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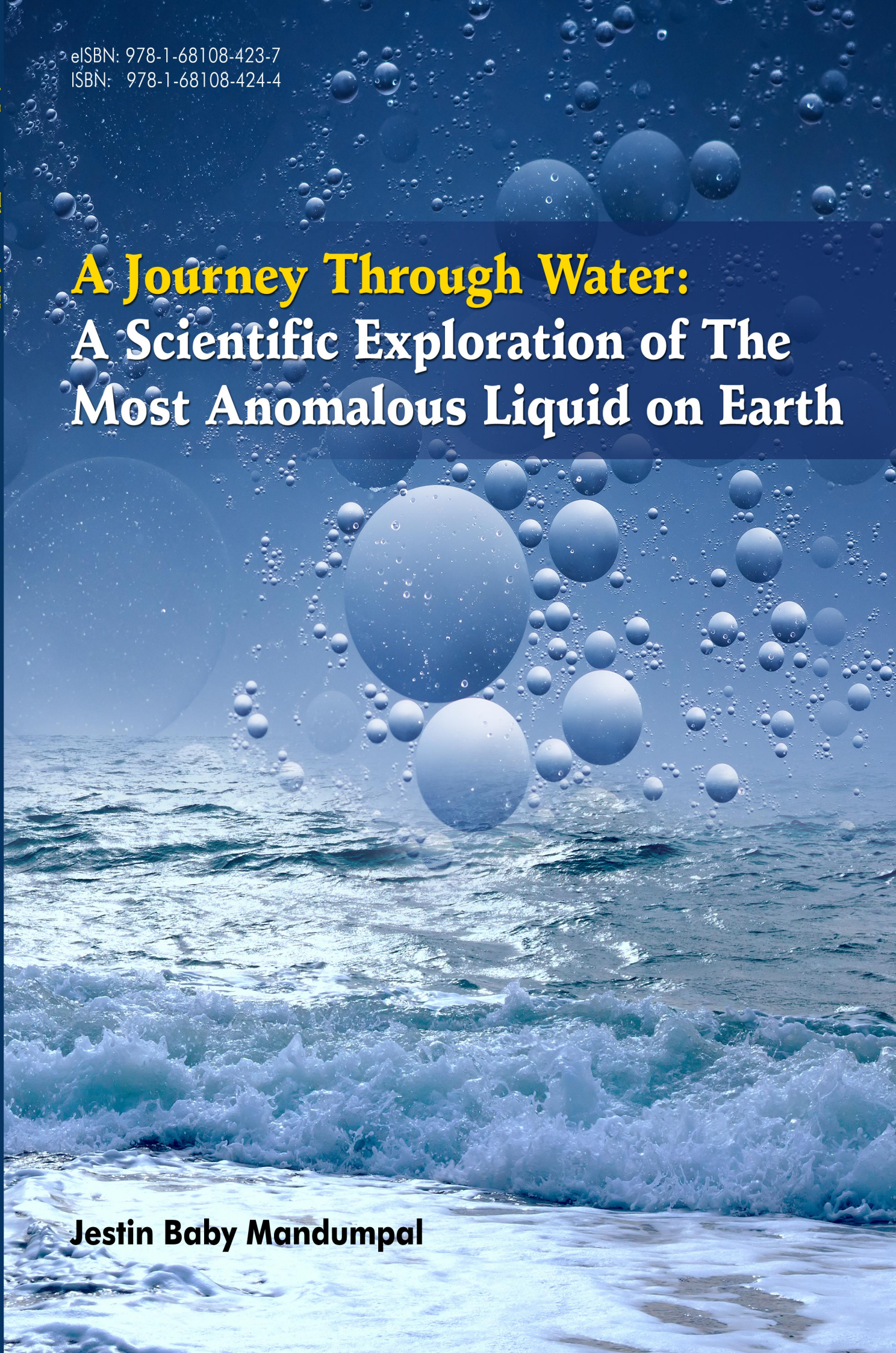
A Journey Through Water: A Scientific Exploration of The Most Anomalous Liquid on Earth



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CONTENTS

FOREWORD

On the surface of the Earth planet, water is everywhere: very visible in oceans, rivers, rain or clouds, less visible in rocks or even in the body of living organisms. Being almost the only easily accessible natural liquid, many processes depend on its properties. No life would be possible without the presence of water in its three states. Moreover, its properties play a major role in seasonal cycles and in weather stability. From the largest scales of ocean currents till the molecular scale of biological reactions the singularity of water is evident. As a consequence, water is at the core of research in a large variety of scientific disciplines, as it is nicely presented in the first chapter of this book.

One may ask why, more than any other substance, is water so important and subject of a huge literature, given the apparent simplicity of both the chemical composition and shape of the molecules. The answer cannot be simple because, indeed, complexity comes from different origins, such as the local tetrahedral arrangement or the intermolecular hydrogen bonds and their fast dynamics.

The great merit of the presentation of J. B. Mandumpal is the gradual introduction of the main concepts of the physics of water, with a pedagogical approach based on experimental results and on computer simulations. The text encompasses essentially all the properties of water from the better known till the still controversial models of supercooled water and glass transition.

Given the amount of data available and the enormous number of research papers (more than 400 publication every day!), the content of the book constitutes a remarkable review of the state-of-the-art in water physics, which will be source of information and inspiration for graduate students, scientists and engineers.

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PREFACE

Water is one of the most puzzling substances on earth despite its relatively small size and simple molecular formula. Importance of water in our life need not mention to the scientific community any further as numerous theoretical and experimental investigations have already been performed on water, and staggering volume of research work has been appeared for last several decades in hundreds of scientific journals and books. The second half of twentieth century witnessed a sudden expansion of scientific repertoire due to the refinement of the existing experimental equipment with better resolution and the introduction of computer simulations into basic and applied sciences. It has been widely accepted by now that both experiments and simulations are not independent subjects; rather they are mutually complimentary disciplines; this warrants much more concerted effort in future for better understanding of complex systems like water. The proposed book, titled, **"A JOURNEY THROUGH WATER: A scientific exploration of the most anomalous liquid on earth",** is an attempt to provide the reader an account of computational and experimental investigations on water.

This work is expected to serve the reader as a useful secondary source of information, with appropriate references to the primary sources, research articles and reviews by pioneers in the field. In addition to the anticipated readers of the book (physicists and chemists), scientists and engineers who indulge in water−based investigations, for example cryobiologists and chemical engineers, can also make use of this work for sharpening their understanding on water. The contents of this book are presented in such a manner that a person with minimal understanding of physics and chemistry can comprehend most of them without much laborious effort. An important feature of this book is the way by which the introductory chapter has been presented, contrary to the traditional approaches: I venture into providing a wider outlook to water from a socio−economic, political and technological perspectives. This, I hope, will make the scientific community much more aware of the importance of their research, and prompt to design their aim according to social needs as well. The first four chapters serve as a platform for the subsequent five core chapters (5-9). Chapters from 2 to 4 are devoted to cater the needs of people who do not have fundamental understanding of various simulation and experimental methods as well as theories that have been developed over the years for explaining the properties of water and liquids in general.

Conceived in the beautiful city of the South African coast, Capetown, I proceeded to write this book part by part in several countries including the Republic of Maldives where I was later appointed as a Teaching Service Officer (TSO) under the Ministry of Education of the Republic, and Baku, where I am living now. Completion of this book was a long haul, and

took more than three years to the present form after several reorganisations of the chapters. Even the title of the book has been revised several times: initially I thought of focussing mainly on computational investigations of water, but had to change my mind since such a move would become futile attempt given the fact that neither experiments nor computer simulations are standalone as I mentioned before, at least in the case of water. I thought to include clathrates suggested by one of the reviewers, but had to abandon this idea due to the never ending task of completion and also non−familiarity of the topic, but it will definitely be included in my future assignments!

This book is dedicated to my departed father Baby Mandumpal, who has been very inspirational in my life, and other family members including my mother Filomina, wife Priyanka and our little daughter Joann. I would like to thank Professor Ricardo L. Mancera at Curtin University for introducing me to this marvellous topic and for the stimulating discussions during my PhD research. I owe much to him for the training I obtained during my stay in Perth in the art of scientific presentations and more importantly structured academic writing. I would like to mention my gratitude to Professor Hamlet Izaxanli, the president of Khazar University, and Professor Hassan Niknafs, rector of Khazar University for inviting me to the wonderful city, Baku. I confer gratitude to my friends Rev. Dr. Paul Kattookaran (Co-ordinator, **Art-i (**Indian Christian Artists' Forum)) for motivating me towards fulfilling this task, Dr. Rajesh Komban (Research Scientist at Center for Applied Nanotechnology (CAN) Hamburg, Germany) and Dr. Thiruvancheril Gopakumar (Assistant Professor at Indian Institute of Technology, Kanpur) for providing numerous manuscripts for the completion of this book. Without these vital supports, this book could not have been materialised. I thank Professor José Teixeira (Laboratoire Léon Brillouin, France) for his willingness for writing an appropriate "Foreword" to this treatise. Finally I thank Bentham Science publishers for inviting me to write this book and in particular their acquisition editors Ms. Dur−e−Shahnaz Shafi and Ms. Humaira Hashmi for reminding me the deadline constantly. In fact, there are more people that I could mention here, I tender my apology for not including all of them here.

