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Free energy landscape of a dense hard-sphere system

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The topography of the free energy landscape in phase space of a dense hard-sphere system characterized by a discretized free energy functional of the Ramakrishnan-Yussouff form is investigated numerically using a specially devised Monte Carlo procedure. We locate a considerable number of glassy local minima of the free energy and analyze the distributions of the free energy at a minimum and an appropriately defined phase-space ''distance'' between different minima. We find evidence for the existence of pairs of closely related glassy minima (''two-level systems''). We also investigate the way the system makes transitions as it moves from the basin of attraction of a minimum to that of another one after a start under nonequilibrium conditions. This allows us to determine the effective height of free energy barriers that separate a glassy minimum from the others. The dependence of the height of free energy barriers on the density is investigated in detail. The general appearance of the free energy landscape resembles that of a putting green: relatively deep minima separated by a fairly flat structure. We discuss the connection of our results with the Vogel-Fulcher law and relate our observations to other work on the glass transition. [S1063-651X(99)00903-4]

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I. INTRODUCTION

When a liquid is cooled to temperatures below the equilibrium freezing temperature at a sufficiently fast rate to prevent crystallization, it enters a metastable supercooled state. As the temperature is lowered further, the supercooled liquid undergoes a glass transition to a state in which it behaves in most ways like a disordered solid. The dynamic behavior of supercooled liquids near the glass transition exhibits many peculiar features [1–3], such as multistage, nonexponential decay of fluctuations and a rapid growth of relaxation times, which are not fully understood theoretically.

An intuitively appealing description that is often used [4,5] for qualitative explanations of the observed behavior near the glass transition is based on the so-called ''free energy landscape'' paradigm. The starting point of this description is a free energy functional that expresses the free energy of a liquid as a functional of the time-averaged local number density. At high temperatures (or at low densities in systems such as those consisting of hard spheres, where the density is the control parameter), this free energy functional is believed to have only one minimum that represents the uniform liquid state. As the temperature is decreased to values near the equilibrium crystallization temperature (or *mutatis mutandi* the density is increased), a new minimum representing the crystalline solid, characterized by a periodic modulation of the local density, should also develop. In the ''free energy landscape'' paradigm, it is assumed that a large number of ''glassy'' local minima of the free energy, characterized by inhomogeneous but aperiodic density distributions, also come into existence at temperatures close to the equilibrium crystallization temperature. If the system gets trapped in one of these glassy local minima as it is cooled rapidly from a high temperature, crystallization does not occur and the subsequent dynamics of the system is governed by thermally activated transitions among a subset of the large number of metastable glassy minima. If the system visits a large number of these minima during its evolution over a relatively long observation time, it behaves like a liquid over such time scales, in the sense that the time-averaged local density remains uniform. However, the dynamic behavior in this regime, being governed by thermally activated transitions over free energy barriers of varying height, is expected to be slow and complex. In this picture, the glass transition occurs when the time scale of transitions among the glassy minima becomes so long that the system remains confined in a single ''valley'' of the landscape over experimentally accessible time scales.

The general features of the free energy landscape posited in this picture would be quite similar to those found in analytic studies [6–8] of certain generalized spin glass models with infinite-range interactions, and also in recent studies [9,10] of spin models with complicated infinite-range interactions, but no quenched disorder. The equilibrium and dynamic behavior of these mean-field models exhibit a striking similarity with the phenomenology of the glass transition. These results suggest that the free energy landscape paradigm may indeed provide a fitting framework for the development of a theoretical understanding of the behavior of supercooled liquids near the glass transition. The development of such a description would obviously require detailed information about the topography of the free energy landscape of dense supercooled liquids. Since the analytic methods used in the aforementioned studies of mean-field models with infinite-range interactions cannot be readily generalized to study physical systems with short-range interactions, in-

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vestigations of the properties of the free energy landscape of simple glass-forming liquids require the use of appropriate numerical methods.

We have carried out a number of numerical studies aimed at elucidating the relation between the dynamic behavior of simple model liquids and the structure of the free energy surface in phase space. These studies, carried out for a dense hard-sphere system, are based on a model free energy functional proposed by Ramakrishnan and Yussouff (RY) [11]. A discretized version of this free energy functional was found [12,13] to exhibit a large number of glassy local minima at densities close to or higher than the value at which equilibrium crystallization occurs. [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 in the fluid phase 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.] From numerical studies [14–16] of a set of Langevin equations appropriate for this system, we found that the nature of the dynamics changes qualitatively at a ‘‘crossover’’ density near $n_x^* = 0.95$. The dynamics of a system initially prepared in the uniform liquid state continues to be governed by small fluctuations near the uniform liquid minimum of the free energy as long as the density is lower than this crossover value. For values of n^* higher than the crossover density, the dynamic behavior is governed by transitions among the glassy minima. The time scales for such transitions were estimated from a standard Monte Carlo (MC) method in Ref. [17] and found to increase rapidly with increasing density.

In this paper, we present the results of a numerical study in which a new approach is used for further investigations of the properties of the free energy landscape of a dense hard-sphere system. This study is based on the discretized free energy functional [11] used in our previous work. The development of an understanding of the dynamics of the system in the regime where it is governed by transitions among the glassy minima of the free energy requires information about properties of the free energy landscape such as the number of glassy minima, the distribution of their free energies and overlaps, the heights of the saddle points that connect different glassy minima, and how the system evolves from one minimum to another through these saddle points. One also needs to determine the dependence of these quantities on the average density which, as mentioned above, is the relevant control parameter for the hard-sphere system. In the present study, we have developed and used a MC procedure to obtain quantitative information about some of these features of the free energy landscape. As described in Sec. II below, this MC procedure enables us to study in detail the process of transition between different glassy minima of the free energy and thus provides valuable information about the topography of the free energy surface in phase space. We have also located a large number of glassy minima of the free energy in the course of this study. This gives us useful information about some of the relevant statistical properties of the collection of glassy minima and the dependence of these properties on the density. The main results obtained from this study are summarized below.

