

# Scaling Behavior in the $\beta$ -Relaxation Regime of a Supercooled Lennard-Jones Mixture

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We have performed molecular dynamics simulations of a supercooled atomic liquid. The self-intermediate-scattering function in the  $\beta$ -relaxation regime has a power-law time dependence and temperature dependence consistent with the mode-coupling-theory prediction of a von Schweidler law, with exponents that are very close to satisfying the exponent relationship predicted by the theory. The diffusion constants have a power-law dependence on temperature with the same critical temperature. The exponents for diffusion differ from those of the relaxation time, a result that is in disagreement with the theory.

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In the last few years a remarkable amount of activity has taken place in the field of the glass transition and the dynamics of supercooled liquids. This activity was mainly spawned by the development of sophisticated theories and novel experimental techniques with which the predictions of these theories could be tested. The most outstanding example of these theories is the so-called mode-coupling theory (MCT) which was proposed by Bengtzelius, Götze, and Sjölander and, independently, by Leutheusser [1]. The central point of MCT is the prediction of the existence of a dynamic singularity when the temperature of a supercooled liquid is lowered below a certain critical temperature  $T_c$ . This point of view is in contrast to other theories that try to make a connection between the sluggish dynamics of glass forming materials in the vicinity of the glass transition and an underlying thermodynamic phase transition.

For temperatures close to  $T_c$ , MCT makes detailed predictions about the behavior of all correlation functions  $\langle X(0)Y(t) \rangle$  whose dynamical variables  $X$  and  $Y$  have a nonvanishing overlap with the density fluctuation  $\rho_{\mathbf{q}}$  for any wave vector  $\mathbf{q}$ . These predictions have been verified in experiments and computer simulations of supercooled liquids on a qualitative basis and also on a quantitative basis. However, there are also experiments and computer simulations which show that the predictions of the theory are not always fulfilled [2,3]. The reader can find a good introduction to the theory in the review articles by Götze and Götze and Sjögren [4] and most of the relevant references to the experiments and simulations in references [3,4].

Since experiments and computer simulations have given mixed results as far as the validity of MCT is concerned, more tests are clearly necessary. Moreover, quantitative tests of the theory would be useful in order to understand whether MCT merely suggests a method for performing scaling analyses of experimental data or whether it is also a correct and accurate theory of the exponents and exponent

relations. Since MCT was originally developed for the description of simple supercooled liquids, we have decided to test in a quantitative way the validity and applicability of the prediction of MCT for such a system and this Letter reports some of our findings.

Some of the most important predictions of MCT deal with the behavior of the correlation functions in the so-called  $\beta$ -relaxation regime. At low temperatures the time dependence of correlation functions of supercooled liquids shows a broad shoulder or even a plateau when plotted versus the logarithm of time. The approach to and the subsequent departure from this plateau defines the  $\beta$ -relaxation regime [5]. One of the main predictions of MCT for the behavior of the correlation functions in this  $\beta$ -relaxation regime is the existence of a von Schweidler law. This law states that a correlation function  $\phi(t)$  can be written in the form

$$\phi(t) = f - A[t/\tau(T)]^b, \quad (1)$$

Here  $f$  is the height of the plateau, often also called the nonergodicity parameter, and  $A$  and  $b$  are positive constants.  $A$  and  $f$  are predicted to be smooth functions of temperature if  $T > T_c$  and to be dependent on the type of correlation function investigated but the exponent  $b$  should be the same for all correlation functions. Furthermore, the theory predicts that the relaxation time  $\tau(T)$  shows a power-law divergence at  $T = T_c$  with an exponent  $\gamma$  which is related to the value of  $b$ . Although the predictions of MCT concerning the von Schweidler law have experimentally been found to be true for some systems, it has so far not been observed convincingly in computer simulations of simple liquids. However, for a lattice gas, such a behavior has been observed [6]. But since a simulation of a different lattice gas has shown remarkable disagreement with the predictions of the theory [3], the application of the results of MCT to these kinds of systems may be problematic. Therefore we decided to perform a large scale computer simulation of a simple liquid in order to

investigate, among other things, the dynamics of supercooled liquids in the  $\beta$ -relaxation regime.

