We have carried out molecular dynamics simulations to understand the dynamics of a tagged pair of atoms in a strongly non-ideal glass-forming binary Lennard-Jones mixture. Here atom B is smaller than atom A ($\sigma_{BB} = 0.88\sigma_{AA}$, where $\sigma_{AA}$ is the molecular diameter of the A particles) and the AB interaction is stronger than that given by Lorentz-Berthelot mixing rule ($\epsilon_{AB} = 1.5\epsilon_{AA}$, where $\epsilon_{AA}$ is the interaction energy strength between the A particles). The generalized time-dependent pair distribution function is calculated separately for the three pairs (AA, BB and AB). The three pairs are found to behave differently. The relative diffusion constants are found to vary in the order $D_{bb} > D_{ab} > D_{aa}$, with $D_{bb} \approx 2D_{aa}$, showing the importance of the hopping process (B hops much more than A). We introduce a non-Gaussian parameter ($\alpha_2^B (t)$) to monitor the relative motion of a pair of atoms, and evaluate it for all the three pairs, with initial separations chosen to be at the first peak of the corresponding partial radial distribution functions. At intermediate times, significant deviation from the Gaussian behavior of the pair distribution functions is observed, with different degree for the three pairs. A simple mean-field (MF) model, proposed originally by Haan [Phys. Rev. A 20, 2516 (1979)] for one component liquid, is applied to the case of binary mixture, and compared with the simulation results. While the MF model successfully describe the dynamics of the AA and AB pair, the agreement for the BB pair is less satisfactory. This is attributed to the large scale anharmonic motions of the B particles in a weak effective potential. Dynamics of next nearest neighbor pairs are also investigated.

I. INTRODUCTION

In dense fluids, there are many interaction-induced phenomena that can be interpreted in terms of the dynamics of the pairs of atoms. For example, nuclear overhauser effect studies the relative motion of the atoms. In addition, an understanding of pair dynamics can be of great importance in the studies of rate of various diffusion controlled chemical reactions in dense fluids. Both the theoretical analysis and computer simulation studies have been carried out extensively to study the dynamics of a pair of atoms in an one component liquid. Surprisingly, however, we are not aware of any explicit study of the dynamics of atomic pairs in binary mixtures whose dynamics generally show strong nonmonotonic composition dependence.

The study of the electronic spectroscopy of dilute chromophores (solutes) in fluids (solvents) is a useful tool for obtaining the information about the structure and dynamics of the solvents in the vicinity of the solute. In an attempt to provide a microscopic foundation of the Kubo’s stochastic theory of the line shape, Skinner and coworkers have recently developed a molecular theory for the absorption and emission line shapes and ultrafast solvation dynamics of a dilute nonpolar solute in nonpolar fluids. Due to the motion of the solvent molecules relative to the chromophore, the chromophore’s transition frequency generally fluctuates in time. Thus the nature of the spectral line shape provide a useful information about the details of the dynamics of the solvent relative to the solute. An approximate treatment of the solvent dynamics allowed the theory to express the transition frequency fluctuation time correlation functions (related to the expressions for the absorption and emission line shapes) solely in terms of the two-body solute-solvent time-dependent conditional pair distribution function. Many other applications of pair dynamics have been discussed by a number of authors.

The dynamics of a liquid below its freezing temperature, that is, in a supercooled state, is far more complex than what one would expect from a naive extrapolation of their high-temperature behavior. One of the most challenging problems in the dynamics of a supercooled liquid is to understand quantitatively the origin of the non-exponential relaxation exhibited by various dynamical response functions and the extraordinary viscous slow-down within a narrow temperature range as one approaches the glass transition temperature from above. Many experimental studies, as well as computer simulations, have been performed to shed light on the underlying microscopic mechanism involved in supercooled liquids. These studies have revealed the evidence of the presence of distinct relaxing domains (spatial heterogeneity) which is thought to be responsible for the non-exponential relaxations in deeply supercooled liquids. Molecular motions in strongly supercooled liquid involves highly collective movement of several molecules. Furthermore, the correlated jump motions become the dominant diffusive mode. The observed heterogeneity of the relaxations in a deeply supercooled liquid is found...
to be connected to the collective hopping of groups of particles\textsuperscript{30}.

The occurrence of increasingly heterogeneous dynamics in supercooled liquids, however, has been investigated solely in terms of single particle dynamics. The study of the dynamics of pair of atoms which involve higher order (two-body) correlations thus can provide much broader insight into the anomalous dynamics of supercooled liquids. In this work, we have carried out molecular dynamics simulations in a strongly non-ideal glass forming binary mixture (commonly known as Kob-Andersen model\textsuperscript{21}) to study the relaxation mechanism in terms of the pair dynamics. The main purpose of the present study is to explore the dynamics in a more collective sense by following the relative motion of three different type (AA, BB, and AB) of nearest neighbor and next nearest neighbor pair of atoms. These three pairs are found to behave differently. The simulation results show a clear signature of hopping motion in all the three pairs. We have also performed simple mean-field (MF) model (as introduced by Haan\textsuperscript{3} for one component liquid) calculations to obtain the time dependent conditional pair distribution functions.

The organization of the rest of the paper is as follows. In Sec. II, we describe the details of the simulation and the model system used in this study. The simulation results are presented and discussed in Sec. III. In Sec. IV, we have presented a mean-field model calculations for pair dynamics in binary mixture and the comparison is made with the simulation results. Finally, we end with a few concluding remarks in Sec. V.