By performing a study of the probability of transition from a particular glassy minimum to any other as a function of the free energy increment (the excess free energy measured from that at the original minimum), we find that the value of the free energy at which transitions to other minima begin to occur with a high probability is nearly the same for different glassy minima. This suggests that the free energy surface in phase space has a ‘‘putting green like’’ topography in which the glassy minima are like ‘‘holes’’ of varying depth embedded in a relatively flat background. The total number of glassy minima is a sensitive function of the discretization scale and the sample size. For ‘‘commensurate’’ (as defined below) values of these quantities, which allow the existence of a crystalline minimum (which, when present, is the global minimum of the free energy at high densities), the number of glassy minima is relatively large. Systems with incommensurate values of the discretization scale and the sample size exhibit no crystalline minimum and a substantially smaller number of glassy minima. For this reason, we have carried out all our studies of the statistical properties of glassy minima for a commensurate system. We find that the total number of glassy minima for such a system remains nearly constant as the density is varied in the range $0.94 \leqslant n^* \leqslant 1.06$. The free energies of the glassy minima are distributed over a wide range between the free energy of the uniform liquid and that of the crystalline solid. The width of this range increases as the density is increased. This observation, together with the result that the number of minima is nearly independent of the density, implies that the number of minima per unit interval of the free energy (the ‘‘density of states’’ of glassy minima) decreases with increasing density. A suitably defined ‘‘phase space distance’’ between two different glassy minima also shows a broad distribution. Our study shows the existence of pairs of glassy minima that differ from each other in the rearrangement of a very small number of particles. The height of the free energy barrier that separates two minima belonging to such a pair is found to be quite small. Such pairs may be identified as ‘‘two-level systems’’ which are believed [18] to exist in all glassy systems. The qualitative features of the free energy landscape found in our study are similar to those of the generalized spin glass models mentioned above. However, some of the details of our results (such as the form of the distribution of the overlap between different glassy minima) appear to be different from the predictions of spin-glass-like theories.

Our study of the probability of transition from a particular glassy minimum to the others as a function of the free energy increment and the MC ‘‘time’’ t allows us to define an effective barrier height that depends rather weakly on t. Some of our results for the dependence of this barrier height on the density have been briefly reported [19] in a recent paper. As described there, we found that the growth of this effective barrier height with increasing density is consistent with a Vogel-Fulcher form [20] appropriate for a hard-sphere system [21]. From our numerical results about how the dependence of the effective barrier height on t changes as the density is increased, we were able to conclude that the growth of the barrier height (and the consequent growth of the relaxation time) is primarily due to entropic effects arising from an increase in the difficulty of finding low-free-energy paths (saddle points) that connect one glassy local minimum with the others. Some of the details not included in

Ref. [19] are provided in the present paper. We also relate the new results described above with the conclusions reached in Ref. [19].

The rest of this paper is organized as follows. In Sec. II, we define the model system studied and describe the numerical methods used. Section III contains a detailed description of the results obtained in our study. Finally, in Sec. IV, we summarize the main conclusions and discuss them in the context of other related work on the glass transition.

II. MODEL AND METHODS

In this section we define the model free energy used in our study, and define the MC method that we have developed as a means of studying the topography of the free energy surface of the model in phase space. We also discuss in detail the initial conditions and parameters used.

A. Free energy

As explained in the Introduction, our system is characterized by a free energy functional $F[\rho]$ which is of the following form [11]:

$$F[\rho]=F_l(\rho_0)+k_BT\left[\int d\mathbf{r}\{\rho(\mathbf{r})\ln(\rho(\mathbf{r})/\rho_0)-\delta\rho(\mathbf{r})\}\right.$$
$$\left.-(1/2)\int d\mathbf{r}\int d\mathbf{r}'\,C(|\mathbf{r}-\mathbf{r}'|)\,\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')\right], \quad (1)$$

where $F_l(\rho_0)$ is the free energy of the uniform liquid at density ρ_0, and $\delta\rho(\mathbf{r})\equiv\rho(\mathbf{r})-\rho_0$ is the deviation of the density ρ at point $\mathbf{r}$ from ρ_0. We take our zero of the free energy at the uniform liquid value; i.e., we set $F_l(\rho_0)$ equal to zero. In Eq. (1), T is the temperature and the function $C(r)$ the direct pair correlation function [22] of the uniform liquid at density ρ_0, which we express in terms of the dimensionless density $n^*\equiv\rho_0\sigma^3$ by making use of the Percus-Yevick [22] approximation. This approximation is known to be quite accurate if the value of ρ_0 is not very high, and should be adequate for all the densities ($n^*\leqslant 1.06$) considered in this study. It is well known [22] that the direct pair correlation function of simple model liquids characterized by an isotropic, short-range pair potential with a strongly repulsive core (such as the Lennard-Jones liquid) is very similar to that of the hard-sphere system at high densities. Therefore, we expect the results obtained from this study to apply, at least qualitatively, to other dense model liquids.

To perform the numerical calculations, we discretize our system by introducing a three-dimensional cubic lattice of size L^3 and mesh constant h in which a discrete set of variables, ρ_i, $i=1,L^3$, are defined as $\rho_i\equiv\rho(\mathbf{r}_i)h^3$, where $\rho(\mathbf{r}_i)$ is the density at mesh point i. It is often convenient, in performing and describing the calculations, to deal with a dimensionless, normalized free energy per particle $f[\rho]$ defined as

$$f[\rho]=\beta F[\rho]/N, \quad (2)$$

where $N=\rho_0(Lh)^3=n^*L^3a^3$ is the total number of particles in the simulation box, $\beta\equiv 1/(k_BT)$, and a is the ratio h/σ.

B. The Monte Carlo method

Our main objective in this work is to find an efficient way to investigate the topography of the free energy landscape of the hard-sphere system described by the discretized form of the free energy functional defined in Eq. (1). Basically, what one would like to do is to start the system in a known free energy state (e.g., a glassy local minimum of the free energy), and then investigate the topography of the free energy surface near the starting point by allowing the system to evolve in time and finding out which configurations it subsequently visits and where it ends up. A conventional Metropolis algorithm MC procedure, as performed at lower densities in our previous work [17], is not the most efficient way of doing this: From a computational point of view, a certain amount of computer time is spent at every step of a conventional MC simulation in evaluating the exponential of the free energy change. More important, in a conventional MC simulation carried out at the rather high densities we will consider here, it would take a very long time for the system to move out of the basin of attraction of the minimum in which it is initially placed. This makes a conventional MC study of the process of transitions among free energy minima prohibitively expensive in the density range we consider.

In order to overcome these difficulties of a standard MC simulation, we have devised another MC procedure that generates a random sampling of configurations for which the total free energy F defined in Eq. (1) is constrained to be lower than a specified value. This procedure works as follows: we choose a trial value of what we call the free energy increment, which we denote by ΔF or, alternatively, by Δf if we are dealing with the dimensionless version of Eq. (2). Then, starting with initial conditions which, as discussed below, correspond to a configuration where the free energy is at a local minimum, we sweep the lattice sites i sequentially. At each step and site, we pick another site j at random from among the ones that lie within a distance σ from the site i. We then attempt to change the values of ρ_i and ρ_j to $p(\rho_i+\rho_j)$ and $(1-p)(\rho_i+\rho_j)$, where p is a random number distributed uniformly in [0,1]. The attempted change is accepted, and this is the crucial point, if and only if the free energy after the change is less than $F_{\max}\equiv F_0+\Delta F$ where F_0 is the initial value, that is, the value of the free energy at the minimum where we start the computation. The simulation proceeds up to a maximum ‘‘time’’ t_m measured in MC steps per site (MCS).

