System size and potential range

Size of the simulated sample depends on:

- correlation length
- range of the potential

liquid: hundreds of molecules
biomolecules: 10^4–10^6
nanostructures, crystals (dislocations): billions

problem: correlation times of many complex phenomena are long

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

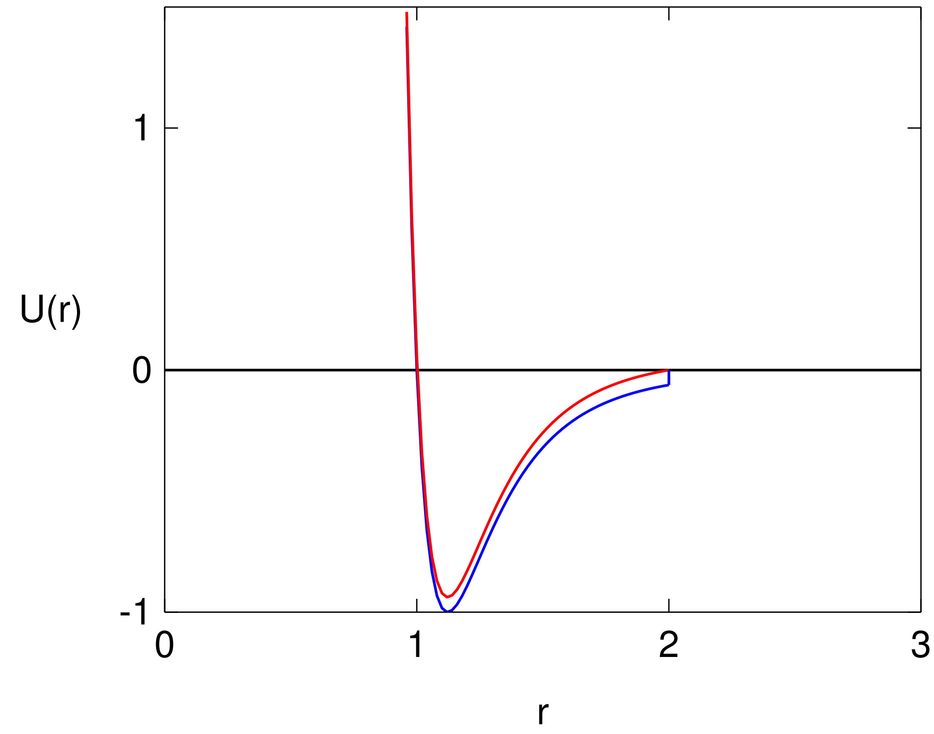
$$u_{\rm simul}(r) = \begin{cases} u(r) & \text{for } r \le r_{\rm c}, \\ 0 & \text{for } r > r_{\rm c}, \end{cases}$$

Usually $r_{\rm c} < L/2$ (L = box size)

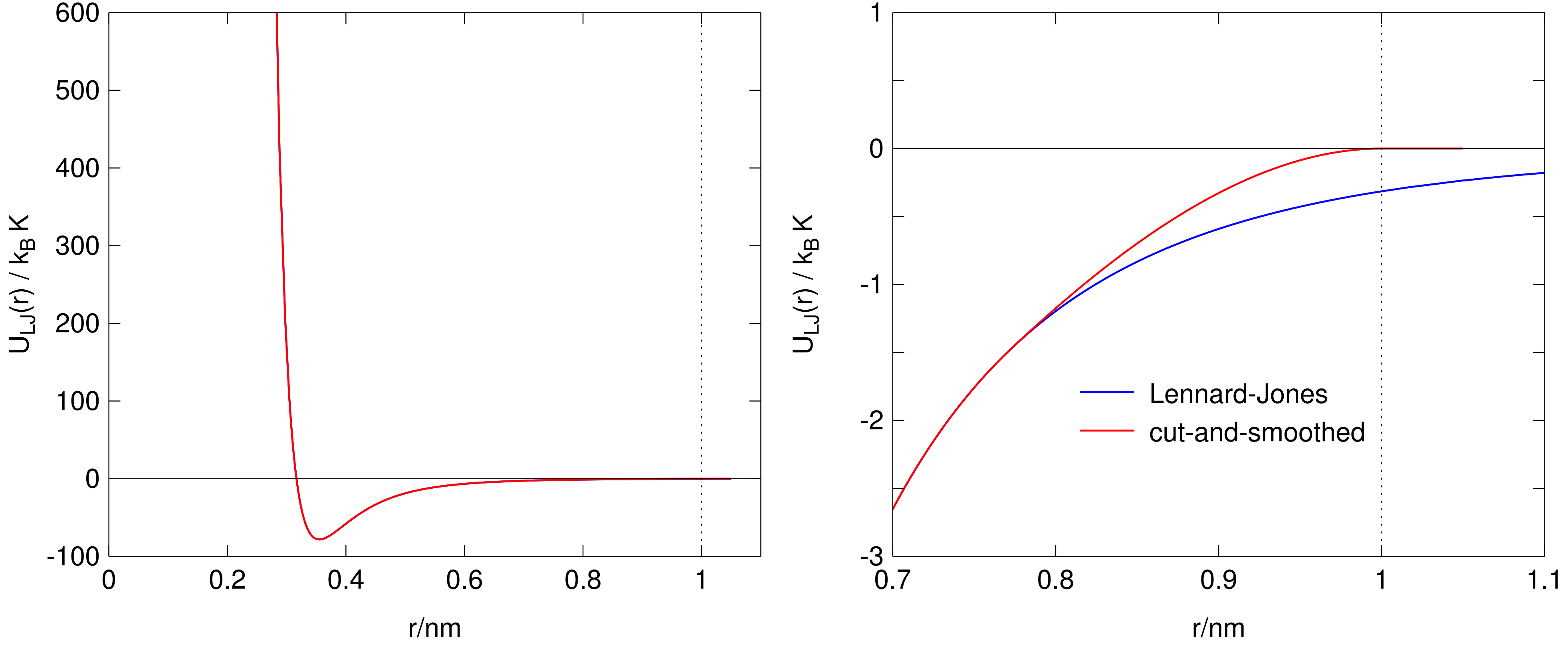
- MD: continuous forces, or at least *cut-and-shift* potential:

