Ewald Summation for long-range potential

Seminar talk for „Computer simulations in statistical physics“
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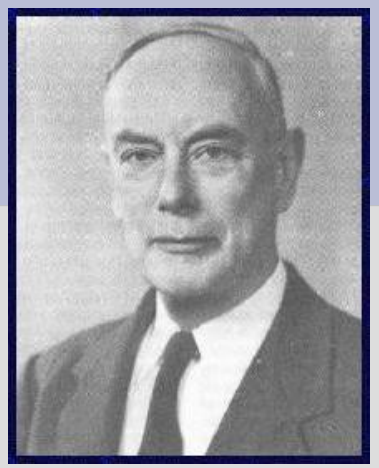
Content

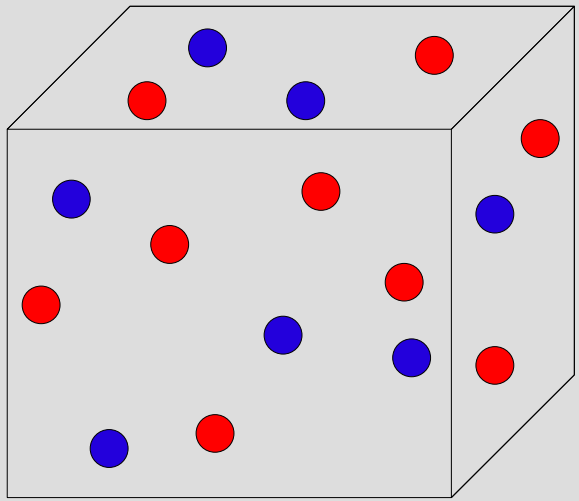


Paul-Peter-Ewald
(1888-1985)
from[4]

- Motivation
- Derivation of the Ewald Sum
- Implementations

Motivation

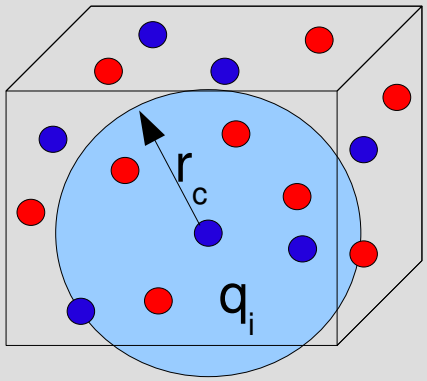
Consider a box of N charged particles with periodic boundary conditions and volume L^3:



Try to calculate the overall potential

Motivation

) Minimum Image (spherical truncation)



Truncate potential at distance r_c

One can show: The contribution of the ignored tail of the potential U(r) can be estimated to be

$$U_{tail} = \frac{N\rho}{2} \int_{r_c}^{\infty} dr\, U(r)\, 4\pi r^2$$

⇨ Tail correction diverges, unless U(r) decays faster than r^{-3}

⇨ Not suitable for e.g. Coulomb potential (r^{-1})

Motivation

Solutions

a) Truncate anyway!

advantage: no costly calculation of long-range-interaction
downside: serious inaccuracies

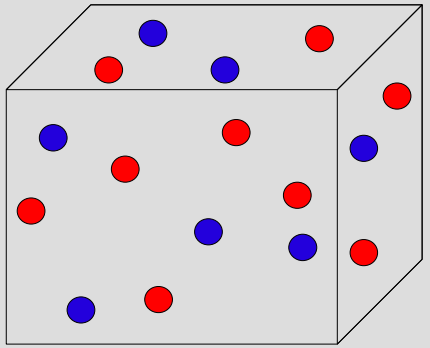
b) Compute long range interactions

Several methods:
i) Ewald sum
ii) Fast Multipole method
iii) Particle-mesh-based techniques

Of these methods, Ewald Summation is still the most widely used one

Ewald Sum

Return to our box:



Assume: System as a whole is electrically neutral

Now compute the contribution to the potential energy of this N-particle system:

$$U_{Coul} = \frac{1}{2} \sum_{i=1}^{N} q_i \phi(r_i)$$

where

$$\phi(r_i) = \sum_{j,\vec{n}}{}' \frac{q_i}{\left| \vec{r}_{ij} + \vec{n}\vec{L} \right|}$$

is the electrostatic potential.

$\vec{n}$ denotes the summation over all periodic images, the prime indicates that the self-potential for i=j is omitted.

