

Size of the simulated sample depends on:

- correlation length
- correlation time
- range of the potential

liquid: hundreds of molecules

biomolecules:  $10^4$ – $10^6$

nanostructures, crystals (defects): 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:  $\sim N^1$

## ● Potential cutoff

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

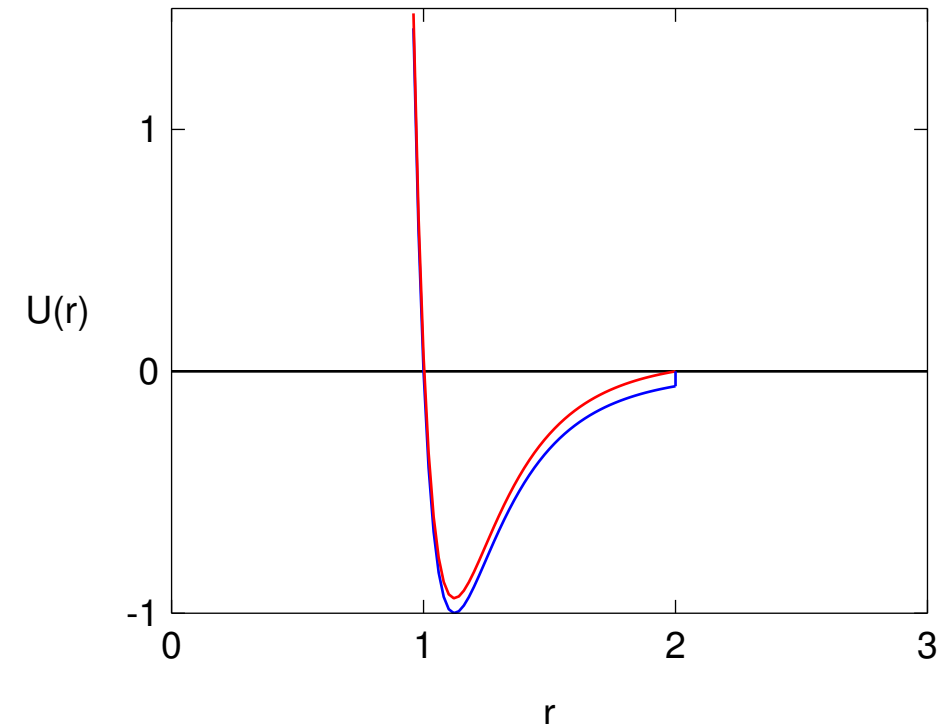
Usually  $r_c < L/2$  ( $L$  = box size)

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

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

⇒ discontinuity (jump) in forces.

