Diffusion in a model metallic glass: Heterogeneity and ageing†

H. R. Schober*

*Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany.
E-mail: H.Schober@FZ-Juelich.de*

We report results of molecular dynamics simulations of a binary Lennard-Jones system at zero pressure in the undercooled liquid and glassy states. We first follow the evolution of diffusivity and dynamic heterogeneity with temperature and show their correlation. In a second step we follow the ageing of a quenched glass. As diffusivity decreases with ageing, heterogeneity increases. We conclude that the heterogeneity is a property of the inherent diffusion of the relaxed state. The variations with ageing time can be explained by annealing of quenched defect structures. This annealing has the same decay constants for both diffusivity and heterogeneity of both components.

I Introduction

Diffusion in glasses and their melts is fundamentally different from diffusion in crystalline lattices. It has been studied in experiment intensively for many years. The increase in computer power in recent years now makes computer simulation studies near and slightly below the glass transition temperature possible. Combining the results from experiment and simulation one increasingly gains insight into the underlying atomic dynamics. Despite this effort, many questions remain and no general agreement on the nature of diffusion and its change at temperatures near the glass transition has been reached, even for simple densely packed glasses, such as binary metallic glasses. However, the research of recent years has greatly improved our understanding and several major issues have been settled; see the recent review.[1]

In a hot liquid, diffusion is by flow, whereas, in glass, well below the transition temperature, it will be mediated by hopping processes. Key question are the transition between the two regimes and also the nature of the hopping process. Are the jumps governed by a vacancy mechanism, similar to diffusion in the crystalline state, or by a mechanism inherent to the disordered structure?

Glasses are thermodynamically not in equilibrium; their properties depend on the production history and one observes ageing. The diffusion coefficient of a glass which has been relaxed for a long time will be considerably lower than the one of an "as quenched" glass. Experimental evidence suggests that this could involve a change of diffusion mechanism.

In the glassy state, diffusion can be described by an Arrhenius law. The activation enthalpies are typically 1 to 3 eV.[1] Other than in crystals the pre-exponential factor varies widely from about 10^{-15} to 10^{+13} m^2 s^{-1}.[1] In the undercooled liquid, diffusion is often described by a Vogel–Fulcher–Tammann law[2,3]

$$D(T) = D_0^{\mathrm{VFT}} \exp - H / k(T - T^{\mathrm{VFT}}) \qquad (1.1)$$

which describes a stronger than exponential decrease of diffusivity upon cooling toward $T^{\mathrm{VFT}} < T_{\mathrm{g}}$ where T_{g} is the glass transition temperature. As $T \to T^{\mathrm{VFT}}$, a residual hopping diffusion eventually becomes essential and the diffusion crosses over to the Arrhenius law. Mode coupling theory gives a different expression for diffusion in the undercooled liquid[4]

$$D(T) = D_0^{\mathrm{MCT}} (T - T_{\mathrm{c}})^\gamma. \qquad (1.2)$$

The critical temperature T_{c}, where viscous flow is arrested according to this expression, lies between the glass transition and melting temperatures, $T^{\mathrm{VFT}} < T_{\mathrm{g}} < T_{\mathrm{c}} < T_{\mathrm{m}}$. Again, hopping terms not included in the simplified expression will become dominant and prevent this freezing. The diffusion data alone can be fitted by both expressions. Neither expression allows a clear insight into the atomic process behind diffusion.

From the pressure dependence of diffusion one finds, in general, apparent activation volumes much smaller than an atomic volume.[1] For vacancy diffusion the activation volumes are of the order of the formation volume, i.e. of the order of the atomic volume. Low activation volumes hint at diffusion without formation of defects, i.e. diffusion by an inherent mechanism. A key to the nature of diffusion was found in measurements of the isotope effect of diffusion E. It is defined by the ratio of the diffusivities, D_α, D_β of two isotopes with masses m_α and m_β, respectively: $E = (D_\alpha / D_\beta - 1) / (\sqrt{m_\alpha / m_\beta} - 1)$.[5] Because of the $1/\sqrt{m}$-dependence of the atomic velocities, E is of order unity for diffusion via single vacancy jumps in densely packed lattices where essentially single atoms jump.[6] In contrast, both in glasses[7] and in undercooled metallic melts[8] nearly vanishing isotope effects were observed. The vanishing isotope effect has a natural explanation if one assumes a collective diffusion mechanism both above and below the glass transition. The usage of the term collective follows the general usage in the field; see e.g. ref. 1. It indicates that groups of atoms jump together as opposed to the usual jumps into vacancies in lattice diffusion.

