Growing length scales in a supercooled liquid close to an interface

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We present the results of molecular dynamics computer simulations of a simple glass former close to an interface between the liquid and the frozen amorphous phase of the same material. By investigating $F_s(q, z, t)$, the incoherent intermediate scattering function for particles that have a distance $z$ from the wall, we show that the relaxation dynamics of the particles close to the wall is much slower than the one for particles far away from the wall. For small $z$ the typical relaxation time for $F_s(q, z, t)$ increases like $\exp(\Delta/(z - z_p))$, where $\Delta$ and $z_p$ are constants. We use the location of the crossover from this law to the bulk behavior to define a first length scale $\bar{z}$. A different length scale is defined by considering the Ansatz $F_s(q, z, t) = F_{s, \text{bulk}}(q, t) + a(t) \exp\left[-(z/\xi(t))^{\beta(t)}\right]$, where $a(t)$, $\xi(t)$, and $\beta(t)$ are fit parameters. We show that this Ansatz gives a very good description of the data for all times and all values of $z$. The length $\xi(t)$ increases for short and intermediate times and decreases again on the time scale of the $\alpha$-relaxation of the system. The maximum value of $\xi(t)$ can thus be defined as a new length scale $\xi_{\text{max}}$. We find that $\bar{z}$ as well as $\xi_{\text{max}}$ increase with decreasing temperature. The temperature dependence of this increase is compatible with a divergence of the length scale at the Kauzmann temperature of the bulk system.

1 Introduction

The idea that the slow dynamics of supercooled liquids is related in some way to the existence of domains in which the dynamics of the particles is cooperative is an old one (Adam and Gibbs 1958). The size of such domains is supposed to grow with decreasing temperature and can in turn be used to explain the slowing down of the dynamics. For a long time it was not clear at all whether or not the idea of such domains has any

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counterpart in real glass formers or whether it is just an appealing theoretical concept. Only in recent years a variety of novel experimental techniques yielded results that gave evidence that such domains do indeed exist in the supercooled state (e.g. Cicerone et al. 1995, Ediger 2000, Hempel et al. 2000, Leheny et al. 1996, Richert 1996, Sillescu 1999, Tracht et al. 1998, Yamamuro et al. 1998). Also computer simulations of two and three dimensional model systems give evidence that in the supercooled state the relaxation dynamics of the particles is very cooperative (Doliwa and Heuer 2000, Donati et al. 1999a/b, Perera and Harrowell 1999, Yamamoto and Onuki 1998). Progress has also been made on the theoretical level in that it was shown that such domains are related to the nonlinear susceptibility of a certain four point correlation function (Franz and Parisi 1998, Franz et al. 1999, Franz and Parisi 2000).

In the present paper we use the fact that the relaxation dynamics of a particle in a confined system depends strongly on its distance $z$ from the wall (Scheidler et al. 2000, Scheidler 2001). By investigating how this influence depends on $z$ and time $t$ we thus can determine a dynamical length scale and study its dependence on temperature.

## 2 Model and Details of the Simulations

The system we study is a binary (80:20) mixture of Lennard-Jones particles, i.e. with an interaction potential $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}\left[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^{6}\right]$. This potential was truncated and shifted at $2.5\sigma_{\alpha\beta}$. The interaction parameters are $\sigma_{AA} = 1.0$, $\epsilon_{AA} = 1.0$, $\sigma_{AB} = 0.8$, $\epsilon_{AB} = 1.5$, $\sigma_{BB} = 0.88$ and $\epsilon_{BB} = 0.5$, where A and B label the type of particle. In the following we will discuss the results in terms of reduced units, using $\sigma_{AA}$ and $\epsilon_{AA}$ as the units of length and energy (setting the Boltzmann constant $k_B = 1$), and $(m\sigma_{AA}^2/48\epsilon_{AA})^{1/2}$ as the unit of time. (Here $m$ is the mass of the particles.)

In the past the static and dynamical properties of this system in the bulk have been analyzed carefully (Kob and Andersen 1995a/b, Gleim et al. 1998) and it was found that its dynamics is described very well by means of the so-called mode-coupling theory (Götz 1999) with a critical temperature around $T_c = 0.435$. Thus this is the temperature at which the dynamics of the bulk system slows down significantly. A further relevant temperature for this system is the Kauzmann temperature $T_K$ which has been estimated to be around 0.3 (Coluzzi et al. 2000a/b, Sciortino et al. 1999).