As one of the prominent theoretical physicists of our era Stephen Hawking in the preface of his seminal book "A brief history of time − from big bang to black holes" mentioned, the more one includes complex mathematical equations in a book, the more readers can be deterred from it. I support for the notion of books written in plain language, especially when they are aimed at general audience, for quick understanding of the subject. As a result, I tried to minimize the number of mathematical equations as far as I can, without losing the rigour of the subject. I have tried my level best to provide the already available research work (most of which are written in academic language with complex physics and mathematics) that has been carried out hitherto on water as much as I can. Nevertheless, the expanding volume of research on water year by year makes this work an endless task. I would therefore encourage

readers for making constructive criticisms on the content of this work. This book's shortcomings, in terms of its contents and style, weigh heavily upon me. I can only say that this book does not serve to account of everything we know about water. Nevertheless, I venture to hope that the readers will enjoy a short journey through this book!

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Baku
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CHAPTER 1

Water, The Centre of Life

Abstract: The ever increasing demand for clean water has prompted the world to consider water scarcity in a serious way. Some regions in the world are already at the brink of war over the ownership of major water resources, and it is feared that the situations may become worse. The marginalised people living in the impoverished regions of the world are struggling to obtain clean water, non−availability of which puts their life in utmost misery. Despite the fact that technological innovation provides some solution to this matter, water's growing demand surpasses what technology can offer. A joint approach unifying various facets of human life is necessary to overcome the issue, and hence they are discussed in detail. It must be appreciated that several organisations including the U. N., representing all nations around the globe, is taking proactive steps to curb this problem by setting up various committees to study the matter in depth and taking appropriate measures to decentralise the resources to all. With the development of robust computer simulation methods, and water models, it is now possible to study water at microscopic level. Together with state−of−the−art experimental techniques the properties of water can be unravelled further. This is expected to have tremendous impact upon improving the quality of water refinement process since most of them are fundamentally of a chemical nature.

Keywords: Disinfection, Filtration, IWMI, MENA, Peptide, Reverse osmosis, Salinity, Solar pasteurisation, Speciation, Water crisis, Water logging, WHO.

INTRODUCTION

Our earth, a blue water planet when observed from space, contains approximately 75% of water, but the vast majority of it (a whopping 97%) is salty and too concentrated to be useful for most of the habitats. This means that the sustainability of life heavily depends on the remaining 3% of water on earth (fresh water). The need for pure water, in particular, creeps through all spheres of life has become foci of our attention: from political summits to economic and scienti-

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fic conferences, as evident from the emergence of specialist academic journals, particularly aimed at discussing different perspectives of water and life [1]. Ever increasing demand for this substance in quality (in its pure state) and in quantity is a challenge for the world in the coming years. Since the global human population is skyrocketing and proportional increase in natural water resources does not seem to be realistic, finding an overarching solution for this problem is a daunting task. The explosion in population also means proportional rise in water−consuming industries, both leading to a reduction in per capita water availability [2]. Other detrimental effects such as climate change, over−exploitation of natural resources and environmental degradation are also associated with them. It has been pointed out by the experts that the demographic explosion generates much more water scarcity than the environmental hazards such as climate change [3]. The studies conducted by Lazarova *et al.* underline this observation: with the environment forecast for the coming 80 years, they demonstrate that the effect of Climate Change does not necessarily have negative influence around the world at the same level [4]. This can be explained by the fact that Climate Change does not reduce amount of rain received on earth, but it only alters volume and timings of river flow, causing damages only at some places. Hence it is very evident that only with proper water management involving the following core principles, namely development of new water technologies, inter basin water transfer, efficient irrigation systems and incurring appropriate charges for water, these issues can be resolved [4]. Before going to a deep analysis of various aspects of water, we need to define "water crisis".

Water Crisis

Water crisis is the shortage of water for internal and external consumption, which occurs due to growing imbalance between supply restricted by stagnated natural resources and demand increased by growing number of consumers. This is a much oversimplified statement because under this definition only human being's needs (internal consumption (for *e.g.* clean drinking water) and external consumption (for *e.g.* irrigation, industry operations and power generation)) are included at the expense of the basic rights of other organisms, inclusion of which magnifies the issue than it is appeared now.

The following facts describe in a nutshell the gravity of water crisis. There are 345 million people living in Africa without proper water access. 3.4 million people (equal to the population of Los Angeles city in the United States) die every year due to water related diseases such as diarrhoea, a potential threat that killed a child in the continent in every 6 seconds between 1980−1990. Every year almost 60 million people migrate to the major cities in the world, overwhelming majority of which live in slums and do not have proper water access [5]. Another issue is the gender discrimination (against women) existing in many parts of the world related to transporting water: to collect water from long distance (usually miles away from their living places) falls upon women's shoulders. One of the World Health Organisation (**WHO**) reports indicates that women and young girls work approximately over 150 million hours a year for just bringing drinking water for their household activities. These distressing facts have been summed up by a report by the International Water Management Institute **(IWMI),** set up for overcoming water crisis in the developing world, according to which approximately 40% percent of people are living in the developing world affected by water shortage [6]. In Fig. (**1.1**), some representative pictures of water crisis have been shown.

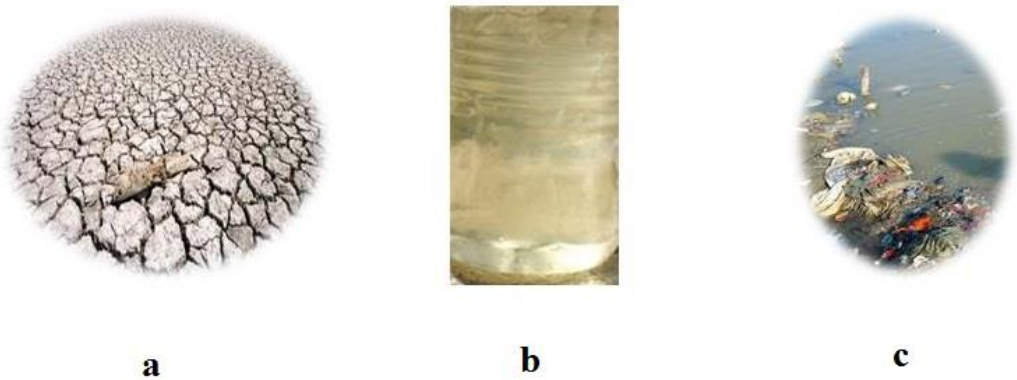

Fig. (1.1). Snapshots of the water crisis. (**a**) Shrinking volume of primary water sources due to human encroachment and climate change. (**b**) A sample of impure, undrinkable water containing pathogens spreading diseases. (**c**) A large chunk of population has only got access to dirty water.

Having rummaged through the introduction section, an intelligent reader may come forward with an immediate solution to the water crisis by stressing upon

CHAPTER 2

A Snapshot of Liquid State

Abstract: Liquid is one the three principal states of matter and its properties are known to be intermediate between gaseous and solid phases. Several types of intermolecular forces, categorised into long range and short range, play important roles in defining liquid structure. Long range forces are of three types, namely electrostatic, induction and dispersion, whilst the short range forces are of quantum chemical nature, due to exchange of electrons. A wide range of materials, including elements, oxides, mixtures of salts and dilute acids, are known to form glasses, which are non−crystalline, amorphous matter. Methods such as lattice theories have been devised long time back to understand the structure of liquids. Several other theories have been put forward as well in order to explain complex behaviour of liquids at lower temperature such as formation of highly viscous glassy materials. Most notable theoretical propositions include Adam – Gibbs theory, Mode Coupling Theory and Energy Landscape theory. Inherent Structure (IS) analysis is a powerful tool to identify the fundamental structures of the system under investigation, and to obtain a pictorial characterisation of the energetics between strong and fragile glasses. Relaxation times exhibit two distinct kinetics, alpha and beta relaxations, which can be properly explained by Mode Coupling Theory. Aqueous solutions of sugars and alkali salts such as lithium chloride are known to be good glass formers, which require only low cooling rates in order to form glasses, bypassing crystallisation.

Keywords: Atactic polymer, Expansion coefficient, Fragile, Freezing, Glass transition, Hole theory, Inherent structures, Kauzmann's paradox, Lindemann ratio, London forces, Metastable, Strong liquids.

INTRODUCTION

The three principal states of matter are solid, liquid and gas, and properties of these states differ in many aspects including molecular arrangement & shape,

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speed of movement, energy and forces of attraction. Major differences in properties among these three states are summarised in Table **2.1**.

Table 2.1. The distinction between the three principal states of matter.

Properties	Solids	Liquids	Gases
Distance between particles	very close	less close	far
Molecular arrangement	regular	irregular	irregular
Shape	well defined	shape of the container	no shape at all
Volume	fixed	Fixed	not fixed
Speed of movement	the slowest	Faster	the fastest
Forces of attraction	the strongest	weaker	the weakest

The principal distinction among these three forms of matter cannot be more accurately explained than by Thermodynamics, in particular entropy, a measure of how available energy in the system is distributed in its constituent particles. When entropy increases, the ways by which the energy can be distributed (degree of disorder) increases. One can clearly see that solids are of high order, followed by liquids and then gases (highest disorder and therefore highest entropy). This is also reflected in higher densities of solids and liquids (collectively known as condensed phases) over gases.

Higher densities of liquids over gases have big impact on the nature of forces that binds molecules in liquid, implying that they are very closely packed compared to gases, and the distance between two molecules in liquid state is simply the molecular diameter. This evidently points in to the significant role of intermolecular forces in binding molecules in liquid phase. Conversely, the distance between two gas molecules are approximately ten times than that of diameters, limiting the role of such forces in gases [44]. Closer packing arrangement (therefore lack of ample free space between molecules) in liquids also implies that they have lower compressibility than gases. When compared to tightly−packed crystalline solids, liquids and amorphous solids do not have long−range order. However, they possess short−range order, as shown by Fig. (**2.1**). Due to the lack of "perfect" order, a vast number of holes or voids can be observed in the micro structure of liquids, suggesting that liquid occupies larger

volume than a solid in general.