In implementing this procedure, the key point is that we perform a sweep over a range of values of ΔF, with the same initial conditions. The objective here is to find the value of ΔF at which the system begins to exhibit transitions to the basins of attraction of other local minima. To find out which basin of attraction the system is in at a certain time t, we save the configurations (i.e., the values of the variables ρ_i) at suitable, relatively frequent, time intervals Δt. These configurations are then used as the inputs in a minimization procedure [12] that determines which basin of attraction the system is in. The entire procedure, that is, running the simulation up to a certain time t_m for a set of values of ΔF, saving the configurations at intervals Δt, and analyzing them, is repeated a certain number of times (typically 10–15) and averaged over. This yields values of the probability

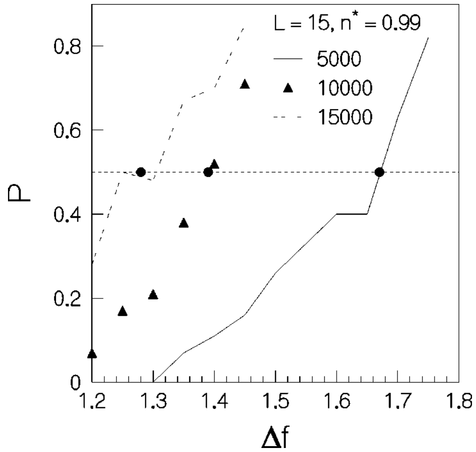

FIG. 1. Example of the determination of the ''critical'' value Δf_c, defined as the value of the free energy increment Δf at which the transition probability P is 1/2. The solid circles mark the intersections of the plots with the line $P=0.5$ (see text for a complete discussion). The data shown are for a sample of size $L=15$.

$P(\Delta f,t)$ that at time t the system has moved to the basin of attraction of a free energy minimum distinct from the one in which it was started. We define [19] a ''critical'' value Δf_c of the free energy increment as the value of Δf for which the transition probability reaches the value 0.5. As an illustration of our numerical procedure, we show in Fig. 1 the results for the transition probability $P(\Delta f,t)$ as a function of the free energy increment Δf for a minimum obtained for a sample with $L=15$ at $n^*=0.99$. The data for three different values of t are shown, and the corresponding estimated values of Δf_c are indicated in the figure.

We have carried out the numerical procedure outlined above at a number of densities in the range $0.94 \leqslant n^* \leqslant 1.06$. We did not consider densities lower than 0.94 because our earlier work [15,16] has shown that the dynamics of the system is governed by transitions among glassy local minima only at higher densities. Since, as mentioned above, the Percus-Yevick approximation used for the direct correlation function $C(r)$ appearing in Eq. (1) becomes less accurate at relatively high densities [22], values of $n^* > 1.06$ were not considered.

C. Initial states and system parameters

Our computations were performed for two different sets of the two computational system parameters—the sample size L and the mesh size h. In one case we took these two parameters to be commensurate with a close-packed lattice and in the other incommensurate. This was done chiefly in order to study the dependence of the structure of the free energy landscape on the commensurability properties of the computational system parameters, as well as on their values. We also considered two different kinds of initial conditions, so that we could investigate the topography of the free energy surface in different regions of phase space. The computationally more intensive part of our simulations was carried out for systems of size $L=15$ with periodic boundary conditions and mesh size $h=\sigma/4.6$. These values of L and σ are incommensurate with a close-packed lattice, and as a result no crystalline minimum was found for these samples. Two kinds of initial conditions were used for such systems. The first kind is the same as that used in Ref. [17]. These are configurations obtained by first allowing the system to evolve from a uniform initial state under Langevin dynamics [14,15] until its free energy (which, we recall, includes a current-dependent term in the Langevin model) reaches zero (indicating the departure of the system from the basin of attraction of the uniform liquid minimum of the free energy), and then using the minimization procedure to reach the minimum whose basin of attraction the system is in at that point. That minimum configuration is then the starting point of the present work. All the minima found this way exhibit glassy structure, as determined by the form of the two-point correlation function (see below) of the local density variables ρ_i. At higher densities, where the Langevin computation is inappropriate, the minima found at lower densities were scaled up by running the minimization program at the higher density using the lower-density configuration (which, of course, is not a minimum at the higher density) as the starting point.

The other portion of the computations was performed for systems with $L=12$ and $h=0.25\sigma$. These values are commensurate with a close-packed (fcc) structure, so that a crystalline minimum is found at sufficiently high densities. Starting configurations used for simulations carried out for such samples were obtained by using the minimization procedure discussed above on randomly inhomogeneous initial configurations. Out of several glassy minima found this way, we selected a few with structures similar to that of the minima used in simulations of the $L=15$ sample. Because of the smaller size of these samples, we were able to explore more extensively several aspects of the problem under consideration.

Our computations for the $L=15$ sample were carried out for a time range $t_m=15\,000$ MCS. Computations for the system with $L=12$ were usually carried out to $t_m=8000$ MCS. In both cases the density range $0.94 \leqslant n^* \leqslant 1.06$ was covered. For the larger size and longer maximum time, an interval $\Delta t=5000$ MCS was used, while a closer spacing, $\Delta t=2000$ MCS, was chosen for $L=12$.

The structure of a local minimum of the free energy may be characterized by the two-point correlation function $g(r)$ of the frozen local density variables ρ_i at the minimum. This function is defined as

$$g(r)=\sum_{i>j}\rho_i\rho_j f_{ij}(r)\Bigg/\left[\rho_{\mathrm{av}}^2\sum_{i>j}f_{ij}(r)\right], \tag{3}$$

where $\rho_{\mathrm{av}}\equiv\Sigma_i\rho_i/L^3$ is the average value of the ρ_i at the minimum (values of ρ_{av} vary from one glassy minimum to another, but are always slightly higher than $\rho_0 h^3$, the value of ρ_i at the uniform liquid minimum), and $f_{ij}(r)=1$ if the separation between mesh points i and j lies between r and $r+\Delta r$ (Δr is a suitably chosen bin size), and $f_{ij}(r)=0$ otherwise. In Fig. 2, we have shown the pair correlation functions for two typical minima used as initial states in our simulations. From the structure of $g(r)$ shown in this figure, it is clear that both these minima are glassy. It is also apparent that the structure of the $L=12$ minimum is quite similar to that of the $L=15$ one. Other minima used in our simulations have a similar structure.

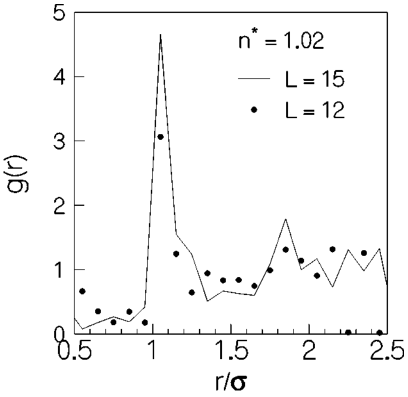

FIG. 2. The density correlation function $g(r)$, as defined in Eq. (3), plotted as a function of distance (in hard-sphere units) for two typical initial configurations. Note the glassy character of the correlations for both lattice sizes.