The vanishing isotope effect is a property of relaxed glasses. Upon quench, defects can be frozen in. These enhance diffusion and can lead to an increased isotope effect which vanishes upon relaxation.[9] Quasi-vacancies can be produced also under irradiation which again enhances diffusion; see ref. 10.

In molecular dynamics simulations one can follow the motion of atoms over periods of several ns and up to μs. Early simulations were restricted to simple model systems, such as Lennard-Jones[11] or soft sphere systems[12] above the glass transition. Now it is possible to simulate real systems such as e.g. NiZr[13] or CuZr.[14] As far as qualitative properties of metallic glasses are concerned the results of the model systems and

† Presented at the 85th Bunsen Colloquium on "Atomic Transport in Solids: Theory and Experiment", Gießen, Germany, October 31, 2003.

the real ones are in full agreement and can be used interchangeably.

Extensive studies of different properties of an undercooled binary Lennard-Jones system (BLS) at constant volume[15,16] showed good agreement with the predictions of MCT. For the pressure derivative this theory predicts a singularity at T_c which should be modified by hopping processes to a sharp cusp of the apparent activation volume at T_c. This was observed in a simulation of a BLS at zero pressure.[17] Both above the cusp, in the undercooled liquid, and below, in the glass, activation volumes of around 0.4 atomic volumes were found. In the hot liquid the activation volume rises to values near the atomic volume, which is expected for binary collisions.

The change of the diffusional isotope effect upon cooling was studied at zero pressure for monatomic Lennard-Jones liquids[18] and for BLS.[19] In a hot liquid one has values $E \approx 1$. Upon cooling, E has already dropped to below 0.1 well above both T_g and T_c. This drop is mainly driven by densification but at different rates for the two components of the BLS.

The small isotope effect can be understood from the elementary step of diffusion, the atomic hopping. In a soft sphere glass, at low temperatures, this atomic hopping was found to be highly collective. Chains of ten atoms and more move together in a jump. Whereas the total jump length, summed over all participating atoms, is of the order of a nearest neighbour distance, a single atom only moves a fraction thereof.[20,21] The same chain-like motion was observed in snap shots of the motion in the undercooled melt.[22–24] This collective motion is similar to the one of a group of people threading their way through a crowd. They will fill whatever space they find in front – small activation volume, and each member will follow instantaneously the one in front – collectivity. Obviously they will get on better as a file than in a broad front. Chain-like motion was observed already in early simulations of melting in two dimensions.[25]

Subsequent atomic jumps are strongly correlated with each other, not only in the case of return jumps,[21] and atoms which have just jumped have a strongly enhanced probability to jump again, leading to local bursts of activity interspersed with times of relative calm.[21,26] These correlations, which are typical of all glasses, not only metallic ones, are closely related to the so called "dynamic heterogeneity" of glasses and undercooled liquids. At any given time only a few atoms are active. The resulting mean square displacements strongly deviate from a Gaussian distribution for long times (non-Gaussianity) before it is finally restored by long range diffusion.

In this paper we will present results for the temperature dependence of the dynamic heterogeneity and then study effects of ageing on both the diffusivity and the dynamic heterogeneity.

II Simulation details

The calculations are done for a BLJ system

$$V_{ij}(R) = 4\varepsilon_{ij}[(\sigma_{ij}/R)^{12} - (\sigma_{ij}/R)^6 + A_{ij}R + B_{ij}]. \quad (2.3)$$

where the subscripts ij denote the two species. The potential cutoff was set at $R_c = 3\sigma$. For the parameters we took the commonly used values of Kob and Andersen:[15] $\varepsilon_{AA} = \varepsilon = \sigma_{AA} = \sigma = 1$, $\varepsilon_{BB} = 0.5$, $\sigma_{BB} = 0.88$, $\varepsilon_{AB} = 1.5$ and $\sigma_{AB} = 0.8$. To avoid spurious cutoff effects we introduce the parameters A_{ij} and B_{ij} to ensure continuity of the potential and its first derivative at the cutoff, similar to the shifted force potential.[27] All masses were set to $m_j = 1$. As usual, in the following, we will give all results in the reduced units of energy ε_{AA}, length σ_{AA}, and atomic mass m_A. To compare with real metallic glasses one can equate one time unit $((\varepsilon/m\sigma^2)^{-1/2})$ roughly to 1 ps.