The confined liquid studied in the present work was set up in the following way: We first equilibrated a system of 3000 particles in a box of dimensions $L_x = L_y = 12.8$ and $L_z = 15$ by applying periodic boundary conditions in all three directions. After equilibration we joined a copy of the configuration in the positive $z$-direction and one in the negative $z$-direction. The particles of these two copies that were in the layer (perpendicular to the $z$-axis) of thickness 2.5 closest to the original system were subsequently frozen and constituted the wall for the confined system (2.5 is the range of the interaction). In this way we thus generated a sandwich geometry in which a fluid system of extension $L_x \times L_y \times L_z$ was confined by two walls of dimension $L_x \times L_y \times 2.5$. (In the direction of the $x$ and $y$ axis we kept the periodic boundary conditions.) The width $L_z$ of the film
was sufficient to make sure that the dynamical bulk properties are realized in the center. Apart from the two mentioned walls we also added a hard-core potential at \(z = 0\) and \(z = L_z\) to avoid a penetration of particles into the wall. It is now straightforward to show that with these types of boundary conditions the equilibrium structure of the confined liquid is identical to the one of the bulk liquid. Hence it is not necessary to equilibrate the confined system after the introduction of the wall. (Note that this procedure was done for all temperatures investigated and hence the structure of the wall depends slightly on temperature.) Moreover, the energy of a particle near to the wall is statistically the same to the one of a particle far from the wall: in general, the presence of such a wall cannot be discovered by looking to quantity measured at one time, but influences only the correlation of quantities measured at two different times.

The lowest temperature investigated was \(T = 0.5\) for which production runs of 16 million time steps were used. Note that the length of these production runs is more than ten times longer than the one needed in a simulation for the bulk (Kob and Andersen 1995a/b), since the relaxation of the system close to the wall is so much slower. Finally, we mention that in order to improve the statistics of the results we averaged them over 8-16 independent runs.

## 3 Results

The dynamical quantity that we investigate is the incoherent intermediate scattering function \(F_s(q, t)\), i.e. a space-time correlation function that is important from the theoretical as well as experimental point of view (Hansen and McDonald 1986). Due to the presence of the walls the system is no longer homogeneous or isotropic and hence we have to consider the \(z\)-dependence of \(F_s(q, t)\). For this we investigate the following generalization of the incoherent intermediate scattering function:

\[
F_s(q, z, t) = \frac{1}{N_\alpha} \left\langle \sum_{j=1}^{N_\alpha} \exp(iq \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))) \delta(z_j(0) - z) \right\rangle
\]

where the \(\delta\)-function on the right hand side makes sure that one considers only particles that at time \(t = 0\) were a distance \(z\) away from the wall. The wave-vectors \(q\) we consider in the following are parallel to the walls and their \(x\) and \(y\) components are chosen such that they are compatible with the periodic boundary conditions. In Fig. 1 we show the time dependence of \(F_s(q, z, t)\) for various values of \(z\). From this figure we see that the relaxation dynamics of the particles close to the walls (curves for \(z \approx 0\)) is much slower than that for particles in the middle of the film (curves for \(z \approx 7.5\)). In an earlier paper we have shown that the typical relaxation time for particles that have a distance \(z\) from the wall, \(\tau(z, T)\), increases like

\[
\tau(z, T) \propto \exp[\Delta/(z - z_p)],
\]

where \(\Delta \approx 7.5\) and \(z_p \approx -0.5\) are constants and the proportionality factor depends on \(T\) (Scheidler et al. 2000, Scheidler 2001). This law is valid for small values of \(z\), i.e. close to
the wall. For large \( z \) we recover instead the bulk relaxation time \( \tau_{\text{bulk}}(T) \). The distance from the wall at which one finds the crossover from the law given by equation (2) to the constant bulk value \( \tau_{\text{bulk}}(T) \) can be used to define a length scale \( \tilde{z} \) (Scheidler 2001). Thus \( \tilde{z} \) is the length scale over which the wall influences the dynamics of the particles and below we will discuss how this scale depends on temperature.

A second approach to investigate the spatial dependence of the structural relaxation is to consider the whole \( t \)- and \( z \)-dependence of the intermediate scattering function within one Ansatz. From figure 2 we see that the \( z \)-dependence of \( F_s(q, z, t) \) is very smooth. In particular it is clear that for \( z \gg 1 \) this function has to converge to the intermediate scattering function for the bulk, \( F_{s\text{bulk}}(q, t) \). Therefore it is reasonable to make an Ansatz of the form

\[
F_s(q, z, t) = F_{s\text{bulk}}(q, t) + a(t) \exp \left[ -(z/\xi(t))^{\beta(t)} \right], \tag{3}
\]

i.e. that the whole \( z \)-dependence of \( F_s(q, z, t) \) is given by a stretched exponential. Here \( a(t) \), \( \xi(t) \), and \( \beta(t) \) are unknown functions of time that can be found from fitting at a given time the \( z \)-dependence of \( F_s(q, z, t) \) with the functional form given by equation (3). Note that \( F_{s\text{bulk}}(q, t) \) is known from the simulations of the bulk and is hence not a fit parameter.

That the Ansatz (3) is indeed able to describe the \( z \)-dependence of \( F_s(q, z, t) \) very well is demonstrated in figure 2 where we show \( F_s(q, z, t) - F_{s\text{bulk}}(q, t) \) as a function of \( z \) for times that span the range from microscopic times to the time of the \( \alpha \)-relaxation, i.e. of the final decay of the correlation functions. We also mention that other simple functional forms, e.g. if the stretching parameter \( \beta \) is set to 1.0, do not give satisfactory fits (Scheidler 2001). Nevertheless such a purely exponential Ansatz leads to a very similar dynamical length scale.

