Microscopic structure and dynamics of glass transition under phase separation in a model linear polymer melt

A THESIS

submitted by

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for the award of the degree

of

DOCTOR OF PHILOSHPY

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

March 2018

dedicated to

my parents

and

my sister

for their love, care, and inspiration.

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.

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Certificate

This is to certify that the thesis entitled **"Microscopic structure and dynamics of glass transition under phase separation in a model linear polymer melt"**, submitted by **Jalim Singh**, 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.

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Acknowledgements

First of all, I would like to express my profound gratitude and deep regards to my thesis supervisor Dr. Prasanth P. Jose for his exemplary and invaluable guidance, monitoring and constant encouragement throughout the course of the thesis work. I am indebted to him for his constant and magnanimous encouragement and support. Throughout my Ph.D., interactions with Dr. Prasanth have taught me various lessons in both academic and non-academic affairs. The blessing, help, and guidance given by him infrequently, shall carry me a long way in the journey of life on which I am about to undertake. The way Dr. Prasanth P. Jose made me think and work will have an everlasting impact on my research career and life.

Next, I am very grateful to IIT Mandi community for a good research environment in the Himalayan region. To the chairperson and teachers of School of Basic Sciences along with all faculty members of IIT Mandi for their constant moral supports, valuable suggestions, and encouragements during my research work. To my teachers, Mr. Ravindra Singh, Mr. R. L. Gupta, Mr. J. C. Maurya, Mr. K. Pandey, Mr. G. Tripathy, Dr. D. K. Mishra, Prof. H. L. Yadav, Prof. C. P. Singh, Prof. R. P. Malik, and Prof. S. Kumar who taught me very well in my school, graduation, and master level and encouraged me to pursue higher study in Physics.

I thank my Doctoral committee members at IIT Mandi, Dr. Hari R. Varma, Dr. Rik Rani Koner, Dr. Chandra Shekhar Yadav, and Dr. Pradyuman Kumar Pathak for their help, support, valuable suggestions, and discussions. I especially thank my former Doctoral committee member, Dr. Aniruddha Chakraborty who inspired me for deep learning and research, and gave me valuable suggestions time to time.

I am grateful to the MHRD, India for providing me the fellowship to carry out this research work. I am also thankful to the high performance computing facility at IIT Mandi due to which I could have been performed this work.

I thank all the staff members of IIT Mandi, especially to Prakash, Sushil, Akshay, Sumit, Kuldeep, Dushyant, Sunil, J. R. Sharma, and C. L. Sharma for their cooperation and help.

I thank my research group members Anna, Shubhanjali, and Duni for their help and moral support. I especially thank Anna and Shubhanjali for their valuable suggestions in all academic affairs.

I have always received cooperation, moral support and constant encouragements from my friends and juniors that cannot be expressed in words and I feel lucky to be blessed with wonderful people like them. I immensely express my heartiest thanks to the close friends Syamantak, Jitendra, Ashish, Rajiv, Manoj Das, Manoj Dhiman, Tushar, Navneet, Arpit, Gourab, Dr. Debarati, Chethna, Dr. Lakshman, Dr. JP, Ritu, Dr. Sohan, Dr. Pankaj, Mohit, Somnath, Punit, Davinder, Ajay, Anna, Sindhu, Shubhanjali, and Pushpendra. Especially, I thank Tushar for his constant support like an elder brother and a good roommate. I thank Jitendra for sharing my ideas and fruitful discussions with him. I thank Manoj Dhiman for his help in the coding and lively discussions with him. I especially thank Syamantak for being an ideal friend in my life. I thank Syamantak for all the scientific, philosophical, and personal discussions with him.

I would like to express heartiest thanks to my fiancée Parul for her encouragement, support, and love. To my dear and lovely sister Pinki for her support and co-operation due to which I have reached up to this position. Last but not the least, I would like to convey my special thanks to my dear parents, brothers, and sisters who tolerated the onslaughts of time to bring me up to this position and for their blessings, continuous encouragement, and moral support. To my dear mother who brought up me from my childhood and gave me constant support due to which I could have accomplished my goals.

Jalim Singh

Abstract

Glass transition is a subject of extensive study due to its relation to the important outstanding problems in physics of complex systems. In this thesis, we present results obtained from molecular dynamics simulations of linear polymer melt system. This thesis mainly focuses on the study of structural and dynamical properties of the system near glass transition temperature at two densities where system phase separate at low temperatures. Dynamics of these systems are compared to a system at a higher density where it undergoes glass transition without inhomogeneity in the density distribution. Cavities are forming in both lower density systems and pressure becomes negative at low temperatures. Higher density system also shows negative pressure at low temperatures. The glassy dynamics of the polymer melt systems under negative pressure and phase separation is rarely studied computationally in literature.

We computed various density distribution functions such as radial distribution functions (intra and inter parts) and the density of monomers from the center of mass of a molecule to the monomers of the same chain and other surrounding chains. These distribution functions show that both lower density systems ($\rho = 0.7$ and 0.85) show phase separation due to the formation of cavities, where pressure becomes negative, while the higher density system ($\rho = 1.0$) shows homogeneous density distributions. We see that the average local density is comparable at low temperatures ($T = 0.5$ to 0.4) for all three densities. The potential of mean force between molecules shows a pronounced long-ranged attractive tail along with the Gaussian potential at shorter distances, showing the importance of attractive interaction during phase separation for both lower density systems, whereas the higher density system shows a short-ranged attractive tail. Finally, the shape and anisotropy of molecules are examined, which shows that the molecular asymmetry is more in both lower density systems than the higher density system. We also find that molecular asymmetry varies in both lower density systems at low temperatures, however, it remains unchanged in the higher density system.