III. RESULTS

In this section, we describe in detail the numerical results obtained from our study, and present our analysis of the numerical data.

A. Monte Carlo dynamics

First, we discuss the qualitative behavior of the system as it evolves in ''time'' under our MC ''dynamics'' from the initial state at $t=0$ to $t=t_m$ as described in Sec. II B. During the evolution of the system, we monitor the dimensionless free energy βF and the maximum and minimum values of the discretized density variables ρ_i, $i=1,L^3$. The maximum value is useful for detecting possible transitions to the neighborhood of the uniform liquid minimum. If the system fluctuates near one of the inhomogeneous minima of the free energy, then the maximum value of ρ_i would be much higher than the value (close to $\rho_0 h^3$) it would have if the system were in the vicinity of the uniform liquid minimum. We find that the system does not move to the neighborhood of the liquid minimum for the values of ΔF considered here. The total free energy is found to remain nearly constant at a value slightly lower than the maximum allowed value, $F_{\max}=F_0+\Delta F$.

In some of the runs, we have also monitored at frequent time intervals a quantity $d(t)$ that measures the ''phase-space distance'' of the system point at time t from the starting point at $t=0$. This quantity is defined as

$$d^2(t)=\sum_i [\rho_i(t)-\rho_i(0)]^2, \tag{4}$$

where $\rho_i(0)$ are the values of the density variables at the minimum from where the simulation is started. By monitoring the time dependence of this quantity, we obtain useful information about how the system explores the free energy landscape as it evolves in time. We find that if the value of the free energy increment ΔF is small enough so that the system remains confined in the basin of attraction of the original minimum over the duration of the simulation, then the phase space distance $d(t)$ saturates (or continues to increase very slowly) after a rapid initial increase. The value at which $d(t)$ levels off increases as ΔF is increased. For values of ΔF that are sufficiently large for the system to be able to move to the basins of attraction of other minima, the transitions to other basins of attraction are usually (but not always) indicated by sudden increases in the value of $d(t)$. Typical results for the time dependence of $d^2(t)$ for three different values of ΔF are shown in Fig. 3. The data shown were obtained for a $L=12$ system at $n^*=1.02$. For $\Delta f=1.0$ and $\Delta f=1.4$, the system was found to remain in the basin of attraction of the initial minimum during the time scale (8000 MCS) of the simulation. In the run with $\Delta f=1.9$, the system was found to have moved to the basin of attraction of a different minimum at $t=2000$ MCS. It moved to the basin of attraction of the crystalline minimum between times $t=2000$ MCS and $t=4000$ MCS, and stayed there for the remaining part of the run. While any signature of the first transition from the initial minimum to the intermediate one is not clearly visible in the time dependence of $d(t)$ [possibly due to the overlap of any such signature with the initial rapid increase of $d(t)$], the subsequent transition to the crystalline minimum is clearly indicated by a rapid rise (and eventual saturation) of $d(t)$.

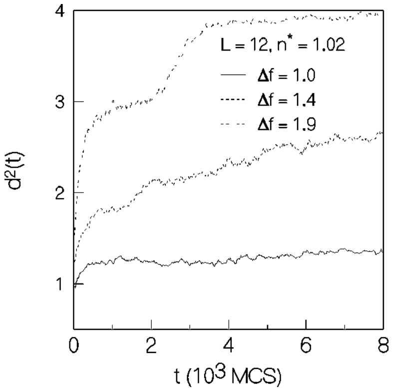

FIG. 3. The quantity $d^2(t)$, which characterizes the ''phase-space distance'' between two points [see Eq. (4)], plotted as a function of Monte Carlo time for three values of the free energy increment. The regions of sharp changes in the curves are discussed in the text.

As mentioned in Sec. II B, the determination of the probability of transition as a function of Δf requires repeating our numerical procedure a number of times for a fixed set of values of Δf. We find that the minima to which the system moves for values of Δf close to or higher than Δf_c are, in general, different for different runs. This is more obvious for $L=12$ samples which, as discussed below, exhibit a larger number of distinct glassy minima. This observation suggests that Δf_c represents a measure of the free energy increment for which a relatively large region of phase space becomes accessible to the system. Another observation that supports this interpretation is that the system almost never returns to the basin of attraction of the initial minimum after making a transition to the basin of attraction of a different one: after having left the initial minimum, the system cannot find its way back. In a few runs, we found transitions at relatively small values of Δf which are *always* to the basin of attraction of the same minimum. In most of these cases, the new minimum was found to be very ''close'' in phase space [as measured by the quantity defined in Eq. (4)] to the initial one. These are examples of so-called ''two-level systems'' discussed in more detail in the next subsection. In a few cases, we found that the new minimum to which all the transitions occur at low values of Δf is not close to the initial one. These are examples of ''special'' paths with low barrier heights which connect the initial minimum with another specific minimum. Since such transitions and the ones between minima which are very close to each other do not correspond to the opening up of large regions of phase space, we did not include such transitions in the calculation of the transition probability.

Finally, we note that although our model and numerical procedure are different from those used in most existing numerical studies of dense liquids (such studies use conventional MC or molecular dynamics to simulate the behavior of models defined by a microscopic Hamiltonian), some of the general features found in existing simulations (and also in experiments) are reproduced in our work. We find that if the value of ΔF is such that $\beta F_{\max}$ exceeds an upper threshold, then the system moves within a few hundred MC steps to the vicinity of the uniform liquid minimum. The value of this upper threshold is found to be close to $\beta F = 5.0$. This is the ''microcanonical'' analog of the melting transition. As mentioned above, this threshold value is not crossed in the simulations from which the results described here were obtained. We also find that in runs with $\beta F_{\max}$ close to, but lower than, the upper threshold, the system moves to the basin of attraction of the crystalline minimum (for $L=12$) with a high probability. This is nothing but the process of annealing: it is well known from experiments and simulations that crystallization may be induced by heating a glassy system to a temperature close to (but lower than) its melting temperature and then cooling it down.

B. Properties of glassy minima

In the course of our computations, we have located many of the glassy minima of the free energy. As mentioned above, for the ''incommensurate'' $L=15$ sample used in our work, the number of minima we have located at each density is not large. The total number of minima found for this sample varies in the range of 4–6, with some tendency to higher values in the lower part of the n^* range considered here. The ''commensurate'' $L=12$ sample exhibits, as we shall see below, a substantially larger number of minima, one of which is crystalline (fcc). For this reason, we consider chiefly the results obtained for $L=12$, for which we can produce significant statistics, in this subsection. A similar sensitivity of the number of local minima to the sample size and boundary conditions has been found in numerical studies [23,24] of the potential energy landscape of model liquids described by simple Hamiltonians. The reason for the relatively strong dependence of the number of minima on the computational system parameters is not clear at present.

