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chapter two

Molecular dynamics

(Part 2)

Titles

2.2 Potentials

❖Unlike human beings(برخلاف انسان), who normally try to have more potential, more money, and higher positions, matter always tries to reduce its potential and to be at the bottom of the potential well. Note that rivers run always to the sea and raindrops always form in sphere-like shapes.

❖ In this section, we will discuss this potential acting on atoms

❖When atoms are near enough to feel each other, the balance between attraction and repulsion takes place, and it is determined by so-called interatomic potential.

❖ Atoms will eventually(در نهایت) settle down at the minimum potential states at the equilibrium distances following Newton's equations of motion.

❖The sum of all forces acting on an atom, F, is

$$F = ma = m\frac{dv}{dt} = m\frac{d^2r}{dt^2} = \frac{dp}{dt} \qquad (2.2)$$

where:

    a is acceleration

    v is velocity

    t is time

    r is position

    p is momentum

❖If the total energy E is constant in time (dE/ dt = 0), which is the case of an isolated system for MD simulations, F is related to the negative gradient of potential with respect to position

$$F = -\nabla U \rightarrow F = -\nabla U(r_1, r_2, \ldots, r_N) \qquad (2.3)$$

where U is the potential.

❖ Therefore, if we know the potential of a system as a function of interatomic distance, then we can have forces on atoms and thus can solve the above equation for time evolution of the system.

❖In this section, two popular types of potentials will be reviewed in some detail: pair potentials, and Tersoff potentials.

2.2.1 Pair potentials

❖In an N-atom system where N is the number of atoms, an atom i interacts with all other atoms at the same time.

❖Let us consider the two-atom pair interactions only.

❖There are *(N − 1)* interactions per atom and the number of atoms is N , thus the number of

pairs, *N* pair, is on the order of *N²*

$$N_{\text{pair}} = \frac{(N-1)N}{2} \propto O(N^2) \tag{2.5}$$

↓

❖Figure 2.4 shows 10 pair interactions in a system of five atoms as an example.

❖A typical example is the Lennard−Jones potential (Lennard−Jones 1924), $U_{LJ}(r)$, expressed in

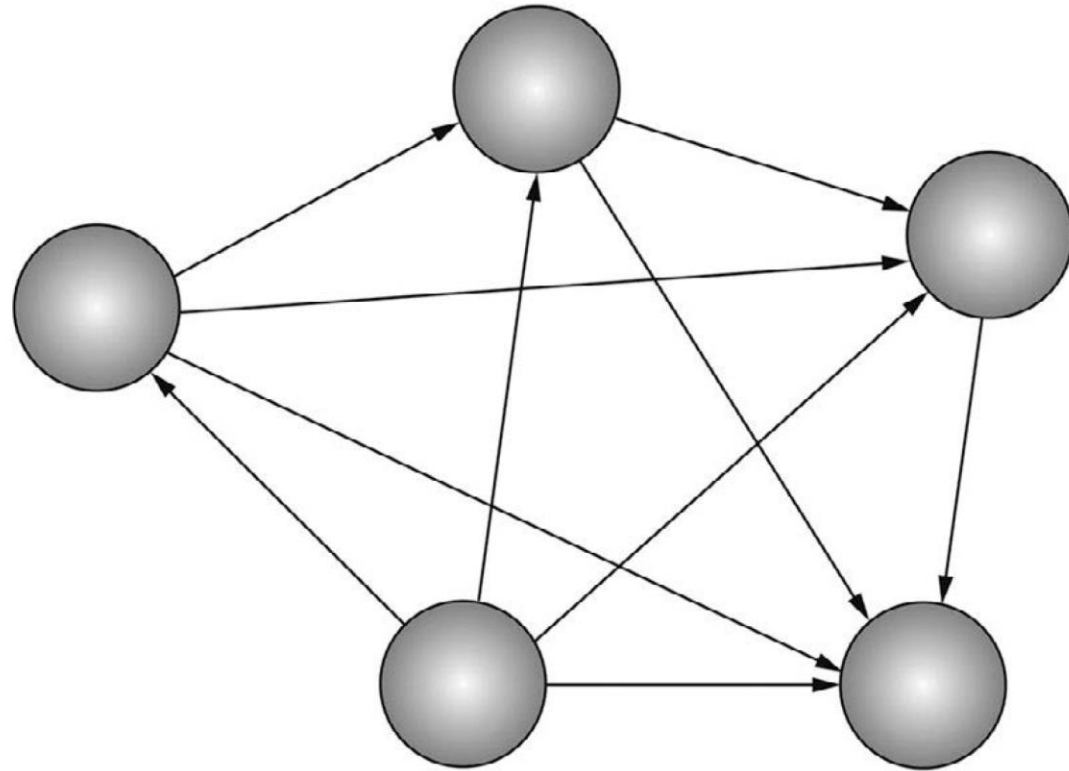terms of interatomic distance, r, with the following two parameters:

