

## Testing mode-coupling theory for a supercooled binary Lennard-Jones mixture: The van Hove correlation function

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(Received 28 November 1994)

We report the results of a large scale computer simulation of a binary supercooled Lennard-Jones liquid. We find that at low temperatures the curves for the mean squared displacement of a tagged particle for different temperatures fall onto a master curve when they are plotted versus rescaled time  $tD(T)$ , where  $D(T)$  is the diffusion constant. The time range for which these curves follow the master curve is identified with the  $\alpha$ -relaxation regime of mode-coupling theory (MCT). This master curve is fitted well by a functional form suggested by MCT. In accordance with idealized MCT,  $D(T)$  shows a power-law behavior at low temperatures. The critical temperature of this power law is the same for both types of particles, and also the critical exponents are very similar. However, contrary to a prediction of MCT, these exponents are not equal to the ones determined previously for the divergence of the relaxation times of the intermediate scattering function [Phys. Rev. Lett. **73**, 1376 (1994)]. At low temperatures, the van Hove correlation function (self as well as distinct part) shows almost no sign of relaxation in a time interval that extends over about three decades in time. This time interval can be interpreted as the  $\beta$ -relaxation regime of MCT. From the investigation of these correlation functions, we conclude that hopping processes are not important on the time scale of the  $\beta$  relaxation for this system and for the temperature range investigated. We test whether the factorization property predicted by MCT holds and find that this is indeed the case for all correlation functions investigated. The distance dependences of the critical amplitudes are in qualitative agreement with the ones predicted by MCT for some other mixtures. The non-Gaussian parameter for the self part of the van Hove correlation function for different temperatures follows a master curve when plotted against time  $t$ .

PACS number(s): 61.20.Lc, 61.20.Ja, 64.70.Pf, 51.10.+y

### I. INTRODUCTION

About a decade has passed since two of the most seminal papers in the recent history of the field of the glass transition and supercooled liquids were published. In these papers, one by Bengtzelius, Götze, and Sjölander and the other by Leutheusser, it was proposed that the glass transition could be understood as the singular behavior of the solution of the equations of motion of the dynamic structure factor, the so-called mode-coupling equations [1]. These equations are the simplified versions of certain nonlinear equations of motion that were derived in the 1970s in order to describe the dynamics of simple liquids at high densities [2]. Subsequently Götze, Sjögren, and many others analyzed these mode-coupling equations in order to work out the details of the singular behavior of their solutions [3–6]. Today the sum of all

these results is known as mode-coupling theory (MCT), and a review of them can be found in some recent review articles [7,8]. The theory has stimulated a remarkable amount of experimental and computer simulation work, with various groups looking for the signs of this singularity in many different kinds of systems [9–20]. The result of all these experiments and simulations is that the theory appears to be able to rationalize the dynamical behavior of some glass forming materials in an amazingly convincing way. However, the dynamical behavior of other glass forming materials seems to be described by MCT only poorly. So far it is still not clear for what kind of system the predictions of the theory hold and for which systems they do not. Even if for a particular system some of the predictions of the theory hold, it is not certain that the other predictions made by MCT will also hold. Therefore it is clear that still much has to be learned about the applicability of this theory. However, it seems that there is agreement on at least one point, namely, that the dynamical singularity predicted by MCT is not the same as the *laboratory* glass transition. The latter occurs at a temperature  $T_g$  that is defined as the temperature at which the viscosity of the material is  $10^{13}$  P. Below this temperature the material can no longer come to thermodynamic equilibrium because its relaxation times are longer than the time scale of typical experiments. How-

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ever, it is found that if experiments manifest a singular behavior that can be interpreted as the singularity predicted by MCT, then the temperature at which this singular behavior is observed is about 30–50 K above  $T_g$ . Furthermore, it has also been found empirically that the predictions of MCT seem to work better for fragile glass formers than for strong glass formers. For fragile glass formers, a plot of the logarithm of the viscosity vs  $1/T$  is curved, and the temperature of the MCT singularity is often near the temperature at which the plot shows a pronounced bend. At this temperature the viscosity changes its behavior from a weak dependence on temperature to a strong dependence on temperature as the temperature is lowered. Thus it can be that this bend in the viscosity is a signature of the singularity predicted by MCT. This bend occurs at viscosities which are about 1–100 P or relaxation times that are around  $10^{-11}$ – $10^{-9}$  s. Thus the singularity predicted by MCT is not the laboratory glass transition but rather is an anomalous dynamic behavior in supercooled liquids for fragile glass forming materials that takes place at temperatures above the glass transition temperature.

Computer simulations are particularly well suited to test the predictions of MCT, since they allow access to the full information on the system at any time of the simulation. This in turn permits the calculation of many different types of correlation functions, some of which are not experimentally measurable but about which the theory makes definite predictions, and thus very stringent tests of the theory become possible. Furthermore, the measurement of these correlation functions is very straightforward in that they are computed directly from the positions and velocities of the particles. Thus no theoretical model or assumption, as has to be used to explain, e.g., the scattering mechanism in light scattering experiments, is needed.

A severe drawback of most computer simulations is the limited range of times over which simulations can be performed. This in effect makes the cooling rates in simulations much larger than those in laboratory experiments. As a result the simulated material falls out of equilibrium at a higher temperature than would the corresponding real material in the laboratory [21]. In other words, the glass transition temperature in the simulation  $T_{g-sim}$  is higher than the laboratory glass transition  $T_g$ . If  $T_{g-sim}$  is too high, the lack of equilibration in the simulation can obscure not only the MCT singularity at  $T_c$  but also the higher temperature signatures of the onset of the singularity. Thus it is important in simulations to have a range of temperatures, extending down as close as possible to  $T_c$ , at which the system can be thoroughly equilibrated and the slow dynamics studied. This requires a significant amount of computation to achieve. In the present paper we will present data for thoroughly equilibrated systems in such a temperature range.

This paper presents the results of a molecular dynamics computer simulation in order to make careful tests of whether the predictions of MCT hold for the system under investigation. In two previous papers we investigated for the same system the scaling behavior of the intermediate scattering function in the  $\beta$ -relaxation regime [15,16].

We found that this correlation function shows many of the features predicted by the theory. In the present paper we will focus on the behavior of the van Hove correlation function and test whether the predictions of MCT hold for these kind of correlation functions as well. In a following presentation [22] we will investigate in detail the time and wave-vector dependence of the intermediate scattering function in the  $\alpha$ - and  $\beta$ -relaxation regimes (defined in the next section) and also the frequency dependence of the dynamic susceptibility. Thus the sum of the results of these investigations will allow us to make a stringent test on whether or not MCT is able to rationalize the dynamical behavior of the system studied.

The present paper is organized as follows. In Sec. II we will summarize those predictions of MCT that are relevant to understand the results of this work. In Sec. III we introduce our model and give some details on the computation. In Sec. IV we present our results and in Sec. V we summarize and discuss these results.

## II. MODE-COUPLED THEORY

In this section we give a short summary of those predictions of MCT that are relevant for the interpretation of the results presented in this paper. An extensive review of the theory can be found in Refs. [7,8].

In its simplest version, also called the idealized version, mode-coupling theory predicts the existence of a critical temperature  $T_c$  above which the system shows ergodic behavior and below which the system is no longer ergodic. All the predictions of the theory which are considered in this paper are of an asymptotic nature in the sense that they are valid only in the vicinity of  $T_c$ . For temperatures close to  $T_c$ , MCT makes precise predictions about the dynamical behavior of time correlation functions  $\phi(t) = \langle X(0)Y(t) \rangle$  between those dynamical variables  $X$  and  $Y$  that have a nonzero overlap with  $\delta\rho(\mathbf{q})$ , the fluctuations of the Fourier component of the density for wave vector  $\mathbf{q}$ , i.e., for which  $\langle \delta\rho(\mathbf{q})X \rangle$  and  $\langle \delta\rho(\mathbf{q})Y \rangle$  are nonvanishing. Here  $\langle \rangle$  stands for the canonical average. In particular, the theory predicts that for  $T > T_c$   $\phi(t)$  should show a two step relaxation behavior, i.e., the correlation function plotted as a function of the logarithm of time should show a decay to a plateau value, for intermediate times, followed by a decay to zero at longer times. The time interval in which the correlation functions are close to this plateau is called the  $\beta$ -relaxation region. Despite a similar name this region should not be confused with the  $\beta$ -relaxation process as described by Johari and Goldstein [23].

Furthermore, the theory predicts that in the vicinity of the plateau the so-called “factorization property” holds. This means that the correlator  $\phi(t)$  can be written in the form

$$\phi(t) = f^c + hG(t) \quad , \quad (1)$$

where  $f^c$  is the height of the plateau at  $T_c$ ,  $h$  is some amplitude that depends on the correlator but not on time, and the function  $G(t)$  depends on time and temperature

but not on  $\phi$ . Thus for a given system  $G(t)$  is a universal function for all correlators satisfying the above mentioned condition. The details of the function  $G(t)$  depend on a system specific parameter  $\lambda$ , the so-called exponent parameter. In principle  $\lambda$  can be calculated if the structure factor of the system is known with sufficient precision, but since this is rarely the case for real experiments it is in most cases treated as a fitting parameter. For all values of  $\lambda$  the theory predicts that for certain time regions the functional form of  $G(t)$  is well approximated by two power laws. In particular, it is found that, for those times for which the correlator is still close to the plateau but has started to deviate from it,  $G(t)$  is given by the so-called von Schweidler law

$$G(t) = -B(t/\tau)^b, \quad (2)$$

where  $B$  is a constant that can be computed from  $\lambda$ . The relaxation time  $\tau$  is the relaxation time of the so-called  $\alpha$  relaxation, i.e., the relaxation at very long times where the correlator decays to zero. The exponent  $b$ , often called the von Schweidler exponent, can be computed if the value of  $\lambda$  is known and is therefore *not* an additional fitting parameter.

