendency to drift downward. Eventually this trend accelerates, the maximum density markedly increases, and, simultaneously, the mean field δF crosses zero. We define τ' as the time at which this occurs. Subsequently, δF becomes negative and the maximum local density begins to increase sharply, as explained above.

The values of τ' obtained in this fashion vary from run to run, but only slightly. The average value as a function of density is plotted in Fig. 1. One clearly sees that τ' decreases very sharply with increasing density, until it becomes approximately independent of n^* beyond $n^* \approx 1$. Since τ , on the other hand, increases with density, the curves for τ and τ' cross, at a density $n^* \approx 0.98$. The main feature is the sharp change in τ' which takes place as the density approaches the crossover value $n_x^* \approx 0.95$.

The evolution of the system beyond time τ' can be inferred in the following way. We use the final state configuration at time τ' , as obtained from the dynamical simulation, as the input in a minimization routine that finds the free energy minimum that is closest in phase space to the initial configuration. We then examine the nature of the distribution of the local density in this free energy minimum. If the minimization procedure is applied to configurations obtained when δF is still positive, the flow is invariably to the uniform liquid minimum. In contrast, the minima to which configurations obtained after δF has become negative converge are found to be highly inhomogeneous, with the density concentrated at only a few points.

We have calculated several quantities which characterize the nature of the density distribution at these minima. One of these quantities is a two-point density correlation function $u(r)$. The function $u(r)$ for a particular minimum reached by the system, characterized by the values $\{n_i\}$ of the dimensionless density variables at the points $\{i\}$, is defined as

$$u(r) = \frac{1}{(n_{\text{av}})^2} \frac{\sum_{i>j} n_i n_j f_{ij}}{\sum_{i>j} f_{ij}}, \quad (17)$$

where n_{av} is the average value of n_i and $f_{ij}(r) = 1$ if the separation between the mesh points i and j of the computational lattice lies between r and $r + \Delta r$ and $f_{ij} = 0$, otherwise. This function describes spatial correlations of the *time-averaged* local density at a local minimum of the free energy. It is different from the more familiar pair distribution function $g(r)$, which describes equal-time cor-

relations of the instantaneous local density. The function $u(r)$ is equal to 1 for all r in the uniform liquid minimum. In an inhomogeneous minimum it is not strictly equal to zero for all $r < \sigma$ because the average density near a point where a particle is localized in such a minimum is smeared out over a region of width $\approx 0.3\sigma$. Results for $u(r)$, averaged over five inhomogeneous minima obtained for $n^* = 0.96$, are shown in Fig. 2. The value of Δr used is 0.1σ . The results in Fig. 2 certainly do not correspond to a liquid. The r dependence of $u(r)$ for $r \leq 2.5\sigma$ (information about larger distances is less reliable for our sample size) looks very similar to that of the pair-distribution function of the “slowly quenched” glassy states found in MD simulations [22] of the hard-sphere system. There appear to be significant differences between the form of $u(r)$ and that of the pair-distribution function $g(r)$ of the imperfect crystalline state obtained via nucleation from the liquid state in MD simulations [22]. In particular, $g(r)$ of the nucleated crystal exhibits a pronounced peak at $r \approx 1.6\sigma$, which is just barely present in our data for $u(r)$. Also, the heights of the peaks of $u(r)$ near $r \approx 1.9\sigma$ and $r \approx 2.3\sigma$ appear to be smaller than the heights of the corresponding peaks of $g(r)$ for the nucleated crystalline state. However, these qualitative differences may very well arise due to differences in sample size, boundary conditions, etc. and in the absence of reliable data on the form of $u(r)$ for larger values of r , it is difficult to decide from this information alone whether the inhomogeneous minima obtained in our simulation are glassy or crystalline with defects.