Figure 2.4 Pair interactions (arrows) in a five-atom system.

$$U_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \qquad (2.6)$$

where:

✓ parameter ε is the lowest energy of the potential curve ($\equiv$ well depth)

✓ parameter σ is the interatomic distance at which the potential is zero as shown in Figure 2.5.

Then its force form of repulsive and attractive term is

$$F_{LJ} = \frac{24\varepsilon}{\sigma} \left[2 \left(\frac{\sigma}{r} \right)^{13} - \left(\frac{\sigma}{r} \right)^{7} \right] \qquad (2.7)$$
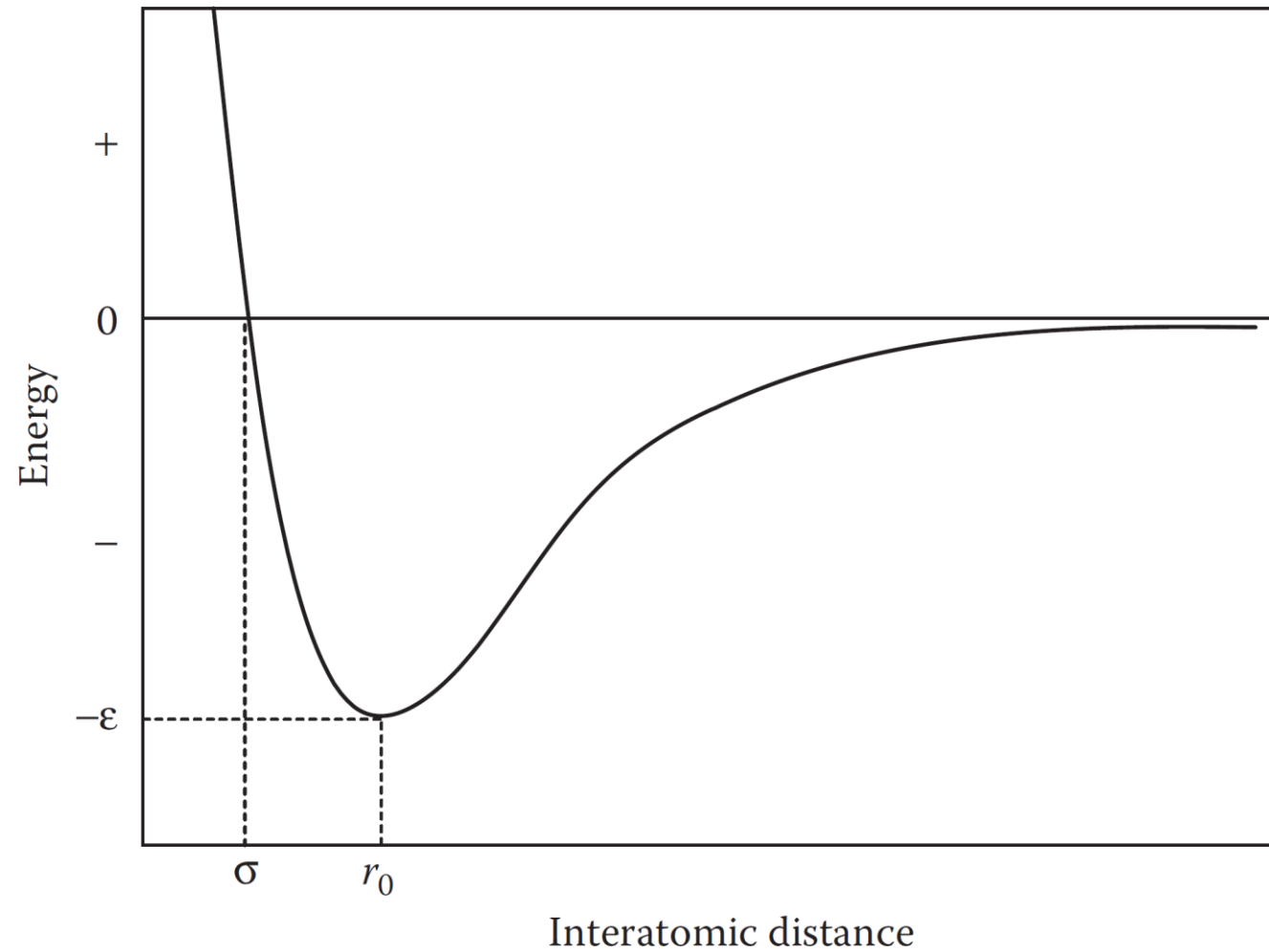
Figure **2.5** Schematic representation of the Lennard–Jones pair potential.