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

$\Rightarrow$ discontinuity (jump) in forces.
Better: smooth (depends on the integrator order) – next slide



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

Typical values r_c: 2.5 to 4 LJ σ, i.e., 8 to 15 Å

Coulomb problem: dipole–dipole: r^{-3}, charge–charge: r^{-1} – ΔU diverges!

Methods:

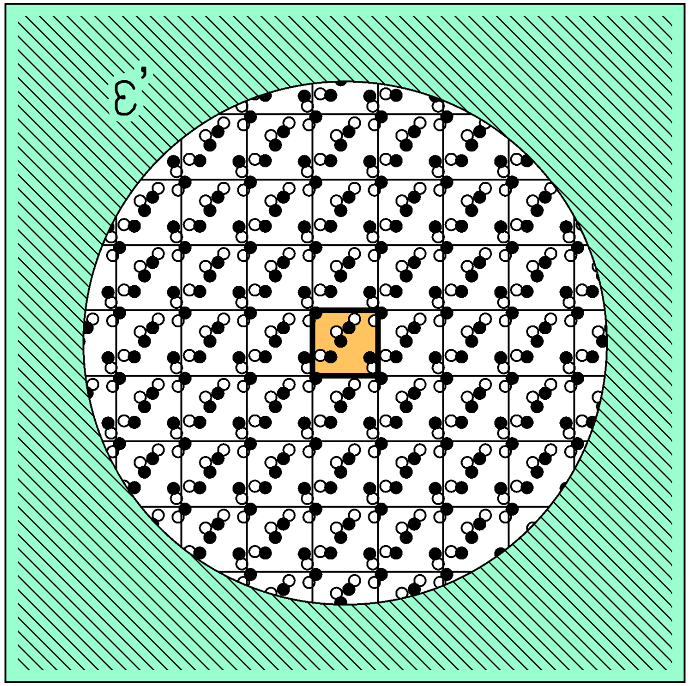
- cut-and-shift, must be done smoothly – cheap, inaccurate, time $\sim N$
  ions: OK for $r_c \gg$ Debye screening length, dipoles: bad correlations
- Ewald summation – golden standard
  standard Ewald: computer time $\propto N^{3/2}$
  particle-mesh (FFT): computer time $\propto N \log N$
- tree-code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

For dipolar systems only:

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

Ewald summation I

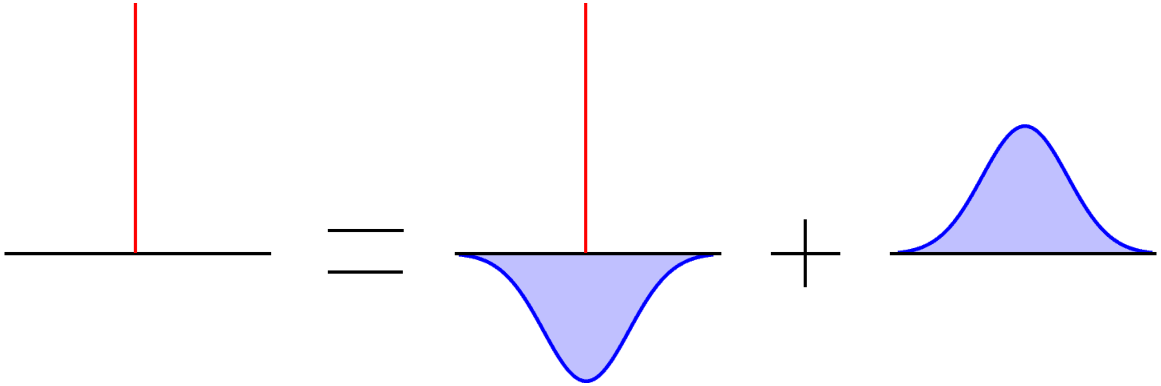
- Periodic boundary conditions surrounded “at infinity” by a dielectric or metal ($\varepsilon' = \infty$, *tin-foil*)



- sum of **all** periodic images:

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

Summation trick:
point charges screened by 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

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

Ewald summation III

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

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

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

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

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

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

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