

Competition between vitrification and crystallization in Lennard-Jones binary mixture: A molecular dynamic simulation study

A THESIS

submitted by

Shubhanjali Pathak

for the award of the degree

of

DOCTOR OF PHILOSOPHY



School of Basic Sciences
INDIAN INSTITUTE OF TECHNOLOGY MANDI
KAMAND, MANDI-175075, INDIA

January 2021

dedicated to

my mother

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 of reporting scientific observations, due acknowledgments have been made wherever the work described is based on finding of other investigators. Any omission which might have occurred by oversight or error in judgement is regretted.

Date:



Shubhanjali Pathak,

School of Basic Sciences,

Indian Institute of Technology Mandi,

Kamand, Mandi, Himachal Pradesh, India - 175005

(Signature of the student)

Certificate

This is to certify that the thesis entitled “**Competition between vitrification and crystallization in Lennard-Jones binary mixture. A molecular dynamics simulation study**”, submitted by **Shubhanjali Pathak**, 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.

Date:

Dr. Prasanth P. Jose,
School of Basic Sciences,
Indian Institute of Technology Mandi,
Kamand, Mandi, Himachal Pradesh, India - 175005
Email: prasanth@iitmandi.ac.in
(Thesis supervisor)

Acknowledgements

First and foremost, I would like to thank my thesis supervisor, Dr. Prasanth P. Jose, for all the guidance, motivation and assistance he has rendered to me. His encouragement and enthusiasm are invaluable for my academic life. There were times that I was unable to cope up with my work parallelly with my personal life. But his constant support and trust kept me going. Under him, I was able to enhance my skills in writing and coding immensely. Also, his concern for my health has always been quite apparent in our interaction. I would always be indebted to him in some aspects of my life, both academically and non-academically.

I can't help thanking IIT Mandi for giving me an appropriate working environment and research facilities. I feel blessed to experience the pristine beauty and stillness of the Himalayas. I was able to regain my focus quickly whenever I faltered, due to the pollution and noise free ambience I got here. I would like to thank the Director, the chairperson and some faculty members here who have been the source of ideas, motivation and encouragement to move forward in work and in life.

I would like to thank my doctoral committee members Dr. Kaustuv Mukherjee, Dr. Suman K. Pal, Dr. Hari Varma, Dr. Chandra Shekhar Yadav and Dr. Anil Kishan. Though not being exactly from my field, they were still able to provide me with their valuable suggestions to move ahead in a smoother manner academically. Dr. C.S. Yadav has been a constant motivator and continuously tracked my progress whenever I happened to interact with him.

I am thankful to the MHRD, India for providing me with the fellowship to carry out my research work. I am also thankful to the high performance computing facility at IIT Mandi because of which I was able to perform this work.

I would like to deeply thank all my dear friends. They have truly been there, backing me up whenever I needed them. I specially thank my IIT friends, in chronological order, Anna, Faria, Indu, Neha, Nidhi, Pragya, Priti, Renu, Tripti and Tulika. . My special mention for Anna, who stayed with me for the most part of my work here. I fall short of words for her humane qualities that I have experienced with her. She mentored me in my work whenever I needed her. She was an adsorbent for variety of my emotional states, without any judgement. I will always cherish her presence in my life.

I would also extend my heartfelt gratitude to my labmate Dr. Jalim Singh, who has been assisting me in my work unconditionally. I am privileged to get his motivation and ideas even without his physical presence here. I would also thank my other labmates, Mr. Duni Chand Thakur and Mr. Keshav.

Last but not the least, I would like to show my gratitude to my family who has constantly supported me in all the terrains in my life. Their unbridled love and faith in me has kept me going in times when life was not rosy. My mother, who left the world in 2015, had been the most important aspect of my life. Without her, I could not imagine my getting into the research. She didn't let the naysayers affect me, so strong was her faith in me. And, I truly believe, she throbs deep inside me and keeps me going. My deepest thanks to my husband Lok, for his care and affection. He has been my backbone from the time he came into my life. His constant motivation and deep involvement in my work propelled me whenever I slowed down, especially during the last but the most crucial stage of my research work.