In the  $\alpha$ -relaxation regime MCT predicts that the correlation functions obey the time-temperature superposition principle, i.e.,

$$\phi(t) = F(t/\tau), \quad (3)$$

where the overwhelming part of the temperature dependence of the right hand side is given by the temperature dependence of  $\tau$ . Equation (3) says that if the correlation functions for different temperatures are plotted versus  $t/\tau(T)$  they will fall onto the master curve  $F(t/\tau)$ . Note that the time range in which the von Schweidler law is observed belongs to the late  $\beta$ -relaxation regime as well as to the early  $\alpha$ -relaxation regime.

In addition MCT predicts that the diffusion constant  $D$  shows a power-law behavior as a function of temperature with the critical temperature  $T_c$ :

$$D \propto (T - T_c)^\gamma, \quad (4)$$

where  $\gamma$  can also be computed once  $\lambda$  is known.

Note that some of these predictions of MCT are valid only for the simplest (or idealized) version of the theory in which the so-called hopping processes are neglected. If these processes are present some of the statements made above have to be modified. However, below we will give evidence that for the system under investigation hopping processes are not important in the temperature range investigated and that therefore the idealized version of the theory should be applicable.

Furthermore, it has to be emphasized that MCT assumes that the system under investigation is in *equilibrium*. Thus great care should be taken to equilibrate the system properly. A recent computer simulation of a supercooled polymer system has shown that nonequilibrium effects can completely change the behavior of the time correlation functions [14]. Thus a comparison of the predictions of MCT with the results of a simulation

in which nonequilibrium effects are still present becomes doubtful at best.

### III. MODEL AND COMPUTATIONAL PROCEDURES

In this section we introduce the model we investigated and give some of the details of the molecular dynamics simulation.

The system we are studying in this work is a binary mixture of classical particles. Both types of particles ( $A$  and  $B$ ) have the same mass  $m$  and all particles interact by means of a Lennard-Jones potential, i.e.,  $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$  with  $\alpha, \beta \in \{A, B\}$ . The reason for our choice of a mixture was to prevent the crystallization of the system at low temperatures. However, as we found out in the course of our work, choosing a binary mixture is by no means sufficient to prevent crystallization, if the system is cooled slowly. In particular, we found that a model that has previously been used to investigate the glass transition [24], namely, a mixture of 80%  $A$  particles and 20%  $B$  particles with  $\epsilon_{AA} = \epsilon_{AB} = \epsilon_{BB}$ ,  $\sigma_{BB} = 0.8\sigma_{AA}$ , and  $\sigma_{AB} = 0.9\sigma_{AA}$ , crystallizes at low temperatures, as evidenced by a sudden drop in the pressure. In order to obtain a model system that is less prone to crystallization, we adjusted the parameters in the Lennard-Jones potential in such a way that the resulting potential is similar to one that was proposed by Weber and Stillinger to describe amorphous  $\text{Ni}_{80}\text{P}_{20}$  [25]. Thus we chose  $\epsilon_{AA} = 1.0$ ,  $\sigma_{AA} = 1.0$ ,  $\epsilon_{AB} = 1.5$ ,  $\sigma_{AB} = 0.8$ ,  $\epsilon_{BB} = 0.5$ , and  $\sigma_{BB} = 0.88$ . The numbers of particles of type  $A$  and  $B$  were 800 and 200, respectively. The length of the cubic box was  $9.4\sigma_{AA}$  and periodic boundary conditions were applied. In order to lower the computational burden we truncated and shifted the potential at a cutoff distance of  $2.5\sigma_{\alpha\beta}$ . In the following all the results will be given in reduced units, i.e., length in units of  $\sigma_{AA}$ , energy in units of  $\epsilon_{AA}$ , and time in units of  $(m\sigma_{AA}^2/48\epsilon_{AA})^{1/2}$ . For argon these units correspond to a length of 3.4 Å, an energy of 120 K  $k_B$  and a time of  $3 \times 10^{-13}$  s.

The molecular dynamics simulation was performed by integrating the equations of motion using the velocity form of the Verlet algorithm with a step size 0.01 and 0.02 at high ( $T \geq 1.0$ ) and low ( $T \leq 0.8$ ) temperatures, respectively. These step sizes were sufficiently small to reduce the fluctuation of the total energy to a negligible fraction of  $k_B T$ . The system was equilibrated at high temperature ( $T = 5.0$ ) where the relaxation times are short. Changing the temperature of the system to a temperature  $T_f$  was performed by coupling it to a stochastic heat bath, i.e., every 50 steps the velocities of the particles were replaced with velocities that were drawn from a Boltzmann distribution corresponding to the temperature  $T_f$ . This was done for a time period of length  $t_{\text{equi}}$ , which was chosen to be larger than the relaxation time of the system at the temperature  $T_f$ . After this change of temperature we let the system propagate with constant energy, i.e., without the heat bath, for a time that was also equal to  $t_{\text{equi}}$ , in order to see that there was no drift

in temperature, pressure, or potential energy. If no drift was observed, we considered the final state to correspond to an equilibrium state of the system at the temperature  $T_f$ , and we used this final state as the initial state for a molecular dynamics trajectory. In this trajectory, there was no coupling to a heat bath; it was a constant energy trajectory, and the results were used to provide the correlation function data discussed below. The temperatures we studied were  $T = 5.0, 4.0, 3.0, 2.0, 1.0, 0.8, 0.6, 0.55, 0.50, 0.475,$  and  $0.466$ . At the lowest temperatures the length of the run was  $10^5$  time units. Thus, again assuming argon units, the present data cover the time range from  $3 \times 10^{-15}$  s to  $3 \times 10^{-8}$  s. At the lowest temperature the equilibration time  $t_{equi}$  was  $0.6 \times 10^5$  time units. Thus, if we define the cooling rate to be the difference of the starting temperature and the final temperature divided by the time for the quench, the smallest cooling rate (used to go from the second lowest temperature to the lowest one) is  $1.5 \times 10^{-7}$ . In the case of argon this smallest cooling rate would correspond to  $6 \times 10^7$  K/s. Thus, although this cooling rate is still very fast, it is smaller than the fastest cooling rate achievable in experiments and about an order of magnitude smaller than the one used in previous computer simulations.

In order to improve the statistics, we performed eight different runs at each temperature, each of which was equilibrated separately in the above described way, and averaged the results. Each of these runs originated from a different point in configuration space. The thermal history of these starting points differed significantly from one to another. In particular, this history sometimes included periods in which we reheated the system after having cooled it to low temperatures and had it equilibrated at these temperatures or, in some other cases, included periods in which we cooled it with twice the normal cooling rate. Despite these different thermal histories the results we obtained from these eight different runs were the same to within statistical fluctuations. Thus we have good evidence that the results reported in this work are all *equilibrium* properties of the system and are not dependent on the way we prepared the system at a given temperature.

Most of the results presented in this paper deal with the van Hove correlation functions (self and distinct part), which are defined below. This space-time correlation function is the one that is most easily obtained from molecular dynamics computer simulations. As mentioned in the previous paragraph we averaged our results over at least eight different runs. Since the resulting correlation functions  $\phi(r, t)$  still showed some short wavelength noise in  $r$  even after we did this averaging, we smoothed the data *in space* by means of a spline under tension [26]. No smoothing was done in time, since the data were so smooth that such a treatment seemed not necessary.

#### IV. RESULTS

In this section we present the results of our simulation. In the first part we will deal with time independent

quantities and in the second part with time dependent quantities.

In many computer simulations dealing with the glass transition it is observed that there exists a temperature  $T_{g-sim}$  at which certain thermodynamic quantities, like, e.g., the potential energy per particle, show some sort of discontinuity (e.g., a rapid change of slope) when plotted versus temperature (see, e.g., [17]). The temperatures where these features are observed have nothing to do with the laboratory glass transition temperature  $T_g$ , the temperature where the viscosity of the material has a value of  $10^{13}$  P, since  $T_{g-sim}$  is usually significantly higher than  $T_g$ . The physical significance of  $T_{g-sim}$  is that at this temperature the system under investigation has fallen out of equilibrium, or in other words has undergone a glass transition, on the time scale of the computer simulation. Obviously  $T_{g-sim}$  depends on the cooling rate with which the system was cooled and on the thermal history of the system.

In Fig. 1 we show the pressure, the total energy, and the potential energy of our system as a function of temperature. In order to expand the temperature scale at low temperatures, we plot these quantities versus  $T^{-1}$ . We recognize from this figure that there is no temperature at which one of these quantities shows any sign of an anomalous behavior. Thus we can conclude that in this simulation the system is not undergoing a glass transition, i.e., that for the effective cooling rates used in this work,  $T_{g-sim}$  is less than the lowest temperature investigated. Thus this is evidence that we are able to equilibrate the system even at the lowest temperatures. Stronger evidence for equilibration will be presented below.

One of the simplest time dependent quantities to measure in a molecular dynamics simulation is the mean squared displacement (MSD)  $\langle r^2(t) \rangle$  of a tagged particle, i.e.,  $\langle r^2(t) \rangle = \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$ . In Fig. 2 we show this quantity for the particles of type A versus time in a double logarithmic plot. The corresponding plot for the

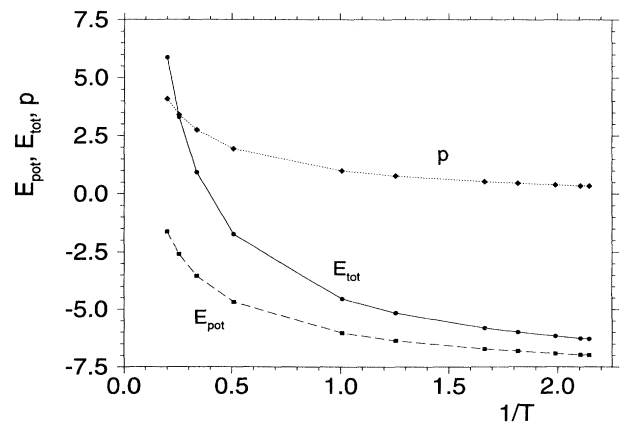


FIG. 1. Total energy (solid line), potential energy (dashed line), and pressure (divided by 10, dotted line) versus temperature  $T$ .

