# Dynamic Heterogeneity of Relaxations in Glasses and Liquids

D. Caprion, J. Matsui, and H. R. Schober
*Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany*

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We report an investigation of the heterogeneity in supercooled liquids and glasses using the non-Gaussianity parameter. We simulate selenium and a binary Lennard-Jones system by molecular dynamics. In the non-Gaussianity three time domains can be distinguished: an increase on the ps scale due to the vibrational (ballistic) motion of the atoms, followed by a growth, due to local relaxations ($\beta$ relaxation) at not too high temperatures, and finally a slow drop at long times. The non-Gaussianity follows in the intermediate time domain a $\sqrt{t}$ law. This is explained by collective hopping and dynamic heterogeneity. We support this finding by a model calculation.

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Although glass is one of the most common materials, its physics and especially its dynamics are still only poorly understood. In addition to sound waves, two level systems [1,2] and quasilocal (resonant) vibrations [3], experiments indicate a wide distribution of relaxations, i.e., nonperiodic changes of the local structure [4,5]. In supercooled liquids one observes, apart from the vibrational (ballistic) motion of the atoms, two types of relaxations with different time scales. These $\beta$ and $\alpha$ relaxations are attributed to short range (cage) motion and diffusion, respectively.

In recent years these relaxations, both in glasses and in liquids, have been studied intensively by experiment [6–9] and theoretically [10–13]. One particular aim was to determine whether the relaxations involve only groups of atoms or are spread over the whole system. The first case, where relaxations are restricted to a few atoms only, is known as the heterogeneous scenario, the other one as the homogeneous scenario.

Spatial heterogeneity is thought to be responsible for the nonexponential relaxations in supercooled liquids [14]. This view has recently been challenged on the basis of inelastic neutron scattering experiments on polymers [6]; however, see also [15].

To understand its effects, it is necessary to know the properties of the "dynamic heterogeneity" itself, e.g., the time and temperature dependence. Qualitatively it is known [6,12,16] that the system becomes homogeneous at all temperatures for sufficiently long times, corresponding to the $\alpha$ regime. In the intermediate time domain, corresponding to the $\beta$ relaxation, heterogeneity becomes more pronounced when the system is cooled down. Here we show that there is for different classes of materials a common law governing heterogeneity at these intermediate time scales which stretch, depending on temperature, over some ps or at least several ns.

This is closely related to collectivity of motion. Measurements of the isotope effect have shown that diffusion both in glasses and in supercooled liquids is highly collective [17,18]. A similar very small isotope effect was also observed in simulations of a Lennard-Jones liquid [19]. In glasses, one observes collective jumps of chainlike structures [20–22]. Similar mobile structures are also observed in the undercooled liquid [23,24].

Following our previous work [16], we investigate the non-Gaussianity behavior, i.e., the heterogeneity, of relaxations in glasses. In this Letter we focus especially on intermediate times, shorter than the typical diffusion time. As shown previously, the non-Gaussianity increases markedly in this time domain. Here we want to go one step further. First we show that molecular dynamics simulations of two different systems, Se and binary Lennard-Jones (LJ), give strikingly the same law for the increase of the non-Gaussianity parameter (NGP), $\alpha_2(t)$ defined below. In this intermediate time domain the non-Gaussianity follows a power law $\alpha_2(t) \propto \sqrt{t}$ for both systems and for both temperatures above and below $T_g$. We propose a simple model based on previous results showing the prevalence of collective hopping of groups of particles.

The simulations for Se and LJ were both done with a velocity-Verlet algorithm, controlling the temperature by velocity adjustment and using the equilibrium volume at the given temperature, i.e., zero average pressure.

We describe Se with a three-body potential [25]. This potential has been used previously to calculate vibrations [26], local relaxations [22,23] and heat transport [27] in amorphous Se. It provides a sound basis for the study of both the atomistic and the electronic structure [28]. We prepared four independent samples of hot liquid, each containing 2000 atoms. These were then quenched to the desired temperatures with rates of $10^{13}$ K/s. Before using the configurations for the measurements, they were aged for several ns. The effective quench rates were thus of order $10^{10}$ K/s. The glass transition temperature is estimated as $T_{\mathrm{g}} \approx 300$ K, and the mode coupling critical temperature $T_c \approx 330$ K. More details are given in Ref. [16].

