A molecular dynamics study of glass transition under phase separation in pure and glass forming binary Lennard-Jones liquids

A THESIS

submitted by

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for the award of the degree

of

DOCTOR OF PHILOSOPHY

School of Basic Sciences
INDIAN INSTITUTE OF TECHNOLOGY MANDI
KAMAND, MANDI-175005, INDIA

November 2018

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 **"A molecular dynamics study of glass transition under phase separation in pure and glass forming binary Lennard-Jones liquids"**, submitted by **Anna Varughese**, 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 her 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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Acknowledgements

I would like to thank my thesis advisor Dr. Prasanth P. Jose for his patience to guide me. I am touched by his commitement to science, hard work, unflinching courage and emphasis towards perfection. I have benefitted from his expertise in coding, knowledge and vision. I appreciate and treasure him for all of these.

My sincere thanks to the Prof. Timothy A. Gonsalves, the director of IIT Mandi for his encouragement and support. I am also thankful to Prof. Ramesh Oruganti for being the chair of my synopsis talk, and for his valuable suggestions. My gratitude goes to the doctoral commmitee members Dr. Bindu Radhamany, Dr. P. Anil Kishan, Dr. Hari Varma, Dr. Pradyuman K. Pathak, Prof. Arghya Taraphder, the dean of academics, and the associate dean for their valuable comments and suggestions.

Next, I would like to thank MHRD for the financial assistance and IIT Mandi for providing the necessary requirements. I also express my gratitude to the IIT Mandi staff for all the helps whenever the need arose.

I would like to express thanks to my labmates Jalim Singh, Shubhanjali Pathak, Duni Chand, Sujeet Jaiswal, and Runa Barik for the fruitful discussions and their help. I owe my thanks to all my friends, well wishers and elders for their care and concern.

I am grateful to my family for their love and support. Above all, I would like to thank Lord Almighty for everything.

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Abstract

As liquid approaches glass transition by a decrease in temperature a small change in the structure of the liquid leads to dramatic slow down of relaxation properties. Many phenomenological relations are used to understand glass transition in liquids. One of the methods to arrive at or improve these relations that governs the structural glass transition is by studying the statistical behaviour of phase space trajectories from molecular dynamic simulations of glass forming models. Structural glass transition has been extensively studied using molecular dynamics simulations at high number density state points, where the particles are constrained to move at low temperatures, thus leading to a structural arrest. Many glasses found in nature exist at low densities, where basic ingredients of glass transition are poorly understood because the role of density induced constraints is not well defined. Recent experimental studies of glass transition on nanopores show that the phenomenological relations connecting variation in alpha relaxation with temperature continuously vary from positive pressure to negative pressure regime without any variation in the boundary at which pressure changes its sign (Phys. Rev. Lett. **115**, 265702 (2015)).

The objective of our work is to understand the supercooled liquid in the phase separated region at steady state that could contribute to some new understanding of glass transition in the low density region. As this phase separation is seen at a comparatively lower density, we look at the effect of pressure which changes from positive to negative during the glass transition on cooling under isochoric condition. We observe a shift to negative pressure in the deeply supercooled temperatures due to the excess volume in the system. This is a representation of glass forming liquids confined to nanopores under negative pressure with neglect of confinement effects.

This study uses extensive molecular dynamics simulations to understand glass transition in binary and pure Lennard-Jones models from the structural perspective and its associated dynamics. We looked at the domain formation in low density where system phase separates on cooling. On sudden quenching at low density, system phase separate and the configuration of the system get trapped in one of the meta-stable states of the system. This study show these metastable states are long lived and unchanging during the time scale of these studies.

We find slow density relaxation in the dense domains at low density that are formed when the system pressure become negative. Contents of the thesis chapters are given below

Chapter 1, presents a brief introduction to outstanding problems in glass transition such as incomplete theoretical understanding, the relation between structure and dynamics *etc.* are discussed. This is followed by a discussion on the importance of glass transition and glassy relaxation in the supercooled liquid in many systems that have useful applications. Then, we discuss theories of glass transition that is useful in understanding properties of the glass transition. First, we discuss ideal mode-mode coupling theory (MCT) and insights provided by MCT in understanding glass transition. The characterization of the system near the glass transition temperatures is described by phenomenological theories of Adam-Gibbs and random first order transition; we give a brief description of these theories. Finally, we look into the free-volume theory which is useful to understand many results presented in this thesis. We present an introduction to liquids and glass transition under phase separation and experimental and theoretical studies performed in such liquids. Many such systems show negative pressure on cooling. Two systems studied in this thesis are: a glass forming Kob-Anderson binary mixture and a pure Lennard-Jones liquid at low densities and temperatures. At low density, the system has an excess volume that is expected to give a difference in glass transition properties as compared to glass transition in a system at high density. These studies are also inspired by many earlier studies which show the connection between local structure and glass transition. The organization of the thesis is given at the last part of this chapter.