Molecular dynamics computer simulations are particularly well suited for testing the predictions of MCT since they allow the measurement of many different types of correlation functions. This freedom allows the performance of more stringent tests of the theory than would be possible for experiments. In addition, simulations allow the measurement of the correlation functions in a very direct way. This is in contrast to experiments, where in most cases a considerable amount of interpretation and manipulation of the raw data has to be done in order to obtain the desired quantities. The main problems with simulations are the limited size of the systems one can study and the time span that a simulation can cover. Since MCT is a theory of equilibrium, it is of utmost importance to make sure that the simulated system is equilibrated at all temperatures investigated. A very recent simulation of a glassy system has shown that failure to equilibrate the system leads to a completely different relaxation behavior [7]. In order to overcome this problem we have performed a simulation that covers a time range that is more than an order of magnitude in time larger than previous molecular dynamics simulations that have studied relaxation in supercooled liquids.

The system we are dealing with 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.,  $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ . The parameters  $\epsilon$  and  $\sigma$  of the various interaction potentials were chosen as follows:  $\epsilon_{AA} = 1.0$ ,  $\sigma_{AA} = 1.0$ ,  $\epsilon_{AB} = 1.5$ ,  $\sigma_{AB} = 0.8$ ,  $\epsilon_{BB} = 0.5$ , and  $\sigma_{BB} = 0.88$ . These potentials were truncated and shifted at a cutoff distance of  $2.5\sigma$ . The number of A particles was 800, and the number of B particles was 200. These potentials are similar to the ones used by Stillinger and Weber for their simulation of amorphous  $\text{Ni}_{80}\text{P}_{20}$  [8]. In the following, all quantities will be expressed in a system of units in which the unit of length is  $\sigma_{AA}$ , the unit of time is  $(m\sigma_{AA}^2/48\epsilon_{AA})^{1/2}$ , and the unit of energy is  $\epsilon_{AA}$ . The equations of motion were integrated with the velocity form of the Verlet algorithm with a step size of 0.01 and 0.02 at high and low temperatures, respectively. The system was equilibrated at high temperatures and, by coupling it to a heat bath, subsequently slowly cooled down to low temperatures. At each temperature the system was equilibrated for a time which was equal to or longer than the time it took all the correlation functions investigated to decay to zero to within the noise. After equilibration, a long molecular dynamics calculation was performed for the calculation of the diffusion constant and the correlation functions. The length of this run was also equal to or longer than the time for the correlation functions to decay to zero. The longest equilibrium runs were those for the lowest temperature and had a duration of  $10^5$  time units, which would correspond for an atomic liquid to a real time of about 30 ns. This is about

an order of magnitude longer than previously reported comparable simulations. To improve the statistics further we determined the correlation functions for at least eight different starting positions in phase space. More details on the simulation will be presented elsewhere [9].

In the following we will mainly concentrate on the investigation of the dynamics in the  $\beta$ -relaxation regime. Since the presence of activated, or hopping, processes will modify the prediction of the simple version of MCT (in which these effects are neglected) [4], one has to determine the importance of these processes for the system under investigation. By studying the self and distinct part of the van Hove correlation function we have found that on the time scale of the  $\beta$ -relaxation there is no secondary peak in the self part and no peak at  $r = 0$  in the distinct part [10]. Thus we conclude that hopping processes are not relevant on the time scale of the  $\beta$ -relaxation and can therefore be neglected in the analysis of the data [9]. Thus the comparison of our results with the simple version of the theory is justified.