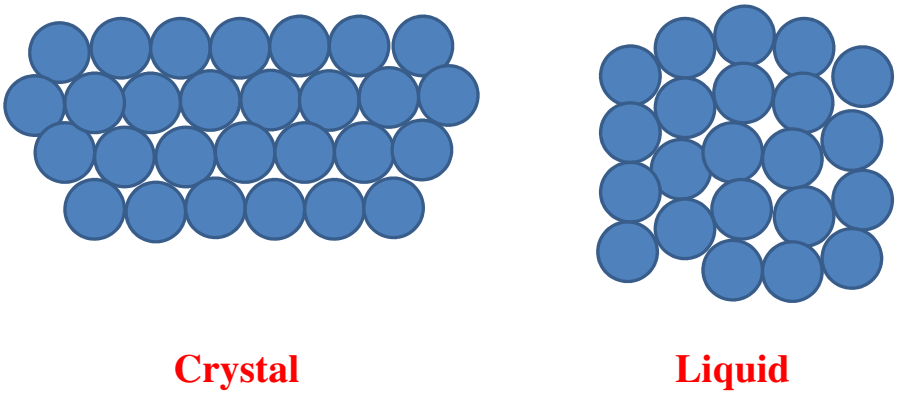

Fig. (2.1). Molecular view of crystal and liquid. The molecules in crystal (shown in the left) have been locked in regular pattern, compared to liquids (shown on right) which possess random arrangement.

Amorphous solids are highly viscous liquids with most of their features akin to liquids. The structural difference between a perfect crystalline and an amorphous phase cannot be better understood than using the tiling model as shown in Fig. (**2.2**).

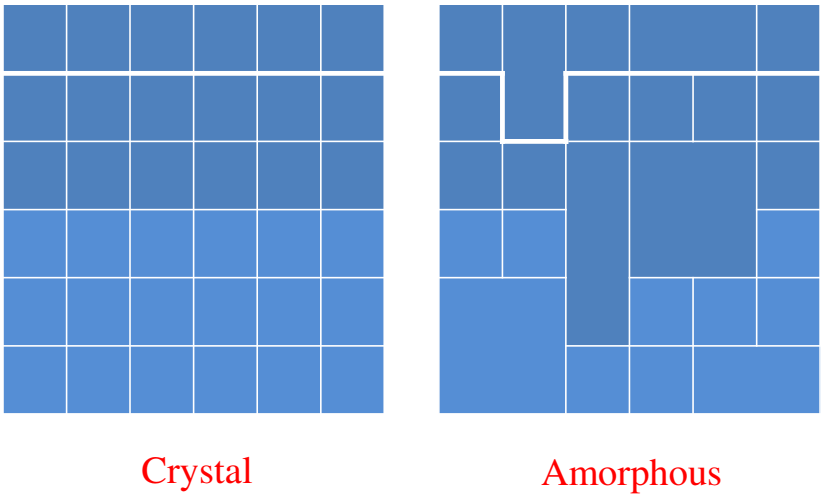

Fig. (2.2). Crystalline and amorphous phases. On the left shown is crystal, represented by arrays of regular periodic squares, and on the right shown is amorphous phase constituted by irregular squares.

As evident from Fig. (**2.2**), in the crystalline structure, the small squares are of

CHAPTER 3

Experimental Tools for Microanalysis of Water

Abstract: A wide range of experimental techniques has been developed and applied for investigating matter at high resolution. Scattering experiments are considered as powerful tools for structure elucidation of liquids including normal water and supercooled water. Employing techniques such as Differential Scanning Calorimetry (DSC), one can record the temperature of phase changes, the glass transition temperature. Quasi Elastic Neutron Scattering (QENS) spectral analysis suggests distinct relaxation behaviour of diffusive motions of water molecules. Nuclear Magnetic Spectroscopy (NMR) is very useful tool in elucidating molecular structures of systems including liquids and aqueous solutions. By Compton Scattering and NMR techniques, estimation of average number of hydrogen bonds has been achieved to a considerable level of accuracy. Extensive studies have been made on water clusters using a sophisticated spectroscopic technique namely Far Infra−Red Vibration−Rotation−Tunneling (VRT) spectroscopy. Optical Kerr Spectroscopy has been employed to investigate the relaxation process at femtosecond and picosecond levels. Properties such as compressibility and diffusion coefficient have been experimentally measured by simple capillary tube techniques. Electron microscopic techniques have become invaluable tools to obtain high resolution of molecular structure materials. Electron microscopic techniques equipped with better resolution can yield further information regarding the microstructure of materials including liquids.

Keywords: Bragg, Compton scattering, Density, Diffraction, DSC, Infra−Red, NMR, QENS, SANS, SEM, Spectroscope, TEM, X−ray, Zeeman.

INTRODUCTION

Obtaining evidence to a claim has paramount importance in science, and experimentation is an integral part of this process. The evidence can be used to further development of theories, thereby increasing our understanding of the world we live in.

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Due to immense growth in instrumentation, which modern science relies heavily on, information can be gathered automatically in areas that are beyond human sense perception [68]. An investigator first finds a research theme, and then carries out his/her investigations after procuring a sound theoretical and practical understanding in relevant experimental procedures. The design of experiments depends on the level of information required. Collection and subsequent analysis of data is followed, and the propositions of solutions to the investigating theme are ensued, before communicating his findings to the scientific community.

The experimental cycle just mentioned now is very helpful to arrive at developing models, by which generalization of data can be achieved, and, more importantly, to derive laws which can be used to make predictions [68]. A considerable understanding of both experimental and theoretical procedures is also required for accurate handling of the data, which evidently points into the fact that both experimentalists and theorists should gain a solid understanding of each other's working tools.

The purpose of this chapter is to provide the reader a general idea about some experimental techniques. These techniques are constantly applied for the investigation of various phases of H_2O. However, several challenges are encountered during experimental investigations on liquids such as water in extreme conditions, due to the high probability of crystallisation as temperature drops [69]. By contrast, performing experiments in normal temperature domain, precisely between melting point of water (ice) 273 K, and boiling point of water, 373 K is rather "straight forward". The chapter will aid a normal reader, who is not familiar with them, in understanding of several following chapters.

Scattering and spectroscopic techniques are the two major tools that are widely employed for understanding water structure. These include X−ray and neutron scattering experiments, Infra−Red (IR), and Nuclear Magnetic Resonance (NMR). In addition, a thermometric technique Differential Scanning Calorimetry, abbreviated as DSC, is widely exploited for investigating phase transitions occurring in materials. In addition to these experimental techniques, a reference has been made to capillary technique, one of the oldest experimental methods for investigating water for quite long time.

SCATTERING EXPERIMENTS

In scattering experiments, a sample (liquid or crystal) is subjected to radiation of a particular wavelength. The radiation is scattered by the sample, the intensity of which is determined as a function of scattering angle. Applying suitable mathematical treatments such as Fourier transformation on the resulting data, properties such as Radial Distribution Function (RDF) can be calculated. RDF is the measure of the probability of finding an atom with respect to another atom. Other quantities such as coordination number and nearest−neighbour distance can also be calculated from scattering experiments. Various crystalline ice forms differ in oxygen−oxygen distance and the angle between three neighbouring oxygen atoms (please refer the chapter 7 on ice), and hence differentiated among themselves in terms of aforementioned physical quantities. This explains why scattering experiment serves as an important tool for identifying various crystalline forms of ice. A simple sketch of scattering experiment protocol (known as Laue method) is shown in Fig. (**3.1**).

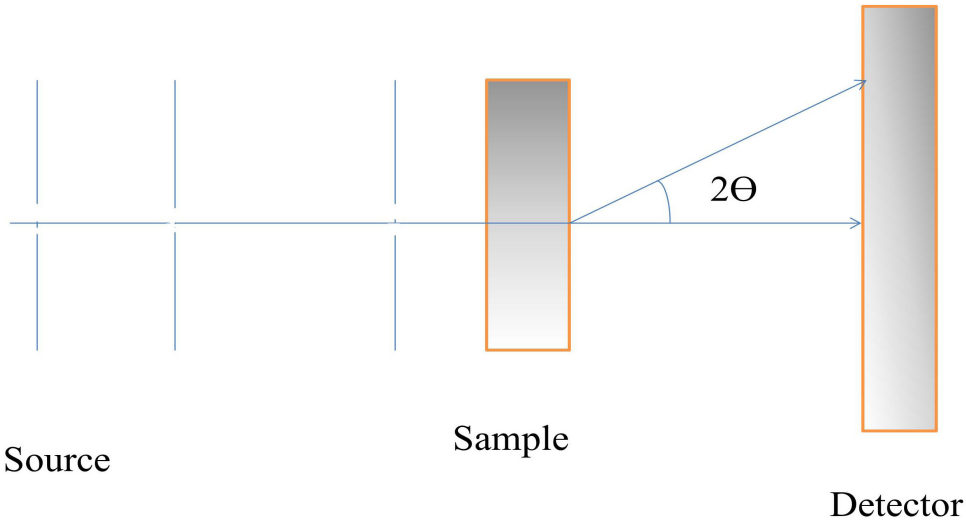

Fig. (3.1). The schematic diagram of scattering experiments. A sample is irradiated with some type of radiation (produced by a source), and the resulting intensity is measured as a function of angle between the incoming beam and scattered beam.