Therefore, to investigate further the nature of the local arrangement of the particles in the inhomogeneous minima, we have calculated the bond-orientational “order parameters” Q_l and W_l , introduced by Steinhardt *et al.* [26]. These quantities are defined for our system in the following way. The mesh points at which the density is peaked in an inhomogeneous minimum of the free energy represent the locations of the hard-sphere particles. Two such particles are considered to be neighbors if the separation between the corresponding mesh points is less than 1.4σ , the approximate value of r at the first

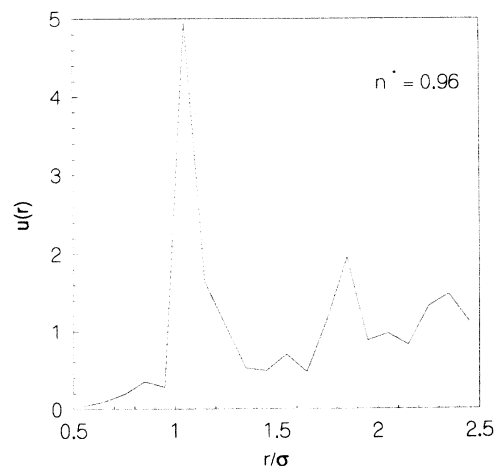


FIG. 2. The function $u(r)$ (see text) averaged over five free energy minima obtained at $n^* = 0.96$.

minimum of $u(r)$. Let \mathbf{R}_i denote the location of such a particle and let $\theta^\alpha(\mathbf{R}_i)$ and $\phi^\alpha(\mathbf{R}_i)$ be the polar and azimuthal angles which specify the orientation of a unit vector pointing from this particle to its α th neighbor. Following Ref. [27], we then define a quantity $Q_{lm}(\mathbf{R}_i)$ for this particle as

$$Q_{lm}(\mathbf{R}_i) \equiv \frac{1}{m_i} \sum_{\alpha} Y_{lm}(\theta^\alpha(\mathbf{R}_i), \phi^\alpha(\mathbf{R}_i)), \quad (18)$$

where m_i is the number of neighbors of this particle and $Y_{lm}(\theta, \phi)$ is a spherical harmonic. The order parameters $Q_l(\mathbf{R}_i)$ and $W_l(\mathbf{R}_i)$ are defined as rotationally invariant combinations of the $Q_{lm}(\mathbf{R}_i)$'s:

$$Q_l(\mathbf{R}_i) \equiv \left(\frac{4\pi}{2l+1} \sum_{m=-l}^l |Q_{lm}(\mathbf{R}_i)|^2 \right)^{1/2} \quad (19)$$

and

$$W_l(\mathbf{R}_i) \equiv \frac{1}{\left(\sum_m |Q_{lm}(\mathbf{R}_i)|^2 \right)^{3/2}} \times \sum_{m_1, m_2, m_3} \begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix} \times \delta_{m_1+m_2+m_3, 0} Q_{lm_1}(\mathbf{R}_i) Q_{lm_2}(\mathbf{R}_i) Q_{lm_3}(\mathbf{R}_i), \quad (20)$$

where $\begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix}$ is a Wigner $3j$ symbol. As pointed out by several authors [26,27], the values of $Q_l(\mathbf{R}_i)$ and $W_l(\mathbf{R}_i)$ for $l = 4$ and 6 provide useful information about the symmetry of the local arrangement of particles surrounding the one at \mathbf{R}_i . In particular, the values of Q_4 , Q_6 , W_4 , and W_6 are $(0.19, 0.57, -0.16, -0.013)$, $(0.036, 0.51, 0.16, 0.013)$, $(0.097, 0.48, 0.13, -0.012)$, and $(0, 0.66, 0, -0.17)$ for fcc, bcc, hcp, and icosahedral clusters, respectively. The results for Q_4 and Q_6 , obtained for the inhomogeneous local minima found in our simulation, are consistent with local fcc order. In particular, the distribution of $Q_4(\mathbf{R}_i)$ peaks near 0.21, which is also the average value of $Q_4(\mathbf{R}_i)$. This value is close to what is expected for a cluster with fcc symmetry. The distribution of $Q_6(\mathbf{R}_i)$ peaks near 0.43 and its average value is close to 0.46. Since all close-packed structures (fcc, bcc, hcp, and icosahedral) have large values of Q_6 , it is not possible to draw any conclusion about the nature of the local bond-orientational order from this observation. The distributions of $W_4(\mathbf{R}_i)$ and $W_6(\mathbf{R}_i)$, obtained for five local minima at density $n^* = 0.96$, are shown in Figs. 3 and 4, respectively. The distribution of W_4 shows significant weight in the region near -0.14 , close to the value (-0.16) expected for a fcc cluster. However, the distribution is fairly wide and the average value of W_4 (≈ -0.026) is rather different from the fcc value. The distribution of $W_6(\mathbf{R}_i)$ exhibits a peak in the neighborhood of the value (-0.013) expected for a fcc cluster, but has significant weight at negative values with a larger magnitude, indicating the presence of a substantial amount

