



Intermolecular Potentials

Professor Richard J. Sadus

Centre for Molecular Simulation

Swinburne University of Technology

PO Box 218, Hawthorn Victoria 3122, Australia

Email: RSadus@swin.edu.au



Overview

This module comprises material for two lectures. The aim is to examine the nature and role of intermolecular potentials used in simulations. This module build is common to both the molecular dynamics and Monte Carlo modules

The specific learning objectives are:

- (a) To understand the role of intermolecular potentials;
- (b) To become familiar with the most commonly used potentials;
- (c) To understand the consequences of short and long range potentials.



Introduction

In Module 1, the need for an intermolecular potential was discussed and the Lennard-Jones potential was introduced. The Lennard-Jones potential is undoubtedly the most widely used intermolecular potential for molecular simulation. It is a simple continuous potential that provides an adequate description of intermolecular interactions for many applications. Although it is treated as a pair-wise potential, it is more accurately described as an “effective” potential and as such it does not truly represent two-body interactions but it also incorporates influence of many-body interactions albeit in a very crude and inaccurate way.

The aim of this Module is to survey intermolecular potentials and provide an awareness of alternatives to the Lennard-Jones potential.



Intermolecular Interactions

- The calculation of the potential energy inevitably involves assumptions concerning the nature of attraction and repulsion between molecules. Intermolecular interaction is the result of both short- and long-range effects.
- Electrostatic, induction, and dispersion effects are examples of long range interactions. In these cases, the energy of interaction is proportional to some inverse power of intermolecular separation. Electrostatic interactions result from the static charge distribution between molecules. The effect can be either attractive or repulsive and it is exclusively pairwise additive. Induction effects are always attractive, resulting from the distortions caused by the molecular fields of neighbouring molecules.
- However, the most important contribution is the attractive influence of dispersion arising from instantaneous fluctuations caused by electron movement. Neither induction nor dispersion are pairwise additive.



Intermolecular Interactions (contd)

- Short-range interactions are characterised by an exponential decay in the interaction energy with respect to intermolecular separation. At small intermolecular separations, there is a significant overlap of the molecular wave functions causing either intermolecular exchange or repulsion. These interactions are not pairwise additive.
- In theory, it is possible to calculate the intermolecular interactions from first principles. However, in practice the first principle or ab initio approach is confined to relatively simple systems. More commonly, the influence of intermolecular interaction is expressed by some type of intermolecular potential.



Intermolecular Interactions (contd)

- The justification for the intermolecular potential is often entirely empirical, although, it is possible to determine an ab initio potential during the course of a simulation.
- The nature of intermolecular forces is discussed in greater detail by Stone (1996).



Effective Potentials

- Before proceeding further, it is important to make the distinction between effective and true two-body potentials. Even though many potentials functionally pairwise (i.e., they only require pair separation as inputs), they are often in reality “effective” potentials that should not be confused with genuinely two-body potentials. Here, we will reserve the word two-body or pairwise, for potentials that genuinely represent only two-body interaction. Therefore, unless otherwise indicated, the potentials discussed below should be treated as “effective.”
- Many effective potentials have been developed (Maitland et al., 1981) and applied to atoms. Historically, an empirical approach was used with the parameters of the potential being obtained from experimental data such as second virial coefficients, viscosities, molecular beam cross sections etc. Conclusions regarding the accuracy of pair potential were made by comparing the properties predicted by the potential with experiment.



Effective Potentials (contd)

- In contrast, computer simulation permits the theoretical rigorous evaluation of the accuracy of intermolecular potentials. However, very few potentials have been tested extensively using molecular simulation. Notable exceptions are the hard-sphere, Lennard-Jones, and exp-6 potentials.
- Effective potentials for atoms are often incorporated into the molecular simulation of platonic molecules and increasingly, macromolecules. Therefore, the atomic pair potential is an important starting basis for predicting molecular properties.
- In view of this, the evaluation of pair potentials by molecular simulation is likely to be increasingly important for the prediction of molecular fluids.



Hard-Sphere Potential

The simplest approximation is to treat atoms as impenetrable hard spheres, i.e.,

$$u(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$

where σ is the hard-sphere diameter. In a molecular simulation, special procedures are required (Allen and Tildesley, 1987) to evaluate the effect of the hard-sphere potential. These problems are more easily overcome by MC than MD. The potential remains of considerably utility as a reference for the development of hard-sphere equations of state.