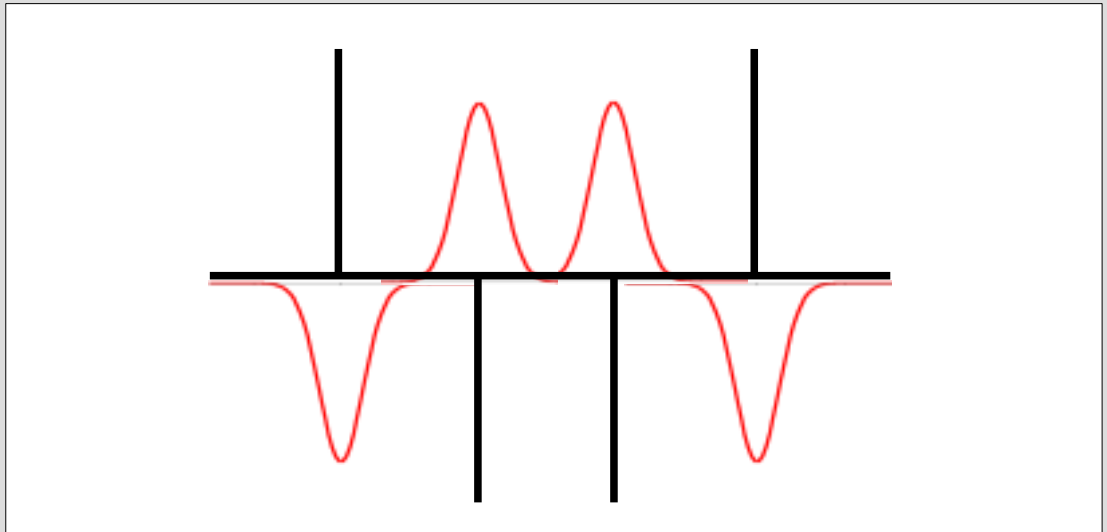
Ewald Sum

Problem:

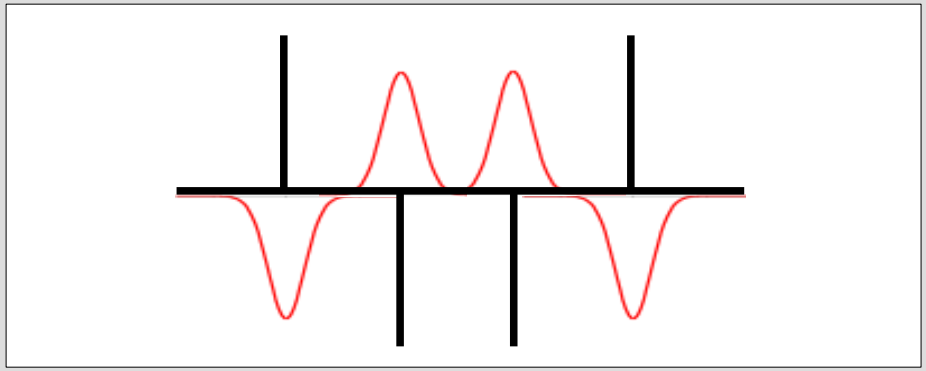
$$U_{Coul} = \frac{1}{2} \sum_{i=1}^{N} q_i \phi(r_i)$$

is only slowly (in fact conditionally) convergent.

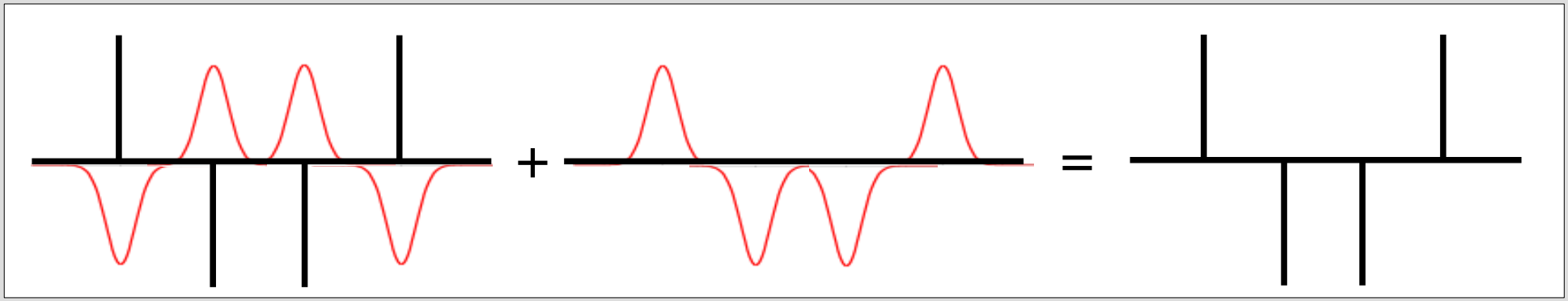
Idea: Consider that every particle q_i is surrounded by a diffuse charge distribution of opposite sign but same magnitude,such that it cancels q_i.