The calculations were done with zero pressure and periodic boundary conditions. The time step was $\Delta t = 0.005$. Control runs with $\Delta t = 0.0005$ showed no significant deviation. A heat bath was simulated by comparing the temperature averaged over 20 time steps with the nominal temperature. At each time step 1% of the temperature difference was adjusted by random additions to the particle velocities. Apart from the very first steps of the ageing procedure the correction, after excursions of the temperature due to relaxations, did not exceed 10^{-4} of the average velocity. This procedure assured that existing correlations between the motion of atoms were only minimally affected. The results did not change when the temperature adjustment was varied within reasonable limits.

Ageing was studied for samples quenched to $T = 0.32\varepsilon/k$, below the glass transition temperature, obtained from the kink in the volume *versus* temperature curve. Ageing leads to densification. However for the parameters adopted the aged system was still sufficiently far from the density of the undercooled liquid to be considered glassy. We proceeded from the samples prepared in our previous work on the pressure dependence of the diffusivity where we had prepared 16 samples for each temperature, eight with slightly positive and eight with slightly negative pressure.[17] Each sample consists of 5488 atoms in a ratio 4:1 of *A*- and *B*-atoms. The samples were then additionally aged for up to 32×10^6 time steps. Measurements were made during runs with constant volume. In all runs pressure and energy were monitored to ensure stability of the configurations. The measured pressure was used to interpolate to zero pressure. The diffusion constant was calculated from the asymptotic slope of the atomic mean square displacements.

Fig. 1 shows the densities and diffusion constants for zero pressure. From the change in slope of the volume expansion we estimate the glass transition temperature as $T_g \approx 0.35\varepsilon/k$. The diffusion constant can be fitted very well with the mode coupling expression, eqn. (1.2), using a value $T_c = 0.36\varepsilon/k$ for both species and $\gamma = 1.87$ and $\gamma = 2.02$, respectively. The two temperatures are very close to each other, $T_g \approx T_c$, but are much lower than the value $T_c = 0.435\varepsilon/k$, reported for simulations at constant density $\rho = 1.2$.[15] This reflects the strong dependence of the glass transition on density or pressure. We find for zero pressure a density of $\rho = 1.16$ at T_g.

The diffusion coefficients depend in a rather intricate way both on temperature and atomic density. This makes a comparison of the present zero pressure values with the the previous isochoric ones[15] difficult. First the BLS becomes at $p = 0$ unstable for $T \approx 1\varepsilon/k$ whereas the high density used in ref. 15 stabilizes the BLS to $T > 51\varepsilon/k$. As mentioned in the introduction the pressure derivative of D (activation volume) has a cusp at T_c this implies that one would have to scale
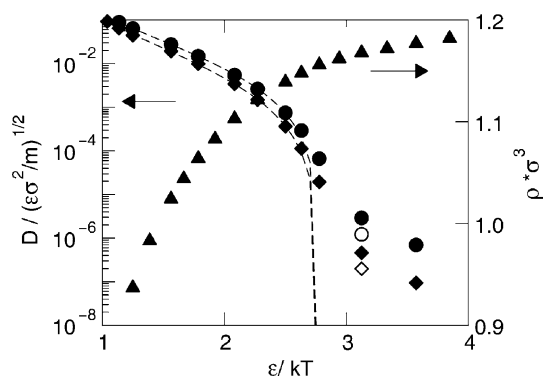

Fig. 1 Diffusion constants (majority A-atoms, diamonds, and minority B-atoms, circles) and density (triangles) at zero pressure against inverse temperature (all in reduced units). The open symbols indicate the extrapolated inherent diffusion coefficients according to eqn. (4.8). The dashed and dash–dotted lines show the fit with the mode coupling expression for atoms *A* and *B*, respectively.

temperature as T/T_c and subsequently scale with pressure which again is complicated by the strong temperature variation of the activation volume which reflects the transition from a thin liquid dominated by binary collisions through the viscous undercooled liquid to the solid like glass.[17] Furthermore it has been shown that both components are affected differently by density. Density is a strong driving force towards cooperative motion. However, in a binary liquid there is no longer a simple proportionality.[19] We have, therefore, not attempted to scale our values over the whole temperature range to the ones of.[15] Doing a rough scaling just above T_c we find qualitative agreement.