As beam (X−ray, neutron, electron or light) passes through the sample (crystal), it

CHAPTER 4

The Fundamentals of Molecular Simulations

Abstract: Computer modelling is a powerful enterprise for the investigation of matter at atomic and molecular levels, and has generally been accepted as a supplementary tool to traditional experimental methods. Its advantages over real experiments are primarily exemplified by its portability and cost effectiveness. Monte Carlo and Molecular Dynamics methods are two principal techniques that have gained a great level of popularity among various computer simulation methods. Numerous mathematical models, popularly known as Forcefields, have been developed in order to investigate water computationally. The application of computer simulation methods is limited by the choice of parameters that define the intra and inter molecular interactions within the framework of Forcefields. *Ab−initio* forcefields are expected to overcome the limitations of other types of water models. Concept of ensemble provides a theoretical basis for deriving physical properties by significantly reducing number of particles in a system. Mathematical devices such as Periodic Boundary Conditions (PBC) bypass the inconsistencies in simulations. Density Functional Theory (DFT) and Wave Function methods are two important classes of quantum chemical methods for investigating matter at electronic level. Born−Oppenheimer approximation provides a fruitful means for separating electronic and nuclear motions, which reduces the complexity of quantum calculations to a great extent. Hartree−Fock (HF) method is the most fundamental wave function procedure for calculating the energy of multi−electronic systems. On the contrary, Density Functional Theory (DFT) is based on the estimation of electron density, which can be validated by experimental means. Combined electronic and classical approaches are increasingly becoming popular in the scientific community.

Keywords: Basis sets, Boltzmann factor, Ensemble, Equilibration, Ergodic, Forcefield, Initialisation, Molecular dynamics, Periodic boundary, Production, Quantum mechanics, Shifting function, Switching function.

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INTRODUCTION

Models are built based on our theoretical understanding of what is observed, and hence, they should serve as complementary tools to the experimental methods. If one wants to test the predictions based on the model created, performing experiments is not the only one option. Due to ever growing availability and capability of computers, it is now customary for researchers to apply various computer simulation protocols to extract physical and chemical properties of the systems of interest. One can represent a system by a model, and with simulation on can track the changes in the model by varying conditions.

Computer simulation is a virtual experiment, in which an abstract model of a system created artificially in a computer. In comparison to the laboratory experiments, it has several advantages: firstly, compared to an experimental set up, a simulation (computer experiment) kit is portable, *i.e.* without much hassle, a person can carry it and any associated instruments (for example printer or scanner) from place to place, and secondly, challenging physical conditions limit the applicability of certain real experiments. For example, performing experiments on liquid water in low temperatures is met with limited success due to its unstable nature with respect to its more stable phase, ice, but mimicking them on a computer (computer simulations) is rather straight forward. Selecting appropriate models, one must supply input structure to the computer software he/she employs, and can extract certain physical or chemical properties without much strenuous efforts. However, this does not imply that computational investigations are superior to experiments.

Despite their advantages, computer experiments too are not without limitations. One major drawback of the computer methods is lack of accuracy of the methods and models employed in the simulations. One can in fact say that models and methods are plenty but one requires a detailed awareness of models and various computational procedures. Certain methods or models might be very efficient for particular type of systems and inefficient for some other types. Therefore, one must be judicious in choosing them prior to running the simulations, and interpreting the results afterwards. On the ground of aforementioned advantages and disadvantages one can say that computational methods do not stand

independently, rather they can supplement existing experimental investigation modes towards enhancing scientific understanding.

It becomes now clear that the role of computational chemists and physicists is to develop novel computational procedures, to perform molecular or atomistic simulations using these methods and to validate the findings when experimental results are available. Important modes of molecular investigations chiefly fall into two types: classical modelling grounded on laws of classical physics and quantum chemical modelling based on the revolutionary quantum mechanics founded in twentieth century. Dynamics of planetary objects (the best example being the motion of earth around the sun) can be explained by the laws of classical physics: that is they follow Newtonian Mechanics, the theoretical framework based on three Newtonian laws of motion. On the contrary, classical physics was proven to be inadequate for dealing with the motions of much smaller atomic particles that could only be described efficiently by a later theoretical development, called quantum mechanics. Important distinction between these two theoretical domains (classical and quantum) lies in the fact that the exact location of a particle (large particles) using classical physics can be estimated in advance without sacrificing accuracy, whereas quantum mechanics offers only a probable location for particles (small particles).

Over the years, more researchers are interested in computational methods as evident from the growing number of scientific articles appearing in national and international journals, and conferences proceedings. However, caution must be exercised in order to avoid pitfalls. For instance, a person without working knowledge of the basis sets will struggle to operate quantum chemical packages efficiently. On the other hand, the choice of appropriate forcefields is necessary to avoid embarrassing results in classical simulations. This demands a basic level of comprehension of computational methods.

The impetus for writing this chapter is to provide the reader a brief conceptual understanding of various computational methods that are being employed in material science. This chapter is organised as follows: firstly, I briefly outline the general simulation protocol. Then I discuss simulation techniques at molecular level (classical molecules); in this section concept of force field is developed and

CHAPTER 5

Water Between Its Freezing and Boiling Points

Abstract: Structural elucidation of water is so fundamental in understanding its roles as a solvent as well as a reagent in facilitating multifarious chemical reactions. The internal structure of water molecule is very "simple" to explain yet the physical and chemical properties of this liquid remains to be elusive in spite of tremendous theoretical and experimental efforts till date. Several propositions have been made in order to account for water structure, in particular its enigmatic hydrogen bonding environment that accounts for its exceptional properties. The concept of uniform distribution of tetrahedral network in water has been emerged from various experimental investigations. Water structure as equilibria of large number of clusters formed by varying number of water molecules has also been proposed based on computer simulations and Raman spectroscopy. Percolation model provides a quantitative picture of hydrogen bonding in liquids. The nature of hydrogen bond is dynamic in nature, spurring sporadic changes in its local structure, which can effectively be probed by various spectroscopic and scattering techniques. Local structure of water molecules is influenced by thermodynamic changes, most notably in temperature and density. Both computational experimental findings reveal that density plays a vital role in determining average number of hydrogen bonds a water monomer can have across wide temperature domain. More importantly, water undergoes a cascade of morphological changes upon alteration in temperature, which is still a fascinating subject for many researchers.

Keywords: Bifurcated hydrogen, Clusters, Coordination number, Density, Electrostatic interaction, Exchange repulsion, NMR, Percolation theory, Raman spectroscopy, VSEPR, Walrafen pentamers.

INTRODUCTION

Liquid water, the substance what we call 'water' in our daily life, exists usually in temperature ranging from 273 to 373 Kelvin. Water, one of the simplest hetero-

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atomic substances, consists of one 'heavy' oxygen atom (atomic mass = 16g/mol) and two lighter hydrogen atoms (atomic mass =1.008 g/mol). The static model, as shown in Fig. (**5.1**), for water is very "simple".

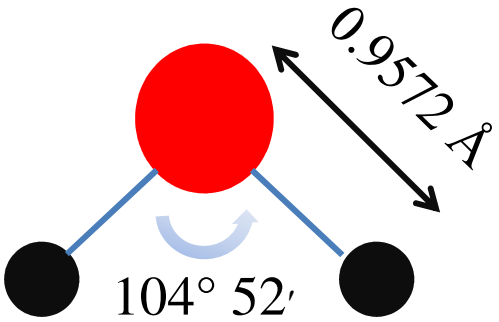

Fig. (5.1). The static geometry water. Water consists of one oxygen atom and two hydrogen atoms connected by two single bonds. The bond length between oxygen and hydrogen atoms in water is 0.9572 Å and the angle between the two oxygen − hydrogen bonds is 104.52°.

A water molecule has two oxygen−hydrogen bonds, and there are two types of oxygen−hydrogen bonds in water too (one of these is an example for strong covalent bond). The distance between hydrogen and oxygen atoms is approximately 0.96 Å with the angle between them 104.52° [121]. This angular deviation in water from a pure covalent bond angle (90°), as a result of repulsion arising from partial ionic character of oxygen−hydrogen bond, may offer a glimpse of its enigmatic properties [122]. It must also be noted that the deviation from the ideal bond angle comes about due to the repulsion between two lone pairs on oxygen atoms, commonly referred as Valence Shell Electron Pair Repulsion (VSEPR) theory.

The static model is however a very crude approximation due to three different modes of vibration of oxygen − hydrogen bonds [121]. They correspond to symmetric and asymmetric stretching (3657 cm^{-1} and 3756 cm^{-1}) and bending vibrational motions (1595 cm^{-1}). The schematic diagrams of these three modes of vibration are shown in Fig. (**5.2**).

The second type of oxygen−hydrogen bonds is weaker intermolecular hydrogen bonds. This is much more significant than the covalent bond in relation to the properties of water, as we will see throughout this book. What is a hydrogen

bond? In order to have hydrogen bond established between two neighbouring molecules, there must be a hydrogen bond donor (D) and hydrogen bond acceptor (A), and it is expected that the angle between DH (donor (D) –hydrogen bond (H)) and AH (acceptor – hydrogen bond) be approximately 180° [87, 92] (An alternative definition to hydrogen bond based on electrostatic interaction has already been given in the introductory chapter).

