Orientational and Translational Hopping in Supercooled Liquids and Glasses: Correlated Dynamics in a Free Energy Landscape

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Abstract

Orientational relaxation (OR) in a viscous, glassy liquid is investigated by carrying out extensive NPT molecular dynamics simulations of isolated ellipsoids in a glass forming binary mixture. Near the glass transition, the OR occurs mainly via correlated hopping, sometimes involving participation of several neighboring atoms, placed in a ring like tunnel. In the glassy state, hopping is found to be accompanied by larger fluctuations in the total energy and the volume of the system. Both orientational and translational hopping are found to be gated, restricted primarily by the entropic bottlenecks, with orientation becoming increasingly slower than translation as the pressure is increased. OR is heterogeneous, with a wide distribution of decay times.

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1 Introduction

Even after intense studies over many decades, several aspects of relaxation in supercooled liquids remain ill-understood and controversial. It is now recognized that anomalies in the relaxation in deeply supercooled liquids arise from an interplay between the dynamical cooperativity between different regions in the liquid (an idea
originally introduced by Adam and Gibbs [1] and the influence of the underlying free energy surface of the liquid which increasingly exerts its influence as the glass transition region is approached [2, 3]. The essence of the dynamical cooperativity can arguably be described by the mode coupling theory [4, 5] which, however, fails to connect to the free energy landscape. There is still no comprehensive treatment of the cross-over from the dynamically cooperative region to the hopping dominated region. The cross-over scenario is intimately connected with other concepts, like the fragility and the super-Arrhenius behavior of the supercooled liquid.

Orientational relaxation in glassy liquid has proved to be the most powerful probe of dynamics. The dielectric relaxation study by Goldstein and Johari first revealed the emergence of the $\alpha$-$\beta$ bifurcation and the disappearance of the $\alpha$ relaxation, as the glass transition is approached from higher temperature [6]. The NMR studies of Ediger and coworkers find an emergence of the a new time scale near glass transition temperature [7]. This new time scale is larger than $\alpha$ relaxation time. Ediger and other workers also found evidence of heterogeneity and decoupling of translational and rotational motions [7].

Theoretical and computer simulation studies have mostly been directed towards understanding spherical systems, like the Lennard-Jones and the hard spheres. In this study, we report detailed MD (constant pressure (P), temperature (T), and constant total number of particles (N)) simulations of orientational relaxation of a few isolated ellipsoids in glass forming binary liquids. The questions we address here are the following: (a) How are the orientational and the translational motions correlated? (b) What is the energy surface for orientational hopping? (c) How local
is the hopping phenomenon? Or in another words, how relevant is the free energy landscape? (d) How sensitive is rotational diffusion to molecular shape? Simulation studies presented here hopefully provide answer to some of these questions.

Our solvent is represented by Kob-Andersen (KA) binary mixture ([8] which is known to be a good glass former and has been extensively studied [9], and our solute probes are prolate ellipsoids. Pressure is kept constant by Andersen’s piston method [10] while in the case of temperature, a damped oscillator method has been adopted which keeps temperature constant at each and every time step [11]. The piston mass involved here is $0.0027(m_A/\sigma_A^4)$ which is regarded as optimum [11, 12]. The interactions between the particles are modeled by different potentials. The interaction between the spheres are given by Lennard-Jones Potential (as in KA Model) and the interaction between two ellipsoids with arbitrary orientations is assumed to be given by the Gay-Berne (GB) potential [13],

$$U_{GB} = 4\epsilon(\hat{r}, \hat{u}_1, \hat{u}_2) \left[ \left( \frac{\sigma_0}{r - \sigma(\hat{r}, \hat{u}_1, \hat{u}_2) + \sigma_o} \right)^{12} - \left( \frac{\sigma_0}{r - \sigma(\hat{r}, \hat{u}_1, \hat{u}_2) + \sigma_0} \right)^6 \right]$$

