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Exchange rates of dynamic heterogeneities in a glass-forming liquid

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Abstract. Dynamic heterogeneities, *i.e.* the presence of molecules with different mobilities, have been established as one of the key features of the physics of supercooled liquids. Here we study in detail how the mobility of an individual molecule fluctuates with time. Our analysis is based on a time series of molecular dynamics simulations for a low molecular weight glass-former, propylene carbonate. We find that the variation of mobility with time of initially slow molecules significantly differs from that of initially fast molecules. We explicitly show the relation to the rate memory parameter which recently has been introduced to quantify the mobility fluctuations as observed *via* multidimensional NMR experiments. In this way qualitative agreement between simulation and experiment can be established although the time scales of simulation and NMR experiment differ by many orders of magnitude.

PACS. 64.70.Pf Glass transitions – 61.20.Ja Computer simulation of liquid structure

1 Introduction

An important property of supercooled liquids is nonexponential relaxation [1]. Many experiments [2–10] and simulations [11–15] have demonstrated that the non-exponentiality results from a superposition of exponential relaxation processes with different relaxation times, giving rise to the notion of “dynamic heterogeneity”. This means that the supercooled liquid contains molecules with different dynamic behavior. This is a non-trivial result because also back- and forth correlations might account for non-exponential relaxation as realised, *e.g.*, for the Rouse model of polymer dynamics [12]. The interesting question arises on which time scale the mobility of some tagged molecules fluctuates *i.e.*, on which time scale the mobility of a molecule is uncorrelated to its initial mobility. With the multidimensional NMR experiments for a few Kelvin above T_g one can determine this fluctuation rate *via* appropriately chosen four time correlation functions [3,4,16]. A dimensionless parameter, Q, was introduced to measure the fluctuations within the heterogeneous distribution of relaxation rates [3,17]. This parameter is denoted *rate memory parameter*. On a qualitative level it is defined as the ratio of the average relaxation rate of slow molecules to the average exchange rate between slow and fast molecules. In the sketch of Figure 1 this corresponds to the average exchange rates, τ_{sf}^{-1}, between fast and slow molecules as compared to the average slow relaxation rate, τ_s^{-1} itself. The rate memory parameter can be interpreted as an average property of the fluctuations, accessible from the NMR correlation functions. It can be shown that for physically reasonable systems $Q \geq 1$ [17].

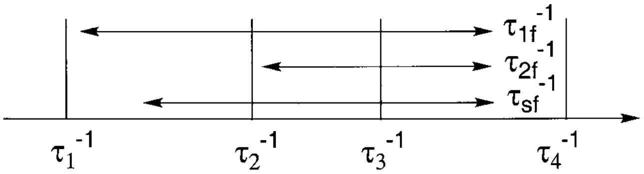

Fig. 1. Sketch of the exchange rates. 1, 2, 3, 4 indicate the molecular groups of extremely slow, slow, fast, and extremely fast, respectively. τ_{1f}^{-1} is the exchange rate between the extremely slow and fast molecules; τ_{2f}^{-1} is the exchange rate between the slow and fast molecules; τ_{sf}^{-1}, the average exchange rate between the slow and fast molecules, which approximately is given by $(\tau_{1f}^{-1} + \tau_{2f}^{-1})/2$; τ_{3s}^{-1}, and τ_{4s}^{-1}, are defined analogously (not shown). τ_i^{-1} correspond to individual relaxation rates. $\tau_s^{-1} = (\tau_1^{-1} + \tau_2^{-1})/2$ is thus the average relaxation rate of slow molecules.

The method, used for the present analysis, is motivated by the ideas, originating from the NMR correlation functions. In a first time interval, a slow (or fast) subensemble is selected. Then, after a second time interval of variable length (waiting time), this subensemble is checked again during a third time interval. Whereas for very long waiting time the selected subensemble behaves like the average, differences are expected for short waiting times, since slow (fast) molecules on average are still slow (fast). In the NMR experiment the first and third time intervals are

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usually chosen equal, denoted as t_{m0}. This parameter determines the size of the initially selected subensemble. Another parameter in the experiment is the evolution time t_p (see Ref. [18]), which can be adjusted to be sensitive to the small or large angle jumps. For the translational motion in this work the analogous parameter is the wave vector q, which corresponds to the length scale on which molecular motion is probed.

