Finite size effects in simulations of glass dynamics

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We present the results of a molecular dynamics computer simulation in which we investigate the dynamics of silica. By considering different system sizes, we show that in simulations of the dynamics of this strong glass former surprisingly large finite size effects are present. In particular, we demonstrate that the relaxation times of the incoherent intermediate scattering function and the time dependence of the mean squared displacement are affected by such finite size effects. By compressing the system to high densities, we transform it to a fragile glass former and find that for that system these types of finite size effects are much weaker. [S1063-651X(96)50712-9]

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The dynamics of supercooled liquids and the related phenomenon of the glass transition have been the focus of interest for a long time. In the last ten years a particularly intense activity could be observed in this field, which was triggered on the one hand by new theoretical developments, such as the so-called mode-coupling theory, and on the other hand by the progress in experimental techniques which allowed one to make new types of experiments to investigate such systems [1]. However, despite all these efforts the underlying mechanism for the dramatic (by some 15 decades) slowing down of the dynamics of the liquid upon cooling is still a matter of debate and thus the focus of many investigations.

In these years the dynamics of supercooled liquids has also been investigated intensively with the help of computer simulations [2]. Because such simulations permit access to the whole microscopic information of the system at any given time, such investigations permit measurement of observables which are not accessible in today's experiments, but for which the theories make predictions that can be tested. Therefore, computer simulations are a very useful addition to theoretical and experimental investigations in the field of supercooled liquids and the glass transition.

With very few exceptions [3–5], the computer simulations that investigated the *dynamical* properties of supercooled liquids focused on models in which the interactions between the particles are short ranged. The reason for this is that only for such simple models was it possible to make sufficiently long simulations to allow the system to equilibrate even at relatively low temperatures and thus to investigate the supercooled regime. By determining the temperature dependence of the diffusion constant or of structural relaxation times it was found (see, e.g., Ref. [6]) that these systems are so-called fragile glass formers [7]. The other extreme in this classification scheme are the so-called strong glass formers [7], and the materials belonging to this class usually have interactions that are long ranged, such as the

Coulomb interaction in SiO_2. Because of the significantly increased cost in computer time that is needed to handle such long range forces, the dynamics of these types of systems has only been investigated by computer simulations in a few cases. In *real* experiments the dynamics of strong glass formers has been investigated for many years already, and it was found that apart from the quantitative difference between the dynamics of strong and fragile glass formers there is also a qualitative difference, in that the spectra of the former show, e.g., a feature which today is called the boson peak [8]. Since the microscopic origin of this feature is still unclear it would be interesting to do computer simulations of strong glass formers in order to gain some insight into the microscopic dynamics of such systems, and some attempts in this direction have already been made [3,4].

Because of the long runs needed to equilibrate the systems at low temperatures it is natural to use systems that are rather small, usually between a few hundred and a thousand particles. Such small systems have generally been thought to be large enough to avoid finite size effects. That this is not *quite* the case was demonstrated by Lewis and Wahnström in a computer simulation of the fragile glass former orthoterphenyl [9], in that they showed that the intermediate scattering function has a small blip at around 5 ps, the time that it takes a sound wave to cross the simulation box. By investigating the dynamics of a larger system, Lewis and Wahnström showed that the observed blip was indeed a finite size effect. However, because of its smallness the authors concluded correctly that this finite size effect can be disregarded when investigating the dynamics of that system.

In the following we will demonstrate that although this finite size effect can be disregarded for *fragile* glass formers, it cannot be neglected in the case of *strong* glass formers, because it is much more pronounced in the latter type of systems.

The potential we use is the one proposed by van Beest *et al.* [10], which seems to be quite reliable to describe amorphous SiO_2 [11]. The total numbers of particles for our simulations, N, were 336, 1002, 3006, and 8016. In order to be able to compare the dynamics of the systems with the

