Molecular-dynamics study of a supercooled two-component Lennard-Jones system

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Molecular-dynamics (MD) simulations have been carried out on a two-component Lennard-Jones system, quenched into supercooled and amorphous states. Two different regimes of viscous behavior are found in the time window accessible in MD simulation studies (of the order of nanoseconds if units appropriate for argon are used). The results for the time dependence of the self-intermediate scattering function $F^{s}(\mathbf{q},t)$ show two different slow relaxation processes, where the slowest (α relaxation) can be represented by a stretched exponential, $a \exp[-(t/\tau_{rel})^{\beta}]$. In the frequency domain this gives rise to a quasielastic peak, and it is found that its area, the nonergodicity parameter $f^{s}(q) \equiv a$, shows an anomalous decrease when increasing the temperature towards a critical value T_c . This happens in the supercooled-liquid regime, and it is one of the basic predictions of the recent mode-coupling theory for the liquid-glass transition problem. In the strongly supercooled-liquid regime the diffusion is of the hopping type, and it is found to be strongly cooperative in nature.

I. INTRODUCTION

If a liquid is cooled rapidly enough below the freezing temperature, it enters the supercooled-liquid regime. If cooled further, the dramatic increase of its viscosity causes the system to reach a state of such high viscosity that it acts effectively like a disordered solid, a glass. The occurrence of a liquid-glass transition is believed to be a more or less universal behavior of matter [1]. A glass transition temperature T_g is conventionally introduced and defined as the temperature where the viscosity reaches the value 10^{13} poise [2]. The relevant structural relaxation times are then macroscopic, of the order of hours. For practical purposes this is a relevant time scale, but there is no evidence for any deeper significance for this particular value. The glass transition temperature T_g only indicates the temperature below which the system behaves like a solid over macroscopic times.

Recently, the dynamics of glass-forming systems on a much shorter time scale has gained considerable interest [3,4]. The impetus was the success of certain nonlinear mode-coupling theories in describing a purely dynamic transition from an ergodic to a nonergodic (structurally arrested) behavior at a well-defined critical temperature T_c [5,6]. It is now recognized and accepted that the critical temperature T_c in the mode-coupling theory should not be identified with the experimental glass transition temperature T_g , but with a temperature where the viscosity is considerably smaller, $10-10^4$ poise. The corresponding time scale is mesoscopic, of the order of nanoseconds.

The notion of the importance of the nanosecond time region for the dynamics of viscous liquids is not new. Goldstein [7(a)] argued that when the shear relaxation time exceeds 10^{-9} s activated processes between local potential-energy minima start to dominate the flow processes, while at higher temperatures, this will no longer

be true. It is also well known [2,8] that the so-called fragile glass-forming liquids show a change of their temperature dependence for the viscosity, when cooling below a temperature where the viscosity is in the range 10-1000poise. It has also been shown [8b] that the Stokes-Einstein relation for the diffusion constant starts to break down for the same values of the viscosity.

Inelastic neutron scattering experiments are well suited for testing the theoretical predictions of the modecoupling theory. In particular, the neutron spin-echo technique has been used in order to reach the nanosecond regime. Extensive investigations have been done on quite different systems, such as ionic systems [9], molecular systems [10], polymers [11], and proteins [12]. The results are in qualitative agreement with the theory and in particular in the case of polybutadiene in quantitative agreement [11d]. Experiments have also been performed on colloidal suspensions [13] and here the relevant length and time scales are such that conventional light scattering and photon correlation measurements can be used. The comparisons with the theoretical predictions are convincing [14].

Molecular-dynamics (MD) simulation can also be used in order to reach the nanosecond regime for simple model systems. This technique is unique in the respect of yielding detailed information on a variety of correlation functions and on single-particle trajectories. Some recent MD work in relation to the liquid-glass transition problem can be found in Refs. [15–26]. In particular, the twocomponent soft-sphere system has been investigated in great detail [18,19].

Here, we will present MD results for a two-component Lennard-Jones system in the supercooled-liquid regime. Careful attention is paid to proper equilibrium of the system and long production runs are performed in order to reveal slow relaxation processes and to be able to obtain good statistics. We concentrate on the self-motion and in particular on the temperature dependence of the area under the quasielastic peak in the dynamic structure factor. This dependence has been in focus in the neutron scattering studies [9-11]. An identification of an anomalous decrease of the strength of the quasielastic peak is a strong indication in favor of the mode-coupling theory. We also try to characterize the processes that are responsible for the increase of the viscosity in the strongly supercooled regime. The statistics is poor due to the limited time region that can be covered in MD simulations, but the question is controversial and highly relevant for further development of the theoretical description.

The paper is organized in the following way. In Sec. II some basic predictions of the mode-coupling theory are briefly summarized. Section III gives some technical details about the MD simulation. The main section, Sec. IV, presents the numerical results together with directly related discussion. The paper is concluded by a summary and concluding remarks in Sec. V. Preliminary results of this work have been presented in Ref. [23(a)].

II. THE MODE-COUPLING THEORY

In this section we would like to present a short outline of the basic ideas behind the mode-coupling theory and the predictions which are relevant for this paper. Thorough reviews can be found in Refs. [3] and [4].

The mode-coupling theory for the liquid-glass transition is a development of theoretical concepts used for the description of the microscopic dynamics of dense liquids [27,28]. It includes explicitly delayed feedback effects, which arise from the fact that in dense systems each particle is hindered in its motion by the surrounding particles. It was found [5,6] that when lowering the temperature this nonlinear effect gives rise to a transition from an ergodic to a nonergodic state at a certain critical temperature T_c . The static quantities are assumed to vary smoothly when crossing the critical temperature T_c and the transition is purely dynamic in origin.

A frozen structure manifests itself in a strictly elastic peak in the dynamic structure factor,

$$S(q,\omega) = 2\pi f(q)S(q)\delta(\omega) + \cdots, \qquad (2.1)$$

where the ellipsis represents "more regular terms." Equivalently, the infinite time value of the intermediate scattering function is nonzero,

$$F(q,t \to \infty) = f(q)S(q) . \qquad (2.2)$$

Here, S(q) is the ordinary static structure factor and f(q) is a continuous positive function, which corresponds to the Debye-Waller factor of a crystalline structure. It may be viewed as an order parameter [29] and we will refer to it as the nonergodicity parameter. The mode-coupling theory makes the prediction that when increasing the temperature for the frozen structure the nonergodicity parameter decreases according to

$$f(q) = f_c(q) + h(q) [(T_c - T)/T_c]^{1/2}, \quad T \le T_c$$
 (2.3)

Equation (2.3) holds in the vicinity of T_c ($T \leq T_c$) and

both $f_c(q)$ and h(q) are temperature independent.