For the binary LJ simulations we take the frequently used parameters of Kob and Andersen [12,29]. The simulations are done with 5488 atoms and a composition of 20% small particles. We quench from appropriately aged samples with a rate of about $10^{11}$ K/s (relating the LJ values to Ar) and subsequently age the samples again. A heat bath was simulated by comparing the temperature averaged over 20 time steps with the nominal temperature. At each step 1% of the temperature difference was adjusted by random additions to the particle velocities. To ease comparison with previous LJ simulations we use, in the following, the usual LJ units. Details of the simulation procedure are analogous to the ones described for the monatomic LJ system [19]. From the diffusion constant we determine $T_c \approx 0.37$. The discrepancy of this value compared to the one in previous simulations [11,29] is due to the difference of densities. The previous work was done for a constant density of $\rho = 1.2$, whereas we find for our equilibrium samples at $T = T_c$ a lower value of $\rho = 1.15$. We also used a slightly larger cutoff of the potentials.

To quantify the heterogeneity of the relaxations we follow previous work [9–11,13,30] and use the NGP [31]:

$$\alpha_2(t) = \frac{3\langle \Delta r^4(t)\rangle}{5\langle \Delta r^2(t)\rangle^2} - 1\,, \qquad (1)$$

where $\langle \cdots \rangle$ denotes time averaging, $\Delta r^2(t)$ is the mean square displacement, and $\Delta r^4(t)$ is the mean quartic displacement. Experimentally the NGP can be determined from the $q$ dependence of the Debye-Waller factor [9]. From simulations the qualitative behavior of $\alpha_2(t)$ is well known. Starting from $\alpha_2(t = 0) = 0$, it rises on a time scale typical for vibrations ($t \approx 1$ ps) to values around $\alpha_2 = 0.2$. In a hot liquid the NGP drops from this value on a ps scale. In undercooled liquids and in glasses the NGP keeps growing and reaches values an order of magnitude larger. Only on the time scale of diffusion or $\alpha$ relaxation does the NGP drop and finally reach, for $t \to \infty$, the limit $\alpha_2 = 0$. This latter limit reflects the ergodicity of the system for long times. From the increase, one concludes that the relaxations are mainly heterogeneous in the intermediate time scale. This becomes more and more pronounced as the system is cooled down [16].

Here we want to stress for this time domain a property which is common to different classes of materials. For this, we plot for Se $\alpha_2(t)$ multiplied by $t$ against time in a log-log representation (Fig. 1). The most interesting feature of this plot is the appearance of an envelope curve for all temperatures stretching over a time domain from $10^{-1}$ to $10^3$ ps, i.e., 4 orders of magnitude. It corresponds to a power law $t^{3/2}$ leading to $\alpha_2(t) \propto \sqrt{t}$.

To check whether this behavior results from the particular structure of amorphous Se, which is constituted from chains and rings, we repeated the calculations for a binary LJ system. This model is frequently used as an idealized dense packed metallic glass. The nearest neighbor coordination is near 12 rather than 2 in Se. We plot the NGP of binary LJ in the same way as for Se, i.e., $t \cdot \alpha_2(t)$ versus $t$ in a log-log plot. As Fig. 2 shows, the time dependence of the NGP follows the same power law $\alpha_2(t) \propto \sqrt{t}$ as seen in Se. Moreover, we observe this behavior not only for the average NGP, shown in Fig. 2, but also for both components separately.

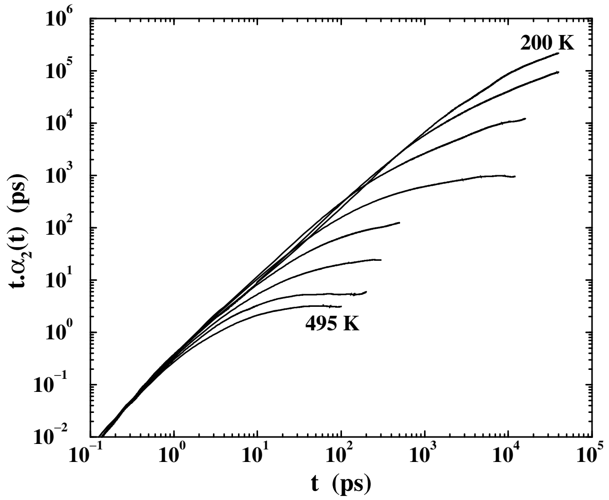

FIG. 1. Non-Gaussianity parameter multiplied by time against time in a log-log representation. The values are obtained from a molecular dynamics simulation of Se at the temperatures (from bottom to top): 495, 445, 400, 355, 330, 290, 255, and 200 K.