\section{II. SYSTEM AND SIMULATION DETAILS}

We performed a series of equilibrium isothermal-isobaric ensemble (NPT) molecular dynamics (MD) simulation of a strongly non-ideal well-known glass forming binary mixture in three dimensions. The binary system studied here contains a total of $N = 1000$ particles consisting of two species of particles, $A$ and $B$ with $N_A = 800$ and $N_B = 200$ number of A and B particles, respectively. Thus, the mixture consists of 80\% of A particles and 20\% of B particles. The interaction between any two particles is modeled by means of shifted force Lennard-Jones (LJ) pair potential\textsuperscript{22}, where the standard LJ is given by

$$u_{ij}^{LJ} = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$ (1)

where $i$ and $j$ denote two different particles ($A$ and $B$). The potential parameters are as follows: $\varepsilon_{AA} = 1.0$, $\sigma_{AA} = 1.0$, $\varepsilon_{BB} = 0.5$, $\sigma_{BB} = 0.88$, $\varepsilon_{AB} = 1.5$, and $\sigma_{AB} = 0.8$. The mass of the two species are same ($m_A = m_B = m$). Note that in this model system the AB interaction ($\varepsilon_{AB}$) is much stronger than both of their respective pure counterparts and $\sigma_{AB}$ is smaller than what is expected from the Lorentz-Berthelot mixing rules. In order to lower the computational burden the potential has been truncated with a cutoff radius of $2.5\sigma_{AA}$. All the quantities in this study are given in reduced units, that is, length in units of $\sigma_{AA}$, temperature $T$ in units of $\varepsilon_{AA}/k_B$, pressure $P$ in units of $\varepsilon_{AA}/\sigma_{AA}^3$. The corresponding microscopic time scale is $\tau = \sqrt{m\sigma_{AA}^2/\varepsilon_{AA}}$.

All simulations in the NPT ensemble were performed using the Nose-Hoover-Andersen method\textsuperscript{52} where the external reduced temperature is held fixed at $T^* = 1.0$. The external reduced pressure has been kept fixed at $P^* = 20.0$. The reduced average density $\rho^*(= \rho\sigma_{AA}^3)$ of the system corresponding to this thermodynamic state point is 1.32. Throughout the course of the simulations, the barostat and the system’s degrees of freedom are coupled to an independent Nose-Hoover chain\textsuperscript{34} (NHC) of thermostats, each of length 5. The extended system equations of motion are integrated using the reversible integrator method\textsuperscript{4} with a time step of 0.002. The higher order multiple time step method has been employed in the NHC evolution operator which lead to stable energy conservation for non-Hamiltonian dynamical systems\textsuperscript{35}. The extended system time scale parameter used in the calculations was taken to be 1.15 for both the barostat and thermostats.

The systems were equilibrated for $2 \times 10^6$ time steps and simulations were carried out for another $10^7$ production steps following equilibration, during which the quantities of interest are calculated.

\section{III. SIMULATION RESULTS AND DISCUSSION}

The three partial radial distribution functions, $g_{AA}(r)$, $g_{AB}(r)$ and $g_{BB}(r)$ obtained from simulations are plotted in figure 1. Due to the strong mutual interaction, the AB correlation is obviously the strongest among the three pairs. The splitting of the second peak of both $g_{AA}(r)$ and $g_{AB}(r)$ is a characteristic signature of dense random packing. The structure of $g_{BB}(r)$ is interestingly different. It has an insignificant first peak which originates from the weak interaction between the B type particles. The second peak of $g_{BB}(r)$ is higher than that of the first peak signifying that the predominant BB correlation takes place at the second coordination shell. The occurrence of the splitted second peak is clearly observed here also.

In the present study, the central quantity of interest is the time-dependent pair distribution function (TDPDF) (first introduced by Oppenheim and Bloom\textsuperscript{1} in the theory of nuclear spin relaxation in fluids), $g_{2}(r_o; r; t)$ which is the conditional probability that two particles are separated by $r$ at time $t$ if that pair were separated by $r_o$ at time $t = 0$. Thus, the TDPDF measures the relative motion of a pair of atoms. For an isotropic fluid, the TDPDF depends only on the magnitudes of $r$, $r_o$, and $\theta$, where $\theta$ is the angle between $r$ and $r_o$. In computer simulation, one can readily evaluate separately the radial and orientational features of the relative motion. In the
following two subsections, we present, respectively, the results obtained for the time evolution of the radial part $g_{2,rad}(r_o, r; t)$ and the angular part $g_{2,ang}(r_o, \theta; t)$ of the TDPDF for the three different pairs (AA, BB and AB).

A. Radial part of the TDPDF, $g_{2,rad}(r_o, r; t)$

In figure 2 we plot the $g_{2,rad}(r_o, r; t)$ for the AA pair with the initial separation $r_o$ corresponds to the first maximum of the partial radial distribution function $g_{AA}(r)$ (that is, pairs which are nearest neighbor) at four different times. While at short time (figure 2(a)) the distribution function has a single peak structure as expected, with increase in time it reaches slowly to its asymptotic limit where additional peaks develop at larger relative separations (see figures 2(b)-2(d)). The microscopic details of the underlying diffusive process (by which it approach to the asymptotic structure) can be obtained by following the trajectory of the relative motions. Figure 3 displays the projections onto an x-y plane of the trajectory of a typical AA pair for the nearest neighbor A atoms over a time interval $\Delta t = 500\tau$. The motion of the AA pair is shown to be relatively localized for many time steps and then move significant distances only during quick, rare cage rearrangements. This is a clear evidence that the jump motions are the dominant diffusive mode by which the separation between pairs of atoms evolve in time.