In this paper we show that the detailed information, obtained *via* computer simulations, allows one to elucidate the nature of the fluctuations in detail. Here we exploit that for simulations one is not restricted to the determination of correlation functions which always involve some kind of average but rather can use the total microscopic information about the dynamics. This approach has been already successfully applied for the elucidation of the cage effect [14] and the quantification of rotational-translational coupling [11]. In this way it is possible to differentiate between slow (fast) and very slow (very fast) molecules and to analyze their respective behavior. In particular, our purpose is to recover and understand the many results obtained so far from measuring the appropriate NMR correlation functions: (i) $Q \approx 1$ for most systems [3–5,12,19], which means that the time scales of the exchange processes and the relaxation process are similar. (ii) Q increases with increasing t_p *i.e.*, angular sensitivity [18]. (iii) Q decreases slightly with increasing t_{m0} *i.e.*, the size of the selected subensemble [18,19]. For this comparison with NMR results one should keep in mind that the difference between the NMR time scale and the simulation time scale is up to 10^9, corresponding to a very different temperature regime. Therefore *a priori* the properties can be very different. However, as we will show in this work, the rate memory seems to have similar properties on a qualitative level. We mention in passing that the optical experiments by the Ediger group [9] show that around T_g Q starts to increase up to $Q \approx 100$.

2 Simulation

We use classical molecular dynamics simulations to generate time series of the dynamics of a glass-forming system, which we choose to be propylene carbonate. For this system we have detailed information about its structure and dynamics [11]. Among other things we corroborated the presence of dynamic heterogeneities at sufficiently low temperatures. Although the NMR experiments were performed for rotational rather than translational dynamics, the previously found strong coupling between rotational and translational dynamics [11] indicates that both types of dynamics should have very similar properties.

The system consists of 1728 molecules (roughly corresponding to a linear dimension of the cubic simulation cell of 60 Å). The parameters describing the interactions within and between the molecules are taken from AMBER (Assisted Model Building with Energy Refinement) [20]. Non-bonded interactions are calculated using a residue based cutoff of 8 Å, where each molecule constitutes a residue. The atomic equations of motion are integrated *via* the half-step leap-frog Verlet algorithm [21] with a time step of 1 fs. Periodic boundary conditions are used. The calorimetric glass transition temperatures is about 158 K. Our simulation was performed at $T = 200$ K. Temperature and pressure (1 bar) were adjusted and maintained constant *via* the weak coupling method due to Berendsen *et al.* [22] (temperature relaxation time = 0.2 ps; pressure relaxation time = 0.2 ps).

3 Results

The mobility of a molecule during the time interval t_{m0} is defined as $\mu = \sum_{i=0}^{N-1} |\mathbf{r}(t_{i+1}) - \mathbf{r}(t_i)|$. Here $t_N - t_0 = t_{m0}$, and $t_{i+1} - t_i = t_{m0}/N$. Note that this definition is different to the pure displacement $|\Delta\mathbf{r}| = |\sum(\mathbf{r}(t_{i+1}) - \mathbf{r}(t_i))| = |\mathbf{r}(t_N) - \mathbf{r}(t_0)|$. The advantage of this definition is that it can distinguish between fast molecules which by chance happen to be at the initial position after t_{m0} although they significantly moved during this time interval and slow molecules which always remained close to this position. In our analysis the length t_{m0} of the first and the third time interval is equal. We choose $t_{m0} = 90$ ps, which is the $\alpha-$relaxation time at this temperature and $N = 90$. The molecules are classified as slow and fast molecules according to their μ. A similar definition has been already used in reference [24].

To detect the fluctuation between the fast and slow molecules, we calculate the probability that after a certain time interval t, a slow molecule becomes fast, or *vice versa*. Figure 2a shows the number of molecules, $A_\mathrm{f}(t)$, which in the first time interval are the first 10% fastest (circles), the second 10% fastest (triangles), or the third 10% fastest (squares), and after the waiting time, t, in the final time interval belong to the 50% slowest molecules. Since we deal with small subensembles of the total system and furthermore we simulate a real molecular system rather than a simple model system the noise is significant which, however, is no problem for the results presented below. The dashed line indicates the equilibrium value that is obtained from simple statistical considerations and is of course approached for large t. The size of the initial amplitude *i.e.* $|A_\mathrm{f}(0) - A_\mathrm{f}(\infty)|$, is largely determined by the probability that molecules, that have been detected as fast (slow) by the above criterion are indeed fast (slow). One could have performed the same procedure also for an ensemble of particles without dynamical heterogeneities, *i.e.* with a single diffusion constant. In this case one would have $|A_\mathrm{f}(0) - A_\mathrm{f}(\infty)| = 0$. Since molecules with an extremely large value of μ are very likely to be indeed fast it is not surprising that only a small fraction of these molecules have a low mobility during the subsequent time interval t_{m0}, as expressed by their large value of $|A_\mathrm{f}(0) - A_\mathrm{f}(\infty)|$. In what follows we mainly concentrate on the time scales of the decay. The individual decay curves have been fitted by standard KWW curves $\exp(-(t/\tau)^\beta)$, yielding average exchange times $\langle\tau\rangle = \tau\beta^{-1}\Gamma(\beta^{-1}) = 110$ ps, 140 ps, and 180 ps for the first, second, and third 10% fastest molecules, respectively. The fastest molecules also display the fastest

