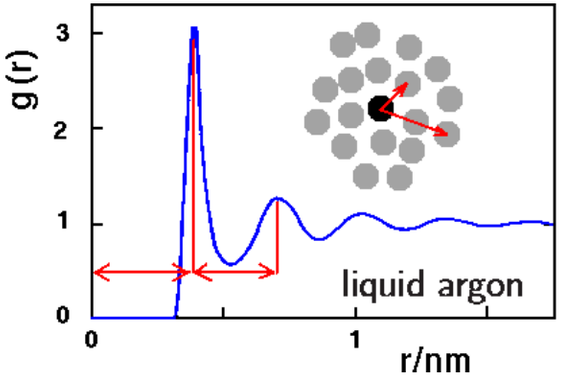
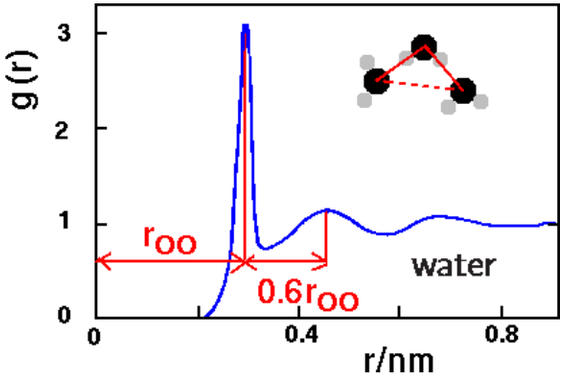
System size and potential range

Size of the simulated sample depends on:

- correlation length (property of the system)
  liquids: a few nm →
- range of the potential (technical aspect)





Simulation **time** depends on:

- correlation time (property of the system): water $t \sim$ ps, polymers: very long
- timestep and code efficiency; “wall time” = time to get my results

correlation lengths and times of complex phenomena are long

Typical scales:

- liquids: N = 100–1000, t = 10–100 ps, ionic liquids: t > 10 ns
- polymers/biomolecules: N > 10 000
  $t \sim$ ns (structure), μs (complex phenomena, binding), ms (protein folding)
- nanostructures, crystals (defects): N = billions, t > ns

Pair potential treatment:

number of operations needed for 1 MD step or 1 attempted move of every particle:

- loop over all pairs (nearest-image): $\sim N^2$
- short-range potential, optimum algorithm: $\sim N^1$

Short-range forces

- Potential cutoff

$$u_{\text{simul}}(r) = \begin{cases} u(r) & \text{for } r \le r_c, \\ 0 & \text{for } r > r_c, \end{cases}$$

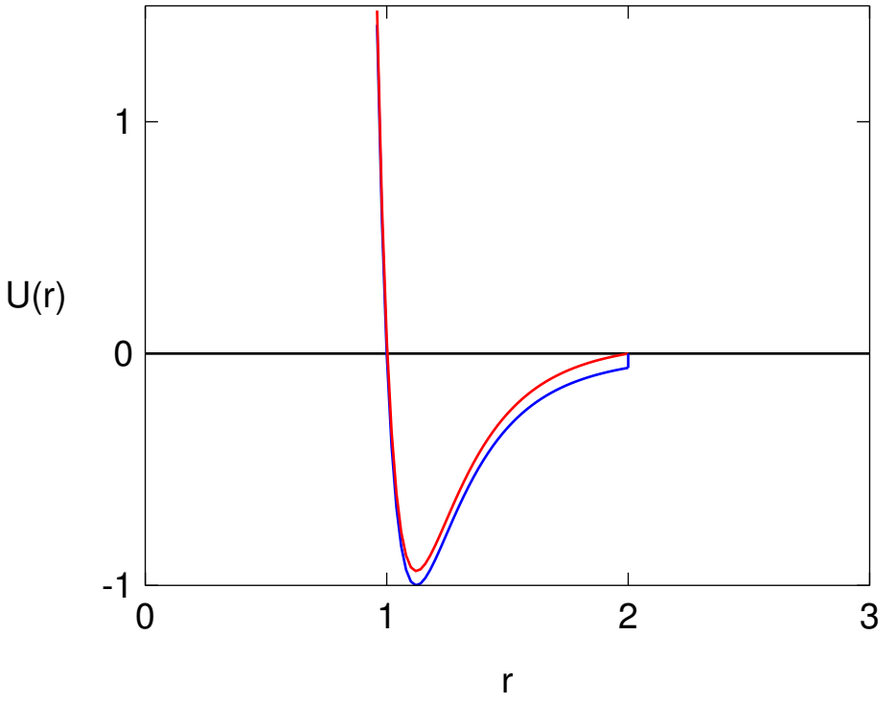
  Usually $r_c < L/2$ (L = box size, in the periodic b.c.)