The behavior of the distribution function $g_{2,rad}(r_o, r; t)$ for the AB pairs (where the interaction being the strongest) is plotted in figure 4 at four different times. The distribution function shows the same qualitative behavior as we observed in the case of AA correlation (figure 2). When compared to the AA correlation function within the same time scale, the decay of the correlation function is found to be faster despite the much strong AB interaction. This must be attributed to the difference in size of the two types of particles. As the B particles are smaller in size than the A particles, they are more mobile. In addition, the AB interaction is such that AB repulsion is felt at relatively small distances ($\sigma_{AB} = 0.8$ instead of 0.94 according to the Lorentz-Berthelot rules). Consequently, the B particles are more prone to make jumps than the A particles (as observed earlier by Kob and Andersen [21]).

The nature of the relative motion of a typical AB pair is illustrated in figure 5(a), which display the trajectory of a typical AB pair (in the x-y plane) that were initially at the nearest neighbor (first peak of $g_{AB}(r)$). The elapsed time is $\Delta t = 500\tau$. The dynamics of the relative motion is again dominated by hooping, the AB pair remain trapped at their initial separation over hundreds of time steps, before jumping to neighboring sites where they again become localized. Further, the jump motion is more frequent for the AB pair than that for the AA pair. The individual trajectory of the A and B particles of the same AB pair within the same time window is shown in figures 5(b) and 5(c), respectively. While both the A and B particles hop, B particles move faster and the effect of caging is weaker (than the A particles) due to its smaller size. In this time window, the net displacement of the AB pair in the x-y plane is found to be quite large as shown in figure 6 and mainly determined by the displacement of the B particle.

In figure 7 we show $g_{2,rad}(r_o, r; t)$ for the BB pair initially separated at the first peak of $g_{BB}(r)$ at four different times. Due to weak interaction among B particles, one expects that the B atoms in the BB pair will fast lose the memory of their initial separation. This is indeed the case for the BB pair shown in figure 7. Once again the jump dynamics is clearly seen in the trajectory of a typical BB pair projected in the x-y plane (figure 8).

We now consider the case where the separation of the initial pairs corresponds to the second peak of their respective partial radial distribution functions of figure 1 (that is, pairs which are next nearest neighbor). The distribution function for the AA pair is plotted in figure 9. It shows a qualitative different behavior because the peak at the nearest neighbor separation develops in a relatively short time. Here also the motion of the pairs are found to be mostly discontinuous in nature, thus motion from second to first nearest neighbor occurs mostly by hopping. In figure 10 we plot the similar distribution function of the AB pair. Since the AB interaction is the strongest, the height of the first peak grows faster than that for the AA pair (compare figures 9(b) and 10(b)).

Next, in figure 11 we plot the distribution function for the BB pair. Contrary to the AA and AB pairs, BB pairs tend to retain their initial separation for a relatively long time compared to the nearest neighbor pair. This can be understood from the predominant BB correlations at the second coordination shell.

B. Angular part of the TDPDF, $g_{2,ang}(r_o, \theta; t)$

In this subsection we present the angular distribution function $g_{2,ang}(r_o, \theta; t)$ for the three different pairs (AA, BB and AB). The initial separation $r_o$ for the three pairs corresponds to the first peak of the respective partial radial distribution functions (figure 1).

In figure 12(a) we show the angular distribution $g_{2,ang}(r_o, \theta; t)$ for the AA pair. We calculate the angular distribution with respect to the initial separation vector $r_o$ and irrespective of the value of the separation at time $t$. The distribution which is a $\delta$-function at $t = 0$, spreads more and more with time and eventually it reaches to a uniform distribution with zero slope. When we compare to the distribution corresponding to the AB pair as shown in figure 12(b), we find that the approach to the uniform value is faster in the case of AB pair. This can be understood again in terms of the mobility of the B particles which is more compared to the A particles. In figure 12(c) we show how the distribution for the BB pair changes with time. The relaxation is seen to be rel-
atively slower at short times compared to the AB pair. This can be understood in terms of the effective potential, discussed later.

### C. Relative diffusion: Mean square relative displacement (MSRD)

In this subsection, we investigate the time dependence of the mean square relative displacement \( \langle |r_{ij}(t) - r_{ij}(0)|^2 \rangle_{r_o} \), the simplest physical quantity associated with the pair motion, where the index \( i \) and \( j \) denote A and/or B particles and the subscript \( r_o \) indicates the ensemble averaging is restricted to the pairs whose initial separation corresponds to \( r_o \). First, we consider the case where the initial separations for the three pairs corresponds to the first peak of the respective partial radial distribution functions (see figure 1). In other words, we consider first those pairs that were initially nearest neighbor pairs.

Figure 13 shows the result for the time dependence of the relative mean square displacement (MSRD) of the three pairs. At long times the MSRD varies linearly with time. However, the evolution of MSRD with time differs for different pairs. As expected, the smaller size of the B particles and the weak BB interaction leads to a faster approach of the diffusive limit of BB pair separation. The time scale needed to reach the diffusive limit is shorter for the AB pair than that for the AA pair.

From the slope of the curves in the linear region one can obtain the values of the relative diffusion constants \( D_R \) of the different pairs. The values thus obtained are the following: \( D_{RA} \approx 0.0032, D_{RB} \approx 0.0048 \) and \( D_{BB} \approx 0.0064 \). One should note that even though the difference in size of the A and B particles is small, \( D_{BB} \) is almost twice of \( D_{RA} \). At sufficiently long time, one would certainly expect the diffusion constant for the relative motion of a pair to be the sum of the individual diffusion constants of the two atoms obtained from the slope of the corresponding mean square displacements at long time. Indeed, we find there is a good agreement.

