Scaling behavior in the dynamics of a supercooled Lennard-Jones mixture

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Abstract

We present the results of a large scale molecular dynamics computer simulation of a binary, supercooled Lennard-Jones fluid. At low temperatures and intermediate times the time dependence of the intermediate scattering function is well described by a von Schweidler law. The von Schweidler exponent is independent of temperature and depends only weakly on the type of correlator. For long times the correlation functions show a Kohlrausch behavior with an exponent \( \beta \) that is independent of temperature. This dynamical behavior is in accordance with the mode-coupling theory of supercooled liquids.

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In the last ten years there has been an impressive increase of our understanding of the dynamics of supercooled liquids. In particular the so-called mode-coupling theory (MCT), proposed by Götze and Sjögren and, independently, by Leutheusser, seems to offer a remarkable theoretical insight into the dynamics of supercooled liquids [1]. However, despite the fact that certain experiments seem to be in remarkable accordance with the theory [2], the applicability of the theory to supercooled liquids is still highly controversial.

In this paper we report some of the results of our efforts to investigate the dynamics of a simple supercooled liquid in order to find out whether the dynamics of this system is in accordance with the predictions of MCT. A more extensive report will be given elsewhere [3,4]. The reader is referred to two review articles by Götze and Götze and Sjögren [5] for a discussion of the predictions of MCT.

The model investigated is a binary mixture of Lennard-Jones particles (800 particles of type A and 200 particles of type B). Both kinds of particles have the same mass. The parameters of the Lennard-Jones potential 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 $\sigma_{BB} = 0.88$. The equations of motion were integrated with the velocity form of the Verlet algorithm with a time step of 0.01 and 0.02 at high and low temperatures respectively. (Throughout the paper we use reduced time units, with the unit of time being $(m\sigma_{AA}^2/48\epsilon_{AA})^{1/2}$, where $m$ is the mass of a particle.) The length of the runs at the lowest temperature was $5 \times 10^6$ time steps, which corresponds to a real time of about 10ns. More details on the simulation will be given elsewhere [4].

In order to investigate the dynamical behavior of the system we computed $F_s(q, t)$ and $F(q, t)$, the self and total intermediate scattering function for wave vector $q$ [6]. We found that at low temperatures these correlation functions, when plotted versus the logarithm of time, show a two-step relaxation process with a well defined plateau at intermediate times, in agreement with the predictions of MCT. The width of the plateau is a strong function of temperature, and at the lowest temperature it extends from about 3 time units to $10^3$ time units [3]. In MCT, the approach to the plateau and the early stages of deviation from it are referred to as the $\beta$-regime, whereas the entire departure from the plateau, from the early stages to infinity, is referred to as the $\alpha$-regime. Even at the lowest temperature all correlation functions that we measured decay to zero within the time of our simulation.
This gives strong evidence that we are able to equilibrate this system at all temperatures investigated. Thus the results reported are all *equilibrium* properties of the liquid.

We defined the $\alpha$-relaxation time $\tau(T)$ as the time required for the correlation function to decay to $e^{-1}$ of its initial value. Figure [1] shows $F_s(q, t)$ for the A particles versus the rescaled time $t/\tau(T)$ for all temperatures investigated (see figure caption). The wave vector $q$ is $q_{\text{max}} = 7.25$, the location of the maximum of the structure factor for the AA correlation. We recognize that for low temperatures the curves follow a master curve that extends throughout the $\alpha$-relaxation regime. Thus this master curve extends over about four orders of magnitude in time and is therefore quite remarkable.