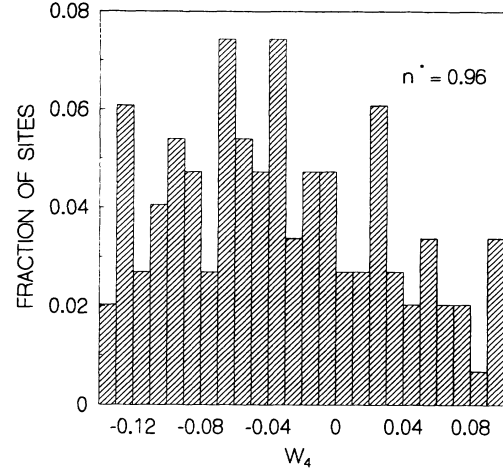


FIG. 3. The distribution of the quantity $W_4(\mathbf{R}_i)$ (see text) averaged over five free energy minima obtained at $n^* = 0.96$.

of local icosahedral order, which is expected [26] in a random close-packed arrangement of hard spheres. The distribution shown in Fig. 4 is qualitatively similar to the distribution of $W_6(\mathbf{R}_i)$ obtained in MD simulations [27] of glassy states of a Lennard-Jones system.

To summarize, our investigation of the nature of the arrangement of the local density in the inhomogeneous minima reached by the system after it makes a transition away from the uniform liquid minimum shows that these minima exhibit a number of features characteristic of a fcc solid. At the same time, some of the features expected for a random close-packed structure also appear to be present. Of course, there is no meaningful difference between the short-range correlations of a glass and those in a very disordered crystal, so that the question of whether our finite-size system is glassy or a very defective crystal is not really well posed.

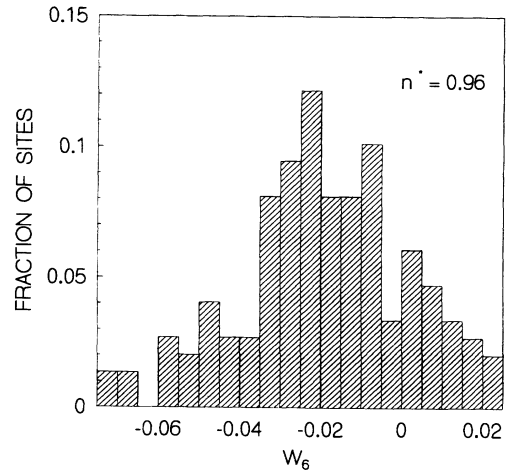


FIG. 4. The distribution of the quantity $W_6(\mathbf{R}_i)$ (see text) averaged over five free energy minima obtained at $n^* = 0.96$.

III. SUMMARY AND DISCUSSION

We first summarize the main results of this study. It is important to recall that for hard spheres the density, rather than the temperature, is the control parameter. From direct numerical integration of a set of Langevin equations which describe the fluctuating hydrodynamics of a dense hard-sphere liquid, we have found a characteristic time scale $\tau'(n^*)$, which corresponds to the amount of time a system, initially prepared in a state close to the uniform liquid minimum of the free energy, spends in the vicinity of this minimum before making a transition to one of the many inhomogeneous local minima of the free energy. This time scale is found to decrease sharply as the dimensionless density n^* is increased above a characteristic value $n_x^* \simeq 0.95$ and it exceeds the time scale of our longest simulation for lower values of n^* . The free energy minima to which the system makes transitions for $n^* > n_x^*$ exhibit, for our finite-size sample, characteristic features expected for *both* crystalline and glassy states. For this reason, we have not been able to determine unambiguously whether they represent crystalline or amorphous states. This, however, is a moot point because there is no meaningful distinction between a finite crystal with many defects and an amorphous solid with short-range crystalline order.

