Time scales for transitions between free-energy minima of a dense hard-sphere system

Chandan Dasgupta
Department of Physics, Indian Institute of Science, Bangalore 560012, India

Oriol T. Valls
*School of Physics and Astronomy and Minnesota Supercomputer Institute, University of Minnesota,
Minneapolis, Minnesota 55455*

Time scales associated with activated transitions between glassy metastable states of a free-energy functional appropriate for a dense hard-sphere system are calculated by using a new Monte Carlo method for the local density variables. In particular, we calculate the time the system, initially placed in a shallow glassy minimum of the free-energy, spends in the neighborhood of this minimum before making a transition to the basin of attraction of another free-energy minimum. This time scale is found to increase as the average density is increased. We find a crossover density near which this time scale increases very sharply and becomes longer than the longest times accessible in our simulation. This time scale does not show any evidence of increasing with sample size.

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I. INTRODUCTION

Although the behavior of supercooled liquids near the glass transition has been studied extensively over several decades [1,2], a complete understanding of some of the observed phenomena is not yet available. Existing theories of the glass transition may be broadly classified into two categories. The first category consists of theories that describe the glass transition as a purely dynamic phenomenon. Mode coupling (MC) theories of the glass transition [3] are the most prominent ones in this class. In MC theories, the slowing down of the dynamics near the glass transition is attributed to a nonlinear feedback mechanism arising from correlations of density fluctuations in the liquid. MC theories provide a detailed and qualitatively correct description of the dynamic behavior observed in experiments [4] and numerical simulations [5] over a temperature range that covers the first few decades of the growth of the characteristic relaxation time of so-called "fragile" [2] liquids in the supercooled regime. The original version of MC theories [6,7] predicts a power-law divergence of the relaxation time at an *ideal glass transition temperature* T_c. Experimentally, however, this divergence is not found, and the predictions of MC theories do not provide a correct description of the actual behavior at temperatures close to or lower than the T_c extracted from power-law fits to the data at higher temperatures. It is generally believed that the breakdown of conventional MC theories at temperatures near T_c arises because "activated processes" become important at such temperatures. The conventional MC formalism has been generalized [8,9] to incorporate in a phenomenological way some of the effects of activated hopping processes, and results of recent light scattering experiments [10] have been interpreted in terms of this extended version of MC theory. However, the microscopic nature of these activated processes has not been fully elucidated so far.

In the second class of theories [11] of the glass transition, the starting point is the assumption that the free energy of the liquid, expressed as a functional of the local average density, develops a large number of "glassy" local mimima as the temperature is decreased below the equilibrium crystallization temperature. These glassy minima, characterized by an inhomogeneous but aperiodic distribution of the local density, are distinct from the (metastable) liquid minimum where the average density is uniform and from the (globally stable) crystalline minimum where the average density is a periodic function of position. During a quench from the liquid state, the system gets trapped in one of these glassy minima from which it eventually relaxes. The relaxation is slow because it involves thermally activated transitions over free-energy barriers. In this picture, therefore, the slow dynamics near the glass transition is attributed to activated transitions among metastable glassy minima of the free energy. This description is similar to that developed in recent years for a number of quenched random systems such as spin glasses [12]. Several authors [13–16] have taken this analogy further and suggested that the behavior observed near the glass transition is the precursor of a true thermodynamic phase transition that would take place at a temperature lower than the conventional glass transition temperature T_g (defined [2] as the temperature at which the viscosity reaches a value of 10^{13} poise) if one could maintain thermodynamic equilibrium all the way down to this temperature. This scenario, however, remains speculative because the existence of such a phase transition has not yet been demonstrated convincingly for any physically realistic system.

Recently, we have carried out a number of investigations [17–20] that suggest that elements of these two apparently dissimilar descriptions of the glass transition should be combined for the development of a full understanding of the observed phenomena. This conclu-

sion was based on the results of a numerical study of a set of Langevin equations that describes the nonlinear fluctuating hydrodynamics of a dense hard-sphere liquid. Information about the static structure of the liquid was incorporated in the Langevin equations considered by us through a free-energy functional of a form suggested by Ramakrishnan and Yussouff [21]. From previous studies [22,23], it is known that this free-energy functional develops a large number of glassy local minima at densities higher than the equilibrium crystallization density. [The control parameter for a hard-sphere system is the dimensionless density $n^* \equiv \rho_0 \sigma^3$, where ρ_0 is the average number density and σ is the hard-sphere diameter; increasing (decreasing) n^* has the same effect as decreasing (increasing) the temperature of systems for which the temperature is the relevant control parameter.] Our numerical study of the dynamics showed [17,18] that for relatively small values of n^* ($n^* < 0.95$), a system initially prepared in the liquid state remains in the vicinity of the metastable liquid minimum during the time scales accessible in the simulation. The dynamic behavior observed in this regime was found to be in good qualitative agreement with the predictions of MC theories. At higher densities (specifically, for n^* greater than a "crossover density" $n_x^* \approx 0.95$), we found [19] a qualitatively different behavior. At these densities, 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 glassy minima of the free energy. This observation implies that the long-time dynamic behavior for $n^* > n_x^*$ is not governed by small fluctuations near the uniform liquid minimum: the glassy local minima of the free energy have to be taken into account in a proper description of the dynamics. In particular, activated transitions among these glassy minima are expected to play a crucial role in the dynamic behavior in this regime. Although a different Langevin simulation method could in principle be developed to study the dynamics in this density range, the methods of Refs. [17–20], which are based on a liquidlike formulation, are not physically appropriate for such a study. In practice, attempts to use these methods at higher densities lead to numerical instabilities associated with large-scale density fluctuations present at the inhomogeneous minima. For this reason, our Langevin dynamics cannot be carried all the way to equilibration at densities higher than n_x^*, although the early and intermediate stages of the system's evolution can still be studied [19]. Therefore, we develop here an alternative method to study the dynamics of the same system at higher densities.