Square-Well Potential

The square-well potential is the simplest intermolecular potential that is capable of representing the properties of liquids

$$u(r) = \begin{cases} \infty & r \leq s \\ -\epsilon & s < r \leq \lambda s \\ 0 & r > \lambda s \end{cases}$$

where λ is some multiple of the hard-sphere diameter and ϵ is a measure of the attractive interaction. The square-well potential represents a mathematically idealised model of molecular interactions. The properties of the square-well fluid have been investigated widely (Haile, 1992) and it remains a useful starting point for the development of fluid state theories.



Yukawa Potential

The square-well potential can be made more realistic by changing the variation of attractive interactions. There have been many such variations of which the Yukawa potential is an important example:

$$u(r) = \begin{cases} \infty & r \leq \sigma \\ -\frac{\epsilon \sigma}{r} \exp\left[-z\left(\frac{r}{\sigma} - 1\right)\right] & r > \sigma \end{cases}$$

where ϵ is an attractive term, σ is the hard-sphere diameter and z is an adjustable parameter. The inverse power dependence of this potential means that it can be applied to ionic systems.



Lennard-Jones Type

Real fluids have a continuous intermolecular potential, which can be approximated by the following empirical relationship:

$$u(r) = \mathbf{e} \left[\left(\frac{m}{n-m} \right) x^{-n} - \left(\frac{n}{n-m} \right) x^{-m} \right]$$

where n and m are constants, $x = r/r_m$, and r_m is the separation corresponding to minimum energy. The most common form of the Lennard-Jones potential is obtained when $n = 12$ and $m = 6$. We note that only the choice of $m = 6$ has a valid theoretical justification (this is how dispersion forces decay).



Truncated Lennard-Jones Potential

It is also common to model the repulsive interactions between hard-spheres by a truncated Lennard-Jones potential defined by

$$u(r) = \begin{cases} 4\mathbf{e} \left[\left(\frac{\mathbf{s}}{r} \right)^{12} - \left(\frac{\mathbf{s}}{r} \right)^6 \right] + \mathbf{e} & r \leq 2^{1/6} \mathbf{s} \\ 0 & r > 2^{1/6} \mathbf{s} \end{cases}$$

The advantage of this potential is that it provides a more realistic representation of repulsive interaction than assuming an infinitely steep potential.



Kihara Potential

The Kihara spherical core potential (Maitland et al., 1981) is a slightly more complicated alternative to the Lennard-Jones potential.

$$u(r) = \begin{cases} \infty & r \leq d \\ 4e \left[\left(\frac{s-d}{r-d} \right)^{12} - \left(\frac{s-d}{r-d} \right)^6 \right] & r > d \end{cases}$$

where d is the diameter of an impenetrable hard core at which $u(r) = \infty$. The Kihara potential can be also applied to non-spherical molecules by using a convex core of any shape. The Kihara potential has been studied extensively and it generally predicts the second virial coefficient more accurately than the Lennard-Jones potential.



Exponential-6 Potential

A great theoretical weakness of all of the preceding potentials is they fail to acknowledge the exponential decay of intermolecular repulsion. Possibly the most widely used intermolecular potential containing an exponential term is the modified-Buckingham or exp-6 potential. The exp-6 potential is based on the Born-Mayer potential. For practical applications, the form of the exp-6 potential is

$$u(r) = \begin{cases} \infty & r \leq r_m \\ \frac{e}{1 - \frac{6}{a}} \left\{ \frac{6}{a} \exp \left[a \left(1 - \frac{r}{r_m} \right) \right] - \left(\frac{r_m}{r} \right)^6 \right\} & r > r_m \end{cases}$$



Exponential-6 Potential (contd)

where α is the repulsive-wall steepness parameter, ϵ is the maximum energy of attraction occurring at a separation of r_m , and λr_m is the distance at which the potential goes through a false maximum. The value of λ can be obtained (Hirschfelder et al., 1954) by finding the smallest root of the following equation.

$$I^7 \exp[\mathbf{a}(1-I)] - 1 = 0$$

The false maximum is an unsatisfactory feature of the exp-6 potential. At $r = 0$ the exponential term has a finite value allowing the dispersion term to dominate at very small intermolecular separation. Consequently, the potential passes through a maximum and then tends to $-\infty$ as $r \rightarrow 0$. Therefore, the condition that $u(r) = \infty$ when $r \leq \lambda r_m$ must be imposed to use the potential meaningfully in a simulation. Alternatively, damping functions for the dispersion term have been proposed which overcome this problem.