The space Fourier transform of the self part of the van Hove correlation function gives the self-intermediate-scattering function  $F_s(q, t)$  [11]. Figure 1 shows the time dependence of  $F_s(q, t)$  for the AA correlation function. The value of  $q$  is  $q_{\text{max}}$ , the location of the first maximum in the structure factor  $S_{AA}(q)$  for the AA correlation function. The following observations can be made: (1) For all temperatures investigated the correlation functions decay to zero to within the noise of the data. This is strong evidence that the runs were long enough to equilibrate the system. (2) For high temperatures the correlation functions decay quickly to zero. When the temperature is lowered the formation of a shoulder at intermediate times (on a logarithmic time scale) can be observed. For the lowest temperatures this shoulder forms almost a plateau and we can clearly observe the two step relaxation behavior observed for strongly supercooled

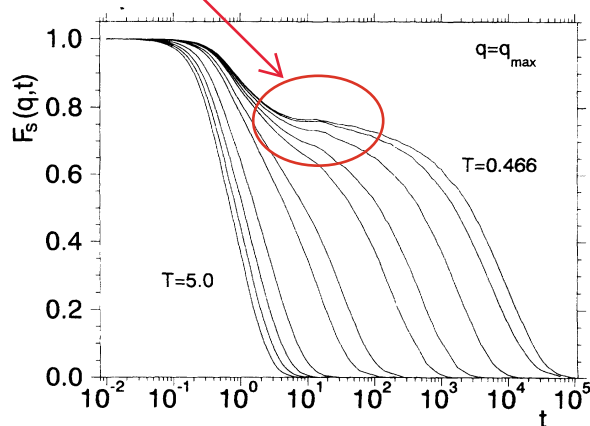


FIG. 1. Self-intermediate-scattering function  $F_s(q, t)$  for A particles vs  $t$ .  $q = 7.251\sigma_{AA}^{-1}$ , the location of the first peak in the structure factor  $S_{AA}(q)$ . Temperatures (from left to right): 5.0, 4.0, 3.0, 2.0, 1.0, 0.8, 0.6, 0.55, 0.5, 0.475, and 0.466.

liquids. (3) For times around 15 time units the correlation functions for low temperatures show a small bump.

In order to test for the presence of a scaling behavior we plotted the data from Fig. 1 versus a rescaled time  $t/\tau(T)$ . The value of the scaling time  $\tau(T)$  was chosen at each temperature such that  $F_s(q, \tau) = e^{-1}$ . In Fig. 2 we show the resulting plot. We can clearly recognize the presence of a master curve. This master curve can be fitted very well by a power law of the form given by Eq. (1) with  $f = 0.783$  and  $b = 0.488 \pm 0.015$ . This fit is included in the plot as well. Since the fit is valid for almost 3 orders of magnitude in rescaled time, it is definitely significant. Thus we find a power law with an exponent  $b$  and an offset  $f$  that are independent of temperature. This is exactly the behavior predicted by MCT for the behavior of the correlation function in the later part of the  $\beta$ -relaxation region, i.e., a von Schweidler law with a nonergodicity parameter  $f$  and an exponent  $b$  that are independent of temperature.

In order to test whether the power law observed in the  $\beta$ -relaxation region is just the short time expansion of a Kohlrausch-Williams-Watt (KWW) law,  $\phi(t) = f \exp[-(t/\tau)^\beta]$ , which is known to be often an excellent approximation for the long time behavior of correlators in glassy materials, we fitted the long time behavior of our correlation functions with such a functional form. We found that such a fit is very good but that the extrapolation of the fit to intermediate times, i.e., to the  $\beta$ -relaxation regime, is not good at all since the fit falls below the data. Thus we can conclude that the power law observed here is not just the short time behavior of the KWW law.

MCT predicts that the scaling time  $\tau$  in Eq. (1) scales with temperature as  $\tau \propto (T - T_c)^{-\gamma}$ . We fitted the relaxation time with such a power law and found, for the A and B particles, the value 0.435 for  $T_c$ . The exponent  $\gamma$  is 2.5 and 2.6 for the A and B particles, respectively. MCT also predicts a relationship between the exponents  $b$  and  $\gamma$ . The value found above for  $b$ , when combined with this

