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Entropic origin of the growth of relaxation times in simple glassy liquids

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Transitions between ''glassy'' local minima of a model free-energy functional for a dense hard-sphere system are studied numerically using a ''microcanonical'' Monte Carlo method that enables us to obtain the transition probability as a function of the free energy and the Monte Carlo ''time.'' The growth of the height of the effective free-energy barrier with density is found to be consistent with a Vogel-Fulcher law. The dependence of the transition probability on time indicates that this growth is primarily due to an increase in the difficulty of finding low-free-energy paths to other minima. [S1063-651X(98)12307-3]

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The dynamic behavior of supercooled liquids near the glass transition [1] is one of the most enigmatic problems of condensed matter physics. The most dramatic feature of the dynamics near the glass transition in so-called fragile systems [2] is an extremely rapid growth of the relaxation time τ, which is reasonably well described by the Vogel-Fulcher law [3] $\tau \propto \exp[C/(T-T_0)]$, where $T_0 < T_g$, the conventionally defined glass transition temperature at which the viscosity attains a value of 10^{13} P. The apparent divergence of τ at T_0 has led to speculations about the possibility of a true thermodynamic transition at this temperature. This is also suggested by the observation [4] that the temperature T_K (the so-called Kauzmann temperature) at which the entropy difference between the supercooled liquid and the equilibrium crystalline solid extrapolates to zero is very close to T_0. The closeness of T_0 and T_K suggests that the growth of the relaxation time near the glass transition is primarily entropic in origin. Heuristic arguments that attempt to relate the Vogel-Fulcher law to entropic effects have been proposed by several authors [5,6]. However, we are not aware of any calculation that provides an explicit demonstration of such effects in simple model liquids.

In this paper we describe the results of a numerical investigation that provides direct evidence for an entropic origin of the growth of the relaxation time in simple liquids near the glass transition. Our computations are based on a model free-energy functional [7] for the hard-sphere system. We use a ''microcanonical'' Monte Carlo (MC) method described below to study transitions between different ''glassy'' minima of a discretized version of this free-energy functional. We determine the probability of transition from one minimum to another as a function of the free-energy increment Δf (the excess free energy per particle measured from that at the original minimum) and MC ''time'' t. This allows us to define an effective barrier height that depends weakly on t. We find that the growth of this effective barrier height with increasing density is consistent with a Vogel-Fulcher form appropriate for a hard-sphere system. Our numerical results about how the dependence of the effective barrier height on t changes as the density is increased indicate clearly 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 another.

The free-energy functional used in our study is of the form proposed by Ramakrishnan and Yussouff [7]:

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

where $\delta\rho(\mathbf{r}) \equiv \rho(\mathbf{r})-\rho_0$ is the deviation of the time-averaged local number density $\rho(\mathbf{r})$ from its value ρ_0 in the uniform liquid state, F_l is the free energy of the uniform liquid, T is the temperature, and $C(r)$ is the direct pair correlation function [8] of the uniform liquid at density ρ_0. $C(r)$ is expressed in terms of the dimensionless density $n^* \equiv \rho_0\sigma^3$($\sigma$ is the hard-sphere diameter) through the Percus-Yevick approximation [8], which is expected to be adequate if ρ_0 is not very high. The free energy of Eq. (1) may also be used to describe other simple liquids with short-range, isotropic interactions in the well-known ''effective hard-sphere'' approximation [8].