An investigation of the behavior of MSRD is also performed for atomic pairs which were initially next nearest neighbor. When compared to the nearest neighbor pairs (figure 13) we find that the slope of the corresponding straight lines are almost identical, although in the case of AA and AB pairs the diffusive limits are reached at shorter times. This has been shown in figure 14. One should remember that the AA and AB correlations are highest at the first coordination shell whereas the highest BB correlations occur at the second coordination shell (see figure 1). Thus, at short time the increase in slope for the AA and AB pairs can be explained in terms of the decrease in correlations at the second coordination shell.

### D. The non-Gaussian parameter for the relative motion

In a highly supercooled liquid, the single particle displacement distribution function \( G_s(r, t) \) (known as the self-part of the van Hove correlation function) has an extended tail and is, in general, non-Gaussian. The deviation from the Gaussian behavior is often thought to reflect the presence of the transient inhomogeneities and can be characterized by the non-Gaussian parameter \( \alpha_2(t) \)

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

where \( \langle \Delta r^2(t) \rangle \) and \( \langle \Delta r^4(t) \rangle \) are the second and fourth moments of \( G_s(r, t) \), respectively. At intermediate time scale, \( \alpha_2(t) \) increases with time and the maximum of \( \alpha_2(t) \) occurs around the end of the \( \beta \) relaxation region. Only on the time scale of diffusion or the \( \alpha \) relaxation, \( \alpha_2(t) \) starts to decrease and finally at very long time limit, it reaches to zero. \( \alpha_2(t) \) calculated for the A and B particles are shown in figure 15. The maximum in \( \alpha_2(t) \) is seen to shift slightly towards left and also the height of the maximum is higher for the B particles. This is a clear evidence that the B particles probe much more heterogeneous environment than does the A particles. This difference can be explained in terms of the smaller concentration of B particles, different sizes of the A and B particles and also from the fact that the interaction between the B particles is much weaker than that between the A particles.

Motivated by these findings for the single particle displacement distribution function, we introduce a new non-Gaussianity parameter for the pair dynamics, denoted by \( \alpha_2^P(t) \). \( \alpha_2^P(t) \) can be a measure of the deviation from the Gaussian behavior of the pair distribution function \( g_2(r_o, r; t) \). It can be defined as,

\[
\alpha_2^P(t) = \frac{3\langle |r_{ij}(t) - r_{ij}(0)|^4 \rangle_{r_o}}{5\langle |r_{ij}(t) - r_{ij}(0)|^2 \rangle_{r_o}^2} - 1, \quad (i, j = A \text{ and/or } B) \tag{3}
\]

where \( \langle |r_{ij}(t) - r_{ij}(0)|^2 \rangle_{r_o} \) and \( \langle |r_{ij}(t) - r_{ij}(0)|^4 \rangle_{r_o} \) are the mean square relative displacement and mean quartic relative displacement of the \( ij \) pair. One should note that \( \alpha_2^P(t) \) is identical to zero for a Gaussian pair distribution function.

In figure 16 we show the behavior of the \( \alpha_2^P(t) \) as a function of time for the three different pairs. We again consider only those pairs that were initially nearest neighbor. The behavior observed for the three pairs is markedly different. The dynamics explored by the BB pair is seen to be less heterogeneous than the AA and AB pairs. Because of the smaller size of the B particles, the B particles reach the average distribution faster, although it explores larger heterogeneity. The AA pair reaches the diffusive limit at longer time scale than that for the AB pair, the AB pair explore more heterogeneous dynamics.
as is clearly evident from the difference in the maximum value of \( \alpha_p^2(t) \).

**IV. THEORETICAL ANALYSIS**

For the motion of an atomic pair in a pure fluid, Haan\cite{2} introduced a simple mean-field level equation of motion for the time-dependent pair distribution function \( g_2 \). This equation was shown to give a quantitatively correct description both at short and long times\cite{13}. This treatment is mean-field in the sense that the two atoms were assumed to diffuse in an effective-force field of the surrounding particles given by the gradient of the potential of mean force. The equation for \( g_2 \) was represented by a Smoluchowski equation and the correct short time description of \( g_2 \) was obtained only by introducing a non-linear time that is related to the mean-squared distance (MSD) moved by a single atom. In other words, an \textit{ad hoc} introduction of a time-dependent diffusion constant \( D(t) \) in the equation of motion gives the correct description at short times.

In the view of its success for one-component liquid, we have performed a similar mean-field model calculations for the binary mixture considered here. The generalization to binary mixture gives the following Smoluchowski equation for the different pairs

\[
\frac{\partial g^{ij}_{2}(\mathbf{r}_o, \mathbf{r}; t)}{\partial \tau_{ij}} = \nabla \cdot \left[ \nabla g^{ij}_{2}(\mathbf{r}_o, \mathbf{r}; t) + \beta g^{ij}_{2}(\mathbf{r}_o, \mathbf{r}; t) \nabla W^{ij}_{o}(r) \right],
\]

where the index \( i \) and \( j \) denote A and/or B particles. \( \beta \) is the inverse of the Boltzmann’s constant \( (k_B) \) times the absolute temperature \( (T) \). \( W^{ij}_{o}(r) \) is the potential of mean force (‘effective potential’) between the \( i \) and \( j \) particles given by

\[
W^{ij}_{o}(r) = -k_BT \ln g^{ij}_{o}(r)
\]

where \( g^{ij}_{o}(r) \) is the partial radial distribution function. In Eq. 4, the ”time” \( \tau_{ij} \) is defined by

\[
\tau_{ij} = \frac{1}{6} \left( | \mathbf{r}_{ij}(t) - \mathbf{r}_{ij}(0) |^2 \right)_{\mathbf{r}_o}
\]

\[
\approx \frac{1}{6} \left[ \left( | \mathbf{r}_{ij}(t) - \mathbf{r}_i(0) |^2 \right)_{\mathbf{r}_o} + \left( | \mathbf{r}_{ij}(t) - \mathbf{r}_j(0) |^2 \right)_{\mathbf{r}_o} \right]
\]

where \( | \mathbf{r}_{ij}(t) - \mathbf{r}_{ij}(0) |^2 \) is the mean square relative displacement (MSRD) of the ‘\( ij \)’ pair. Note that an approximation is made in the above equation by neglecting the cross-correlation between the two particles (‘\( i \)' and ‘\( j \)’) and the MSRD is replaced by the sum of individual particle’s mean square displacement (MSD).

