CHAPTER 3

POTENTIAL FUNCTIONS

The reliability of results obtained from a computer simulation of Monte Carlo or Molecular Dynamics type depends strongly on the quality of the potential functions used. A potential function describes the interaction energy among particles in that system. In general, the total interaction energy of N particles of the system can be written as

$$\Delta E = \sum_{i}^{N} v_1(r_i) + \sum_{i}^{N} \sum_{j>i}^{N} v_2(r_i, r_j) + \sum_{i}^{N} \sum_{j>i}^{N} \sum_{k>j>i}^{N} v_3(r_i, r_j, r_k) + \ldots \qquad (3.1)$$

where the first term in eq. (3.1), $v_1(r_i)$, represents the effect of an external field (e.g. the container walls) on the system. The second term, v_2, called the pair potential is the most contribution term. In practice, one assumes ΔE to be equal to this term only, known as the pair-wise additive approximation, whereas the remaining terms are often referred to as non-additive corrections. The third term,v_3, called three-body connecting interaction which sometime 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 to v_2 and v_3.

3.1 Pair Potential

As mentioned above, most of simulations which available at the time being approximates ΔE simply by the pair potential term. So far, there have been several types of pair potentials used in computer simulations. The most commonly used is the Lennard-Jones 12-6 pair potential [30] which has the form

$$v^{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{3.2}$$

The Lennard-Jones potential contains just two adjustable parameters: the collision diameter σ (the separation for which the energy is zero) and the well depth ε. These parameters are graphically illustrated in Figure 3.1.

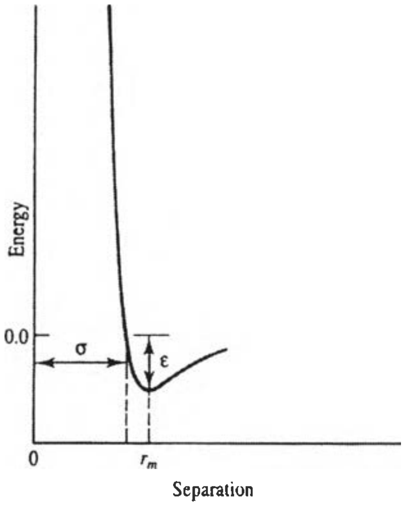

Figure 3.1 The Lennard-Jones potential.

The Lennard-Jones equation may also be expressed in term of the separation at which the energy passes through a minimum, r_m. At this separation, the first derivative of the energy with respect to the internuclear distance is zero (i.e. $\partial v / \partial r = 0$) from which it can easily be shown that $r_m = 2^{1/6}\sigma$. We can thus also write Lennard-Jones 12-6 potential function as follows,

$$\nu^{LJ}(r) = \varepsilon\left[\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right] \tag{3.3}$$

or

$$\nu^{LJ}(r) = \frac{A}{r^{12}} - \frac{C}{r^{6}} \tag{3.4}$$

where A is equal to εr_m^{12} (or $4\varepsilon\sigma^{12}$) and C is equal to $2\varepsilon r_m^{6}$ (or $4\varepsilon\sigma^{6}$).

The Lennard-Jones potential is characterised by an attractive part that varies as r^{-6} and a repulsive part as r^{-12}. These two components are drawn in Figure 3.2.

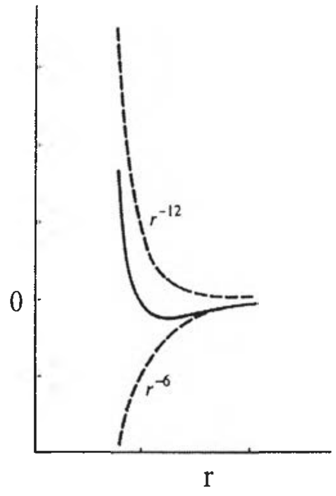

Figure 3.2 The Lennard-Jones potential as a sum of a repulsive (Ar^{-12}) and attractive (Cr^{-6}) components.

The other forms of pair potential, which are very simple and convenient to use in computer simulation and in liquid-state theory, are:

a) The hard-sphere potential

$$\upsilon^{HS}(r) = \begin{cases} \infty & (r < \sigma) \\ 0 & (r \geq \sigma) \end{cases} \tag{3.5}$$

b) The square-well potential

$$\upsilon^{SW}(r) = \begin{cases} \infty & (r < \sigma_1) \\ -\varepsilon & (\sigma_1 \leq r < \sigma_2) \\ 0 & (r \geq \sigma_2) \end{cases} \tag{3.6}$$

c) The soft-sphere potential

$$\upsilon^{SS}(r) = \varepsilon\left(\frac{\sigma}{r}\right)^{\kappa} = ar^{-\kappa} \tag{3.7}$$

where κ is a parameter, often chosen to be an integer. The soft-sphere potentials contain no attractive part. These three potentials are shown in Figure 3.3.

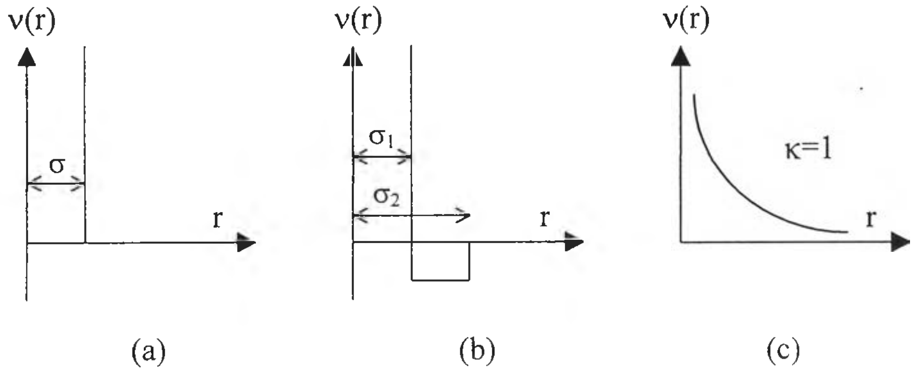

Figure 3.3 (a) the hard-sphere potential, (b) the square-well potential and (c) the soft-sphere potential with repulsion parameter κ=1.

3.2 Analytical Form of Potential Functions

In the energy fitting step, a suitable mathematical function is selected. Given two molecules M and N, the pair interaction potential E_{MN} might contain explicitly both angular and radial dependency. In practical way, however, one normally use only the radial function depending on the interatomic distance $r_{i,j}$ with i and j being atoms belonging to molecules M and N, respectively. For accuracy and flexibility reasons, one would like to use a fairly long series of terms. On the other hand, the longer series, the larger number of associated fitting parameters, and the larger number of machine cycles required to compute interaction energies in the simulation. In general, the form of potential function can be expressed as

$$E_{MN} = \sum_{i}^{m}\sum_{j}^{n}\left(\frac{A_{ij}}{r_{ij}^{x}} + \frac{B_{ij}}{r_{ij}^{y}} + \frac{q_i q_j}{r_{ij}}\right) \qquad (3.8)$$

where m and n are number of atoms on molecules M and N, respectively, A_{ij} and B_{ij} are fitting parameters which represent interaction between atom i and atom j, and q is atomic charge of each atom.

Once the analytical form of the potential has been chosen, a fitting procedure then will be carried out.