Role of attractive interactions in the dynamics of a supercooled binary mixture: a molecular dynamics simulation study

A THESIS

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dedicated to

my family, Guide

and

my friends

for their love, care inspiration and support.

Declaration

I hereby declare that the entire work embodied in this thesis is the result of investigations carried out by me in **School of Basic Sciences, Indian Institute of Technology Mandi, Kamand, Mandi** under the supervision of **Dr. Prasanth P. Jose**, and that it has not been submitted elsewhere for any degree or diploma.

In keeping with the general practice, due acknowledgments have been made wherever the work described is based on finding of other investigators. Any omission which might have occured by oversight or error in judgement is regretted.

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Certificate

This is to certify that the thesis entitled **"Role of attractive interactions in the dynamics of a supercooled binary mixture: a molecular dynamics simulation study"**, submitted by **Duni Chand Thakur**, to the Indian Institute of Technology Mandi, Kamand, Mandi for the award of the degree of **Doctor of Philosophy**, is a bonafide record of the research work done by him under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other institute or university for the award of any degree or diploma.

In keeping with the general practice, due acknowledgments have been made wherever the work described is based on finding of other investigators.

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Duni Chand Thakur

Abstract

Liquid under fast cooling or fast compression undergoes a glass transition; while, a glass is an unconventional phase unlike liquid, gas, and solid. These phases are formed during the change of the thermodynamic parameters such as temperature or pressure at infinitely slow rate where the system relaxes to its lowest Gibbs free-energy minima and remains there. When thermodynamic parameters change, all systems move away from equilibrium, which at a long time relaxes to new minima. This simple view of the phase changes considerably get altered when the relaxation process slows down. Glasses are formed when a system is cooled or compressed at a higher rate than the relaxation can occur. The specification of how fast the compression or cooling is required to form glasses depends on the relaxation time of the liquids, which vary with intermolecular potentials. Glass transition occurs in the dense systems and glass has the same structure as that of a liquid with arrested dynamics. Many systems with different complex potentials show similarities in the relaxation process irrespective of complexity in the potential. One of the ways to develop theories of glass transition is by extending the theories of the liquid state. Investigations of Weeks-Chandler-Andersen (WCA) (J. Chem Phys. 54,5237(1971)) showed that dense Lennard-Jones systems can be well described by the repulsive part of the potential. A test of this by Berthier and Tarjus (Phys. Rev. Lett. 103, 170601(2009)) on the Kob-Andersen (Phys. Rev. Lett. 73, 1376(1994)) glass-forming binary mixture (A (80%) and B(20%) components) and its WCA variant (without the attractive part of the interaction) show that dynamics considerably vary at lower temperatures. There are many following investigations which looks into various aspect of the role of attractive interactions in glass transition. Inspired from results of these earlier studies, we attempt to explain the origin of the difference in dynamics as the interplay of the barriers of three interactions, namely, A-A, A-B, and B-B. We have looked into various aspects of glass transition and its density dependence with an emphasis on the role of attractive interaction.

Chapter 1: Presents a short introduction to the present understanding of the glass transition and difficulties in various theoretical formalisms, especially the relation between structure and dynamics *etc.* which is missing from the earlier studies. This is followed by a discussion on correlations on basic liquid state theory and their relevance in understanding

the relaxation and connection to glassy domain formation without attractive interactions. Basic theories of glass transition that are relevant to understand the problems addressed in this thesis is discussed: the schematic mode-coupling theory (MCT), the phenomenological Vogul-Fulcher-Tammann relation, Adam-Gibbs theory, random first-order transition theory, and free-volume theory. Next, the motivation for the studies presented in the thesis which details earlier studies that look into the role of attractive interactions in the system.

Chapter 2: Computer simulations bridges the gap between the theoretical models and experimental observations. A comprehensive theoretical understanding of glass transition is still elusive, while, different experiments support different theoretical models; thus, a detailed microscopic understanding is desirable to build theories that can explain the glass transition. Despite the complexity of the system that undergoes glass transition, many features of the glass transitions have an underlying universal features such as steps like slow relaxation. Simple computational models, such as Kob-Andersen models have given light on many aspects of the glass transition. To look at density-dependent features of glass transition and also the effect of attractive interaction on the properties of glass transition, we have simulated Kob-Andersen model binary mixture and its WCA variant from low to higher density i.e. ρ =0.8 to 1.8, to understand, how various glass transition properties vary with density. The simulations are from high to low temperature in density grids in microcanonical ensemble to obtain dynamics driven by the unperturbed Hamiltonian. The lowest temperature in the grid in each set of density is set close to the mode-coupling theory glass transition temperature.

