

CHAPTER 2

LITERATURE REVIEW

Chapter 1 has explained how computer simulations can be a powerful tool for developing our understanding of molecule system at the atomic/molecular level. However, there are two major limitations preventing computer simulations from fulfilling their true potential in providing scientific insights and aiding the industrial development of new materials. The first problem is that simulations require considerable computing resources; this limitation is rapidly being overcome by the hardware and software development. The second problem is the accuracy of the fundamental input into the simulations, i.e., the intermolecular model potential, which quantifies the forces acting between the particles.

Since the quality of the results from the simulations definitely depend on the quality of the input, it is important to be able to assess the likely accuracy of an intermolecular potential. Intermolecular potentials are well known with very high accuracy for the rare gases. Much current work on deriving accurate intermolecular potentials is concentrating on small rigid polyatomic molecules. Due to the shortage of reasonable intermolecular potentials, the development in the field of solution research by means of computer simulations seem to be slower than it should be according to technological advances.

Early simulation works were aimed at understanding general features of, for example, liquid behavior, and so idealized model potentials were appropriate. Nowadays, many simulations are undertaken in order to model real systems. The simulations seek to produce results which are in agreement with experiment. The first stage in such a computer simulation is to find a model for the intermolecular interactions in the chosen system, which is sufficiently realistic to give worthwhile

results. There are, of course, difficulties to do so since there are no generally reliable simple procedures for developing intermolecular potentials. Mostly, one must choose which potentials are suitable for the intended simulation by considering the nature of the system. In order to improve this situation, more accurate intermolecular potentials, which are reliably transferable from study to study, must be constructed.

2.1 Definitions and Approximations

2.1.1 Pair interaction approximation

An intermolecular pair potential $E(r_i, r_j)$ is defined as the energy of interaction of a pair of molecules as a function of distance r . The pair potential depends only on the magnitude of the pair separation $r_{ij} = |r_i - r_j|$, so it may be written $E(r_{ij})$. In practice, one assumes ΔE to be equal to this term only, known as the pair-wise additive approximation. Some assumptions are needed in order to approach the intermolecular potential with pair-wise additive approximation.

(a) First, molecules are treated as rigid molecules. This is usually a closed approximation for small molecules. Sometimes the potential is also a function of the intramolecular bond-lengths and bond-angles for studying the transfer of energy between translational and vibration motions. Organic molecules are not usually rigid, so it is usual to model their intermolecular forces by approximating the molecule as a set of fragments and assuming that contributions from each fragment do not depend on the molecular conformation. This assumption will only be valid if the charge density associated with each fragment does not change with the conformation of the molecule.

(b) The total interaction energy of a many- $(N-)$ molecule system based upon the pair-wise additive approximation can be calculated as

$$\Delta E = \sum_i^{N-1} \sum_{j>i}^N E(r_{ij}) \quad (2.1).$$

Indeed, an exact interaction energy of the system does not only sum over all possible pairs, but also other higher-order non-additive terms. The exact interaction energy of a system consisting of N rigid molecules is given by

$$\Delta E = \sum_i^N E_1(r_i) + \sum_i^N \sum_{j>i}^N E_2(r_i, r_j) + \sum_i^N \sum_{j>i}^N \sum_{k>j>i}^N E_3(r_i, r_j, r_k) + \dots \quad (2.2)$$

where the first term in equation (2.2), $E_1(r_i)$, represents the effect of an external field (for example, the container walls) on the system. The second term, $E_2(r_i, r_j)$ is the previously outlined intermolecular pair potential describing the interaction of two molecules, and three-body term, E_3 , four-body term, E_4 , etc., often referred to as non-additive corrections. The third term, E_3 connecting interaction which becomes very significant in case of condensed systems. In most of published simulation, however, they were not included, due to the large computer time needed. Four-body (and higher) terms are expected to be small in comparison with E_2 and E_3 .

Fortunately, the pairwise approximation gives a remarkably good description of liquid properties because the average three-body effects can be partially included by defining an 'effective' pair potential. To do this, we rewrite equation (2.2) in the form

$$\Delta E \approx \sum_i^N E_1(r_i) + \sum_i^N \sum_{j>i}^N E_2^{\text{eff}}(r_{ij}) \quad (2.3).$$

The pair potential appearing in computer simulations are generally to be regarded as effective pair potentials of this kind, representing all the many-body effects; for simplicity, we will just use the notation $E(r_{ij})$ or $E(r)$. A consequence of this approximation is that the effective pair potential needed to reproduce experimental data may turn out to depend on the density, temperature etc., while the true two-body potential $E_2(r_{ij})$ of course does not.

2.1.2 The Isotropic Atom-Atom Approximation

The intermolecular interaction energy between a pair of molecules is assumed as a sum of interactions between every intermolecular pair of atoms, and these interactions depend only on the separation of the atoms. As shown in equation 3.12 in Chapter 3.