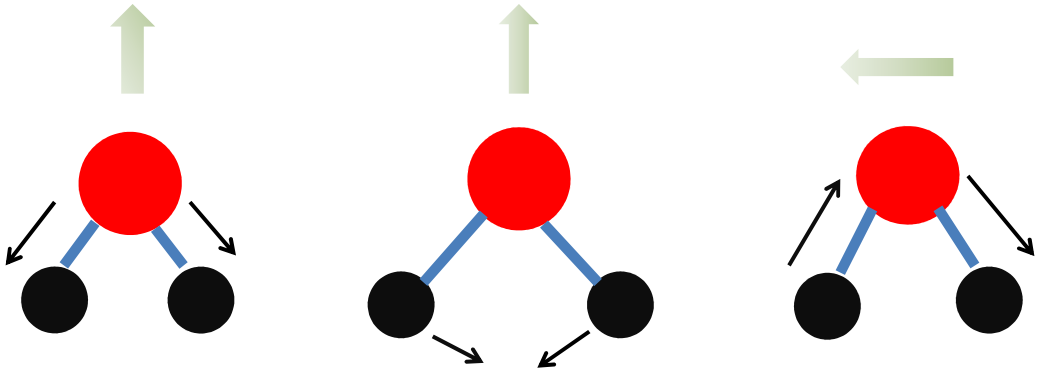

Fig. (5.2). Three different modes of vibration in water molecules. In the left is shown symmetric stretching vibrations occurring at a frequency of 3657cm^{-1}. In the middle and on the right are shown bending vibration and asymmetric stretching with a frequency of 1595 cm^{-1} and 3756 cm^{-1} respectively.

Hydrogen bond is a distant dependant, and several quantum mechanical forces contribute to it. These forces include Exchange Repulsion (ER) due to electron exchange from two neighbouring molecules, and Electron Delocalisation (ED) due to charge transfer from an occupied orbital of one molecule to unoccupied orbital of its neighbouring molecule [123]. It has been found that hydrogen bonds are replicated due to electronic redistribution, a signature of cooperative coupling in water [124].

Hydrogen bonds are formed in variety of chemical species, organic compounds including carbohydrates, proteins, nucleic acids and other numerous biological molecules, as well as a wide array of inorganic compounds. Based on strength of bonding, hydrogen bonds have been classified as weak (with energies between −2.4 and −12 kcal/mol), strong (with energies between −12 and −24 kcal/mol), and very strong (with energies more than −24kcal/mol) [125]. The range of hydrogen bond energy, the energy required to break one mole of hydrogen bonds

CHAPTER 6

Supercooled & Glassy Water

Abstract: The roles of two low temperature and non−crystalline forms of water, (supercooled and glassy water) are very pivotal in supporting the existence of several microorganisms below 0°C, although they are very metastable with respect to the stable crystalline form of water, ice. In the supercooled regime, the hydrogen bond lifetime of a single hydrogen bond and water clusters are found to be significantly higher than in higher temperatures. Diffusion coefficient and configurational entropy show a distinct maximum at density 1.15g/cm^3. Two inter−convertible forms of supercooled water, known as Low Density Liquid (LDL) and High Density Liquid (HDL), are found to coexist at temperatures below the freezing point of water. If water is cooled at very fast rate, it becomes glassy, the most profound form of water in the universe, bypassing the formation of ice. Polyamorphism is one of the characteristics observed in glassy water. Glass transition temperature in water has sparked debate in the scientific community. Different experimental procedures as well as water models produced varying values for the glass transition temperatures in water. It has been experimentally monitored and computationally simulated the transition between the two glassy phases of water, HDA and LDA. The transition is terminated at a critical point, according to Liquid−Liquid Critical Point (LLCP) theory. The concept of strong and fragile glasses is very powerful tool in furthering our understanding of the dynamics of glassy materials. It is interesting to note that a transition from strong to fragile occurs in water.

Keywords: Aerodynamics, Aviation, Crystallisation, Desterilisation, Diffusion, Glass transition, HDA, HDL, Inherent structure, LDA, LDL, Nucleation temperature, Polyamorphism, SANS.

INTRODUCTION

In addition to its three well known, standard and stable states (solid, liquid and gas) water also exists as supercooled and glassy (two of its known metastable forms) which are vital ingredients in sustaining life to numerous microorganisms

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at low temperatures. Investigation of supercooled water is gaining attention among the scientific community mainly due to the following reasons: firstly, water's anomalies are more pronounced in supercooled regime, and therefore a detail understanding of supercooled water can shed more light on its elusive behaviour in this temperature range, and secondly, supercooled water impacts on certain technologies including pharmaceutical and food industries, and cryopreservation, the technique of preserving organs and other biomaterials in low temperature (a discussion of various aspects encompassing cryopreservation can be found in [37]). Further, supercooled water instils a growing interest among aeronautical engineers due to its pivotal role in aviation industry which transfers millions of people annually from place to place worldwide. The growth of supercooled water droplets outside the aeroplane results in the formation of larger ice crystals (as shown in (Fig. **6.1**)), known as ice accretion, which causes numerous malfunctions in aircraft engine and the aircraft itself [154]. These include increase in the weight of aircraft resulting in altering the aerodynamics of side and rear, malfunctioning of landing gear and communication systems, decreasing flight lift, increase in propeller vibrations, making errors in instruments which provide vital information about aircraft such as air speed, altitude, and vertical speed, and reduction in visibility. The problems related to the formation of ice on aircrafts are severe in winter than in summer. It is interesting to note the fact that it is supercooled water in the subzero conditions, not the tiny ice crystals present in clouds, that causes the aforementioned disastrous effects.

The first part of this chapter examines the structure of supercooled water, which is followed by the important methods of its preparation. The discussion ends with a reference to diffusive motions of H_2O molecules. In the second part of this chapter, a detail discussion on glassy water is provided. This includes various glassy forms of water, experiments on the transition between the two known phases of glassy water, and glass transition temperature. The chapter is concluded with an important property that occurs in water at the glass transition temperature, Fragile Strong Crossover (FSC).

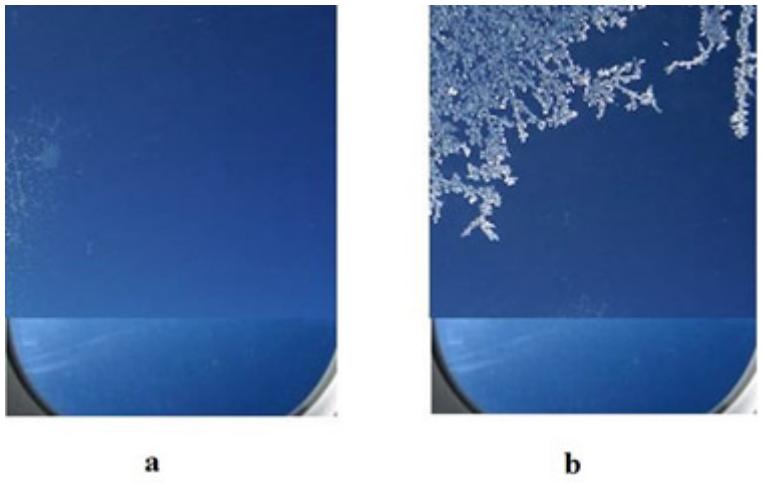

Fig. (6.1). Ice formation on aircraft body. Ice formation on the aircraft can result in serious malfunctions during the flight. Aircraft window without (left) and (right) with the formation of ice (picture trimmed for clarity).

STRUCTURE OF SUPERCOOLED WATER

Water forms a strong tetrahedral network between the nucleation temperature, T_H (the temperature at which nucleation of water molecules occurs) and the melting temperature, T_m [155]. Computer simulations carried out by Stanley *et al.* reveal the fundamental differences in the structure of water at lower temperatures and higher temperatures [156]. Sciortino *et al.* have investigated the relationship between the fraction of molecules and coordination numbers employing traditional Molecular Dynamics and Inherent Structure (IS) simulations. Inherent Simulation techniques are based on Energy Landscape Theory (ELT), discussed in chapter 2. In IS simulations, the structure corresponds to the local potential energy minimum can be accurately mapped. They noted that as the temperature approached 210 K, a large number of water molecules attain a stable four −coordinated state (Fig. **6.2**). On the contrary, within the temperature range of 300K and 700 K, there is little difference in the fraction of tetragonal coordinated water molecules.

It is very difficult to discern the impact of the density upon the number of neighbours around a water molecule from these simulations. However, it appears that as the density increases, more water molecules attain four−coordinated state

CHAPTER 7

Ice, The Crystalline Phase of Water

Abstract: Transition from water to ice is very crucial in many natural and artificial processes on which our lives depend. No other substance exhibits more crystalline forms than ice, the solid phase of water. Several ice polymorphs are found to exist in pairs, corresponding to high temperature proton disordered state and low temperature proton ordered state. Hexagonal ice is the dominant form of ice at ambient conditions. Ice X is highly symmetrical ice polymorph with hydrogen atoms exactly positioned equidistant to the two adjacent oxygen atoms. Five and seven membered rings of water molecules are observed in ice XII. The orientation of hydrogen bonds plays important roles in assigning the geometries of various forms of ice as in the case of normal and supercooled waters. The largest hydrogen bond bending is observed in ice VI. Orientations of hydrogen atoms result in Bjerrum and ionisation defects in ice crystals, which are responsible for dielectric effects. Auto ionisation, leading to the generation of hydronium and hydroxyl ions in water, promotes ionisation defects. Catalytic properties of ice are found to be remarkable in large number of reactions. TIP4P water model and its variants seem to be the popular models for simulating ice phase of water. Rotational motion of oxygen−hydrogen bonds is responsible for the destruction of ice lattice as temperature increases, leading to the melting of ice. Ice exhibits excellent electrical, optical, mechanical, thermal & surface properties. Thanks to its exceptional thermal properties, ice has been successfully employed as a better alternative to the traditional air cooling systems.

Keywords: Auto ionisation, Bjerrum, Clusters, D defect, Ferroelectric, Heterogeneous, Homogeneous, imidazole, L defect, polymorph, Polytype, Rectifier, Semiconductor, Thermoluminescence, Tyndall.