Notabene, the present values for the diffusivity below T_g, in the glass, are somewhat lower than the ones published previously[17] which is an effect of the additional ageing as we will discuss further down.

III Dynamic heterogeneity

In isotropic diffusion the atomic displacements show a Gaussian distribution. In undercooled liquids and in glasses Gaussianity is violated over long time scales. This non-Gaussianity indicates different mobilities of different atoms over long time scales, the so called dynamic heterogeneity. This effect is quantified by the non-Gaussianity parameter[28]

$$\alpha_2(t) = \frac{3\langle \Delta r^4(t) \rangle}{5\langle \Delta r^2(t) \rangle^2} - 1, \qquad (3.4)$$

where $\langle \ldots \rangle$ denotes time averageing, $\Delta r^2(t)$ is the mean square displacement and $\Delta r^4(t)$ the mean quartic displacement. This parameter is defined so that it is equal to zero when the atomic motion is homogeneous. Experimentally it can be obtained from the q-dependence of the Debye–Waller factor.[29] It has been calculated in numerous molecular dynamics simulations of liquids, e.g..[12,15,30–33] There are three time regimes of $\alpha_2(t)$. First it increases from $\alpha_2(t = 0) = 0$ on a ps time scale due to heterogeneities of the atomic vibrations. The maximal value of $\alpha_2(t)$ in this vibrational regime is small, less than 0.2. Depending on temperature this is followed by a strong increase during the time of the so called β-relaxation. At times, corresponding to the α-relaxation time, $\alpha_2(t)$ reaches a maximum and drops for $t \to \infty$ to $\alpha_2(t = \infty) = 0$. The strong increase seems to follow a $\sqrt{t}$-law, independent of the material. This $\sqrt{t}$-law has been shown to be a direct consequence of the collectivity of the diffusional jumps and the correlation between subsequent jumps.[32] This general behavior holds both below and above T_g.

In Fig. 2 we show the maximal value of the non-Gaussianity as function of inverse temperature. In the hot liquid $\alpha_2(t)_{max}$ is
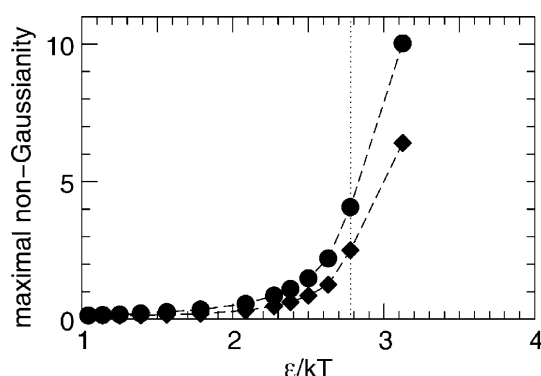
0.12 and 0.14 for the two components, respectively. This corresponds more or less to the vibrational contribution with very little from jump processes. The hot liquid is, as expected, nearly homogeneous with respect to diffusion. Cooling down, we observe a marked increase of $\alpha_2(t)_{max}$ in the undercooled melt which accelerates approaching T_c. At T_c the maximal non-Gaussianity is already 2.5 and 4 for the two components, respectively. In the glass, just about 10% below T_c, these values have doubled and reach $\alpha_2(t)_{max} \approx 10$ for the smaller component. This value is still an underestimate due to ageing effects, see next section. The non-Gaussianity is strongly pressure dependent. We define a pressure coefficient as

$$\beta_\alpha(T) = \frac{2}{p_1 - p_2} \frac{\alpha_2(T, p_1) - \alpha_2(T, p_2)}{\alpha_2(T, p_1) + \alpha_2(T, p_2)} \qquad (3.5)$$

with p_1 and p_2 two different applied external pressures. We find for $T = 0.32$ $\beta_\alpha(T) = 0.27$ and $0.35\varepsilon/\sigma^3$ for the two components, respectively. There is no drastic effect near T_c ($\beta_\alpha(T) = 0.27$ and $0.35\varepsilon/\sigma^3$).