Chapter 2, describes the details of the model liquids and interaction potential. This chapter is an overview of molecular dynamics simulation. We integrate Newton's equation of motion using velocity Verlet algorithm in the NVE ensemble to reproduce dynamics driven by unperturbed Hamiltonian. This chapter further describes model systems we studied, features of its phase diagram and other technical details such as how we ensured time invariance of the simulation results especially under phase separation.

Chapter 3, presents the structural analysis of binary Lennard-Jones system. This chapter looks at static correlation functions and equilibrium structure. The theories on geometrical frustrations points to the importance of structures in the glassy system. We start with the conventional static measure, radial distribution function, of the particles to distinguish whether they are in the liquid state, supercooled liquid state or in a deeply supercooled arrested state. As the temperature is lowered, the first peak of radial distribution function goes sharper, which shows an increase in the number of neighbors in the first shell of a typical particle. We observe a split in the second peak on cooling, which is an evidence of multiple secondary structures within the system. We compute the partial peak height density of both phases separated regime and glassy phase at high density to check whether the local

geometry is similar to what found at low densities. In our system, we observe a difference in local geometry as there is a difference in peak height density in the phase separated regime at low density and glassy regime at high density. At high density, particles are constrained to be in the volume and show glass behavior, but at low density, particles are in the arrested state because of the attractive interaction between the particles. We also look into the effect of pressure in this region in comparison with the effect of pressure at high density. We further looked at the local molecular packing from the nearest neighbor distributions; the presence of local liquid-like or vapor-like clusters are identified from nearest neighbor distribution. Nearest neighbor distributions fall in the range 8-17, which is sufficient to form well known structures like, cube, tetrahedra, icosahedra, *etc*. For a deeper understanding of this local structural density, we discretized the simulation box into a number of cells and computed coarse grained density, which is defined in the work of Berthier et. al. (J. Chem. Phys. **140**, 164502 (2014)). Coarse grained density clearly shows domain formation and a preferable range of density for a glass forming liquid at low density similar to that of high density, which is already known to undergo glass transition. Explicit structural analysis has been performed using bond-order parameters introduced by Nelson (Phys. Rev. B, **28** 784 (1983)) *et. al.* which shows explicit structural similarity in the local structures of this glass forming liquid. Thus we see that local structure of the glasses are considerably similar under external constraints at high density and self generated internal constraints at low density which is a new finding in simulation studies of the glass transition. In our system, the local bond order shows structures of hcp, icosahedral, and various mixed structures.

Chapter 4, presents studies on relaxation dynamics of the model binary liquid. The dynamics of the system is characterized using mean squared displacement. In the phase separated regime near glass transition mean squared displacement shows ballistic, sub-diffusive, and near diffusive regimes. Presence of subdiffusive region shows cage formation that is a signature of a glassy system. The diffusion constant, cage radius, *etc.* are computed from mean squared displacement. From the fit of variation of the diffusion constant with temperature, MCT transition temperature is determined. We compute the incoherent intermediate scattering function ($F_s(k,t)$), to study the variation in the density relaxation properties of the system. We observe both alpha and beta relaxation in the phase separated regime. The nonexponential relaxation of $F_s(k,t)$ is due to the emergence of glassy domains. We have tested the phenomenological relations connecting Debye-Waller factor and the relaxation properties of the system to establish the validity of these relations across glass transition in homogeneous to phase separated region.

Chapter 5, discuss the glass-like properties found in the phase separated regime of simple Lennard-Jones system. This system is known for crystallization properties under cooling.

We analyze the system using above mentioned structural (chapter 3) and dynamic (chapter 4) measures and compare it with that of binary Lennard-Jones system. The radial distribution function shows the higher number of neighbors in the first shell as the temperature is lowered. Coarse grained density shows a shift to higher density as the temperature is lowered and the density range is comparable to binary Lennard Jones system. Using bond order parameter, we observe the existence of individual and multiple local structures within the system. Dynamics measures like mean squared displacement, and incoherent intermediate scattering function shows an arrested state in the phase separated regime. We discuss the connection between relaxation dynamics and structure.

Chapter 6, is a study on an application of a binary liquid with components that have masses differ considerably over a liquid substrate. This simulation work is to mimic an experiment where Fullerene in solution evaporate to form a thin film. We have studied formation a film of heavy solutes on the liquid substrate surface as result of the nonequilibrium evaporation of one of the lighter component. Our study is of two parts: the first one is the generation of the droplet in its vapor and second is evaporation of droplet over a substrate. We reproduce some aspects of the experimental observation with this minimalistic model.

Results of the thesis are summarized in chapter 7.

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