The discretized version of this free-energy functional exhibits [9] a large number of ''glassy'' minima (local minima of F at which the density is inhomogeneous but aperiodic) for $n^* > n_f^*$, where $n_f^* \simeq 0.85$ is the density at which equilibrium crystallization occurs. Numerical studies [10,11] of Langevin equations appropriate for this system show that the dynamic behavior is governed by thermally activated transitions among these glassy minima if n^* exceeds a ''crossover'' value that is close to 0.96. The time scales for such transitions were estimated from a standard MC method in Ref. [12] and found to rapidly increase with increasing density. Here we have used a different numerical method that is

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more efficient than the canonical MC method and provides information about the origin of the growth of the time scale of these thermally activated transitions. The increase of this time scale may be due to one or both of two factors: (a) an increase of the heights of the free-energy barriers that separate a glassy minimum from the others and (b) an increase of the difficulty in finding low-free-energy paths to other minima. Considering the free-energy functional as an effective Hamiltonian for the system, these two factors may be called energetic and entropic [13], respectively. The canonical MC method does not provide much information about the relative importance of these two factors in the observed growth of the time scales. As described below, the numerical method used in this study allows us to distinguish between energetic and entropic effects. It also allows us to follow the growth of the barrier-crossing time scale over about ten decades, which would not be possible in a canonical MC calculation.

We discretize our system on a cubic lattice of size L^3 and mesh constant h with dimensionless density variables defined as $\rho_i \equiv \rho(\mathbf{r}_i) h^3$. Periodic boundary conditions are used and the constraint that the sum of the variables ρ_i must be a constant N, the number of particles in the sample, is enforced during the simulation. We define a dimensionless free-energy per particle $f[\rho]$ as

$$f[\rho] = \beta F[\rho] / n^* L^3 a^3, \tag{2}$$

where a is the ratio h/σ and $\beta = 1/k_B T$.

Our numerical method, which may be called microcanonical MC if the free-energy functional is considered to be an effective Hamiltonian, involves the following steps. Each run is started from a glassy local minimum of the free energy. We choose a trial value of what we call the free-energy increment Δf and then perform a MC simulation in which we sweep the sites i of the lattice sequentially. At each step and site, we pick another site j at random from 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 *only if the dimensionless free energy after the change is less than* $F_{min} + N\Delta f$, where F_{min} is the dimensionless free energy βF at the minimum where the simulation is started. This procedure generates a random sampling of configurations whose free energy lies within $N\Delta f$ of that of the glassy minimum under consideration. The simulation proceeds up to a maximum time t_m, of MC steps per site. At regular intervals along the evolution of the system, we use a minimization procedure [9] to determine whether the system has moved to the basin of attraction of a different local minimum of the free energy. Obviously, if $N\Delta f$ is smaller than the lowest-free-energy barrier between the starting minimum and any other minimum, the system remains in the basin of attraction of the starting minimum. As Δf is increased, one begins to find transitions to other accessible minima, that is, minima that the system can find within a time $t \leqslant t_m$, which are separated from the initial one by a barrier of height less than $N\Delta f$. Repeating this procedure a number of times (typically 10–20) for a fixed set of values of n^*, Δf, and t_m, we obtain $P(n^*, \Delta f, t)$, the probability of a transition to a different minimum within time t for free-energy increment Δf, as the fraction of the number of runs in which a transition is found. This probability is calculated for a suitable range of values of n^*, Δf, and t and the whole procedure is repeated for several glassy minima of the free energy (see below). We define a ''critical'' value $\Delta f_c(n^*, t)$ of the free-energy increment as the value of Δf for which $P(n^*, \Delta f, t) = 0.5$. Clearly, $N\Delta f_c$ represents an effective barrier height for transitions to other local minima. This is the quantity that we use to present our results.

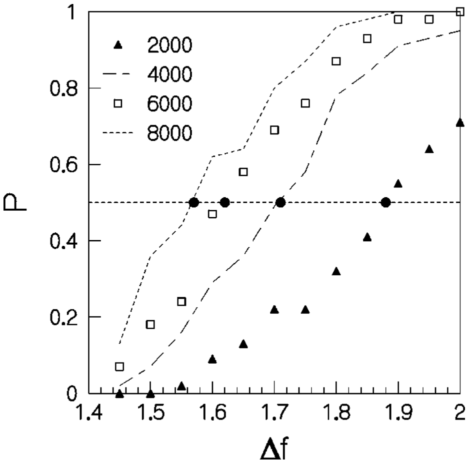

FIG. 1. Transition probability P (see the text) as a function of the free-energy increment Δf for four values of the time t. The data shown are for a $L = 12$ minimum at $n^* = 1.04$. The values of Δf_c are indicated by the filled circles.