The increase of the maximal value is concomitant with an increase of the time this value is reached, $t_{max}(T)$; see Fig. 3. In the hot liquid $t_{max}(T)$ is of the order of vibrational times and increases by four orders of magnitude upon cooling to $0.9\ T_c$. This slowing down reflects the general slowing of the diffusional dynamics as shown in Fig. 1. To check the correspondence between the diffusion time and t_{max} we calculate the dimensionless quantity

$$C_{\text{D-NG}}(T) = D(T)\rho(T)^{2/3} t_{max} \qquad (3.6)$$

where $\rho(T)$ is the density of the system at zero pressure. In defining $C_{\text{D-NG}}(T)$ it is assumed that the non-Gaussianity is mainly caused by the same atomic motion as diffusion, which is indicated by the rise of $t_{max}(T)$ above the vibrational times upon undercooling. $C_{\text{D-NG}}(T)$ should then become independent of temperature. Indeed the large variation of $t_{max}(T)$ by orders of magnitude nearly vanishes. We find, for both components, $C_{\text{D-NG}}(T = 0.56) \approx 0.015$, at the onset of undercooling, dropping to $C_{\text{D-NG}}(T = 0.32) \approx 0.004$ just below T_c. This correlation between $t_{max}(T)$ and diffusivity is related to the one with the onset of the α-relaxation, reported earlier.[16] The drop of $C_{\text{D-NG}}(T)$ is probably partially a result of the increasing separation of relaxation and diffusion, the first one being less sensitive to eventual return events than the long range diffusion. Another contribution could be a change of the shape of the non-Gaussianity *versus* time curves.

As mentioned in the introduction, there is a general $\sqrt{t}$-law governing the increase of $\alpha_2(t)$ above its vibrational value.[32] From this, one could assume that $\alpha_2(t)_{max}/\sqrt{t_{max}(T)}$ should be approximately constant in the undercooled and glassy regimes. This holds fairly well in the undercooled melt above
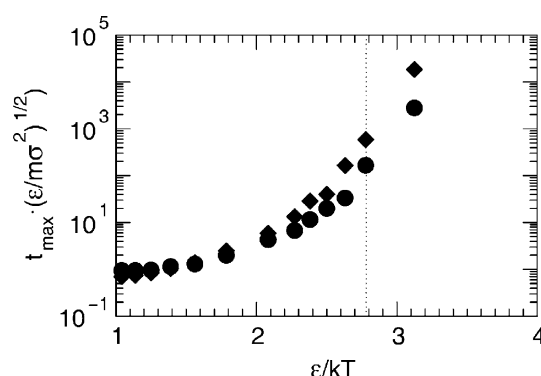

Fig. 2 Maximum value of the non-Gaussianity (majority A-atoms, diamonds, and minority B-atoms, circles) at zero pressure against inverse temperature. The dotted line indicates T_c. The dashed lines are guides to the eye only.

Fig. 3 Time, t_{max}, elapsed till the maximum of the non-Gaussianity is reached (majority A-atoms, diamonds, and minority B-atoms, circles) at zero pressure against inverse temperature. The dotted line indicates T_c.

T_c but breaks down below. Part of this might be due to ageing but inspection of the actual $\alpha_2(t)$-curves shows that it is mainly due to an increased flattening near the maximum which separates $t_{max}(T)$ from the $\sqrt{t}$-increase.

IV Ageing

We have seen that there is a close connection between diffusivity and dynamic heterogeneity. It is well known that glasses are not in thermodynamic equilibrium and are subject to ageing. In experiment one sees upon rapid quenching a drop of the diffusivity on a time scale of hours.[34] Ageing, it is generally assumed, leads to a more "ideal" glass. The "excess volume" drops which indicates annealing of defects - whatever they are. This poses the question of the relationship of dynamic heterogeneity and idealness. If the dynamic heterogeneity is an inherent property of the glassy state one expects it to increase with ageing as the diffusivity decreases.

A simulation over real times of hours is of course impossible. To circumvent this, ageing effects have been studied by instantaneous quenches from high temperatures, thus producing large effects.[35,36] We adopted a softer procedure: samples equilibrated at $T = 0.34\varepsilon/k$ were quenched at a rate of $Q = 10^{-4}$ to $T = 0.32\varepsilon/k$. The quench amounted to about 5% of T_c. The quenched samples were then aged and the diffusion constant was determined in subsequent intervals. To determine the diffusion constant at time t we calculated the average mean square displacement in the interval $[t - \delta/2, t + \delta/2]$. The diffusion coefficient was then obtained by the standard procedure from the long time slope in that interval.