In this paper, we present the results of a study in which we develop a Monte Carlo method and use it to determine the characteristic time scales of transitions between glassy free-energy minima for $n^* \geq n_x^*$. The Monte Carlo method, described in detail in the following section, is much simpler to implement than the Langevin simulation method. The numerical instabilities mentioned above are not present in the Monte Carlo procedure used by us. This simplification, however, is achieved at the cost of abandoning the physical (coarse grained) dynamics embodied in the Langevin equations (that is, the nonlinear

hydrodynamics equations) in favor of a somewhat artificial Monte Carlo dynamics. In particular, some of the results obtained in the present study indicate that the nonlinear feedback mechanism that causes the growth of relaxation times in the MC description is not operative when the artificial Monte Carlo dynamics is used. However, since the Monte Carlo method obeys the principle of detailed balance, it should provide a correct description of the process of thermal activation over free-energy barriers. Therefore, a Monte Carlo calculation of the characteristic time for transition from one local minimum of the free energy to another one can be expected to provide a correct estimate of the height of the free-energy barrier that separates the two local minima.

In this work, we use this Monte Carlo dynamics to study the process of thermally activated transitions from a shallow glassy minimum of the free energy to regions near other, more ordered minima. On general grounds, one expects that a system initially prepared in a glassy state with relatively high free energy would evolve toward a crystalline state that corresponds to the global minimum of the free energy at the densities of interest here. It is also expected that the transition of the system from the initial glassy minimum to a crystalline one would not, in general, be a single-step process: the system would sample a number, possibly large, of additional free-energy minima during its evolution toward equilibrium. This manifestly nonstationary process of approach to equilibrium is what we are interested in here. In our study, we start the system off in one of the shallow glassy free-energy minima obtained from our Langevin work [19] and use the Monte Carlo procedure to evolve it in time (as measured in Monte Carlo steps) until it makes a transition to a different free-energy minimum. Using a set of criteria described in detail in the next section, we find that the new minima to which the system moves generally have a lower free energy and are more "crystalline." The characteristic time for such transitions increases as the density is increased. We find a second "crossover" density n_y^* near which the time for transition from one glassy minimum to another increases very sharply and becomes longer than the times accessible in our simulation. A limited investigation of the dependence of this barrier crossing time scale on the size of the simulation sample does not show any evidence of its growing with increasing system size. As far as we know, this study is the first one that provides explicit and unambiguous information about the time scales for transitions between different glassy free-energy minima of the hard-sphere system. In molecular dynamics (MD) simulations [24,25], which provide most of the existing numerical data on the dynamics of this system, it is not possible to determine unambiguously whether the system fluctuates near the uniform liquid minimum of the free energy or near an inhomogeneous glassy minimum at a particular instance of time. For this reason, MD simulations do not provide information about the time scales associated with transitions between different glassy minima.

The remaining part of this paper is organized as follows. Section II contains descriptions of the Monte Carlo method, the procedure used by us to monitor the tran-

sition of the system from one local minimum to another, and the criteria we use to specify the degree of crystalline order present in a free-energy minimum. The results obtained from this work are described in detail in Sec. III. In Sec. IV we summarize the main conclusions, compare our findings with MD results, and discuss the implications of our results on the interpretation of experimental and numerical data on the dynamics of supercooled liquids.

II. METHODS

The basic ingredient of our study of the dynamics of a dense hard-sphere system is the functional relating the free energy F to the density field $\rho(\mathbf{r})$. We take for this the Ramakrishnan-Yusouff [21] (RY) functional:

$$F[\rho] = F_l[\rho_0] + k_B T \left[\int d\mathbf{r}\{\rho(\mathbf{r})\ln[\rho(\mathbf{r})/\rho_0] - \delta\rho(\mathbf{r})\} \right.$$
$$\left. - (1/2) \int d\mathbf{r} \int d\mathbf{r}' C(|\mathbf{r} - \mathbf{r}'|)\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}') \right], \quad (2.1)$$

where $\delta\rho(\mathbf{r}) \equiv \rho(\mathbf{r}) - \rho_0$ is the deviation of the number density from its average value ρ_0, k_B is Boltzmann's constant, F_l the free energy of a uniform liquid of density ρ_0, T the temperature, and $C(|\mathbf{r} - \mathbf{r}'|)$ is the direct pair correlation function [26], which is taken to be given in the Percus-Yevick [26] approximation for hard spheres. It can then be expressed in dimensionless form in terms of the density parameter $n^* \equiv \rho_0\sigma^3$.

In our previous work [17–20] we studied the dynamical properties of this model by introducing the appropriate Langevin dynamics. Briefly, one introduces the additional current field $\mathbf{g}(\mathbf{r})$ and the total free energy:

$$F_{Tot}[\rho, \mathbf{g}] = (m_0/2) \int d\mathbf{r} \frac{|\mathbf{g}(\mathbf{r})|^2}{\rho_0} + F[\rho], \quad (2.2)$$

and then one proceeds to derive the Langevin equations by using the fields ρ and $\mathbf{g}$ as the "slow" variables, evaluating the needed Poisson brackets, and adding the appropriate dissipative and noise terms. This derivation [20] results in a system of integro-differential equations with stochastic terms, which can then be solved numerically.

The Langevin formulation of the dynamics is appropriate to the physical situation where deviations of the local density from its spatial average are small. As was shown in Ref. [19], the Langevin dynamics used in our previous studies is inadequate when very large scale density fluctuations are present. In practice, this means [19,20] that the Langevin dynamics will lead to equilibration at very long times for densities $n^* \leq n_x^*$, where $n_x^* \simeq 0.95$. At higher densities, if one starts with liquidlike initial conditions, the Langevin dynamics does not evolve all the way to equilibrium: after a certain time has elapsed, the density inhomogeneities grow strong, indicating a transition of the system from the vicinity of the uniform liquid minimum to the neighborhood of one of the inhomogeneous local minima of the free energy. As was seen in Ref. [19], the time τ' at which this transition occurs can

be characterized as the time at which the quantity δF, defined as

$$\delta F \equiv F[\rho] - F_l[\rho_0], \quad (2.3)$$

becomes negative. This quantity can be evaluated as a function of time given the density distribution at that time and Eq. (2.1). This has a simple physical interpretation: at higher densities the system is trying to reach an inhomogeneous state, which may be crystalline or glassy. The value of the free energy when this inhomogeneous state is reached will be, at higher densities, lower than the free energy of the reference homogeneous liquid. Therefore δF will start to become negative as soon as the larger local density fluctuations characteristic of a crystalline or glassy state become prevalent.