The role of local structure and local density in the arrested dynamics of the supercooled linear polymer melt are compared at three different densities mentioned above. We find that local density at the first coordination shell obtained from the radial distribution function is

related to the $\alpha-$relaxation time, Debye-Waller factor, and the dynamic correlation length. We proposed an exponential relation between the local density, ρ_{loc} and $\alpha-$relaxation time, $\tau_\alpha \propto \exp(\rho_0/(\rho_0-\rho_{loc}))$ (ρ_0 is a critical local density). It found that the local density and Debye-Waller factor $\langle u^2\rangle$ have a fractional power-law relation ($\langle u^2\rangle \propto (\rho_0-\rho_{loc})^\alpha$). These relations state that if local density approaches ρ_0, the $\alpha-$relaxation time diverges and the Debye-Waller factor becomes zero. Additionally, the relation between dynamical quantities *e.g.*, $\alpha-$relaxation time, Debye-Waller factor, and dynamic correlation length are examined at three different densities.

Violations of Stokes-Einstein (SE) and Debye-Stokes-Einstein (DSE) relations are presented in the supercooled state of the linear polymer melt. The role of multiple lengths and time scales in the violation of SE and DSE relations is revealed from the various time correlation functions in the supercooled state of the system at three number densities. The incoherent scattering function examines the non-exponential relaxation dynamics, which attributes to the caged monomers and molecules in the system. The NGP shows a pronounced peak at low temperatures of lower density system compared to the higher density system. This pronounced peak appears due to the large disparity in the mean squared displacements of the monomers and molecules in both lower density systems. The self-part of von-Hove correlation functions for monomers and molecules show a major peak at a smaller distance and a hump at a distance equal to the diameter of the monomers and molecules. This shows that particles with two type of mobilities are present in the supercooled state of the linear polymer melt system. The SE relation violates in the supercooled regime for all three densities. However, the pronounced violations are observed in both lower density systems. The end-to-end vector and reorientational correlation functions, and the trajectories of the orientational unit vector of a randomly selected polymer chain show that DSE relation is obeyed for higher density system, while it violates for both lower density systems. This violation of DSE relation is attributed to the step-like orientational relaxations and jump like motion of the orientational unit vector. Finally, the violations of SE and DSE relations are attributed to both the mobile and caged particles, which agrees with the existing literature.

Local order, shear stress correlations, and its fluctuations. The computed local bond orientational order parameters show that this system of linear polymer chains exhibits a mixture of incomplete local face-centered cubic and body-centered cubic crystalline structures, which are similar for both densities ($\rho = 1.0, 0.85$) and could be a reason for the slow down of the dynamics. Various stress correlations show that its oscillations are decaying at the vibrational time scale, which are localized at low temperatures because the amplitude becomes smaller. The trajectories of shear stress show that the stress is more localized in the lower density system compare to the higher density system at low temperatures.

Table of contents

1 Introduction **1**

1.1 General introduction to glass transition 1
1.2 Theories of glass transition 4
1.2.1 Mode coupling theory 6
1.2.2 Free volume theory 7
1.3 Correlation functions 8
1.4 Simple polymer liquids 14
1.5 Polymer melts 15
1.6 Phase separation 15
1.7 Liquids at negative pressure 16
1.8 Polymer glasses 17
1.8.1 Structural properties 18
1.8.2 Dynamical properties 18
1.9 Relevance of local structure in glasses 20
1.10 Local dynamics 20
1.11 Organization of thesis 21
1.12 Concluding remarks 23

2 Model and simulation details **25**

2.1 Introduction 25
2.2 Polymer model 26
2.3 Reduced units 26
2.4 Initial configuration 26
2.5 Force calculation 27
2.5.1 Molecular potentials 27
2.6 Trajectory of the system 28
2.6.1 Velocity Verlet algorithm 29
2.7 Equilibration and production runs 30

2.8 Summary 33

3 Structure of linear polymer melt 35
3.1 Introduction 35
3.2 Comparison of the structure 36
3.2.1 Static structure factor 37
3.2.2 Pressure 38
3.2.3 Radial distribution functions 39
3.2.4 Density distribution from center of mass 44
3.2.5 Local density 47
3.2.6 Potential of mean force 48
3.2.7 Shape descriptors of polymer chains 50
3.3 Concluding remarks 56

4 Local structure and its relation to the dynamics 59
4.1 Introduction 59
4.2 Comparative study on dynamics 61
4.2.1 Incoherent scattering function 61
4.2.2 Non-Gaussian parameter 63
4.2.3 Structural dynamic susceptibility 64
4.2.4 Local density and its relation to the dynamics 65
4.3 Concluding remarks 69

5 Violation of Stokes-Einstein and Debye-Stokes-Einstein relations 71
5.1 Introduction 71
5.2 Temperature dependent Structural changes 73
5.3 Polymer relaxations 76
5.3.1 Translation 76
5.3.2 Orientation 89
5.4 Concluding remarks 95

6 Bond orientational order and shear stress 99
6.1 Introduction 99
6.2 Bond orientational order parameters 100
6.3 Shear stress 102
6.4 Concluding remarks 105

7 Summary, conclusions and future directions 107
7.1 Summary and conclusions 107
7.2 Future directions 109

Appendix A Cell list and parallel programing 125
A.1 Cell list 125
A.2 Parallel programming 126
A.2.1 Trajectory generating code 127
A.2.2 Trajectory analysis code 127

List of Publications 129
Refereed Journal Papers 129

Conferences Attended 131