Several features are noted here when two Lennard–Jones atoms (such as inert element Ar) approach each other from a long distance:

At $r = \infty$, U_{LJ} and F_{LJ} are zero.

When they get closer, dipole–dipole attraction takes place, and the r^{-6} term best describes this van der Waals interaction.

When they get even closer, the Pauli repulsion due to overlapping electron clouds takes place, and the arbitrary r^{-12} term describes this steep increase in repulsion.

At equilibrium interatomic distance, r_0 (= $2^{1/6}$ σ = 1.122 σ), two forces are balanced to a net force of zero, and the corresponding energy becomes minimum ($dU_{LJ}/dr = 0$).

The energy passes through 0 at $r = \sigma$ and increases steeply as r decreases further due to the Pauli repulsion.

❖This simple pair potential can express the atomic interactions of noble gases (Ne, Ar, Kr, etc.).

However, this potential cannot be applied to metals, semiconductors, and other solids.

2.2.2 Tersoff potential

❖ Covalent solids have less closely-packed (often with a coordination number of only 4) and have strong directional bonds of equivalent strength.

❖ Diamond or zincblende(ZnS) structures belong to this group of solids and are characterized by a bond angle of ~109.47° and bonds of the sp^3 hybridization of orbitals. Therefore, bond angle and bond order are the prime characteristics of these materials.

❖ Tersoff (1988) recognized this geometrical fact and developed a potential in the following general form:

$$U_{\text{Tersoff}} = \frac{1}{2}\sum_{i\neq j} U_R(r_{ij}) + \frac{1}{2}\sum_{i\neq j} B_{ij}U_A(r_{ij}) \tag{2.12}$$

where:

U_R and U_A represent repulsive and attractive potentials

B_{ij} is the bond order for the bond between atom i and j, which is normally a decreasing function of the coordination number, N_{coor}, as

$$B_{ij} \propto \frac{1}{\sqrt{N_{\text{coor}}}} \tag{2.13}$$

❖In other words, the bonding B_{ij} of atom i with atom j is reduced by the presence of another bond B_{ik}.

❖The degree of weakening depends on where this other bond is and what is the angle.

❖ With a good parameterization, this potential has worked quite well and has been applied to various covalently bonded solids and molecules such as SiC, Si, diamond, amorphous carbon and hydrocarbons.