All quantities that couple to the density are predicted to show behavior similar to that in Eq. (2.3). In particular, we have for the self-motion a corresponding nonergodicity parameter, $F^{s}(q,t \rightarrow \infty) \equiv f^{s}(q)$, which fulfills the relation

$$f^{s}(q) = f^{s}_{c}(q) + h^{s}(q) [(T_{c} - T)/T_{c}]^{1/2}, \quad T \leq T_{c}$$
 (2.4)

The small q values of $f^{s}(q)$ determine the mean square displacement of localization length r_0 of the particles, according to

$$f^{s}(q \to 0) = 1 - (r_{0}q)^{2}$$
 (2.5)

At the liquid side, $T > T_c$, the theory predicts that the viscosity η diverges as a power law,

$$\eta = \eta_0 [T_c / (T - T_c)]^{\gamma} , \qquad (2.6)$$

where γ is a nonuniversal, system-dependent exponent. Besides Eqs. (2.3) and (2.6) the theory makes nontrivial predictions for the time dependences of the density correlation functions F(q,t) and $F^{s}(q,t)$. In the vicinity of T_{c} two different slow relaxation processes appear, the α and the β relaxation, besides the conventional fast microscopic one. The former, the α relaxation, is arrested below T_{c} , while the latter, the β relaxation, shows up as a subtle low-frequency singularity in the part of the spectrum denoted by the ellipsis in Eq. (2.1).

The transition from an ergodic to a nonergodic behavior at T_c is a result of the assumption that the relaxation kernel in the mode-coupling theory can be expressed in terms of only density modes [5,6]. We will refer to this as the ideal transition. Already in one of the original papers [6] it was argued that certain kinds of density fluctuations, connected with strong local anisotropies, have been left out and may cause a smearing of the sharp ideal transition. Later [30] it was shown that independently of the number of density modes included in the relaxation kernel, the transition is sharp, ideal.

By extending the original density-mode approximation and including also current contributions into the relaxation kernel it was shown that the transition is smeared out to a more continuous crossover and a strict nonergodic solution becomes impossible [31(a), 32(a)]. The density correlation functions F(q,t) and $F^{s}(q,t)$ will decay to zero for sufficiently long times also when $T < T_c$, but for intermediate times they will level off at a constant nonzero value. The strictly elastic peak in the spectra broadens to a quasielastic line, the α peak, and the viscosity does not diverge to infinity. The strength of the α peak is directly related to the plateau value of the corresponding density correlation function. However, it was found [32(b)] that for temperatures $T > T_c$ the basic dynamics did not change and the task is to find systems where it is possible to come close enough to the critical point, i.e., where the additional processes that restore ergodicity for $T < T_c$ (referred to as hopping processes or jump diffusion events) are sufficiently infrequent around T_c . The theoretical predictions from the theory for the

ideal transition can then be tested. In particular, we have that the strength of the α peak is given by Eqs. (2.3) and (2.4), respectively, for $T < T_c$. For $T > T_c$ the strength varies smoothly with temperature. This prediction will be tested in Sec. IV B 4.

An important issue is the location of the critical temperature T_c . The statement that T_c is located in a temperature region where the viscosity is of the order $10-10^4$ poise is based on experimental evidence [9-12]. It is possible to calculate the value for the critical temperature T_c only for very simple model systems, using a microscopic description. For realistic glass-forming liquids it has not been possible to perform calculations. The viscosity range $10-10^4$ poise corresponds to a moderately supercooled liquid.

In the strongly supercooled region $(T_g < T < T_c)$ the origins of the transport properties are evidently not the nonlinear couplings introduced in the original densitymode approximation. The validity of the proposed extension of the original theory is unsettled. It is possible to obtain an Arrhenius dependence for the viscosity at temperatures well below T_c [32(c)], in accordance with experiments. On the other hand, it has been stated [31(b)] that in order to come in contact with the conventional glass transition $(T \simeq T_g)$ one has to generalize the theory and allow for the underlying thermodynamic liquid-solid transition. In any case, for further development of the theoretical description it is important to be able to characterize correctly the processes that are responsible for the increase of the viscosity in the strongly supercooled-liquid state. In Sec. IV B 5 we present some information in that direction.

III. MODEL AND MOLECULAR-DYNAMICS PROCEDURE

We consider a binary mixture of $N_1 = 250$ particles of mass m_1 and diameter σ_{11} and $N_2 = 250$ particles of mass m_2 and diameter σ_{22} . For the interaction between all pairs of particles the Lennard-Jones potential is used,

$$v_{\alpha\beta}(r) = 4\varepsilon \left[\left[\frac{\sigma_{\alpha\beta}}{r} \right]^{12} - \left[\frac{\sigma_{\alpha\beta}}{r} \right]^{6} \right], \qquad (3.1)$$

where α and β are equal to 1 or 2, denoting the two different types of particles. The only differences between the two types of particles are that their masses and diameters differ, $m_2/m_1=2.0$ and $\sigma_{22}/\sigma_{11}=1.2$. The cross-interaction diameter is given by the Lorentz-Berthelot mixing rule, $\sigma_{12}=(\sigma_{11}+\sigma_{22})/2$.

Nucleation is easily bypassed in a binary mixture and that is the motivation for using a two-component system [18(a)]. The Lennard-Jones potential is used for its simplicity and the parameter values are chosen in the same way as in some previous MD studies on the binary soft-sphere mixture [18,19], where the interaction is given by $v_{\alpha\beta}(r) = \varepsilon (\sigma_{\alpha\beta}/r)^{12}$. By comparing with these previous studies the effect of the attractive part in the Lennard-Jones potential can be studied [24].