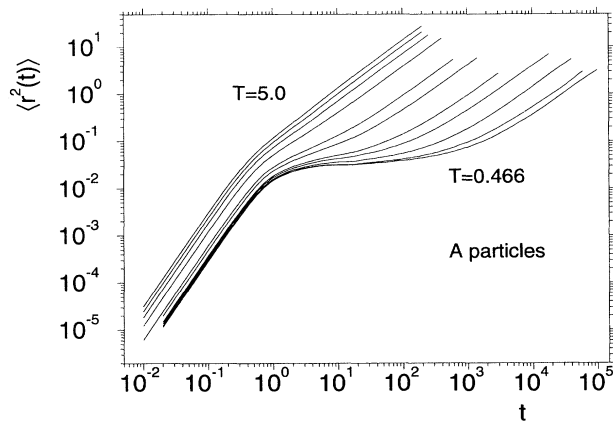


FIG. 2. Mean squared displacement versus time for A particles for all temperatures investigated.

B particles is very similar. The curves to the left correspond to high temperatures and those to the right to low temperatures. We recognize that for short times all the curves show a power-law behavior with an exponent of 2. Thus this is the ballistic motion of the particles. At high temperatures this ballistic motion goes over immediately into a diffusive behavior (power law with exponent 1). For low temperatures these two regimes are separated by a time regime where the motion of the particles seems to be almost frozen in that the MSD is almost constant and thus shows a plateau. At the lowest temperature this regime extends from about 1 time unit to about  $10^3$  time units. Only for much longer time (note the logarithmic time scale) do the curves show a power law again, this time with unit slope indicating again that the particles have a diffusive behavior on this time scale. The fact that the length of our simulation is long enough in order to see this diffusive behavior even at the lowest temperature is a further indication that we are able to equilibrate the system at all temperatures. The reader should note that for the discussion of these different time regimes it is most helpful to plot the curves of the MSD with a *logarithmic* time axis. Only in this way is it possible to recognize that the dynamics of the system is very different on the various time scales.

Note that the value of the MSD in the vicinity of the plateau is about 0.04, thus corresponding to a distance of about 0.2. We therefore recognize that on this time scale the tagged particle has moved only over a distance that is significantly shorter than the next nearest neighbor distance (which is close to 1, see below). Thus it is still trapped in the cage of particles that surrounded it at time zero, and it takes the particle a long time to get out of this cage. The initial stage of this slow breakup of the cage is exactly the type of process MCT predicts to happen during the  $\beta$  relaxation. (We will later elaborate more on this point in the discussion of the self part of the van Hove correlation function.) Thus we can identify the time range where we observe the plateau in the MSD with the  $\beta$ -relaxation regime of MCT.

From the MSD it is now easy to compute the self diffusion constant  $D(T)$  of the particles. (Using a plot such as Fig. 2, a straight line, with unit slope, fitted to the long time behavior of the data intersects a vertical line at  $\log_{10} t = 0$  at a height of  $\log_{10} 6D$ .) Since MCT predicts that diffusion constants should have a power-law dependence on temperature at low temperatures [see Eq. (4)], we tried to make a three parameter fit with such a functional form. In Fig. 3 we show the result of this fit by plotting  $D$  versus  $T - T_c$  in a double logarithmic way. We clearly observe that, in accordance with MCT, for temperatures  $T \leq 1.0$  the diffusion constants follow a power-law behavior. The value of  $T_c$  is 0.435, independent of the type of particle. This independence of  $T_c$  of the type of particles is in accordance with the prediction of MCT. From the value of  $T_c$  we now can compute the small parameter of the theory, i.e.,  $\epsilon = |T - T_c|/T_c$ . At the lowest temperature  $\epsilon$  is 0.07 and thus quite small and therefore it is not unreasonable to assume that we are already in the temperature range where the asymptotic results of the theory hold. At  $T = 1.0$  the value of  $\epsilon$  is 1.3, which seems rather too large for the asymptotic expansion to apply. However, it has been found in experiments that for some systems the predictions of MCT hold for values of  $\epsilon$  of at least 0.5 [19]. Therefore our finding is not very astonishing. Also, by investigating the relaxation time of the intermediate scattering function we found that the asymptotic behavior at low temperatures is obtained for this quantity only for  $T \leq 0.6$  [15,22]. This corresponds to a value of  $\epsilon$  of 0.4, which is comparable to the values found in experiments. Thus we see that the upper temperature for which the asymptotic behavior can be

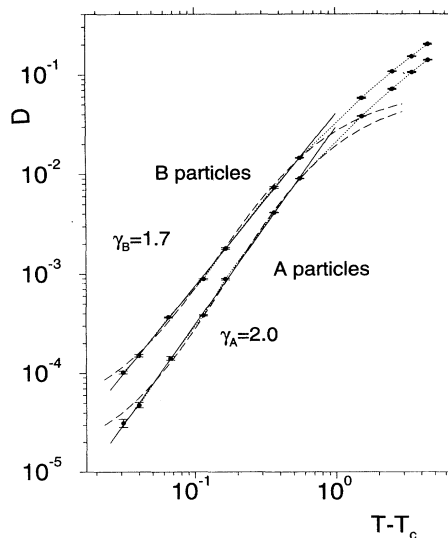


FIG. 3. Diffusion constant  $D$  for A and B particles (lower and upper curve, respectively) versus  $T - T_c$ . The critical temperature  $T_c$  is 0.435. Also shown are the power-law fits with exponents 2.0 and 1.7 for the A and B particles, respectively. The dashed lines are the best fits with a Vogel-Fulcher law.

observed clearly depends on the quantity investigated. Note that this observation is in accordance with MCT since the theory predicts that the magnitude of the corrections to the asymptotic behavior will depend on the quantity considered.

The exponent  $\gamma$  of the power law for  $D(T)$  [see Eq. (4)] is 2.0 for the  $A$  particles and 1.7 for the  $B$  particles. Although MCT predicts these two exponents to be the same, a 10% deviation from an asymptotic result is not surprising and therefore not a severe contradiction to this prediction of the theory. However, in a different work [15] we have analyzed the temperature dependence of the  $\alpha$ -relaxation time  $\tau$  [see Eq. (2)] and found, in accordance with the prediction of MCT, that at low temperatures  $\tau$  shows a power-law behavior. MCT predicts that the exponent of the power law for  $\tau(T)$  and the exponent in the power law for  $D(T)$  should be the same. Since we found that the former is about 2.6 [15] and we now find that the latter is around 1.9 we conclude that this prediction of the theory is not correct for our system.

Since the connection proposed by MCT between the von Schweidler exponent  $b$  and the critical exponent  $\gamma$  [7] would imply  $\gamma=2.8$  (using  $b = 0.49$ , which we determined in Ref. [15]) we tested whether a plot of  $D^{1/\gamma}$  with  $\gamma = 2.8$  versus  $T$  gives a straight line in some temperature interval. This would imply that in this temperature interval a power law with exponent 2.8 would fit the data well. We found that for the  $A$  particles the data points for  $T \leq 0.6$  lie reasonably well on a straight line. This is not the case for the  $B$  particles in any range of temperatures. Furthermore, the critical temperature that is obtained for the  $A$  particles is around 0.40. This is significantly smaller than the critical temperatures we determined by other means and which were all around 0.435 [15,22]. Thus we think that a power law with an exponent of 2.8 and a temperature around 0.435 is inconsistent with our data for the diffusion constant. From the theoretical point of view it is, of course, interesting to find that the relaxation times of the intermediate scattering function for nonzero values of  $q$  behave the way MCT predicts [15,16,22] whereas the diffusion constants, related to quantities at  $q = 0$ , do not follow these predictions as closely. To understand this observation it probably will be necessary to increase our understanding of the corrections of the asymptotic expressions of the theory for small values of  $q$  and we hope that some progress will be possible in this direction in the future.

Also included in Fig. 3 is the result of a fit to the diffusion constants with a Vogel-Fulcher law, i.e.,  $D \propto \exp[-B/(T - T_0)]$ . The Vogel-Fulcher temperature  $T_0$  is 0.268 and 0.289 for the  $A$  and  $B$  particles, respectively. These two temperatures are significantly lower than the critical temperatures found for other quantities, which were all around 0.435 [15,22]. Also, as can be seen from Fig. 3 in our case the quality of the Vogel-Fulcher fit is inferior to the one with a power law. This shows that our data are good enough to distinguish between the two functional forms and that therefore the power law we found is really significant. Note that this finding is not in contradiction with the situation often encountered in experiments, where the viscosity, or a relaxation time, is

fitted well by a Vogel-Fulcher law over many orders of magnitude. The temperatures for which these fits are done are usually closer to the laboratory glass transition temperature  $T_g$  than the temperatures we deal with here. Thus the viscosity is much larger than the viscosity one would obtain at the lowest temperature investigated in this work. Hence our statement is that *in the temperature region investigated here* the diffusion constant is better fitted by a power law than by a Vogel-Fulcher law and at present nothing can be said about its behavior at lower temperatures.