While studying the process of transitions among the minima, we carried out a large number of minimization runs with many different initial states. The total number of such runs is of the order of 10^3 for each of the values of n^* studied. While our procedure does not correspond to an exhaustive search for all the local minima of the system, the fairly large number of initial states considered for each value of n^* ensures that, for $L=12$ at least, we did locate a large fraction of the local free energy minima of the system. So the statistical information obtained from our study can be expected to be representative of the full collection of local minima.

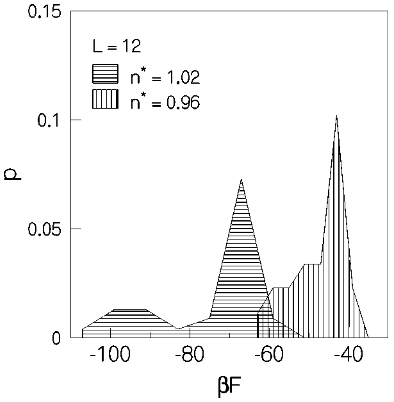

FIG. 4. The ''density of states'' for glassy free energy minima, defined as the probability of finding a glassy minimum with free energy in a given range (see text). Results for $L=12$ samples at two densities are shown.

The total number of local minima of the $L=12$ system remains nearly constant as the density is varied in the range $0.96 \leqslant n^* \leqslant 1.06$. This number is close to 25. The numbers for different values of n^* show small variations, but there is no clear systematic trend in the dependence of this number on the density. In most cases, a minimum found at a particular density may be ''followed'' to higher or lower densities by using the values of ρ_i at the minimum at the first density as inputs to the minimization program at the new density. In a few cases, we find that a minimum disappears as the density is increased or lowered, but such occurrences are rare. From these observations, we conclude that the total number of glassy minima does not exhibit any strong dependence on the density. Our limited investigation of the variation of the free energies of the glassy minima with density suggests that the ordering of the free energies remains the same (i.e., free energies of different minima do not cross) as the density is changed.

The free energies of these minima are distributed in a band that lies between the free energy of the uniform liquid (which, we recall, is taken to be the zero of the free energy scale) and that of the crystalline solid. The width of this band increases with increasing n^*. Since the number of minima is approximately independent of the density, this implies that the ''density of states'' of the glassy minima decreases as n^* is increased. Specifically, let $p(\beta F)\delta$ be the probability of finding a glassy minimum with dimensionless free energy between $\beta F - \delta/2$ and $\beta F + \delta/2$. We have calculated this quantity from our data at different values of n^*. Representative results at two densities, $n^* = 0.96$ and $n^* = 1.02$, are shown in Fig. 4. The values of δ used are 4.0 and 8.0 for $n^* = 0.96$ and $n^* = 1.02$, respectively. While the distributions for the two densities are qualitatively similar, the range of βF over which $p(\beta F)$ is nonzero is clearly wider at the higher density. The consequent decrease in the values of $p(\beta F)$ with increasing density is also clearly seen. Both distributions show peaks near the upper end and tails extending to substantially lower values. However, the lowest free energy of the glassy minima is substantially higher than the free energy of the crystalline minimum (for the crystalline minimum, $\beta F=-102.4$ for $n^*=0.96$ and $\beta F=-167.4$ for $n^*=1.02$). If the probability of finding the system in a glassy minimum is assumed to be proportional to the Boltzmann factor $e^{-\beta F}$, then only those minima with free energies lying near the lower end of the band would be relevant in determining the equilibrium and dynamic properties of the system. Our results indicate that the number of such ''relevant'' minima decreases with increasing n^*.

In the present study, we find certain correlations between the free energy of a glassy minimum and its structure. Similar correlations were also found and described in some detail in Ref. [15]. Specifically, we find that minima with lower free energies have more ''structure'' [as indicated by, e.g., the heights of the first and second peaks of the correlation function $g(r)$ defined in Eq. (3)] and higher density than those with lower free energies.

We have also studied how the distributions of the local density variables in two distinct glassy minima differ from one another. To do this, we need a measure of the difference between the distributions of ρ_i in two glassy minima. This measure should satisfy the requirement that it yield a zero value for the difference between two configurations if one of them can be mapped to the other by a symmetry operation of the computational mesh. The symmetries of the cubic mesh used in our computation include the 48 symmetry operations of a simple cubic lattice and all translations, taking into account the periodic boundary conditions. The quantity $d_m(1,2)$ that we have used to measure the difference in the density distributions at two minima labeled ''1'' and ''2'' is defined as follows:

$$d_m(1,2)=\frac{1}{2}\min\{\mathbf{R}\}\sum_i \,[\rho_i^{(1)}-\rho_{\mathbf{R}(i)}^{(2)}]^2, \qquad (5)$$

where $\rho_i^{(1)}$ and $\rho_i^{(2)}$ are the discretized densities at two minima, $\mathbf{R}$ represents one of the symmetry operations mentioned above, $\mathbf{R}(i)$ is the mesh point to which mesh point i is transformed under $\mathbf{R}$, and $\min\{\mathbf{R}\}$ means that the $\mathbf{R}$ that minimizes the quantity on the right is to be taken. Since the variables ρ_i in an inhomogeneous minimum are close to one at the mesh points corresponding to the locations of the ''particles'' and close to zero at the other mesh points, the quantity d_m basically measures the number of particles whose positions are different in the two minima being compared. In Fig. 5, we display in histogram form the results for the distribution of d_m at two values of the density. The two distributions are qualitatively similar. Both are small at small values of d_m and exhibit peaks near $d_m=15$, which corresponds to about half of the total number of particles having different locations in the two minima. From these results, we conclude that most of the glassy minima are rather different from one another. The arrangement of the particles in the glassy minima is also very different from that in a crystalline minimum, as indicated by the observation that the value of d_m almost always lies above 15 if one of the two minima being compared is glassy and the other one is crystalline.

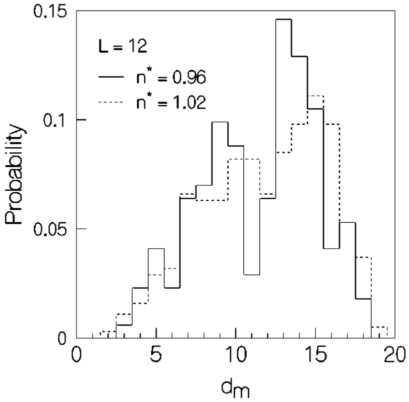

FIG. 5. Histogram representing the fraction of pairs of free energy minima found to differ in their real-space density configurations by an amount d_m as defined in Eq. (5). Results for $L=12$ samples are shown at two different densities.

