How Does the Relaxation of a Supercooled Liquid Depend on Its Microscopic Dynamics?

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Using molecular dynamics computer simulations we investigate how the relaxation dynamics of a simple supercooled liquid with Newtonian dynamics differs from the one with a stochastic dynamics. We find that, apart from the early β-relaxation regime, the two dynamics give rise to the same relaxation behavior. The increase of the relaxation times of the system upon cooling, the details of the α relaxation, as well as the wave-vector dependence of the Edwards-Anderson parameters, are independent of the microscopic dynamics. [S0031-9007(98)07644-3]

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If the logarithm of a transport quantity, such as the viscosity, of a good glass former is plotted versus T_g/T, where T is temperature and T_g is the glass transition temperature, it becomes obvious that this temperature dependence is not universal, since some materials show essentially an Arrhenius behavior whereas others show a strong non-Arrhenius behavior [1]. Also more microscopic dynamical properties, such as the Raman spectrum, depend strongly on the material, in that, i.e., the so-called boson peak is much more pronounced in strong glass formers than in fragile glass formers [2]. Thus we can say that it is well established that the macroscopic as well as the microscopic dynamics of supercooled liquids is not universal at all and must be considered as a material specific property. This insight is, of course, not surprising, since the materials differ in their structure, the masses of the individual atoms, etc., and thus it can be expected that these microscopic quantities will give rise to a different relaxational and vibrational dynamics.

What is much less obvious, however, is how the *microscopic dynamics* affects the vibrational and relaxational dynamics of the system, i.e., whether the relaxational dynamics is different if the microscopic dynamics is, e.g., a Newtonian one or a Brownian one. The answer to this question is most important since it will allow us to gain insight to understand which aspects of the relaxation behavior are, for a given system, universal and which ones are not. This information is in turn relevant for testing the applicability of theories that attempt to describe the slowing down of the system upon cooling, i.e., the mechanism for the glass transition.

In real experiments it is of course difficult to investigate how the microscopic dynamics affects the dynamics of the system at long times, since usually it is not possible to change the former without also influencing other microscopic quantities like, e.g., the masses of the particles or the interaction between the atoms. Experimentally a Brownian type dynamics can be realized, e.g., by colloidal fluids [3], while atomic liquids have a Newtonian dynamics. However, the structure and interparticle forces in these two types of systems are quite distinct from each other, and thus it is not surprising that the two corresponding dynamics are different. For computer simulations it is, however, most simple to change, for a given system, the dynamics, and they are therefore ideally suited to investigate such questions. The only investigation in that direction we know of is a pioneering study by Löwen *et al.* [4]. In that work the authors compared the relaxation dynamics of a polydisperse system of charged particles which move according to a Newtonian dynamics to the one moving according to a Brownian dynamics. The outcome of that study was that the relaxation dynamics depends, on the time scale of the β relaxation, on the microscopic dynamics. However, due to the limited length of the runs and the lack of statistics, no stringent test could be made as to whether or not the α relaxation depends on the microscopic dynamics. If such a dependence would also exist in the α relaxation regime it would be in contrast to the prediction of the so-called mode-coupling theory (MCT) [5,6], according to which the relaxation dynamics at long times should be independent of the microscopic dynamics. Since there is very good evidence that this theory gives, in the vicinity of the MCT-transition temperature $T_c > T_g$, a reliable description of the dynamics of supercooled simple liquids and even network forming liquids (see [7–9] and references therein), such a disagreement between theory and computer simulation would be quite disturbing since it would show that certain *fundamental* aspects of the theory are not correct. Because of the availability of better computers and algorithms it is possible today to do simulations which are more than a hundred times longer than the ones done by Löwen *et al.* Therefore it is possible to investigate the question of how the long-time dynamics of a system depends on the microscopic dynamics on a qualitatively completely different level, and in the present paper we report the results of such an investigation.