Since the inverse of the constant of diffusion gives a time scale, we plotted the MSD versus  $tD(T)$ . The resulting plot is shown in Fig. 4. The curves to the left correspond to low temperatures and those to the right to high temperatures. We recognize from this figure that for intermediate and low temperatures the curves fall onto a master curve. A comparison with Fig. 2 shows that this master curve is present for those times that fall into the  $\alpha$ -relaxation regime. Thus it can be expected that the master curve has something to do with the time-temperature superposition principle [see Eq. (3)]. We thus used as an ansatz a functional form that is an interpolation between the von Schweidler behavior at short rescaled times and a diffusive behavior at long rescaled times, e.g.,

$$\langle r^2(t) \rangle = A[r_c^2 + (Dt)^b] + Dt. \quad (5)$$

Here  $r_c$ ,  $A$ , and  $b$  are fit parameters. The best fit for the  $A$  particles is included in Fig. 4 as a dashed line. We recognize that the functional form given by Eq. (5) leads to a quite satisfactory fit in the time region where the master curve is observed. For the best value of  $b$  we obtained 0.48 and 0.43 for the  $A$  and  $B$  particles,

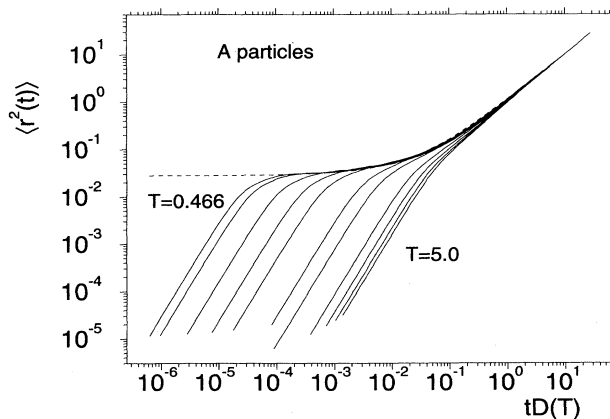


FIG. 4. Mean squared displacement versus  $tD(T)$  for the  $A$  particles (solid lines) for all temperatures investigated. The low temperatures are to the left and the high ones to the right. Dashed curve: Best fit to the master with the functional form of Eq. (5).

respectively. These values are in accordance with the value for the von Schweidler exponent which we found for this system to be around  $b = 0.49$  [15,16,22]. Thus MCT is able to rationalize this master curve quite convincingly.

We now turn our attention to a closer examination of the motion of the particles. This is done conveniently with the help of  $G_s^\alpha(\mathbf{r}, t)$  and  $G_d^{\alpha\beta}(\mathbf{r}, t)$  ( $\alpha, \beta \in \{A, B\}$ ), the self and distinct part of the van Hove correlation function [27]. Here and in the following we assume that the system is isotropic and therefore only the modulus of  $r$  enters the equations.  $G_s^\alpha(r, t)$  is defined as

$$G_s^\alpha(r, t) = \frac{1}{N_\alpha} \left\langle \sum_{i=1}^{N_\alpha} \delta(r - |\mathbf{r}_i(0) - \mathbf{r}_i(t)|) \right\rangle \xrightarrow{t, r \rightarrow \infty} \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right), \quad (6)$$

where  $\delta(r)$  is the  $\delta$  function. If  $G_s(\mathbf{r}, t)$  depends only on the modulus of  $\mathbf{r}$  the angular integration can be carried out and thus one usually considers not  $G_s(\mathbf{r}, t)$  but  $4\pi r^2 G_s(r, t)$ .

The distinct parts  $G_d^{\alpha\beta}(r, t)$  are defined by

$$G_d^{\alpha\alpha}(r, t) = \rho g_{\alpha\alpha}(r, t) = \frac{N_A + N_B}{N_\alpha(N_\alpha - 1)} \left\langle \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\alpha} \delta(r - |\mathbf{r}_i(0) - \mathbf{r}_j(t)|) \right\rangle \xrightarrow{t, r \rightarrow \infty} 1 \quad (7)$$

and

$$G_d^{AB}(r, t) = \rho g_{AB}(r, t) = \frac{N_A + N_B}{N_A N_B} \left\langle \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \delta(r - |\mathbf{r}_i(0) - \mathbf{r}_j(t)|) \right\rangle \xrightarrow{t, r \rightarrow \infty} 1. \quad (8)$$

Here  $\rho$  is the density of the system. The prime in the second sum of Eq. (7) means that the term  $i = j$  has to be left out. Note that we define  $G_d^{\alpha\alpha}(r, t)$  in a slightly different way than it is usually done in the literature (see, e.g., [27]) in that we divide on the right hand side of Eq. (7) by  $N_\alpha(N_\alpha - 1)$  instead of the usual  $N_\alpha^2$ . For a finite system this choice makes  $g_{\alpha\alpha}(r, t)$  approach 1 for  $r$  and  $t$  large instead of  $1 - 1/N_\alpha$  as is the case with the usual definition.

In Fig. 5 we plot  $4\pi r^2 G_s(r, t)$  for the  $A$  particles for a high (a), an intermediate (b), and a low temperature (c). The function is presented only for  $0 \leq r \leq 0.6$  since this is the most relevant region at low temperatures. In each panel the topmost curve is for  $t \approx 0.32$ . The lower curves are then each a factor of approximately 2 in time apart. From this figure we recognize that at high temperatures the self part of the van Hove correlation function decays in a regular way, e.g., as in a normal liquid. This changes slightly for intermediate temperatures. Here we see that for times in the range  $5 \leq t \leq 80$  the curves show a weak tendency to cluster for  $0.05 \leq r \leq 0.25$ . This effect is much more pronounced at the lowest temperature investigated, where it can be observed for times in the range  $2.4 \leq t \leq 640$ , which belong to the  $\beta$ -relaxation regime [15,22]. This clustering is the signature that the movement of the particles has dramatically slowed down in this time interval. We note that this slowing down takes place for small distances; thus the particle has not yet left the cage formed by the particles that surrounded it at time zero. The particle is typically able to leave this cage, i.e., to move for net distances of the order of unity, only on a much longer time scale. Thus the process that takes place in the time window corresponding to the late  $\beta$  relaxation is related to the breaking up of this cage. MCT predicts that in this time window the

correlation functions should show a power-law behavior in time [see, e.g., Eq. (2)]. That this is indeed the case is demonstrated in Refs. [15,16,22]. Note that these distances are comparable to the one that we found for the height of the plateau in the MSD (see Fig. 2) and that also the time window in which we observe the clustering of the correlation functions is the same as the one in which we observed the plateau in the MSD. Thus this is a confirmation that the plateau in the MSD is indeed a signature of the  $\beta$ -relaxation process.

The idealized version of MCT is based on the assumption that the so-called "hopping processes" are not important contributors to the relaxation. This version of the theory makes a number of straightforward and easily testable predictions that can be compared with experiments or computer simulations. The more general version of the theory that takes hopping processes into account is more difficult to test and thus this has been done only on a few occasions [18–20]. We now present evidence that for our system such hopping processes are not important in the temperature range we have studied. This justifies the use of the idealized theory to interpret the data.

In Fig. 6(a) we show  $4\pi r^2 G_s(r, t)$  for the  $A$  particles for times  $1.16 \leq t \leq 100\,000$  at  $T = 0.466$ , the lowest temperatures investigated. The times corresponding to the different curves were chosen in such a way that the ratio of the times belonging to two consecutive curves is approximately constant. Thus these times are, on a *logarithmic* time axis, equidistant. Analogous pictures for a binary soft sphere system or a binary Lennard-Jones system show that for intermediate times, i.e., a few hundred time units, the correlation function shows a small peak at distances around 1 (see, e.g., Fig. 3 in Ref. [10] or Fig. 4 in Ref. [13]). The existence of this peak was in-

terpreted as an activated process in which a particle hops to the position formerly occupied by one of the particles in the cage that surrounded it at  $t = 0$  [10]. (In this process, the latter particle, or perhaps some other particle forming the initial cage, presumably hops into the center

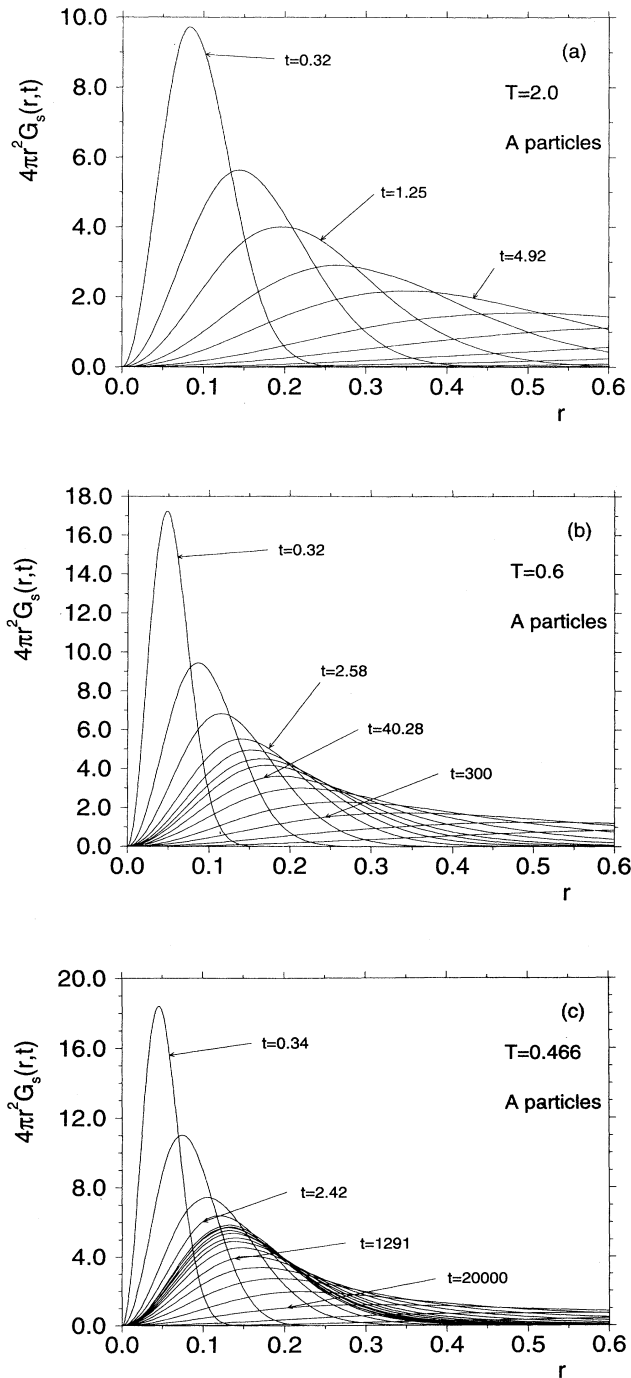


FIG. 5.  $4\pi r^2 G_s(r, t)$  for the *A* particles versus  $r$  for times  $t \approx 0.32 \times 2^n$  with  $n = 0, 1, 2, \dots$ . (a)  $T = 2.0$ , (b)  $T = 0.6$ , and (c)  $T = 0.466$ .