The distributions shown in Fig. 5 extend down to values of d_m as small as 2 or 3, indicating that there are a few pairs of glassy minima which are very similar to each other. For each value of n^*, we find a small number (3–5) of such pairs of minima. To take an example, for $n^*=0.96$, we have found two minima, with free energies $\beta F=-47.7$ and -47.0, for which the value of d_m is 2.4. A detailed examination of the density distributions at these two minima reveals that the main difference between their structures comes from small displacements of just two particles. Of course, these displacements also produce small changes in the values of ρ_i at neighboring mesh points. We believe that these pairs of minima are examples of ''two-level systems'' whose existence in glassy materials was postulated [18] many years ago in order to account for some of the experimentally observed low-temperature properties. The height of the free energy barrier that separates two members of a two-level system is expected to be low. Our observations are consistent with this expectation. For the pair of minima mentioned above, we find that if we start the system from the minimum with $\beta F_0=-47.7$ and carry out our numerical procedure for finding transitions to other minima, the system begins to show transitions to the minimum with $\beta F_0=-47.0$ as the value of Δf is increased above 0.7. For $0.7\leqslant\Delta f\leqslant 1.4$, *all* the transitions are to the other member of the two-level system. Transitions to other minima begin to appear only for higher values of Δf. (As noted above, we did not include transitions between the members of a two-level system in our calculation of Δf_c.)

The degree of similarity between two different minima may also be quantified in terms of their ''overlap'' [8]. For the discretized system considered here, the dimensionless overlap $q(1,2)$ between two minima labeled ''1'' and ''2'' may be defined in the following way:

$$q(1,2)=\frac{1}{\rho_{\mathrm{av}}L^3}\max\{\mathbf{R}\}\sum_i \,[\rho_i^{(1)}-\rho_{\mathrm{av}}][\rho_{\mathbf{R}(i)}^{(2)}-\rho_{\mathrm{av}}], \qquad (6)$$

where ρ_{av} is the average value of the ρ_i, which is assumed to be the same in the two minima, and $\max\{\mathbf{R}\}$ means that the $\mathbf{R}$ that maximizes the quantity on the right is to be taken. Using the aforementioned fact that at the glassy minima found in the density range considered here the values of ρ_i are close to one at a small number of mesh points and close

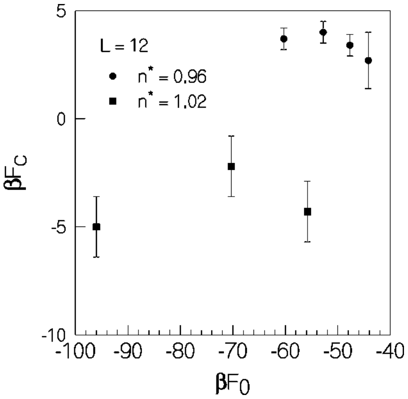

FIG. 6. The value F_c of the free energy at which transitions to other minima begin to occur with a high probability, plotted as a function of F_0, the free energy at the starting minimum. Results are shown for $L=12$ at two densities. One can see that, at a given n^*, the dependence of F_c on the starting value is quite weak.

to zero at others, the following approximate relation between q and d_m may be derived easily:

$$q(1,2)\simeq 1-d_m(1,2)/N-\rho_{\rm av}, \tag{7}$$

where $N\equiv\rho_{\rm av}L^3$ is the total number of particles in the simulation box. The observation that the distribution of d_m has a peak near $d_m=N/2$ then implies that the distribution of q peaks near the value 0.5.

We have also looked at how the quantity $F_c=F_0+\Delta F_c$, which measures the value of the total free energy at which transitions to other minima begin to occur with a high probability, varies from one minimum to another. As exemplified by Fig. 6, where we present the results for βF_c for four minima at $n^*=0.96$ and for three minima at $n^*=1.02$, the value of this quantity is nearly constant for each value of n^*. While the values of βF_0 vary over a range of about 15 at $n^*=0.96$, and over a range of about 40 at $n^*=1.02$, the calculated values of βF_c are nearly the same (within the error bars) for the different minima at both densities. This observation suggests a ''putting-green-like'' free energy landscape in which the local minima are like ''holes'' of varying depth in a nearly flat background. This structure also implies that there is a strong correlation between the depth of a minimum and the height of the barriers that separate it from the other minima: the barriers are higher for deeper minima.

C. Vogel-Fulcher law and entropic effects

The dependence of Δf_c on n^* and t was analyzed in detail in Ref. [19], where it was first pointed out that there is a direct connection between our results and the Vogel-Fulcher law [20]. We summarize this connection here. The basic point is that the results for Δf_c are consistent with the form

$$\Delta f_c(n^*,t)=\frac{a(t)}{n_c^*-n^*}+b, \tag{8}$$

where $a(t)$ is a weak function of t, b is a constant, and the ''critical'' density n_c^* is found to be independent of t within the accuracy of our results. In Fig. 7, we show the data for Δf_c for a $L=15$ minimum at times 5000, 10 000, and 15 000 MCS, and also the best fits of the data to the form of Eq. (8) with $b=0$. The parameter values for the best fits are $a=0.31$, $n_c^*=1.19$ for $t=5000$; $a=0.30$, $n_c^*=1.22$ for $t=10\,000$; $a=0.27$, $n_c^*=1.23$ for $t=15\,000$. The form of Eq. (8) leads at once to the Vogel-Fulcher law appropriate for a hard-sphere system [21] since the characteristic time should be proportional to the exponential of $\beta\Delta F_c$. The values of n_c^* obtained from the fits, particularly at later times, are very close to the random close packing density, $n_{\rm rcp}^*\simeq 1.23$. This is in agreement with the results of molecular dynamics simulations [21]. The $L=12$ data yield similar values of n_c^*, but with $b\simeq 1.0$.

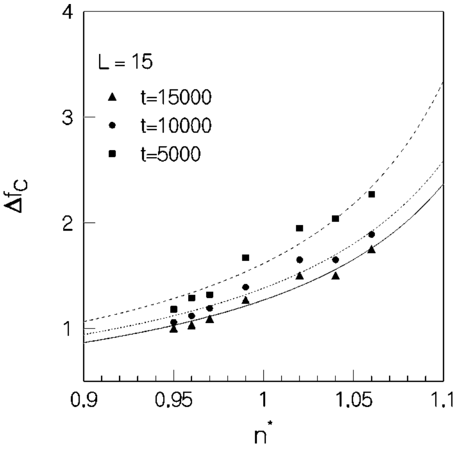

FIG. 7. Vogel-Fulcher fits of the data for Δf_c obtained for a $L=15$ minimum at three different values (5000, 10 000, and 15 000 MCS) of t. The solid lines are the best fits of the data to the form of Eq. (8) with $b=0$. The parameter values for the best fits are given in the text.

