

CHAPTER 1

INTRODUCTION



1.1 Computer Simulation : Motivation and Applications

Solutions and the liquid state, especially aqueous solutions play an important role in many chemical processes in nature. Life as we know must have evolved in the liquid phase, and our bodies are kept alive by chemical reactions occurring in liquids. 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.

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. At the same time, theoreticians have tried to construct models which explain how liquids behave. Contrary to the other states of the matter, the liquid state has resisted rigorous theoretical treatment for a long time. In the solid state, the microscopic interparticle interactions are usually rather strong (say compared to $k_B T$) while in the gaseous state these interactions are usually weak or altogether negligible. This facilitates the theoretical models of these two extreme cases. In liquids, the microscopic interparticle interactions are of intermediate strength resulting a short to

medium range spacial and time correlation, and a nonlinear governing equations. The difficulties are further increased if particles with long range electric interactions are present in the liquid in finite concentrations.

Early models of liquids involved physical manipulation and analysis of packing of a large number of gelatine balls, representing the molecules; this resulted in a surprisingly good three-dimensional picture of the structure of a liquid, or perhaps a random glass, and later applications of the technique have been described [1]. Even today, there is some interest in the study of assemblies of metal ball bearings, kept in motion by mechanical vibration [2]. However, as the use of large numbers of physical objects to represent molecules can be very time-consuming, there are obvious limitations on the type of interactions between them, and the effects of gravity can never be eliminated. The extension of this approach is to use a mathematical rather than a physical model, and to perform the analysis by computer. This method of mathematical analysis has been known for a long time as "computer simulation," whose technique has been developed in two different ways, Monte Carlo(MC) and Molecular Dynamics (MD).

Some decades ago, investigation of solution and liquid structure was mainly a 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 solvent exchange takes place very fast, or when the molecular interactions are so weak that the input energy from the spectroscopic apparatus exceeds that of the interactions. In addition, solvation numbers of ions or liquids produced by these analysis depend on the method being used [3,4]. 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 [5-7]. Further, capacity of these methods is also limited by the complexity

of the investigated system.

Computer simulations using Monte Carlo, originally introduced by Metropolis [8], and Molecular Dynamics method, introduced by Alder [9], have overcome some limitations of the experimental approach. The availability of high processing-capacity computers provide simulations of rather large number of molecules. Therefore, theoretical investigations of the liquid state and solutions have been rapidly developed and numerous studies based on Monte Carlo and Molecular Dynamics simulations for solution have been published [10-35]. Most of the investigations were, however, based on statics and dynamics properties concerning the first hydration shell structure. It is also interesting to obtain data how far influence of an ion acts beyond this first solvation shell, as this gives interesting information about the further structure and the microscopic properties of solutions. Monte Carlo and Molecular Dynamics simulations allow 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 percentual contribution of various coordination numbers to the average solvation number of ions or solvent molecules. The access to angular distribution of neighbour molecules is also an important means of these methods for the evaluation of structural factors in solution. In addition, Molecular Dynamics simulations can give a lot of details of dynamics properties such as translational motion, librational or rotational motion, infrared spectrum etc.

Computer simulations have been expanded at a tremendous speed [36] and applications of these and other simulation methods have emerged in almost every field of physics, chemistry, biosciences and engineering sciences. Because of the underlying approach, which is in philosophy often close to the experimental approach, simulations are also sometimes called 'computer experiments'. On the one hand, the

results of computer simulations can 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, which provides a test of theories. 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, and between models and experimental results, is illustrated in Fig. 1.1 .