of the cage.) These types of processes are not included in the idealized version of MCT but are approximately accounted for in the extended version of the theory. A close inspection of Fig. 6(a) shows that for the *A* particles there is no hint of the presence of a small secondary peak at distances around 1 (the location of the nearest neighbor shell). Thus we can conclude that for the *A* particles hopping processes in the above mentioned sense are not present at all. For the *B* particles the situation is slightly different. In Fig. 6(b) we show  $4\pi r^2 G_s(r, t)$  for the *B* particles for the same time interval as in Fig. 6(a). We see that for times around 15 000 time units we observe a secondary peak located around  $r = 1.0$ . Thus we can conclude that the *B* particles show some kind of jump motion. The reason for this difference in the dynamics of the *A* and *B* particles is probably the difference in size of the two types of particles. Since the *B* particles are smaller than the *A* particles, they are more mobile, as can also be recognized from the fact that the diffusion constant for the *B* particles is larger than the one for the *A* particles, and that they therefore are able to make

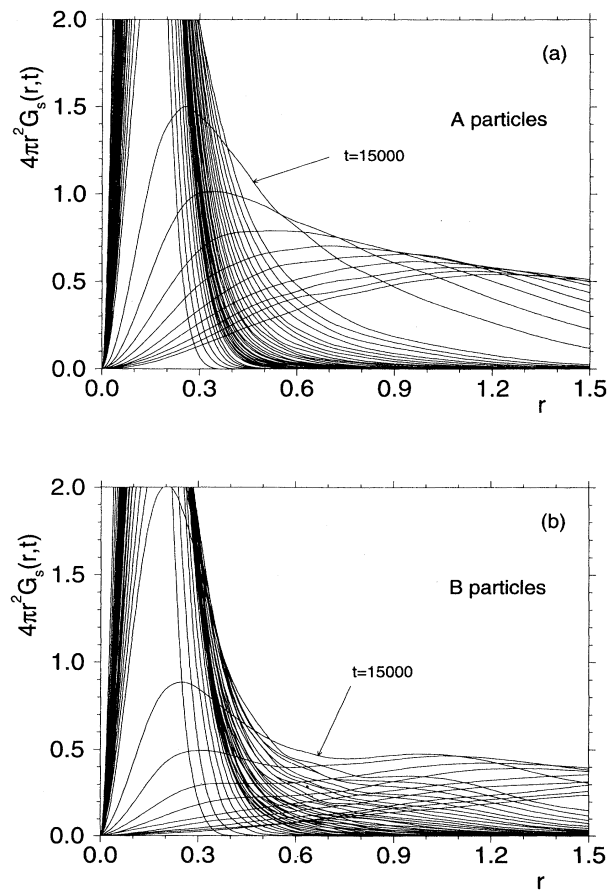


FIG. 6.  $4\pi r^2 G_s(r, t)$  for the *A* particles (a) and the *B* particles (b) at  $T = 0.466$  for times between 1.16 and  $10^5$  time units. Note the presence of a small secondary peak for times around 10 000 for the *B* particles. No such peak is observed for the *A* particles.



some movements (jumps) that the  $A$  particles cannot do. However, despite the fact that the  $B$  particles show the occurrence of hopping processes we also recognize from the figure that no secondary peak is observed for times less than  $10^4$ , i.e., that these processes are effective only on the time scale of  $10^4$  time units or more. For the temperatures investigated in this work this time scale belongs to the time scale of the late  $\alpha$  process. Therefore the  $\beta$  process is not affected by these hopping processes at all and hence it is reasonable to analyze all the data that belong to the  $\beta$ -relaxation region with the *idealized* version of MCT. We will come to a similar conclusion when we study the distinct part of the van Hove correlation function.

In Fig. 5(c) we see that in the  $\beta$ -relaxation region the various correlation functions for different times seem to cross all in one common point, namely, at  $r \approx 0.21$ . MCT can rationalize such a behavior by means of the factorization property stated formally in Eq. (1). If we apply this equation to the correlation function  $\phi(r, t) = 4\pi r^2 G_s(r, t)$  we obtain

$$\phi(r, t) = F(r) + H(r)G(t) \quad (9)$$

Here  $F(r)$  and  $H(r)$  are the  $r$  dependent offset  $f^c$  and amplitude  $h$ , respectively, from Eq. (1). Thus if  $H(r)$  becomes zero for some value of  $r$  the whole time dependence of the right hand side disappears and for this particular value of  $r$  the correlation functions are independent of time (note that this statement is true only in the  $\beta$ -relaxation region). This is exactly what happens around  $r \approx 0.21$ .

In order to make a more stringent test on whether the factorization property, as stated in Eq. (9), really holds we applied a test which was proposed by Signorini *et al.* [11]. If  $t$  and  $t'$  are two different times in the  $\beta$ -relaxation regime it is easy to show that if the factorization property holds we have

$$\frac{\phi(r, t) - \phi(r, t')}{\phi(r', t) - \phi(r', t')} = \frac{H(r)}{H(r')} \quad (10)$$

where  $r'$  can be chosen arbitrarily. Hence the left hand side of Eq. (10) is independent of  $t$  and depends only on  $r$ . Signorini *et al.* showed in their simulation of a molten salt that if  $t'$  is 180 ps the left hand side is indeed independent of  $t$  in the range  $20 \leq t \leq 40$  ps and thus the factorization property holds over this time span.

In Fig. 7(a) we show the left hand side of Eq. (10) for the  $A$  particles in the range  $0 \leq r \leq 1.5$  at the lowest temperature investigated, i.e., for  $T = 0.466$ . For  $r'$  and  $t'$  we chose 0.13 and 3000 time units, respectively. The time range covered is  $0.02 \leq t \leq 100\,000$  and for clarity we show only every second curve in time (as in Fig. 6 the times for which we plot the curves are spaced evenly on a *logarithmic* time axis). From the figure we recognize that if  $t$  varies over this time range (i.e. from microscopic times up to times at the end of the  $\alpha$  relaxation) the left hand side of Eq. (10) shows a significant dependence on time. To show this a bit more clearly we plotted the curves belonging to the time range before the  $\beta$  relaxation as dotted lines, the curves belonging to the  $\beta$  relaxation as solid lines, and the curves for times after the  $\beta$  relaxation as dashed lines. To see whether the factorization property holds for times in the  $\beta$ -relaxation regime we plot in Fig. 7(b) only those curves that correspond to

laxation as solid lines, and the curves for times after the  $\beta$  relaxation as dashed lines. To see whether the factorization property holds for times in the  $\beta$ -relaxation regime we plot in Fig. 7(b) only those curves that correspond to

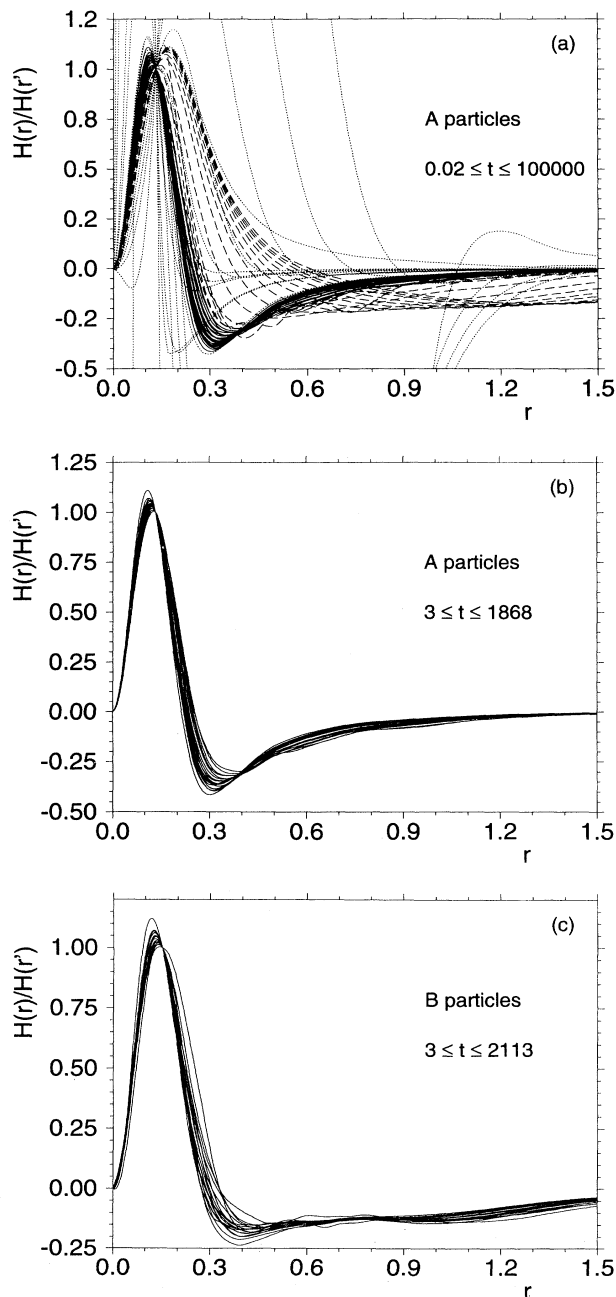


FIG. 7. Normalized critical amplitude  $H(r)/H(r')$  for  $0 \leq r \leq 1.5$  [see Eq. (10)] for  $T = 0.466$ ,  $t' = 3000$ . (a)  $A$  particles:  $0.02 \leq t \leq 100\,000$  (only every second correlation function is shown),  $r' = 0.13$ . Dotted lines:  $0.02 \leq t < 3$ , solid lines:  $3 \leq t \leq 1868$ , dashed lines:  $1868 < t \leq 100\,000$ . (b)  $A$  particles  $3 \leq t \leq 1868$  (only every third correlation function is shown),  $r' = 0.13$ . (c)  $B$  particles:  $3 \leq t \leq 2113$  (only every third correlation function is shown),  $r' = 0.15$ .