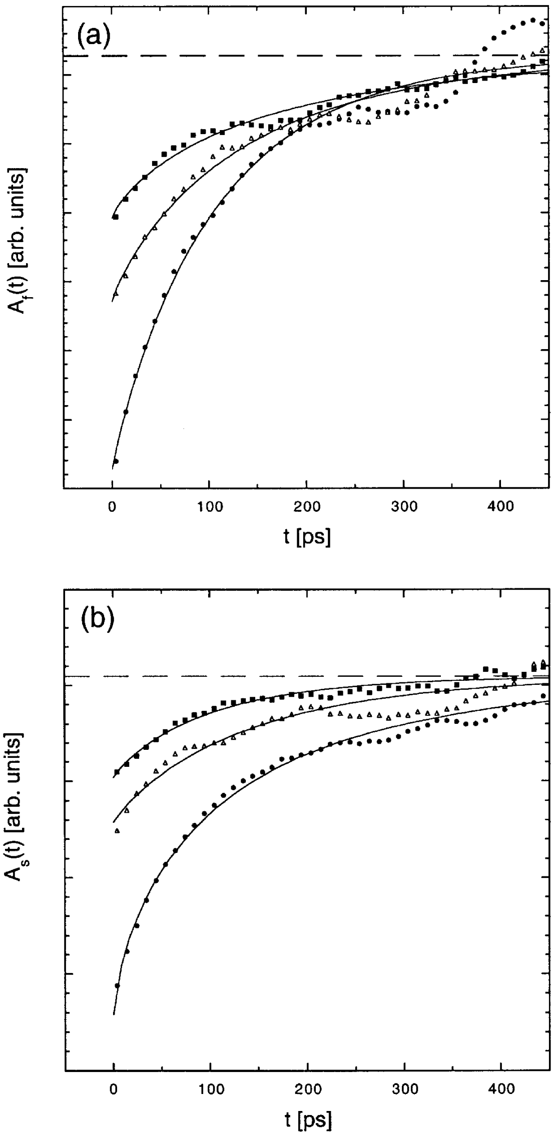

Fig. 2. (a) $A_{\mathrm{f}}(t)$, the number of molecules, which belong to the 10% fastest (circles), the second 10% fastest (triangles), and the third 10% fastest (squares) during the first time interval, and to the 50% slowest during the third time interval. (b) Analogously $A_{\mathrm{s}}(t)$ describes the equilibration of the slow molecules.

exchange processes *i.e.* $\tau_{4\mathrm{s}}^{-1} > \tau_{3\mathrm{s}}^{-1}$. This scenario has to be compared with Figure 2b, where the quantity $A_{\mathrm{s}}(t)$ shows how slow molecules change to fast ones. In analogy to above the first, second, and third 10% slowest molecules are displayed. Interestingly, all three curves show rather similar exchange times (146 ps, 143 ps, and 133 ps, respectively). Thus the exchange processes among slow and fast molecules as well as extremely slow and fast molecules are identical within statistical error *i.e.*, $\tau_{1\mathrm{f}}^{-1} \approx \tau_{2\mathrm{f}}^{-1}$. The exchange time between slow and fast molecules is therefore a well-defined quantity and can be estimated to be close to 140 ps.