All the simulation results are reported in dimensionless units; energy is measured in ε , length in σ_{11} , and time in $\tau \equiv (m_1 \sigma_{11}^2 / \varepsilon)^{1/2}$. Assuming the 1 particles to be argon, $\tau=2.2$ ps and $\epsilon/k_B=120$ K. We will call this argon units. The equations of motion are integrated with periodic boundary conditions using the velocity version of Verlet's algorithm [33], with the time step being equal to $\Delta t=0.01\tau$. The calculations are carried out at constant total energy and the particle concentration n=N/V is kept fixed at the value $n^*=n\sigma_{11}^3=0.75$ and V denotes the total volume.

Due to the slow relaxation processes the phase space may be poorly sampled and that can become a serious problem in MD simulations, where small systems during short time periods have to be studied by necessity. To test this we have performed three independent series of calculations (a, b, and c). Each series is initiated by generating a random configuration of 500 particles at a high temperature $T^* \equiv k_B T/\epsilon = 2.0$. The system is then cooled quasicontinuously by scaling the velocities.

When the temperature is reduced to about $T^*=0.7$ the collection of data is started. First the velocities are scaled at each consecutive time step $\Delta t = 0.01\tau$ for the time t_{scale} (see Table I) to obtain a chosen temperature. The system is then left to evolve in time for the time t_{eq} (see Table I) in order to equilibrate the system properly. Temperature, pressure, and the static pair distribution functions $g_{\alpha\beta}(r)$ are monitored and only minor changes are observed. In the beginning of the equilibrium run these static properties are drifting slightly. Also the mean square displacements for the two different types of particles are determined and compared in consecutive time intervals of the size 200τ . The values for these

TABLE I. Different times used in the three different series of the MD simulation (a, b, and c); t_{scale} —time for scaling the velocities, t_{eq} —time for equilibration, t_{prod} —time for producing data. The time unit is equal to 2.2 ps if argon units are assumed.

No.	t_{scale}^*	$t_{\rm eq}^*$	$t_{\rm prod}^*$
<i>a</i> 1	10	0	100
<i>a</i> ₁	10	400	1200
a2	10	400	1200
u ₃	20	400	1200
a_4	40	800	1200
a_5	40	1200	1200
a_6	40	1200	2400
<i>a</i> ₇	40	1200	1200
\boldsymbol{b}_1	10	0	100
b_2	10	400	1200
<i>b</i> ₃	20	400	1200
b_4	20	800	2000
b ₅	20	800	1600
b_6	20	800	1600
b_7	20	1600	2000
b_8	20	1600	2000
c_1	10	0	100
c_2	20	400	1200
<i>c</i> ₃	20	800	1600
<i>c</i> ₄	20	800	1600
<i>c</i> ₅	20	800	1600
<i>c</i> ₆	20	1200	1600
<i>c</i> ₇	20	2000	1600

time-dependent correlation functions are drifting when comparing them in the first few time intervals of the size 200τ , indicating a nonequilibrium situation. After some time they stabilize and show a more fluctuating behavior. We then regard the sample to be in the supercooledliquid state and the following time period t_{prod} (see Table I) is used for evaluating static and dynamic quantities. At the lowest temperatures the system is frozen. The last

configuration for the next temperature. The cooling rate is considerably less than is generally used in MD studies. The equivalent cooling rate for argon would be of the order 10^9 K/s, which is comparable to those achieved by the fastest experimental techniques.

configuration at one temperature is used as initial

In no case have we seen any sign of crystallization. This has been verified by monitoring the time dependences of the instantaneous pressure and temperature. One state c_5 seems to be in error [23(a)]. Pressure, temperature, and pair distribution functions behave normally, but the mean square displacement for the 1 particles is too small compared with the corresponding displacement for the 2 particles [23(a)]. The reason can be the small size of the system we are using. The data evaluated from this state are not shown in the figures that follow.

IV. RESULTS AND DISCUSSION

A. Static quantities

1. The total energy

The simulation is carried out at constant volume. At low temperatures, where the system is frozen and its vibrational motion approximately harmonic, the total energy per particle u should depend linearly on the temperature,

$$u = u_0 + 3k_B T$$
 (4.1)

The slope, the heat capacity at constant volume, is given by the law of Dulong and Petit. In Fig. 1 we show the temperature dependence of the total energy. The different symbols correspond to the three independent series of calculations (a, b, and c) with different starting configurations. The dashed straight line is fitted to the low-temperature values and has the slope 3, in accordance with Eq. (4.1). When the temperature is increased there is a change of the temperature dependence around $T^*=0.5$. We have indicated this by fitting a dotted straight line to the high-temperature values.

The crossover temperature $T^* \simeq 0.5$ marks the change from solidlike to liquidlike behavior for the heat capacity. For $T^* < 0.5$ the system is solidlike for the relevant "experimental" time scale t_{prod} . In our case it is equal to nanoseconds if argon units are assumed. By extending the simulation in time we expect the temperature points below $T^* \simeq 0.5$ to change slightly and the crossover temperature to move to lower temperatures. The location of the crossover temperature depends strongly on the pressure. At zero pressure the transition is located around $T^* \simeq 0.35$ [24], which coincides with the findings in Ref. [15(b)].



FIG. 1. The temperature dependence of the total energy per particle u for the different states defined in Table II. The dashed line is fitted to the low-temperature points and has the slope 3 [cf. Eq. (4.1)]. The dotted line is fitted to the hightemperature points. The arrow indicates the location of the temperature (the critical temperature T_c) where the dynamic anomalies are most pronounced.

For the low-temperature states time averaging becomes ineffective in sampling the relevant phase space, particularly for the small systems that are used in computer simulation studies. The problem is that the system becomes nonergodic. Proper ensemble averaging is very costly on a computer. We have tried to test if the nonergodicity is a major problem by using the three independent series of calculations (a, b, and c). We have found no significant difference between these three series.

2. The pair distribution function

A fundamental assumption behind the mode-coupling approach for the liquid-glass transition problem is that static quantities are assumed to change smoothly. Only by inspecting dynamic quantities can one identify if a system is in the supercooled-liquid or glassy state. This identification also depends on the time (frequency) window that is being used.

