

CHAPTER 1

INTRODUCTION

The study of metal-ammonia solutions has been conducted for over a century in history [Weyl 1864; Seely 1871; Taft 1933; Naiditch 1964]. The rich variety of properties is observed as the concentration of metal is changed. For an example, it has a large wide range of electric conductivity, from 10^{-8} to $10^4 \Omega^{-1}\text{cm}^{-1}$ [Schroeder, Thompson, and Oertel 1969]; immiscibility of concentrated and dilute solutions; and liquid metal like properties of concentrated solutions. A lot of structure and dynamical properties were measured by x-ray, neutron diffraction, IR and UV absorption techniques. However, more understanding of the physical phenomena of such systems is still needed. The models of the molecular system were built and the simulations have been performed. Better method and tools, the high performance computers, have rapidly been developed.

Nowadays, in the globalization age, computer technology has been integrated into every field in science. It has been penetrated and expanded by computational methods. The availability of fast computers in the past decades has opened solutions to a lot of computational research, formerly restricted to limited applications, simple chemical model systems and specialized theoretical chemistry. These tools, mainly quantum calculations and statistical mechanics simulations, are widely applicable, and now to very large molecular systems. Especially for investigation of micro-structures formed in solution, these tools are nowadays sometimes even superior to experimental methods, and in systems for which experiments cannot be performed, e.g., arbitrary dilution, these computer simulations can be employed.

A new branch of science, computational science, has been developed to fill the gap between theoretical and experimental science. With the computer simulation many quantities can be computed and provide details of systems in microscopic through macroscopic properties. These results can also be compared with those from real

experiments. If the model is good, it is expected that the simulation results are compatible with experimental results. On the other hand, the predictions of some complicated theoretical models can also be tested with simulation results. The relation

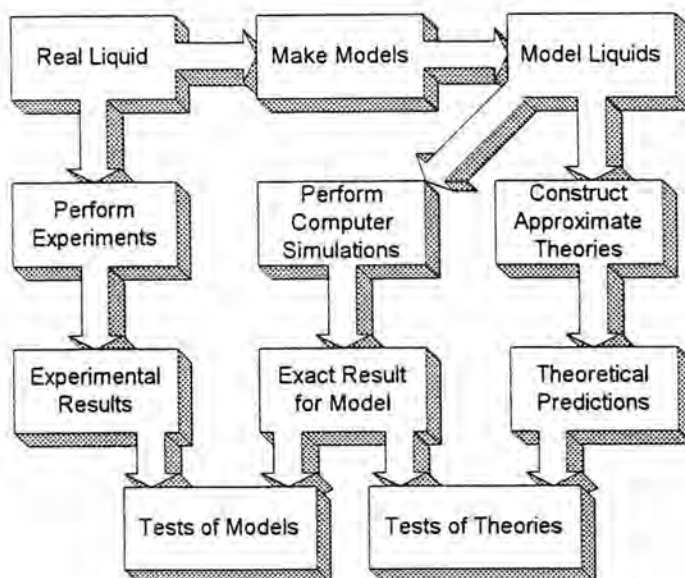


Figure 1.1. The connection between experiment, theory, and computer simulation.

between all these is illustrated in Figure 1.1

1.1 Metal-Ammonia Solutions

Metal-liquid ammonia solutions consist of ammonia molecules, metal ions and (sometimes) free electrons. The presence of free electrons is a special feature of metal-ammonia systems. It is necessary to treat these electrons as quantum particles. This gives rise to considerable difficulties in computer simulations of metal-liquid ammonia solutions. The following are examples of properties which indicate why metal-liquid ammonia solutions have been of interest for a long time.

- At concentrations over 6 mole percent, the solutions behave like liquid metal, especially in electrical properties [Cusack 1963; Faber 1972] in some regions of metal concentration, except they cover a range of very low density of free electron [Allgaier 1970].
- They show unusual physical properties in the region of the phase instability [Teoh, Antoniewicz, and Thompson 1971].

1.1.1 Properties

There are many available data of metal ammonia solution electrical conductivity [Schroeder et al. 1969]. They show that electrical conductivity increases with concentration (Figure 1.2) and it is almost a linearly increasing function of temperature. The conductivity ranges from 10^{-8} to $10^4 \Omega^{-1}\text{cm}^{-1}$, which comparable to that of liquid mercury at room temperature [Schroeder et al. 1969]. The Hall effect

studies show that in the metal-ammonia solutions containing more than 8 mole percent of a metal, the electron density is equal to the density of metal valence electrons and it is independent of temperature [Nasby and Thompson 1970]. These indicate that free electrons exist in the concentrated solution.