Now the integration of the \( g^{ij}_{2}(\mathbf{r}_o, \mathbf{r}; t) \) over the solid angles \( \hat{\Omega}_o \) and \( \hat{\Omega} \) corresponding to the initial and final positions, respectively, gives the radial part of the full distribution function (the zeroth-angular moment of \( g^{ij}_{2}(\mathbf{r}_o, \mathbf{r}; t) \))

\[
g^{ij}_{2,rad}(r_0, r; t) = \frac{1}{4\pi} \int d\hat{\Omega}_o \int d\hat{\Omega} g^{ij}_{2}(\mathbf{r}_o, \mathbf{r}; t)
\]

Note that the normalization of this function is

\[
\int_{0}^{\infty} dr r^2 g^{ij}_{2,rad}(r_0, r; t) = 1
\]

The equation of motion for \( g^{ij}_{2,rad}(r_0, r; t) \) (derived from Eq. 4) is solved numerically (by Crank-Nicholson method) for the different pairs and the results obtained from this model calculations are compared with the simulation results. The partial radial distribution functions \( g^{ij}_{o}(r) \) and the mean-square displacements of the A and B particles (required as input) are obtained from the present simulation.

Figures 17 and 18 compare model calculations with the simulated distribution functions for the AA and AB nearest neighbor pairs. The time evolution of the distributions are described well by the simple mean-field model. The underlying effective-potential energy surfaces are plotted in figure 19. Thus relative diffusion in these cases can be considered as overdamped motion in an effective potential, which takes place mainly via hopping (as shown in figures 3 and 5), which governs the time evolution of the distributions for the AA and AB pair.

Unfortunately, the good agreement observed above between simulation and theory for the AA and the AB pairs, does not extend to the BB pair. This is shown in figure 20. As the number of B particles present in the system is much less (20 %) and the interparticle interaction is weak, the effective potential for a B atom interacting with a nearest neighbor atom is unfavorable (see the figure 19). Consequently, the nearest neighbor BB pairs execute highly anharmonic motions. Thus, the fluctuations about the mean-force field experienced by the BB pair are large and important. These fluctuations are neglected here, as in other mean-field level description.

The extension of the calculations to the case of next nearest neighbor pairs also been carried out and compared with the simulated distributions. It should be noted that compared to the nearest neighbor pairs, the AA and AB pairs are now executes motions in a relatively weak, shallow potential, whereas the motions of the BB pairs takes place in a relatively strong, bound potential well (see the figure 19). Thus, for the BB pairs, one expects a better agreement with the simulated distributions compared to the earlier case (nearest neighbor BB pairs). Indeed, the agreement is better for the BB pairs, as shown in figure 21 (compare with figure 20). We have found that the MF model provides a good description of the dynamics of the AA and AB pairs, although the agreement is not as satisfactory as for the nearest neighbor pairs.

Thus, it is evident that the MF description for the time dependent pair distribution functions is reasonably good for the AA and AB pairs. Simulation results have shown that the relative diffusion of an AB pair is higher than that for an AA pair. We noted that this due to
more frequent hopping of B particles than the A particles. Our main objective now is to see whether the frequent jump motions of the B particles, as predicted by the simulations, can be explained in terms of the MF model described above.

We have performed an approximate calculation to get an estimate of the transition rate between the first two adjacent minima in the effective potential energy surface of the AA and AB pairs (see the figure 21). In other words, the rate of crossing from the deep minima located at the nearest neighbor pairs, to the adjacent minima (corresponds to the next nearest neighbors). As the motion of a pair in the effective potential was treated by (corresponds to the next nearest neighbors). As the motion of a pair in the effective potential was treated by a Smoluchowski equation, we use the corresponding rate expression in the overdamped limit to calculate the escape rate. Thus, we have an expression for the escape rate given by

\[ k_S \cong \frac{\omega_{\text{min}}^* \omega_{\text{max}}^*}{2\pi \zeta} \exp \left( -\frac{\Delta W}{k_B T} \right) \]  

(9)

where \( \Delta W = W(r_{\text{max}}) - W(r_{\text{min}}) \) is the Arrhenius activation energy and \( \omega_{\text{min}}^* \), \( \omega_{\text{max}}^* \) are the frequency at the minima \( r_{\text{min}} \) and maxima \( r_{\text{max}} \) in the effective potential \( W(r) \), respectively. The diffusion coefficient \( D \) is related to the friction \( \zeta \) by \( D = k_B T/\zeta \).