The system considered is a 80:20 mixture of 1000 Lennard-Jones particles consisting of two species of particles, A and B. All the particles have the same mass m and the interaction between two particles of type $\alpha, \beta \in \{A, B\}$ is given by $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^{6}]$ with $\epsilon_{AA} = 1.0$, $\sigma_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\sigma_{AB} = 0.8$,

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$\epsilon_{BB} = 0.5$, and $\sigma_{BB} = 0.88$, with a cutoff radius of $2.5\sigma_{\alpha\beta}$. In the following we will always use reduced time units with σ_{AA} and ϵ_{AA} the units of length and energy, respectively (setting the Boltzmann constant k_B equal to 1.0). Time is measured in units of $\sqrt{\sigma_{AA}^2 m/48\epsilon_{AA}}$. The volume of the box is kept constant with a box length of 9.4. Two types of microscopic dynamics are investigated: a Newtonian one and a stochastic one (described below). In the Newtonian dynamics (ND) we integrate Newton's equation of motion with the velocity form of the Verlet algorithm with a time step of 0.02. After equilibrating the system in the canonical ensemble we turn off the heat bath and start the production run in the microcanonical ensemble. For this kind of dynamics the temperature dependence of the relaxation behavior has already been studied in great detail in the temperature range $5.0 \geq T \geq 0.466$ [8]. Because of an improvement of the hardware and computer codes it is, however, possible today to perform simulations which extend over a time range that exceed the ones of the previous investigations by a factor of 8, giving now a total of 4×10^7 time steps, and thus allowing us to equilibrate the system at lower temperatures than has been possible before, and hence to perform more accurate tests. Therefore we have determined the dynamics of the system also at $T = 0.452$ and 0.446.

The stochastic dynamics (SD) we considered is defined as follows: Apart from the deterministic forces that originate from the interaction potential given above, each particle j is also subject to a Gaussian distributed white noise force $\vec{\eta}_j(t)$ with zero mean, i.e., $\langle \vec{\eta}_j(t) \rangle = 0$, and a damping force which is proportional to the velocity of the particle. Thus the equation of motion for particle j reads

$$m\ddot{\vec{r}}_j + \nabla_j \sum_l V_{\alpha_j \beta_l}(|\vec{r}_l - \vec{r}_j|) = -\zeta \dot{\vec{r}}_j + \vec{\eta}_j(t), \quad (1)$$

where the damping constant ζ is given from the fluctuation dissipation theorem, i.e., $\langle \vec{\eta}_j(t) \cdot \vec{\eta}_l(t') \rangle = 6k_B T \zeta \delta(t - t')\delta_{jl}$. The value of ζ was set to 10, which is sufficiently large that the presented results for the SD do not depend on ζ anymore (apart from a trivial change of the time scale). Equations (1) were solved with a Heun algorithm [10]. The time step used was 0.008, which is small enough to ensure that the *equilibrium* properties of the system are the same for the ND and the SD. Also for this dynamics the runs at the lowest temperature extended over 4×10^7 time steps. At the lowest temperatures the SD is so slow that, within the time span of the runs, the system does not equilibrate. Therefore we used at each temperature the ND to equilibrate the system, and used the SD only for the (equilibrium) production runs. In order to improve the statistics of the results we averaged at each temperature over eight independent runs (ND as well as SD). The temperatures investigated were 5.0, 4.0, 3.0, 2.0, 1.0, 0.8, 0.6, 0.55, 0.5, 0.475, 0.466, 0.452, and 0.446.