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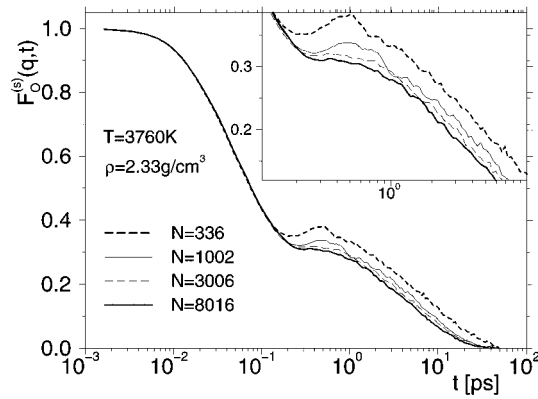
FIG. 1. Time dependence of the incoherent intermediate scattering function for oxygen for all system sizes investigated. $E = -18.0345$ eV, $T = 3760$ K, $\rho = 2.33$ g/cm^{-3}. Inset: Enlargement of the main figure.

different sizes, we needed a well defined ensemble. In such simulations it is common to use the (N,p,T) ensemble or the (N,V,T) ensemble. However, for the type of question investigated here, these ensembles are not very useful, since the only way to realize them for finite systems is to introduce an *artificial* dynamics (fluctuating shape of the simulation box or coupling to a heat bath). Since our goal is to study the finite size effects of the *real* dynamics of the system, we therefore decided to fix instead the density and the total energy per particle.

The equations of motion were integrated with the velocity form of the Verlet algorithm with a step size of 1.6 fs. The systems were first equilibrated at a temperature of 5200 K, a temperature at which the relaxation times of silica are very short. Subsequently, the velocities of the particles were changed such that the mean total energy per particle was -18.0345 eV, which corresponds to a temperature of around 3760 K. At this energy the system was propagated for at least 50 000 time steps in order to allow it to reach equilibrium. After that, the production run of 30 000 steps was started and the quantities of interest measured. In order to improve the statistics of the results we used 20, 10, 5, and 2 independent runs for the $N = 336$, 1002, 3006 and the $N = 8016$ systems.

Subsequently, we changed the energy of the system to a value of -18.6627 eV, which corresponds to a temperature around 1600 K. We let the system propagate again for 100 000 time steps in order to allow it to relax from the quench. However, at this low temperature the relaxation time of the system exceeds by far this equilibration time; thus the resulting configurations were in some way relaxed from the quench, but not typical equilibrium configurations for that energy.

One of the natural quantities to investigate the dynamics of a fluidlike system is the incoherent intermediate scattering function $F_i^{(s)}(q,t) = \langle \delta\rho_i(q,0)\delta\rho_i^*(q,t)\rangle$, where q is the wave vector and $i \in \{Si,O\}$. In Fig. 1 we show the time dependence of this function for the oxygen particles for all system sizes investigated. The wave vector q is 2.8 Å^{-1}, the location of the maximum in the structure factor of the O-O pairs. From the main figure we see that for short times, i.e., less than 0.1 ps, the curves for the different system sizes fall

on top of each other. Thus for these short times there are no finite size effects. This is not the case for longer times, since we find that for $t > 0.2$ ps the curves for the different system sizes show two types of size dependence (see inset of Fig. 1): The first one is that the smaller the system, the longer it takes the corresponding relaxation function to decay to zero. This effect is most pronounced for the smallest system, for which we see that the relaxation is slower by more than a factor of 1.5 compared to the largest systems, but is also easily recognizable for the system with $N = 1002$. The second type of size dependence is that the curves for the smaller systems show a local minimum at $t = 0.2$ ps, which is followed by an oscillatory behavior that is damped out only for times larger than 2 ps. For the larger systems this feature is not observed at all, showing that it is a pure finite size effect. Since this local minimum is believed to be related to the boson peak [3,4], care has to be taken to not confuse the finite size effect with a real feature in the dynamics of strong glass formers.

Although we present here only the results for the wave vector $q = 2.8$ Å^{-1}, we have found a similar behavior also for different values of q (for 1.7 Å$^{-1} \leqslant q \leqslant 5.3$ Å^{-1}). In particular, we note that the time at which the blip is observed, as well as its amplitude is independent of q.

What is the reason for the occurrence of the oscillatory time dependence in the correlation function for small systems? Lewis and Wahnström have pointed out that a disturbance that propagates through the system will leave and reenter the box due to the periodic boundary conditions after a time of L/c, where L is the size of the box and c is the typical velocity of the sound wave [9]. This disturbance is likely a sound wave with a small value of q (since modes with large values of q are strongly damped). Because of nonlinear effects this sound wave also couples to modes with larger values of q and thus gives rise to an echo for these values of q as well. The returning wave thus gives rise to an additional signal in the correlation function and hence the latter shows a slowed down decay, as is observed. The reason why this effect is so much stronger in the system investigated here than in the molecular system studied by Lewis and Wahnström is that in our system the damping of the acoustic wave is significantly smaller than in their system, probably due to the nature of the tetrahedral network in this strong glass former as compared to the closed packed structure in fragile glass formers.