BFW Two-Body Potential

The square-well, Lennard-Jones, and exp-6 potentials, are generic potentials which can be applied to a wide variety of fluids with a varying degree of accuracy. In contrast, considerable effort has been made in developing highly accurate intermolecular potentials that are specific to a particular atom or class of atoms. The noble gases have been the main focus of this work. A feature of all true body potentials is that repulsion is treated via an exponential term. For example, the Barker-Fisher-Watts potential for argon is:

$$u(r) = e \left[\sum_{i=0}^5 A_i (x-1)^i \exp[\mathbf{a}(1-x)] - \sum_{j=0}^2 \frac{C_{2j+6}}{\mathbf{d} + x^{2j+6}} \right]$$



BFW Two-body Potential (contd)

In the BFW potential, $x = r/r_m$ and the other parameters are obtained by fitting the potential to experimental data for molecular beam scattering, second virial coefficients, and long-range interaction coefficients. The contribution from repulsion has an exponential-dependence on intermolecular separation and the contribution to dispersion of the C_6 , C_8 and C_{10} coefficients are included.



Ab Initio Potentials

Historically, most true two-body potentials were obtained from empirical fits to experimental two-body data. An alternative is to obtain an intermolecular potential by fitting a carefully chosen function to data obtained from ab initio calculations. For example, Eggenberger et al. used ab initio calculations to obtain the following potential for the interactions between neon atoms

$$u(r) = a_1 \exp[-a_2 (r / a_0)^2] + a_3 \exp[-a_4 (r / a_0)^2] \\ + a_5 \exp[-a_6 (r / a_0)^2] + a_7 (r / a_0)^{-10} + a_8 (r / a_0)^{-8} + a_9 (r / a_0)^{-6}$$

where a_0 is the Bohr radius and the remaining parameters do not have any physical meaning.



Ab Initio Potentials (contd)

It is interesting to compare the functional similarity of this potential with with accurate empirical two-body potentials such as the BFW potential. By doing so, we can observe that all of these potential have an exponential term and contributions from r^{-6} , r^{-8} and r^{-10} intermolecular separations.



Ionic and Polar Potentials

Unlike atoms, molecules are associated commonly with permanent multipole moments or charges which result in electrostatic interactions. The theoretical basis of electrostatic interactions is well known (Hirschfelder et al., 1954). The application of Coulomb's law of electrostatic interaction between charges q , dipole moments μ and quadrupole moments Q between molecules a and b yields

$$u^{(q,q)}(r) = \frac{q_a q_b}{r}$$

$$u^{(q,m)}(r) = -\frac{q_a \mathbf{m}_b \cos \theta}{r^2}$$



Ionic and Polar Potentials (contd)

$$u^{(q,Q)}(r) = \frac{q_a Q_b (3\cos^2 \mathbf{q}_b - 1)}{4r^3}$$

$$u^{(mm)}(r) = -\frac{m_a m_b (2\cos \mathbf{q}_a \cos \mathbf{q}_b - \sin \mathbf{q}_a \sin \mathbf{q}_b \cos(\mathbf{f}_a - \mathbf{f}_b))}{r^3}$$

$$u^{(mQ)}(r) = \frac{3m_a Q_b}{4r^4} \left[\cos \mathbf{q}_a (3\cos^2 \mathbf{q}_b - 1) - 2\sin \mathbf{q}_a \sin \mathbf{q}_b \cos \mathbf{q}_b \cos(\mathbf{f}_a - \mathbf{f}_b) \right]$$

$$u^{(Q,Q)}(r) = \frac{3Q_a Q_b}{16r^5} \left[1 - 5\cos^2 \mathbf{q}_a - 5\cos^2 \mathbf{q}_b - 15\cos^2 \mathbf{q}_a \cos^2 \mathbf{q}_b + 2[\sin \mathbf{q}_a \sin \mathbf{q}_b \cos(\mathbf{f}_a - \mathbf{f}_b) - 4\cos \mathbf{q}_a \cos \mathbf{q}_b]^2 \right]$$



Ionic and Polar Potentials (contd)

Where θ_a , θ_b , Φ_a and Φ_b define the various orientation angles between the molecules.

At this stage it should be noted that most of the above interactions are long-ranged and as such special techniques described below are required otherwise the minimum image convention would be violated.



