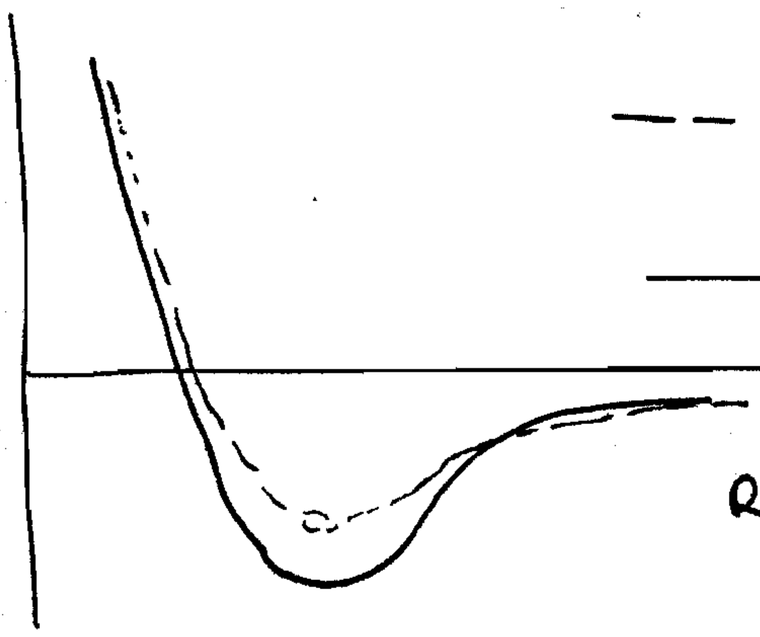
Atomic systems

$$V = \sum_i v_1(\vec{r}_i) + \sum_i \sum_{j>i} v_2(\vec{r}_i, \vec{r}_j) + \sum_i \sum_{j>i} \sum_{k>j>i} v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \cdots$$

Most simulations stop at pair-wise additive terms.

Common form of model potential:



– – – – $v(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$

——— "real" potential for Ar (pairwise!)

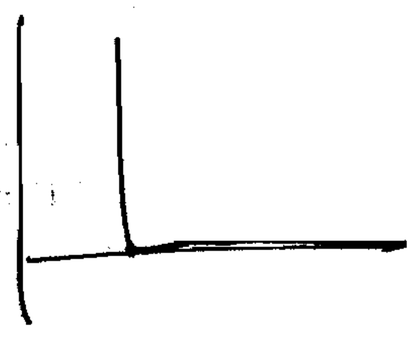
Reduced units: $\rho^* = \rho\sigma^3 \quad T^* = \frac{k_B T}{\epsilon}$

$p^* = p\sigma^3/\epsilon \quad E^* = E/\epsilon$

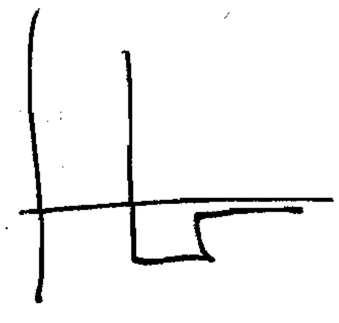
The difference between "true" (pairwise) potential and the effective potential must need to be introduced in a simulation to reproduce the properties of a liquid is significant!

Some even less realistic potentials:

$$v^{HS}(r) = \begin{cases} \infty & r < \sigma \\ \phi & \sigma \leq r \end{cases}$$



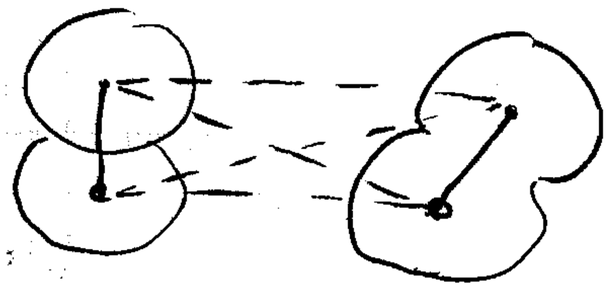
$$v^{SW}(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma \leq r < \lambda\sigma \\ \phi & r \geq \lambda\sigma \end{cases}$$



λ: range

Molecular systems

Often, site-site approximation, with fixed bond lengths (and torsional or bond angles?)