times that are in this regime, thus  $3 \leq t \leq 1868$ . In order not to overcrowd the figure, only every third curve in time is shown. We clearly see that for this time range the curves show only a weak dependence on time and that therefore the factorization property holds. The master curve we find is quite similar to the one predicted by MCT for a binary mixture of soft spheres [5] or for hard spheres [6]. We have to emphasize that MCT does not predict that  $H(r)/H(r')$  is a universal function. In general it will depend on the system under investigation and also on the type of particle considered. That  $H(r)/H(r')$  is actually dependent on the type of particle is shown in Fig. 7(c) where we show the same quantity as in Fig. 7(b) but this time for the  $B$  particles, for  $r' = 0.15$  and the time interval  $3 \leq t \leq 2113$ . Again we find a master curve if the time lies in the  $\beta$ -relaxation regime. Although the general shape of this master curve is similar to the one we found in the case for the  $A$  particles there are quantitative differences. For example, we recognize that the two master curves become zero at a different value of  $r$  thus showing that the master functions are not universal. Finally we mention that we found that the form of these master curves for  $H(r)/H(r')$  depends only weakly on the particular choice of  $r'$  and  $t'$ , an observation that is also in accordance with MCT.

A different way to analyze the behavior of the self part of the van Hove correlation function is by means of the non-Gaussian parameters  $\alpha_n(t)$ ,  $n = 2, 3, \dots$  [28]. These parameters are measures of the deviation of a distribution function from a Gaussian form, and it has been proposed that the first of these parameters, i.e.,  $\alpha_2(t)$ , can be used as an order parameter for the glass transition occurring at  $T_{g-sim}$  [29]. The definition of  $\alpha_2(t)$  is given by

$$\alpha_2(t) = \frac{3\langle r^4(t) \rangle}{5\langle r^2(t) \rangle^2} - 1 \quad . \quad (11)$$

In Fig. 8 we show  $\alpha_2(t)$  as a function of  $t$  for the  $A$  and  $B$  particles at intermediate and low temperatures. We see that at these temperatures the self part of the van Hove correlation function clearly shows a strongly non-Gaussian behavior. This effect becomes more and more pronounced the lower the temperature is. Also, a comparison with Fig. 1 shows that the maximum of  $\alpha_2(t)$  occurs around the end of the  $\beta$ -relaxation region. Furthermore, we observe that in the interval that starts at  $t \approx 1$  and ends just before the curves attain their maximum the individual curves seem to follow a master curve. Although this master curve is not very well defined for the  $A$  particles [Fig. 8(a)] it is quite well defined for the  $B$  particles [Fig. 8(b)] and should therefore be considered as a real effect and not just some sort of coincidence. Note that no scaling or fitting is involved to generate these master curves. We have tried to determine of what functional form these master curves are but due to the noise in the data we were not able to come to a convincing conclusion.

Since the interval in which the master curves are observed coincides well with the interval in which we observe the  $\beta$ -relaxation behavior (see, e.g., Fig. 1) we are

strongly tempted to think that these master curves have something to do with the scaling behavior observed in the  $\beta$ -relaxation region (see, e.g., Fig. 4 or Ref. [15,16,22]). However, one should note that all the scaling behavior we have discussed previously occurs only when the time axis is scaled by a relaxation time that is strongly dependent on temperature. This is not the case in Fig. 8, where we observe the scaling when we plot the curves versus (unscaled) time. So far it is not clear whether MCT is able to rationalize our finding and therefore theoretical work in this direction would certainly be most useful. Furthermore, it would also be worthwhile to check whether the observed scaling behavior is also observed for different kinds of systems. Unfortunately all published data we are aware of only show  $\alpha_2(t)$  versus time on a *linear* scale and not versus the *logarithm* of time. Thus the master curve, if present, is not observable, since on a linear time scale it is shifted very close to the origin. Finally we mention that we observed a very similar behavior for the non-Gaussian parameter  $\alpha_3(t)$ , thus showing that this phenomenon is not just a peculiarity of  $\alpha_2(t)$ .

We turn our attention now to the distinct part of

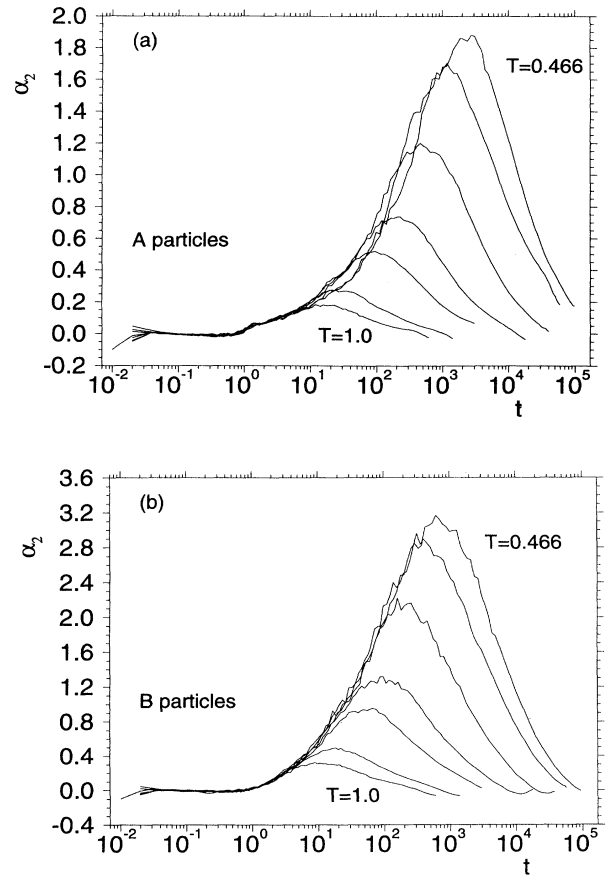


FIG. 8. Non-Gaussian parameter  $\alpha_2$  versus  $t$  for the  $A$  particles (a) and the  $B$  particles (b). Temperatures from right to left: 0.466, 0.475, 0.5, 0.55, 0.6, 0.8, 1.0.

the van Hove correlation function  $G_d^{\alpha\beta}(r, t)$ , defined in Eqs. (7) and (8). In Fig. 9 we show  $G_d^{\alpha\beta}(r, t)/\rho$  at  $t = 0$ , which is the same as the radial distribution function  $g_{\alpha\beta}(r)$ , for the  $AA$ , the  $AB$ , and the  $BB$  correlations for all temperatures investigated. For clarity the individual curves for different temperatures have been displaced

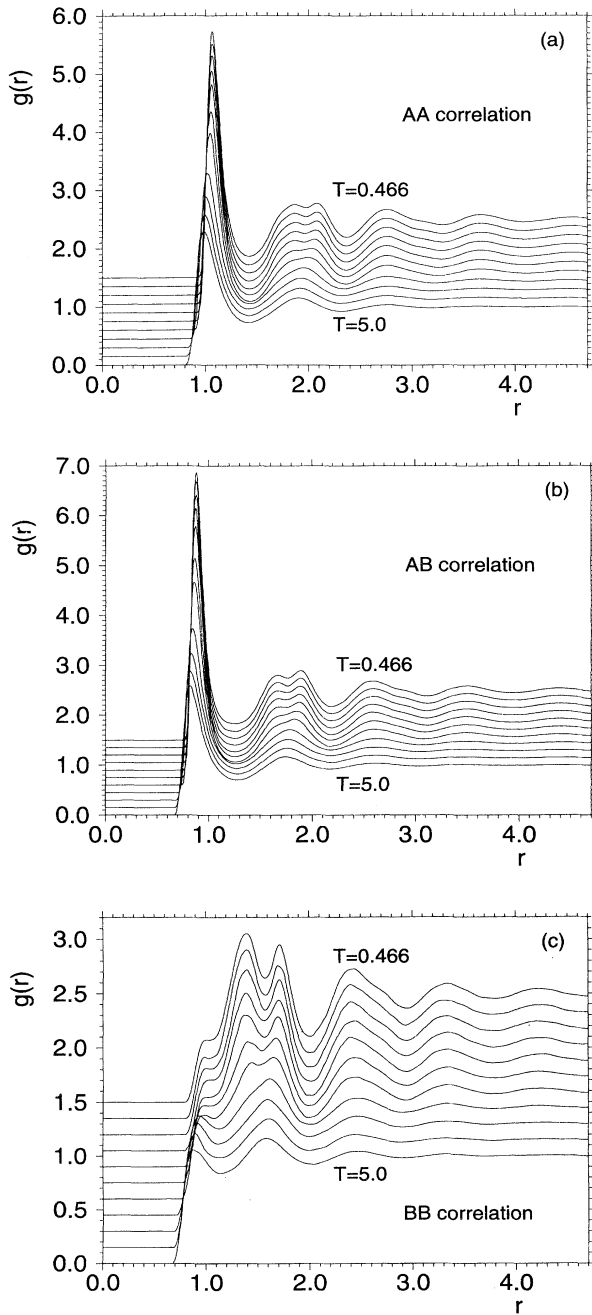


FIG. 9. Radial distribution function  $g(r)$  for  $AA$  (a),  $AB$  (b), and  $BB$  (c) correlation for all temperatures investigated. For clarity the individual curves have been shifted vertically by  $0.15n$ ,  $n = 1, 2, 3, \dots$

vertically (see the figure caption for details). For the  $AA$  and  $AB$  correlations we see that, when the temperature is lowered, the first neighbor peak becomes narrower. In addition the second neighbor peak starts to split around  $T = 0.8$ , a feature often observed for supercooled liquids. Since we have given evidence above that in this simulation the system does not undergo a glass transition, i.e., that  $T_{g-sim}$  is less than the lowest temperature investigated here, we can conclude that the occurrence of a split second neighbor peak has nothing to do with  $T_{g-sim}$ , but is just a feature of a strongly supercooled liquid.