In Fig. 2 we show the partial pair distribution function $g_{11}(r)$ for the 1 particles and at three different temperatures. When lowering the temperature the second peak evolves into a double peak, the characteristic signature of dense random packing. These three curves correspond to a large temperature change. The self-diffusion constant changes with two orders of magnitude over the same temperature interval. In a similar computer simulation study of a two-component Lennard-Jones system [15(b)] it was found that the structure changed slightly and local five-fold symmetry became more prominent when lowering the temperature. It is difficult to judge if these kinds of changes of static quantities are crucial for the description of the liquid-glass transition.



FIG. 2. The pair distribution function $g_{11}(r)$ for the 1 particles at three widely separated temperatures.

B. Dynamic quantities: Single-particle properties

This paper concentrates on the dynamic quantities of the simulated system. We have chosen to present results only for the single-particle properties. The statistics for these are better than for the corresponding collective ones. Also when comparing with the mode-coupling theory there is no essential difference between singleparticle and collective properties.

1. The self-diffusion constant

In all our simulations we have determined the mean square displacements of the particles. From the slope of these curves we have evaluated the self-diffusion constant D_{α} and the relevant data are collected in Table II. At low temperatures the uncertainty is large, but it is difficult to give a proper error bar. An indication of the magnitude of the error can be obtained by comparing the result from the three different series of calculations. For the two states with lowest temperature the diffusion is too small to be detectable. One can compare these values for the self-diffusion constant with the corresponding value for a one-component Lennard-Jones system near the triple point which is $D^* = 3.3 \times 10^{-2}$ [34].

2. The velocity correlation function

We have also determined the velocity correlation function for the two species $\Phi_{\alpha}(t)$. In Fig. 3 the result for the 1 particles is shown at the same temperatures as in Fig. 2. The behavior is typical of a dense system. There is a strong backscattering effect and some weak oscillations. This indicates a temporal confinement in a cage built up by the surrounding particles.

The behavior is surprisingly similar at the three different temperatures. In the next subsection we will show that at the highest temperature (a_2) the dynamics at a mesoscopic time scale $(t^* \sim 10^3)$ is liquidlike, while at the lowest temperature (a_6) the system is frozen. These differences are not visible in the velocity correlation function. The time window used in Fig. 3 defines the typical

TABLE II. Temperature T, pressure P, and total energy per particle u for the three different series of calculations (a, b, and c). Also the self-diffusion constants D_{α} for the two different species are shown, determined from the slope of the mean square displacements. All results in reduced units.

No.	T*	P*	u *	D [*] ₁	D_{2}^{*}
<i>a</i> ₁	0.8023	5.042	-5.375		
a_2	0.6886	4.145	-5.755	2.9×10^{-3}	1.9×10^{-3}
<i>a</i> ₃	0.6229	3.513	-6.006	9.4×10^{-4}	6.1×10^{-4}
a ₄	0.5662	3.047	-6.202	4.7×10^{-4}	2.7×10^{-4}
a_5	0.5229	2.598	-6.372	5.8×10^{-5}	3.8×10^{-5}
a ₆	0.4335	1.998	-6.644	2.0×10^{-5}	5.2×10^{-6}
<i>a</i> ₇	0.2042	0.535	-7.320		
\boldsymbol{b}_1	0.7999	4.999	-5.388		
b_2	0.7038	4.207	-5.719	2.8×10^{-3}	1.9×10^{-3}
b_3	0.6213	3.396	-6.040	5.5×10^{-4}	3.1×10^{-4}
<i>b</i> .	0.5664	3.023	-6.204	3.0×10^{-4}	2.0×10^{-4}
b.	0.5457	2.832	-6.279	2.4×10^{-4}	1.0×10^{-4}
b,	0.5512	2.880	-6.266	2.8×10^{-4}	1.6×10^{-4}
b_{7}	0.5051	2.417	-6.457	6.9×10^{-5}	1.9×10^{-5}
b_8	0.3549	1.463	-6.898		
<i>C</i> ₁	0.8134	5.171	-5.325		
C ₂	0.7043	4.215	-5.718	3.0×10^{-3}	2.1×10^{-3}
C ₃	0.6355	3.590	-5.970	1.3×10^{-3}	7.1×10^{-4}
C _A	0.6164	3.244	-6.087	5.0×10^{-4}	2.3×10^{-4}
C 5	0.5853	2.907	-6.219	1.9×10^{-4}	8.8×10^{-5}
c,	0.5578	2.809	-6.278	1.8×10^{-5}	7.5×10^{-5}
$\tilde{c_7}$	0.4058	1.766	-6.738	4.1×10^{-6}	1.3×10^{-6}



FIG. 3. The velocity correlation function $\Phi_1(t)$ for the 1 particles at the same temperatures as in Fig. 2.

microscopic time scale. It is of the order $t^* \simeq 0.1$ $(2 \times 10^{-13} \text{ s if argon units are assumed})$. We can compare our results for the velocity correlation function with the corresponding result for the soft-sphere system [18(b)]. In that case the oscillations are somewhat more pronounced.

3. The Van Hove self-correlation function

A more detailed picture of the single-particle motion can be obtained from the Van Hove self-correlation function

$$G_{\alpha}^{s}(\mathbf{r},t) = \frac{1}{N_{\alpha}} \sum_{i=1}^{N_{\alpha}} \left\langle \delta(\mathbf{r}_{i}(t) - \mathbf{r}_{i}(0) - \mathbf{r}) \right\rangle , \qquad (4.2)$$

where $\mathbf{r}_i(t)$ denotes the position of particle *i* of species α at time *t*. Both for a liquid in the hydrodynamic limit and a frozen system in the harmonic approximation, the van Hove self-correlation function is a Gaussian,

$$G_{\alpha}^{s}(\mathbf{r},t) = \frac{1}{\left[\pi w_{\alpha}^{2}(t)\right]^{3/2}} \exp\left[-\frac{r^{2}}{w_{\alpha}^{2}(t)}\right].$$
 (4.3)

The width function $w_{\alpha}(t)$ is given by $w_{\alpha}^{2}(t)=2D_{\alpha}t$ and $w_{\alpha}^{2}(t>t_{D})=A_{\alpha}T$, respectively, where D_{α} is the selfdiffusion constant for species α , A_{α} a constant that depends on the vibrational properties of the system, and Tis the temperature. The time t_{D} is a microscopic time, of the order of an inverse Debye frequency, $t_{D} \sim 1/\omega_{D}$. The mean square displacement is given by the second moment of $G_{\alpha}^{s}(\mathbf{r}, t)$.

