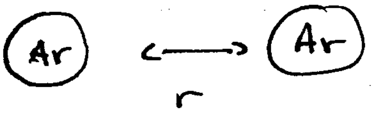
MSS- Ch-22

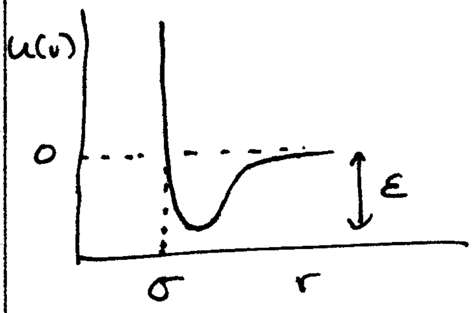
"Practical" Statistical Mechanics → Simulations

Classical force fields



Lennard-Jones potential

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



- r^{-6} dispersion forces (vdw) are correct limiting behavior
- r^{-12} is arbitrary - can you guess why it was adopted? [exponential repulsion from electron cloud overlap]

Assuming pair-wise additivity, with "effective" interactions to capture multi-body effects:

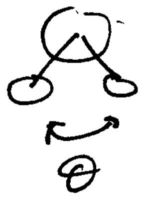
$$u(\vec{r}^N) = \sum_i \sum_{j>i} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

For unlike interactions in mixtures, need combining rules:

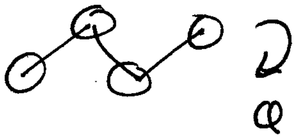
$$\left.\begin{aligned} \sigma_{AB} &= \frac{\sigma_A + \sigma_B}{2} \\ \varepsilon_{AB} &= \sqrt{\epsilon_A \epsilon_B} \end{aligned}\right\} \text{Lorentz-Berthelot (empirical)}$$

More complex molecules/interactions:

bond stretching, e.g. $u_b = k_b(r - r_0)^2$

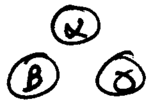


bond bending (angle) $u_a = k_a \cdot (\theta - \theta_0)^2$



torsional angles $u_t = k_t \left[1 + \cos[\varphi - \varphi_0]\right]$

Many-body interactions



$$u_{\alpha\beta\gamma} = f(\vec{r}_{\alpha\beta}, \vec{r}_{\alpha\gamma}, \vec{r}_{\beta\gamma})$$

Coulombic $u_c = \dfrac{q_\alpha q_\beta}{4\pi\varepsilon\varepsilon_0 r_{\alpha\beta}}$

$\hookrightarrow$ typically $\varepsilon = 1$

etc for dipolar, quadrupolar interactions

Polaritability

[non-additive]

Forces are obtained from energy function:

$$f_{i,x} = -\frac{\partial u(\vec{r}^N)}{\partial x_i} \qquad f_{i,y} = -\frac{\partial u(\vec{r}^N)}{\partial y_i} \qquad f_{i,z} = -\frac{\partial u(\vec{r}^N)}{\partial z_i}$$

or $\vec{f}_i = -\dfrac{\partial u(\vec{r}^N)}{\partial \vec{r}_i}$

If only pair-wise interactions,

$$f_{i,x} = -\frac{\partial u}{\partial x_i} = -\frac{\partial}{\partial x_i}\sum_{j\neq i} u(r_{ij}) = -\sum_{j\neq i}\frac{\partial r_{ij}}{\partial x_i}\frac{\partial u(r_{ij})}{\partial r_{ij}} \quad ①$$

$$r_{ij}^2 = (x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 \Rightarrow 2r_{ij}\frac{\partial r_{ij}}{\partial x_i} = 2(x_i - x_j)$$

$$\Rightarrow \frac{\partial r_{ij}}{\partial x_i} = \frac{x_i - x_j}{r_{ij}}$$

From ① $f_{x,i} = - \sum_{j \neq i} \frac{x_i - x_j}{r_{ij}} \frac{du(r_{ij})}{\partial r_{ij}}$ + similarly for y, z

These expressions are used in:

Molecular Dynamics Simulations

- Setup a system in an initial (plausible) configuration
- Solve Newton's equations of motion

$$\frac{d^2 \vec{r}_i}{dt^2} = \frac{\vec{f}_i}{m_i} \qquad i = 1, 2, \ldots N$$

- measure properties after system has reached equilibrium, e.g. energy E, pressure P, T_{kin}, pair correlation functions, ... {from virial expr.}