Shubhanjali Pathak

Abstract

When a liquid is cooled slowly, it attains minimum energy by searching through all the possible configurations, consequently forming a crystal at the freezing point. When there is an increase in the cooling rate, the system visits a lesser number of probable configurations, which increases the disorder in the solid. The tendency to find equilibrium further reduces with an increase in the complexity of the constituent particles, that is, the shape or relative change in their concentrations in multicomponent systems. There is an increased tendency to settle in multiple local minima, which eventually leads to glass transition on further cooling. The state of glass is highly disordered, structurally similar to liquids, but mechanically similar to solids. Single component Lennard-Jones (LJ) liquid at lower temperatures crystallizes whereas, LJ binary mixture used in the study of Kob and Andersen (Phys. Rev. Lett. 73, 1376 (1994)) (KALJ) with 20% minority component (B particle) undergo glass transition on cooling. At compositions of the minority component ($\leq 10\%$), the binary mixture crystallizes in the studies by Valdes *et. al.* (J. Chem. Phys. 130, 154505 (2009)). In this work, molecular dynamics simulations of the pure Lennard-Jones system and the Kob-Andersen model with the variations in the composition of the minority component B in the range 0% – 15% are performed to see the effects of increment in B (impurity) on the structures and relaxation dynamics. The glass transition is characterized by the dynamics, while studies on crystallization focus on the structure. Therefore, both structural and dynamical studies are done to understand crystallization, vitrification, and the competition between them.

To study glass transition, we have generated low-temperature state points by a fast quenching and looked at the structural variations for each composition at different temperatures. Pressure variations at B particle's concentration as 0%, 1%, 5%, 7.5%, 10%, 12.5%, and 15% show a linear decrease in pressure on cooling due to an increase in particles' mutual affinity on the successive increment of B particles. We define a characteristic temperature called T_{LS} for each composition studied, which is the lowest temperature where a system can stay supercooled in a typical long-time trajectory which is much longer than the α -relaxation time. It is considered as the temperature of the last supercooled state. We find that T_{LS} reduces linearly with an increase in B concentration. Below this temperature, a system shows a sudden transition in the order identifiable from the global bond-order parameter Q_6 , which

differs at different B concentrations. The typical Q_6 value diminishes with an increase in the B concentration. The reduction of the order is also clearly visible from the radial distribution functions $g(r)$, whose first peak gets taller; besides, the second peak gets broadened due to the formation of the multiple secondary structures on supercooling. We have analyzed the partial radial distribution function $g_{AA}(r)$, which shows that at all compositions, A component undergoes crystalline ordering below T_{LS} . As temperature reduces, the first peak of the $g(r)$ increases in height, showing enhancement in the caging that is quantified using ρ_{loc} , which is the local density at the first peak of $g(r)$. When the local density increases as temperature reduce, it shows enhancement of the barrier height and reduction in free-volume available to the particles for relaxation. The crystalline state just below T_{LS} serves as a free energy minimum of the configuration for a system. Comparison of the $g(r)$ in this state shows that there is a difference in the positions and heights of various peaks, which vary non-monotonically with composition. The analysis of partial $g(r)$ shows that the $A - B$ interaction locally destabilizes the lattice by inducing local defects; hence, the lattice formation gets destabilized. Eventually, with more concentration of B, the crystallization suppressed to support the glass transition at deeper supercooling with stabilization of local structures.

The hallmark of a glass-forming system is the cage formation and the associated dynamic heterogeneities. The mean square displacements at T_{LS} show a prolonged sub-diffusive regime, which gets more prolonged as impurity increases; thus, give a qualitative comparison of the formation of dynamical cages that enhances collective relaxation. The comparison of the non-Gaussian parameter $\alpha_2(t)$ near T_{LS} shows that its peak height increases as B concentration increases, signifying deepening of the dynamic heterogeneity. This increase of height and peak position of $\alpha_2(t)$ of B induces growth of $\alpha_2(t)$ of A, thus, showing competition between both the species in establishing order and disorder at lower temperatures. The overall or average $\alpha_2(t)$ is largely influenced by the $\alpha_2(t)$ of B particle. As temperature reduces at all compositions, the cage size reduces. Near a critical cage size, there is a trigger of crystallization, around $r_{cage} \sim 0.23$, at all compositions. $F_s(q, t)$ at all the supercooled states show KWW-exponent $\beta \sim 0.9$ signifying a nearly exponential relaxation. At 15% B, the variation of the $F_s(q, t)$ shows a considerable slowdown of the relaxation process. By computing β of A and B, we find that as B composition increases, the heterogeneity in the relaxation of B component decreases, and that of A increases leading to the mixing of collective relaxation process in the supercooled state. This study shows that no sharp boundary exists from crystallization towards vitrification when the B concentration increases. The transition from a system that prefers crystallization to the one that prefers glass transition is gradual. Hence, we predict T_{LS} for a couple of nearby higher B concentrations by linear extrapolation of B% versus T_{LS} . We have computed the mode-coupling theory glass transition

