COMPUTATIONAL STUDIES OF NETWORK-FORMING LIQUIDS: MULTIPLE TIME-SCALE BEHAVIOR AND WATER-LIKE ANOMALIES

BY

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To Daddy and Amma

Certificate

This is to certify that the thesis titled **"COMPUTATIONAL STUDIES OF NETWORK-FORMING LIQUIDS: MULTIPLE TIME-SCALE BEHAVIOR AND WATER-LIKE ANOMALIES"** is being submitted by **Ms. Ruchi Sharma** to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy**. This thesis is a record of bona-fide research work carried out by her under my guidance and supervision. In my opinion, the thesis has reached the standards fulfilling the requirements of the regulations relating to the degree.

The results contained in this thesis have not been submitted to any other university or institute for the award of any degree or diploma.

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New Delhi **Ruchi Sharma**

Abstract

Network-forming liquids are characterized by the presence of strong, highly directional interatomic interactions, resulting in the formation of open, random networks. This thesis employs classical molecular dynamics and Monte Carlo simulations to study the network-forming liquids, primarily focusing on characterizing their complex network dynamics and studying the water-like anomalous properties in fluids other than water.

Chapter 1 provides an overview of those aspects of the literature which are of relevance to this thesis. Section 1.1 defines simple and the network-forming liquids giving examples. Section 1.2 reviews the work on power spectral analysis as a means for characterizing liquid state dynamics in network-formers. Section 1.3 summarises the relationship between structural order and water-like anomalies for different types of liquids. In order to connect structure, entropy and mobility in network-forming liquids, we have found it useful to draw upon two different aspects of the theory of simple liquids, which are reviewed in Sections 1.4 and 1.5. Section 1.4 focuses on multiparticle expansions of the excess entropy of a fluid, defined as the difference in entropy between the fluid and the corresponding ideal gas under identical temperature and density conditions. Section 1.5 describes the concept of excess entropy scaling of transport properties of fluids. The motivation for the presented set of investigations and the organization of the thesis are described in section 1.6.

Chapter 2 deals with the computational details which are relevant to the presented set of studies. Section 2.1 discusses the canonical ensemble partition function for simple liquids and the evaluation of various thermodynamic and transport properties in this ensemble. Section 2.2 discusses the potential models used for the various systems we study in this thesis, viz. methanol, silica, beryllium fluoride and two-scale ramp fluid. The interaction potentials in the case of CH_3OH, SiO_2 and BeF_2 are a combination of Coulombic and

short-range interaction term, while the two-scale ramp (2SRP) fluid is described using a very simple, isotropic pair potential. Periodic boundary conditions and the long range forces are discussed in Section 2.3 and 2.4 respectively. Algorithms of molecular dynamics (MD), implemented in this thesis and carried out using the DL_POLY simulation package is described in Section 2.5. Section 2.6 discusses the Metropolis Monte Carlo (MC) algorithm in the canonical (NVT) ensemble as applicable to simple isotropic liquids. We have employed MC simulations only for studying the 2SRP system.

Chapter 3 discusses the characterization of the multiple time-scale behavior of liquid methanol, focusing primarily on the power spectrum of the tagged particle potential energy. Methanol presents an interesting contrast to the systems like water and silica since hydrogen bonding results in formation of one-dimensional chains, rather than a three-dimensional network. Unlike water, methanol does not show any anomalous liquid state properties. It is therefore interesting to compare the manner in which the multiple time-scale behaviour of methanol and water differ. In this chapter, canonical ensemble molecular dynamics simulations of the H1 model of liquid methanol, modeled using a rigid-body, pair-additive potential, have been used to compute the static distributions and temporal correlations of tagged molecule potential energies as a means of characterising the liquid state dynamics. Section 3.1 contains details of the molecular dynamics simulations as well as of the power spectral analysis. Section 3.2 defines the criteria for defining the hydorgen bonds and presents the analysis of the hydrogen bonding statistics at the state points studied. Section 3.3 discusses the static distributions of tagged molecule potential energy. Power spectral analysis of the tagged molecule potential energies is discussed in Section 3.4. We compare the power spectra of methanol with that of water and discuss its variation with temperature and density. We also present the effect of modifying the hydrogen bond strength on the static

distributions and the power spectra of tagged energies. Section 3.5 establishes a quantitative connection between the complex dynamics of the fluctuating hydrogen-bonded network and a long-time averaged transport property, such as diffusivity. Section 3.6 presents the key conclusions of this study.