The weak dependence of Δf_c on t was also analyzed in detail in Ref. [19] where it was found that this dependence for all values of n^* and all the minima studied is well described by the form

$$\Delta f_c(n^*,t)=c(n^*)t^{-\alpha}+\Delta f_0, \tag{9}$$

with α in the range 0.24–0.40, and Δf_0 nearly independent of n^*. The coefficient $c(n^*)$ was found to increase with increasing n^*. Fits of the data to the form of Eq. (9) are shown in Fig. 2 of Ref. [19]. [This form agrees with Eq. (8) if $a(t)\propto t^{-\alpha}$ and $c(n^*)\propto 1/(n_c^*-n^*)$; our data are consistent with these conditions.] This result suggests a physical interpretation of the observed Vogel-Fulcher behavior. The quantity Δf_0 (the value of Δf_c in the $t\to\infty$ limit) provides a measure of (β/N times) the height of the lowest-free-energy barriers that must be crossed in order to reach some of the other local minima of the free energy from the one under consideration. As discussed in detail in Ref. [19], the coefficient $c(n^*)$ may be interpreted as a measure of the difficulty of finding low-free-energy paths to other minima. The observation that $c(n^*)$ increases with n^* while Δf_0 is nearly independent of n^* then implies that the increase of the effective barrier height with increasing n^* is primarily due to ''entropic'' effects associated with the difficulty of finding low-lying saddle points that connect a minimum with the others.

Therefore, a picture emerges from our work as to the origin of the Vogel-Fulcher divergence. As the system evolves over longer and longer times, the probability that it will find paths to other minima involving jumps over lower- and lower-free-energy barriers increases. At early times, the system can only explore nearby paths and must then jump over whatever barrier is available in that region. At longer times, a wider region is explored and the chances of finding a path with a lower barrier increase. What our argument shows is that the Vogel-Fulcher law follows from the fact that the difficulty of finding such low-free-energy paths to other minima increases with increasing n^*.

IV. SUMMARY AND DISCUSSION

We have developed and used in this work a numerical method to study the topography of the free energy surface of a dense hard-sphere system characterized by a model free energy functional. At the relatively high densities considered in this study, this system exhibits a complex free energy landscape characterized by the presence of many glassy local minima. The number of accessed glassy local minima is found to depend strongly on the commensurability properties of the discretization scale h and the sample size L used. For fixed values of these parameters, the number of minima is nearly independent of the density in the range studied. In the case where L and h are commensurate, a crystalline minimum is found and the number of glassy minima accessed is large enough to allow for statistical study. The free energy values at its minima are distributed over a broadband whose width increases with increasing density. The phase-space distance between different minima shows a broad distribution with a peak near the high end. However, there are a few pairs of minima which are very close to each other in phase space and are separated by low-free-energy barriers. These, we believe, are examples of ''two-level systems'' which are expected to be present in all glassy materials. We have found in all cases a strong correlation between the depth of a minimum and the effective height of free energy barriers that separate it from the other minima: deeper minima have higher barriers. The observed density dependence of the effective barrier height is consistent with the Vogel-Fulcher law. Our results indicate that this Vogel-Fulcher growth is primarily due to an increase in the difficulty of finding low-free-energy paths to other minima as the density is increased.

Our results have close connections with those of a number of recent studies of the equilibrium and dynamic properties of dense supercooled liquids. We first discuss the relation of our observations with spin-glass-like theories [7,8,25] of the structural glass transition. These theories are based on the similarity between the phenomenology of the structural glass transition in so-called ''fragile'' [3] liquids and the behavior found in a class of generalized mean-field spin glass models [6,26] with infinite-range interactions, and also in certain mean-field spin models with complicated multispin interactions but no quenched disorder [9,10]. At high temperatures, the free energy of these mean-field models, expressed as a function of the single-site magnetizations, exhibits only one minimum—the ''paramagnetic'' one at which all the site magnetizations are zero. As the temperature is lowered, an exponentially large number of nontrivial local minima come into existence, and a ''dynamic transition'' characterized by a breaking of ergodicity occurs at a temperature T_d. At this ''transition,'' the system gets trapped in the basin of attraction of one of the newly developed local minima and remains confined in this basin for all subsequent times because the free energy barriers between different local minima diverge in the thermodynamic limit in these models. This ''dynamic transition'' does not have any signature in the equilibrium behavior of the system. A thermodynamic phase transition occurs at a lower temperature T_c at which the configurational entropy associated with the exponentially large number of free energy minima becomes nonextensive.

In the suggested analogy between these models and the structural glass transition, the paramagnetic minimum of the free energy is identified with the one that represents the uniform liquid, and the role of the nontrivial local minima of the free energy is played by the glassy local minima of the liquid free energy. The ''dynamic transition'' found at T_d in the mean-field spin models is thought to be smeared out in liquids. This is because the free energy barriers between different minima are expected to remain finite in physical systems with finite-range interactions. It has been suggested [7,8,25] that the temperature T_d should be identified with the ''ideal glass transition'' temperature of mode-coupling theories [27] of the dynamics of dense liquids. This temperature is supposed to signal the onset of activated processes in the dynamics. The temperature T_c is interpreted as the ''Kauzmann temperature'' [28] at which the difference in entropy between the supercooled liquid and the crystalline solid extrapolates to zero. The relaxation time of the supercooled liquid is supposed to diverge at the same temperature. Heuristic arguments that suggest that this divergence is of the Vogel-Fulcher form have been proposed [8,25]. These arguments are based on an entropic mechanism associated with the vanishing of the configurational entropy at T_c.

The behavior found in our numerical study is in qualitative agreement with this scenario. We find a characteristic density (we recall once more that the density plays the role of the temperature in the hard-sphere system we consider) at which a large number of glassy minima of the free energy come into existence. We do not yet know whether the number of glassy minima depends exponentially on the sample volume—a study of this question is difficult due to the dependence of the number of minima on the commensurability of h and L. While the number of glassy minima for fixed h and L remains nearly constant as the density is increased, the configurational entropy associated with these minima decreases with increasing density because the width of the band over which the free energy of these minima is distributed increases with density. As discussed above, we have also found evidence for a Vogel-Fulcher-type growth of relaxation times driven by an entropic mechanism.

There are, however, a number of differences between the details of our findings and the predictions of spin-glass-like theories. In our earlier work [15,16] on the Langevin dynamics of the model system considered here, we found that the dynamic behavior is governed by activated processes if the dimensionless density n^* exceeds a crossover value, n_x^*, of about 0.95. This value is substantially higher than the value of n^* (≈ 0.8) at which the glassy minima make their first appearance. These two densities are expected to be close to each other in spin-glass-like theories. Another difference lies in the values of the free energy of the glassy minima relative to that of the uniform liquid. We find that the free energy of a glassy minimum becomes lower than that of the uniform liquid minimum as the density is increased above a value that is only slightly higher than the density at which the glassy minimum comes into existence. In particular, the free energies of the glassy minima are substantially lower than that of the uniform liquid one for values of n^* near n_x^*. This is different from the behavior found in the spin glass models. In these systems, the free energies of the nontrivial local minima remain higher than that of the paramagnetic one over the entire temperature range $T_c < T < T_d$. Our results for the distribution of the overlap between different minima are also somewhat different from those for the spin glass models. We cannot rule out that some of these differences arise from finite-size effects which may be significant for the rather small samples considered in our study. Another possibility is that these differences arise in our system from the effects of small fluctuations about a local minimum, which are unimportant in models with infinite-range interactions. A careful investigation of these issues would be very interesting.