INTRODUCTION

When liquid water freezes, its crystalline polymorph ice forms, and this transition has profound impact on many processes that have direct relevance to our lives. Like water, ice is also subjected to immense scholarly activities due to its critical

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role in many fields including our planetary system, food preservation, *etc.* [189].

A wide variety of structures of ice, have been identified, as water molecules orient themselves in specific patterns in order to minimise energy upon changing physical conditions (pressure and temperature) [190]. The presence of ice in atmosphere and its role in the creation of cloud formation have made ice an interesting topic for geologists and other environmental specialists [72,189]. It has also been found that rheology of ice has profound impact upon the existence and appearance of several planetary objects [189b]. In food technology, ice has already occupied a prime position in preserving food materials domestically and commercially since ancient times [191]. Ice morphology dictates texture and physical properties of frozen materials and the popular cold sweet food ice cream [192]. Ice also has excellent adhesion properties on solid surface, which is relevant to the aviation industry and ship navigation as ice crystals are developed on aeroplanes and ships during their journey through supercooled clouds and storms respectively, which was discussed earlier [72].

Thus, it is very crystal clear that further multi−dimensional investigations on ice are very much needed for the betterment of the standard of our daily lives. Following a discussion on supercooling and supercooled water in the previous chapter, we are going to discuss the structure, properties and applications of ice in depth in this chapter. Although I mentioned about the connection between supercooling and crystallisation in the previous chapter, a repetition is unavoidable sometimes as these two states (metastable states) are inextricably linked to each other.

The supercooled state is a metastable state, highly unstable and can give away to more stable state, ice in the case of water, which is much more ordered solid species [193]. We saw in the previous chapter that water droplets can form clusters, which are so abundant in supercooled water, and the decrease in temperature promotes clustering of water molecules [160]. Clusters are grown in size as temperature drops by, and the movement of water molecules becomes sluggish. Some of the clusters attain a critical size by growing around themselves (a process known as nucleation). This leads to the transformation of supercooled water to large block of ice, and this process is known as crystallisation. Three

other alternative routes to crystallisation have also been suggested as shown in Fig. (**7.1**). The diagrams indicate that crystallisation can occur as a result of the contact between ice nucleus and water droplet, which can be inside or outside the water droplet [194]. Here, we must remember that a water droplet consists of thousands of water molecules.

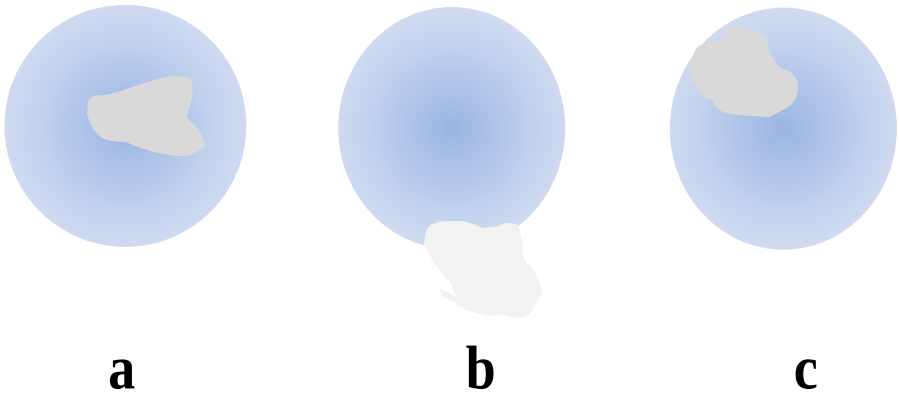

Fig. (7.1). Crystallisation of water droplet. Three ways by which ice nucleus promotes crystallisation of water droplet (shown in sky-blue circle): (**a**) ice nuclei inside a water droplet, (**b**) nominal contact between ice nuclei and water droplet (**c**) ice nuclei inside the water droplet.

Thus, the formation of ice is preceded by a process known as nucleation [195] which can either due to the electrostatic interaction of polar part of water (known as homogenous nucleation) or due to the presence of substance other than water considered as impurities (known as heterogeneous nucleation). The homogenous temperature of water is 231 K, below which it readily undergoes crystallisation under normal conditions (at very low cooling rate and at low pressures). It is very noteworthy that at higher temperature (close to the freezing temperature of water), the critical radius for homogenous nucleation is five times higher than the critical radius required for nucleation at 231K. Consequently, the number of particles required for attaining critical radius is also significantly less shown in Table **7.1**. At the same time, as mentioned earlier, the number of water molecules participating in the process of crystallisation increases as temperature drops by. Computer simulations show that for a drop in temperature from 240 K to 235 K, the number of water molecules that are part of "ice building" increases by a whopping amount of 40% [196].

CHAPTER 8

Water Above its Boiling Point

Abstract: Water beyond its boiling temperature has been investigated by numerous theoretical and experimental tools including classical and quantum simulations, Neutron Scattering, Nuclear Magnetic Resonance, Infra−Red, and a more recent Tetrahertz Vibrational−Rotational−Tunnelling spectroscopic technique. Water becomes Super Critical Water (SCW) when it reaches temperature 647 K with critical pressure and density at which vapour and liquid phases coexist. SCW has been found to have exceptional properties such that many chemical reactions can be efficiently carried out without the presence of catalysts, and hence is considered as a better alternative to many of the traditional reagents, which are currently being used in organic synthesis. It is also effective in biofuel production and in burying toxic waste products by converting them to water and CO_2. Simulations and experiments point into dramatic changes in the intermolecular structure of water at elevated temperatures signalled by depletion of tetrahedral hydrogen bonding network, which gives rise to higher population of water clusters than found in ambient water, with varying size and geometry. Cyclic water isomers are found to be stable up to clusters containing five water molecules, whereas three dimensional cage structures are found to be stable in higher analogues. Density along with temperature plays a vital role in determining diffusive properties of SCW. It has been demonstrated by numerous experiments and computer simulations that a proportional increase in hydrogen bonding is observed as density increases. On the contrary, diffusive motion of water molecules is retarded upon a hike in density.

Keywords: *Ab-initio*, Aldol, Benzamide, Cannizzaro, Density, Dimers, Friedel Craft, Hexamer, IR, NMR, Pentamer, SCW, Tetrahedral, Tetramer, Trimer, Water Clusters.

INTRODUCTION

Liquid water becomes water vapour beyond its boiling point, 373 K, under normal heating. The boiling temperature of water is inextricably linked to the upper limit

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of the temperature at which organisms can survive, 100°C (373 Kelvin): animals can survive temperature up to 51°C (324 Kelvin); Eucaryotic microorganisms can live bit longer (333 K), while photosynthetic procaryotes continue to exist up to temperatures around 350 K [223]. Certain bacteria can survive bit further, up to 373 Kelvin.

However, in analogy of supercooled water (below melting point of ice), liquid water can exist as superheated without being converted into vapour above its boiling point. Water beyond its boiling point becomes Super Critical Water (SCW) by attaining its critical temperature 647 K (374 °C), pressure 22.1 MPa and density 0.17 g/cm^3, and behaves like a gas−like fluid. Physical quantities such as dielectric constant (ε) and specific heat capacity (C_p) can take their anomalous values at these conditions, ~6 and 29.2 kJkg^{-1}K^{-1} respectively [224].

On the contrary, the role of Super Critical Water (SCW) in biological activities is almost negligible. However, it offers numerous unremitting applications, which have high economical, industrial and environmental impact. In this chapter, I venture into reviewing the applications and properties of water beyond its boiling point (in particular Super Critical Water) and major experimental and computational investigations on it. The chapter concludes with an analysis of small water clusters that are believed to exist at super critical regime.

APPLICATIONS OF SUPER CRITICAL WATER

The role of Super Critical Water (SCW) has been reported in the scientific literature principally as a reaction medium. Super Critical Water (SCW) can be useful in several ways: first it can act as solvent medium in several types of reactions including hydrolysis, dehydration, hydration and partial oxidation [224, 225]. Sub Critical Water (water heated beyond its boiling point without being boiled) is also found to be effective for better product conversion rate in certain aforementioned reactions [224, 226]. Enhanced reactivity in SCW can be exploited for chemical waste disposal since SCW can oxidise highly hazardous chemicals without any trace [227]. Hydrothermal technologies based on Super Critical Water (SCW) and Sub Critical Water can replace the traditional power generation methods to a greater extent [226].

Hydrolysis is one of the most common reactions in organic synthesis and the roles of SCW are remarkable in these types of reactions in terms of percentage yield and reaction kinetics. Hydrolysis of the ester 1,4−butanedioldiacetate is a typical example. Under normal conditions, hydrolysis of this ester gives only 38% yield. Amazingly with SCW, the yield can be increased to almost 100% [224]. Certain hydrolysis (for example benzamide hydrolysis) conducted in the presence of SCW occurs at faster rate. Similarly, in the dehydration reactions, for example ethanol to ethylene and glycerol to acrolein, SCW offers better yields than conventional free radical reactions. The exceptional catalytic activity of SCW is due to its ionic properties which spur on specific heterolytic bond cleavages [228]. Similar trends have also been observed in other two types of reactions just mentioned before. One of the exceptional properties of SCW is high feasibility of certain reactions without the presence of acidic or basic medium, which do not occur with normal water. Dehydration of 1,4−butanediol, a key industrial reaction to produce Tetra Hydro Furan (THF), is a prime example. There are several disadvantages, namely corrosion and generation of chemical waste, associated with the traditional synthetic routes of THF synthesis, due to the use of numerous chemicals including acids and salts. But with SCW the conversion from diols to THF can be achieved with high yield with minimal chemical waste [224]. Notable example for enhanced oxidation in the presence of SCW is catalytic reforming whereby methane, stable up to 723 K, is oxidised yielding CO_2 and H_2 with 90% conversion rate [226]. A large number of well−known reactions can be conducted with SCW without the support of catalysts: Cannizzaro reaction, Friedel−Craft reactions, Aldol condensation and to name a few [229]. This has a profound advantage in chemical industry if you consider the cost of chemicals and chemical industries polluting environment. Furthermore, as the world becomes more environment conscious, this “green” route is expected to replace traditional chemical methods polluting our healthy life. It is believed that this enhanced auto catalytic activity is due to the storage of vast amount of energy in SCW and to the fact that the concentrations of H^+ and OH^- ions in SCW is 30 times higher than ambient water [79, 229]. In addition, advanced computer simulation studies indicate that dissociation of acid and alkali increases in Super Critical Water [230].