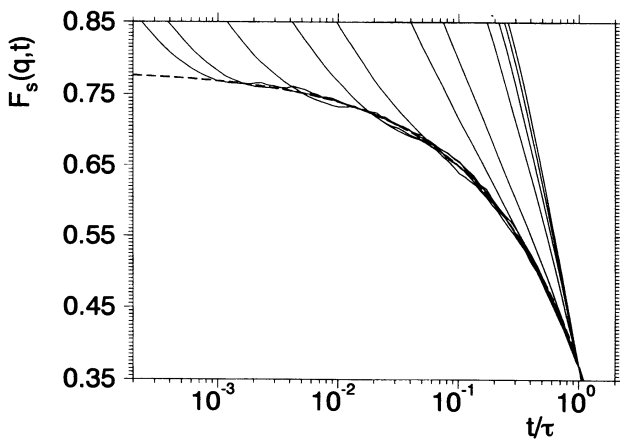


FIG. 2. Self-intermediate-scattering function for the A particles for  $q = 7.251\sigma_{AA}^{-1}$  vs rescaled time  $t/\tau(T)$  (solid lines). Dashed curve: Fit with von Schweidler law. Temperatures (from right to left) as in Fig. 2.

relationship, predicts that  $\gamma = 2.7$ , which is very close to what we actually found. Thus the exponent relationship of MCT is confirmed to within the precision with which we can obtain the exponents. In Fig. 3 we plot  $\tau^{-1}$  versus  $T - T_c$  (dotted curves). From this plot we recognize that the power-law behavior is observed for  $0.466 \leq T \leq 0.6$ . Although this range is not that large we recognize from Fig. 2 that it is only for this temperature range that the curves follow the master curve. Thus from the point of view of MCT we have a consistent picture with respect to this range. A fit to the data with a Vogel-Fulcher law gave accordance with the data over a temperature range which is a bit larger than the one where the power law is observed [9]. However, this observation is not in contradiction with MCT since the main point is that the theory works where it is supposed to work, namely, close to  $T_c$ .

MCT predicts that the von Schweidler law should be present not only for  $q = q_{\max}$  but all values of  $q$  and that the exponent  $b$  should be independent of  $q$ . We tested this prediction by computing  $F_s(q, t)$  for different values of  $q$  in the range  $6.5\sigma_{AA}^{-1} \leq q \leq 9.6\sigma_{AA}^{-1}$ , i.e., from  $q$  values a bit less than  $q_{\max}$ , the location of the peak in the structure factor  $S_{AA}(q)$ , to values up to the first minimum of  $S_{AA}(q)$ . In Fig. 4 we plot these correlation functions vs  $t^b$  with  $b = 0.488$ . The part of the curves that are straight lines are power laws with exponent  $b$ . We recognize that this is the case for  $t^b$  lying between 2–3 and about 60. This corresponds to a time interval of 4–9 time units to 3600 time units. Thus we find that this prediction of MCT also holds for this system.

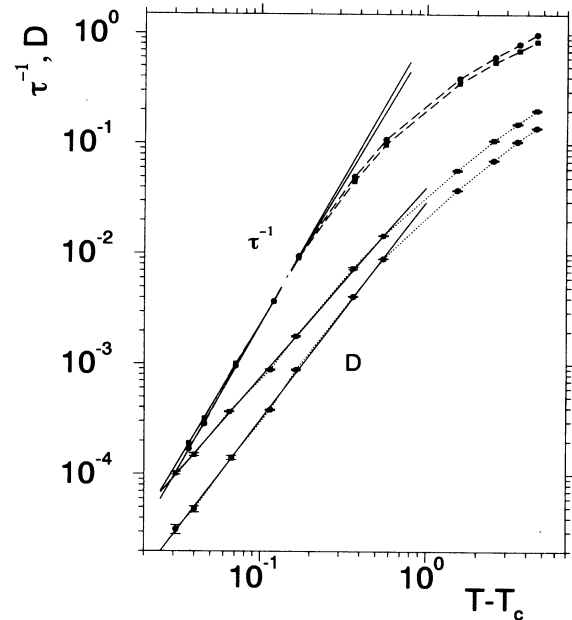


FIG. 3. Inverse relaxation time (dashed curves,  $T_c = 0.430$ ) and self-diffusion constant with error bars (dotted curves,  $T_c = 0.435$ ) for A (circles) and B (squares) particles vs  $T - T_c$ . Also shown are the fits with a power law (solid lines).