- MD: continuous forces, or at least *cut-and-shift* potential:

$$u_{\text{simul}}(r) = \begin{cases} u(r) - u(r_c) & \text{pro } r \le r_c, \\ 0 & \text{pro } r > r_c, \end{cases}$$

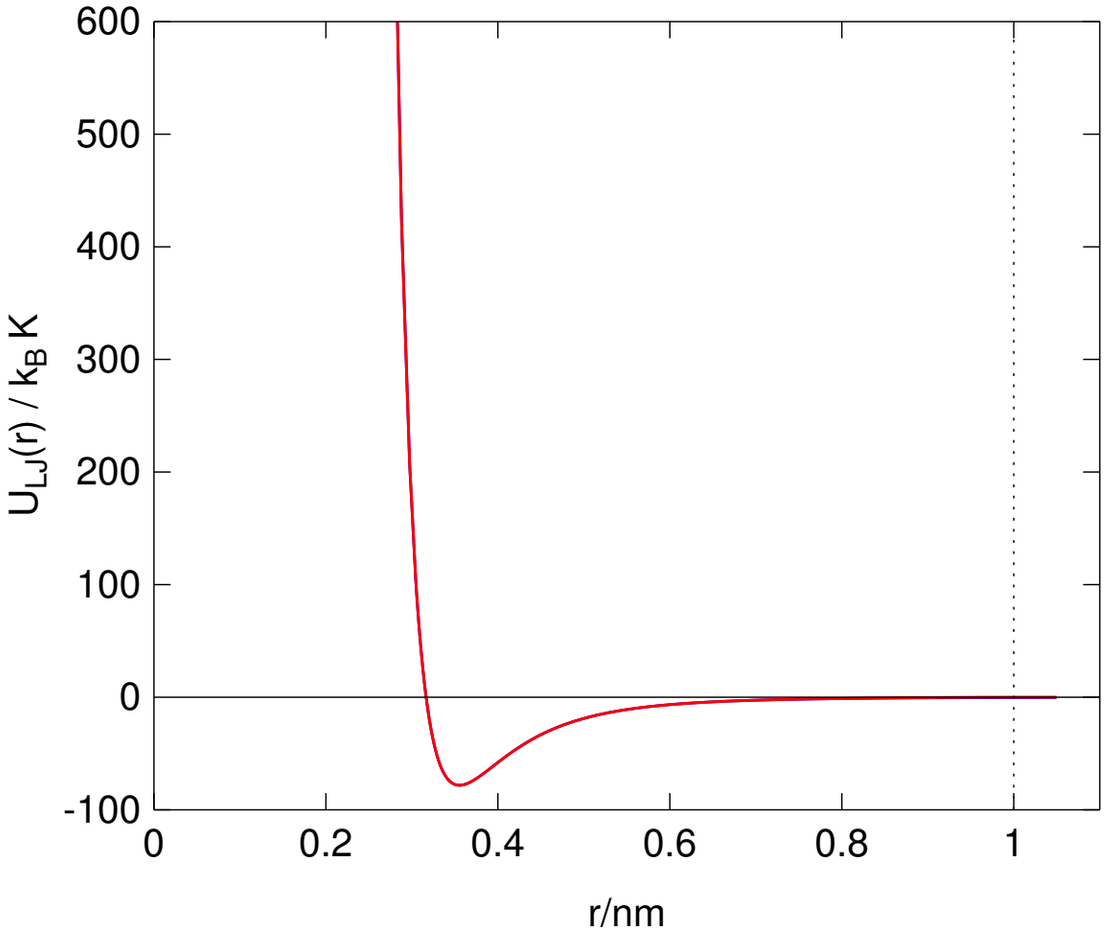
  ⇒ discontinuity (jump) in forces.