Better: smooth (depends on the integrator order) – next slide

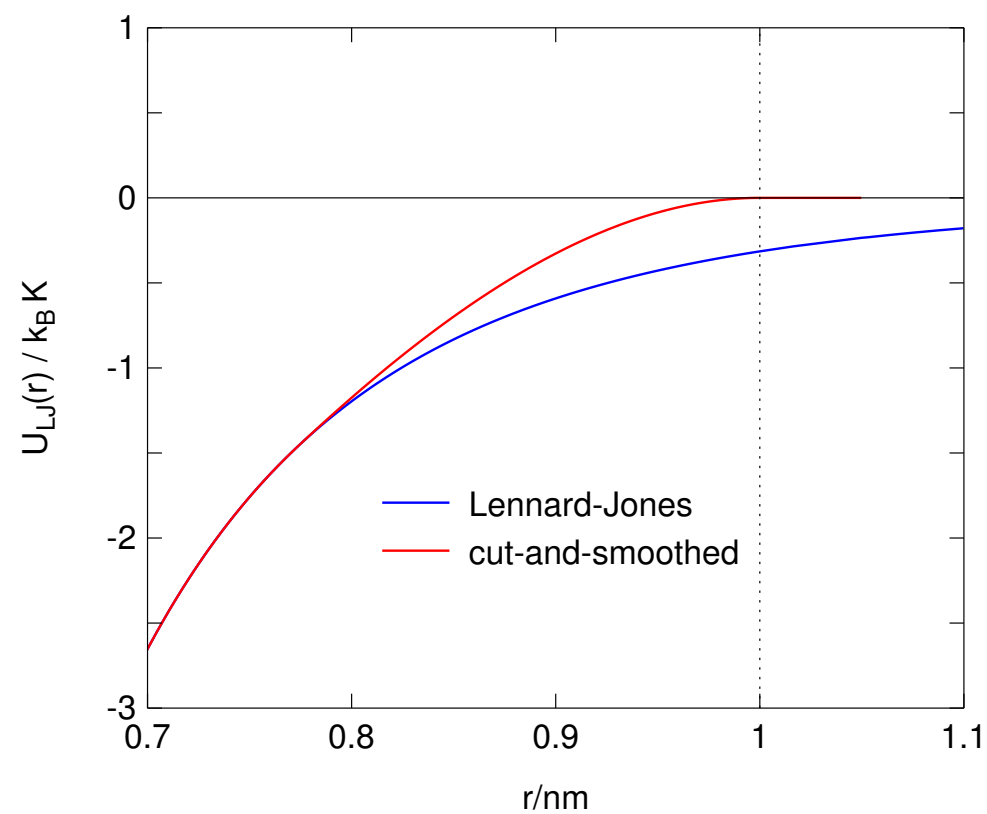
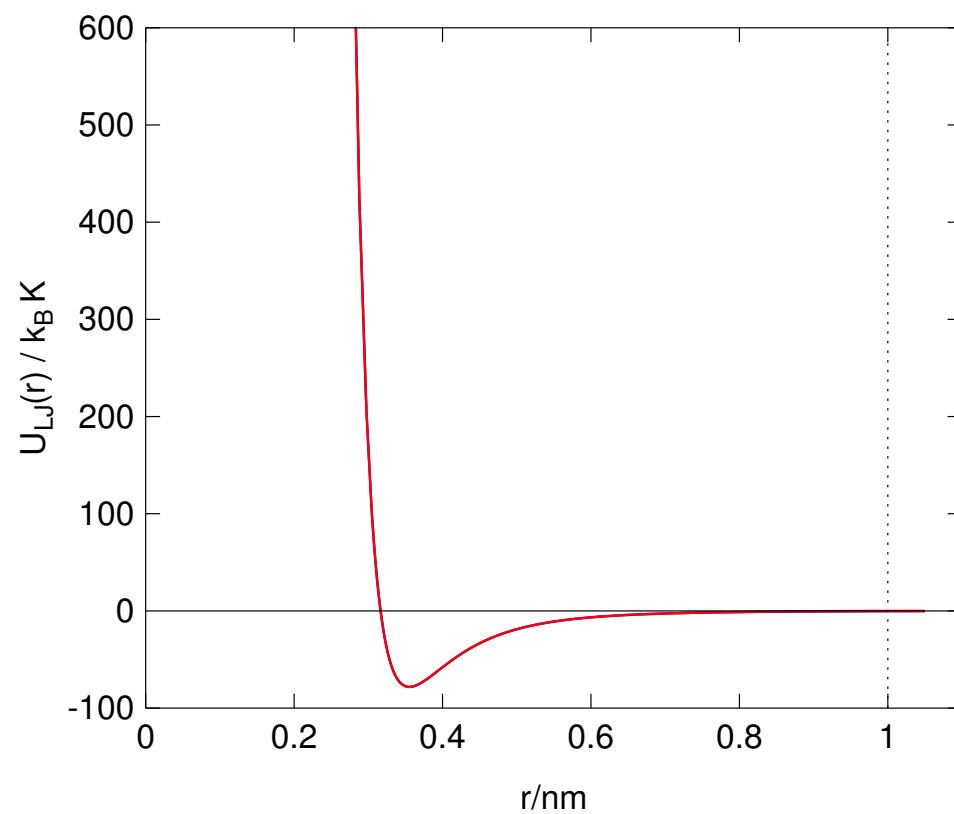


# Smooth cutoff

[simul/plotspcelj.sh]



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

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

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  $\sigma$ , i.e., 8 to 15 Å

