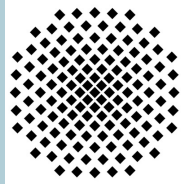
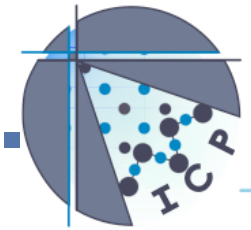


University of Stuttgart
Germany



INSTITUTE FOR
COMPUTATIONAL
PHYSICS

Electrostatic Solvers

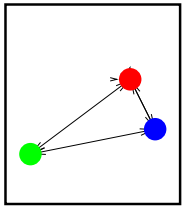
Christian Holm

Institut für Computerphysik, Universität Stuttgart
Stuttgart, Germany

Overview

- Statement of the problem
- Standard Ewald Sum
- Particle-Mesh-Ewald => P^3M
- ScaFaCoS Library
- Partially periodic geometries
- Dealing with dielectric interfaces
- Constant Potential Methods

Electrostatics is long ranged



Coulomb energy

Pair energy summation

$$U = \frac{l_B}{2} \sum_{i,j=1}^{N}{}' \frac{q_i q_j}{|\mathbf{r}_{ij}|}$$

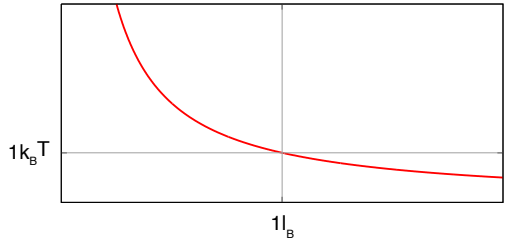
- summing up $1/r$ Coulomb pair potential
- Bjerrum length l_B

costly: $T_{CPU} \propto N^2$

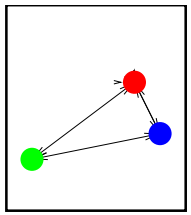
Bjerrum length

$$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}$$

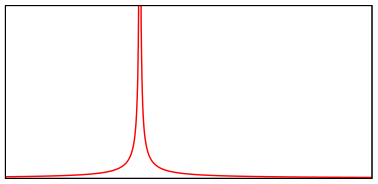
- electrostatic prefactor $\propto$ inverse temperature
- for two unit charges:



Electrostatics in Open Boundaries



Coulomb energy



Pair energy summation

$$U = \frac{l_B}{2} \sum_{i,j=1}^{N}{}' \frac{q_i q_j}{|\mathbf{r}_{ij}|}$$

- summing up $1/r$ Coulomb pair potential
- Bjerrum length l_B

Potential summation

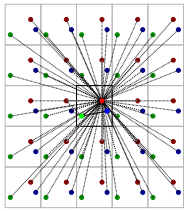
$$U = \frac{1}{2} \sum_{i=1}^{N} q_i \phi(\mathbf{r}_i)$$

- potential from solving Poisson's equation

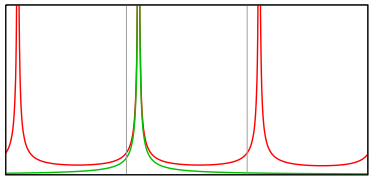
$$\nabla^2 \phi(\mathbf{r}) = -4\pi l_B \sum_{j=1}^{N} q_j \delta(\mathbf{r}_j - \mathbf{r})$$

equivalent approaches

Electrostatics in Periodic BC



Coulomb energy



Pair energy summation

$$U = \frac{l_B}{2} \sum_{S=0}^{\infty} \sum_{\mathbf{m}^2=S} \sum_{i,j=1}^{N}{}' \frac{q_i q_j}{|\mathbf{r}_{ij} + \mathbf{m}L|}$$

- conditionally convergent — summation order important
- numerically difficult
- *U not* periodic in coordinates $\mathbf{r}_i$