An alternative method to study the dynamics of the system with free energy (2.1), which is valid at times $t > \tau'$, must be sought. Here we use a Monte Carlo dynamics implemented in a way that we now describe:

We consider a computational lattice as used for the Langevin study: a cubic lattice with lattice constant h. The lattice constant of the computational lattice is taken to be incommensurate with σ, which has the effect of inhibiting the formation of an ordered crystal. In this lattice the density field is described as a set of N^3 numbers ρ_i representing the density at each lattice point multiplied by h^3. We sweep the lattice considering each site i. Given the site i we select at random a site j, which is among the neighbors of i, that is, such that the distance between these sites is less than the hard-sphere diameter σ. We then evaluate the quantity $s_{ij} = \rho_i + \rho_j$, generate a random number p distributed uniformly between 0 and 1, and attempt to change the values of ρ_i and ρ_j to ps_{ij} and $(1 - p)s_{ij}$, respectively. Clearly this exchange conserves particle number. The exchange is accepted or rejected according to a standard Metropolis algorithm with

$$W_{ij} = \exp -[\lambda\beta\Delta F], \quad (2.4)$$

where ΔF is the change in the free energy F as given in (2.1), which would be produced by the attempted exchange, β the usual inverse temperature, and λ the appropriate ratio between the number of lattice degrees of freedom and the number of spatial degrees of freedom of the actual continuum system: $\lambda \equiv 1/(3n^*a^3)$, where $a \equiv h/\sigma$ is the ratio of the computational lattice constant to the hard-sphere diameter.

In an approximate sense, this dynamics may be thought to represent the diffusion processes that would characterize the later stages of the evolution of the system. It has two additional advantages: it can handle density fluctuations of any size, and it is algorithmically very efficient. One inconvenience of the procedure we follow, however, is that the Langevin and Monte Carlo time scales are not directly comparable. The difficult question of their comparison has been discussed in the past for simpler systems [27,28]. We will return to this question in Sec. III. For many purposes it suffices to make comparisons in terms of time scales obtained from the same dynamics, and we take this course when possible.

As follows from the Introduction, the present study covers densities $n^* \geq 0.94$. In this density range, one can proceed with Langevin dynamics until one reaches the point where $\delta F = 0$, as explained above. We then construct our initial conditions for the Monte Carlo dynamics in the following way: we consider the state of the system at Langevin time τ' (the Langevin simulation having been started [17,18] from a perfectly disordered state), and, as in Ref. [19], we consider the density configuration of the system at that time. We use this configuration as the input in a minimization routine [22] that determines the minimum in the free energy F [Eq. (2.1)], which is closest to that configuration in the sense that it is the local minimum the system moves to when one attempts to find a minimum by making successive small changes in the density in a way that always lowers the free energy. The free-energy minimization procedure used by us is similar in spirit to the conjugate gradient method developed by Weber and Stillinger [29], but with a crucial difference. The work of Weber and Stillinger involves finding local minima of the Hamiltonian of the system under study, whereas our procedure finds local minima of the free energy which are obviously the correct quantity to consider at nonzero temperatures. The free-energy minimum obtained as the output of the minimization routine corresponds, evidently, to a negative value of δF when the input is chosen as described above. This configuration is then that which corresponds to the local minimum of the free-energy "basin" in configuration space that the system is in when the density fluctuations begin to be large, that is, when the system has dynamically evolved away from the uniform liquid minimum. The configurations at these local minima are [19] glasslike. We take these local minimum configurations (obtained at each density studied) as the initial configurations for the Monte Carlo simulations in the main studies reported in this work. Thus, our initial conditions correspond to having the system in a local minimum of F, which is close to the liquid state. Our objective here is to find out how long the system remains in the basin corresponding to such minima as it evolves. We call the time characterizing this evolution τ_1 and it is one of the main quantities of interest here. To determine τ_1 we begin our Monte Carlo study with the initial conditions described above. As we proceed, we monitor the value of the free energy, and other relevant quantities. At periodic intervals, we run the minimization routine to find out if it still leads to the initial configuration. When it no longer does (the precise criteria will be given in the next section), we know that the system has evolved to another basin of the free energy, and that it will eventually evolve to another, more ordered state after possibly sampling a number of additional free-energy regions.

We emphasize that in the work described here, the time evolution of the system is simulated by the Monte Carlo dynamics only. The Langevin dynamics used in our previous studies [17–19] is used (in conjunction with the free-energy minimization routine, as described above) only in the determination of the initial configurations to be used in the Monte Carlo simulations. Since our goal in the present study is to estimate the characteristic time

for thermally activated transitions from shallow glassy minima to deeper, more ordered ones, a proper choice of the initial state is important. However, the particular way in which the initial state is obtained should not matter. The combination of Langevin dynamics and free-energy minimization described above provides a convenient way of locating appropriate initial configurations. This procedure, however, is obviously not unique. In fact, as described in the next section, we also consider initial configurations corresponding to similar (negative) values of δF and density distributions to those described above, but obtained simply by a random search for local minima instead of through the Langevin intermediate step. We also note that in the simulations described in this paper, the free-energy minimization procedure is used only to determine the minimum near which the system fluctuates at a given time: it plays no role in the simulation of the time evolution of the system.