In figure 3 we show the time dependence of the stretching parameter \( \beta(t) \) for all temperatures investigated. From this figure we recognize that at low temperatures \( \beta(t) \) shows at short times \( (\approx 3 \text{ time units}) \) a rapid decrease from values around 1.5 to a value around 1.2. Subsequently it remains at this latter value for a time span that corresponds roughly to the \( \beta \)-relaxation, i.e. the time window during which the correlation functions for small \( z \) remain close to the plateau and which extends at the lowest temperature over roughly three decades in time (see figure 1). For longer times \( \beta(t) \) increases again to values above 1.4. For intermediate and high temperatures the time dependence of \( \beta(t) \) remains qualitatively the same as the one we just described. The main difference is that the length of the plateau at intermediate times is shortened significantly, in agreement with the fact that also the correlation functions show only a short plateau at high temperatures (Scheidler 2001). Note that the fact that at intermediate times \( \beta(t) \) is larger than 1.0 shows that the \( z \)-dependence of the \( F_s(q, z, t) \) is rather strong, i.e. it is not just an exponential dependence. Additionally we observed in thin films that the influence of two walls on the dynamics of the particles between them is not just the superposition of two laws of the form given by equation (3). This is thus evidence that the slowing down of the dynamics is related to the presence of a strongly non-linear process such as, e.g., the non-linear feedback process of mode-coupling theory.
In figure 4 we show the time dependence of the parameter $\xi(t)$ for all temperatures investigated. We see that for short and intermediate times this length scale increases, attains a maximum around a time that corresponds to the $\alpha$-relaxation time of the bulk system, and then starts to decrease again. The value of $\xi$ at its maximum can thus be used to define a new length scale $\xi_{\text{max}}(T)$. Note that the time at which this maximum is attained is roughly in the time window in which $\beta(t)$ has a minimum, i.e. is relatively small. This implies that at this time the influence of the wall on the dynamics of the particles in the fluid extends over the largest range.

Finally we discuss the temperature dependence of the length scales $\tilde{z}$ and $\xi_{\text{max}}$. These quantities are shown in figure 5 as a function of temperature. We see that both length scales increase with decreasing temperature but that this increase is relatively modest. In the temperature interval $0.5 \leq T \leq 1.0$, where the relaxation times of the system in the bulk increases by about a factor of 500, this increase is only around 2.5 for the case of $\xi_{\text{max}}$ and a factor of 4 for $\tilde{z}$. Due to the slow relaxation of the particles close to the wall it is presently not possible to study the relaxation dynamics of these particles at significantly lower temperatures and hence it is also not possible to determine neither $\tilde{z}$ nor $\xi_{\text{max}}$ at low temperatures. Due to this relatively weak increase of the length scales it is difficult to make precise statements on whether or not these length scales diverge or not and if yes, at which temperature this would be expected to happen. Furthermore it is presently not even clear whether such a divergence occurs at the same temperature, since the ratio $\tilde{z}/\xi_{\text{max}}$ depends on temperature (see inset of figure 5). Since previous simulations have identified two relevant temperatures, the critical temperature $T_c$ of mode-coupling theory at $T_c = 0.435$ and the Kauzmann temperature $T_K$ at around $T_K = 0.29$ (Coluzzi et al. 2000a/b, Sciortino et al. 1999) we have tried to see whether the increasing length scale is compatible with a power-law divergence at one of these two temperatures. Whereas it seems that no such divergence occurs at $T_c$, the data is indeed compatible with a critical behavior at $T_K$ with an exponent of the power-law around 1, both for $\tilde{z}$ and $\xi_{\text{max}}$. This result is in agreement with a theoretical approach to describe the temperature dependence of the size of cooperatively rearranging region in the concept of configurational entropy (Huth et al. 2000). However, it is also possible that the divergence occurs only at $T = 0$ since also this temperature is compatible with our data. Hence we conclude that although we are able to identify a growing length scale it is presently not yet possible to give a definite answer regarding the precise temperature dependence of the scale. Therefore simulations at lower temperatures as well as some theoretical guidance on this matter would be highly desirable.

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Figure 1: Time dependence of the generalized incoherent intermediate scattering function from equation (1) for the A particles for $T = 0.55$. The curves are for $q = 7.18$, the location of the main peak in the static structure factor. The different curves correspond to different distances $z$ from the wall (see label of curves).

Figure 2: The time dependence of $F_s(q, z, t) - F^\text{bulk}_s(q, t)$ is shown to check the validity of the Ansatz given by equation (3) (the value of $q$ is the same as in figure 1). The symbols are the data from the simulations and the smooth curves are the fits with the functional form given by equation (3).
Figure 3: Time dependence of the stretching parameter $\beta(t)$ from equation (3) for all temperatures investigated.

Figure 4: Time dependence of the scale $\xi(t)$ from equation (3) for all temperatures investigated. The value of the maximum of the curves is used to define the length scale $\xi_{\text{max}}$. 
Figure 5: Temperature dependence of the two length scales $\tilde{z}$ and $\xi_{\text{max}}$. The inset shows the ratio between these two quantities.