The function $f_{\alpha}(r,t) \equiv 4\pi r^2 G_{\alpha}^s(|\mathbf{r}|,t)$ is equal to the probability of finding a particle of species α at time t at the distance r from its location at time 0. For a liquid in the hydrodynamic limit the location of the maximum of $f_{\alpha}(r,t)$ as function of r is changing in time according to $r_{\alpha}^{\max}(t) = (2D_{\alpha}t)^{1/2}$. In a frozen structure $r_{\alpha}^{\max}(t)$ reaches a constant value after a short time,

$$r_{\alpha}^{\max}(t > t_D) = (A_{\alpha}T)^{1/2}$$
, (4.4)

valid in the harmonic approximation.

In Fig. 4 we show the Van Hove self-correlation function for the 1 particles at three different temperatures. At each temperature $f_1(r,t)$ is shown for several different times in order to reveal the character of the diffusive motion. At high temperatures (a_3) the function has a single peak which is moving to larger distances with increasing time. This is the typical behavior for a liquid.



FIG. 4. The Van Hove self-correlation function $G_1^s(|\mathbf{r}|,t)$ for the 1 particles at three different temperatures. The spatial dependences of the function $f_1(\mathbf{r},t) \equiv 4\pi r^2 G_1^s(|\mathbf{r}|,t)$ are shown for five different times. At the lowest temperature we show also the last curve ($t^* = 1000$) increased by a factor 10.

At low temperatures (a_5) the peak becomes arrested and a gradual increase of a second as well as a third peak is visible. For these temperatures and times the system is essentially frozen. The second and third peaks are due to rare jump diffusion events. The crossover between these two types of behavior occurs near $T^*=0.55$.

Similar behavior has been found previously for the binary soft-sphere system and the crossover is designated as the "kinetic glass transition" [18(f),18(h)]. The simulation data on the soft-sphere system [18(f),18(h)] strongly suggest that the observed transition is an intrinsic property of the system, independent of the quenching history. It is identified as a smeared version of the ideal glass transition, predicted by the mode-coupling theory.

According to the mode-coupling theory for the ideal transition the mean square displacement should increase as a power law when increasing the temperature towards the critical temperature T_c . At the critical temperature $T = T_c$ the mean square displacement reaches a constant value r_c . To test this prediction one would like to extract the dynamics of the frozen structure. A better candidate for the mean square displacement of the frozen structure than the second moment of $G_{\alpha}^s(\mathbf{r},t)$ is the location of the maximum of $f_{\alpha}(\mathbf{r},t)$. The latter quantity is less influenced by the rare jump diffusion events, which are supposed to smear and partly destroy the theoretical ideal transition.

We have determined the location of the maximum r_1^{max} and the result for the squared quantity is shown in Fig. 5. At high temperatures (a_2-a_3) , where $f_1(r,t)$ has a single peak, the identification of the peak with a frozen structure is questionable. At low temperatures (a_5-a_7) , however, we have a well-defined peak, associated with the frozen structure. For intermediate temperatures (a_4) we can identify a peak, at least for $t^* < 400$, that reflects the frozen structure. We have indicated the behavior for a harmonic system, Eq. (4.4), with the dashed straight line. The slope A_1 is adjusted to value with the lowest temperature (a_7) and it is equal to $A_1^* = 0.045$. The full circles



FIG. 5. The location of the first maximum r_1^{max} of the function $f_1(r,t) \equiv 4\pi r^2 G_1^s(|\mathbf{r}|,t)$ at different temperatures. The squared quantity $(r_1^{\text{max}})^2$ is shown at several different times. The dashed line is the result for a frozen harmonic system [cf. Eq. (4.4)].

show the result at $t^*=4$. This time scale is microscopic and we may associate the departure from the straight line with conventional nonharmonic effects. By considering longer times we notice a substantial further increase of r_1^{max} for $T^* > 0.5$.

By using r_1^{max} instead of the mean square displacement the effects of the jump diffusion events are reduced, but not eliminated. Ideally one would like to study the dynamics for the frozen system, uninfluenced by the jump diffusion events. This is not possible here. The present model system, as well as the similar soft-sphere system, is not ideal for testing the mode-coupling theory. However, it is tempting to identify the anomalous increase of r_1^{max} around $T^*=0.55$ with the prediction from the modecoupling theory, given in Eqs. (2.4) and (2.5).

4. The self-intermediate scattering function

In neutron scattering experiments one measures the density correlation functions. The quantity that is obtained directly in the neutron spin-echo technique is the intermediate scattering function. Its incoherent part, the self-intermediate scattering function $F^s_{\alpha}(\mathbf{q},t)$, is given by the Fourier transform in space of the van Hove self-correlation function $G^s_{\alpha}(\mathbf{r},t)$.

We have determined the self-intermediate scattering function $F_{\alpha}^{s}(\mathbf{q},t)$ for both species at the temperatures given in Table II. At each temperature $F_{\alpha}^{s}(\mathbf{q},t)$ is evaluated for times $0 \le t^* \le 1000$ and for eight different wave vectors. In Fig. 6 the result is shown for several different temperatures (a_2-a_7) and for two different wave vectors. The smallest wave vector $q^*=6.47$ is located slightly below the main peak in the static structure factor, which is centered around $q^* \simeq 7$.

The dramatic slowing down of the time decay is clearly seen in Fig. 6 (notice the logarithmic scale). This effect has been observed previously in several MD studies [16-20]. At the highest temperature shown (a_2) , the self-diffusion constant is already an order of magnitude less than the value near the triple point for a onecomponent Lennard-Jones system $(D^*=3.3\times10^{-2})$. At the lowest temperature the system is completely frozen and $F_{\alpha}^{s}(\mathbf{q},t)$ is constant for times $t^* \gtrsim 10$. The slowing down of the time decay reflects itself in the decrease of the self-diffusion constant (see Table II).