The free energy F has a large number of minima at the densities of interest. The state of the system at such minima is to a varying degree glassy or crystalline, and it is important to have at least a rough criterion to separate the more glassy from the more ordered states. The minima can be characterized first by the value of the free energy. This is conveniently done for computational (i.e., finite) systems in terms of the dimensionless free energy per particle f:

$$f[\rho] = \beta F[\rho]/(n^* N^3 a^3). \qquad (2.5)$$

One expects that smaller (i.e., more negative) values of f would correspond, at the same density, to more ordered states. One would like to verify and quantify this statement. The primary detailed measure of order is the spatial correlation function $u(r)$ [as defined in Eq. (17) of Ref. [19]], which can be calculated from the density distribution at each minimum. This function describes correlations of the time-averaged local densities at two points as a function of their separation. In Fig. 1 we show two examples (solid and dashed lines) of this correlation function for two different free-energy minima at the same density ($n^* = 0.95$). These were obtained numerically for the same computational lattice ($N = 15$ and $a = 1/4.6$) as was used in our previous Langevin work. One can see from this figure that the height of the first maximum is not a very good measure of the degree of ordering, but that the second and particularly the third maxima are markedly more prominent for the minimum with the lower free energy. While the two minima shown in these two curves have different degrees of short-range order, neither of them is truly crystalline. To make this point clear, we have shown in Fig. 1 (symbols and dotted line) the function $u(r)$ for a perfectly crystalline minimum obtained for a sample with $N = 12$, $a = 0.25$, and the same density. (We could not find any exactly crystalline minimum for samples with $N = 15$ and $a = 1/4.6$, due to the incommensurability [17,18] of the computational lattice with a fcc one.) The function $u(r)$ for the crystalline minimum has very sharp peaks at values of r corresponding to the lattice vectors of a fcc structure and is very close to zero at all other values of r. These
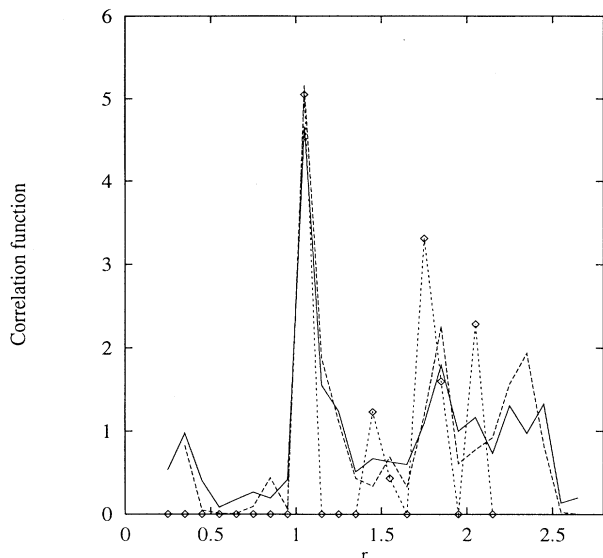
FIG. 1. Radial correlation function [called $u(r)$ in the text] as a function of distance r (measured in units of σ). All curves correspond to the same density $n^* = 0.95$. The solid and dashed lines (without symbols) correspond to glassy states with $N = 15$ and $a = 1/4.6$. The solid line refers to a minimum having a free energy per particle $f = -1.78$, while the dashed line is for the case of a lower f, $f = -2.12$. For comparison we include also a plot (symbols and dotted line) corresponding to the crystalline case with $N = 12$ and $a = 0.25$.

FIG. 2. Correlation between three measures of degree of order and the free energy per particle at a given minimum. This plot is for $n^* = 0.95$, similar plots can be made at other densities. Three different quantities are plotted as functions of the free energy per particle f. These quantities are: Top (diamonds and solid line), the height of the second peak in $u(r)$ times ten; middle (squares and short dashes), percentage density increase (see text); bottom (crosses and long dashes), height of the first peak in $u(r)$ times two. The factors are chose so as to clearly separate the three plots. The symbols are in all cases the actual results for nine different free-energy minima and the lines just connect the dots.

features are clearly very different from what is found for the other two minima.

One can proceed with this study in a more systematic way. In Fig. 2 we show, for the same density and computational lattice as in the previous figure, the relation between the value of the free energy at a given minimum and three different measures of the degree of order at that minimum. The comparison includes nine different minima. The quantities plotted are the height of the second peak in $u(r)$ (which is one-tenth of the quantity represented by the top line in the figure), the increase in the average density that occurs as one evolves (under the minimization procedure) from the homogeneous liquid state to the minimum (middle line) and the height of the first peak (which is half of the value plotted as the lower line). We can see that, while the relationship is not simple, it is generally true that lower free-energy values are associated with a higher degree of order. In particular, the free-energy minimum of Fig. 1 with $f = -2.12$ corresponds to a state at the left end of Fig. 2, whereas the one with $f = -1.78$ sits at the right end. In this work, when we refer to glassy free-energy minima corresponding to "more ordered" or "more disordered" states, we mean states near the left and right ends, respectively, of Fig. 2 or of the corresponding situations at other densities. A similar classification of glassy states on the basis of the degree of short-range positional order was also made in MD studies [24] where it was found that glassy states obtained after a fast quench from high temperatures or low densities generally exhibit a lower degree of positional order than those obtained after a slow quench.
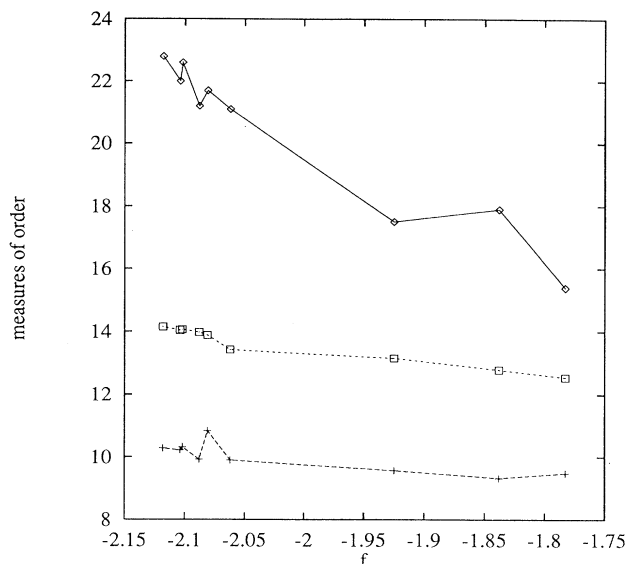
The differences in the structures of glassy minima corresponding to the two ends of Fig. 2 are, in fact, quite similar to the differences in the structures of the "slow" and "fast" glasses of Ref. [24]. As explained above, our Monte Carlo runs use one of the more disordered states (typically those obtained from Langevin dynamics and the procedure explained above) as the initial condition. We turn now to the results in the next section.

