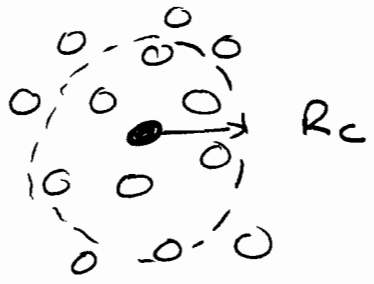
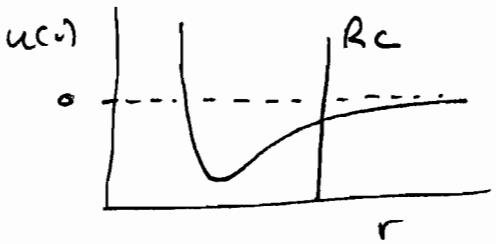
Ref.: Ch. 12 in F+S

Long-Range Interactions



e.g. $u(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$



Why cutoff interactions? → Box Length L
→ Simulation efficiency

"Tail" corrections $\frac{\Delta U}{N} = \frac{1}{2}\int_{R_c}^{\infty} u(r)\,\rho\,g(r)\,4\pi r^2 dr$ (1)

Assume $g(r) = 1$ for $r > R_c$

obtain (for LJ potential) $\frac{\Delta U}{N} = \frac{8\pi}{3}\rho\varepsilon\sigma^3\left[\frac{1}{3}\left(\frac{\sigma}{R_c}\right)^9 - \left(\frac{\sigma}{R_c}\right)^3\right]$

But... for potentials that decay with distance slower than r^{-3}, the integral in (1) diverges!

Especially severe issues for Coulomb potential,

$u(r_{ij}) = \frac{q_i q_j}{r_{ij}}$ (in Gaussian units to make notation easier to follow – factor of $\frac{1}{4\pi\varepsilon_0}$ omitted)

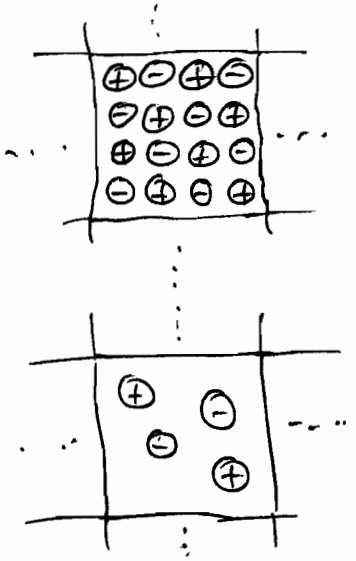
In early days of simulation, several approaches were tried to address this issue - e.g. "standard" truncation w/o any corrections, "spherical" truncation, corrections made by assuming a mean-field dielectric surrounding central cell etc. None of these methods works well: artifacts due to neglect of long-range interactions, system size dependence.

Systems affected:

* electrolyte solutions, ionic liquids etc
* dipolar fluids (e.g. H_2O)
* models w/ partial charges (e.g. CO_2)