Whereas the distinct parts of the van Hove correlation function for the  $AA$  and  $AB$  correlations are very similar to the one found for a one component simple liquid, the correlation function for the  $BB$  correlation is quite a bit different. This is probably due to the fact that the  $B$  particles are in the minority in this system and also smaller than the  $A$  particles. Thus their packing structure in a dense environment is quite different from the one of a simple one component liquid. We recognize from Fig. 9(c) that when the temperature is lowered the first neighbor peak is reduced to a small shoulder. This can be understood by remembering that the attraction between two  $B$  particles is smaller than the one between an  $AA$  pair or an  $AB$  pair. Thus at low temperature two  $B$  particles will try to stay apart and thus the first neighbor peak will become smaller. Contrary to this trend the second neighbor peak becomes much larger and, similar to the corresponding peak in the  $AA$  and  $AB$  correlation functions, splits at temperatures around 0.8.

We also investigated the time dependence of the distinct part of the van Hove correlation function. In Fig. 10 we show the dependence of  $G_d^{\alpha\beta}(r, t)/\rho$  for the  $AA$  particles for three different temperatures. For relatively high temperatures [ $T = 2.0$ , Fig. 10(a)] the correlation function decays without showing any particular feature. (As in Fig. 6 the times for which we plot the curves are spaced evenly on a *logarithmic* time axis.) This changes when we lower the temperature to  $T = 0.6$  [Fig. 10(b)]. Now we observe that for intermediate times the correlation functions start to cluster. This effect is even more pronounced at the lowest temperature [ $T = 0.466$ , Fig. 10(c)]. This clustering is again the result of the  $\beta$  relaxation in which the relaxation is severely slowed down. From this figure we also recognize that in the time interval of the  $\beta$ -relaxation regime the correlation hole at  $r = 0$  is still there. Thus no particle from the nearest neighbor shell of the particle at  $r = 0$  (or somewhere else) has managed to enter this hole. We find a small peak at  $r = 0$  only for times that are appreciably larger than the ones belonging to the  $\beta$ -relaxation regime, namely, for  $t \geq 10^4$  time units. This observation is further support for our conclusion made above that on the time scale of the  $\beta$  relaxation, which starts at a few time units and ends at a few thousand time units, the hopping processes are not important. In Fig. 11(a) we show the same type of correlator as in Fig. 10 and at the same temperature as in Fig. 10(c) but this time for the  $AB$  correlation function. We see that in the  $\beta$ -relaxation regime the behavior of this correlation function is very similar to the one for the  $AA$  correlation function. However, even for times that

belong to the  $\alpha$  relaxation regime we do not see any sign of a peak at the origin. Thus we have evidence that for this correlation function hopping processes are not important even on the time scale of the  $\alpha$  relaxation. This does not seem to be the case for the  $B$  particles. In Fig. 11(b) we show the function for the  $BB$  correlation. For intermediate times we find again the clustering of

the curves and no peak at the origin. However, for longer times there is a pronounced peak at small distances. This peak is definitely larger than the one observed for the  $AA$  correlation [Fig. 10(c)]. Thus this finding is in accordance with the conclusion we made above with regard to the self part of the van Hove correlation function, namely, that in the time region of the  $\alpha$  relaxation the hopping processes are more important for the dynamics of the  $B$  particles than for the  $A$  particles.

We now proceed to test whether the factorization property holds also for the distinct part of the van Hove correlation function. We do this in the same way we tested this property for the self part, i.e., by checking whether the left hand side of Eq. (10) is independent of time. In Fig. 12 we show the result of this kind of analysis. Figure 12(a) shows the left hand side of Eq. (10) for the  $AA$  correlation. The value of  $r'$  is 1.05 and the one of  $t'$  is 3000 time units. The curves are shown for times in the range  $2.7 \leq t \leq 700$ , thus covering almost two and a half decades in the  $\beta$ -relaxation regime. We clearly see that the curves lie on a master curve. A comparison with the prediction of MCT for the master curve of a hard sphere system [4] shows that the form of this master curve is qualitatively similar to the one we find. A similar re-

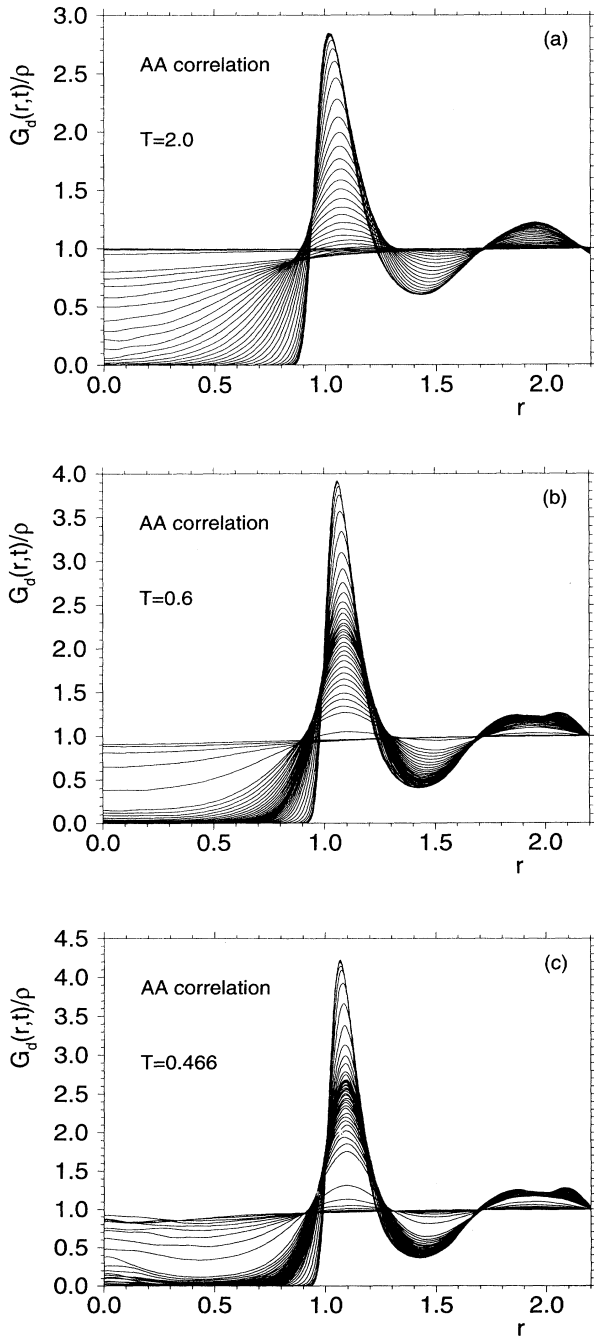


FIG. 10.  $G_d(r,t)/\rho$  for the  $AA$  correlation function. (a)  $T = 2.0$ ,  $0 \leq t \leq 400$ ; (b)  $T = 0.6$ ,  $0 \leq t \leq 3000$ ; (c)  $T = 0.466$ ,  $0 \leq t \leq 100\,000$ .

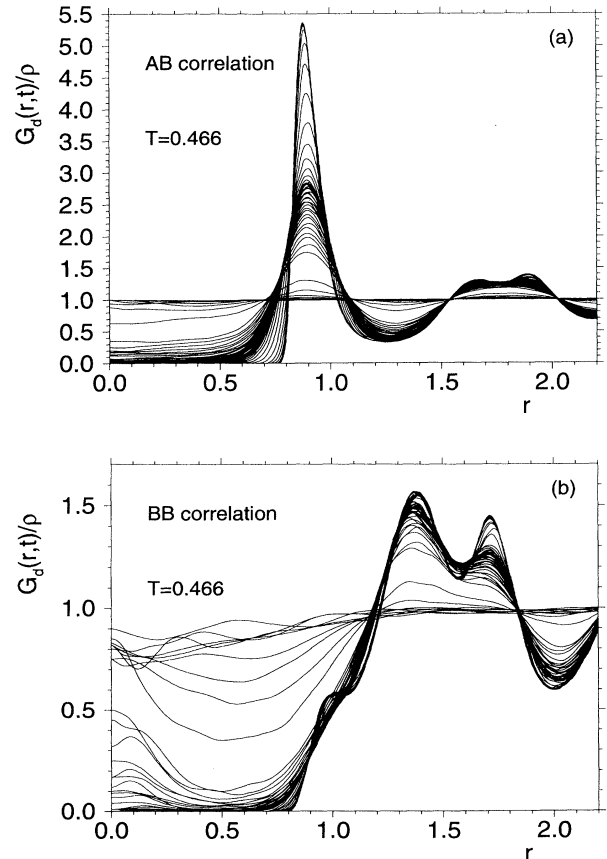


FIG. 11.  $G_d(r,t)/\rho$  for  $T = 0.466$  and  $0 \leq t \leq 100\,000$ . (a)  $AB$  correlation and (b)  $BB$  correlation.