Thus, to calculate the transition rate we need to know the values of the frequencies \( \omega_{\text{min}}^* \), \( \omega_{\text{max}}^* \), and the barrier height \( \Delta W \), which are different for the AA and AB pairs. For the AA pairs, these parameters are found to be \( \omega_{\text{min}}^* \simeq 16.5, \omega_{\text{max}}^* \simeq 6.5 \) and \( \Delta W_{\text{AA}} \simeq 2.25k_B T \), whereas for the AB pairs they are \( \omega_{\text{min}}^* \simeq 17.8, \omega_{\text{max}}^* \simeq 7.4 \) and \( \Delta W_{\text{AB}} \simeq 2.45k_B T \). The relative diffusion of the two pairs are \( D_{\text{AA}}^R \simeq 0.0032 \) and \( D_{\text{AB}}^R \simeq 0.0048 \). Using all these parameters, the escape rate calculated for the AA and AB pairs are (in reduced units) \( k_S^{AA} \simeq 5.9 \times 10^{-3} \) and \( k_S^{AB} \simeq 8.8 \times 10^{-3} \), respectively (in terms of time \( \tau \), which is equal to 2.2 ps for argon units).

Even though the barrier height \( \Delta W_{\text{AB}} > \Delta W_{\text{AA}} \), the transition rate for the AB pair is larger than that for the AA pair. Thus, the jump motions are much more frequent for the AB pair, due to the large diffusion of the B particles in the potential energy surface (which mainly occurs via hopping mode).

V. CONCLUSIONS

Let us first summarize the main results of this study. We have presented the molecular dynamics simulation results for the time dependent pair distribution functions in a strongly non-ideal glass forming binary Lennard-Jones mixture. In addition, a mean-field description of the pair dynamics is considered and the comparison is made with the simulated distributions. The main goal of this investigation was to explore the dynamics of the supercooled liquids in a more collective way, by following the relative motion of the atoms rather than absolute motion of the atoms. We find that the three pairs (AA, BB and AB) behave differently. The analysis of the trajectory shows a clear evidence of the jump motions for all the three pairs.

The relative diffusion constant of the BB pair \( (D_{\text{BB}}^R) \) is almost twice the value for the AA pair \( (D_{\text{AA}}^R) \). This clearly suggests the importance of the jump dynamics for the B particles and indeed, we find that the motion of the B particles is mostly discontinuous in nature, while the A particles show occasional hopping. The dynamic inhomogeneity present in a supercooled liquid is generally characterized by the well-known non-Gaussian parameter \( \alpha_2(t) \), which describe the deviations from the Gaussian behavior in the motion of a single atom. In this paper, we have generalized this concept and introduce a non-Gaussian parameter for the pair dynamics \( (\alpha_2^p(t)) \), to measure the deviations from the mean behavior in the relative motion of the atoms. At intermediate times, all the three pair distribution functions for the three pairs show significant deviations from the Gaussian behavior, with different degree.

It is found that for the nearest neighbor AA and AB pairs, which are confined to a strong effective potential and merely makes anharmonic motions in it, the dynamics can be treated at the mean-field level. However, as the motion of a nearest neighbor BB pair is highly anharmonic, one must include the effects of the fluctuations about the mean-force field, in order to get a correct description of the dynamics.

While the mean-field treatment provides reasonably accurate description of pair dynamics (at least for AA and AB pairs), it must be supplemented with the time dependent diffusion coefficient \( (D(t)) \). This is a limitation of the mean-field approach because at present we do not have any theoretical means to calculate \( D(t) \) from first principles. The mode coupling theory (MCT) does not work because it neglects hopping which is the dominant mode of mass transport in deeply supercooled liquids, even when the system is quite far from the glass transition. As we discussed recently, the hopping can be coupled to anisotropy in the local stress tensor \( \Sigma \). The calculation of the latter is also non-trivial. Work in this direction is under progress.

Acknowledgments

This work was supported in part by the Council of Scientific and Industrial Research (CSIR), India and the Department of Science and Technology (DST), India. One of the authors (R.K.M) thanks the University Grants Commission (UGC) for providing the Research Scholarship.
[1] I. Oppenheim and M. Bloom, Can. J. Phys. 39, 845 (1961).
[2] J. A. Bucaro and T. A. Litovitz, J. Chem. Phys. 54, 3846 (1971); A. J. C. Ladd, T. A. Litovitz, and C. J. Montrose, ibid. 71, 4242 (1979); A. J. C. Ladd, T. A. Litovitz, J. H. R. Clarke, and L. V. Woodcock, ibid. 72, 1759 (1980).
[3] M. S. Miller, D. A. McQuarrie, G. Birnbaum, and J. D. Poll, J. Chem. Phys. 57, 618 (1972).
[4] S. A. Adelman, Adv. Chem. Phys. 53, 61 (1983).
[5] J. T. Hynes, R. Kapral, and G. M. Torrie, J. Chem. Phys. 72, 177 (1980).
[6] S. W. Haan, Phys. Rev. A 20, 2516 (1979).
[7] C. D. Boley and G. Tenti, Phys. Rev. A 21, 1652 (1980).
[8] U. Balucani and R. Vallauri, Physica A 102, 1652 (1980).
[9] U. Balucani, R. Vallauri, C. S. Murthy, T. Gaskell, and M. S. Woolfson, J. Phys. C: Solid State Phys. 16, 5605 (1983); U. Balucani, R. Vallauri, T. Gaskell, and M. Gori, ibid. 18, 3133 (1985).
[10] H. Posch, F. Vesely, and W. Steele, Mol. Phys. 44, 241 (1981).
[11] G. T. Evans and D. Kivelson, J. Chem. Phys. 85, 7301 (1986).
[12] Ten-Ming Wu and S. L. Chang, Phys. Rev. E 59, 2993 (1999).
[13] G. Srinivas, A. Mukherjee, and B. Bagchi, J. Chem. Phys. 114, 6220 (2001).
[14] R. K. Murarka and B. Bagchi, J. Chem. Phys. 117, 1155 (2002).
[15] J. G. Saven and J. L. Skinner, J. Chem. Phys. 99, 4391 (1993); M. D. Stephens, J. G. Saven, and J. L. Skinner, J. Chem. Phys. 106, 2129 (1997).
[16] A. D. Santis, A. Ercoli, and D. Rocca, Phys. Rev. E 57, R4871 (1998); Phys. Rev. Lett. 82, 3452 (1999).
[17] P. G. Debenedetti and F. H. Stillinger, Nature 410, 554 (1998).
[18] B. Doliwa and A. Heuer, Phys. Rev. Lett. 80, 4915 (1998); J. Qian, R. Hentschke, and A. Heuer, J. Chem. Phys. 110, 4514 (1999).
[19] C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Phys. Rev. Lett. 80, 2338 (1998).
[20] S. Bhattacharyya and B. Bagchi, Phys. Rev. Lett. 89, 25504 (2002).
[21] S. Bhattacharyya, A. Mukherjee, and B. Bagchi, J. Chem. Phys. 117, 2741 (2002).
[22] C. Oligschleger and H. R. Schober, Phys. Rev. B 59, 811 (1999).
[23] H. Miyagawa, Y. Hiwatari, B. Bernu, and J. P. Hansen, J. Chem. Phys. 88, 3879 (1988).
[24] D. Caprion, J. Matsui, and H. R. Schober, Phys. Rev. Lett. 85, 4293 (2000).
[25] M. P. Allen and D. J. Tildesley, Computer Simulation of Liquids (Oxford University Press, Oxford, 1987).
[26] G. J. Martyna, D. J. Tobias, and M. L. Klein, J. Chem. Phys. 101, 4177 (1994); H. C. Andersen, J. Chem. Phys. 72, 2384 (1980); S. Nose, Mol. Phys. 52, 255 (1984); W. G. Hoover, Phys. Rev. A 31, 1695 (1985).
[27] G. J. Martyna, M. E. Tuckerman, and M. L. Klein, J. Chem. Phys. 97, 2635 (1992).
[28] M. E. Tuckerman, G. J. Martyna, and B. J. Berne, J. Chem. Phys. 97, 1990 (1992).
[29] G. J. Martyna, M. E. Tuckerman, D. J. Tobias, and M. L. Klein, Mol. Phys. 87, 1117 (1996).
[30] R. Zwanzig, Non-equilibrium Statistical Mechanics (Oxford University Press, New York, 2001).
Figure Captions