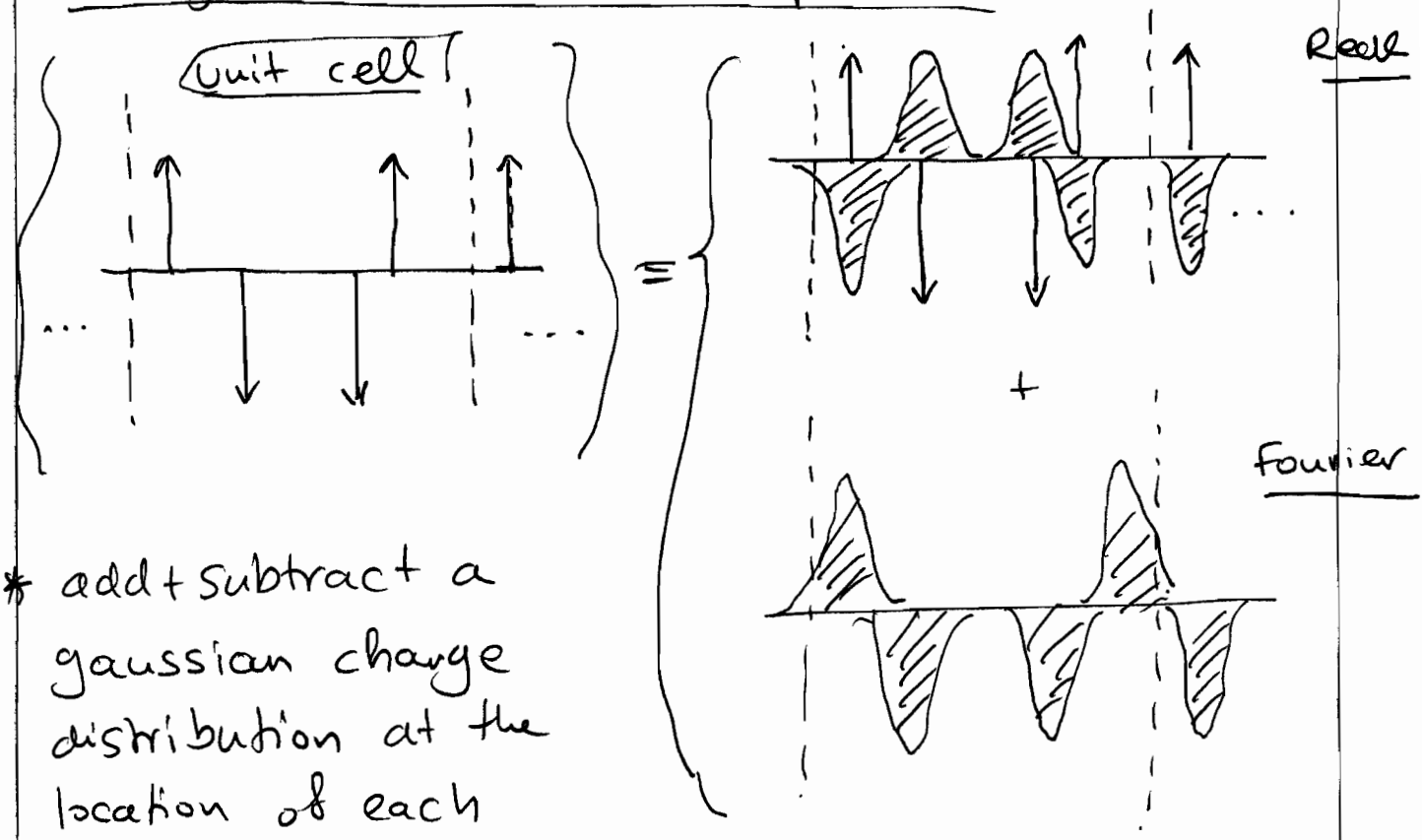
Ewald Sums

Now universally accepted as the only valid simulation approach for systems with electrostatic interactions



* Originally developed to compute energy of ionic crystals - (actually periodic systems)
* Take artificial periodicity of simulations literally, perform summations for ∞ periodic array

Charge distribution - 1D periodic



* add + subtract a gaussian charge distribution at the location of each original charge.

* The top part (marked "Real") now has only short-range interactions, as each charge is compensated by the opposite distribution outside the range of the Gaussian

* The bottom part (marked "Fourier") is a periodic array of smoothly varying charge density and the energy can be computed by a rapidly converging fourier series

$$\rho_{Gauss}(r) = q_i \left(\frac{\alpha}{\pi}\right)^{3/2} \exp(-\alpha r^2) \qquad \text{width } \sqrt{\frac{2}{\alpha}}$$

↳ free parameter

Poisson's Equation $\nabla^2 \varphi = -4\pi \rho_{Gauss}$

In spherical coordinates, $\frac{1}{r} \frac{\partial^2 r\varphi(r)}{\partial r^2} = -4\pi \rho(r)_{Gauss}$

$$\Rightarrow \frac{\partial^2 r\varphi(r)}{\partial r^2} = -4\pi r \rho_{Gauss}(r) \Rightarrow \frac{\partial}{\partial r} r\varphi(r) = -\int_{\infty}^{r} 4\pi r \rho_{Gauss}(r)\, dr$$

$$= +2\pi q_i \left(\frac{\alpha}{\pi}\right)^{3/2} \int_{r}^{\infty} \exp(-\alpha r^2)\, dr^2 = 2q_i \left(\frac{\alpha}{\pi}\right)^{1/2} \exp(-\alpha r^2)$$

2nd integration: $r\varphi(r) = 2q_i \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{0}^{r} \exp(-\alpha r^2)\, dr \Rightarrow$

$$\Rightarrow \boxed{\varphi(r) = \frac{q_i}{r} \operatorname{erf}(\sqrt{\alpha}\, r)}$$

Potential of Gaussian charge distr.