III. RESULTS

In this section we present the results obtained from the Monte Carlo simulations. One of our main objectives is to find out whether our hard-sphere system, if initially quenched in a free-energy minimum corresponding to a glassy state, will evolve towards a more ordered final state.

Except for the investigation of size effects described later in this section, our Monte Carlo work was done for the same system as the Langevin work of Refs. [17–20]. We use the same lattice size $(N = 15)$, the same incommensurate value of a, and, in all $N = 15$ cases, an initial state obtained from the same Langevin runs using the procedure indicated in the previous section.

We focus on the quantity τ_1. As explained in the previous section, this quantity measures the time the system spends in an initial, shallow, "glassy" minimum. To de-

fine τ_1 and to evaluate it explicitly we follow the following algorithm: We begin the MC simulation, with the initial conditions as described, and at periodic intervals t_i separated by intervals $\Delta t \equiv t_{i+1} - t_i$ (all times from now on are given in terms of Monte Carlo attempts per site, MCS), we save the current density configuration and run the minimization routine to find out if the system is still within the initial basin. We wish τ_1 to represent the time at which the system definitely leaves the initial basin to move to other regions of phase space on its way, eventually, to a more ordered state (presumably after sampling a large number of minimum basins in phase space). To prevent fluctuations, arising from situations where the system is evolving along saddle type regions separating minima, from giving incorrect small values of τ_1 for a given run, we define τ_1 algorithmically as the time after which the system is found by the minimization procedure at a minimum different from the initial one for $N_i = 3$ consecutive times t_i with $\Delta t = 400$ MCS. By continuing the runs to longer times, we find that with this criterion the system does not return to the basin of attraction corresponding to the initial minimum. Such continuing runs were used to determine by trial and error the appropriate values of Δt and of N_i. In addition to thus representing the desired physical quantity, this procedure has the advantage of reducing run to run fluctuations.

The results for τ_1 obtained by the above procedure, and for the system and lattice sizes described, are plotted in Fig. 3. For $n^* \leq 0.98$ the symbols plotted represent the average over five runs, and the error bars the standard deviation. For $n^* = 0.99$ only one run out of five led to a finite τ_1, as defined above, with a value corresponding to the lower end of the arrowlike "error bar" plotted. The other runs yielded only lower bounds $\tau_1 > 120\,000$ MCS, that is, the system remained in the domain of attraction of the initial minimum. We did not need to calculate τ_1 for $n^* \leq 0.93$ because our previous studies [17,18] showed that for such densities, a system initially prepared in the liquid state, remains in the vicinity of the uniform liquid

minimum for all time scales accessible in our Langevin simulations. We see from Fig. 3 that τ_1 increases slowly for $0.94 \leq n^* \leq 0.98$, but it then grows extremely fast and at the vicinity of $n^* = 0.99$ it becomes longer than any reasonable measurement time. Thus, there will be a density $n_y^* \approx 0.99$ such that, if the system is quenched to a density $n^* > n_y^*$, then it cannot reach the equilibrium crystalline state in time scales accessible in simulations. It would be interesting to determine whether the observed growth of τ_1 with increasing density is described by one of the various functional forms (e.g., the Batchinski-Hildebrand [30] form, the Vogel-Fulcher [31] form, and the power-law form) used in the literature to describe the growth of time scales in dense liquids. Due to the limited accuracy and range of our data for τ_1, we did not attempt to fit them to these functional forms. Such fits would be meaningful only if much more accurate data for τ_1 spanning several decades of its growth were available. Given the computational complexity of the numerical method used here (approximately 200 CPU hours of a Cray 2 machine were required for carrying out the calculations described here) and the very high degree of statistical accuracy required to distinguish among the proposed forms, generation of such data appears to be computationally impossible at the present time.

As we monitored the system to evaluate τ_1, we also kept track of other relevant quantities. In particular, we continued many of the runs to times well beyond τ_1 to verify the condition of nonreturn to the vicinity of the initial state. We found that over time scales of the order of several times the value of τ_1, the system sampled several free-energy minima (more accurately, the basins associated with several free-energy minima). The characteristic time spent in one of these basins showed a wide variation, with values ranging from a small fraction of τ_1 to several times the value of τ_1. The results seem to hint at the existence of a continuum or a hierarchy of time scales, rather than a single scale characterized by some dwelling time.

We monitored also the free energy F as a function of time. The results are very suggestive. We show here the results for four runs, two at $n^* = 0.94$ (Fig. 4) and two at $n^* = 0.95$ (Fig. 5). We see that the free energy first increases, and eventually begins a slow decrease, passing therefore through a rather shallow but definite maximum. We find that the time at which this maximum occurs corresponds to a very good approximation to the value of τ_1 obtained for the particular run under consideration. In other words, at times earlier than that at which the maximum in F occurs, the minimization routine indicates that the system is still in the phase-space neighborhood of the initial minimum, while for times beyond the maximum, it is elsewhere in phase space. This meshes well with the intuitive observation that the system must cross over some free-energy barrier in order to move from basin to basin in phase space. The lack of clearly defined maxima at latter times in these two plots agrees well with the remark in the preceding paragraph that there is no statistically well defined single time scale for the dwelling time in different basins beyond the original one.