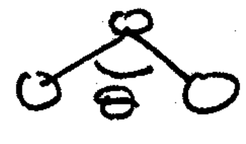


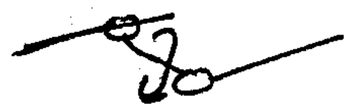
Bond vibrations are of very high frequency, difficult to handle.

$$v(\vec{r_{ij}}, \vec{o_i}, \vec{o_j}) = \sum_a \sum_b v_{ab}(r_{ab})$$

Common potential for polymeric systems

$E_b = \frac{1}{2} k_b (\ell - \ell_0)^2$ harmonic, bond vibration

$E_\theta = \frac{1}{2} k_\theta (\cos\theta - \cos\theta_0)^2$ bond bending 

$E_\phi = \sum_{n=0}^{5} a_n \cos^n \phi$ torsional 

$E_{ub} = 2D$

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

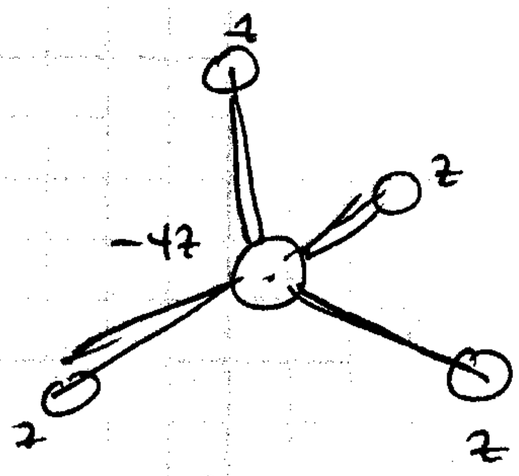
$$U_{GB} = 4\epsilon(\vec{r}, \vec{o_1}, \vec{o_2}) \cdot \left(\left[\frac{\sigma_0}{r - \sigma(\vec{r}, \vec{o_1}, \vec{o_2}) + \sigma_0} \right]^{12} - \left[\quad \right]^{6} \right)$$

two parameters in orientation-dependent σ and ϵ:

k: ratio of molecular length to breadth

k': ratio of potential well depths for side-by-side and end-to-end configurations

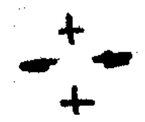
Polar forces → partial charges or multipoles



CH_4

(octopole is first non-vanishing moment)

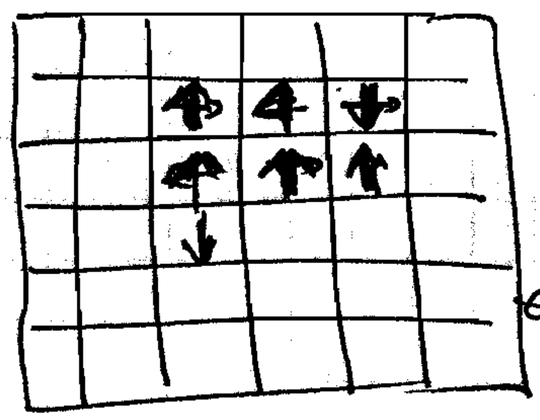
→ dipole



quadrupole.

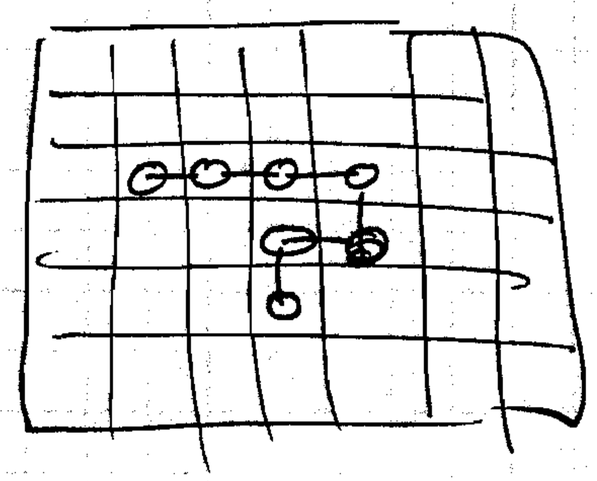
Lattice models

Spin models (such as Ising)



← cubic lattice.

relevant for solids, magnetism, important for theoretical physics



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