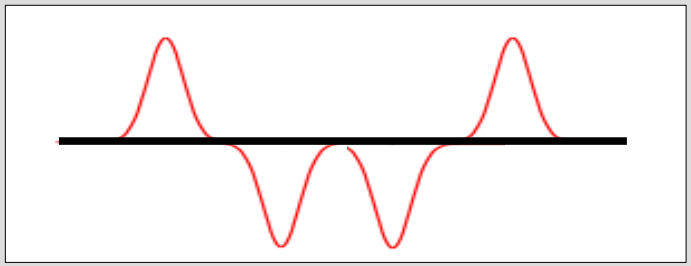
Ewald Sum



Now the interaction becomes short-ranged, as the diffuse distribution screens some part of the charge.
Of course we have to correct for the fact, that we added a potential by adding another potential with the same sign as the original potential:



Ewald Sum



The compensating charge density varies smoothly in space and is periodic, hence can be represented by a (rapidly converging Fourier series).

⇨ General idea of Ewald Summation:

i) Sum screened particle interactions in real space

ii)Subtract compensating potential in Fourier space.

put differently: $$\frac{1}{r} = \frac{f(r)}{r} + \frac{1-f(r)}{r}$$

Ewald Sum

$$U_{Coul} = \frac{1}{2V} \sum_{\vec{k} \neq \vec{0}} 4 \frac{\pi}{k^2} \left| \rho(\vec{k}) \right|^2 \exp\left(\frac{-k^2}{4\alpha} \right)$$

Fourier contribution

$$- \left(\frac{\alpha}{\pi} \right)^{\frac{1}{2}} \sum_{i=1}^{N} q_i^{\,2}$$

Self-potential correction

$$+ \frac{1}{2} \sum_{i \neq j}^{N} \frac{q_i q_j \, erfc\left(\sqrt{\alpha} r_{ij} \right)}{r_{ij}}$$

Real-space contribution

$$+ \frac{2\pi}{(2\epsilon' + 1)V} \left| \sum_{i=1}^{N} \vec{r}_i q_i \right|^2$$

Boundary effects

Basics for implementation

Standard Ewald implementation scales like N^2

Most costly part: Fourier transformation

⇒ Process can be speeded up by a method called „Fast Fourier Transformation“ (FFT)

3 popular algorithms, that implement FFT:

1) Particle-particle-particle mesh (P^3M)
2) Particle mesh Ewald (PME)
3) Smooth particle mesh Ewald (SPME)

Basics for implementation

Implementation steps

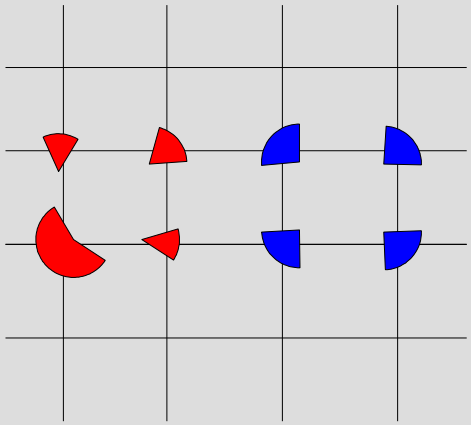
All 3 algorithms implement 4 steps:

1) Charge assignment
2) Solving Poisson's Equation
3) Differentiation
4) Back-Interpolation

Basics for implementation

Charge Assignment

FFT is a finite and discrete Fourier transformation, thus point charges with continuous coordiates have to be replaced by a grid based charge density.



Define an even function $W(\vec{x})$ such that the fraction of charge at position $\vec{x}$ is given by $W(\vec{x}_p-\vec{x})$, where $\vec{x}_p$ is a mesh point.