Other potentials may have a variety of other terms, where atom-atom potential can be a complex function of r_{ij} [6]. With regard to the aforementioned definition of the intermolecular pair potential as a function of molecule pair separations and orientation, the orientation dependence is implicit used an isotropic atom-atom assumption. The isotropic atom-atom approximation is fairly good approximation considering its convenience and reliability, which recognizes just the relative positions of the atoms within the molecule as the major factor in determining the interaction energy between pairs of molecules. In addition, the isotropic atom-atom approach may allow transferring the potential parameters for a particular atom in a molecule to others. This assumption completely neglects the effects of attached atoms, which implies that every atom is treated as spherical shape. Therefore, some errors may occur. These errors can be partly absorbed into the parameters, according to which parts of the intermolecular potential are sampled in fitting. There is considerable cancellation of errors between different components

of the potentials, so taking some parts of potentials, and combining them with other term, can make the overall scheme useable. Hence, it is not possible to state which parameter set is best, except in the sense that it has been fitted and tested against the widest range of data. The only way of establishing which potential will be best for the purposes of a given simulation is by trying a variety of functional forms.

2.1.3 Contributions to the Intermolecular Potential

The intermolecular forces all have an electronic origin and are fundamentally the same as the forces involved in chemical bonding; although magnetic and gravitational effects do exist, they can normally be neglected. There is no general description of what components are composed in a potential. Thus, it is dependent upon how it has been established. An intermolecular potential which is derived from empirical data may contain different parts by fitting quantum-mechanical energies. In principle, each intermolecular potential consists of an attractive and a repulsive potential. The attractive potential reflects the long-range interaction, while the repulsion dominates the short-range interaction. In general, most intermolecular potentials are usually described by a repulsive potential, a dispersion term, point-charge Coulombic interaction, and sometimes general polarization terms. Morokuma [7] has successfully developed a method of separating the Hartree-Fock energy into several components, including electrostatic, exchange repulsion, charge-transfer, and polarization components. The importance of what components represent the main interaction varies from system to system. In hydrocarbon systems, the hydrogen-hydrogen repulsive forces dominate the interaction energy [8]. On contrary, hydrogen bonding interaction is most important in water.

2.2 Classification of Intermolecular Potentials

Intermolecular potentials fall roughly into three classes namely, model potential, empirical potential, and quantum-mechanical potential. The model potential is the most simple one, but it has also the specific intention of showing that the structure of simple liquids is more or less universal and could be well approximated by the interaction of rigid spherical particles. It dominated in the early literature of Molecular Dynamics [2,9] Monte Carlo [10,11] simulations as presented in the work of van der Waals and also in the hard-sphere glasses built from ball bearings by Bernal [12]. As time goes on and computers becomes more powerful, the focus of such simulation shifted away from the general properties of liquids to the more specific, leading to the need of more realistic models to an increasing extent. At present, intermolecular potentials employed in most simulations are empirical and quantum-mechanical intermolecular potentials. The latter one seems to be of advantage in both aspects of its accuracy and transferability.

2.2.1 Model Intermolecular Potentials

Model intermolecular potentials have also known as “idealized” intermolecular potentials for the reason that they do not represent realistic interactions between molecules pair. For the purpose of investigating general properties of liquids and solutions and for comparison with theory, they may be, however, of value. Thus, it is very common to use them in computer simulations. There are forms of the model intermolecular potentials; the hard-sphere potential, the square-well potential, and the soft-sphere potential. Because of their mathematical simplicity, many of the empirical intermolecular potentials are derived from them with refining of experimental data.

(a) The hard-sphere potential

This model represents molecules as rigid spheres of diameter σ : two such molecules will bounce off each other elastically if their centers approach to a distance σ , but otherwise do not interact at all. The potential can be written in the form

$$U^{\text{HS}}(r) = \begin{cases} \infty & (r < \sigma) \\ 0 & (r \geq \sigma) \end{cases} \quad (2.4)$$

as shown in Figure 2.1(a). This model takes account of only the short-range repulsion which is always infinitely large in the inner space of the molecule sphere. Due to its simplest form, it has the greatest advantage compared to other model potentials, so that simulations with this model can be carried out with relative ease. In many cases such simulations give a good qualitative picture of the effects of molecules collisions. This is especially true at relatively high temperatures, where molecules have enough kinetic energy that they encounter mainly the upper portion of the repulsive curve. Most principles of kinetic theory can be developed with only this model.

(b) The square-well potential

This is one of the simplest potentials including both attractive and repulsive contributions, as shown in Figure 2.1(b), a hard-sphere surrounded by an attractive well of constant depth. The square-well potential is defined by the equations

$$v^{sw}(r) = \begin{cases} \infty & (r < \sigma_1) \\ -\varepsilon & (\sigma_1 \leq r < \sigma_2) \\ 0 & (r \geq \sigma_2) \end{cases} \quad (2.5)$$

with the three adjustable parameters σ_1 , σ_2 and ε . This model is a good compromise between mathematical simplicity and the model realism.