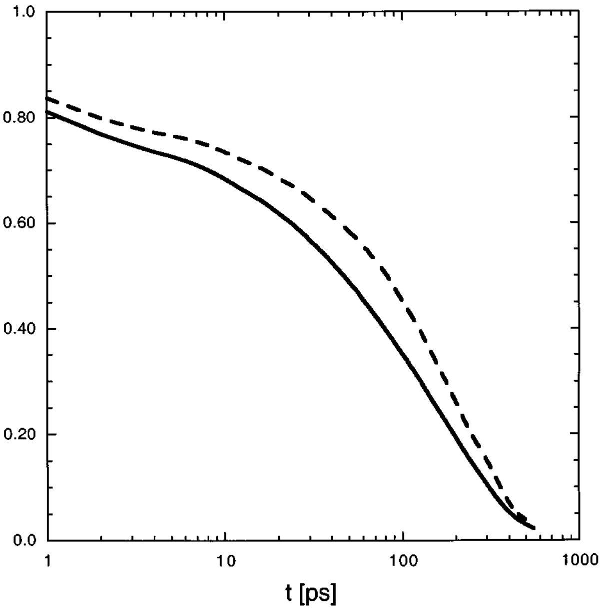

Fig. 3. Two time correlation function $\langle \cos(\mathbf{q} \cdot \Delta\mathbf{r}) \rangle$ for the bulk (solid line) and 30% slowest molecules (dashed line). $q = 1.55$ Å^{-1}, which corresponds the maximum structure factor position.

In addition, we can relate our calculation to the rate memory [3,17] and obtain the dependence on the wave vector, $q \equiv |\mathbf{q}|$. In Figure 3, we present the two time correlation function, $\langle \cos(\mathbf{q} \cdot \Delta\mathbf{r}) \rangle$. The solid line is for the bulk system, while the dashed line is for the 30% slowest molecules. They are selected according to their μ during a time interval t_{m0}, which starts at the same time as the correlation function. $|\mathbf{q}| = 1.55$ Å^{-1}, which is close to the maximum of the structure factor. The curves are again fitted by the KWW function, yielding an average relaxation time $\langle \tau_{\mathrm{R}} \rangle \approx 127$ ps. One can obtain the average relaxation time $\langle \tau_{\mathrm{R}} \rangle_{\mathrm{s}}$ for the 30% slowest molecules using the same procedure. Figure 4 shows $\langle \tau_{\mathrm{R}} \rangle_{\mathrm{s}}$ for the slow molecules as a function of q. We also fit the two correlation function for the entire system by two-state model, $0.3 \exp(-t/\tau_{\mathrm{R,s}}) + 0.7 \exp(-t/\tau_{\mathrm{R,f}})$. Similar values were obtained *i.e.*, $\tau_{\mathrm{R,s}} \approx \langle \tau_{\mathrm{R}} \rangle_{\mathrm{s}}$. The dashed line in the figure indicates the average exchange time of 140 ps between slow and fast molecules. Because in the present notation the value of the rate memory parameter, Q, is given by $Q \approx \langle \tau_{\mathrm{R}} \rangle_{\mathrm{s}}^{-1} / \tau_{\mathrm{sf}}^{-1}$, one can estimate how Q depends on the wave vector q. Figure 4 shows that $\langle \tau_{\mathrm{R}} \rangle_{\mathrm{s}}$ decreases with increasing q *i.e.*, the rate memory Q, increases with decreasing length scale whereas $Q \approx 1$ for $q = 1.55$ Å^{-1}. Actually, experimental variation of the angular sensitivity, t_{p}, in the NMR experiment [18], which is analogous to the variation of q, has also revealed an increase of Q with increasing q. For example for $q = 5$ Å^{-1} one would have $Q \approx 10$.

At this point one can conclude that the environment (and thus the resulting dynamics) of a molecule is uncorrelated to its initial environment after moving around one typical inter-molecular distance. For the same system

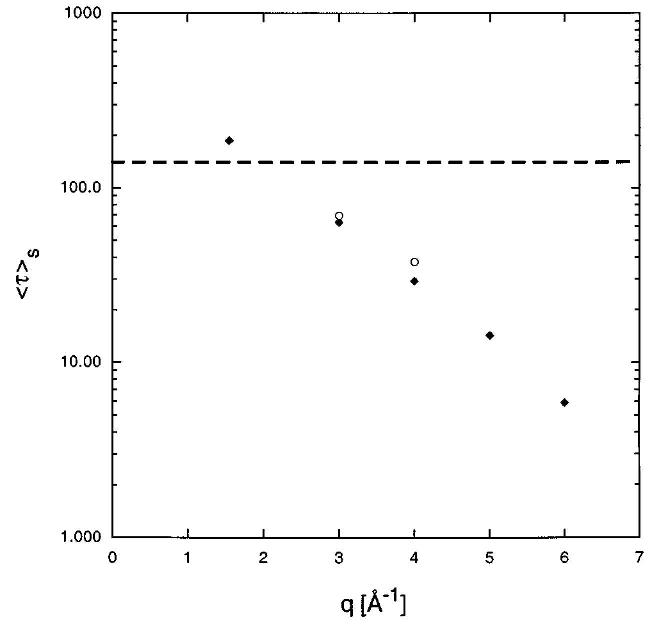

Fig. 4. Average relaxation time $\langle\tau\rangle_\mathrm{s}$ for the 30% slowest (solid diamonds) and 10% slowest (empty circles) molecules. The dashed line indicates the average exchange time between the fast and slow molecules.