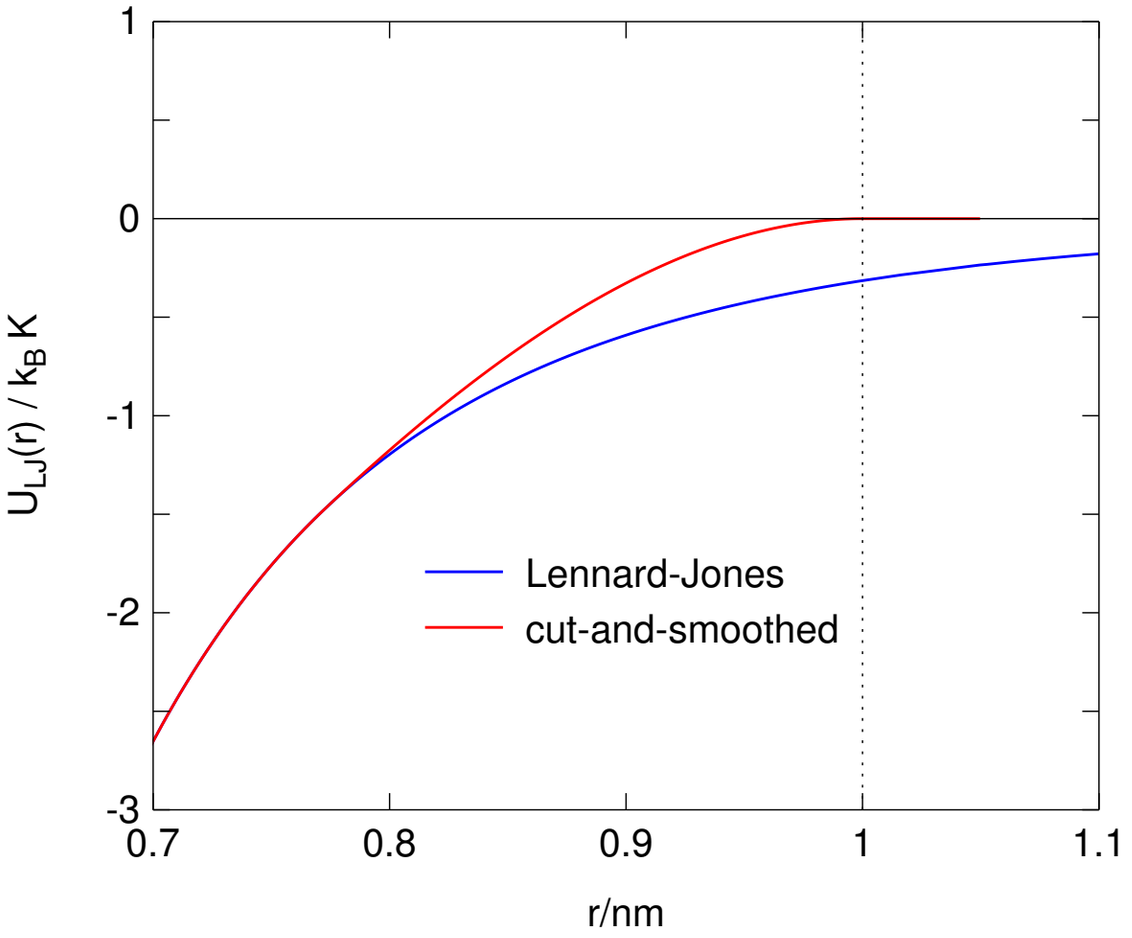
  Better: smooth (depends on the integrator order)