CHAPTER 9

A Brief Review of Water Anomalies

Abstract: Numerous anomalies of water have been reported in the literature. Anomalous behaviour of liquid water is so striking when it is supercooled below the melting temperature of ice, T_m. Several physical properties have been found to be diverging in the supercooled liquid phase, including isobaric heat capacity, isothermal compressibility, relaxation time and thermal expansion coefficient. Interestingly hydrogen bond life times show a divergence at this temperature, indicating its connection to these singularities. Liquid water exhibits both density maximum and minimum, the latter has been discovered by a recent Small Angle Neutron Scattering (SANS) experiments, considered to be two of its most notable thermodynamic anomalies. Unlike other liquids, translational and diffusive motions in water exhibit contrasting behaviour and product of these two diffusive constants is found to be insensitive to temperature and density. Formation of water clusters of varying sizes dictates the nature of diffusion in supercooled water. Several propositions have been made in order to account for water's anomalies, which include Liquid−Liquid Critical Point theory, Singularity Free hypothesis, Critical Point−Free hypothesis and Stability Limit conjecture. In bulk phase, water shows its most of the anomalies. In addition, it exhibits several other anomalous characters when confined to nanoscale geometries and is near to macromolecular surface. It has to be noted that in the vicinity of non−polar solutes the strength and lifetimes of water network increases.

Keywords: Boltzmann constant, Critical point, Entropy, Hydrophobic hydration, Isochore, Isotherm, Life times, Short range, Singularity−free, Spinodal, TMD, Well depth, Widom line.

INTRODUCTION

Anomalies of water were known to the scientific community for centuries. There are numerous anomalies that have been reported for water, several of them have been studied in much depth by experimental and computational methods.

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As mentioned in chapter 5, water is a very small molecule, containing three atoms with molar mass just over 18 g per mole. However, there is no other material that possesses large number of anomalous properties as water does. Most of the anomalous behaviour exhibited by water is in the supercooling range, between the melting point of ice, T_m, and the temperature of homogenous nucleation, T_H, and therefore much of the efforts have been made to understand the nature of water in this region. In the remaining portion of this chapter, I wish to discuss about notable anomalies of water as a liquid, which are thermodynamic, kinetic and structural in nature. The chapter is concluded with four major interpretations that have been suggested to interpret anomalous behaviour of water.

WATER AS LIQUID

The most notable unusual property of water is its very existence as a liquid at normal temperature domain [121]. The interaction that dominates water is undoubtedly hydrogen bonding, whose interaction strength (20 kJ/mol or 5 kcal/mol approximately) is higher than van der Waals forces and lower than ionic bonding. The hydrogen bonds can overpower thermal fluctuations (one tenth of the former) in water, and provides vital strength to water to be remained as liquid [121].

HIGH ENERGY OF DISSOCIATION

I briefly mentioned in chapter 2 about the role of pair interaction functions in modelling liquids in general. Water under normal thermodynamic conditions is a classic example of matter in condensed phase. Water has an amazing pair potential well depth. This means that there exist forces that bind the molecules together. Classically these forces can be categorised into two: long range electrostatic forces and short range van der Waals forces (non− bonded interactions) (I have mentioned about these forces briefly in chapter 2). The short range forces heavily depend upon the distance between the molecules, and are attractive at larger distances but very repulsive at shorter distances. This suggests that there exists an effective distance which corresponds to a minimum in energy, lower than zero. The potential well depth (ε) is the distance between the energy minimum and the point at which energy is zero, which is also the approximate

energy required to separate a pair molecules that are close to each other in a condensed liquid such as water. Values of potential well depth for some smaller molecules and water are given (as $(\varepsilon/k_B)/K$, where K_B is the Boltzmann constant) in the following Table **9.1**.

Table 9.1. Pair potential well depth.

Atom/Molecule	$(\varepsilon/k_B)/K$	Boiling Point/K
He	11	4.2
Ar	142	87
Xe	281	166
CH_4	180-300	111.5
H_2O	2400	373.2

It can be seen from Table **9.1** that water possesses high energy of dissociation (the energy required to break its condensed phase into constituent molecules), almost 8 times than that of methane (CH_4). The boiling point also increases dramatically. The high pair potential well depth of water explains another anomalous behaviour of water: high boiling point.

DENSER LIQUID PHASE

Most of the solids are denser than their corresponding liquids and therefore these solids cannot float in their corresponding liquid phases. On the contrary, normal water is denser than its solid form, ice, and the latter floats in liquid water; this is a signature of water's volumetric anomaly [271]. Enthusiastic readers can verify themselves this fact by comparing how ethanol cubes behave in liquid ethanol [272]. Like ethanol, other hydrogen−bonded liquids, for example, dinitrogen tetroxide (N_2O_4) or hydrogen peroxide (H_2O_2) too do not behave like water does, so this points to the fact that water's exceptional properties do not solely lie in its ability to form hydrogen bonds, rather how it forms. In liquid state, water can have numerous configurations, forming clusters with varying number of water molecules (for example, hexamer and decamer) as we saw before. Nevertheless, as temperature drops by, in particular below the melting point of ice, nearly all of the water monomers prefer to have four nearest neighbours with linear oxygen – hydrogen – oxygen angles.

CHAPTER 10

A Journey Through Water - A Review

Abstract: Recent advances in computing and development of sophisticated experimental techniques have enabled us to make giant leaps in understanding the microstructure of water. The structure of water in normal temperature range is still shrouded in Continuum-Mixture model controversy while new characterisation methods are reported on yearly basis, leaving water an interesting and controversial theme for ever. A multifaceted approach, amalgamating social, economic, political, geographical and technological aspects, is required to alleviate the issues related to the scarcity of water to considerable extent. Centres have been established for performing cutting edge research on water across the globe in order to develop efficient technologies in response to chronic water scarcity. Molecular scientists can greatly contribute to the technological advances that could allay the problems related to fresh water, and influence the policy makers at various organisation levels.

Keywords: Gel, Moor's law, Supramolecular chemistry, UNESCO, Water models.

INTRODUCTION

Our journey ends with this chapter. The motive of writing this chapter is twofold: to summarise the major landmarks throughout this journey and to provide an outlook on future actions for combating the problems related to the availability of fresh water. In the first part of this chapter (from 2 through 4), a review of theoretical and experimental background of molecular investigations and theories on water is provided. The remaining portion of this part is devoted to important research findings on various forms of H_2O, described in chapters from 5 through 9.

In the second part of this chapter, pragmatic approaches, from a molecular scientist's point of view, are discussed in relation to tackling water crisis. This

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includes application of confinement techniques within the framework of nanotechnology. The chapter is concluded by two important recommendations for increasing the participation of molecular scientists in international stage, and for offering much more effective solutions to water−based problems the world faces.

VARIOUS STAGES OF THE JOURNEY

In this section, I present the essence of what have been discussed in the nine previous chapters. This will help the reader quickly rewind the whole book and understand "water" in a wider perspective.

Water, the Centre of Life

In the first chapter, at the beginning of our journey, the central role of water plays in our life was discussed. I presented water in social, political, economic and technological landscapes, the dimensions of which provide rather bleak picture unless a serious and focussed approach is taken. It advocates the importance of considering water in a broader perspective in order to solve one of the chronic problem our world faces, the scarcity of clean drinking water. This approach combines political consensus among different groups standing for solving water crisis. Although water's growing demand surpasses what any solutions can offer, the crisis will become worse without the development and implementation of efficient technology comprising all aspects of water, and molecular scientists can provide a strong support in achieving this aim in the different parts of the world.

A Snapshot of Liquid State

Water is used the most when it is in liquid state, and therefore in the second leg of the journey, the discussion was centered on liquids, starting from their elementary properties. The major portion of this journey is devoted to intermolecular forces, and it would be appropriate here to paraphrase what professor Anthony Stone opined about the applicability of some crude potential forms such as Lennard Jones model in molecular simulations in his seminal book "The theory of intermolecular forces" [47]: having made a great progress in diagnosing what the intermolecular forces are, it is high time to replace such a model, though still useful, for betterment of estimation of various physical properties. The remaining

section in this part of the journey was centered on supercooled water, which we would again visit later in the book. Theoretical tools of glass physics have been applied to investigate the glassy water, and a considerable level of progress has been made to understand the behaviour of the puzzling supercooled water. These brilliant theoretical works include Adam – Gibbs theory, Mode Coupling Theory (MCT) and Energy Landscape theory, and most of them are delicate mix of kinetics and thermodynamics.

Experimental Tools for Microanalysis of Water

Third leg of our journey offers us a tour on a wide range of experimental techniques that have already been employed for the microstructural elucidation of water. A closer look at the experiments on water reveals that three major techniques have been widelyemployed in the investigation of various phases of water: scattering, spectroscopicand calorimetric techniques.

