STRUCTURE, ENTROPY AND TRANSPORT IN NETWORK-FORMING LIQUIDS

BY

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Certificate

This is to certify that the thesis titled **"STRUCTURE, ENTROPY AND TRANSPORT IN NETWORK FORMING LIQUIDS"** is being submitted by **Mr. Manish Agarwal** 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 him 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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To My Parents

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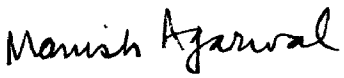

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Abstract

Network-forming liquids have random, open networks, mostly with local tetrahedral or octahedral ordering, resulting from presence of strong, directional interactions. In this thesis, classical molecular dynamics simulations are used to study the relationship between structure, entropy and mobility of two sets of tetrahedral network-forming liquids: (a) namely ionic melts with partial covalent character and local tetrahedral ordering (BeF_2 and SiO_2) and (b) water, as represented by widely used rigid body models. Interconnections between different types of dynamical properties in ionic melts is illustrated by the behaviour of diffusivity, viscosity and ionic conductivity. Restructuring of the liquid-state network in water in the vicinity of a solute is studied using hydration of a small peptide as a test system is an additional theme of this work.

Chapter 1 provides an overview of important aspects of the liquid state, as well as introduces key concepts relevant to this work. Section 1.1 reviews the statistical mechanics of liquids with a view to define important structural and dynamical properties that can be obtained from both computer simulations and experiments. Section 1.2 deals with the idea of order metrics to characterise the local structural order in liquids. Section 1.3 discusses the multiparticle correlation expansion of the excess entropy of a fluid. Section 1.4 discusses estimation of transport properties from computer simulations. Section 1.5 discusses the applicability of excess entropy scaling of transport properties, originally formulated for

simple liquids, to network-forming and anomalous melts. Section 1.6 discusses how multi-particle expansions of the excess entropy, in conjunction with entropy-scaling of transport properties, provide a convenient framework for understanding the emergence of water-like thermodynamic anomalies in systems with very diverse underlying interactions. Recent work suggesting a close connection between the existence of liquid-state anomalies of water and hydrophobic hydration is discussed in Section 1.7. The motivation and organization of this thesis are outlined in Section 1.8.

Chapter 2 presents the computational details relevant to the present set of studies. Section 2.1 discusses the canonical ensemble partition function for simple liquids. Section 2.2 discusses in detail the various potential energy models employed for the systems studied in thesis, viz. ionic melts (beryllium fluoride, sodium chloride and silica), water models (SPC/E, TIP3P, TIP4P, TIP5P, and TIP4P/2005), and peptides (β-hairpin of 2GB1 and α-helix of deca-alanine). Computational strategies to handle short-range forces via minimum image convention and electrostatic long range forces via Ewald summation are dealt with in Sections 2.3 and 2.4 respectively. Section 2.5 describes molecular dynamics algorithms used in this thesis as implemented in the DL_POLY and NAMD packages. This section also deals with strategies to handle rigid body motion. Estimation of entropy using thermodynamic integration for water models and ionic melts is given in Sections 2.6 and 2.7 respectively. Section 2.8 discusses calculation of various transport properties, e.g. self diffusivity, shear viscosity and ionic conductivity.

Chapter 3 focuses on determining anomalous structural and thermodynamic properties of molten BeF_2 using molecular dynamics simulations with a transferable rigid ion model (TRIM) potential. The region of phase diagram on which the simulations are performed are described in Section 3.1. Section 3.2 maps out the density anomaly over a wide range of

temperatures and pressures, analogous to that seen in water and silica. Section 3.4 establishes the region of excess entropy anomaly in BeF_2, within which excess entropy rises on isothermal compression. Section 3.5 extends the idea of multiparticle expansions of excess entropy to ionic melts and further illustrates the pair correlation entropy anomaly. The next section (3.6) discusses the density variation of local structural order in BeF_2, and maps out the structural anomaly. The order map shows a band of state points where the the orientational order and pair correlation order are highly correlated. The interrelationships between the excess entropy and structural anomalies are discussed in Section 3.7. Section 3.8 highlights BeF_2 as a tetrahedral, network-forming liquid with properties intermediate between those of water and SiO_2, and presents other conclusions pertinent to this chapter.