In order to see how the magnitude of these finite size effects depends on temperature we decreased the total energy per particle to a value of -18.6627 eV, which resulted in a temperature of around 1600 K. The time dependence of $F_O^{(s)}(q,t)$ for this lower temperature is shown in Fig. 2. We see again that for short times the curves for the different system sizes coincide, whereas for larger times significant differences occur. We see that now the local minimum at $t \approx 0.2$ ps is present for all system sizes, thus indicating that this is now a real feature of the dynamics of this system (and one that, as we will show elsewhere [12], is related to the boson peak).

For larger times the oscillations in the curves for the two smallest systems are now much more pronounced, which shows that the damping of the sound waves becomes smaller when the temperature is decreased. Since therefore the magnitude of the signal that is added to the correlation function,
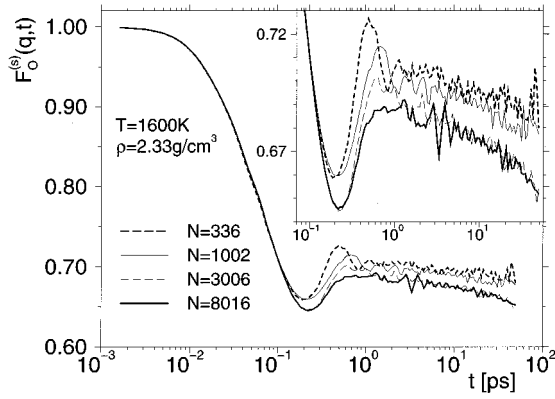
FIG. 2. Time dependence of the incoherent intermediate scattering function for oxygen for all system sizes investigated. $E = -18.6627$ eV, $T = 1600$ K, $\rho = 2.33$ g/cm^{-3}. Inset: Enlargement of the main figure.
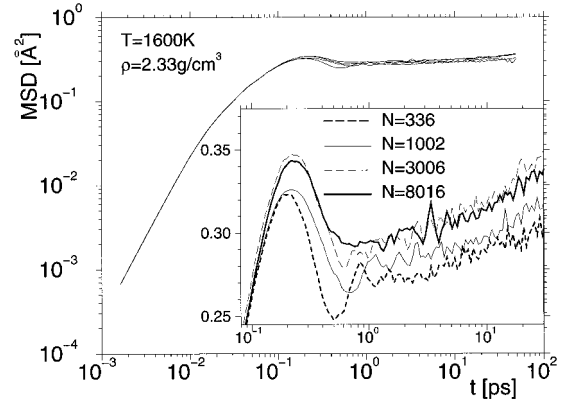

FIG. 3. Time dependence of the mean squared displacement for oxygen for all system sizes investigated. $E = -18.6627$ eV, $T = 1600$ K, $\rho = 2.33$ g/cm^{-3}. Inset: Enlargement of the main figure.

after the disturbance has crossed the box, increases with decreasing temperature, the decay of the correlation function is more delayed the lower the temperature is. In particular we see that the difference in relaxation times between the system with $N = 336$ and the system with $N = 8016$ is now around 4.0, thus significantly larger than it was at the higher temperature. (This value was obtained by assuming that the main effect of the finite size is to shift the curves horizontally, which is in accordance with the observation in Fig. 1. A similar value is obtained from the mean squared displacement, Fig. 3.) Such large differences are not tolerable if one makes semiquantitative calculations in order to test whether or not a given model is a good approximation to the real material.

Since we have shown that the magnitude of the finite size effects depends on temperature, it follows that if the temperature dependence of the relaxation times is determined from a simulation of a small system, this dependence will be different from the one for a large system. This means that also quantities like the glass transition temperature, which is defined as the temperature at which a relaxation time attains a certain value, will also depend on the system size.

In order to show that the observed effects occur not only in the incoherent intermediate scattering function, we have also investigated the mean squared displacement (MSD) of a tagged particle, since this quantity is commonly used to compute the diffusion constant. The results for the oxygen atoms are shown in Fig. 3. As in the case of the intermediate scattering function, we find that the curves for the different system sizes coincide for short times but show a clear system size dependence for intermediate and large times. From this figure we also recognize that in order to avoid finite size effects it is necessary to use system sizes that are larger than 1000 particles.