Potential summation

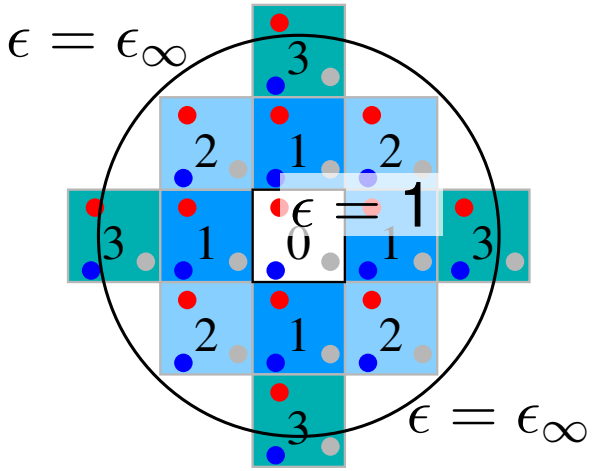
$$U = \frac{1}{2} \sum_{i=1}^{N} q_i \phi_{\text{per}}(\mathbf{r}_i)$$

- solve Poisson's equation imposing periodic boundaries
- *U is* periodic in coordinates $\mathbf{r}_i$

these two calculate something different!

What is the Difference?

- assume summation in periodic shells
- surrounded by polarizable material of dielectric constant ϵ_∞



Pair energy summation

vacuum around: $\epsilon_\infty = 1$

Potential summation

periodic: $\epsilon_\infty = \infty$

- difference to periodic solution is nonperiodic dipole term

$$U^{(d)} = \frac{2\pi}{(1+2\epsilon_\infty)L^3}\left(\sum_i q_i \mathbf{r}_i\right)^2$$

- metallic boundary conditions $\epsilon_\infty = \infty$ always safe
- never use $\epsilon_\infty < \infty$ for conducting systems

The Standard Ewald Method

- Paul Peter Ewald (1888-1985)
- Taught from 1921 – 1933 at the TH Stuttgart
- Theory of X-ray crystallography

Calculating the Coulomb potential yields two difficulties:

1. Singular at each particle position
2. The tail is very slowly decaying

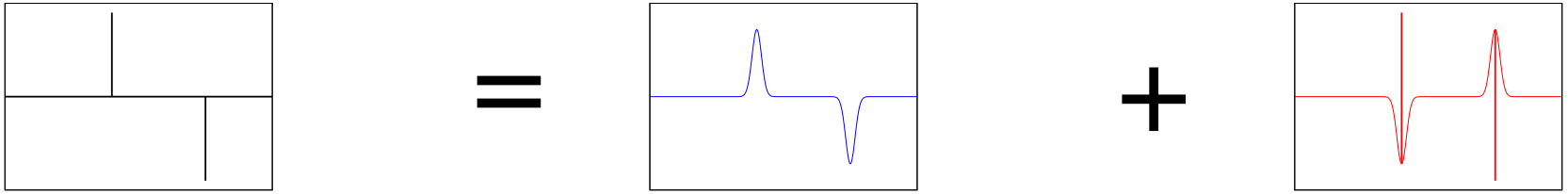
Idea: separate the two problems!

- Calculate the fast decaying short range part in real space
- Calculate the smooth long-distance part in Fourier space

Splitting the Potential

charge distribution

$$\rho = \sum_{\mathbf{n} \in L\mathbb{Z}^3} \sum_{i=1}^{N} q_i \delta(\mathbf{r} - \mathbf{r}_i - \mathbf{n})$$



replace δ by Gaussians of width α^{-1}:

$$\rho_{\text{Gauss}}(\mathbf{r}) = \left(\alpha/\sqrt{\pi}\right)^3 e^{-\alpha^2 r^2}$$

$$\delta(\mathbf{r}) = \rho_{\text{Gauss}}(\mathbf{r}) + [\delta(\mathbf{r}) - \rho_{\text{Gauss}}(\mathbf{r})]$$

The Ewald Formula

$$U = U^{(r)} + U^{(k)} + U^{(s)} + U^{(d)}$$

$$U^{(d)} = \frac{2\pi}{(1+2\epsilon_\infty)L^3}\left(\sum_i q_i \mathbf{r}_i\right)^2$$

exponentially convergent sums!

with

$$U^{(r)} = \frac{l_B}{2}\sum_{\mathbf{m}\in\mathbb{Z}^3}{\sum_{i,j}}' q_i q_j \frac{\mathrm{erfc}(\alpha|\mathbf{r}_{ij}+\mathbf{m}L|)}{|\mathbf{r}_{ij}+\mathbf{m}L|}$$

real space correction

$$U^{(k)} = \frac{l_B}{2L^3}\sum_{\mathbf{k}\neq\mathbf{0}} \frac{4\pi}{k^2} e^{-k^2/4\alpha^2} |\widehat{\rho}(\mathbf{k})|^2$$