The results described above are in qualitative agreement with those obtained from MD simulations [22] of the hard-sphere liquid. These simulations show that the hard-sphere system cannot be locally equilibrated in the supercooled liquid state if the density n^* exceeds a “critical value” $n_s^* \simeq 1.08$. If the liquid is allowed to evolve in time at a density equal to or higher than n_s^* , then it spontaneously freezes into an imperfect fcc solid during the time scale of the simulation. If, on the other hand, the system is rapidly compressed from the liquid state at a density lower than n_s^* to a density close to the random close packing density ($n^* \simeq 1.23$), then it ends up in an amorphous state. The degree of “glassiness” of this amorphous state increases with the rapidity of the process of compression. These results look similar to the behavior observed in our simulation if we identify the crossover density n_x^* obtained from our simulation with the critical density n_s^* found in the MD simulation. The value of n_x^* obtained from our simulation ($n_x^* \simeq 0.95$) is somewhat different from the result ($n_s^* \simeq 1.08$) of MD simulations. This difference probably arises due to the fact that the value of n^* at which the discretized version of the Ramakrishnan-Yussouff free energy functional used in our calculation exhibits a thermodynamic crystallization transition ($n_f^* \simeq 0.83$) [20,21] is substantially lower than the crystallization density obtained in MD simulations ($n_f^* \simeq 0.943$) [22]. The value of the ratio $n_x^*/n_f^* \simeq 1.14$ obtained in our simulation is, in fact, quite close to the value of n_s^*/n_f^* ($\simeq 1.15$) obtained in the MD simulation.

The fact that in MD simulations carried out at densities equal to or greater than n_s^* the liquid is able to freeze into a state which is close to the crystalline one indicates that the free-energy minima which represent

near-crystalline states must be fairly easy to reach. Otherwise, the system would not be able to bypass the large number of glassy minima whose presence is indicated by the fact that the system does get trapped into one of them if it is compressed rapidly. The same is probably true in our simulation, although we cannot rule out the possibility that the free energy minima into which the system makes a transition after leaving the vicinity of the liquid minimum represent amorphous states rather than imperfect crystalline ones. There are other simple model systems [7] which, according to MD simulation results, exhibit nucleation of the crystalline phase at sufficiently high degrees of supercooling. This suggests that a similar picture is valid for these models too.

The dynamics of these systems in the supercooled regime can then be expected to exhibit the following general behavior: For densities lower than the crossover density n_x^* (alternatively, for temperatures higher than a crossover temperature T_x when the temperature T is the control parameter), the system remains in the vicinity of the uniform liquid minimum during the time scale of observation. The dynamics in this regime is therefore governed by small fluctuations about the liquid minimum. Nonlinear interactions of these density fluctuations lead to a growth of the relaxation time as the density is increased (temperature is decreased). MC theories are believed to provide a good description of the nonlinear feedback mechanism that causes this growth of the relaxation time. Therefore, the dynamic behavior of the system in this regime is presumably well described by MC theories. As the density is increased above n_x^* (the temperature is decreased below T_x), the system undergoes a transition from the liquid minimum to a near-crystalline one within the time scale of observation and remains in its vicinity for all later times. Typically, the value of n_x^* (T_x) is found to be lower (higher) than that of n_c^* (T_c) extracted from power-law fits to the data at lower densities (higher temperatures). For example, the value of n_x^* obtained from MD simulations [22] of the hard-sphere liquid is close to 1.08, whereas power-law fits to the MD data [28] for the diffusion constant [29] and our own data [17,18] for the relaxation time yield values of n_c^* in the range 1.10–1.15. Thus questions about a crossover near n_c^* (T_c) do not arise in these systems and the dynamics over the entire accessible supercooled regime is well described by MC theories. All existing simulation data, including our own, on these systems are consistent with this scenario.