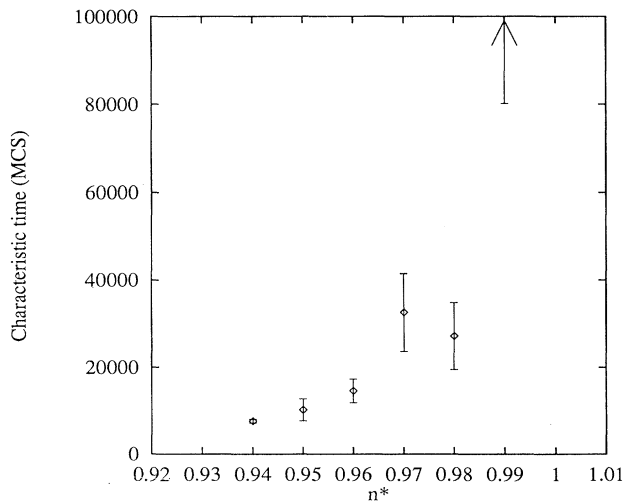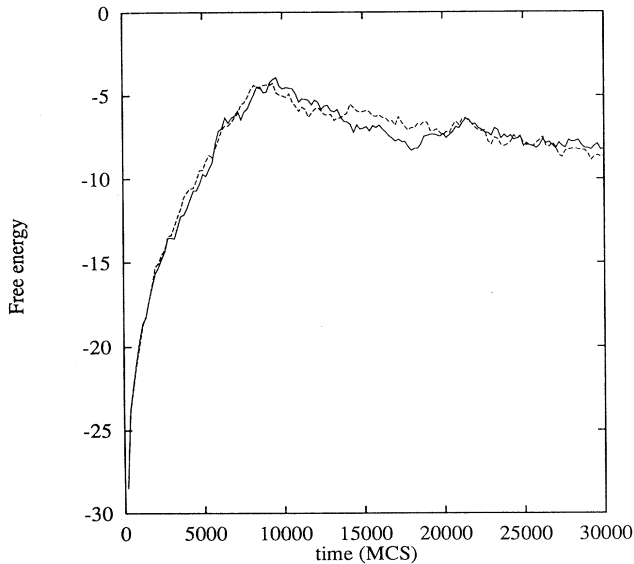We have also monitored the correlation function $u(r)$

FIG. 3. Quantity τ_1 as specified in the text, plotted as a function of density. At $n^* = 0.99$ the lower end of the arrow represents a lower bound

FIG. 4. Dimensionless free energy βF plotted vs time for two runs at $n^* = 0.94$.

at all the different minima reached by the system in any given run. With a few exceptions, the new minima to which the system moves under the Monte Carlo dynamics are found to have lower free energy and a higher degree of order than the minimum from which the run was started. All the minima corresponding to points near the left end of Fig. 2 were obtained in this way. Although the minima near which the system fluctuates for times greater than τ_1 usually have free energies lower than that of the initial minimum, the measured free energies plotted in Figs. 4 and 5 for values of $t > \tau_1$ are higher than the free energy at $t = 0$. This result, which at first may seem paradoxical, may be understood in the following way. The state of the system at time $t = 0$ coincides with the configura-
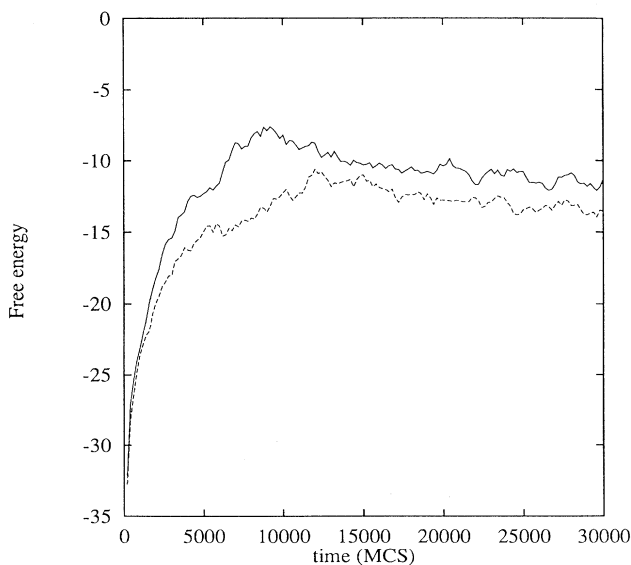

FIG. 5. Dimensionless free energy βF as in Fig. 4, but for $n^* = 0.95$.

tion at a free-energy minimum. So, the free energy at $t = 0$ shown in Figs. 4 and 5 is just the free energy of the minimum from which the Monte Carlo run is started. At later times, the Monte Carlo procedure generates fluctuations about the free-energy minimum. Therefore, the free energy measured at a later time may be viewed as the sum of the free energy of the minimum near which the system happens to reside at that time and the free energy associated with fluctuations about this minimum. The second contribution, which is always positive, may be roughly estimated to be about $1.5k_BT$ per particle in a harmonic phononlike approximation. Due to the presence of this additional contribution, the measured free energy at times greater than τ_1 remains higher than the free energy at $t = 0$ unless the free energy of the minimum near that the system fluctuates at these later times is very much lower than that of the initial minimum. This may happen at very long times when the system reaches the vicinity of the crystalline state. The time scales accessible in our simulations are, however, too short for this behavior to be seen. In our simulations, we can study only the initial part of the evolution of the system toward the crystalline state that is the true equilibrium state of the system at the densities considered here.

We turn now to the question of the dependence of τ_1 on the size of the simulated sample. It is important to check whether τ_1 is size independent or not. If, for example, it was found that τ_1 increases with system size, that is, if it were divergent in the thermodynamic limit, then we would have to conclude that in the region of interest the crystalline state is never accessible. This is not the case. We have computed τ_1 for different sample sizes at the density $n^* = 0.96$, a value that is in the intermediate range of densities considered. Since the Langevin results are available only for samples with $N = 15$ and it would have been too expensive to obtain the necessary results for other values of N, we used for our initial conditions for $N \neq 15$ the density distribution at shallow free-energy minima (as explained in connection with Fig. 2) obtained from a large number of minima located using the minimization routine and random initial conditions. It was not possible to obtain shallow minima with glassy density distributions for the same value of a used at $N = 15$ because the commensurability conditions are different for different values of N. However, the results quoted here for $N = 12$ and $N = 18$ do correspond to the same value of a (=0.25) and can therefore be directly compared with each other. The correlation functions for the minima actually used are shown in Fig. 6. One can see that despite the difference in size the distributions are extremely similar. We again averaged the results for τ_1 over five runs and we found that this quantity is, within statistical error, independent of size, even though the number of particles is 3.375 times greater for the larger value of N. We conclude then that at least for $n^* < n_y^*$, τ_1 remains finite in the thermodynamic limit. This result is in agreement with suggestions made in earlier studies [11,32] of similar systems.