Basics for implementation

Charge Assignment

Properties of a suitable charge assignment function W:

- charge conservation
- finite and possibly small support
- localisation of discretisation error
- smooth
- minimisation of aliasing errors
- easy and transparent implementation

⇨ Not all properties can be achieved at the same time

Basics for implementation

Solving Poisson's Equation

$$-\Delta \phi(\vec{r}) = 4\pi \rho(\vec{r})$$

- by no means trivial

- different realisations in the three algorithms

Basics for implementation

Differentiation

To obtain the Forces exerted on the particles are obtained by differentating the potential. For the Fourier space part there exist several possibilities:

1) Differentation in Fourier space
   (relatively easy, computationally demanding)

2) Analytic differentiation of the assignment function in real space
   (very fast, does not conserve momentum)

3) Discrete differentiation on the mesh in real space
   (fourier part fast, nonlocal)

Basics for implementation

Back-interpolation

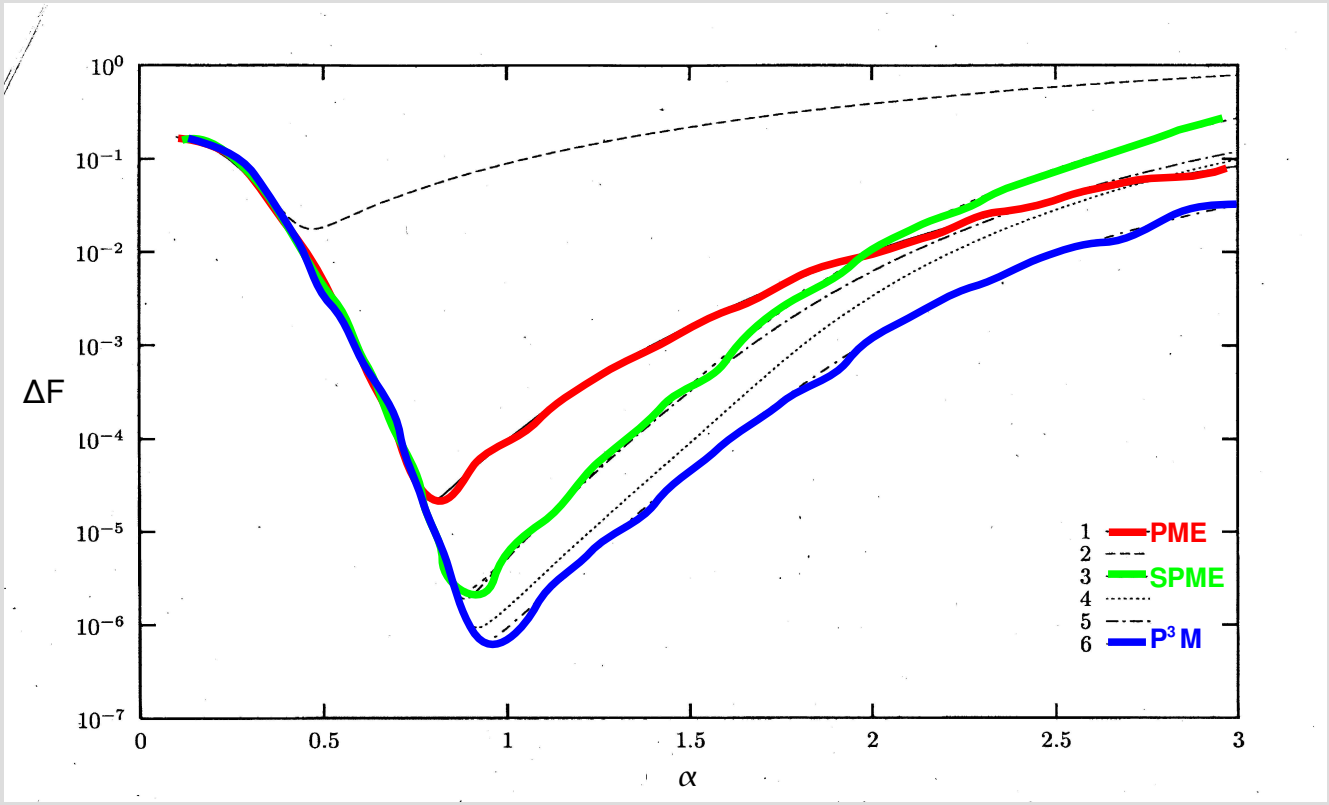
At one point one has to interpolate the mesh based results back to the actual particles.

This is done similarly to the charge distribution via some assignment function W.

It is convenient to use the *same* assignment function onto and from the mesh.

Basics for implementation

Comparison of the algorithms and the significance of α



from [3]

Time to say...

Thank you!

References

- [1] D. Frenkel/ B.Smit „*Understanding Molecular Simulations*“ , Academic Press, San Diego, 2002

- [2] Allen / Tildsley : „*Computer Simulation of Liquids*“

- [3] M. Deserno / C. Holm „*How to mesh up Ewald sums (I)*“ , J. Chem. Phys. 109, 7678(1998)

- [4] http://www.xray.cz/