temperature T_c from the schematic mode-mode coupling theory and the dynamics divergence temperature T_0 of Vogel-Fulcher-Tammann relation from the fit of the τ_α versus temperature. T_c is always between T_{LS} and T_0 . The slope of variation of T_{LS} with composition is the highest, therefore, it will cross variation in T_c and T_{LS} at higher concentrations of $\sim 17\%$ and $\sim 23\%$ respectively. As the growth of the order parameter Q_6 weakens with B, for higher concentrations of B, T_{LS} may not be meaningful. We extrapolated the value of T_c at well-known composition 20% of B to be 0.47, which is closer to the reported value 0.435 with an 8% deviation.

The length and time scale of the dynamic heterogeneity is related to the variation of the 4-point correlator $\chi_4(q, t)$. The peak height of $\chi_4^P(q, t)$ quantifies the correlated motion between the particles. We have proposed a power-law fit $\chi_4(q, t) = a \left(\frac{\tau_\alpha}{\tau_0} \right)^d$ which works reasonably well. We have proposed and tested a power-law relation of the form connecting the peak height to excess density $\chi_4^P(k, t) = A (\rho_0 - \rho_{loc})^k$ that relates the correlated motion with the stability of the cages.

Table of contents

1	Introduction to molecular modeling of vitrification and crystallization	1
1.1	Introduction	1
1.1.1	Applications and features of glass transition	2
1.2	Structural correlation functions	4
1.2.1	Radial distribution functions and structure factor	4
1.2.2	Bond orientational order parameter	5
1.3	Correlations for microscopic dynamics	6
1.3.1	Mean square displacement and non-Gaussian parameter	6
1.3.2	Incoherent intermediate scattering function and four-point correlations	8
1.4	Phenomenology and theories in glass transition	9
1.4.1	Kauzmann Paradox and temperature and fragility	9
1.4.2	Adam-Gibbs Theory	11
1.4.3	Random first-order transition theory	12
1.4.4	Free volume theory	14
1.4.5	Mode coupling theory	14
1.5	Vitrification, crystallization in model systems	18
2	Model and simulation details	23
2.1	Introduction	23
2.2	Model system	23
2.2.1	Molecular dynamics algorithms	27
2.2.2	Reduced Units	27
2.3	Periodic boundary condition and optimization method	28
2.4	Lower limits of the temperature grids	29
2.5	Summary	30
3	Comparison of structures with varying composition	31
3.1	Introduction	31

3.2	Pressure variation in the supercooled state	32
3.3	Microscopic structure from particle distributions	34
3.3.1	Total radial distribution function	34
3.3.2	Local density	37
3.3.3	Partial structures of A and B components	39
3.3.4	System configuration from snapshots	47
3.3.5	Near Neighbour Distribution	51
3.3.6	Global order parameter and distribution of the local order	55
3.3.7	Static Structure Factor	57
3.4	Summary and conclusion structural analysis	58
4	Variation in Single Particle Dynamics with increase in Impurity	63
4.1	Introduction	63
4.2	Variation in the dynamic heterogeneity	64
4.2.1	Characterization of dynamic heterogeneity from diffusion	64
4.2.2	Partial non-Gaussian behavior of the components	74
4.2.3	Caging with a successive increase of impurity	75
4.2.4	Single-particle density relaxation	77
4.2.5	Four-Point Correlation Function	94
4.3	Viscosity and Stokes-Einstein relations	103
4.3.1	Stokes-Einstein Violation	106
4.4	Summary and concluding remarks	109
5	Summary and Conclusions	113
	List of Publications	137
	Refereed Journal Papers	137
	Conferences Attended	139