(1)

where $\hat{u}_1 \hat{u}_2$ are the axial vectors of the ellipsoids 1 and 2. $\hat{r}$ is the vector along the intermolecular vector $r = r_2 - r_1$, where $r_1$ and $r_2$ denote the centers of mass of ellipsoids 1 and 2 respectively. $\sigma(\hat{r}, \hat{u}_1, \hat{u}_2)$ and $\epsilon(\hat{r}, \hat{u}_1, \hat{u}_2)$ are the orientation-dependent range and strength parameters respectively. $\sigma$ and $\epsilon$ depend on the aspect ratio $\kappa$. Finally, the interaction between a sphere and an ellipsoid is accounted for by a modified GB-LJ potential given below [15]

$$U_{Ei} = 4\epsilon_{Ei} \left[ \left( \frac{\sigma(\theta)_{Ei}}{r} \right)^{12} - \left( \frac{\sigma(\theta)_{Ei}}{r} \right)^6 \right]$$

(2)

where 'E' denotes the ellipsoids and 'i' can be 'A' or 'B'. The expression for $\sigma(\theta)_{Ei}$ is available [15, 14].
The ellipsoid in binary mixture system with the above mentioned potential is a well behaved system and it can also exhibit the experimentally observed anomalous viscosity dependence of the orientational correlation time [14]. Four ellipsoids were placed far from each other in a binary mixture of 500 particles with number of 'A' particles, \( N_A = 400 \) and number of 'B' type particles \( N_B = 100 \). The reduced temperature is expressed as, \( T^* = \frac{k_B T}{\epsilon_A} \), the reduced pressure as, \( P^* = \frac{P \sigma_A^3}{\epsilon_A A} \), and the reduced density as \( \rho^* = \frac{\rho \sigma_A^3}{\epsilon_A A} \). The time is scaled by \( \sqrt{\frac{m_A \sigma_A^2}{\epsilon_A A}} \). The time step of the simulation is \(.002 \tau\) and the system is equilibrated for \(1.5 \times 10^5\) steps.

Systematic simulations of the Kob-Andersen model (with \( T^* = 0.8 \)) have been carried out by varying pressure over a large range to study the system from its normal liquid regime to the glassy state. The dynamical nature of the system at different pressures can be characterized from the value of the viscosity and the nature of the translational hopping of all the particles and orientational hopping of the ellipsoids. At \( P^* = 2.0 \), the system is in the normal liquid regime. Here the reduced density is 1.13 and the reduced viscosity is 13.446. Here motion is continuous and orientational correlation decays like in a normal liquid. Both the probability distributions for spatial displacement, \( P^i(r) \), and for angular displacement, \( P(\theta) \), are Gaussian in the long time. This behavior changes as pressure is increased.

At \( P^* = 5 \) where \( \eta^* = 479.5 \), it is a viscous liquid. In figure 1(a) we plot \( P(\theta) \) at pressures 5 and 6. At \( P^* = 5 \), the rotational motion is mostly continuous and at long time \( P(\theta) \) is Gaussian. However, at \( P^* = 6 \) viscosity \( \eta \) is about 2340. At long time \( P(\theta) \) has one peak at small angle and there is also another peak between 160°-
180° The trajectory at pressure 5 shows continuous change where as that at pressure 6 shows sharp 180° rotations.

Figures 1(b) and 1(c) show $P(r)$ at two different pressures, each plot showing the same for both the larger (A) and the smaller (B) particles. While at $P^\ast= 5$ (not shown), both $P^A(r)$ and $P^B(r)$ are Gaussian, at pressure 6 the $P^B(r)$ is still Gaussian but $P^A(r)$ shows two peaks. This is because at this pressure although most of the small ‘B’ particles still have continuous motion with some amount of hopping, the ‘A’ particles move primarily through hopping. At pressure 8, both $P^A(r)$ and $P^B(r)$ show multiple peaks. At this pressure the density is around 1.36 and hopping is the dominant mode of transport for all the particles. A small peak observed in $P^B(r)$ at higher $r$ value (2.5$\sigma$) signifies correlated hopping. The peak at 0.2$\sigma$ describes the vibrational motion within the cage. The cross-over from continuous to hopping dominated regime is accompanied by a dramatic slow down in the decay of the stress auto-time correlation function (not shown here) and the sharp rise in the value of the viscosity. From the above analyses, we conclude that the larger (A) particles freeze near $P^\ast=6$ while the smaller (B) particles freeze near $P^\ast=7$.