Fig. 4 shows a drop of both diffusivities by about an order of magnitude over the ageing interval of 80 000 time units. The rapid initial drop of $\log D(t)$ is followed by a seemingly linear part, dashed lines. Such a behavior is consistent with the assumtion that the diffusivity is the sum of two terms

$$D(t) = D_{\text{inh}} + D_{\text{def}}c_{\text{def}}(t) \qquad (4.7)$$

where D_{inh} is a time independent inherent diffusion coefficient, D_{def} is a defect mediated diffusion constant and $c_{\text{def}}(t)$ is the defect concentration. If the defects are slowly annealed, with some rate α_{def} during the ageing at constant temperature, we get

$$D(t) = D_{\text{inh}} + D_{\text{def}}c_{\text{def}}(0)e^{-\alpha_{\text{def}}t}. \qquad (4.8)$$

Assuming one type of defect, the same decay constant α should apply to both components whereas the combination $D_{\text{def}}c_{\text{def}}(0)$ can vary between them. Eqn. (4.8) gives, appart from the short time behaviour, an excellent fit of the data of Fig. 4, dashed line. The short time behaviour cannot be expected to be reproduced by such a simple model of independent defects. We find a decay constant $\alpha_{\text{def}}(T = 0.32) = 4.15 \times 10^{-5}$, and for the
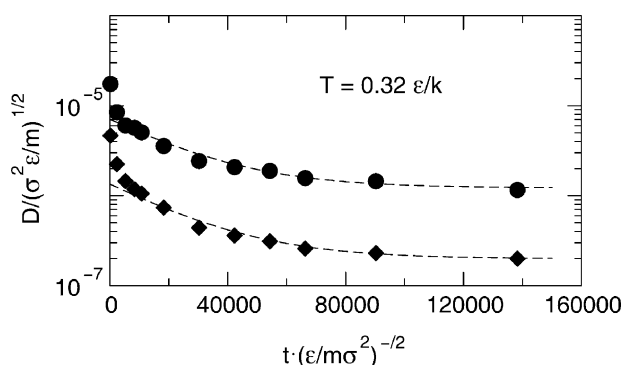
combination $D_{\text{def}}c_{\text{def}}(0)$ we find values of 1.45×10^{-6} and 5.84×10^{-6} for the large and small component respectively. Eqn. (4.8) allows us to extrapolate to the inherent diffusivity which should be reached after long time ageing. These values are shown by the open symbols in Fig. 1.

Soon after the quench, the first values of the diffusion coefficients equal within 10% the ones before the quench, at the higher temperature. There are two effects which seem to cancel each other. On the one hand, due to densification and temperature reduction, diffusion should slow down. On the other hand, the quench drives the system further away from equilibrium which accelerates diffusion processes. It should be noted that diffusion in this short time interval is not necessarily long range.

During the ageing the glass is densified. The volume reduction per atom is $\Delta\Omega \approx 2 \times 10^{-3}\Omega$ where Ω stands for the average atomic volume at that temperature. There is no direct proportionality with the drop in diffusivity. By the time the rapid drop finishes ($t \approx 30\,000$) only about 20% of the excess volume, $\Delta\Omega$, is gone. The raised diffusivity can, therefore, not be attributed to simple quasi-vacancies but to more intricate "defects".

The slowing down of diffusion is accompanied by a monotonic increase of the non-Gaussianity, eqn. (3.4), by a factor of two over the ageing period, Fig. 5. Immediately after the quench the values of $\alpha_2(t)_{max}$ are considerably below the ones of the starting temperature $T = 0.34\varepsilon/k$. This is again consistent with the above picture that the quench produces some "defects" which are annealed during ageing. This is described in analogy to eqn. (4.8) by

$$\alpha_2(t) = \alpha_2^{\text{inh}} + \alpha_2^{\text{def}}c_{\text{def}}(0)e^{-\alpha_{\text{def}}t}. \qquad (4.9)$$

Assuming that the slowing down of diffusion and the increase of heterogeneity are caused by the same mechanism, we take for the decay constant the value obtained from the diffusivity. The resulting fit is shown by the dashed lines in Fig. 5. Considering the obvious scatter the fit is again excellent. The resulting values are for the inherent value $\alpha_2^{\text{inh}} = 6.2$ and 10.0 and for the defect part $\alpha_2^{\text{def}}c_{\text{def}}(0) = -4.0$ and -5.1 for the two components, respectively.