Figure 1. The radial distribution function \( g(r) \) for the AA, AB, and BB correlation is plotted against distance. The solid line is \( g_{AA}(r) \), the dashed line is \( g_{AB}(r) \), and the dot-dashed line is \( g_{BB}(r) \). For details, see the text.

Figure 2. The radial part of the time-dependent pair distribution function \( g_{2, rad}(r_o, r; t) \) for the AA pair as a function of separation \( r \) at four different times: (a) \( t = 20 \tau \), (b) \( t = 50 \tau \), (c) \( t = 100 \tau \), and (d) \( t = 300 \tau \). The initial separation \( r_o \) corresponds to the first maximum of \( g_{AA}(r) \). Note that the time unit \( \tau = 2.2 \text{ps} \) if argon units are assumed.

Figure 3. Projections into x-y plane of the trajectory of a typical nearest neighbor AA pair over a time interval \( t = 500 \tau \). Note that the time unit \( \tau = 2.2 \text{ps} \) for argon units.

Figure 4. The radial part of the time-dependent pair distribution function \( g_{2, rad}(r_o, r; t) \) for the AB pair as a function of separation \( r \) at four different times: (a) \( t = 20 \tau \), (b) \( t = 50 \tau \), (c) \( t = 100 \tau \), and (d) \( t = 300 \tau \). The initial separation \( r_o \) corresponds to the first maximum of \( g_{AB}(r) \). The time unit \( \tau = 2.2 \text{ps} \) for the argon units. For further details, see the text.

Figure 5. (a) Projections into x-y plane of the trajectory of a typical nearest neighbor AB pair over a time interval \( t = 500 \tau \). (b) Trajectory of the A particle of the same AB pair as in (a), within the same time window. (c) Trajectory of the B particle of the same AB pair.

Figure 6. The net displacement of an AB pair into x-y plane \((\Delta L_{xy})\) as shown in figure 5(a), in the same time interval. Note that the displacement is quite large.

Figure 7. The radial part of the time-dependent pair distribution function \( g_{2, rad}(r_o, r; t) \) for the BB pair as a function of separation \( r \) at four different times: (a) \( t = 20 \tau \), (b) \( t = 50 \tau \), (c) \( t = 100 \tau \), and (d) \( t = 300 \tau \). The initial separation \( r_o \) corresponds to the first peak of \( g_{BB}(r) \).

Figure 8. Projections into x-y plane of the trajectory of a typical nearest neighbor BB pair over a time interval \( t = 500 \tau \).

Figure 9. The radial part of the pair distribution function \( g_{2, rad}(r_o, r; t) \) for the AA pair at four different times: (a) \( t = 4 \tau \), (b) \( t = 20 \tau \), (c) \( t = 100 \tau \), and (d) \( t = 300 \tau \). Here the initial separation \( r_o \) is chosen at the second peak of \( g_{AA}(r) \).

Figure 10. The radial part of the pair distribution function \( g_{2, rad}(r_o, r; t) \) for the AB pair at four different times: (a) \( t = 4 \tau \), (b) \( t = 20 \tau \), (c) \( t = 100 \tau \), and (d) \( t = 300 \tau \). Here the initial separation \( r_o \) corresponds to the second peak of \( g_{AB}(r) \).