Although computer simulations have several advantages over real experiments as we would see in chapter 4, we must not underestimate the role of experiments as the "final word" on any scientific matter. Stanley and his co−workers have summarised this fact in one of their review papers: "one experiment is enough to kill a hypothesis" [182]. This statement was based on several recent experimental observations, which refute several already existing theoretical propositions. For example, with the experimental report that claims the observation of the third form of supercooled water, the existence of Liquid−Liquid Critical Point (LLCP) theory that advocates only two phases in supercooled water has been challenged. Further, recent findings on the structure of water reveal that water is structured up to five hydration shells. It is interesting to note that the first and fourth shells are almost without any significant change upon alteration in temperatures [180]. This is indeed very opposite to the traditional view point that the "overall" water structure is disrupted.

Development in nanotechnology opened up new horizons of empiricism, hybridisation of various experimental tools. The recent discovery of the 18th stable phases of ice, by exploiting the properties of graphenes, is a perfect example for this approach [104]. A more recent method to investigate the formation of

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Glossary

Amplifier: An electronic equipment that increases input signal to the desired level as output

Auto ionisation: A process by which a molecule ionises itself into constituent cations and anions (in the case of water, hydronium ions and hydroxyl ions)

Basis set: A set of functions that represent molecular orbitals by the linear combination of atomic orbitals

Bifurcated Hydrogen Bond (BHB): The bonding pattern by which a hydrogen atom can participate in two hydrogen bonds, rather than the conventional one

Binding energy: The energy required to crush a molecule/atom into its constituents

Boiling point: The temperature at which a substance converted to its vapour phase

Bond cleavage: The splitting or breaking of a chemical bond

Born−Oppenheimer approximation: The approximation that the movement of nucleus is negligible with respect to electrons so that their motions can be separated

Bragg's equation: The mathematical condition that connects the wavelength, inter planar spacing and angle of incident wave to the surface

Catalytic activity: The action of catalysts for enhancing the rate of reaction by reducing activation energy

Chemical Vapour Decomposition (CVD): The process by which a chemical substrate is subject to vapours in order to make the surface coated with the material contained in the vapour

Climate change: The change in weather pattern

Clusters: Association of molecules constituted in a regular fashion

Coefficient of compressibility: The measure of variation in volume with respect to pressure at constant temperature

Coefficient of thermal expansion: the measure of variation of volume of a material with respect to temperature at constant pressure

Coordination number: The number of neighbours of a given atom

Critical Pressure: The minimum pressure that must be applied to bring about the liquefaction at the critical temperature (see critical temperature)

Critical Temperature (T_c): The temperature of a substance above which its gas form cannot be made to liquefy regardless of the pressure applied. Critical temperature is the highest temperature at which a substance can exist as a liquid

Critical Solution Temperature (CST): The temperature above which water and solute are completely miscible

Crystallisation: A process by which a solid (crystal) is formed

D-defect: A defect in hydrogen bond caused by the presence of two protons in it

Density: The ratio of mass to volume

Deterministic: A system that evolves without randomness

Dimer: a chemical structure formed as a result of the union of two identical sub units, without needing to have bond with each other

Electric field: Electric force per unit charge

Electromagnetic wave: The wave resulted when an electric wave combines with a magnetic wave

Electronic correlation: The interactions between electrons in a system

Electrostatic interactions: The interactions exerted by charged species, positively charged and negatively charged

Entropy: The measure of a system's disorder, which stands for the unavailable thermal energy in the system which cannot be converted to mechanical work.

Ergodic hypothesis: The theory posits that every possible micro states of a surface of constant energy have equal probability to be visited by the system

Forcefield: The mathematical form and parameter sets required to calculate the potential energy of a system

Foulants: The matter absorbed onto the membranes (filers) used in the water

Filtration process: The process of the separation of suspended solid particles from a liquid by passing it through a filter

Fragile Liquids: The liquids whose dynamics do not slow down linearly towards glass transition temperature

Free energy: The maximum energy that can be converted to work

Freezing point: The temperature at which a liquid freezes

Gaussian function: This is a function that takes a bell shaped curve. Three constants in the function indicate the height, width and the centre of the curve

Gaussian type orbitals: One of the types of orbitals that are used for generating molecular orbitals

Glass transition: The transition from liquid state to highly viscous amorphous state

Greenhouse gas: A gas that can absorb Infra−Red (IR) rays, thereby increasing the temperature of the atmosphere

Hamiltonian: An operator that represents the total energy of the system

Hartree−Fock calculation: The fundamental theoretical method for the determination of energy and wave function of a system

HDA (High Density Amorphous): A high density amorphous form of water

Hexamer: A chemical structure formed as a result of the union of six identical sub units, without needing to have bond with each other

Hole theory: An interpretation to account of for the properties of liquids, accounting for vacant spaces between particles

Hydrolysis: The process by which a chemical bond is broken by the addition of water

Hydrophobic hydration: Hydration of non−soluble compounds

Hydrophilic: A substance that has strong affinity towards water

Hyperquenching: Very high cooling of materials

Intermolecular forces: Forces of attraction between molecules

Infra−Red: An electromagnetic radiation that has higher wavelength than the visible light

Kauzmann temperature: The temperature at which the entropy of liquid would be lower than that of a solid

Kinetic energy: The energy acquired by an object due to motion.

LDA: Low Density Amorphous form of water (observed at lower temperatures)

Lattice theory: A proposition designed to understand the behaviour of liquids

L Defect: A defect that leaves a hydrogen bond with no proton in it

Ligands: It is a group or molecule that binds to central atom to form a coordination compound

Lipids: A group of naturally occurring organic compounds

London force: The weakest intermolecular force

Long range forces: Types of forces are even experienced at long distance

Magnetisation: The degree to which a material magnetised

Means square displacement: Measure of deviation over time between the position of a particle and some reference particle

MENA: Abbreviation for Middle East and North Africa, the countries within this region

Metastable: The state of pseudo stability, which gives way to more stable state upon the action of external forces

Molecular Dynamics: A computational algorithm that is used to investigate the time dependent properties of molecules

Monomer: The smallest unit (one molecule) in a polymer

Moor's law: It states that the number of transistors per square inch of Integrated Circuits double every year

NMR: A technique that is used to characterise the internal structure of a material, exploiting magnetic properties of the material

Octamer: A chemical structure formed as a result of the union of eight identical sub units,

without needing to have bond with each other

Orbital: Holder of electrons

Pentamer: A chemical structure formed as a result of the union of five identical sub units, without needing to have bond with each other

Peptide bond: A covalent chemical bond between two amino acid molecules

Phase: A region of uniform chemical composition and unique physical properties

Phonon: A unit of vibrational energy arising due to the vibration of oscillating atoms within a crystal

Polytype: A crystal being in more than one form

Proton Hopping: The jumping of one proton in one molecule to the other

Puckering: The distortion of certain atoms in a compound from the molecular plane

Radial distribution function: A function that describes the variance of density with respect to the distance

Raman scattering: A type of inelastic scattering of a photon upon interaction with matter

Rayleigh scattering: Elastic scattering of light by particles having much lower wavelength

Schrödinger equation: A differential equation which shows the dependence of a state of system with time

Self Consistent Field theory: A numerical approach used to employ for solving many particle (many electron) problems in chemistry and physics

Short range forces: A type of force that is confined to very short distances

Slater type orbitals: One of the types of orbitals that are used for generating molecular orbitals

Spectroscopy: A group of techniques that are employed for the characterisation of molecules

Spinodal line: The locus of points that refers to the limit of local stability with respect to small fluctuations

Stochastic event: An event that is unpredictable due to randomness

Stokes line: The radiation of particular wavelength associated with Raman Scattering

Strong Liquids: The liquids that show a systematic variation in certain physical properties (for example relaxation times) upon variation of temperature

Supercooled: A state achieved by lowering temperature of a liquid, without being converted to a solid

Superheated: A state achieved by increasing temperature of a liquid, without being converted to a vapour

Thermoelectric effect: Conversion of the temperature gradient to the differences in voltage

Thermodynamics: A branch of physical science concerning heat and temperature

Thermoluminescence: Emission of light that is not resulted from heat

Tetramers: A chemical structure formed as a result of the union of four identical sub units, without needing to have bond with each other

Trimer: A chemical structure formed as a result of the union of three identical sub units, without needing to have bond with each other

Tyndal flowers: Small cavities (often in hexagonal shape) that are appeared in ice crystals

Van der Waal force: A type of attractive or repulsive force exerted between neighbouring molecules

Vogel−Fulcher−Tamman (VFT) equation: An equation described for the description of temperature dependence of viscosity

Walrafen pentamers: A water cluster consists of five water molecules wherein four water molecules occupying the corners of regular tetrahedron linked to a water molecule at the centre

Water crisis: A situation that affects most part of the world due to the availability of clean water

Widom line: A line emanating from critical points in phase diagram, on which certain physical quantities show maximum

SUBJECT INDEX

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D

O

P

Q

R

S

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Dr. Jestin Baby Mandumpal is a Lecturer in the Department of Chemistry & Chemical Engineering, Khazar University, Baku, Azerbaijan. As a physical and computational chemist, he has worked on a wide spectrum of research themes employing quantum and classical methodologies on solids, liquids and aqueous solutions. His research endeavours have produced several high quality research articles & a book (The Molecular mechanism of solvent Cryoprotection), in the fields of computational material science and education. Besides, he has procured invaluable teaching experience in chemistry from several countries. Currently he is leading a research group at newly established Khazar Computing Research Center. His research interests include the development of faster computer simulation methods and their applications in simulating liquids and aqueous solutions, and development and application of software for novel material design. He is also interested in history and philosophy of science, and how society is shaped by science and technology.