At $P^\ast = 10$ the system is so densely packed that there hardly remains any signature of liquid like region. The reduced density of this system is 1.41. In this highly dense system, each ellipsoid has about 22 neighbors. Here we found primarily two different kinds of translational motions, one is many particle correlated hopping and the other is motion in a ring like tunnel. We also found correlated orientational and translation hopping. Figures 2 and 3 show the displacement of the 1st and 2nd ellipsoid in reduced time and the change in their instantaneous orientation.
Study of the first ellipsoid and its neighboring particle dynamics reveal that about 5-6 particles translate (greater than 0.525 \( \sigma \)) during (or just prior to) the time the ellipsoid hops. The OCF decays considerable amount only during this period.

Analyzing the dynamics of the second ellipsoid and its neighboring particles and their neighbors, we found that 5 particles (including the 2nd ellipsoid) have similar trajectories (around 1650 \( \tau \)). All these particles are not the neighbor of the ellipsoid, they are consecutive neighbors and are placed in a ring like tunnel. Thus although the ellipsoid translates considerable amount in this tunnel, the orientational dynamics is constrained, leading to less decay of the OCF (only upto 0.82). We also find that hopping of the particle is associated with larger fluctuation in volume and total energy in this glassy system.

The study of the OCF at different pressures show that at high pressures (\( P^* \geq 6 \)) the OCF decays only through hopping and there is a distribution of relaxation times. While the average orientational correlation function is non-exponential, decay of each ellipsoid is found to be only weakly non-exponential, with widely different relaxation times, often differing by more than one order of magnitude at pressure \( P^* = 6 \). In two different runs the average OCF is also found to be drastically different, although the average energy and volume of the different runs remain the same. Thus, the local minimum explored by each probe ellipsoid are different.

In an ordinary liquid rotational relaxation time, \( \tau_R \) is of the order of \( 10^{-11} sec \) whereas the time taken to translate 1 molecular diameter, \( \tau_T \) is about \( 10^{-10} sec \). In a supercooled liquid both translation and rotation slows down. From the mean square displacement we found that \( \tau_T \) of the ellipsoid is of the order of \( 10^{-5} sec \).
Since the orientational correlation function does not decay much it is difficult to make an estimate of $\tau_R$. We found that even at 1200 $\tau$ the OCF does not decay below 0.55. Thus it can be safely concluded that in our system $\tau_{2R} >> \tau_T$. This observation is similar to that reported by Ediger and co-workers where they found that the molecule translates hundreds of molecular diameter before it rotates once [7].

Figure 4 shows the variation of the single particle potential energy during hopping as a function of distance traversed, both for the ellipsoid and two of its neighbors. The study of the energetics (during orientational and translation hopping) reveals that both kinds of hopping are gated process, where the free energy barrier (or the saddle) is entropic in nature. The ellipsoid hopping is associated with instantaneous rearrangement (significant displacement) of surrounding molecules. At high pressure the particles are densely packed and trapped in regions separated by small windows (entropic bottlenecks) [16]. If the motion of the ellipsoid is in the x-direction then the surrounding particles are found to move in the perpendicular plane. Thus only rearrangements or displacement of surrounding molecules open up the gate and allow the ellipsoid to move as envisaged in the Zwanzig model [16]. In the process of creation of the gate some of the particles register a small rise in energy (shown in figure 4(b) and 4(c)). However the sum of energies of the ellipsoid and its neighbors remains the same.

The present study shows that orientational relaxation in a viscous liquid near glass transition, involves collective motion which, although complex, has certain regular and understandable features. For example, hopping of a particle in question
is gated. There is clearly a waiting time distribution of this collective event to happen, although even very close to glass transition these events are certainly not rare. Therefore, these are expected to play important role in the relaxation of glassy liquids. A complete theory of these highly collective processes would be non-trivial, and would perhaps first require a “coarse-grained” theory of the type discussed by Xia and Wolynes[17].

We find that orientational relaxation occurs increasingly on slower time scale, compared to translation, as the glass transition is approached. This is because molecules can hop preserving its orientation and also 180° orientational hopping does not change 2nd rank harmonics, often probed in experiments. In the glassy state the hopping of ellipsoid is non-local. Finally, we note that the present simulations can reproduce several behavior observed in recent experiments on orientational relaxation in deeply supercooled liquids.

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References

[1] G. Adam and J. H. Gibbs, J. Chem. Phys. 43, 139 (1965).

[2] F. H. Stillinger and T. A. Weber, Phys Rev A 25, 978 (1982); Science 225, 983 (1984).