Figure 11. The radial part of the pair distribution function \( g_{2, rad}(r_o, r; t) \) for the BB pair at four different times: (a) \( t = 4 \tau \), (b) \( t = 20 \tau \), (c) \( t = 100 \tau \), and (d) \( t = 300 \tau \). Here the initial separation \( r_o \) is chosen at the second peak of \( g_{BB}(r) \).

Figure 12. (a) The angular part of the time-dependent pair distribution function \( g_{2, ang}(r_o, \theta; t) \) for the AA pair at four different times. (b) \( g_{2, ang}(r_o, \theta; t) \) for the AB pair. (c) \( g_{2, ang}(r_o, \theta; t) \) for the BB pair. In all the three cases, we consider only those pairs which were initially separated at the nearest neighbor distance. For further details, see the text.

Figure 13. Time dependence of the mean square relative displacement (MSRD) for the AA, AB and BB pair (in units of \( \sigma_{AA}^2 \)). The initial separation \( r_o \) of the three pairs corresponds to the first peak of the respective partial radial distribution functions. The solid line represents the result for the AA pair, the dashed line AB pair, and the dotted line for the BB pair. For the detailed discussion, see the text.

Figure 14. (a) Comparison of the mean square relative displacement (MSRD) for the AA pair with different initial separations. The solid line represents the nearest neighbor AA pair and the dashed line represents the next nearest neighbor AA pair. (b) Same as in (a), but for the AB pair. (c) For the BB pair. For details, see the text.

Figure 15. The behavior of the non-Gaussian parameter \( \alpha_2^P(t) \) as a function of time for the A and B particles. The solid line is for the A particles and the dashed line for the B particles.

Figure 16. The behavior of the non-Gaussian parameter \( \alpha_2^P(t) \) as a function of time for the AA, AB, and BB pairs, initially separated at the nearest neighbor distance. The solid line represents the result for the AA pair, the dashed line for the AB pair, and the dot-dashed line for the BB pair.

Figure 17. The simulated distribution \( g_{2, rad}(r_o, r; t) \) for the AA pair is compared with the mean-field model calculations at three different times: (a) \( t = 10 \tau \), (b) \( t = 50 \tau \), and (c) \( t = 100 \tau \). The initial separation \( r_o \) corresponds to the first maximum of \( g_{AA}(r) \). The histogram represents the simulation results and the dashed line represents the results of the model calculations. Note that the time unit \( \tau = 2.2 \text{ps} \) if argon units are assumed.

Figure 18. The simulated distribution \( g_{2, rad}(r_o, r; t) \) for the AB pair is compared with the mean-field model calculations at three different times: (a) \( t = 10 \tau \), (b) \( t = 50 \tau \), and (c) \( t = 100 \tau \). The initial separation \( r_o \) corresponds to the first maximum of \( g_{AB}(r) \). The histogram represents the simulation results and the dashed line represents the results of the model calculations.

Figure 19. The potential of mean force \( W(r) \) for the AA, AB and BB pairs in the Kob-Andersen model at the reduced pressure \( P^* = 20 \) and the reduced temperature \( T^* = 1.0 \). The solid line represents for the AA pair, the dashed line for the AB pair, and the dot-dashed line for the BB pair.

Figure 20. The simulated distribution \( g_{2, rad}(r_o, r; t) \) for the BB pair is compared with the mean-field model calculations at three different times: (a) \( t = 10 \tau \), (b) \( t = 50 \tau \), and (c) \( t = 100 \tau \). The initial separation \( r_o \) corresponds to the first peak of \( g_{BB}(r) \). The histogram represents the simulation results and the dashed line represents the results of the model calculations.

Figure 21. The simulated distribution \( g_{2, rad}(r_o, r; t) \) for the BB pair is compared with the mean-field model
calculations at two different times: (a) $t = 10\tau$ and (b) $t = 100\tau$. Here the initial separation $r_\circ$ corresponds to the second peak of $g_{BB}(r)$. The histogram again represents the simulation results and the dashed line represents the results of the model calculations. For further details, see the text.
$g_{2,\text{rad}}(r_0, r; t)$

(a) $t = 10\tau$

(b) $t = 50\tau$

(c) $t = 100\tau$

(d) $t = 300\tau$

$r / \sigma_{AA}$
\( \Delta L^{xy} \) vs. time (in \( \tau \))
\[ \sigma_{AA}^3 g_{2,\text{rad}}(r, r; t) \]

(a) \( t = 10\tau \)

(b) \( t = 50\tau \)

(c) \( t = 100\tau \)

(d) \( t = 300\tau \)
\begin{align*}
\sigma_{AA}^3 \cdot g_{2,\text{rad}}(r_0, r; t) & \quad t = 4\tau \\
\sigma_{AA}^3 \cdot g_{2,\text{rad}}(r_0, r; t) & \quad t = 20\tau \\
\sigma_{AA}^3 \cdot g_{2,\text{rad}}(r_0, r; t) & \quad t = 100\tau \\
\sigma_{AA}^3 \cdot g_{2,\text{rad}}(r_0, r; t) & \quad t = 300\tau
\end{align*}
\[ \sigma_{AA}^3 g_{2,\text{rad}}(r_o, r, t) \]

(a) \( t = 4\tau \)

(b) \( t = 20\tau \)

(c) \( t = 100\tau \)

(d) \( t = 300\tau \)
\[ g_{2,\text{ang}}(r_o, \theta; t) \]

- \( t = 10\tau \)
- \( t = 50\tau \)
- \( t = 100\tau \)
- \( t = 500\tau \)

\( \cos \theta \)
MSRD

AB pair

(b)

time (t)
$\sigma_{AA}^3 g_{2,\text{rad}}(r_0,r,t)$

depending on $t$:

(a) $t = 10\tau$

(b) $t = 50\tau$

(c) $t = 100\tau$
