Pressure dependence of diffusion in simple glasses and supercooled liquids

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Using molecular dynamics simulation, we have calculated the pressure dependence of the diffusion constant in a binary Lennard-Jones Glass. We observe four temperature regimes. The apparent activation volume drops from high values in the hot liquid to a plateau value. Near the critical temperature of the mode coupling theory it rises steeply, but in the glassy state we find again small values, similar to the ones in the liquid. The peak of the activation volume at the critical temperature is in agreement with the prediction of mode coupling theory.

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Diffusion in glasses and their melts has been studied intensively for many years. These efforts are stimulated both by the technological importance of glassy and amorphous materials and by the desire to understand the physics of disordered systems in general and the liquid to glass transition in particular. Despite this effort there is still no agreement on the nature of diffusion on an atomic level or on its change at temperatures near the glass transition. This even holds for simple densely packed glasses, such as binary metallic ones, see for recent reviews Refs. 1, 2, 3, 4, 5.

In a hot liquid, diffusion is by flow, whereas, in the glass well below the transition temperature, it will be mediated by hopping processes. One key question is the transition between the two regimes. For fragile glasses, such as most polymers and amorphous metallic glasses, mode coupling theory (MCT) predicts an arrest of the homogeneous viscous flow in the undercooled melt at a temperature $T_c$, well above the glass transition temperature $T_g$. Hopping processes will suppress the predicted singularities and will become the dominant diffusion process near $T_c$.

The nature of the hopping process is another issue of controversy. Is it by a vacancy mechanism, similar to diffusion in the crystalline state, or is it via a collective process inherent to the disordered structure? Investigations are hampered by the fact that glasses are thermodynamically not in equilibrium, and one observes aging. The diffusion constant of a glass which has been relaxed dynamically not in equilibrium, and one observes aging. It is interpreted in terms of a collective diffusion mechanism for thermally activated diffusion the formation volume drops from high values in the hot liquid to a plateau value. Near the critical temperature of the mode coupling theory it rises steeply, but in the glassy state we find again small values, similar to the ones in the liquid. The peak of the activation volume at the critical temperature is in agreement with the prediction of mode coupling theory.

Using $V = \partial G/\partial p$ with $G = H - TS$ one obtains the activation volume for a diffusion by a single jump process

$$V_{act} = -kT \left[ \frac{\partial \ln D}{\partial \mu} \right]_T + kT \left[ \frac{\partial \ln D_0}{\partial \mu} \right]_T.$$ (2)

In crystals one finds that the second term is only a minor correction which can be neglected. For diffusion mediated by defects, the activation volume splits into two terms, $V_{act} = V^f + V^m$, a formation volume $V^f$ and a migration volume $V^m$.

For diffusion via thermal vacancies the formation volume dominates and $V_{act}$ varies between 0.6Ω and 1Ω, where Ω is the average atomic volume. For the migration part one estimates $V^m \sim 0.1Ω$. Concomitantly in crystals high values of $V_{act}$ are taken as a signature of a thermally activated diffusion mechanism.

Assuming that also in the glass the first term in Eq. 2 dominates, one usually describes, also in amorphous materials, the pressure dependence of diffusion by an apparent activation volume

$$\dot{V}_{act} = -kT \left[ \frac{\partial \ln D}{\partial p} \right]_T.$$ (3)

Experiments on a number of metallic glasses give a large spread of values in the range of 0.05 to 1 Ω. Low values were, e. g., observed in Co$_{81}$Zr$_{19}$ [8] where no significant isotope effect is observed [9]. This result can be interpreted in terms of a collective diffusion mechanism inherent to the glassy structure. The situation is not so clear for the case of large activation volumes $V_{act}$. The activation volume of 0.9 Ω for diffusion of Zr in Co$_{93}Zr_{8}$ was interpreted as indication of diffusion via vacancy like defects [8] rather than by an inherent mechanism as in the case Co. Values of around 0.5Ω have been observed in several materials [8, 11, 12]. Such values are also found in materials where the vanishing isotope points to diffusion by collective jumps. Whether collectivity can induce migrational activation volumes of the order 0.5 to 1 Ω is still open.
In the liquid state the diffusion constant can be fitted by a Vogel-Fulcher-Tammann law (VFT)

\[ D_{\text{VFT}}(T) = D_0^{\text{VFT}} \exp \left[ -E_{\text{VFT}}/(T - T_{\text{VFT}}) \right] \]  

(4)

From this we get the activation volume

\[ \hat{V}^{\text{VFT}}_{\text{act}} = -kT \left[ \frac{\partial \ln D_{\text{VFT}}}{\partial p} - \frac{1}{k(T - T_{\text{VFT}})} \frac{\partial E_{\text{VFT}}}{\partial p} \right] + 1 \frac{E_{\text{VFT}}}{k^2(T - T_{\text{VFT}})^2} \frac{\partial T_{\text{VFT}}}{\partial p} \]  