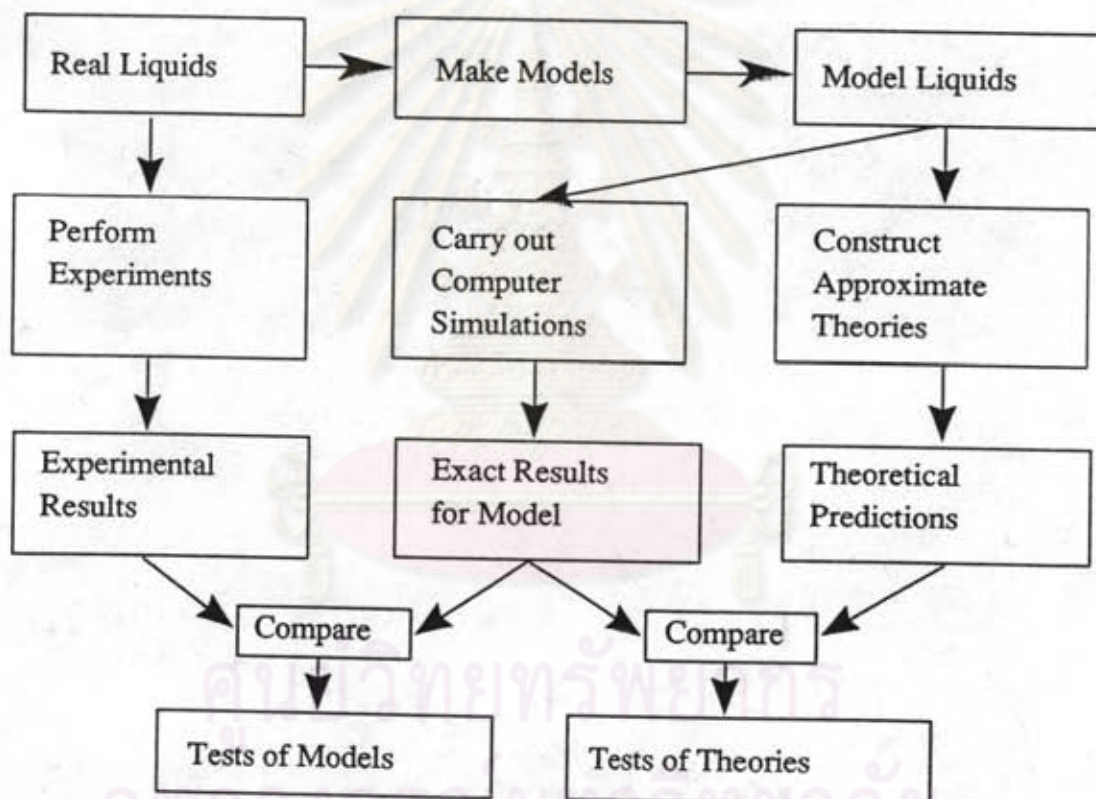


Fig 1.1 The connection between experiment, theory, and computer simulation. [37]

1.2 Ammonia : One of the Most Common Solvents

The archetypal solution for man is salt in water and the major thrust of most solution research has been the elucidation of the properties of similar solutions. When



dealing with non-aqueous solutions, however, one must consider the differences between water and the solvent of interest. Several differences immediately appear when water and ammonia are compared. Water has the higher relative permittivity (80 versus 22 at 0°C) and the lower polarizability (1.45 \AA^3 versus 2.26 \AA^3). Hydrogen bonding is more important in solvent-solvent interactions in H_2O than NH_3 . Finally, the ammonia molecule is more stable against dissociation in the liquid than the water. In water the equilibrium concentrations of H^+ and OH^- ions are near 0.1 ppm. as compared to H^+ and NH_2^- concentrations of 10^{-10} ppm. in ammonia. On the other hand, the H_2O molecule is more stable in the vapour phase.

The study of metal-ammonia solutions has a long and venerable history [38-40]. Most study has focused on the solution of alkaline or alkaline earth metal in liquid ammonia because of their remarkable properties such as high electrical conductivity. Alkaline and alkaline earth metal can be dissolved to large amounts in liquid ammonia, showing the characteristics of liquid metals whereas other metals are hardly dissolved or not. As a result, alkaline and alkaline earth metal in liquid ammonia have been the subject of extensive research by means of both experimental and theoretical methods. In contrast, the study of most other metals in liquid ammonia is impossible in the view of experimental investigations as the experimental apparatus is not capable of giving results for very dilute solution. The solution of one metal ion in a solvent serves as a good model for an infinitely dilute solution. In addition, infinitely dilute solution is a useful tool to understand the effect of a cation or an anion to the solvent species around it, without perturbation by any other ion field.

In this work, a Molecular Dynamics simulation of Zn(II) ion in liquid ammonia will be performed on a high performance workstation (DEC 3100 at the Austrian-Thai Center for Chemical Education and Research, Chulalongkorn University). As mentioned above, the simulation of Zn(II) -ammonia is an attempt to

extend the study of metal-ammonia solutions and of idealized solution models. This work should also provide, therefore, a better understanding of ammonia solution behaviour, and aim at developing a suitable intermolecular potential for cation/solvent interaction.

Details of this intermolecular potential, are given in CHAPTER 2, where the quantum chemical ab initio method, which is one of the most helpful tools for constructing intermolecular potentials, is also outlined. The Molecular Dynamics method is presented in CHAPTER 3, comprising the basic background of statistical mechanics theory and its technical details. CHAPTER 4 contains the various simulation results, and their discussion is presented in CHAPTER 5.



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