There are, however, many cases to which this simple scenario is not applicable. Many model systems, such as two-component mixtures with spherically symmetric interactions [30–32], do not show any sign of crystallization during the time scale of MD simulations. There is also a large number of experimentally studied systems (so-called good glass-forming liquids [4]) which can be maintained in the liquid state for long times at high degrees of supercooling without the occurrence of crystallization. We close with a discussion of the implications of the results obtained in our simulation on the interpretation of the observed dynamic behavior of such systems.

As T is lowered below the equilibrium freezing tem-

perature T_f , the appropriate free energy functional describing the system is expected to develop a large number of inhomogeneous local minima. Some of these minima have crystalline or near-crystalline structures and the others are amorphous. At temperatures well below T_f , all of these minima are expected to have free energies lower than that of the uniform liquid minimum. The conventional mean field description of metastability suggests that the typical height V of the free-energy barriers which separate the liquid minimum from these inhomogeneous minima should decrease as the temperature is lowered.

Further, there exists a large amount of experimental data (summarized in Ref. [2]) which suggest that the dynamics of the liquid at temperatures close to and lower than T_c is dominated by processes associated with the exploration of a large part of the full phase space (excluding the regions near the equilibrium crystalline states). These observations suggest that the time scale τ' in these systems becomes comparable to typical experimental time scales at a temperature T_x which is higher than T_c . If this is so, then the following scenario is expected for the dynamics of the system in the supercooled regions. For temperatures higher than T_x , a system initially prepared in the liquid state remains in the vicinity of the liquid minimum for long times and its dynamic behavior is well described by MC theories. Since temperatures higher than T_x are substantially higher than T_c , the temperature dependence of the relaxation time in this regime would follow the power-law form predicted in the original version of MC theories. We believe that all temperatures at which a liquid can be equilibrated within the time scale accessible in MD simulations lie in this regime. This would explain the observed agreement between the results obtained from MD simulations [30,31,33] and the predictions of MC theories. The growth of relaxation times in this regime is a purely kinetic phenomenon, not related to or caused by the growth of any spatial correlation. This is consistent with two recent numerical studies [32,34] which looked for a growing correlation length in this regime and did not find any evidence for its existence.

The dynamic behavior for temperatures lower than T_x would be qualitatively different. At these temperatures, the system would make a transition from the liquid minimum to one of the inhomogeneous minima of the free energy during the time scale of observation. In good glass-forming liquids, these inhomogeneous minima are much more likely to be glassy than crystalline. Since these free energy minima are expected to have lower free energies than that of the uniform liquid minimum at tem-

peratures lower than T_x , the liquid minimum would not play any significant role in the dynamics at later times.

Not much information is available about the typical height of the free-energy barriers which separate different glassy minima of the free energy. Approximate calculations [35] and the experimental observation that the system behaves like a liquid over a substantial range of temperatures below T_c suggest that these barrier heights remain finite in the thermodynamic limit at these temperatures. The system would then visit many such minima during its evolution over a long time. It would therefore behave like a liquid over such time scales, in the sense that the time-averaged local density would be uniform. However, the dynamics of the system would be very different in this regime because the decay of density fluctuations will be determined primarily by activated transitions among various glassy local minima of the free energy. Thus the presence of a crossover in the dynamic behavior of the system near a temperature T_x , which is higher than the temperature T_c obtained from power-law fits to the data obtained at higher temperatures, would follow naturally in this scenario. The dynamics of the system at temperatures lower than T_x would have many similarities with that of quenched random systems such as spin glasses, which are known [36] to exhibit a large number of local minima of the free energy at low temperatures. In particular, the suggestion [14-16] that a true thermodynamic phase transition would take place at a lower temperature T_g if thermodynamic equilibrium could be maintained all the way down to this temperature would become a distinct possibility in this scenario.

In the absence of any direct corroborative evidence, this description of the dynamics of good glass-forming liquids in the supercooled region remains essentially speculative. It would be very interesting to look for evidence for or against this scenario in experiments and simulations.

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