Considering the results described above and taking also into account those obtained from our previous work [17–20], we obtain the following description of the
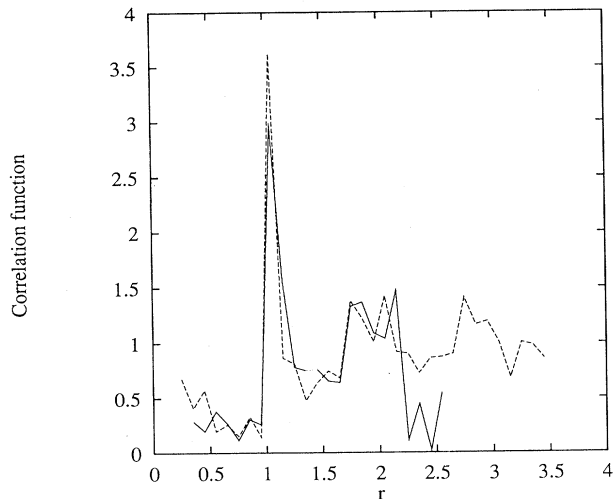
FIG. 6. The radial correlation functions $u(r)$ for the free-energy minima used as initial conditions in the Monte Carlo simulations at sizes $N = 12$ (solid line) and $N = 18$ (dashed line). The density is $n^* = 0.96$ in both cases.

dynamics of a dense hard-sphere system in a rather wide density range. For the discretized version of the Ramakrishnan-Yussouff free-energy functional considered by us, the equilibrium transition to a crystalline phase occurs at a density $n_f^* \simeq 0.83$ [22,23]. The uniform liquid minimum of the free energy, however, remains locally stable for a large range of densities above n_f^*. Our Langevin work [17,18] shows that a system initially prepared in the liquid state remains in the direct vicinity of the liquid minimum over all accessible time scales if the density is lower than a *first crossover density* $n_x^* \simeq 0.95$. The dynamic behavior for $n^* < n_x^*$ is, therefore, governed by small fluctuations about the uniform liquid minimum. The results of our previous study [17,18] show that the dynamics in this regime is described fairly well by MC theories. For $n^* > n_x^*$, on the other hand, the system moves away from the liquid minimum over numerically accessible time scales [19]. The minima to which the system moves are usually found to be glassy according to the criteria described in Sec. II. At subsequent times, the system moves toward states with a higher degree of crystalline order because such states generally have lower free energy. This process is slow because it involves thermally activated transitions over free-energy barriers. Our present calculation shows that the typical time scale τ_1 associated with this process increases with density. The initial increase of τ_1 with n^* is slow, but it increases very sharply as n^* approaches a *second crossover density* $n_y^* \simeq 0.99$. At higher densities, the time scale τ_1 becomes longer than the longest time scales accessible in our simulation. This observation implies that a hard-sphere liquid quenched from a low density to a density $n^* > n_y^*$ would remain stuck in a glassy free-energy minimum for all time scales accessible in numerical simulations. For $n^* < n_y^*$, on the other hand, the system would move to states with a higher degree of crystalline order during simulational time scales. Our calculation indicates that

the time scale τ_1 is an intrinsic property of the system in the sense that it does not depend strongly on the size of the system considered in the simulation. Therefore, the general description outlined above should remain valid in the thermodynamic limit.

We also carried out a limited study of the Monte Carlo dynamics of the system in the vicinity of the uniform liquid minimum for a number of densities in the range $0.93 \leq n^* \leq 0.99$. In these simulations, the initial state of the system was taken to be uniform. The Monte Carlo procedure was then used to simulate the dynamic behavior for a few hundred MCS. The relaxation time obtained from the observed initial decay of the nonequilibrium density autocorrelation function from the uniform state (defined as $\langle [\rho_i(t_0 + t) - \rho_0 h^3][\rho_i(t_0) - \rho_0 h^3] \rangle$, where the average is over all sites i and a range of initial t_0) was found to be very short (a few MCS) and only weakly dependent of the density for values of n^* in the range studied. Thus, the nonlinear feedback mechanism of MC theories that predicts a rapid growth of the relaxation time of small-amplitude density fluctuations near the liquid minimum does not appear to be operative for the Monte Carlo dynamics. An explanation of this result, which may appear surprising, is provided in the next section. Since the dynamic behavior of the system in the vicinity of the liquid minimum was studied in detail in our previous work [17–20] using a dynamics (Langevin equations of fluctuating hydrodynamics) that is physically appropriate for this liquidlike situation, we did not think it useful to carry out a more detailed study of the Monte Carlo dynamics, which is clearly not the appropriate one for describing the physics in this regime.

We now address the issue of relating the Monte Carlo time unit (1 MCS) to the Langevin time unit, which is close to [17] the Enskog collision time. It would appear that a "calibration" of the Monte Carlo time step might be obtained by comparing the results obtained for the same physical time scale by using both Monte Carlo and Langevin dynamics. As mentioned in the Introduction, the Langevin scheme cannot be used to calculate the time scale τ_1. However, the relaxation time of small-amplitude density fluctuations near the liquid minimum can be calculated for both Monte Carlo and Langevin dynamics, and we have the results for the Langevin relaxation time for $n^* \leq 0.93$ from our previous work [17,18] and for the Monte Carlo relaxation time from the present work. For example, the Langevin relaxation time at $n^* = 0.93$ is 2300 in the units of Ref. [17], whereas the Monte Carlo relaxation time at the same density is about 2 MCS. These results may be used to obtain a rough correspondence between the two time units. However, such a comparison must be viewed with extreme caution because one should not really compare nonequilibrium time scales obtained from two completely different dynamics. The difficulty in making such a correspondence is exemplified by the fact that the correspondence factor obtained this way would depend strongly on the density because the Langevin relaxation time increases rapidly with increasing density while the Monte Carlo relaxation time remains nearly constant in the density range studied.