We have also done similar calculations for the  $B$  particles and found a similar behavior as reported here for the  $A$  particles. The von Schweidler exponent  $b$  for the  $B$  particles is about  $0.445 \pm 0.015$ , and thus quite close to the one of the  $A$  particles. Since MCT predicts these two exponents to be the same, this observation is also in accordance with the theory. Note that this kind of universality, i.e., the presence of a von Schweidler law for all types of correlators and that the von Schweidler exponent is independent of, or only weakly dependent upon, the correlator, is one of the main predictions of the theory.

So far we have dealt only with the behavior of the correlators in the  $\beta$ -relaxation regime. But MCT also proposes an intimate connection between this regime and the relaxation on the longest time scale, the so-called  $\alpha$ -relaxation regime. For example, the theory predicts that the constant of diffusion  $D$  should show a power-law divergence at  $T_c$  with an exponent  $\gamma$  that is the same as the one for the relaxation times. We have determined  $D$  by fitting a straight line to the long time asymptote of the mean squared displacement. We have fitted  $D$  with a power law of the form  $D \propto (T - T_c)^\gamma$  and for both types of particles found the critical temperature  $T_c$  to be 0.435. The exponent  $\gamma$  was 2.0 for the  $A$  particles and 1.7 for the  $B$  particles. These results are shown in Fig. 3, where we plot  $D$  versus  $T - T_c$  in a double logarithmic way (dashed curves). Thus, in accordance with MCT, we find that the critical temperature for the constant of diffusion is the same as the one we found for the relaxation time  $\tau$ . However, the  $\gamma$  exponents are slightly different for the diffusion constants of the two species, and both values are significantly different from the  $\gamma$  obtained from the scaling time. These findings are in contradiction to the predictions of MCT.

In the range where the data show a power-law behavior (i.e.,  $T \leq 1.0$ ) we also tried to fit it with a Vogel-Fulcher law, i.e.,  $D \propto \exp[-E/(T - T_0)]$  and found that this type of fit is clearly inferior to the one with the power law.

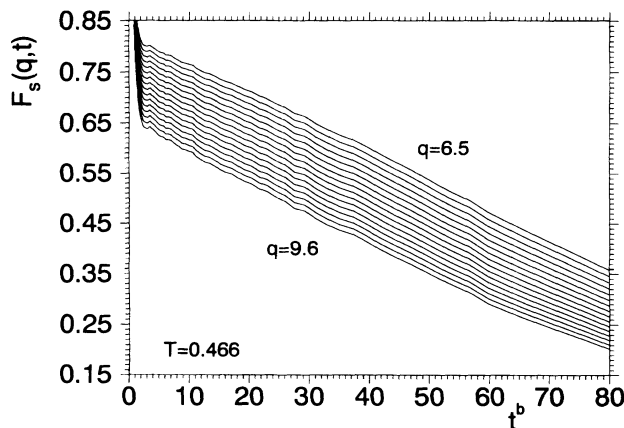


FIG. 4. Self-intermediate-scattering function for  $A$  particles for  $6.5\sigma_{AA}^{-1} \leq q \leq 9.6\sigma_{AA}^{-1}$  (from top to bottom) vs  $t^b$  with von Schweidler exponent  $b = 0.488$ ,  $T = 0.466$ .

In summary, the predictions of MCT concerning the von Schweidler law are fulfilled in quite an impressive way for the system investigated here, but the relationship predicted by MCT between the temperature dependence of the von Schweidler relaxation time and the temperature dependence of diffusion do not hold. For the  $\beta$ -relaxation regime we have presented only the results of the simulation that deal with the departure of the correlation functions from the plateau. But to make a stringent test of the theory it is clearly necessary to check not only a few predictions of the theory but as many as possible. We have done this and the results will be presented in Ref. [9]. These results seem to indicate [9] that the behavior of the correlation functions in the first part of the  $\beta$ -relaxation, i.e., the critical decay, is not as well described by the theory as the second part, which is described in this Letter. Nevertheless, considering the approximations that have to be made in order to derive the statements of the theory, the accordance of its predictions with the results presented here is most remarkable.

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