Atomic systems

\[ V = \sum_i v_i(r_i) + \sum_{i > j} v_{ij}(r_{ij}) + \sum_{i > j > k} v_{ijk}(r_{ijk}) + \cdots \]

Most simulations stop at pair-wise additive terms.

Common form of model potential:

\[ U(v) = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} \left( \frac{\sigma}{r} \right)^{6} \]

"Real" potential for Ar

(pairwise !)

Reduced with:

\[ \rho^* = \rho_0^3 \quad \tau^* = \frac{k_B T}{\varepsilon} \quad \rho^* = \rho_0^3 / \varepsilon \quad \varepsilon^* = \varepsilon / \varepsilon \]

The difference between "true" (pairwise) potential and the effective potential must need to be introduced in a simulation to reproduce the properties of a liquid is significant!

Some even less realistic potentials:

\[ U^{\text{HS}}(r) = \begin{cases} \infty & r < \sigma \\ \phi & \phi < r \end{cases} \]

\[ U^{\text{sw}}(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma \leq r < 2\sigma \\ \phi & r \geq 2\sigma \end{cases} \]

\( \lambda \): range
Molecular systems

Often, site-site approach, with fixed bond lengths and torsional or bond angles?

Bond vibrations are of very high frequency, difficult to handle.

Common potential for polymeric systems

\[ E_B = \frac{1}{2} k_B (r - R_0)^2 \] harmonic, bond vibration

\[ E_\theta = \frac{1}{2} k_\theta (\cos \Theta - \cos \Theta_0)^2 \] bond bending

\[ E_\Phi = \sum_{n=0}^{5} \alpha_n \cos^n \Phi \] torsional

\[ E_{\text{ub}} = LD \]

For larger systems, site-site approach becomes prohibitively expensive - Orientation-dependent potentials (Oey and Berne).

\[ U_{6B} = 4 \epsilon \left( \frac{r}{\delta_1, \delta_2} \right) \left( \frac{1}{r-\delta_1(r, \delta_1, \delta_2)} \right) \]

two parameters in orientation-dependent \( \sigma \) and \( \epsilon \):

- \( k \): ratio of molecular length to breadth
- \( \kappa' \): ratio of potential well depth for side-by-side and end-to-end configurations
Polar forces → partial charges or multipoles

\[ \rightarrow \quad + \quad - \]
dipole / quadrupole.

CH4
(octopole is first non-vanishing moment)

Lattice models

Spin models (such as Ising)

relevant for solids, magnetism, important for theoretical physics

polymer models (Flory Theory)
important because of speed of coding.