- Nearest image boundary conditions

Smooth cutoff





Cutoff corrections

Correction of energy of a selected atom (assuming: $g(r) = 1$ for $r > r_c$):

$$\Delta U = \int_{r_c}^{\infty} u(r) \rho \, 4\pi r^2 \, \mathrm{d}r \qquad \text{for the whole box : } N\Delta U/2$$

Dispersion forces: $u(r) \propto 1/r^6$, $\Delta U \propto 1/r_c^3$; for $r_c = L/2$ we get error $\propto 1/N$

Typical values r_c: 2.5 to 4 LJ $\sigma \approx$ 8 to 15 Å

Coulomb problem: dipole–dipole: $1/r^3$, charge–charge: $1/r$ – ΔU diverges!

Methods:

- cut-and-shift, must be done smoothly – cheap, inaccurate, time $\sim N$
  ions: OK for $r_c \gg$ Debye screening length
- Ewald summation – golden standard
  standard Ewald: computer time $\propto N^{3/2}$
  particle-mesh (FFT): computer time $\propto N \log N$
- tree-code (Greengard–Rokhlin)

a similar method for cutoff corrections exists for Lennard-Jones

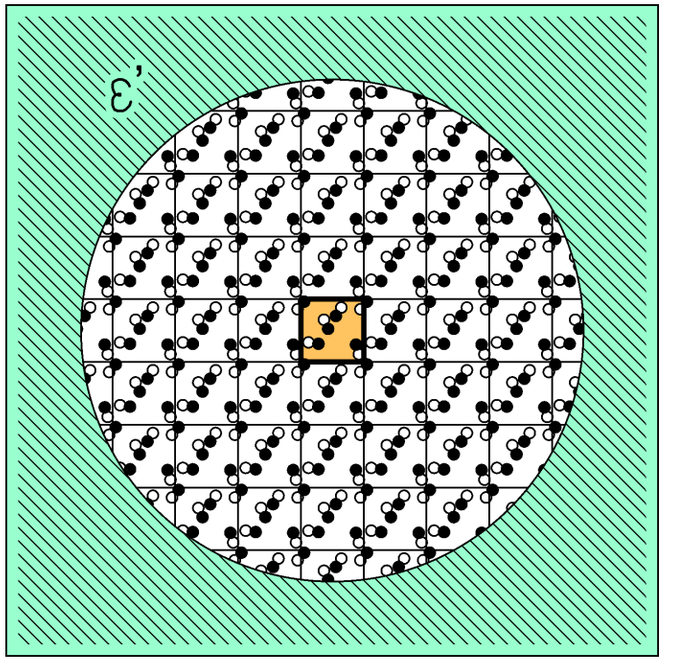
For dipolar systems only:

- reaction field: dielectric response beyond cutoff, computer time $\propto N$

Ewald summation I

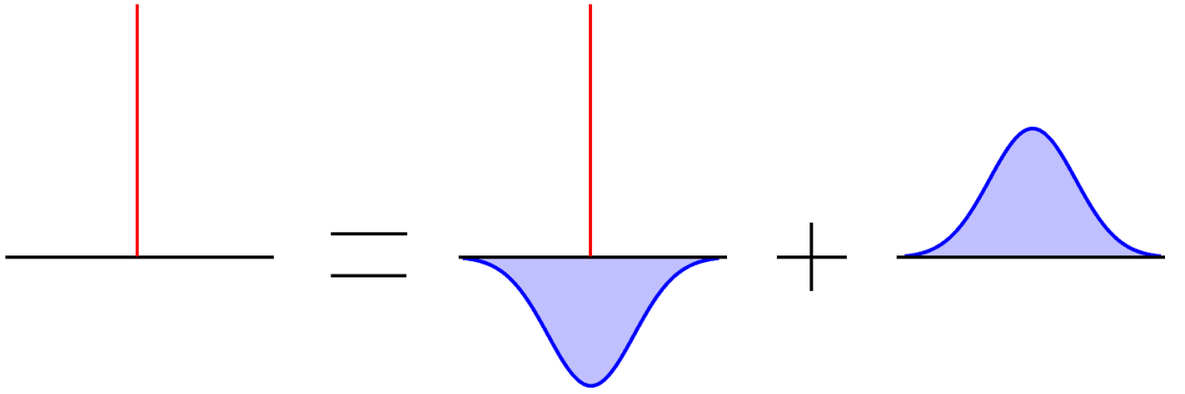
- Periodic boundary conditions surrounded “at infinity” by a dielectric or metal ($\varepsilon' = \infty$, *tin-foil*)
- sum of **all** periodic images:

