CHAPTER I

INTRODUCTION

Review of Liquid State

A simple operational definition of a liquid is that it is a medium which takes the shape of a container without necessarily filling it. In contrast, a gas both takes the shape and fills the container whilst a solid neither takes the shape nor fills it. There are, however, materials which are difficult to place on this definition. A few polymeric materials appear to be solid but with time they will flow to the shape of a container. Glasses behave similarly although their flow rate may be immeasurably slow at normal temperatures.

Solutions and the liquid state play an important role in many chemical process in the nature. According to advantages in energy exchange and reaction mechanism, most of the chemical operations such as synthesis, mixing, purification and separation are performed in the liquid state in laboratory and industry. There are many fascinating details of liquid-like behaviour, covering thermodynamics, structure, and motion. For example, liquids flow, although they may be very viscous. They may be transparent, or they may scatter light strongly. Liquids may be found in bulk, or in the form of tiny droplets. They may be vaporized or frozen. Life as we know it probably evolved in the liquid phase, and our bodies are kept alive by chemical reactions occurring in liquids.

The study of the liquid state of matter has a long and rich history, from both the theoretical and experimental standpoints. From early observations of Brownian motion to recent neutron scattering experiments, experimentalists have worked to improve the understanding of the structure and particle dynamics that characterize liquids. Frank and Wen [1] presented a simple model to describe the structural aspects of ions in aqueous solutions. They proposed three different regions, A, B and C, of the solvent molecules surrounding ions. In region A, the solvent molecules are strongly oriented by the powerful short-range forces acting between solute and solvent, and the influence of Coulombic forces is significant as well. The solvent structure in region C is the same as in bulk water. Region B, which interfaces regions A and C, is assumed in order to allow a continuous transition between these structures. It is generally called "region", according to macroscopic observations. The most interesting area is of course the

region A, which is called "solvation shell", where spectroscopic measurements can provide structural data.

The concept of solvation is often used in general to describe the structure of a solution where the geometrical arrangements are significantly different from the bulk structure of the solvent itself. The dynamical stability depends on the combination of forces acting between homogeneous and heterogeneous molecules of which the solution consists. On one hand, a discrete solvation shell can be based on a solute-solvent interaction which is so strong that the exchange rate is much lower in the first solvation shell than among solvent even when the interaction between solute and solvent is weaker than the solvent-solvent interaction. In this case density and mobility effects in the solution are the dominant factors rather than the binding forces between particles.

Some decades ago, investigation of solution and liquid structure was mainly domain of spectroscopical methods such as X-ray and neutron diffractions and NMR etc. However, they encounter some difficulties of producing and interpreting data when the sample is very dilute or when the solution is unstable, or when the molecular interactions are so weak that the input energy from the spectroscopic apparatus exceeds that of the interactions. Moreover, solvation numbers of ions or liquids produced by these analyses depend on the method being used. Data from the diffraction methods seem to supply the most well-defined results, while interpretations of the diffraction data seem to be very difficult and of high error. Further, capacity of these methods is also limited by the complexity of the investigated system.

Evolution of Computer Simulations

Meanwhile the experimental testing has been performed, theoreticians have tried to construct simple models and explained how liquids behave. A successful theory of the liquid state will be one that explains the bulk properties of the liquid from a knowledge of the intermolecular potential. In the bulk we are dealing with a very large number if molecules ($\sim10^{23}$) and we know by the principles of statistics that at equilibrium the time fluctuations of bulk properties will be very small and can generally be ignored. Statistical thermodynamics provides the analytical connection between the intermolecular potential and thermodynamic observables such as pressure and free

energy. Non-equilibrium statistical mechanics provides a similar connection for time-dependent properties such as viscosity and thermal conductivity.

The statistical equations can be solved exactly or with high accuracy for gases and solids but they are very difficult to solve for liquids. An alternative approach to a theory of liquids has been thought the use of physical model which has been developed by Bernal [2] and others [3]. These models have improved our conceptual understanding of the nature of liquids but they have not proved very helpful for the quantitative prediction of liquid-state properties.

In recent years a method has been developed for modelling liquids [4] which has been conceptually valuable and has proved capable of giving a quantitative interpretation of bulk properties. This method uses a modern computer with fast operation and large core store to simulate the behaviour of a large number of atoms or molecules interacting under some assumed potential function. No computer is large enough (nor likely to be) to handle directly the interaction of 10^{23} particles but techniques exist for dealing with much smaller numbers (10^2-10^3) which will give results not significantly different from the true bulk. This method of mathematical analysis has been known as "computer simulation", whose technique has been developed in two different ways, Monte Carlo (MC) and Molecular Dynamics (MD).