Chapter 4 maps out the structural and thermodynamic properties of five rigid geometry water models using molecular dynamics simulations over a large range of state points in the respective liquid regimes. Various simulation details for the water models are presented in Section 4.1. The region of density anomaly is mapped out for all five models and is presented in Section 4.2. Structural order metrics and order maps are discussed in Section 4.3, where all water models are shown to occupy the same region in the order metric plane. The excess entropy anomaly is mapped out for the five water models in Section 4.4. The pair correlation entropy anomaly is identified in Section 4.5. Entropic analogues of the order metrics are explored in Section 4.6. A parallel "order map" is constructed from these analogues. Section 4.7 discusses the relation of phase diagram of the TIP4P/2005 and SPC/E models to the anomalous regime, showing that the region of liquid state anomalies is very similar, while the shape and qualitative nature of the phase diagram changes drastically. Concluding remarks are presented in Section 4.8, suggesting that ideas of structure-entropy-mobility relationships might be experimentally verifiable, and help in improvement of model

parameters. Among the five models, TIP4P/2005 was found to be the best in representing experimental observations of water. However, rigid-body, fixed charge models might have an inherent limitation in reproducing both the liquid and structure at once.

Chapter 5 deals with the comparison of various single particle and bulk measures of mobility in the two AB_2 ionic melts (BeF_2 and SiO_2). The diffusional anomaly for the five water models is mapped out. Semi-empirical scaling relations connecting entropy and dynamics are explored in this chapter. Computational details are briefly outlined in Section 5.1. The three mobility anomalies, namely diffusional, viscosity and ionic conductivity anomalies are discussed in Section 5.2 for the AB_2 ionic melts. The Arrhenius behaviour of shear viscosities and ionic conductivities are also illustrated. Section 5.3 shows that the Stokes-Einstein is valid for ionic melts, while the Nernst-Einstein shows large deviations in the anomalous regime. In Section 5.4, the diffusional anomaly is systematically mapped out for all five models, and found to be quite varied when compared along the 300K isotherm. Excess entropy scaling of various transport quantities for ionic melts and water models is discussed in Section 5.5. Section 5.6 correlates pair entropy estimates with Rosenfeld scaled transport properties. In the next section (5.7), the cascade picture introduced in Chapter 3 is extended to include envelopes of viscosity and diffusional anomalies, illustrating that BeF_2 has the same sequence of onset of anomalies as SiO_2. Section 5.8 concludes that the ionic conductivity has very different behaviour in comparison to self-diffusivity and shear visocity in the case of ionic melts. The strong Nernst-Einstein deviation, as well as very short relaxation times point towards involvement of strong ion-pair interactions in both melts. Usefullness of the structure-entropy-mobility relationships in AB_2 ionic melts and water in terms of Rosenfeld scaling of transport quantities is discussed, with emphasis on the accuracy of structural estimators of excess entropy.

The organization of water at biomolecular interfaces is crucial for understanding the role of water as a solvent in biological processes. **Chapter 6** examines the extent to which the local energetics and structure are modified by the presence of a biomolecular solute. The strong, fluctuating hydrogen bonded network of water undergoes significant alterations when foreign molecules are introduced. In the case of large, complex solutes such as proteins, the structure and dynamics of the hydration layer is a subject of considerable experimental and theoretical interest. We consider two peptides chosen to represent the two main categories of secondary structures observed in proteins, namely the deca-alanine α-helix and the 16-residue β-hairpin fragment of 2GB1. Computational details for this chapter are described in Section 6.1. The bulk properties of TIP3P and SPC/E water are discussed in Section 6.2. Section 6.3 describes the tagged potential energy and tetrahedral order as a function of distance from the biomolecular interface. These static measures of local order and energetics were found to have interesting correlations. Section 6.4 shows that the residue-dependent variations in the tagged potential energy of water molecules within the hydration layer are dependent on the chemical nature of the residue, and are weakly anticorrelated. Summarizing our results in Section 6.5, we conclude that local measures of order, energetics and residence times are of considerable importance in measuring the perturbations in the network of water.

Chapter 7 summarizes the main conclusions from Chapters 3 to 6 and discuss some of the implications for future work.

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