A number of numerical studies of ''aging'' phenomena in the nonequilibrium dynamics of simple model liquids have been reported recently [29–31]. In these studies, the system is quenched from a relatively high temperature to a temperature lower than the numerically determined glass transition temperature, and is then allowed to evolve at this low temperature for a certain ''waiting time'' t_w. Then, the two-time correlation function $C(t_w, t_w+t)$ of an appropriate fluctuating quantity is measured and the dependence of this correlation function on t and t_w is analyzed. The simulations show that the decay of $C(t_w, t_w+t)$ as a function of t becomes slower as t_w is increased. Our results about the topography of the free energy landscape provide a qualitative explanation of this observation. When the system is rapidly quenched to a low temperature (or compressed to a high density in our hard-sphere system), it is likely to get trapped in the basin of attraction of one of the glassy local minima that are close in phase space to the initial configuration. Such minima would not, in general, have the lowest free energies. As the system evolves during the waiting time t_w, it can be expected to move progressively to the basins of attraction of minima with lower free energies because such minima would have a higher Boltzmann weight. Since the effective barrier height is higher for deeper minima (this follows from the ''putting-green-like'' structure of the free energy landscape), the time scale for subsequent relaxation is expected to increase with increasing t_w. This is precisely the behavior found in the aging simulations mentioned above.

Our study is rather similar in spirit to numerical investigations of the ''potential energy landscape'' [23,24,32–36] of model liquids characterized by simple Hamiltonians. In such studies, a numerical minimization procedure (e.g., the conjugate gradient method) is used to find the local minima of the total potential energy of small samples as a function of the coordinates of the particles. The potential energy function is generally found to exhibit a large number of local minima. These local minima and the potential energy barriers that separate them define a complex ''potential energy landscape.'' Recently, there have been several attempts [34–36] to relate the properties of this landscape to the dynamic behavior of the liquid. While the similarities between these investigations and our work are obvious, there are several important differences between these two approaches, some of which we now discuss. A study of the potential energy landscape is based on a microscopic Hamiltonian defined in terms of the coordinates of the particles, whereas our work involves a model free energy which is a functional of a coarse grained (both in space and time) density field. Information about the microscopic interactions is incorporated in our description through the direct pair correlation function $C(r)$ appearing in Eq. (1). The free energy of a thermal system is, of course, equal to the potential energy at zero temperature. Therefore, the potential energy landscape of such systems becomes identical to the free energy landscape at $T=0$. There are some mean-field spin glass models (e.g., the p-spin spherical spin glass [37]) in which the correspondence between the local minima of the energy and the free energy extends also to nonzero temperatures. Such a correspondence is not likely to be generic, however. A description based on the potential energy landscape is certainly appropriate at low temperatures where entropic effects are relatively unimportant. But it would, in general, be difficult to extend such a description to higher temperatures where entropic effects play a crucial role. In particular, information about the energy landscape alone would not be sufficient to describe the behavior near a phase transition (such as the melting transition of a solid and the order-disorder transition in magnetic systems) driven by a competition between energetic and entropic effects. In contrast, a description based on a model free energy that includes entropic contributions provides a convenient and intuitively appealing starting point for studying the behavior near such phase transitions. For example, the free energy functional used in our work is known [11] to provide a correct description of the crystallization transition of simple liquids. Another well-known example is the Curie-Weiss theory of magnetism (our approach is analogous to an inhomogeneous version of the Curie-Weiss theory). For these reasons, we believe that our free-energy-based approach is more suitable for a description of the behavior of liquids near the glass transition than approaches based on the potential energy landscape.

Another important difference between free energy and potential energy landscapes is that the former changes as the appropriate control parameter (density or temperature) is changed, whereas the latter, being determined completely by the Hamiltonian of the system, remains unchanged. Specifically, some of the local minima of the free energy may appear or disappear as the control parameter is varied (for example, the inhomogeneous minima of the free energy used in our study disappear at sufficiently high densities). Also, the heights of free energy barriers between different local minima may change with the control parameter (see, e.g., Fig. 7 where the dependence of the height of a typical free energy barrier on the density is shown). In contrast, the potential energy landscape does not show any such variation as the temperature is changed. This difference may be important in understanding some of the results found in recent studies [24,36] based on the energy landscape of simple model liquids. In Ref. [36], an approximate description of the dynamics of a Lennard-Jones system in supercooled and glassy regimes is developed in terms of the numerically determined properties of the local minima of the potential energy and the energy barriers between them. While this description is found to reproduce several interesting features of glassy dynamics, it *does not* show the expected faster than Arrhenius growth of the viscosity at low temperatures. This may be due to the energy barriers in this description not changing with temperature. It is possible that a free-energy-based description in which the barrier heights change with temperature would lead to a faster than Arrhenius growth of the viscosity. This possibility is clearly illustrated in our study which shows that the dependence of the heights of free energy barriers on the appropriate control parameter leads to Vogel-Fulcher behavior. Reference [24] describes a numerical study of the local minima and the saddle points of the potential energy surface of small Lennard-Jones clusters. One of the quantities calculated in this paper is an ''entropic ratio'' R that approximately quantifies the entropic effects on the rate of thermally activated transitions between two local minima of the potential energy function. Values of $R>1$ indicate entropic suppression of the transition rate, whereas $R<1$ corresponds to an enhancement. The probability of R having values greater than 1 is found to be small. This result is interpreted as evidence for entropic effects being relatively unimportant. In particular, the authors mention that this observation contradicts our conclusion (described in detail in Ref. [19] and summarized in Sec. III C above) that the growth of relaxation times in simple glassy liquids is primarily entropic in origin. In our opinion, the results reported in Ref. [24] do not necessarily contradict our conclusion. The difference between our conclusion and that of Ref. [24] about the importance of entropic effects is probably just a reflection of the aforementioned fact that the free energy landscape changes with the control parameter, but the potential energy landscape does not. We find in our free-energy-based study that the *growth* of the height of a typical effective *free energy* barrier with increasing density is primarily due to entropic effects arising from an increase in the difficulty of finding low-free-energy paths to other minima. This effect is closely related to *changes* in the topography of the free energy landscape as the density is changed. In contrast, the potential energy landscape studied in Ref. [24] *does not* depend on the temperature which is the appropriate control parameter for the Lennard-Jones system considered there. In particular, the calculated values of the height of the potential energy barrier between two minima and the entropic factor R *do not* change as the temperature is changed. Therefore, there is no direct connection between our results (which, as explained above, are about the *changes* of these quantities as the appropriate control parameter is changed) and those reported in Ref. [24].

We end with a word of caution. Because of the computational complexity of numerical studies of free energy and potential energy landscapes, such studies have been restricted to rather small samples which may exhibit finite-size effects. In our work, we found that certain features of the free energy landscape are quite sensitive to the commensurability properties of the discretization scale and the sample size. Strong dependences on the sample size and the boundary condition have also been found [23,24] in studies of the potential energy landscape. One should, therefore, be careful in extrapolating the results obtained from such studies to the thermodynamic limit.

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