(5)

From MCT one derives alternative expressions

\[ D_{\text{MCT}}(T) = D_0^{\text{MCT}} (T - T_c^{\text{MCT}})^\gamma \]  

(6)

\[ \hat{V}^{\text{MCT}}_{\text{act}} = -kT \left[ \frac{\partial \ln D_{\text{MCT}}}{\partial p} - \gamma \frac{1}{(T - T_c^{\text{MCT}})} \frac{\partial T_{\text{MCT}}}{\partial p} \right. \]

\[ \left. + \ln (T - T_c^{\text{MCT}}) \frac{\partial \gamma}{\partial p} \right] \]  

(7)

In both expressions the diffusion constant extrapolates to zero, however, with one crucial difference. In the VFT-expression, Eq. 4, this happens at \( T_{\text{VFT}} \), far below \( T_g \), whereas in MCT diffusion vanishes at, \( T_c^{\text{MCT}} \), well above \( T_g \). Due to the crossover to the glass the difference between the two expressions is normally not sufficient to distinguish between them with certainty. This is different for the pressure dependence where both expressions give singularities, below and above \( T_g \), respectively.

There is only one measurement of \( \hat{V}_{\text{act}} \) in the undercooled melt. Knorr et al. find for Ni diffusion in the bulk metallic glass melt Zr₄₆₇₅Ti₈₂₅Cu₇₅Ni₁₀Be₂₇₅ values between 0.35 and 0.64 Ω.

Whereas experiment so far only provides circumstantial evidence for the diffusion mechanism, molecular dynamics simulation can give both the quantities seen in experiment and show the underlying atomic processes. In a previous simulation on NiZt the activation volume was estimated as 0.36 Ω from the change of barrier height. The underlying process was a collective jump of a chain of atoms.

The aim of the present paper is to present a systematic study of the pressure dependence of diffusion as function of temperature. In order to relate closely to other work the simulations were done for the well studied binary Lennard-Jones system (LJ), described by the interatomic interaction:

\[ V_{ij}(R) = 4\epsilon_{ij} \left[ (\sigma_{ij}/R)^{12} - (\sigma_{ij}/R)^6 + A_{ij} R + B_{ij} \right] \]  

(8)

For the parameters \( \epsilon_{ij} \) and \( \sigma_{ij} \) we took the commonly used values of Kob and Andersen [16] \( \epsilon_{AA} = \epsilon = \sigma_{AA} = \sigma = 1, \epsilon_{BB} = 0.5, \sigma_{BB} = 0.88, \epsilon_{AB} = 1.5 \) and \( \sigma_{AB} = 0.9 \). Different from these authors we use a larger cutoff radius \( R_c = 3\sigma \). To avoid spurious cutoff effects we introduce, similar to the shifted force potential [17], the parameters \( A_{ij} \) and \( B_{ij} \) to ensure continuity of the potential and its first derivative at the cutoff. All masses were set to \( m_j = 1 \). In the following, we will give all results in the reduced units of energy, \( \epsilon_{AA} \), length, \( \sigma_{AA} \), and atomic mass \( m_A \).

We have used this potential previously to calculate the diffusional isotope effect parameter in the liquid [18] and the evolution of the dynamic heterogeneity both below and above the glass transition [19]. From these calculations we had well aged samples at different temperatures for zero external pressure.

The calculations were done at each temperature with constant volume, corresponding to zero pressure, and periodic boundary conditions. The pressure was monitored. The time step was \( \Delta t = 0.005 \). 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. This procedure assured that existing correlations between the motion of atoms were only minimally affected. At each temperature we had 8 independent samples, each of 5488 atoms in a ratio 4 : 1 of A- and B-atoms. The diffusion constants were calculated from the asymptotic slope of the atomic mean square displacements

\[ D(T) = \frac{1}{6t} \lim_{t \to \infty} \langle (R^2(t) - R^2(t'))_{t',t} \rangle \]  

(9)

where \( \langle \ldots \rangle_{t',t} \) indicates averaging over all atoms of the particular species and over starting times.

Fig. 1 shows the densities and diffusion constants for the zero pressure configurations. From the change in slope of the volume expansion we estimate the glass transition temperature as \( T_g \approx 0.35 \epsilon/k \). The diffusion con-
The resulting pressure change after aging was 2% at the highest and 0.5% at the lowest temperature. As starting configurations which were then compressed each temperature the zero pressure samples were taken in runs with higher and lower densities, respectively. At this point we assume that the VFT expression, Eq. 5. One can clearly distinguish four temperature regions together with the fit with the VFT-expression, Eq. 4. From our previous work \[T^2\] and from the work on the LJ-system under high pressure \[T^2\] we expect a predominance of chain motion with increasing chain length upon cooling. At these temperatures diffusion exhibits a pronounced dynamic heterogeneity over times of several \[100 (\text{me}^2/\epsilon)^{1/2}\]. The time scale of this heterogeneity, in turn, correlates with time scale of the transition from \(\beta\) - to \(\alpha\)-relaxation.