Plotting, as in Fig. 1, the NGP obtained recently in a simulation of supercooled orthoterphenyl [32] we find the same envelope curve over 2 orders of magnitude in time. From this and the above we conclude that the NGPs of different types of structural glasses and supercooled liquids follow at intermediate times the same time dependence: $\alpha_2(t) \propto \sqrt{t}$. Therefore, we think that the mechanism responsible for the increase of the NGP, i.e., of the heterogeneity, is common to many kinds of glass-forming materials.

In our previous investigation of the non-Gaussianity [16], we have clearly shown that the increase of non-Gaussianity is due to relaxations. Moreover, it has also been shown that in undercooled liquids and in the glassy phase, clusters of so called mobile particles exist [21–24].

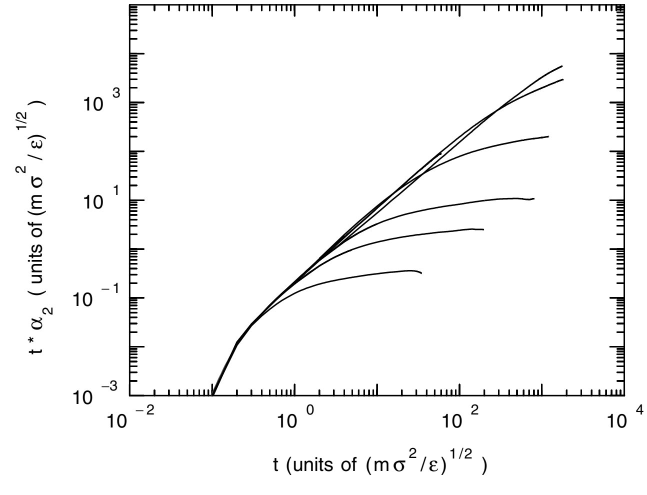

FIG. 2. Non-Gaussianity parameter multiplied by time versus time obtained from molecular dynamics simulation of a binary Lennard-Jones system at the temperatures (from bottom to top) 0.88, 0.56, 0.48, 0.40, 0.36, and 0.32.

These move in a given time over greater distances than the average. Successive jumps are strongly correlated, showing that the major part of the atoms jumping collectively, but not all of them, will participate in a following jump [21]. We further know from experiments [6] and simulations [16] that on the long time scales of diffusion the NGP drops, which indicates that the heterogeneity decays.

Using these results, we build a simple model which explains the time dependence of the NGP. We make three assumptions, all based on previously known results. First, all atoms have a vibrational mean square displacement, increasing with temperature $\propto T$ and giving an initial $\alpha_2(t) \approx 0.2$. Second, there are groups of mobile atoms which jump collectively. And third, after such a jump some atoms can leave while others enter a mobile group. Figure 3 depicts such a collective jump schematically.

In order to make this model more tractable we use the most simple approximations. We have, however, checked carefully that the results do not depend on these details. We consider a system formed of several groups, each group containing ten atoms. Each of these groups of atoms can jump collectively over some barrier into an adjacent configurational minimum position of the underlying energy landscape [33–36]. For simplicity we take a constant distribution of the activation energies. Furthermore, we take a constant probability for jump reversal, ranging from 0.1 to 0.5. A backward jump means that the group of atoms returns to the previous positions. Each time a group of atoms jumps, one atom of the group is exchanged with an atom of another randomly chosen group. This accounts approximately for the changed local environment of the atoms after the jump which will cause some atoms to be in more stable neighborhoods and some others to become more unstable in turn. In the long time limit, this exchange procedure leads to the reduction of the heterogeneity since each atom will ultimately participate in the diffusion. To be effective, an energy barrier has to have a minimum height, depending on temperature. If the system is at a sufficiently high temperature the hopping over the lowest barriers will merge with the anharmonic vibrations. The atoms will instead be restrained by the next barrier of sufficient height. Seen the other way round, when the system is cooled down, it becomes affected by more and more fine details of the energy landscape. To take this into account, we define at each temperature a minimum height for a barrier to be effective for relaxations, $E_{\min} = k_B T$. Lower barriers are replaced randomly by barriers above this threshold, keeping a flat distribution of barrier heights. Finally, the vibrations are accounted for by an "instantaneous" mean square displacement of the atoms. We solve this simple model by a Monte Carlo simulation.