We now would like to test the prediction in Eq. (2.4). To do that one has to extract the nonergodicity parameter $f_{\alpha}^{s}(q)$ from the MD data. In the idealized situation $f_{\alpha}^{s}(q) \equiv F_{\alpha}^{s}(q, t \to \infty)$, but for a real system $F_{\alpha}^{s}(q, t)$ always decays to zero for sufficiently long times. The quantity $f_{\alpha}^{s}(q)$ should then be identified with the plateau value of $F_{\alpha}^{s}(q, t)$ at intermediate times. The conventional way to extract this value is to fit the slow decay of $F_{\alpha}^{s}(q, t)$ to a stretched exponential, $f(t)=a \exp[-(t/\tau_{rel})\beta]$. The nonergodicity parameter is then identified with the amplitude a, $f_{\alpha}^{s}(q)\equiv a$, i.e., with the strength of the corresponding quasielastic peak in the frequency spectrum.

At low temperatures the amplitude a can be determined unambiguously, but at higher temperatures the plateau is less well developed. To bias the data as little as possible we use the following procedure. A nonlinear fit is performed at each temperature and all three parameters $(a, \beta, and \tau_{rel})$ are allowed to vary independently. The time interval $10 \le t^* \le 1000$ is used and each point in this time interval (9900 equidistant points with spacing $\Delta t^*=0.1$) is assumed to have the same weight. At the higher temperatures $F^s_{\alpha}(\mathbf{q},t)$ decays to zero before $t^*=1000$ and in the fitting procedure a lower upper limit for the time interval is used. The procedure becomes dubious at the highest temperature and for the largest wave vectors, which is clearly seen in Fig. 6(b). Relevant data are collected in Table III and the fitted stretched exponentials are shown as dashed lines in Fig. 6.

In Fig. 7 we show the result for the logarithm of $f_1^s(q)$ as a function of temperature. The results for the 1 particles at two different wave vectors are shown and similar results are obtained for other wave vectors as well as for the 2 particles. The results from the three independent



TABLE III. Different parameters in the stretched exponential $f(t)=a \exp[-(t/\tau_{rel})^{\beta}]$, obtained by a fitting to the MD data for the 1 particles. The results from series *a* and for two different wave vectors are shown. The time unit is equal to 2.2 ps if argon units are assumed.

No.	a	β	$ au_{ m rel}^{m *}$
	q*	=6.47	
a_2	0.597	0.807	16
a_3	0.611	0.741	77
a_4	0.618	0.789	225
a_5	0.695	0.632	6 206
a_6	0.780	0.430	51 757
a_7	0.890		
	q*	=12.9	
a_2	0.264	0.610	4
a_3	0.165	0.807	40
a_4	0.194	0.881	121
a_5	0.286	0.551	4 0 8 1
a_6	0.385	0.448	14 068
a_7	0.640		



FIG. 6. The self-intermediate scattering function $F_1^s(\mathbf{q},t)$ for the 1 particles at six different temperatures (see Table II). The results for two different wave vectors are shown. The main peak in the static structure factor is located around $q^* \sim 7$. The dashed lines show the fitted stretched exponentials. Notice the logarithmic time scale. The time unit is equal to 2.2 ps if argon units are assumed.

FIG. 7. The temperature dependence of the logarithm of the nonergodicity parameter $f_1^s(q)$ for the 1 particles. The results for two different wave vectors are shown. The main peak in the static structure factor is located around $q^* \sim 7$. The dotted lines indicate the behavior predicted by the mode-coupling theory [cf. Eq. (2.4)] and the dashed lines show the result for a frozen harmonic system [cf. Eq. (4.5)].

series of calculations (a, b, and c) coincide reasonably well. The spread of the data points at high temperatures, $T^* > 0.60$, is mainly due to the problem of fitting $F_{\alpha}^s(\mathbf{q}, t)$ to the stretched exponential. For a frozen harmonic system we have a linear temperature dependence for

$$\ln f_{\alpha}^{s}(q) = -\frac{A_{\alpha}}{4}q^{2}T , \qquad (4.5)$$

where A_{α} is the same quantity as in Eq. (4.4). This behavior is shown as dashed lines in Fig. 7 and the slope, $A_1^* = 0.042$, is adjusted to the value with lowest temperature. This value for A_1 is not identical with the value used in Fig. 5, but very close.

For temperatures $T^* > 0.5$ the system becomes strongly anharmonic and the mode-coupling theory is aiming at explaining this in terms of a dynamic phase transition. According to the theory the nonergodicity parameter $f_{\alpha}^{s}(q)$ should show a square-root decrease when increasing the temperature towards the critical temperature T_{c} [cf. Eq. (2.4)]. We have indicated this behavior with dotted lines in Fig. 7. The parameters $f_{c}^{s}(q)$, $h^{s}(q)$, and T_{c} are determined by fitting to the MD data points and the obtained values are given in Table IV. The MD data do not prove the square-root dependence in Eq. (2.4), but they are certainly consistent with the prediction by the mode-coupling theory.

The relaxation processes that are responsible for the anomalous decrease of the nonergodicity parameter are also responsible for the increase of r_{α}^{max} , shown in Fig. 5. The relevant time scale for the relaxation processes is of the order $t^* \sim 10$. Conventional anharmonic effects are associated with a much shorter time scale.

5. The dynamics in the strongly supercooled liquid

We have also tried to characterize the single-particle motion in the strongly supercooled liquid. At the lowest temperatures $(T^* < 0.35)$ nothing happens within the time scale of the MD simulation, besides small amplitude vibrational motion of the particles around local equilibrium locations. At slightly higher temperatures $(T^* \sim 0.40)$ some dynamic events with larger displacements occur. When the temperature is further increased these kinds of events become more frequent.

To quantify this we have followed the trajectory of each single particle in detail. The displacements

$$\Delta R_i(t_1 + t_0) \equiv |\mathbf{R}_i(t_1 + t_0) - \mathbf{R}_i(t_0)|$$
(4.6)

are determined in time intervals of the size 100τ , $0 \le t_1 \le 100\tau$. The displacements are measured with

TABLE IV. Different parameters in Eq. (2.4) obtained by fitting to the MD data in Fig. 7.

q*	$f_c^s(q)$	$h^{s}(q)$	T_c^*
6.47	0.612	0.431	0.566
12.9	0.213	0.477	0.566

respect to the location $\mathbf{R}_i(t_0)$ of the particles at the beginning of each separate time interval. In each time interval we have determined the maximum displacement, $\Delta R_i^{\max} \equiv \max[\Delta R_i(t_1)]$, and we have counted the number of particles with $\Delta R_i^{\max} < 0.75\sigma_{11}, 0.75\sigma_{11} < \Delta R_i^{\max} < \sigma_{11}$, and $\sigma_{11} < \Delta R_1^{\max}$, respectively. In Table V the result is shown from the simulation no. a_6 ($T^* = 0.4335$). We also show the time dependence of $\Delta R_i(t)$ for a few numbers of particles in two different time intervals in Figs. 8 and 9. All these particles are 1 particles, except the particle denoted by I in Fig. 9, which is a 2 particle.