Error function $\longrightarrow 1$ as $r \to \infty$ $\quad \varphi(r) \to q_i/r$

$\longrightarrow \sqrt{\frac{\alpha}{\pi}}$ as $r \to 0$

Real Space Sum

$$\varphi_{short\text{-}range}(r) = \frac{q_i}{r} - \frac{q_i}{r} \operatorname{erf}(\sqrt{\alpha} \cdot r) =$$

$$= \frac{q_i}{r} \operatorname{erfc}(\sqrt{\alpha}\, r)$$

This is a short-range function, provided that the parameter $1/\sqrt{\alpha}$ is shorter than $L/2$

In many simulations using Ewald Sums, the width parameter is chosen so that $\sqrt{\alpha} L = 5$ ($= \kappa$) (kappa) so that the erfc function has the value at $\frac{L}{2}$: $\text{erfc}\left(\frac{\sqrt{\alpha} L}{2}\right) = \text{erfc}(2.5) = 0.0004$.

The <u>total</u> interaction of all charges in real space is then

$$U_{\text{real space}} = \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{q_i q_j}{r_{ij}} \text{erfc}(\sqrt{\alpha} \cdot r_{ij})$$

<u>Fourier Space Sum</u>

(for derivation, see F+S §12.1 ; need Fourier transforms)

$$U_{\text{reciprocal space}} = \frac{1}{2V} \sum_{\vec{k} \neq 0} \frac{4\pi}{k^2} |\rho(\vec{k})|^2 \exp(-k^2/4\alpha)$$

sum over all k vectors

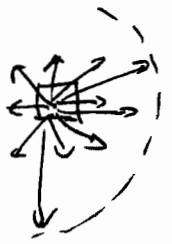
where $\rho(\vec{k}) \equiv \sum_{i=1}^{N} q_i \exp(i\vec{k} \cdot \vec{r}_i)$

The fourier space sum contains $k_{vec} \times N$ terms (where k_{vec} is the number of vectors used in k-space);
Complex arithmetic for its computation

k-vectors

(ix, iy, iz) indices

$\sqrt{ix^2+iy^2+iz^2} \leq Kmax$

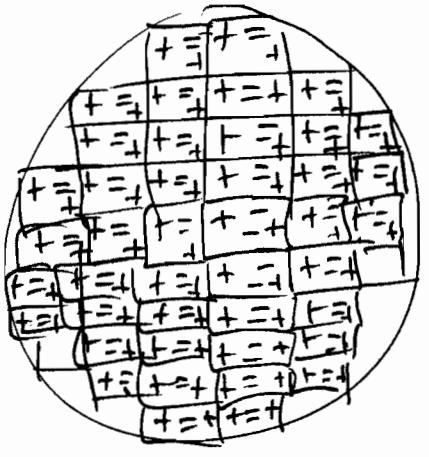


Kmax	Number of k vectors
4	152
5	297
6	518
...	...
10	2,242

Self-interaction

The reciprocal space sum contains a term due to the interaction of the Gaussian charge distribution with itself (in the unit cell + all its images). This needs to be subtracted from the total energy.

Boundary Condition at ∞



Strange as it may sound, the boundary condition at infinite distance can have a contribution to the total energy – because the net dipole is generally non-zero ($\varepsilon_\infty = \infty$)

This is avoided by selecting conducting boundary conditions

Total Energy ($\varepsilon_\infty = \infty$)

$$U = \sum_{i=1}^{N} \sum_{j>i} \frac{q_i q_j}{r_{ij}} \operatorname{erfc}(\sqrt{\alpha} \cdot r_{ij}) - \sqrt{\frac{\alpha}{\pi}} \sum_{i=1}^{N} q_i^2$$

real space — self interaction corr.

$$+ \frac{1}{2V} \sum_{k \neq 0} \frac{4\pi}{k^2} |\rho(\vec{k})|^2 \exp(-k^2/4\alpha)$$

fourier space

Optimal Selection of α, k_{max}

For a given accuracy ε, find distance S so that $\varepsilon = \exp(-S^2)/S^2$

(e.g. for $\varepsilon = 10^{-5}$, $S = 3$)

Selecting $\sqrt{\alpha} \cdot L = K = \left(\frac{T_R \pi^3 N}{T_F} \right)^{1/6}$

T_R, T_F: computational time in real + reciprocal space

equalizes errors in real + reciprocal space

(for $N = 100$, $T_R \simeq T_F \Rightarrow K \simeq 4$; $N = 1000 \Rightarrow K = 5.6$)

$$k_{max} = \frac{SK}{2} \quad (= 6 \text{ in our example})$$

for $\varepsilon = 10^{-8}$ $S = 4$, $K = 4$, $k_{max} = 8$

Fast algorithms: Particle/Particle Mesh Ewald (PPPM)