Molecular Force Fields

To properly describe the physics of interactions of real molecules, apart from bonded interactions we must consider intramolecular interactions. In general, the total interaction energy can be calculated by summing the various contributions, e.g:

$$E(r,l,\mathbf{q},\mathbf{t},\mathbf{c}) = \sum_{\text{nonbonds}} u_{nb}(r) + \sum_{\text{bonds}} u_b(l) + \sum_{\text{bending}} u_q(\mathbf{q}) + \sum_{\text{dihedral}} u_t(\mathbf{t}) + \sum_{\text{out-of-plane}} u_c(\mathbf{c}) + \sum u_{el} + \dots$$

where u_{nb} is the non-bonded potential, u_b is the bond potential, u_q is the bond angle potential, u_τ is the torsional potential, u_χ is the out-of-plane bending (improper torsional) potential, and u_{el} is the Coulombic potential. This equation only includes “diagonal terms” but it can be extended to include contributions from “cross terms” such as bond-angle or angle-angle interactions.



Molecular Force Fields (contd)

There are many examples of such force fields. A popular model is AMBER:

$$\begin{aligned}
 E = & \sum_{bonds} \frac{K_l}{2} (l - l_0)^2 + \sum_{angles} \frac{K_q}{2} (\mathbf{q} - \mathbf{q}_0)^2 \\
 & + \sum_{dihedrals} \sum_n \frac{V_n}{2} [1 + \cos(n\mathbf{t} - \mathbf{g})] + \sum_{i < j} 4\mathbf{e}_{ij} \left[\left(\frac{\mathbf{s}_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\mathbf{s}_{ij}}{r_{ij}} \right)^6 \right] \\
 & + \frac{1}{vdW_{scale}} \sum_{i < j}^{1,4terms} \left[\left(\frac{\mathbf{s}_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\mathbf{s}_{ij}}{r_{ij}} \right)^6 \right] + \sum_{H-bonds} \left[\frac{C_{ij}}{r_{ij}^{12}} - \frac{D_{ij}}{r_{ij}^{10}} \right] \\
 & + \sum_{i < j} \frac{q_i q_j}{\mathbf{e} r_{ij}} + \frac{1}{EE_{scale}} \sum_{i < j}^{1,4terms} \frac{q_i q_j}{D r_{ij}}
 \end{aligned}$$

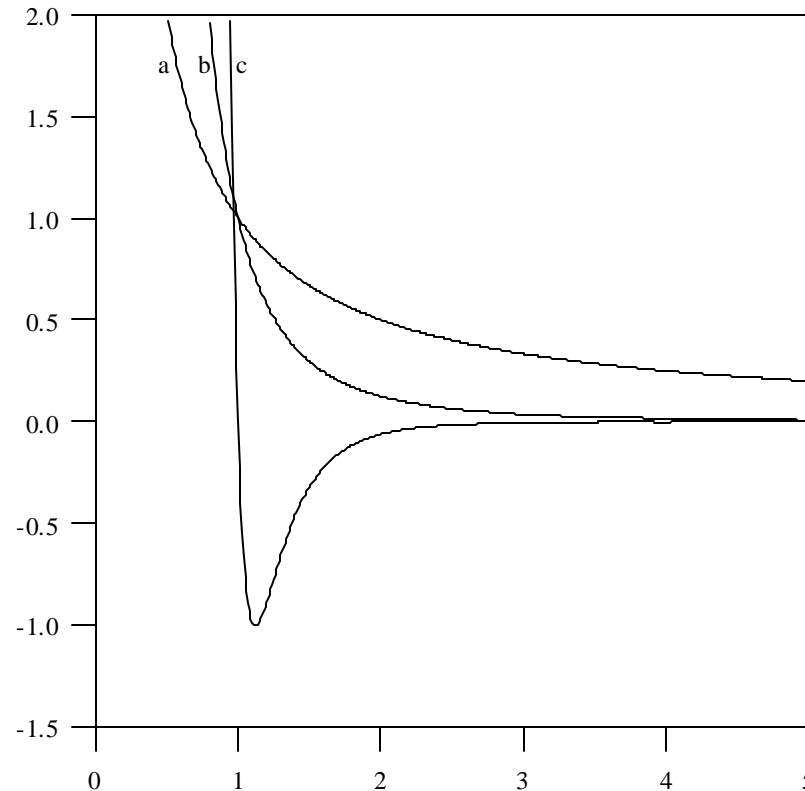


Long Range Interactions

The use of periodic boundary conditions is a standard feature of the molecular simulation of bulk properties using short-range intermolecular potentials. It avoids inaccuracies caused by surface effects and it also provides the additional benefit that computation time is reduced significantly by using cut-off corrections instead of calculating the interactions of all periodic images. However, long-range interactions such as Coulombic or dipolar interactions typically exert an influence which is much greater than half the length of the simulation box. The decay of the Coulombic, Stockmayer, and Lennard-Jones potentials as a function of intermolecular separation are compared in the figure below. It is apparent that the Coulombic and, to a lesser extent, the Stockmayer potentials, are non-zero for quite large intermolecular separations. The obvious solution is to use a very large simulation box, however, this approach is prohibitive computationally. Instead, various computational procedures have been devised and some of the alternatives are discussed below.