**Coulomb problem**: dipole–dipole:  $r^{-3}$ , **charge–charge**:  $r^{-1}$  –  $\Delta U$  diverges!

## Methods:

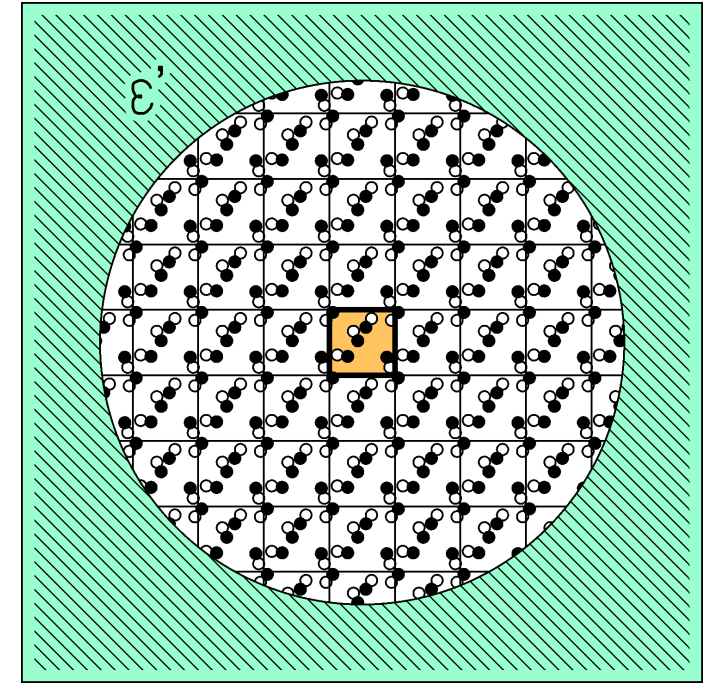
- cut-and-shift, must be done smoothly – cheap, inaccurate, time  $\sim N$   
ions: OK for  $r_c \gg$  Debye screening length, dipoles: bad correlations
- Ewald summation – golden standard  
standard Ewald: computer time  $\propto N^{3/2}$   
particle-mesh (FFT): computer time  $\propto N \log N$
- tree-code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

## For dipolar systems only:

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

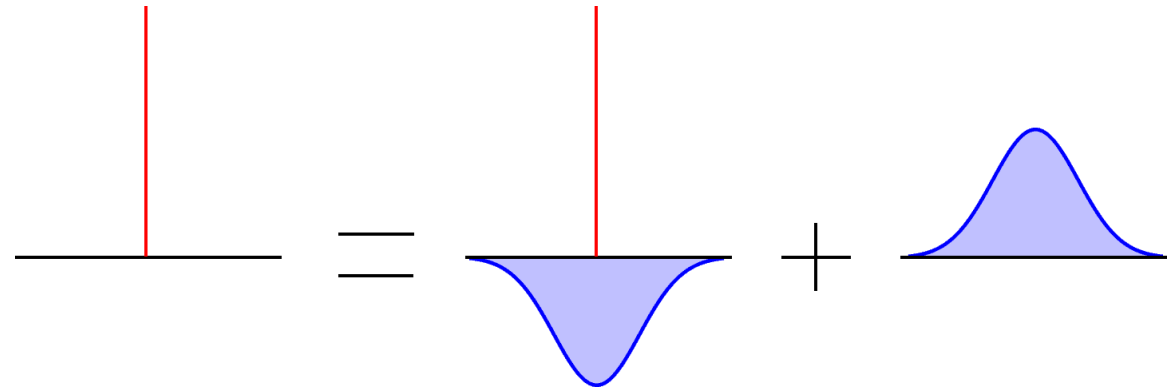
- Periodic boundary conditions surrounded “at infinity” by a dielectric or metal ( $\epsilon' = \infty$ , *tin-foil*)
- sum of **all** periodic images:

$$U = \sum_{\vec{n}}' \sum_{1 \leq j \leq l \leq N} \frac{1}{4\pi\epsilon_0} \frac{q_j q_l}{|\vec{r}_j - \vec{r}_l + \vec{n}L|}$$



## 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

Oops! The infinite sum does not converge absolutely

$$U = \lim_{s \rightarrow 0} \sum'_{\vec{n}} \exp(-s\vec{n}^2) \sum_{1 \leq j \leq l \leq N} \frac{1}{4\pi\epsilon_0} \frac{q_j q_l}{|\vec{r}_j - \vec{r}_l + \vec{n}L|}$$

Tricks used in the derivation:

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

1st term: 3× the Poisson summation formula

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

where

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

2nd term leads to the function

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

$$4\pi\epsilon_0 U = \sum_{\vec{n}}' \sum_{1 \leq j \leq l \leq N} \frac{q_j q_l \text{Erfc}(\alpha |\vec{r}_j - \vec{r}_l + \vec{n}L|)}{|\vec{r}_j - \vec{r}_l + \vec{n}L|} \\ + \sum_{\vec{k}, \vec{k} \neq \vec{0}} \frac{\exp(-\pi^2 k^2 / \alpha^2 L^2)}{2L\pi k^2} |Q(\vec{k})|^2 + \frac{2\pi}{2\epsilon_r' + 1} \frac{\vec{M}^2}{L^3} - \frac{\alpha}{\sqrt{\pi}} \sum_{j=1}^N q_j^2$$

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

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

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

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

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