The majority of particles perform small amplitude vibrational motion and are counted in the first group I, $\Delta R_i^{\max} < 0.75\sigma_{11}$. These particles do not contribute to the diffusive motion but they give rise to the dominant contribution to average properties. To make a contribution to diffusion the particles have to make larger displacements. At $T^*=0.4335$ the number of these particles is small and it is possible to analyze these events in some detail. We concentrate on the particles belonging to group III, $\sigma_{11} < \Delta R_i^{\max}$.

In the time interval $300 < t^* < 400$ four particles make large displacements. We denote these by B, C, D, and E. The corresponding functions $\Delta R_i(t)$ are shown in Fig. 8 together with the typical behavior of a particle belonging to group I, denoted by A. Three particles C, D, and E make a large displacement nearly instantaneously and they do not return to their previous equilibrium locations. At the same time particle B makes a large displacement but it returns. These four particles are located in the vicinity of each other. This can be seen in Fig. 10 where the instantaneous locations of particles are shown at three different times. Imagine that the 1 and 2 particles are represented by spheres with the radius equal to σ_{11} and σ_{22} , respectively. Figures 10 and 11 then show the result from an artificial cut through the liquid. The small circles correspond to particles which are located slightly above or below the artificial plane. The letters show the location of the same particles as are shown in

TABLE V. Number of particles with maximum displacements $\Delta R_1^{\max} \equiv \max[\Delta R_i(t_1)]$ [cf. Eq. (4.6)] in different spatial intervals defined by I: $\Delta R_i^{\max} < 0.75\sigma_{11}$; II: $0.75\sigma_{11} < \Delta R_i^{\max} < \sigma_{11}$; III: $\sigma_{11} < \Delta R_i^{\max}$. The results are taken from simulation No. a_6 ($T^* = 0.4335$) and the displacements are measured with respect to the location of the particles at the beginning of each time interval.

Time interval	Ι	II	III
$0 < t^* < 100$	498	2	0
$100 < t^* < 200$	497	3	0
$200 < t^* < 300$	499	1	0
$300 < t^* < 400$	481	15	4
$400 < t^* < 500$	498	2	0
$500 < t^* < 600$	496	4	0
$600 < t^* < 700$	488	11	1
$700 < t^* < 800$	471	22	7
$800 < t^* < 900$	488	10	2
$900 < t^* < 1000$	468	23	9



FIG. 8. The time dependence of the displacements $\Delta R_i(t \equiv t_1 + t_0) \equiv |\mathbf{R}_i(t_1 + t_0) - \mathbf{R}_i(t_0)|$ for five particles in the time interval $300 < t^* < 400$, taken from simulation No. a_6 ($T^* = 0.4335$). Particle A shows the typical behavior.



FIG. 9. Same as in Fig. 8 but for seven other particles and in the time interval $900 < t^* < 1000$.

Figs. 8 and 9, respectively. It is not possible to locate a plane where all five particles A-E are visible at the same time. In Fig. 10 particle B is located above the plane at a distance slightly larger than $\sigma_{11}/2$, but in the vicinity of C-E. Figures 8 and 10 show that the motion of C, D, and E is strongly correlated. They perform a type of "chain" motion; (1) C moves to a new position, (2) D moves to the initial location of C, and (3) E moves to the initial location of C, and (3) E moves to the initial location of D. There is no clear time ordering of the events (1)-(3). At the same time particle B and other particles in the vicinity, counted in group II, make large displacements, but they all return to their initial equilibrium locations. After this event no large displacements.

In the time interval $600 < t^* < 700$ one particle makes a large displacement. However, this particle returns to its initial equilibrium location and its motion is very similar to the one shown in Fig. 8 for particle B. In general, we find several events where particles make large displacements but then return. Sometimes these events are directly correlated to large "irreversible" displacements as in Fig. 8, but not always. This motion is strongly anharmonic. The particle makes a displacement much larger than the mean displacement and for an extended time period, several vibrational periods. This gives rise to a further relaxation and the relevant relaxation time is given by the extension of the time period of the excursion, which is of the order $\tau^* \sim 10$. At the present temperature too few of these events occur to really be visible in average quantities, such as, for instance, the van Hove self-correlation function. At higher temperatures the events are more frequent but it then becomes more difficult to make a detailed analysis of individual trajectories. It is very difficult to settle if this kind of motion can be connected to a distinct secondary slow relaxation process. We will make some more comments on this in the last section.

In the time interval $700 < t^* < 800$ seven particles make large displacements and four of these do not return to their initial equilibrium locations. In the interval $800 < t^* < 900$ two particles make a "chain" type of motion similar to the one in the time interval $300 < t^* < 400$.

In the time interval $900 < t^* < 1000$ nine particles make large displacements. Six of these, denoted by F-K, are located in the vicinity of each other (see Figs. 9 and 11). Around $t^*=940$ F and G make large displacements but they return. Later, at $t^*=966$, they again make large displacements but at this time the motion is "irreversible." At the same time three particles, L-N, are involved in a "chain" type of motion some interparticle distances away from particles F-K. The motion of these two groups of particles seems to be directly correlated, but they are not located in the immediate vicinity of each other. Also when the periodic boundary conditions, used in the simulation, are taken into account the distance between F-K and L-N is several interparticle distances.

In conclusion, the diffusive motion is complicated and strongly cooperative in nature. All events that we have observed differ from ordinary interstitial diffusion in solids, where a single particle makes a jump and the surrounding particles only make small readjustments. We argue that there may be a tendency for a secondary slow relaxation process, seen as large "reversible" displacements. Qualitatively, the same kind of motion has been seen in the two-component soft-sphere system [18(c)]. It

is only possible to analyze comparatively few events in detail and the statistics become poor. Hopefully, the present data show some typical events occurring in the strongly supercooled liquid.





