COMPUTATIONAL STUDIES OF HYDROGEN BOND NETWORK DYNAMICS IN WATER

BY

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Water – hydrogen bond network

Certificate

This is to certify that the thesis titled **"Computational Studies of Hydrogen Bond Network Dynamics in Water"** is being submitted by **Mr. Anirban Mudi** 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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Abstract

This thesis employs classical molecular dynamics simulations and power spectral analysis of fluctuations in tagged particle quantities to understand hydrogen-bond network dynamics and the connection between various anomalies of water. It also explores the usefulness of power spectral analysis to characterise hydrogen bond dynamics in aqueous solutions.

The first chapter presents an overview of the complex macroscopic properties of water, as exemplified through the unusual phase diagram and thermodynamic and transport properties of water. To understand the connection between the intermolecular interactions and the macroscopic properties, it is necessary to employ computer simulations. The possible approaches currently available for computing intermolecular interactions in water, as a necessary input for computer simulation studies, are discussed. The literature on computer simulations of water is reviewed. These simulations have yielded important insights into the relevant features of the potential energy surface and the degree of accuracy required in order to model different macroscopic aspects of water. In the final section of this chapter, the motivation for this work and the organisation of the thesis are described.

Chapter 2 discusses the relevant methodological and computational aspects of this thesis. Details of the microcanonical ensemble (NVE) molecular dynamics simulation techniques for integrating Newton's equations of motion are discussed. The Verlet, SHAKE and the quaternion algorithm used in this work are discussed. Canonical ensemble (NVT) ensemble and isothermal-isobaric (NPT) ensemble molecular dynamics simulation techniques also used is this work are described. Analysis of molecular dynamics trajectory data, with particular emphasis on power spectral techniques, is described in some detail. The equation

of state calculations for SPC/E and TIP5P-E, as well as extensive set of tests of the effect of the Berendsen thermostat on the dynamics of SPC/E water, are presented here.

Chapter 3 describes how the multiple time-scale behaviour of power spectra is used to establish a quantitative connection between the complex dynamics of the fluctuating hydrogen bond network and a long-time averaged transport property, such as the diffusivity. Molecular dynamics simulations of SPC/E water are used to show that monitoring of $1/f^{\alpha}$ behaviour is a simple and direct method for linking phenomena on three distinctive length and time scales: the local molecular environment, hydrogen bond network reorganisations and the diffusivity.

Chapter 4 explores the connection between the structural, kinetic and thermodynamic anomalies of water by analysing dynamical correlations in the fluctuations of local tetrahedral order and local configurational energy. The boundaries of the diffusionaly anomalous region have been mapped out using the maxima and minima of the multiple time-scale exponent of the tagged potential energy fluctuations. Higher moments of the order parameter distribution are shown to be useful indicators of the transition from the anomalous to normal density regime. The final section of the chapter focuses on the compressibility anomaly and explores it's connection with the order map of water.

Chapter 5 examines the effect of ionic solutes on the hydrogen bond network dynamics by power spectral analysis and by monitoring static distributions of tagged potential energies. The local environment of solvent and solute ions has been analysed based on the power spectral data. This approach provides a simple route to characterise the dynamical differences between hydrophobic and hydrophilic solutes. In the case of hydrophilic solutes, such as NaCl, strong correlations between the exponents of the multiple time-scale region and the diffusivities of the anions, cations and water molecules have been observed, similar

to those seen in bulk water.

Chapter 6 gives a summary of the essential results contained in Chapters 3 to 5. The scope for extending power spectral analysis to study networked liquids such silica, beryllium fluoride and zinc chloride, is examined. Implications of this work for experimental work on water and aqueous solutions have been discussed.

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