Lennard–Jones Potential and Reduced Units

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1 Lennard–Jones potential

Lennard-Jones potential is one of the most famous pair potentials for van der Waals systems, which was initially proposed for liquid argon (Ar).

$$V_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{1}$$

The parameter ε governs the strength of the interaction and σ defines a length scale. The r^{-12} term, which is the repulsive term, describes Pauli repulsion at short ranges due to overlapping electron orbitals, and the r^{-6} term, which is the attractive long-range term, describes attraction at long ranges (van der Waals force). This potential is strongly repulsive at short distances and it passes through 0 at $r = \sigma$, $V_{LJ} = 0$.

Whereas the functional form of the attractive term has a clear physical justification, the repulsive term has no theoretical justification. It is used because it approximates the Pauli repulsion well and is more convenient due to the relative computing efficiency of calculating r^{-12} as the square of r^{-6}.

Due to its simplicity, it is often used to describe the properties of gases and to model dispersion and overlap interactions in molecular models. It is especially accurate for noble

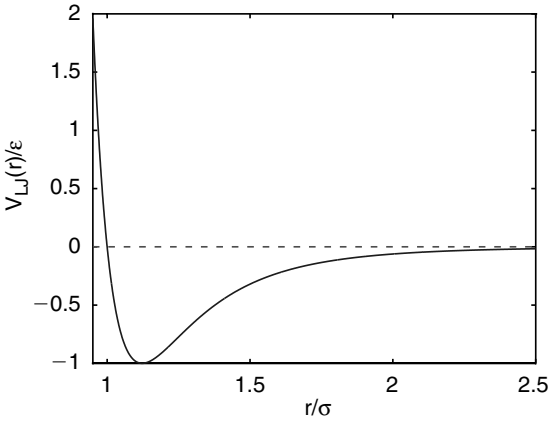

Figure 1: The Lennard–Jones potential.

Table 1: Units used in MD simulations of Lennard-Jones potential of Ar.

Physical quantity	Unit	Value for Ar
length	σ	3.4×10^{-10} m
energy	ε	1.65×10^{-21} J
mass	m	6.69×10^{-26} kg
time	$\sigma(m/\varepsilon)^{1/2}$	2.17×10^{-12} s
velocity	$(\varepsilon/m)^{1/2}$	1.57×10^{2} m/s
force	ε/σ	4.85×10^{-12} N
pressure	ε/σ^3	4.20×10^{7} N $\cdot$ m^{-2}
temperature	ε/k_B	120 K

gas atoms and is a good approximation at long and short distances for neutral atoms and molecules.

These parameters can be fitted to reproduce experimental data or accurate quantum chemistry calculations. Due to its computational simplicity, the Lennard-Jones potential is used extensively in computer simulations even though more accurate potentials exist.

2 Reduced Units

It is convenient to work in dimensionless or reduced units, also called MD units. In MD units $k_B = 1$ is considered.

Assume that the potential energy of the system can be written as a sum of pair interactions. The (effective) intermolecular potential can be written in the form $\varphi(r) = \varepsilon V(r/\sigma)$, where ε is a characteristic energy (*e.g.* the well depth) and σ a characteristic length (*e.g.* the value of r for which $\varphi(r) = 0$). The mass of the atoms is denoted by m. It is good practice to express all physical quantities in term of the units ε, σ and m.

In this way one avoids discovering the law of corresponding states the hard way. From these fundamental units one may derive all other units, *e.g.* the unit of time: $t_0 = \sigma(m/\varepsilon)^{1/2}$. To give a specific example: for Lennard-Jones (Ar) ($\varepsilon/k = 119.8$ K, $\sigma = 3.405$ Å, $m = 39.95/6.02 \cdot 10^{23}$ g) the time unit is $t_0 = 2.156 \cdot 10^{-12}$ s, the unit of velocity $v_0 = \sigma/t_0$ $= 1.579 \cdot 10^{4}$ cm $\cdot$ s^{-1}. The time unit t_0 is roughly the timescale of one atomic vibration period in Ar lattice.