$$U = \sum_{\vec{n}}{}' \sum_{1 \le j \le l \le N} \frac{1}{4\pi\varepsilon_0} \frac{q_j q_l}{|\vec{r}_j - \vec{r}_l + \vec{n}L|}$$



Summation trick: point charges screened by a Gaussian charge distribution of opposite sign

- the screened charge interaction is short-ranged
- Gaussians are summed in the k-space



Ewald summation II

Oops! The infinite sum does not converge absolutely

$$U = \lim_{s\to 0} {\sum_{\vec{n}}}' \exp(-s\vec{n}^2) \sum_{1\le j\le l\le N} \frac{1}{4\pi\varepsilon_0} \frac{q_j q_l}{|\vec{r}_j - \vec{r}_l + \vec{n}L|}$$

Tricks used in the derivation:

$$\frac{1}{r} = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp(-t^2 r^2)\mathrm{d}t = \frac{2}{\sqrt{\pi}} \int_0^\alpha \exp(-t^2 r^2)\mathrm{d}t + \frac{2}{\sqrt{\pi}} \int_\alpha^\infty \exp(-t^2 r^2)\mathrm{d}t$$

1st term: 3× the Poisson summation formula

$$\sum_{n=-\infty}^{\infty} f(x+nL) = \frac{1}{L} \sum_{k=-\infty}^{\infty} \hat{f}(k/L)\mathrm{e}^{2\pi i k x/L}$$

where

$$\hat{f}(k) = \int_{-\infty}^{\infty} f(x)\mathrm{e}^{-2\pi i k x/L}\mathrm{d}x$$

2nd term leads to the function

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty \exp(-t^2)\mathrm{d}t$$

Ewald summation III

$$4\pi\varepsilon_0 U = \sum_{\vec{n}}{}' \sum_{1\le j\le l\le N} \frac{q_j q_l \operatorname{erfc}(\alpha|\vec{r}_j - \vec{r}_l + \vec{n}L|)}{|\vec{r}_j - \vec{r}_l + \mathrm{n}L|}$$

$$+ \sum_{\vec{k},\vec{k}\neq\vec{0}} \frac{\exp(-\pi^2 k^2/\alpha^2 L^2)}{2L\pi k^2} |Q(\vec{k})|^2 + \frac{2\pi}{2\varepsilon'_r + 1}\frac{\vec{M}^2}{L^3} - \frac{\alpha}{\sqrt{\pi}}\sum_{j=1}^{N} q_j^2$$