Chapter 3: One of the simple methodology to understand the difference in the dynamics of KA and KAWCA model is in terms of the inter-molecular interactions, this is because in the Kob-Andersen binary mixture, the minority component is introduced to induce frustrations that prevent crystallization, which is smaller in the size in its interaction to the major component. We have looked at this qualitative view and attempted a quantitative relation between structure and dynamics. In these studies lower densities ρ =0.8 and 1 are where attractive interactions lead to a phase-separated system at a lower temperature when attractive interactions are present. The relative difference in the pressure between KA and KAWCA models to total pressure reduces as density increases.

The studies of the partial radial distribution function $g_{AA}(r)$ shows enhancement of the peak height at densities, where system phase separates at lower temperatures. Similar features were observed in A-B partial radial distribution function $g_{AB}(r)$, which is the strongest among the three interactions. The $g_{BB}(r)$ of both models differs considerably at all densities at lower temperatures, they are comparable at the highest density in this study at ρ =1.8. Comparison of average radial distribution function $g(r)$ with the partial one show that the highest peak

arises at the same position of the highest peak of $g_{AA}(r)$ which shows that here the density remains high, thus, can be considered as the origin of the free-energy barrier.

Comparison of the variation of α relaxation time for KA and KAWCA models at these densities with reduction of temperature shows that there is a direct correlation between the growth of the peak height of the $g(r)$ and the relaxation time. The mean force distribution in the radial direction on a reference particle show that in all densities at high temperature the force distribution is identical for KA and KAWCA models, at these state points the relaxation dynamics of these systems are also identical. We have proposed a relation connecting the density relaxation and density at the peak position of the first coordination shell in similar arguments of the free-volume theory. This exponential function $\tau_\alpha \propto exp(\rho_0/\rho_0 - \rho_{loc})$ which predict a critical local peak height density ρ_0, where the relaxation dynamics diverges. We have shown that this critical density increase from lower density to higher. This critical density also shows similar variation and crossover to KAWCA models at a high density which is observed for T_c and T_o thus similar to the predictions of existing models.

Chapter 4: For a system that undergoes glass transition, the phenomenological models divide the system into regions where the dynamics of the systems differ. There are many investigations in the Kob-Andersen binary mixture that looks into various aspects of the dynamical heterogeneities in the system, earlier investigations of glass transition extensively used mean square displacements as a primary tools to characterize the cages formed near the glass transition. In this chapter, we first look at the detailed characterization of the microscopic dynamics of the KA and KAWCA models to look for density dependence of dynamics. Here we use mean square displacement as the primary measure to characterizes cage formation near the glass transition.

The partial diffusion coefficients of A and B differ in their values as the density increases at high temperatures and they become nearly equal at low temperatures due to enhancement of collective rearrangement and its effect on diffusion. At density 1.2, the comparison of growth in the non-Gaussian parameter of A and B with the reduction of the temperature shows that the non-Gaussian parameter of B grows at a higher rate than A which is different from density 1 and 0.8, is because of structural inhomogeneities in the distribution of A at the interface of the phase-separated domains. In higher densities the growth of non-Gaussian parameter of B always higher than that of A.

We compare the variation of the β relaxation time from the comparison of the peak time of the non-Gaussian parameter. At the highest density of this study, at 1.8 the mean square displacements of KA and KAWCA nearly fall on each other. The cage radius r_{cage} is small even at high temperatures, which further reduces as temperature drops. At this density, average diffusion coefficient D is nearly the same for KAWCA and KA models

which shows the negligible contribution from the attractive interactions. It is interesting to look at the variation of the stretched exponential relaxation exponent β of $F_s(k,t)$ and identify the heterogeneity in the relaxation from the variation in the limit $0 < \beta < 1$. In this study our investigations are limited till the lowest temperature near T_c , therefore the low value of the β below 0.5 is not observed. Next, the thesis looks at the growth of the correlated volume from analysis of the four-point correlation functions. There is a growth of the peak of the four-point correlation function for A and B, when compared in the densities where system phase separates for the KA model shows that they are identical but magnitude differs for the KA model, while that for KAWCA model the signatures of growth is absent. At high densities, there is the growth of the four-point correlation function as the pressure in the KAWCA model grows larger as the repulsive forces are propagated at a larger distance in this system, similar to jammed granular systems. Finally, we have looked at Stokes-Einstein relations at all densities in this study which show complex correlation between observed heterogeneity in the system.

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