Our values for the activation energy in the glass are of similar magnitude as the estimate of Teichler \[T^2\] for the NiZr system. We find higher activation volumes for less well aged samples. In other simulations of metallic glasses collective jumps of chains of atoms \[T^2\] have been observed, an indication of an inherent collective diffusion mechanism.

The experimental values for Ni diffusion in the bulk glass \[Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}\] \[T^2\] show an increase of the activation volume below \(T = 704\) K. When we plot (open circles in Fig. \[T^2\]) the experimental values in LJ units by scaling with the temperature where the break in the diffusion constant occurs, i. e. without a free parameter, they closely follow the LJ result. In particular, they show the strong increase of \(V_{\text{act}}\) upon cooling towards \(T^2\). This apparent agreement poses, however, some questions. The two temperatures \(T^2\) and \(T^2\) nearly coincide in the LJ system, under the present quench and aging times. There is experimental evidence that in \[Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}\] the two temperatures differ strongly: \(T^2 = 592\) K and \(T^2 \approx 875\) K. According to these numbers the increase of the activation volume would occur at \(T^2\) and not at \(T^2\) and, therefore, would not be the effect predicted by MCT. The experimental evidence is not sufficient to clear this point. There is a large experimental uncertainty on the measured values of the activation volume, the apparent increase might be an artifact of the fitting. Also the MCT critical temperature might be overestimated. Clearly better experimental values are needed.

As we have seen above, both VFT and MCT expressions predict the onset of a divergence in \(V_{\text{act}}(T)\). The dotted line in Fig. \[T^2\] shows a fit with the VFT expression, Eq. 4. We assume that the VFT temperatures are the same for both components, independent of pressure. The fit works relatively well. However, the resulting parameters are somewhat odd. We find: \(\partial T^2/\partial p = 0.3\) and \(\partial E^2/\partial p = 0\) for both compo-

\[\text{FIG. 2: Calculated activation volume (majority A-atoms, diamonds, and minority B-atoms, circles) versus temperature. The open circles represent the experimental data on Ni diffusion in a bulk glass melt, scaled to LJ-units. The dashed and dotted lines are fits with the VFT expression, with one or two VFT temperatures, respectively.}\]
nents and \[\partial \ln D_c^{\text{VFT}} / \partial p = -0.329\] and \[-0.2561\] for the the A and B-components, respectively. That means, according to the fit there is very little change of the “activation energy” and a strong change of the pre-factor. Allowing for different values of \[\partial T^{\text{VFT}} / \partial p\] the fit is somewhat improved. Its main shortcoming, the too slow rise, remains.

The alternative fit with the MCT-expression, Eq. 7, is displayed in Fig. 3. As above, we assume a common value of \(T_c^{\text{MCT}}\) for both components and all pressures. We omitted in the fit the logarithmic term in Eq. 7, i.e. we neglected the weak dependence on a possible pressure variation of \(\gamma\). We get an excellent fit (dashed line) with \[\partial T^{\text{MCT}}_c / \partial p = 0.028\] for both components and \[\partial \ln D_0^{\text{MCT}} / \partial p = -0.338\] and \[-0.278\] for A and B atoms, respectively. The square deviation for this fit is an order of magnitude less than the one using the VFT-expression. Contrary to the VFT case it reproduces the sharp uprise. We take this as an indication that the divergence of the activation volume would in deed be at \(T_c^{\text{MCT}}\) and not at \(T^{\text{VFT}}\). Of course the glass transition intervenes before the divergence is reached.

Kob and Andersen [14] report for their constant volume simulation a pressure of \(p \approx 2.5\) at their \(T_c^{\text{MCT}} = 0.435\). Extrapolating our value using the fitted pressure derivative we find \(T_c^{\text{MCT}}(p = 2.5) \approx 0.43\) in excellent agreement with Kob and Andersen’s value.

In conclusion, we find, both in the liquid and the glass, activation volumes of around 0.3 atomic volumes. This correlates with a high collectivity seen in the isotope effect. In the hot liquid, where diffusion is no longer by collective motion, the activation volume rises to about 0.6 atomic volumes. Cooling towards the critical temperature mode coupling theory predicts a \(1/(T - T_c)\) singularity, cut off by the glass transition. This is clearly observed in the simulation. This singular behavior can, e. g. be used to test whether there is one or several critical temperatures in a multicomponent system.

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