We have used two sizes $L = 15$ and $L = 12$. In the first case we have taken $a = 1/4.6$ so that L and a are incommensurate with a close-packed lattice and no crystalline minimum of the free energy is found. The total number of inhomogeneous minima is then about 10 and all of them exhibit glassy structure as determined by the two-point correlation function of the local density. The minima we have used as our starting point in this case were also used in Ref. [12]. These are the minima to which the system moves [11] in the course of its time evolution under Langevin dynamics [10] when it is started from the uniform liquid state. For $L = 12$ we took $a = 0.25$ so that the sample is commensurate. It admits a crystalline minimum that has the lowest free energy for the values of n^* considered here. The number of glassy minima is substantially larger (about 30) in this sample. Out of those we chose a few with structure similar to that of the minima of the $L = 15$ sample. For both cases, the minima found at lower densities were ''followed'' to higher densities by running the minimization program at the higher density using the lower density configuration (which is of course not a minimum at the higher density) as the starting point. The values of t_m are 15 000 for $L = 15$ and 8000 for $L = 12$. The transition probability was calculated at time intervals of 5000 in the first case and 2000 in the second case. In both cases, the density range covered was $0.94 \leqslant n^* \leqslant 1.06$. Higher values of n^* were not considered because the Percus-Yevick approximation then becomes [8] inaccurate.

Typical results for P are shown in Fig. 1, where data for $L = 12$ and $n^* = 1.04$ are plotted for four different values of t. The value of Δf was incremented in steps of 0.05, which is

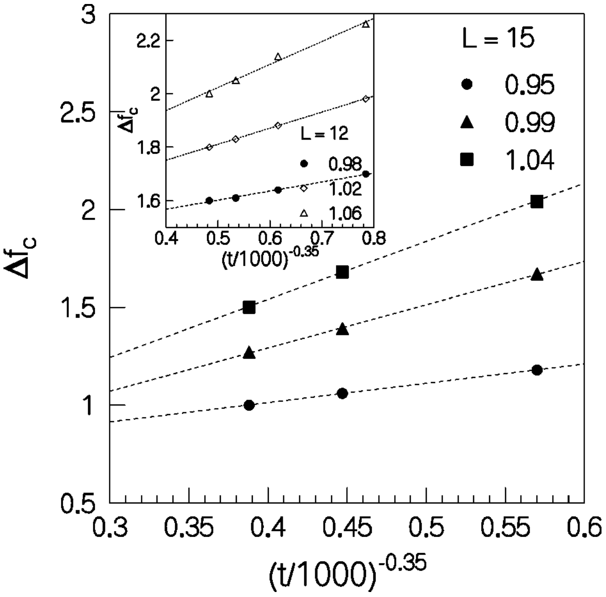

FIG. 2. Plots of Δf_c, obtained for a $L=15$ minimum, against $(t/1000)^{-0.35}$ for three values of n^*. The dashed lines are the best straight-line fits. Similar plots for a $L=12$ minimum are shown in the inset.

also the estimated uncertainty in the determination of Δf_c. The transition probability grows from zero as Δf is increased and eventually saturates at one for sufficiently large values of Δf. For a fixed value of Δf, the transition probability increases as t is increased: Transitions to other minima are more likely if the system is allowed to explore a larger number of configurations. Since P is an increasing function of both Δf and t, $\Delta f_c(n^*,t)$ (the value of Δf where $P=0.5$, as defined above) decreases as t is increased. In agreement with the previously observed [12] growth of the barrier-crossing time scale with n^*, we find that Δf_c is an increasing function of n^*.