we have checked that slow molecules (and correspondingly fast molecules) are clustered together [23]. Similar results have been found in previous simulations, see, *e.g.*, reference [24]. Interestingly, also multidimensional NMR experiments have revealed some kind of clustering for temperatures around T_g [25]. Thus one has the interesting situation that, on the one hand, a typical slow molecule becomes fast after moving one inter-molecular distance but, on the other hand, is surrounded at a given time by a larger number of other slow molecules. This, for the first time, suggests that the slow clusters do not move around in the liquid but rather stay immobile (thus displaying only very little relaxation) until they eventually dissolve. Thus our results show an interesting facette of the nature of the cooperativity of this complex many-particle problem.

Hence by separate consideration of the relaxation and exchange time scales we could obtain direct information about the rate memory of the system. As shown in [17] the value of Q may depend on the fraction of selected slow molecules. As mentioned before this fraction can be adjusted experimentally by choosing an appropriate t_{m0}. Interestingly, if the exchange rates τ_{ij}^{-1} are proportional to the individual relaxation rates τ_i^{-1} and τ_j^{-1} of subensembles i and j (for all subensembles) the value of Q does not depend on the size of the subensemble. A simple physical model, yielding $\tau_{ij}^{-1} \propto \tau_i^{-1}\ \tau_j^{-1}$, is the case of *active* exchange process [17,26]. In this scenario a particle gains a new relaxation rate after performing a relaxation process. Qualitatively this means that a variation in environment of a tagged molecule would *not* be related to a variation of the structure of the neighborhood but rather be a consequence of its own dynamics. Validity of this relation would imply that slow molecules have larger exchange rates than extremely slow molecules. In contrast, in the present system the slow and extremely slow molecules have the same exchange rate, whereas the relaxation rates of the first 10% slowest and the third 10% slowest molecules differ by 50% (they were evaluated for $q = 3$ Å^{-1} which is the smallest $q-$ value where $\langle\cos(\mathbf{q}\cdot\Delta\mathbf{r})\rangle \approx 0$ for $t > t_{m0}$). This rules out a strictly active scenario. As a direct conclusion the value of Q is smaller, if only determined for the extremely slow subensemble. Figure 4 also shows $\langle\tau\rangle_\mathrm{s}$ for 10% slowest molecules, which corresponds to an increase of t_{m0} in the NMR experiment. We observe the decrease of Q with decreasing size of the selected subensemble. On a qualitative level, this behavior has been already observed for the Fredrickson model [19] and in NMR experiments [18].

A possible explanation for the different behavior between the fast and the slow molecules is as follows. The slow and extremely slow molecules form clusters which display cooperative motion. After some time the clusters dissolve, and the slow and extremely slow molecules become fast on the same time scale. A different picture might apply for the fast molecules. Molecules traveling a very long distance during the first time interval are more likely to encounter a new environment during the next time interval. Thus the extremely fast molecules have a higher probability to become slow than the fast molecules. Definitely this interpretation needs more detailed studies.

In summary, the present analysis has elucidated unprecedented information about the nature of the exchange processes within the heterogeneous distribution of relaxation rates. On the one hand, it confirms in detail previous results of multidimensional NMR experiments (the value of the rate memory parameter as well as its dependence on the different experimental parameters), on the other hand, it yields additional insight about the explicit time scales for the different subensembles, thus suggesting a more detailed picture of the dynamics close to the glass transition. For example it turns out that a molecule moves approximately one inter-molecular distance before it changes its dynamical status (in terms of fast and slow). Having in mind the largely different temperatures for the NMR experiments and simulations ($\tau_\alpha^{\mathrm{exp.}}/\tau_\alpha^{\mathrm{sim.}} \approx 10^9$), this work also shows that the properties of dynamic heterogeneities, as opposed to other properties like the transport coefficients, only mildly change with temperature when approaching T_g from above. As mentioned before, whether or not these properties change when crossing T_g is still a matter of debate.

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