Chapter 4 presents the results obtained by carrying out molecular dynamics simulations for the BKS model of liquid silica to demonstrate the strong parallels in the complex dynamics of silica and water. Both silica and water form tetrahedral network and exhibit anomalous density and diffusional anomalies, though the underlying interactions in the two systems are different. Section 4.1 discusses the simulation details regarding the the potential model and molecular dynamics simulations. Section 4.2, 4.3 and 4.4 discuss the density, diffusional and the structural anomalies respectively. These sections essentially reproduce the earlier work in the literature on the water-like anomalies of BKS silica. Section 4.5 and 4.6 present the configurational energy and the static distribution of tagged particle energy in liquid silica. Power spectra of tagged potential energy of Si^{4+} and O^{2-} ions is discussed in Section 4.7. Section 4.8 discusses the correlation between diffusivity and multiple time-scale behaviour in the tetrahedral melt. We also compare the MTS behavior of methanol, water and silica. The conclusions of this study are summarized in Section 4.9.

Chapter 5 presents the computational strategy for estimating the thermodynamic excess entopy of ionic melts (silica and beryllium fluoride) using the thermodynamic integration method, with a view to assessing the accuracy of the pair correlation approximation to entropy for ionic melts. Section 5.1 provides the details of the TRIM potential used for BeF_2. Section 5.2 and 5.3 present the computation of the entropy of ionic melts using the thermodynamic integration and structural correlations, respectively. The density and temperature dependence of the excess entropy is discussed in Section 5.4 and 5.5. The

correlation between the thermodynamic excess entropy and the pair correlation estimate of the entropy is explored in Section 5.6. Residual multiparticle entropy (RMPE) of a fluid is defined to as the contribution to total excess entropy from three-particle and higher-order multiparticle correlations. Section 5.8 uses RMPE to test the accuracy of pair correlation approximation to entropy and correlates it with the local orientational order in ionic melts. Section 5.9 summarizes the key conclusions.

Chapter 6 maps out the structural and thermodynamic properties of a core-softened system, the two-scale ramp (2SRP) fluid. The pair interaction is characterized by two length scales: the hard-core diameter, σ_0, and a softer repulsion in the form of a linear ramp with a characteristic length scale, σ_1. It is known that the 2SRP system displays water-like density and diffusional anomalies. We focus on the density and temperature dependence of internal energy and the tagged particle energies, and the computation of structural order metrics and the pair-correlation entropy. Section 6.1 provides the computational details. The behavior of the configurational energy and the tagged particle potential energy is discussed in Section 6.2 and 6.3, respectively. Variations in the pair correlation entropy with density and temperature are discussed in Section 6.4. The structural order metrics and the order map for the 2SRP fluid are given in Section 6.5, 6.6 and 6.7. Section 6.8 summarizes the key conclusions.

Chapter 7 studies the connection of a single quantity, the excess entropy, with water-like density, diffusional and structural anomalies, using the BKS model of liquid silica and the two-scale ramp potential. We show that the common feature that all systems with water-like anomalies share, is the existence of an excess entropy anomaly. Section 7.1 shows how simple thermodynamic ideas relate the excess entropy with the density anomaly. Section 7.2 relates excess entropy to the diffusivity of silica and 2SRP fluid using excess entropy

scaling relationships. Section 7.3 connects the excess entropy anomaly to the local order. Section 7.4 points out that while the excess entropy and associated water-like anomalies are common to network-forming and core-softened fluids, the relationship between entropy and the internal energy is qualitatively different for the two categories. Section 7.5 presents the conclusions.

Chapter 8 summarizes the principal conclusions of Chapter 3 to 7 and discusses the possible future extensions of this work.

Contents