One of the simplest quantities to characterize the dynamics of the system is the diffusion constant D_α of the particles, which we calculated from the mean squared displacement of a tagged particle. For the ND the temperature dependence of D_α has been determined before [8] and it was shown that, at low temperatures, it is given by a power law, i.e., $D_\alpha \propto (T - T_c)^\gamma$, a functional form predicted by MCT. (Here $T_c > 0$ is the so-called critical temperature of MCT.) It is, however, desirable to compare the temperature dependence of D_α for the ND with the one for the SD without making reference to any theory, and thus we calculated the ratio $D_{A,\mathrm{ND}}/D_{A,\mathrm{SD}}$ and show its temperature dependence in Fig. 1. Note that we plot this ratio versus $T - T_c$, where $T_c = 0.435$ is the critical temperature from the MCT analysis [8], instead of T, but we emphasize that this representation of the data has nothing to do with MCT but is only a convenient way to expand the abscissa at low temperatures. From this figure we see that this ratio shows a noticeable temperature dependence at high temperatures but becomes essentially constant (within the error bars) for temperatures $T \leq 0.8$. We note that in the temperature interval $0.446 \leq T \leq 0.8$ the diffusion constants change by almost three decades [11]. Since the ratio $D_{A,\mathrm{ND}}/D_{A,\mathrm{SD}}$ stays constant to within about 30% we conclude that the temperature dependence of the diffusion constants is independent of the microscopic dynamics to within a few parts in 10^4. A similar result is found for the B particles. We also mention that at the two lowest temperatures the diffusion constants do no longer follow the power law found at slightly higher temperatures. This is indirect evidence that also the processes that destroy this power law are independent of the microscopic dynamics.

A further quantity that is very useful to characterize the dynamics of the system is the (incoherent) intermediate scattering function $F_s(q,t)$ for wave vector q [8]. For the SD we show the time dependence of this quantity in

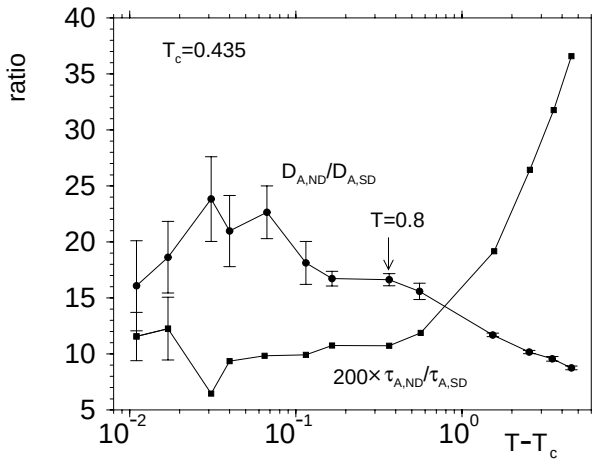

FIG. 1. Temperature dependence of the ratio of the diffusion constant for the A particles for the ND and SD (circles). Squares: Ratio for the α-relaxation time of the incoherent intermediate scattering function.

Fig. 2 for all temperatures investigated (solid lines). The value of q is 7.20, the maximum of the static structure factor for the A-A correlation [8]. It can be seen that on lowering the temperature the relaxation behavior changes qualitatively in that at high temperatures the decay of $F_s(q,t)$ is essentially an exponential (apart from the time dependence at very short times), whereas it shows a plateau at low temperatures. The time for which the correlation function decays to zero increases quickly with decreasing temperature, indicating the dramatic slowing down of the relaxation dynamics of the system upon cooling. This strong dependence of the dynamics on temperature has also been seen in the case of the ND [8]. We emphasize that these curves are all *equilibrium* curves.

Also shown in the figure is $F_s(q,t)$ for the ND at three different temperatures (dashed curves). We first compare the SD and ND in the α-relaxation regime, i.e., the time regime where the correlation function decays, at low temperatures, from the mentioned plateau. From the figure we see that at the highest temperature ($T = 5.0$) the ND gives rise to a relaxation that is about a factor of 7 faster than the one for the SD. This factor increases upon cooling the system and reaches about 20–30 at low temperatures. Thus from the point of view of the *absolute values* of the α-relaxation times $\tau(T)$, the two types of dynamics are very different. [$\tau(T)$ can be defined, e.g., as the time the correlator takes to decay to e^{-1} of its initial value.] However, if we look at the *temperature dependence* of $\tau(T)$, we come to a different conclusion. In Fig. 1 we also show the ratio $\tau_{A,\mathrm{ND}}/\tau_{A,\mathrm{SD}}$ and find that this ratio becomes independent of T for temperatures smaller than 1.0. Thus the ratio shows a similar dependence on temperature as the one for the diffusion constants.