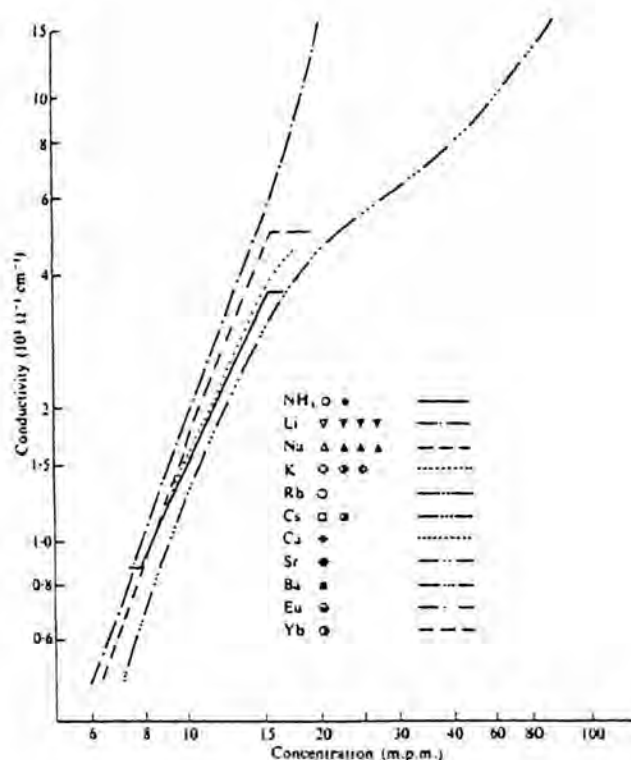


Figure 1.2 Electrical conductivities of solutions of several metals in liquid ammonia at 240 K [Schroeder et al. 1969].

In general, at very low concentrations of metals in ammonia solution, 0-2 mole percent, the solutions behave much as salt solutions do. The experimental data show that valence electrons are solvated [Hallada and Jolly 1963; Burow and Lagowski 1965]. At higher concentrations, at 3-8 mole percent, the solutions show an interesting, metal-insulator transition state. The solution separates into two immiscible fluid phases, metallic and electrolytic [Teoh et al. 1971]. The more concentrated, metallic phase floats above the low concentration, electrolytic phase. Their interface layer is sharp and easily observed. However, this occurrence disappears at temperatures above, approximately, 230 K. For concentrations greater than 8 mole percent, the behavior of the solution can be compared with that of a common liquid metal [Wong 1966; Schroeder et al. 1969; Teoh et al. 1971].

1.1.2 Ca-NH₃ solutions

The first experimental report on calcium-ammonia solutions was by Mossian [1904]. The concentrated solutions have metallic properties. The phase diagram of calcium-ammonia solution is shown in Figure 1.3. It presents five major zones.

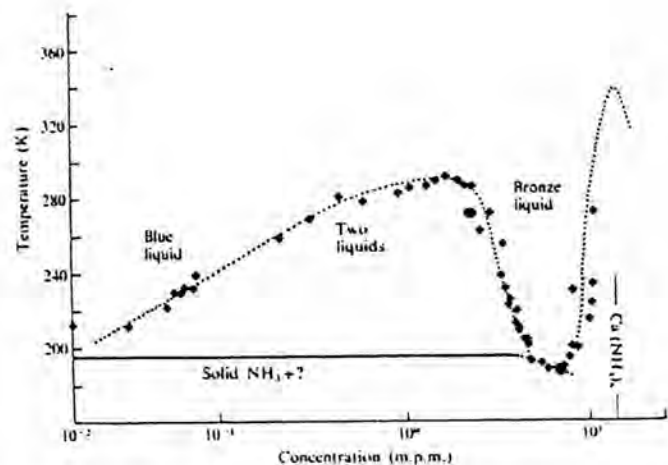


Figure 1.3 Phase diagram of calcium-ammonia solution [Thompson 1976].

- i) Inky-Blue liquid, dilute solution nonmetallic liquid.
- ii) Bronze liquid, concentrated solution homogenous metallic liquid.
- iii) Two liquids, a miscible solution cannot be made at this temperature and concentration.

iv) Solid ammonia.

v) Excess solid metal.

1.1.2.1 Dilute solutions

There have been less data reported for solutions with concentrations below the two phase region. However, from optical absorption, it was shown that both valence electrons of calcium ion in the dilute solution are solvated. [Hallada et al. 1963]. Their mechanical properties, such as the density, are close to the value of pure ammonia.

1.1.2.2 Concentrated solutions

Solutions are taken to be concentrated when the concentration exceeds 3 mole percent. The experimental densities of calcium-ammonia solutions are contained in the dissertation of Wa She Wong [1966] (Figure 1.4). The data on electronic properties indicate that the electrons are free and the mean free paths are sufficiently long for a metallic description to be justified at least near saturation.