Long Range Interactions (contd)



Comparison of the decay of (a) Coulombic ($q_a q_b / \epsilon \sigma = 1$), (b) Stockmayer ($\mu_a \mu_b / \epsilon \sigma^3 = 1$, $\theta_a = 90^\circ$, $\theta_b = 90^\circ$ and $\phi_a = \phi_b$), and (c) Lennard-Jones (u / ϵ) reduced potentials (u^*), as a function of reduced intermolecular separation ($r^* = r / \sigma$).



Long Range Interactions (contd)

Special techniques must be used in conjunction with potentials that are long range. Two popular techniques are the Ewald summation and the reaction field method. Details of the Ewald summation are given elsewhere (Sadus, 1999). Here we will describe the use of the reaction field method.

Firstly, we assume that every molecule is at the centre of an imaginary sphere the size of which is determined by the cut-off radius r_c . The sphere is inside a homogeneous medium with a characteristic dielectric constant ϵ_s . The energy resulting from interaction of the central molecule with all other molecules within the sphere are calculated fully:



Long Range Interactions (contd)

$$E(short)_i = \sum_{j:r_{ij} \leq r_c} u(r_{ij})$$

This corresponds to the short-range contribution of dipolar interaction. The long-range contribution to the energy results from interaction with the medium beyond the sphere. The contribution to energy caused by the surrounding medium is

$$E(long)_i = -\frac{\mu_i(\epsilon_s - 1)}{2\epsilon_s + 1} \left(\frac{1}{r_c^3} \right) \sum_{j:r_{ij} \leq r_c} \mu_j$$

where μ_i is the dipole moment of the central molecule and μ_j is the dipole moment of neighbouring molecules within the sphere. Consequently, the total energy experienced by each molecule is evaluated from:



Long Range Interactions (contd)

$$E_i = E(\text{short})_i + E(\text{long})_i$$

It should be noted that a discontinuity in energy is generated when molecules enter or leave the sphere. Therefore, it is usual practice to taper the interactions at the sphere's surface by applying a weighting factor $f(r_{ij})$ that approaches zero continuously at $r_{ij} = r_c$. Several different tapering functions have been proposed. In many cases, a simple linear function is appropriate

$$f(r_{ij}) = \begin{cases} 1 & r_{ij} < r_t \\ \frac{r_c - r_{ij}}{r_c - r_t} & r_t \leq r_{ij} \leq r_c \\ 0 & r_c < r_{ij} \end{cases}$$

where $r_t = 0.95r_c$.



Long Range Interactions (contd)

- The advantage of the reaction field method is that it can be incorporated easily into a conventional molecular dynamics or Monte Carlo simulation with a minimal increase in computation time.
- The main disadvantages of the method are the potential discontinuity in energy arising from molecules entering and leaving the sphere, and the need to know the external dielectric constant in advance.



Problems

1. Devise an NVT algorithm that assumes a hard sphere intermolecular potential.
2. Determine the value of λ for the square-well potential that gives a reasonable approximation of the well-width of the Lennard-Jones potential. Hint: do this graphically.
3. Find a relationship between the hard-sphere diameter and the energy-minimum separation for Lennard-Jones type intermolecular potential.
4. Suggest an approximate intermolecular potential for interactions that consist pure of a combination of hard-sphere repulsion and dispersion interactions.
5. Suggest a modification of the 12-6 Lennard-Jones potential to improve the calculation of dispersion interactions.
6. Devise an algorithm to implement a reaction field into an NVT ensemble simulation.



Reading Material

The material covered in this module is discussed in greater detail in the following books:

Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., *Molecular Theory of Gases and Liquids*, John Wiley & Sons, New York, 1954.

M.P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, OUP, Oxford, 1987.

Hockney, R. W. and Eastwood, J. W., *Computer Simulation Using Particles*, Adam Hilger, Bristol, 1988.

Haile, J. M., *Molecular Dynamics Simulation. Elementary Methods*, John Wiley & Sons, New York, 1992.

D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press, San Diego, 1996, pages.

Stone, A. J., *The Theory of Intermolecular Forces*, Clarendon Press, Oxford, 1996.

R.J. Sadus, *Molecular Simulation of Fluids: Theory, Algorithm and Object-Oriented*, Elsevier, Amsterdam, 1999.