In the last part of the $\beta$-regime, which overlaps the early part of the $\alpha$-regime, MCT predicts this master curve to show a von Schweidler behavior, i.e. that the correlator $\phi(t)$ is of the form $\phi(t) = f_c - A(t/\tau)^b$ with $A > 0$. The constant $f_c$ is called nonergodicity parameter and the positive exponent $b$ is called the von Schweidler exponent. We made a fit to the master curve with this functional form and the best fit obtained is included in the figure as well. It is clear that the von Schweidler law describes the relaxation behavior of the correlation function over about three decades of rescaled time, which is remarkably long. For the value of the von Schweidler exponent we obtained 0.49. In the later part of the $\alpha$-regime, MCT predicts that the decay of the correlation functions is well described by a Kohlrausch-Williams-Watt-law (KWW), i.e. by $\phi(t) = A \exp\left(-\left(t/\tau(T)\right)^\beta\right)$. The best fit with this functional form is included in the figure as well and we recognize that this type of fit gives a good representation of the data. Note that the value of the KWW exponent $\beta$ is 0.83 and therefore definitely different from the value of the von Schweidler exponent $b$, as predicted by MCT. Thus we can conclude that the power-law observed for short rescaled time is not just the short time expansion of the KWW function.

MCT predicts that the von Schweidler exponent $b$ should be independent of the value of the wave vector $q$ and also of the type of correlator. In a separate work [3] it was shown that for the self intermediate scattering function of the A particles the value of $b$ is almost independent of $q$ for values of $q$ between $q_{\text{max}} = 7.25$ and $q_{\text{min}} = 9.61$, where $q_{\text{min}}$ is the location of the first minimum in the structure factor for the AA correlation. Thus this prediction of the theory seems to hold for the system under investigation.
Figure 2 shows the self intermediate scattering function $F_s(q,t)$ for the B particles versus rescaled time $t/\tau(T)$. The relaxation time $\tau(T)$ is defined here in the same way as for the case of the A particles. The value of $q$ is 5.75, the location of the maximum of the structure factor for the BB correlation. As in the case of the A particles we observe that at low temperatures the correlator fall onto a master curve. Also included in the figure is the result of a fit with a von Schweidler law to this master curve in the appropriate range of times (see above). The von Schweidler exponent is in this case 0.47 and thus very close to the one found for the A particles. Also in this case the long time behavior of the correlation functions at low temperatures can be fitted well with a KWW function. The best fit is included in the figure as well.

Figure 3 shows the total intermediate scattering function $F(q,t)$ for the A particles versus rescaled time $t/\tau(T)$. For $q$ we chose again $q_{\text{max}}=7.25$. Again we observe the presence of a master curve that can be fitted well with a von Schweidler law. For this correlator the von Schweidler exponent is 0.52 which is reasonably close to the value we reported above for the values of the von Schweidler exponent. Also for this correlation function the long time behavior could be fitted well with a KWW function.

In summary we can conclude, that the system investigated here seems to exhibit a dynamical behavior that is in accordance with the predictions of mode-coupling theory. In particular we find that the correlation functions show a two-step relaxation behavior. Furthermore, we find that in the late $\beta$-regime or early $\alpha$-regime the correlation functions investigated show a von Schweidler law. The von Schweidler exponent is only a weak function of the wave vector $q$ and of the type of correlation function. Thus with respect to this the predictions of MCT seem to hold. Also the observation that the later stages of $\alpha$-relaxation of the correlation functions can be fitted well by a KWW function, with an exponent $\beta$ that is independent of $T$, is in accordance with the theory.

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FIGURES

FIG. 1. Self intermediate scattering function for A particles versus rescaled time $t/\tau(T)$ (solid curves). Temperatures (from left to right in the upper part of the figure): 0.466, 0.475, 0.5, 0.55, 0.6, 0.8, 1.0, 2.0, 3.0, 4.0, 5.0. Dashed curve: von Schweidler law $0.783 - 0.407(t/\tau)^{0.49}$. Dotted curve: KWW $0.69\exp(-(t/\tau)^{0.83})$.

FIG. 2. Self intermediate scattering function for A particles versus rescaled time $t/\tau(T)$ (solid curves). Temperatures as in Fig. 1. Dashed curve: von Schweidler law $0.804 - 0.438(t/\tau)^{0.47}$. Dotted curve: KWW $0.72\exp(-(t/\tau)^{0.78})$.

FIG. 3. Intermediate scattering function for AA correlation versus rescaled time $t/\tau(T)$ (solid curves). Temperatures as in Fig. 1. Dashed curve: von Schweidler law $0.867 - 0.475(t/\tau)^{0.52}$. Dotted curve: KWW $0.81\exp(-(t/\tau)^{0.85})$. 