A discussion of the relative merits of the Monte Carlo

method used here and the standard MD method would be interesting from a methodological point of view. It is difficult to determine which algorithm is "faster" because the answer seems to depend on the nonequilibrium process being studied. The process of crystallization appears to be faster in MD than in our Monte Carlo simulations. MD simulations often show [24] nucleation of the crystalline state during simulation time scales at high densities, whereas we seldom see crystallization in our Monte Carlo simulations at similar densities. On the other hand, small fluctuations near the uniform liquid minimum relax faster in the Monte Carlo dynamics than in MD. Our Monte Carlo method has the advantage of being able to relate the observed behavior to different local minima of the free energy. This cannot be done in MD simulations.

IV. CONCLUSIONS AND DISCUSSION

The main result obtained in this work is the determination of the time scale τ_1 associated with activated transitions between glassy metastable minima of the free energy of a dense hard-sphere system. The observed dependence of τ_1 on the dimensionless density parameter n^* (Fig. 3) establishes the existence of a crossover density $n_y^* \simeq 0.99$ with the property that systems quenched to densities higher than n_y^* would remain stuck in a glassy state for all time scales accessible in simulations. We emphasize that the growth of τ_1 with density is *not* caused by the MC mechanism that is responsible for the growth of relaxation times for values of n^* lower than the other crossover density n_x^* mentioned above. That the nonlinear feedback mechanism of MC theories is not present in the Monte Carlo dynamics used in the present work is explicitly demonstrated by the observation that the relaxation time of small-amplitude density fluctuations near the liquid minimum is very short (of the order of a few MCS) and approximately independent of the density when the system evolves under the Monte Carlo dynamics. This result arises because in the Monte Carlo algorithm we use, two cells that are within a distance σ, but not necessarily nearest neighbors, are selected at random and the densities at these two cells are changed by random amounts. These changes, although conserving the total mass, are not governed by an equation of continuity containing the divergence of a current field. Therefore, the physics that arises as a consequence of the coupling of the density field to the current field through the equation of continuity is not expected to be present in the results obtained by using this algorithm. Since the nonlinearities that lead to the feedback mechanism of MC theories come from the coupling of the density field to the current field and from the nonlinearities present in the equation of motion of the current field, it is not surprising that the slowing down of the kinetics predicted in MC theories (and observed in our previous Langevin work [17,18]) is not found in the Monte Carlo dynamics used in the present work.

Therefore, the present work establishes the existence of two distinct regimes for the dynamics of the dense hard-sphere liquid: in the first regime, $n^* \leq n_x^*$, which

covers the first few orders of magnitude of the growth of relaxation times, the slowing down of time scales is a consequence of the nonlinear feedback mechanism described by MC theories. In the second regime, $n^* > n_x^*$, the slow relaxation arises from thermal activation over free-energy barriers between different inhomogeneous minima of the free energy. The growth of relaxation times with increasing density in this regime must be attributed to an increase of the characteristic height of these free-energy barriers.

The results of the present study are in qualitative agreement with the observations of existing MD studies [24,25] of the same system. MD simulations show that the system spontaneously freezes into a near-crystalline state if it is allowed to evolve in time at densities higher than a "first critical density" $n_s^* \simeq 1.08$. If, on the other hand, the system is rapidly quenched from the liquid state at a density lower than n_s^* to a density above a "second critical density" $n_t^* \simeq 1.2$ (which is close to the random close packing density, $n^* \simeq 1.23$), then it ends up in a glassy state with little crystalline order. In our previous work [19], we identified the density n_x^* with n_s^*. The present work suggests that the new crossover density n_y^* should be identified with the density n_t^* found in MD simulations. As mentioned in Sec. III, we find that the minima to which the system moves over the time scale τ_1 are generally more crystalline than the initial ones. This result is consistent with the observation [24], made in MD simulations, that the degree of order present in the glassy states obtained by quenching the system to densities higher than n_t^* increases as the quenching rate is decreased. The value of n_y^* obtained here ($n_y^* \simeq 0.99$) is substantially lower than the result for n_t^* ($\simeq 1.2$) obtained in MD simulations. As mentioned in Ref. [19], this difference is likely due to the fact that the value of n^* at which the discretized version of the free-energy functional used by us exhibits a thermodynamic crystallization transition ($n_f^* \simeq 0.83$) is substantially lower than the crystallization density obtained in MD simulations ($n_f^* \simeq 0.943$) [24]. Indeed, the ratios n_x^*/n_f^* and n_y^*/n_f^* that we find for our system are quiet similar to the corresponding ratios n_s^*/n_f^* and n_t^*/n_f^* as found in the MD work.

We conclude with a few remarks on the implications of the results of the present study on the interpretation of experimental data on the dynamics of good glass forming systems. In contrast to the hard-sphere system for which near-crystalline states are relatively easy to reach if n^* lies between n_x^* and n_y^* (as indicated by MD results and our observation that the minima to which the system moves during its evolution under the Monte Carlo dynamics usually have higher degrees of crystallinity), the ordered state is expected to be highly inaccessible in good glass forming liquids such as two (or more) component mixtures. In such systems, the transitions described by the time scale τ_1 may not take the system closer to the ordered state. Instead, the system may continue to wander among various glassy minima of the free energy. In the long-time limit, such a system may still be a liquid in the sense that the time-averaged local density may still be uniform. However, the dynamics of such a liquid

(governed by the time scale τ_1 defined above) would be quite different from that of the same system at densities lower than n_x^*, for which the dynamics is governed by the MC time scales. We suggest that this picture may provide an explanation of the "crossover" in the dynamics observed [1,2] near the ideal glass transition temperature T_c in experiments on fragile liquids.

A question that naturally arises in this context is whether the present study has anything to say about the possibility of a true second order glass transition in such systems. Such a transition would correspond to a true divergence of the time scale τ_1 in the thermodynamic limit. Our investigation of the dependence of τ_1 on sample size does not show any evidence for such a divergence. However, our study of sample-size dependence was rather limited in scope. In particular, we only considered glassy local minima that are rather shallow. We found some evidence (although this aspect was not studied in any detail) that suggests that the time scales for transitions from deeper glassy minima are longer than the values of τ_1 quoted above. A more comprehensive study of this and other related issues would be most interesting.

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