sult was found by Signorini *et al.* in a simulation of a molten salt [11]. A qualitatively similar master curve is obtained for the *AB* correlation function, which is shown in Fig. 12(b). Here we chose  $r' = 0.90$  and  $t' = 3000$ . The time range covered is  $3.1 \leq t \leq 1142$ . Although the

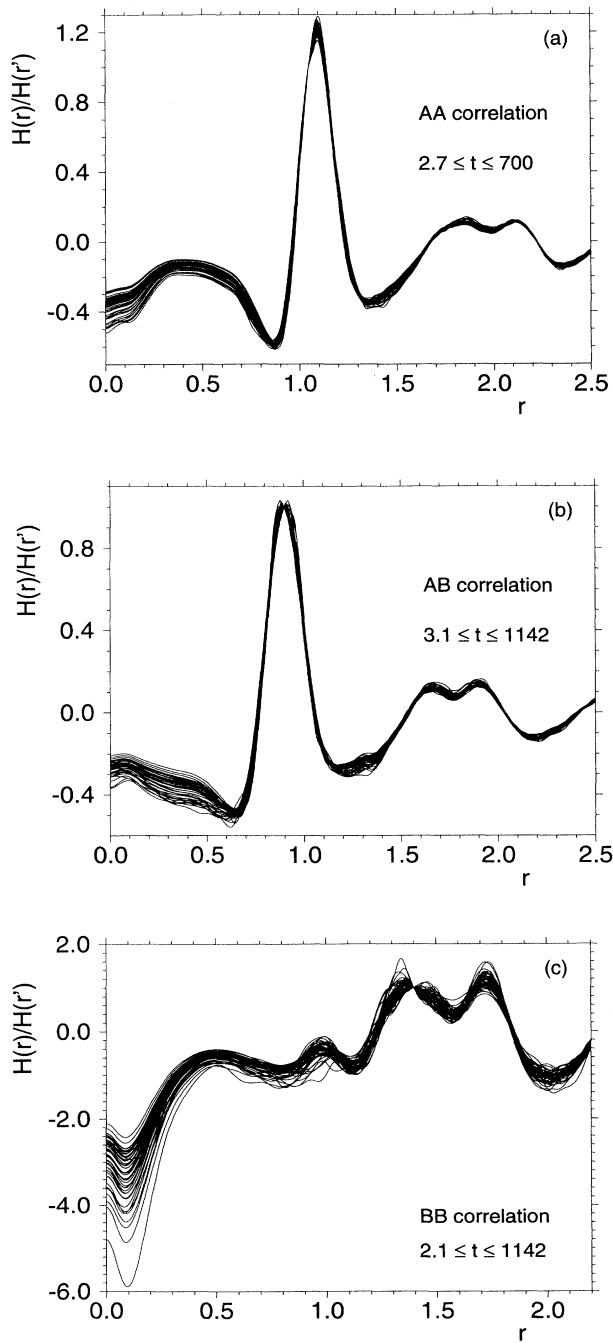


FIG. 12. Normalized critical amplitude  $H(r)/H(r')$  for distinct part of the van Hove correlation function at  $T = 0.466$  [see Eq. (10)].  $t' = 3000$ . (a) *AA* correlation;  $r' = 1.05$ ,  $2.7 \leq t \leq 700$ . (b) *AB* correlation;  $r' = 0.90$ ,  $3.1 \leq t \leq 1142$ . (c) *BB* correlation;  $r' = 1.40$ ,  $2.1 \leq t \leq 1142$ .

master curve is of similar shape as the one for the *AA* correlation the details of the two master curves differ, thus showing again, as in the case of the self part of the van Hove correlation function, that these master curves are not universal but depend on the type of correlator investigated. This is shown even more clearly with the master curve found for the *BB* correlation function [Fig. 12(c)]. To compute it we chose  $r' = 1.40$  and  $t' = 3000$ . The time range shown is  $2.1 \leq t \leq 1142$ . We recognize that for this correlation function the shape of the master curve is very different from the ones for the *AA* and *AB* correlation functions, and it would be interesting to see whether MCT is able to rationalize also a master curve like this.

## V. SUMMARY AND CONCLUSIONS

We have presented the results of a large scale computer simulation we performed in order to test the correctness of the predictions of MCT for a supercooled binary Lennard-Jones liquid. In this work we concentrated on the investigation of the mean squared displacement of a tagged particle and on the van Hove correlation function. The results can be compared with some of the findings of our investigations of the intermediate scattering function [15,16,22] in order to test whether MCT is able to give a correct description of the dynamics of the system investigated.

We have strong evidence that for *all* temperatures investigated these results are all *equilibrium* properties of the system and are therefore independent of cooling rates or the thermal history of the system. This evidence includes the observation that the pressure and the potential energy of the system are smooth functions of temperature, i.e., show no sign of a singularity of some sort. Furthermore, we show that the mean squared displacement (MSD) of a tagged particle shows a diffusive behavior at long times. Moreover, we find that all correlation functions investigated decay to zero within the time span of our simulation.

We find that, for low temperatures, the curves of the MSD collapse onto a master curve when they are plotted versus  $tD(T)$ , where  $D$  is the constant of diffusion. This master curve is observed in a time range where we find that also the intermediate scattering function shows a scaling behavior and which has been identified with the  $\alpha$ -relaxation regime [15,16,22]. The master curve is fitted well by an interpolation formula between the von Schweidler behavior at short rescaled times and the diffusive behavior at long rescaled times. The exponent of the von Schweidler law in this interpolation formula is close to the value we found for the von Schweidler exponent of the intermediate scattering function of this system [15,16,22]. This is further evidence that the scaling behavior in the MSD is a consequence of the scaling behavior predicted by MCT in the  $\alpha$ -relaxation region.

The diffusion constant of both types of particles shows a power-law behavior at low temperatures. The critical temperature  $T_c$  is the same for both species and also the critical exponents  $\gamma$  differ only by about 10%. Thus this is in accordance with MCT. However, the value of  $\gamma$

does not match the value of the critical exponent that we found for the divergence of the relaxation time of the intermediate scattering function. [15,22]. Thus this result is in disagreement with MCT.

Note that this disagreement is rather surprising since we have shown in Refs. [15,22] that various correlators show a scaling behavior with a scaling time that shows a power-law dependence on temperature. The critical exponent of this power law fulfills the connection predicted by MCT between this exponent and the von Schweidler exponent  $b$ , which was extracted from the scaling behavior of the correlators. Here we find now that the MSD shows a scaling behavior too. The scaling function seems to be in accordance with the one found for the correlators. The corresponding time scale, i.e., the inverse of the diffusion constant, shows a power-law behavior with the same critical temperature as the relaxation times of the mentioned correlators. However, the exponent is *not* the same and thus the MCT connection between  $b$  and the  $\gamma$  extracted from  $D(T)$  is not obeyed.

The analysis of the self part of the van Hove correlation function showed that the  $\beta$ -relaxation regime can be recognized in this quantity as well. With the help of this function we also gave evidence that hopping processes are unimportant for the dynamics on the time scale of the  $\beta$  relaxation. This justifies use of the idealized version of MCT, which neglects such hopping processes, to interpret the data. Also on the time scale of the  $\alpha$  relaxation we do not see any indication that these hopping processes are present for the  $A$  particles. However, for the  $B$  particles we see that on the time scale of the *late*  $\alpha$  relaxation a second neighbor peak appears and that therefore hopping processes become relevant. Note that this observation, namely, that hopping processes affect different quantities in different degrees, is not in contradiction with MCT.

We have tested whether the factorization property proposed by MCT, see Eq. (10), holds for this type of correlation function. This test was performed in a way proposed by Signorini *et al.* [11]. We found that in the time region of the  $\beta$ -relaxation regime the factorization property actually holds. Thus we confirmed the prediction of MCT on the existence of this property and the time range in which it is supposed to hold. Also the form of the curve of the critical amplitude  $H(r)$  is in qualitative agreement with the prediction of MCT for a binary soft sphere system [5].

The investigation of the three parts of the distinct part

of the van Hove correlation function, i.e., the  $AA$ , the  $AB$ , and the  $BB$  correlation functions, led to similar conclusions as in the case of the self part, thus confirming the existence of the  $\beta$ -relaxation regime and the absence of hopping processes on the time scale of this regime. Also in this case we found that the factorization property holds in the time range of the  $\beta$ -relaxation regime and that the critical amplitude  $H(r)$  is qualitatively similar to the one predicted by MCT for a hard sphere system [4].

In addition to these observations, which can all be rationalized in the framework of MCT, we have also found that the non-Gaussian parameters  $\alpha_2(t)$  and  $\alpha_3(t)$  show a master curve when they are replotted versus time, i.e., *not* versus *rescaled* time. So far it is not clear whether this observation can be understood with the help of MCT or whether it is in contradiction to the theory. Therefore it would certainly be important to see whether this feature is found also in different types of systems.

In summary we can say that there are a fair number of features in the dynamics of the Lennard-Jones mixture investigated that can be rationalized in the framework of the idealized version of the MCT. The idealized version predicts the existence of a dynamical singularity at a temperature  $T_c$  and predicts several signatures of this singularity in the behavior of the system above  $T_c$ . These signatures include, for example, apparent power-law dependence of relaxation rates on temperature and the factorization property in the  $\beta$ -relaxation regime. The Lennard-Jones mixture studied exhibited many of these signatures in a temperature range corresponding to a value of  $\epsilon = (T - T_c)/T_c$  between about 0.07 and 0.8. (The singularity is not actually observed, but its apparent temperature is inferred from the higher temperature data.) Thus we conclude that the idealized MCT is able to describe some essential features of relaxation in supercooled liquids.

## ACKNOWLEDGMENTS

We thank Dr. J. Baschnagel, Dr. M. Fuchs, and Professor W. Götze for many useful discussions and a critical reading of the manuscript. Part of this work was supported by National Science Foundation Grant No. CHE89-18841. We made use of computer resources provided under NSF Grant No. CHE88-21737.

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