(c) The soft-sphere potential

A somewhat more realistic representation of the repulsive energy is given by the potential

$$v^{ss}(r) = \varepsilon \left(\frac{\sigma}{r} \right)^\kappa = ar^{-\kappa} \quad (2.6)$$

where κ is a parameter, often chosen to be an integer. The soft-sphere potential becomes progressively 'harder' as κ is increased. Soft-sphere potentials contain no attractive part. Figure 2.1(c), where a is a positive constant [13]. This model recognizes the fact that more energetic molecules can approach each more closely before being repelled, and thus can represent some of the temperature dependence of properties. But it again neglects the attractive part of the molecular interaction, and is mainly recommended because of the mathematical convenience. These three potentials are shown in Figure 2.1.

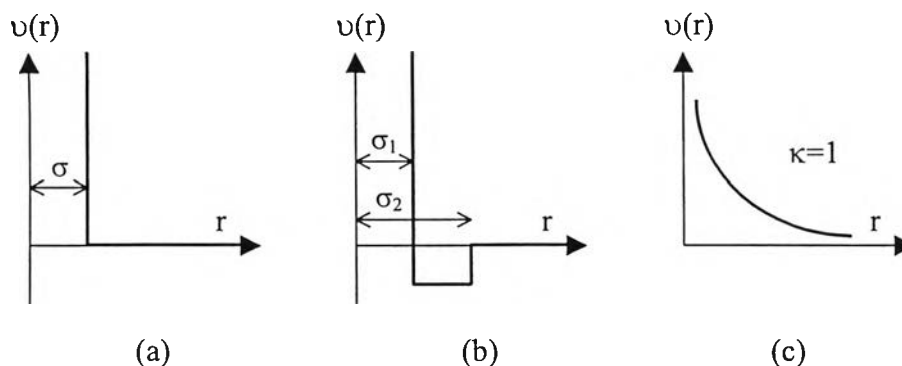


Figure 2.1 (a) the hard-sphere potential, (b) the square-well potential and (c) the soft-sphere potential with repulsion parameter $\kappa=1$.

2.2.2 Empirical Intermolecular Potentials

The empirical model for intermolecular potentials has been developed in order to remedy the problems of non-realistic model of the intermolecular potential for many years before the *ab initio* calculation became possible for calculating molecular energies with high accuracy. Most empirical intermolecular potentials are derived by fitting only one observed property, such as lattice constants [14], or vibrational spectra [15], to a potential function. Those potentials are not sufficient to describe the interaction energies when the system enhances its complexity. However, fitting a wide variety of experimental data is very difficult because the observed properties sometimes does not correlate altogether. Limited attempts have been made to combine several different types of properties in one potential [15,16], but this has been done only for a small class of systems. Need of a large amount of experimental data for highly accurate potential hinders development of the empirical model. Moreover, there are no experimental data available for large classes of systems.

To determine an empirical intermolecular potential requires,

- (i) some experimental data for some properties of the molecular solid, liquid or gas, which is sensitive to the intermolecular potential,
- (ii) a quantitative theory to propose those properties to be an intermolecular potential, and
- (iii) an assumed functional form for the intermolecular potential which contains some adjustable parameters.

Most of the early models were based on the Lennard-Jones potential of the form

$$v^{\text{LJ}}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2.7)$$

which has only two parameters, the minimum energy separation σ and the well depth ε . It has a reasonable functional form at long range, as the dominant term in the dispersion energy is r^{-6} . The r^{-12} term for the repulsive wall was chosen purely for mathematical convenience (an exponential one would be sometimes more realistic). This model potential is then fitted to experimental data by first guessing initial values for ε and σ , calculating the property from the guessed potential, comparing with the experimental values, and thereby deriving an improved estimate of ε and σ , using fitting criteria such as a least squares minimization. The set of parameters which gives the 'best' agreement with experiment defines the potential, which will be used in the simulation.

2.2.3 Quantum Mechanical Intermolecular Potentials

According to difficulties in obtaining highly accurate empirical intermolecular potentials, the advantages of modern and fast computers is utilized more and more for the energy calculations of chemical system, and quantum-mechanical intermolecular potentials now become a helpful tool to computer simulations. In the view of quantum mechanics, the intermolecular energy is assumed to be the difference of the supermolecule (dimer or complex) energy and the energies of its constituents.

$$E(\text{intermolecular}) = E(\text{supermolecule}) - E(\text{constituents}) \quad (2.8).$$

Since the intermolecular potentials employed in the simulations of this study have been derived by quantum chemical method, in the following two sections some details of quantum mechanics as well as the construction procedure are presented.