FIG. 10. The instantaneous location of particles at an artificial cut through the liquid. The 1 and 2 particles are represented by spheres with the radius equal to σ_{11} and σ_{22} , respectively. Small circles correspond to particles which are located slightly above or below the artificial plane. The letters show the location of the same particles as shown in Fig. 8.

FIG. 11. Same as in Fig. 10 but for the particles in Fig. 9.

V. DISCUSSION AND CONCLUSIONS

We have investigated the dramatic slowing down of the structural relaxation in a simple supercooled liquid, a two-component Lennard-Jones fluid. Two different regimes of viscous behavior are found in the time window accessible in MD simulations.

At high temperatures $(T^* > 0.6)$, but still within the supercooled-liquid regime, the behavior is "liquidlike." This is seen by monitoring the time evolution of the van Hove self-correlation function $G_{\alpha}^{s}(\mathbf{r},t)$ which shows the behavior typical of a dense liquid [cf. Fig. 4(a)]. The difference between the supercooled liquid and an ordinary dense liquid is merely quantitative, the supercooled liquid is more viscous, and the corresponding structural relaxation times are longer.

At low temperatures $(T^* < 0.5)$ the system is essentially frozen for times $t^* < 10^3$. The position of the peak in $f_{\alpha}(r,t) \equiv 4\pi r^2 G_{\alpha}^s(|\mathbf{r}|t)$ remains unchanged after an initial microscopic time. A tail in $f_{\alpha}(r,t)$ at larger distances is built up gradually at the expense of a slow decay of the strength of the peak [cf. Fig. 4(c)]. This is caused by hopping processes, which are investigated in some detail in Sec. IV B 5. The hopping processes are found to be strongly cooperative in nature. Many particles participate and several of them, but not all, make instantaneously large displacements, of the order of interparticle distances, and they do not return to their initial equilibrium locations. The motion of these particles contributes to the diffusion processe.

The transition between the two types of viscous behavior is rather abrupt and it is located around $T^*=0.55$. This temperature is identified with the critical temperature T_c in the mode-coupling theory. The corresponding time scale for structural relaxations is $\tau_{\rm rel} \sim 250\tau$ (0.5 ns if argon units are assumed) and it coincides with the conjecture by Goldstein [7(a)] that the viscous behavior changes in a qualitative way when the shear relaxation time exceeds 10^{-9} s. It is important to notice that this transition is an intrinsic property of the system. We have found no evidence for a dependence on the cooling rate, provided it is sufficiently slow. The same conclusion is also obtained in the study of the two-component softsphere system [18].

A conventional glass transition is obtained if the time scale for structural relaxations becomes comparable to or longer than the "experimental" time scale. In our case this occurs at about the same temperature. The drop of the heat capacity around $T^*=0.5$ (cf. Fig. 1) is the classical indication of a conventional glass transition. In laboratory studies on real glass-forming systems structural relaxations can also occur at lower temperatures and for those systems there is then a more clear distinction between the critical temperature T_c and the glass transition temperature T_g (cf. Ref. [15(b)]). Only the location of the latter temperature depends on the "experimental" time scale and on the cooling rate. Strong indications in favor of this statement are now available through the recent and extensive neutron scattering data [9-11].

We have found no qualitative difference between the

present model system and the two-component soft-sphere system. In our case we can vary two of the parameters, density, pressure, and temperature, independently. To investigate the effect of the attractive part of the interparticle interaction we have performed calculations keeping the pressure constant and equal to zero [24]. The transition between the two types of viscous behavior is then located around $T^*=0.39$ but we do not find any noticeable difference in the dynamical behavior. In this respect these two systems seem to behave similarly.

Next, we consider the mode-coupling theory. One of the basic theoretical predictions is the anomalous decrease of the nonergodicity parameter when increasing the temperature towards T_c . The present MD data do not prove the square-root dependence in Eq. (2.4), but the data are certainly consistent with the theoretical prediction. Similar behavior is obtained with the neutron scattering technique [9–11], but then on much more complicated systems.

In the theory, the anomalous decrease of the nonergodicity parameter is associated with a secondary slow relaxation process, the β relaxation. The primary relaxation, α relaxation, is responsible for the diffusive motion and here that was taken into account by fitting to the stretched exponential. It is difficult to judge if the anomalous decrease, shown in Fig. 7, can be associated with a distinct relaxation process or if a more proper interpretation is in terms of a conventional but strong anharmonic effect.

To investigate this in more detail we have determined the self-dynamic susceptibility, which is given by the Fourier transform in time of $F_{\alpha}^{s}(\mathbf{q},t)$. A broad feature in the imaginary part of the susceptibility, the spectrum, is visible in between the diffusive peak (α peak) and the microscopic peak (the vibrational motion) [23(b)]. The mode-coupling theory makes detailed scaling predictions for the behavior of the spectrum in the vicinity of T_c . From the present MD data it was not possible to test these scaling relations [23(b)]. The main problem is that, assuming the mode-coupling theory to be correct, the transition in our model system is too smeared out and a detailed test becomes impossible. This is clear from the fact that at $T_c F^s_{\alpha}(\mathbf{q},t)$ has decayed to zero already around $t^* = 1000$. Our results for $F^s_{\alpha}(\mathbf{q}, t)$ in Fig. 6 agree qualitatively with the numerical results from a model calculation by Götze and Sjögren [cf. Fig. 1(b) in Ref. [32(b)]], where additional processes have been included which smear the ideal transition. The theory becomes more involved and another separation parameter δ enters. A main issue for future investigations is to study these real transitions and in particular to include the relevant processes in an appropriate way in the theory. MD simulation studies can then be of great value and the result in Sec. IV B 5 is a small step in that direction.

The theoretical prediction of two distinct slow relaxation processes, not associated with the microscopic details of the system, is amazing. It is well known that many glass-forming systems show two different slow relaxation processes. The commonly accepted explanation for the fastest, the secondary relaxation, is that it is connected to the microscopic molecular details of the glass [1] J. Jäckle, Rep. Prog. Phys. 49, 171 (1986).

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