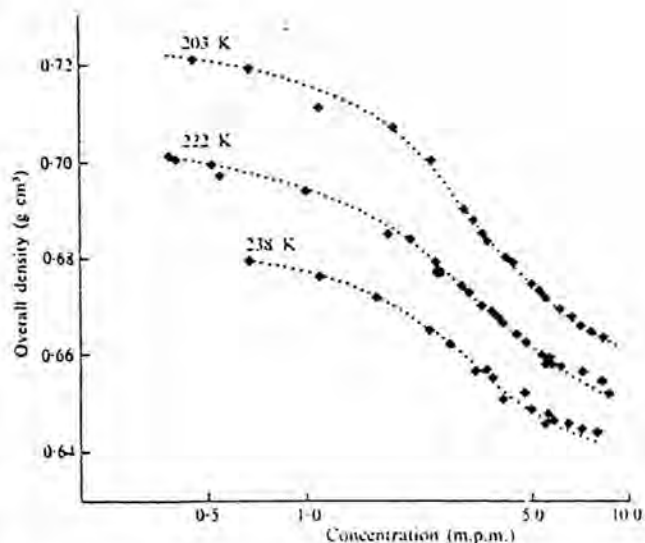


Figure 1.4 Density of calcium-ammonia solutions [Wong 1966].

In $\text{Ca}(\text{NH}_3)_6$, the ammonia molecules have a different geometry from that of the normal pyramid shape. They are nearly planar, with H-N-H angles of 122° and 115° with one shorter N-H distance, 1.94 \AA , and two longer distance, 1.39 \AA [Glaunsinger et al. 1984].

1.2 Computer Simulation

It was over 40 years ago that the first computer simulation of a liquid was carried out at the Los Alamos National Laboratories [Metropolis et al., 1953]. They presented a general method, afterward called the Monte Carlo method, for calculating the properties of any substance which may be considered as composed of interacting individual particles. A few years later, another method was introduced to precisely calculate the behavior of several interacting classical particles in a liquid system, called the Molecular Dynamics method [Alder and Wainwright 1957].

1.2.1 Monte Carlo (MC) simulation

This technique was called Monte Carlo (MC) because of that city's famous gambling casinos, and the role that random numbers play in the method of calculation. One famous example of the MC technique is a method, called hit and miss integration, to evaluate π . This can be easily done by finding the area of a circle inscribed in a square, as shown in Figure 1.5.

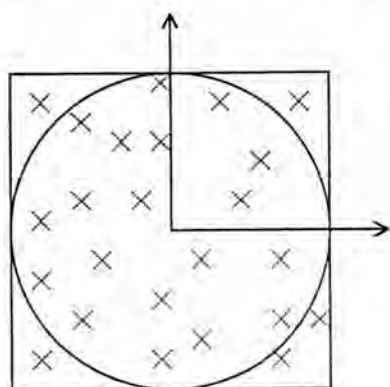


Figure 1.5 The geometry for the hit and miss integration to find the area of the circle. For this illustration the ratio of hits in circle:square is 19:24. It gives a value of $\pi \approx 3.17$, whereas the precise value is $\pi \approx 3.14159$.

A number of trial shots is generated in the square. Two independent random numbers are chosen from a uniform distribution. These numbers are used as the coordinates of points in the square. The value of π can be evaluated from

$$\frac{\pi}{4} = \frac{\text{area of circle}}{\text{area of square}} \approx \frac{\text{number of trial points in circle}}{\text{number of trial points in square}}$$

The accuracy of the estimate of π depends on the number of random trial shots that are used.

1.2.2 Molecular Dynamics (MD) simulation

This method traces all particle trajectories in system using Newton's equations of motion. Technically, it is very easy to get a numerical solution for classical n-body problem. This method can provide both structural and dynamical properties of the solution. The numerical calculation technique called the Predictor-Corrector algorithm was used to perform the simulations in this research.

1.2.3 Comparison between MC & MD

Both simulation methods can be used to evaluate many properties of systems, included some data inaccessible by experimental techniques. However, MD can also calculate dynamical properties of the system, while MC can only provide the time-independent information.

1.3 Summary of This Work

This dissertation deals with calcium-ammonia solutions, using the molecular dynamics method. The primary requirement for the simulation is the potential function description of interactions in the system. The pair, Ca(II)-NH₃, and three-body, NH₃-Ca(II)-NH₃, potential functions have been newly developed. For the concentrated solution, the pseudopotential effect was included. Ammonia-ammonia interactions were taken from the well developed literature [Gurskii, Hannongbua, and Hienzinger 1993]. The results of simulations have been analyzed in the form of radial distribution functions, velocity autocorrelation functions and their Fourier transforms.

This thesis consist of two principal parts. Chapters 1-4 review the fundamental theories needed for this study. The second part, chapters 5-7, report and

discuss the application of those theories to computer simulations and the results obtained from the calculations.

The quantum mechanics theories will be reviewed in the next chapter. The procedure of molecular dynamics methods is reviewed in chapter 3, and the pair potential, three-body correction, and pseudopotential method are described in chapter 4. The method of calculation and the way to manipulate the simulation are shown in chapter 5. Chapter 6 shows the results and comparison with some other works. The final conclusions are presented in chapter 7.