The close connection between collective jumps and heterogeneity gives a hint of the possible nature of what we loosely call defects. Defect here does not mean a simple structure such a vacancy but more likely a local center of strain. These local strains can be relaxed by a less collective motion than in the relaxed glass. This was found earlier by tracer experiments which investigated the effect of ageing on the isotope effect.[9] This additional motion apparently is more homogeneous than the one inherent to the relaxed glass. At the early stages or after a large rapid quench, collectivity might be fully destroyed
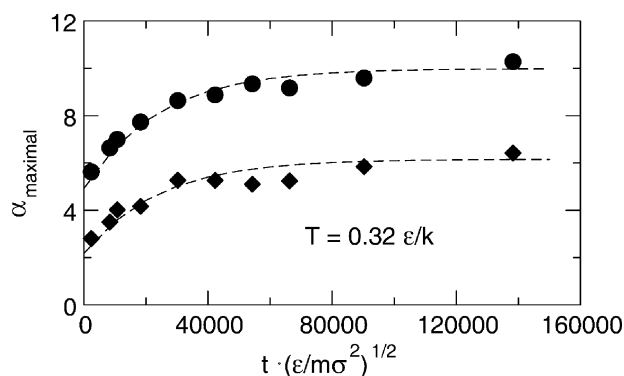

Fig. 4 Diffusion coefficient as function of ageing time (majority A-atoms, diamonds, and minority B-atoms, circles). The dashed lines show the fit with the exponential annealing expression, eqn. (4.8).

Fig. 5 Maximal value of non-Gaussianity as function of ageing time (majority A-atoms, diamonds, and minority B-atoms, circles). The dashed lines show the fit with the exponential annealing expression, eqn. (4.9).

for some jumps. In a simulation of a BLJ glass at constant density single particle jumps have been observed after a rapid quench.[37]

Finally, checking the correlation, eqn. (3.6) we find a drop by a factor of 2–3 during ageing, similar to the one found in the temperature dependence. We interpret this as an indication that the excess diffusivity produced in the quench shows less decoupling between diffusion and relaxation than the inherent one.

V   Summary

We investigate by molecular dynamics the relation between diffusivity and dynamic heterogeneity. We use a binary Lennard-Jones-like system as a simple model of a metallic glass and of a metallic melt. This model system has been extensively studied, mostly at constant volume. In this study the volume is varied to ensure zero pressure conditions. The diffusion coefficients in the melt are in accordance with mode coupling theory with a single critical temperature T_c. In the undercooled melt and, even more so in the glass, diffusion is strongly heterogeneous over long times. The distribution of atomic displacements deviates from the Gaussian distribution found for random walks.

The non-Gaussianity parameter increases, from its small starting value due to vibrations, initially with a $\sqrt{t}$-law before long range diffusion finally restores homogeneity. The time of the maximum non-Gaussianity is given approximately by the diffusion time. However, the correlation factor between the two times decreases systematically with reducing temperature. This may indicate a decoupling between relaxations and long range diffusion as has been observed in studies of viscosity *versus* diffusivity. Below T_g the $\sqrt{t}$-increase does no longer determine the maximal value of the non-Gaussianity since the maximum rapidly flattens.

After quenching below T_c we find a drop of the diffusion coefficients by an order of magnitude with ageing at constant temperature. This can be explained in terms of defects which are produced in the quench and are subsequently annealed. These defects lead to faster diffusion and lower heterogeneity. In this simple system, defect probably means some center of local strain which allows for a less collective motion. In a more complicated system "defects" could, *e.g.*, be different molecular conformations.[38] This general picture is supported by the fact that in the present binary system the ageing of both, diffusivities and heterogeneity, of both components can be described by a single decay constant. This can be used to extrapolate to the inherent diffusion coefficients of the ideal glass at the given temperature. At the temperatures accessible to simulation this ideal glass would actually still be an undercooled liquid, alas with $T < T_c$. The heterogeneity increases with ageing. We conclude that it is an inherent property of the relaxed glass which is suppressed by defects.