The conclusion that entropic effects play a crucial role in the growth of the effective height of the free-energy barriers stems from the observation that the t dependence of Δf_c becomes *stronger* as n^* is increased (see Fig. 2). The t dependence of Δf_c is clearly related to the probability of finding the saddle points that connect the starting minimum with other minima. If such paths were relatively easy to find, then the transition probability would be insensitive to the value of t as long as it is not very short. If, however, paths to other minima are few, a large number of configurations have to be explored before one of them is found. The t dependence of Δf_c would then be more pronounced and extend to larger values of t. To make the idea more concrete, we ignore the correlations (which are short range in time) among the configurations generated in a MC run and assume that they represent t independent samplings of configurations with free energy less than $F_{min}+N\Delta f$. Let us also assume that the system does not return to the basin of attraction of the starting minimum after a transition to a different basin of attraction. We find that a return to the original basin of attraction is indeed very rare. The transition probability may then be estimated as $P(n^*,\Delta f,t)=1-[1-p(n^*,\Delta f)]^t \simeq 1-\exp(-tp)$, where $p(n^*,\Delta f)\ll 1$ is the probability that a randomly chosen configuration with $\beta F \leqslant F_{min}+N\Delta f$ belongs in the basin of attraction of a different minimum. One expects p to be zero if $\Delta f \leqslant \Delta f_0(n^*)$, where $N\Delta f_0$ is the height of the lowest free-energy-barrier, and $p=g(n^*,\Delta f-\Delta f_0)$ for $\Delta f>\Delta f_0$, where $g(n^*,x)$ grows continuously from zero as x is increased from zero. Combining this with the definition of Δf_c, we obtain the relation $g(n^*,\Delta f_c(n^*,t)-\Delta f_0(n^*))=\ln 2/t$. Our observation that the difference $\Delta f_c(n^*,t_1)-\Delta f_c(n^*,t_2)$ for fixed $t_1<t_2$ *increases* with n^* then leads to the conclusion that the function $g(n^*,x)$ *decreases* (i.e., the difficulty of finding paths to other minima increases) as n^* is increased at fixed x.

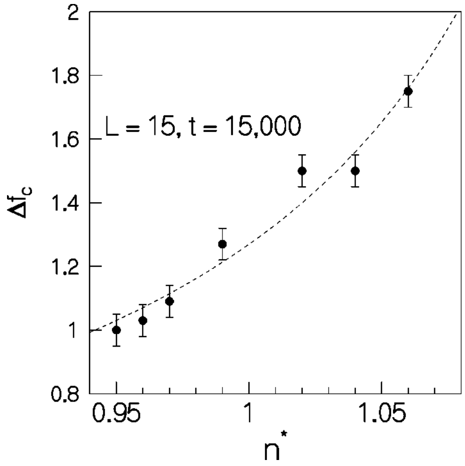

FIG. 3. Dependence of $\Delta f_c(n^*,t=15\,000)$ on n^* for $L=15$. The dashed line shows the best fit to a Vogel-Fulcher form (see the text).

The observed t dependence of Δf_c for all values of n^* and all the minima in our study is well represented by

$$\Delta f_c(n^*,t)=\Delta f_0(n^*)+c(n^*)t^{-\alpha}, \tag{3}$$

with α in the range 0.25−0.40. Typical fits to this form with $\alpha=0.35$ for two minima with $L=15$ and $L=12$ are shown in Fig. 2. The values of Δf_0 obtained from such fits with a fixed value of α are nearly independent of n^*, but exhibit a dependence on the value of α, varying between 0 and 0.5 for the $L=15$ minimum and between 1.3 and 1.5 for the $L=12$ minimum of Fig. 2. The quantity $c(n^*)$ increases with n^*. This corresponds to the function $g(n^*,x)$ having the form $g(n^*,x)\sim A(n^*)x^{1/\alpha}$, with $A(n^*)$ decreasing with increasing n^*. These results imply that (a) the lowest barrier height $N\Delta f_0$ is *nearly independent* of n^* and (b) for a fixed small positive value of $\Delta f-\Delta f_0$, the probability of finding a saddle point to other minima *decreases* as n^* is increased. We conclude from these observations that the growth of the effective barrier height with increasing n^* is primarily due to an entropic mechanism associated with an increase of the difficulty in finding low-lying saddle points that connect different glassy local minimum. This conclusion is consistent with the canonical MC results of Ref. [12], where we found that while the time scale of transitions between minima increases dramatically with n^*, the free-energy increment at the transition point remains essentially independent of n^*.