It is now about 40 years since the first computer simulation of a liquid was carried out at the Los Alamos National Laboratories in the United States. Due to the rapid development of computer technology, computer simulations have been expanded at a tremendous speed [5] and application of these and other simulation methods have penetrated in almost every field of physics, chemistry, biosciences and engineering sciences. Results of the simulations may also be compared with those of real experiments. In the first place, this is a test of the underlying model used in a computer simulation. Eventually, if the model is a good one, the simulator hopes to offer insights to the experimentalist, and assist in the interpretation of new results. This dual role of simulation, as a bridge between models and theoretical predictions on one hand, and between models and experimental results on the other, is illustrated in Figure. 1.1 . Because of this connecting role, and the way in which simulations are conducted and analysed, these techniques are often termed " computer experiments ".
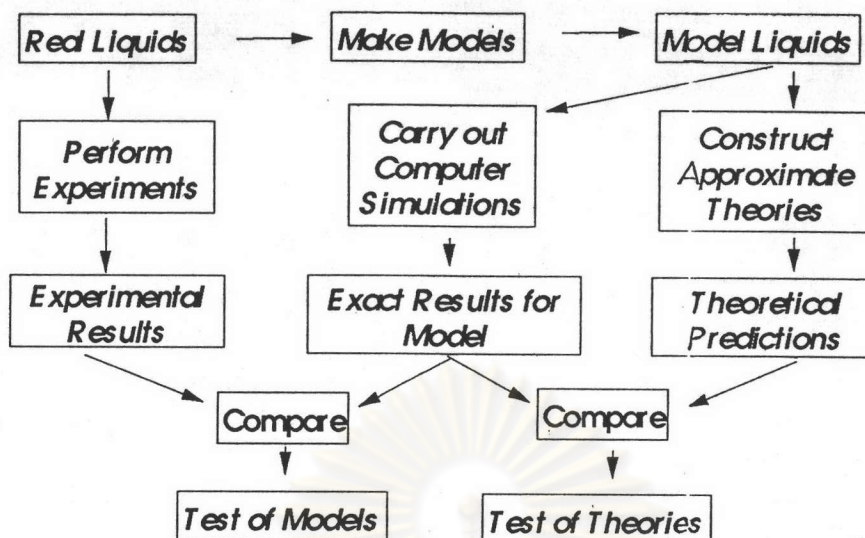
Figure 1.1 The connection between experiment, theory and computer simulation

Since Monte Carlo and Molecular Dynamics simulation have been overcome some limitations of the experimental approach and the availability of high performing capacity of computer provides simulations of rather large number of molecules. Therefore, theoretical investigations of liquid state and solutions have been rapidly developed and numerous studies based on these methods for solution have been published [6-10]. Most of the investigations were, however, based on the structural and dynamic properties concerning the first solvation shell.

Monte Carlo simulation allows not only to evaluate solvation numbers and solute-solvent distances from computed radial distribution functions, but give also access to data not available from any experimental technique so far, as for example an analysis of the perceptual contribution of various coordination numbers to the average solvation number of ions or solvent molecules. The access to the angular distribution of neighbour molecules is also an important means of these methods for the evaluation of structural factors in solution.

In this study, the solvation structure of the solution has been investigated for three systems, one lithium ion (Li^+), one chloride ion (Cl^-) and 1 LiCl molecule in liquid hydroxylamine (NH_2OH), by the method of Monte Carlo simulation. Hydroxylamine has been chosen for several reasons. First, being still a relatively small

molecule, it allows the application of sufficiently accurate ab initio calculations. Second, chemically situated between water and ammonia [11] and being a good solvent for electrolytes, MC and/or MD simulations of ions in hydroxylamine as solvent will be of particular interest for comparisons with similar simulations for water [12], ammonia [13] and water ammonia mixtures [6] as solvents. Third, the possibility of forming several types of hydrogen bonds and the existence of two possible coordination sites for ions make this molecule an especially versatile and challenging example for a theoretical approach, as experimental methods for structural investigations of hydroxylamine solutions meet several restrictions that could be overcome by the quantum chemical and statistical simulation treatment.

The theoretical and analytical requirement for this work are described in chapter II. The construction of an analytical pair potential function and the MC simulation for the two systems of Li^+-NH_2OH and Cl^--NH_2OH are presented in chapter III and IV, respectively. The simulation of the last system studied here, 1 LiCl molecule in liquid NH_2OH, is given in chapter V. Results and discussion are presented in its own chapter. In the last chapter, the conclusion of this study is reported according to the results discussed .