$$Q(\vec{k}) = \sum_{j=1}^{N} q_j \exp(2\pi i \vec{k}\cdot\vec{r}_j/L)$$

$$\vec{M} = \sum_{j=1}^{N} \vec{r}_j q_j \quad \text{(watch point charges!)}$$

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty \exp(-t^2)\mathrm{d}t$$

with optimized parameters: computing cost $\sim N^{3/2}$

with *particle mesh* for the k-space part: computing cost $\sim N \log N$

Reaction field I

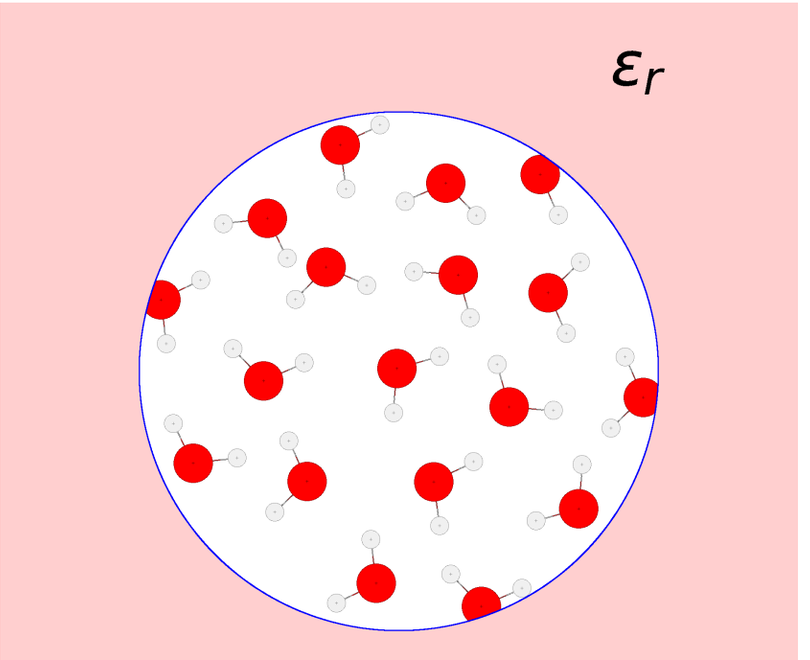
For dipolar systems without free charges: dipoles beyond spherical cutoff replaced by response of continuous dielectric

Neutral molecules with point partial charges:

$$u_{\mathrm{RF}}(i,j) = \frac{1}{4\pi\varepsilon_0} \sum_{a\in\{i\}} \sum_{b\in\{j\}} \begin{cases} \dfrac{q_{i,a}q_{j,b}}{|\vec{r}_{i,a}-\vec{r}_{j,b}|}\left[1+\dfrac{\varepsilon_r-1}{2\varepsilon_r+1}\left(\dfrac{|\vec{r}_{i,a}-\vec{r}_{j,b}|}{r_{\mathrm{c}}}\right)^3\right], & r_{ij}<r_{\mathrm{c}} \\ 0, & r_{ij}>r_{\mathrm{c}} \end{cases}$$

MD: Smoothing needed!

Caveat: forces are not central



Reaction field II

Energy of dipole $\vec{\mu}_i$ with a dielectric outside an r_c-sphere:

$$-\frac{1}{4\pi\varepsilon_0}\vec{\mu}_i \cdot \frac{\varepsilon'_r - 1}{2\varepsilon'_r + 1}\frac{1}{r_c^3}\vec{M}'_i$$

where

$$\vec{M}'_i = \sum_{j, r_{ij}<r_c} \vec{\mu}_j, \quad \vec{\mu}_i = \sum_{a\in\{i\}} q_{i,a}\vec{r}_{i,a}, \quad \sum_{a\in\{i\}} q_{i,a} = 0$$

Trick:

$$\begin{aligned}
-\vec{\mu}_i \cdot \vec{\mu}_j &= -\sum_{a\in\{i\}} q_{i,a}\vec{r}_{i,a} \cdot \sum_{b\in\{j\}} q_{j,b}\vec{r}_{j,b} + 0 + 0 \\
&= -\sum_{a\in\{i\}} q_{i,a}\vec{r}_{i,a} \cdot \sum_{b\in\{j\}} q_{j,b}\vec{r}_{j,b} \\
&\quad + \frac{1}{2}\sum_{a\in\{i\}} q_{i,a} \cdot \sum_{b\in\{j\}} q_{j,b}|\vec{r}_{j,b}|^2 + \frac{1}{2}\sum_{a\in\{i\}} q_{i,a}|\vec{r}_{i,a}|^2 \cdot \sum_{b\in\{j\}} q_{j,b} \\
&= \frac{1}{2}\sum_{a\in\{i\}}\sum_{b\in\{j\}} q_{i,a}q_{j,b}|\vec{r}_{i,a} - \vec{r}_{j,b}|^2
\end{aligned}$$