References

1   F. Faupel, W. Frank, M.-P. Macht, H. Mehrer, V. Naundorf, K. Rätzke, S. K. Sharma, H. R. Schober and H. Teichler, *Rev. Mod. Phys.*, 2003, **75**, 237.
2   G. S. Fulcher, *J. Am. Ceram. Soc.*, 1925, **8**, 339.
3   G. Tammann and W. Hesse, *Z. Anorg. Allgem. Chem.*, 1926, **156**, 245.
4   W. Götze and A. Sjölander, *Rep. Prog. Phys.*, 1992, **55**, 241.
5   A. H. Schoen, *Phys. Rev. Lett.*, 1958, **1**, 138.
6   H. Mehrer, *Landolt Börnstein, New Series, Group III*, Springer, Berlin, 1990, vol. 26, p. 1.
7   F. Faupel, P. W. Hüppe and K. Rätzke, *Phys. Rev. Lett.*, 1990, **65**, 1219.
8   H. Ehmler, A. Heesemann, K. Rätzke, F. Faupel and U. Geyer, *Phys. Rev. Lett.*, 1998, **80**, 4919.
9   K. Rätzke, P. W. Hüppe and F. Faupel, *Phys. Rev. Lett.*, 1992, **68**, 2347.
10   W. Frank, U. Hamlescher, K. Kronmüller, P. Scharwaechter and T. Schuler, *Phys. Scr., T*, 1996, **66**, 201.
11   G. Wahnström, *Phys. Rev. A*, 1991, **44**, 3752.
12   H. Miyagawa, Y. Hiwatari, B. Bernu and J. Hansen, *J. Chem. Phys.*, 1988, **88**, 3879.
13   H. Teichler, *Defect Diffus. Forum*, 1997, **143–147**, 717.
14   M. Kluge and H. R. Schober, *Defect Diffus. Forum*, 2001, **194–199**, 849.
15   W. Kob and H. Andersen, *Phys. Rev. E*, 1995, **51**, 4626.
16   W. Kob and H. Andersen, *Phys. Rev. E*, 1995, **52**, 4134.
17   H. R. Schober, *Phys. Rev. Lett.*, 2002, **88**, 145901.
18   M. Kluge and H. R. Schober, *Phys. Rev. E*, 2000, **62**, 597.
19   H. R. Schober, *Solid State Commun.*, 2001, **119**, 73.
20   H. R. Schober, C. Oligschleger and B. B. Laird, *J. Non-Cryst. Sol.*, 1993, **156**, 965.
21   C. Oligschleger and H. R. Schober, *Phys. Rev. B*, 1999, **59**, 811.
22   H. R. Schober, C. Gaukel and C. Oligschleger, *Defect Diffus. Forum*, 1997, **143–147**, 723.
23   H. R. Schober, C. Gaukel and C. Oligschleger, *Prog. Theor. Phys. Suppl.*, 1997, **126**, 67.
24   C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole and S. C. Glotzer, *Phys. Rev. Lett.*, 1998, **80**, 2338.
25   B. J. Alder and T. E. Wainwright, *Phys. Rev.*, 1962, **127**, 359.
26   H. Teichler, *J. Non-Cryst. Solids*, 2001, **293–295**, 339.
27   J. J. Nicolas, K. E. Gubbins, W. B. Streett and D. J. Tildesley, *Mol. Phys.*, 1979, **37**, 1429.
28   A. Rahman, *Phys. Rev., Sect. A*, 1964, **136**, 405.
29   R. Zorn, *Phys. Rev. B*, 1997, **55**, 6249.
30   B. Doliwa and A. Heuer, *Phys. Rev. Lett.*, 1998, **80**, 4915.
31   D. Caprion and H. R. Schober, *Phys. Rev.B*, 2000, **62**, 3709.
32   D. Caprion, J. Matsui and H. R. Schober, *Phys. Rev. Lett.*, 2000, **85**, 4293.
33   K. Vollmayr-Lee, W. Kob, K. Binder and A. Zippelius, *J. Chem. Phys.*, 2002, **116**, 5158.
34   J. Horvath, K. Freitag and H. Mehrer, in *Proceedings of the 5th International Conference on Rapidly Quenched Metals*, ed. S. Steeb and H. Warlimont, Elsevier, Amsterdam, 1985, p. 751.
35   W. Kob and J.-L. Barrat, *Phys. Rev. Lett.*, 1997, **78**, 4581.
36   U. Müssel and H. Rieger, *Phys. Rev. Lett.*, 1998, **81**, 930.
37   K. Vollmayr-Lee, *Mater. Res. Soc. Symp. Proc.*, 2003, **754**, CC3.19.1.
38   R. Chelli, G. Cardini, P. Procacci, R. Righini and S. Califano, *J. Chem. Phys.*, 2003, **119**, 357.