Natural ensemble: NVE, equations of motion preserve E

Time Step (numerical) solution – Verlet algorithm

$$r(t+\delta t) = r(t) + \frac{dr(t)}{dt}\delta t + \frac{d^2 r(t)}{\partial t^2}\frac{\delta t^2}{2} + \frac{d^3 r(t)}{dt^3}\frac{\delta t^3}{6} + \mathcal{O}(\delta t$$

$$= r(t) + v(t)\delta t + \frac{f(t)}{m}\frac{\delta t^2}{2} + \frac{d^3 r(t)}{dt^3}\frac{\delta t^3}{6} + \mathcal{O}(\delta t^4)$$

$$r(t-\delta t) = r(t) - v(t)\delta t + \frac{f(t)}{m}\frac{\delta t^2}{2} - \frac{d^3 r(t)}{dt^3}\frac{\delta t^3}{6} + \mathcal{O}(\delta t^4)$$

Add:

$$r(t+\delta t) = 2r(t) - r(t-\delta t) + \frac{f(t)}{m}\delta t^2 + \mathcal{O}(\delta t^4)$$

This requires knowing positions at two time steps, not so great, but doable w/ appropriate initialization.

A slight variation is the "velocity Verlet" algorithm:

$$r(t+\delta t) = r(t) + v(t)\delta t + \frac{f(t)}{2m}\delta t^2$$

$$v(t+\delta t) = v(t) + \frac{f(t+\delta t)+f(t)}{2m}\delta t$$

These algorithms are implemented efficiently (in parallel) in many open-source packages, e.g. Gromacs, LAMMPS

How does one pick δt? [frequency of fastest motion]

Too small – simulation too slow

Too large – no energy conservation, unstable

For flexible bonds, typical $\delta t \simeq 0.5-1$ fs

(for rigid bonds, $\delta t \simeq 2-3$ fs, but one needs special methods to keep lengths constant)

Recall $1\ \text{fs} = 10^{-15}\ \text{s}$

$1\ \text{ns} = 10^{-9}\ \text{s} = 1{,}000{,}000$ time steps

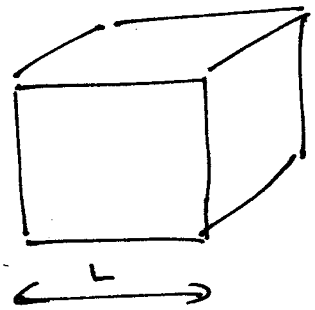
So that sets a limit as to how long a time one could simulate

Initialization

- Avoid large forces due to overlaps, need to construct configuration w/o them
- Assign velocities from Maxwell-Boltzmann distribution:

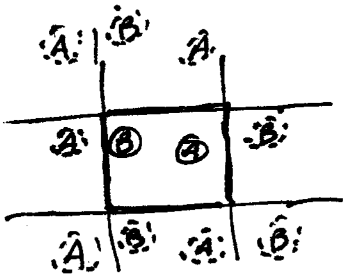
$$\mathcal{P}(v_{x,i}) = (2\pi\sigma_v^2)^{-1/2}\exp\left(-\frac{v_{x,i}^2}{2\sigma_v^2}\right) \qquad \sigma_v^2 = \frac{k_BT}{m_i}$$

Practical Considerations – Periodic Boundary Conditions

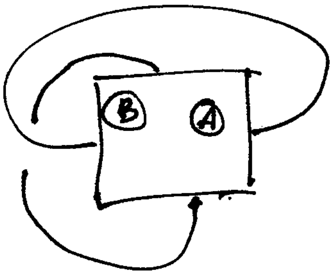


A cube with $L \simeq 10\sigma$ contains ~ 800 LJ particles at the triple-point liquid density. If there are hard walls, <u>most</u> are within 2-3 σ from the walls

Solution → periodic boundary conditions



[2D version]



or "torroidal" geometry

- avoid "edge" effects, space is continuous
- artificially periodic, usually not detrimental (except for simulations of solids)
- We still need to count a finite number of interactions in $\sum_i \sum_{j>i} u_{ij}$

→ Minimum Image Convention: only take into account neighbor that is closest.

$$\delta x = |x_A - x_B|$$

$$\delta x \leftarrow \min\{\delta x, L - \delta x\}$$

$$\delta r^2 = \delta x^2 + \delta y^2 + \delta z^2$$