From Fig. 2 we also see that the shape of the correlation functions *in the α-relaxation regime* is independent of the microscopic dynamics. This can be recognized by the fact that the curve for $T = 0.466$ for the ND lies almost on top of the curve for the SD for $T = 0.55$, *and* by the fact that for both types of dynamics the time-temperature superposition principle holds (see Refs. [8] and [11]), i.e., that for a given dynamics the shape of the correlation function does, in the α-relaxation regime, not depend on temperature. Therefore we conclude that not only is the temperature dependence of the time scale of the α relaxation independent of the microscopic dynamics but also those details of the (α-)relaxation process that give rise to the stretching of the correlation function. The same result is found for the coherent intermediate scattering function and other values of q.

We now turn our attention to the β relaxation, i.e., the relaxation regime in which the correlation function is in the vicinity of the plateau. From Fig. 2 we recognize that, for low temperatures, the way the curves approach the plateau depends strongly on the microscopic dynamics in that for the SD this approach is very gentle, whereas for the ND it is quite abrupt. This difference does not exist for the *late β* relaxation, i.e., when the correlation functions start to fall under the plateau. This can be seen by plotting the relaxation functions versus $t/\tau(T)$, which is done in Fig. 3 for the SD and the ND for the lowest temperature investigated. We see that this scaling of time makes the two correlation functions fall on top of each other in the late β-relaxation regime.

MCT predicts that *in the β-relaxation regime* and asymptotically close to the critical temperature T_c the shape of the correlation functions is given by the so-called β correlator, a function that can be computed within the framework of the theory [5]. The form of this β correlator depends on one parameter, the so-called exponent parameter λ, which has been computed for the present system to be $\lambda = 0.71$ [12]. Using this theoretical value of λ we fitted the correlation curves in the β regime

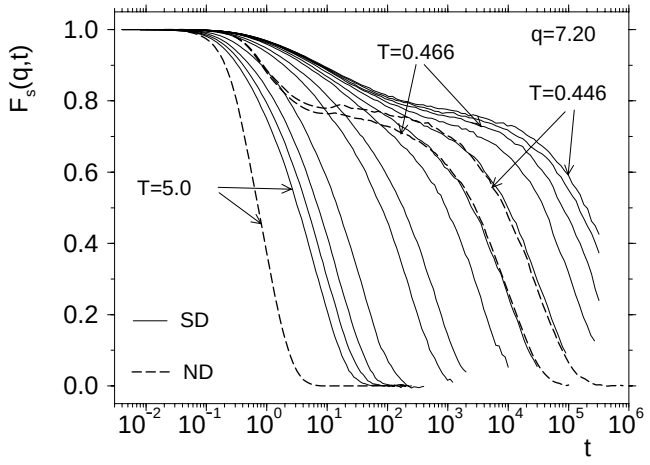

FIG. 2. Time dependence of the incoherent intermediate scattering function for the SD for all temperatures investigated (solid lines) and the ND for selected temperatures (dashed lines).

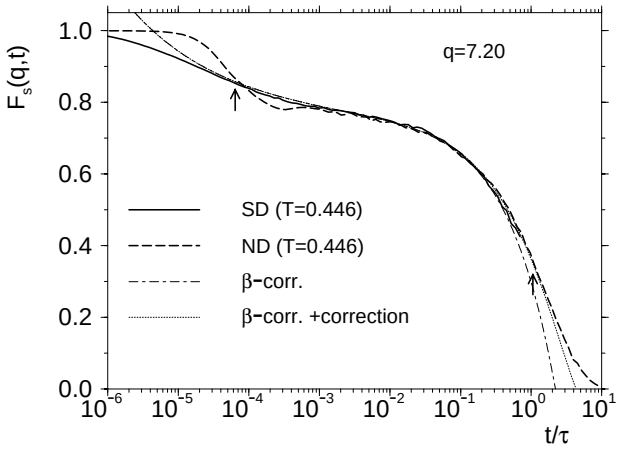

FIG. 3. $F_s(q,t)$ at the lowest temperature investigated versus rescaled time $t/\tau(T)$ for the SD (bold solid line) and the ND (bold dashed line). Dashed line: β correlator for $\lambda = 0.71$. Dotted line: β correlator + leading corrections at long times.