[3] R. Zwanzig, J. Chem. Phys. 79, 4507 (1983); E. Rabani, J.D. Gezelter, and B.J. Berne, Phys. Rev. Lett. 82 3649 (1999); T. Keyes, G. V. Vijayadamodar and U. Zurcher, J. Chem. Phys. 106, 4651 (1997).

[4] W. Gotze, in Liquids, Freezing and the Glass Transition, edited by D. Levesque, J. P. Hansen, and J. Zinn-Justin (North-Holland, Amsterdam, 1990); W. Gotze and L. Sjogren, Phys. Rev. A 43, 5442 (1991).

[5] B. Bagchi and S. Bhattacharyya, Adv. Chem. Phys. 116, 67 (2001).

[6] G. P. Johari and M. Goldstein, J. Chem. Phys. 53, 2372 (1970); ibid, 55, 4245 (1971).

[7] M.D. Ediger, C. A. Angell and S. R. Nagel, J. Phys. Chem. 100; M. T. Cicerone and M. D. Ediger, J. Chem. Phys. 104, 7210, 103, 5684 (1996); G. Heuberger and H. Sillescu, J. Chem. Phys. 100, 15255 (1996).

[8] W. Kob and H. C. Andersen, Phys. Rev. E, 51, 4626 (1995); W. Kob and H. C. Andersen, Phys. Rev. Lett, 73, 1376 (1994).

[9] S. Sastry, P. G. Debenedetti and F. H. Stillinger, Nature 393, 554 (1998); S. Sastry, Phys. Rev. Lett. 85, 590 (2000); S. Sastry, Nature
[10] H.C. Andersen et al. Rapport d’activite scientifique du CECAM, pp 82-115 [7.4, 7.4.3].

[11] D. Brown and J. H. R. Clarke, Mol. Phys. 51, 1243 (1984).

[12] J. M. Haile and H. W. Graben, J. Chem. Phys. 73, 2412 (1980)

[13] J. G. Gay and B. J. Berne, J. Chem. Phys., 74, 3316 (1981).

[14] S. Bhattacharyya and B. Bagchi, J. Chem. Phys., in press

[15] S. Ravichandran and B. Bagchi, J. Chem. Phys., 111, 7505 (1999).

[16] H.-X. Zhou and R. Zwanzig, J. Chem. Phys., 94, 6147 (1991); J. Machta and R. Zwanzig, Phy. Rev. Lett. 50, 1959 (1983).

[17] X. Xia and P. G. Wolynes, Phys. Rev. Lett., 86, 5526 (2001).
Figure Captions

Figure 1 (a) Dashed and Solid lines show variation of $P(\theta)$ against angular displacement $\theta$ for pressure $P^* = 5.0$ and $P^* = 6$, respectively. At $P^* = 6$ the distribution is bimodal with a second peak appearing around 160$^\circ$. (b) Distribution of $P(r)$ against displacement ($r^*$) for two different types of particles (’A’ and ’B’) at pressure $P^* = 6.0$. Solid line and dashed line denote bigger and smaller particles, respectively. (c) Same plot as 1(b) but at pressure $P^* = 8.0$.

Figure 2 (a) Displacement of an ellipsoid (tag 1) occurs only by hopping at around 300$\tau$. (b) Dot product of instantaneous orientation and the orientation at the time t=0 shows that orientational and translational hopping happen at the same time. (c) Decay of $C_{2R}(t)$ in different time intervals are plotted. The arrow points to the OCF which shows prominent decay during the time interval of the hopping.

Figure 3 (a) Displacement of another ellipsoid (tag 2) where it undergoes motion in a ring like tunnel. (b) Dot product of the instantaneous orientation and the orientation at time t=0. Both the orientational hopping and translational motion are correlated. (c) Decay of $C_{2R}(t)$ in different time intervals are plotted. Although, the ellipsoid translates about 1$\sigma$ distance, due to constrained orientational dynamics in the ring like tunnel the OCF decays only upto 0.82. The arrow points to the OCF, obtained during the period of hopping.

Figure 4 (a) Variation of the single particle potential energy (SPPE) of the ellipsoid with time around hopping signifies gated diffusion. (b) and (c) shows variation of SPPE of two neighboring particles of the above ellipsoid.