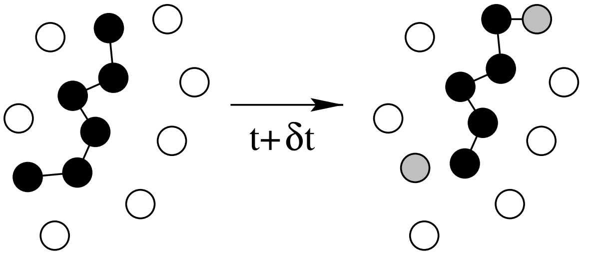

FIG. 3. Schematic representation of a collective jump (left configuration to right configuration). Mobile and immobile atoms are indicated by full and empty circles, respectively. The grey circles show the atoms which have changed their group. After the jump one previously mobile atom has left the group; i.e., it will not participate in the next jump. Another atom has joined the group instead.

We build a system of 2000 atoms, divided into 200 groups having different activation energies. At each time step we check for each group $i$ whether this group will jump with the associate probability $\exp(-E_i/k_B T)$. If the group jumps, we move all the atoms of this group by a nearest neighbor distance and then exchange one atom of the group with another atom. We have checked that neither the exchange rate, nor the probability of jump reversal, nor the jump length change the exponent of the power law. They merely affect the absolute value of the NGP. We repeat this procedure for several time steps and random numbers. During these simulations the NGP is computed at different temperatures from $T = 0.42$, corresponding to the liquid, to $T = 0.14$ below $T_g$. Figure 4 shows the result of these simulations.

This simple model reproduces the power law $\alpha_2(t) \propto \sqrt{t}$, found in the molecular dynamics simulation, which is striking due to the simplicity of the model and even more so to the fact that all details of the interaction in the materials are neglected. In other words, the model can be applied to many kinds of glass-forming material, once one believes in collective hopping of groups of particles. Therefore, we think that the behavior of the non-Gaussianity parameter will also be observed in oxide glasses such as silica and

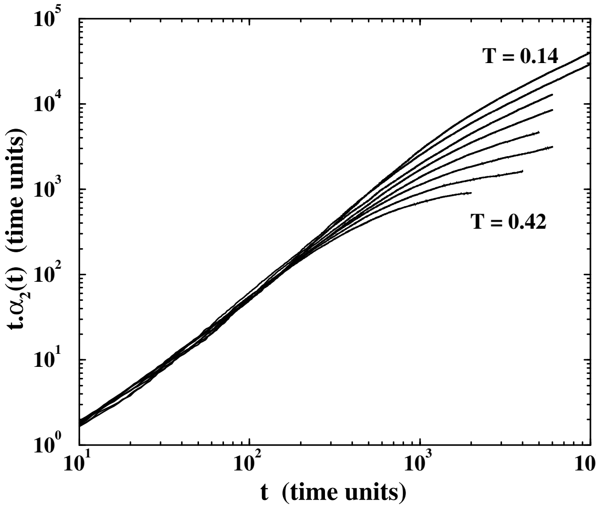

FIG. 4. Non-Gaussianity parameter multiplied by time versus time, computed for a simple model of relaxation (see text) at different temperatures in the supercooled liquid and in the glass.

in polymeric glasses. In polymer glasses the long chains will probably limit the displacement of the atoms in the $\beta$-relaxation regime which might result in smaller maximal values of the NGP.

In this work we have concentrated on the intermediate time regime which is more easily accessible to experiment. There remain some other interesting questions. Comparing Fig. 2 with the predictions of the trapping diffusion model [37] we see a difference for long times. The decay of the NGP in the simulation is clearly slower than the predicted $1/t$. The reason for this is not yet understood. Another open question is the NGP at temperatures much below $T_g$. Lowering the temperature the spectrum of the activation energies should eventually become important.

To conclude we have presented the results of two independent molecular dynamics simulations on completely different systems and of a simple model. All these results show the same power law for the non-Gaussianity in the intermediate time range, corresponding to the $\beta$ relaxations in undercooled liquids and in glasses. This increase of the non-Gaussianity, i.e., of the heterogeneity of the relaxations, proportional to $\sqrt{t}$, can be understood as resulting from the collective hopping of groups of particles. Assuming that this mechanism is common to all kinds of glass formers, we believe that heterogeneity will always increase in the intermediate time regime domain following the power law $\sqrt{t}$, at all temperatures and in many types of materials.

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