with the corresponding β correlator, and the resulting fit is shown in Fig. 3. It has been shown that, for temperatures slightly above T_c, the time window in which the theoretical curve describes the data well can be extended considerably, if also the *corrections* to the β correlator are taken into account [5,9]. The result of a fit to our SD data with the β correlator and the first correction at long times is included in Fig. 3 as well. We recognize that the fit with the β correlator alone describes the SD data well over about 3.5 decades in time. This time window is expanded at large times by about half a decade by taking into account the corrections to the β correlator (time window between the two arrows). From the figure we see that the theoretical curves fit the ND data well only in the *late* β-relaxation regime, whereas they do a poor job in the early β-relaxation regime since the asymptotic law is completely obscured by the phonons [8]. For the SD, however, the early β relaxation is described very well by MCT in that the approach to the plateau is described well by the β correlator. The reason for this better agreement is that in the SD the phonons are strongly damped and thus interfere much less with the asymptotic laws of the theory on the time scale in which the correlators approach this plateau. Thus we find that the relaxation dynamics of the SD is qualitatively much more similar to the one of colloidal systems [3] than is the one for the ND.

The last quantity we discuss is the q dependence of f_c, the so-called Edwards-Anderson or nonergodicity parameter (NEP). This quantity is related to the height of the plateau in the correlation functions and can be measured, e.g., in neutron scattering experiments (see, e.g., Ref. [13]). f_c is one of the fit parameters for the β correlator and was thus obtained by performing such fits to the time correlation functions. In Fig. 4 we show the q dependence of $f_c^{(s)}(q)$ and $f_c(q)$, and the NEP for the coherent (A-A) and incoherent intermediate (A) scattering function. We see that for all q considered the two NEPs for the SD are very close to the ones for the ND, thus showing that this quantity also does not depend on the microscopic dynamics. Also included in the figure are the two curves that correspond to the q dependence of f_c as predicted by MCT [12]. We see that these two theoretical curves agree very well with the ones measured in the simulation. The reader should appreciate that in the calculation of these theoretical curves *no* free fit parameter was involved, since the only input to the MCT calculations was the temperature dependence of the partial structure factors, which were determined from the simulation. Thus we conclude that the NEPs do not depend on the microscopic dynamics and can be calculated with high precision from MCT.

In summary, we conclude that at low temperatures the α-relaxation dynamics of this system is independent of the microscopic dynamics, whereas the early β-relaxation dynamics does depend on it. We find that in the β-relaxation regime the relaxation behavior for the SD is in very good agreement with the one predicted by MCT and that this theory is also able to give a very accurate prediction of the q dependence of the nonergodicity parameters.

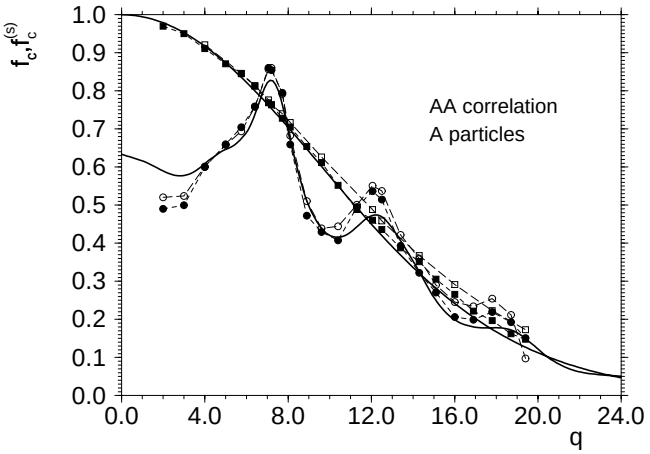

FIG. 4. Wave-vector dependence of the nonergodicity parameter for the SD and ND (filled and closed symbols, respectively). The squares and circles correspond to the incoherent and coherent intermediate scattering functions, respectively. The two solid lines are the prediction of MCT for this system.

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