Our results for the dependence of Δf_c on n^* are consistent with the Vogel-Fulcher law [3], which assumes the following form [14] for our system:

$$\Delta f_c(n^*) = a + b/(n_c^* - n^*), \tag{4}$$

where a and b are constants and n_c^* is expected to be close to the random close-packing density $n_{rcp}^* \simeq 1.23$. There is some ambiguity in trying to fit our data to this form because our values of Δf_c depend weakly on the time t. However, the value of n_c^* obtained from fits of our data for $\Delta f_c(n^*,t)$ to Eq. (4) with fixed a is nearly independent of t. This is consistent with the form of Eq. (3) if $a = \Delta f_0$, $b \propto t^{-\alpha}$, and $c \propto 1/(n_c^* - n^*)$. Δf_0 is indeed nearly independent of n^* and the t dependence of b and the n^* dependence of c are in agreement with the other two conditions. For the $L=15$ case, we can fit the data for Δf_c at $t = 15\,000$ to the form of Eq. (4) with $a = 0(\Delta f_0 = 0)$. The best fit, shown in Fig. 3, corresponds to $n_c^* = 1.225$, very close to the expected result. The best fit to the $L=12$ data with $a \simeq 1.0$ (the difference between the values of Δf_0 for the $L=12$ and $L=15$ minima is about 1.0) also yields a similar value of n_c^*. So we conclude that the observed growth of the effective barrier height is consistent with the Vogel-Fulcher form. The increase in the effective barrier height as n^* is increased from 0.94 to 1.06 is about $25 k_B T$, corresponding to a growth of the characteristic time scale of about ten orders of magnitude. Thus the range of time scales covered in our study is comparable to that used in Vogel-Fulcher fits of experimental data and much wider than what can be achieved in standard MC or molecular dynamics simulations.

In summary, our study demonstrates that the Vogel-Fulcher–type growth of relaxation times in simple glassy liquids is primarily entropic in origin, the underlying mechanism being an increase in the difficulty of encountering low-lying saddle points that connect different glassy local minima of the free energy.

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[1] For a review see *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier, New York, 1991).

[2] C. A. Angell, J. Phys. Chem. Solids **49**, 863 (1988).

[3] H. Vogel, Z. Phys. **22**, 645 (1921); G. S. Fulcher, J. Am. Ceram. Soc. **8**, 339 (1925).

[4] W. Kauzmann, Chem. Rev. **48**, 219 (1948).

[5] J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys. **28**, 373 (1958); G. Adams and J. H. Gibbs, *ibid.* **43**, 139 (1965).

[6] T. R. Kirkpatrick and P. G. Wolynes, Phys. Rev. B **36**, 8552 (1987); T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, Phys. Rev. A **40**, 1045 (1989).

[7] T. V. Ramakrishnan and M. Yussouff, Phys. Rev. B **19**, 2775 (1979).

[8] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).

[9] C. Dasgupta, Europhys. Lett. **20**, 131 (1992).

[10] L. M. Lust, O. T. Valls, and C. Dasgupta, Phys. Rev. E **48**, 1787 (1993).

[11] C. Dasgupta and O. T. Valls, Phys. Rev. E **50**, 3916 (1994).

[12] C. Dasgupta and O. T. Valls, Phys. Rev. E **53**, 2603 (1996).

[13] The term *entropic* refers to the number of paths, which may be related [6] to the *configurational entropy*. It is unrelated to the free energy, which is in a different sense, purely entropic in a hard-sphere system.

[14] L. V. Woodcock and C. A. Angell, Phys. Rev. Lett. **47**, 1129 (1981).