Finally we come back to the point made above that the finite size effects presented here are much weaker in fragile glass formers. In order to test this hypothesis, we transformed the system into a fragile glass former. This can be done by applying an external pressure, since at sufficiently high pressure the tetrahedral network of silica is destroyed and is replaced by a structure with a higher coordination number that is more similar in nature to a simple liquid, i.e.,

a system of hard spheres or a Lennard-Jones fluid, than the tetrahedral network is. Since simple liquids are generally fragile or intermediate glass formers [6], it follows that compressing silica will increase the fragility of the system and evidence for this has indeed been found [3,4,13]. Therefore we increased the density of the system to 3.94 g/cm^3 and repeated all of the calculations for this new density.

In Fig. 4 we show the time dependence of $F_O^{(s)}(q,t)$ for this new density for all system sizes investigated. The value of q is 3.0 Å^{-1}, close to the location of the maximum in the O-O structure factor at this density. Two sets of curves are shown. The first one is for a total energy per particle of -17.7343 eV, which corresponds to a temperature of about 3760 K, the same temperature at which we investigated the dynamics in the low density phase (see Fig. 1). The second set is for a total energy per particle of -18.0586 eV, and corresponds to a temperature of about 2860 K. At this temperature the α relaxation time of the system is comparable to the relaxation time of the system in the low density phase at $T = 3760$ K. From this figure we see that the dynamics of the system is now indeed very different from the dynamics in the low density phase, in that the relaxation times are now much shorter. In addition, we also see that the system size depen-
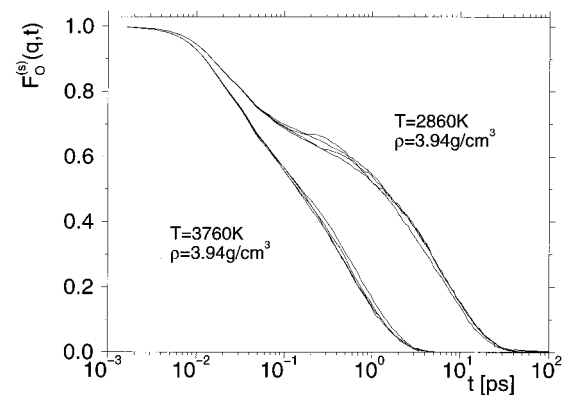

FIG. 4. Time dependence of the incoherent intermediate scattering function for oxygen for all system sizes investigated. $\rho = 3.94$ g/cm^{-3}. Lower set of curves: $E = -17.7343$ eV, $T = 3760$ K. Upper set of curves: $E = -18.0586$ eV, $T = 2860$ K.

dence of the curves is now significantly smaller than in the case at low density, since the relaxation time for the smallest system is now only 15% larger than the one for the largest system. Also the temperature dependence of this remaining finite size effect is now much weaker, if present at all, than it was for the system at low density. Thus if we use the result that the high density phase is indeed more fragile than the low density phase, we can conclude that the investigated finite size effects are much smaller in fragile glass formers than in strong glass formers.

Before we conclude a few remarks are appropriate: (i) Although we have presented here only the results concerning the dynamics of oxygen, the same conclusions also hold for the silicon atoms. (ii) It has to be emphasized that the finite size effects presented here do not at all affect the results of simulations in which *static* quantities are investigated. (iii) Although we have investigated this sort of finite size effect only for periodic boundary conditions, it can be expected that they are also present for open boundary conditions or fixed boundary conditions. (iv) We have also investigated

whether structural quantities, such as the radial distribution functions or the partial structure factors, show a dependence on system size and have found no such dependence. This is in contrast with the results of Nakano *et al.*, who found in their simulation of silica that the total structure factor depends on the size of the system [14]. The reason for this discrepancy is that these authors compute the structure factor from a Fourier transform of the radial distribution functions, which leads to truncation effects, whereas we computed it directly from the particle positions.

In this work we have shown that for a simple model for silica surprisingly large finite size effects are present in the dynamics. This result is likely to hold also for other strong glass formers and therefore has to be taken into account in future computer simulations of such systems.

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