Gaussians in *k*-space

$$U^{(s)} = -\frac{\alpha l_B}{\sqrt{\pi}}\sum_i q_i^2$$

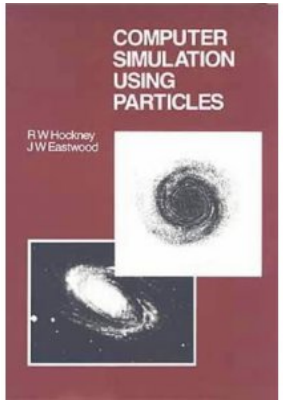
Gaussian self interaction

forces from differentiation

$$\mathbf{F}_i = -\frac{\partial}{\partial \mathbf{r}_i} U$$

Complexity of $\mathrm{O}(N^{3/2})$

Particle Mesh Ewald Methods

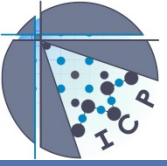


...The Bible...
written by the *evangelists*
R.W. Hockney, J.W. Eastwood, 1988

- Near field: standard Ewald
- Far field: replace Fourier space sum by the discrete FFT on a regular mesh
- Computational order $\mathcal{O}(N \log N)$
- The wheel got reinvented:
  P^{3}M (Hockney, Eastwood, 1973)
  PME (Darden et al. 1993)
  SPME (Essmann et al., 1995)

Particle-Particle-Particle-Mesh ♫♭ Simply the best.....

See also: M. Deserno, C. Holm, J. Chem. Phys. **109**, 7678-7693 (1998)

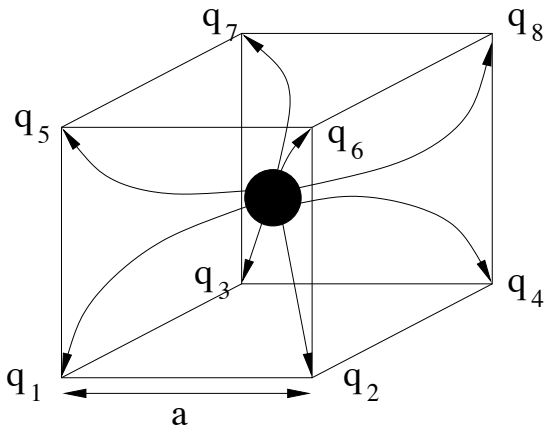


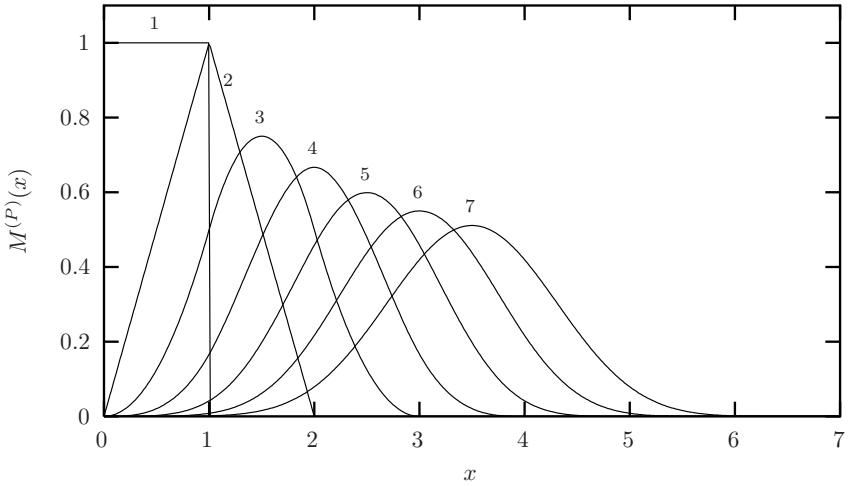
Steps of the P^{3}M

1. $\{\mathbf{r}_i, q_i\} \rightarrow \rho(\mathbf{r})$: interpolate charges onto a grid
   (window functions: cardinal B-splines)
2. $\rho(\mathbf{r}) \rightarrow \widehat{\rho}(\mathbf{k})$: Fourier transform charge distribution
3. $\hat{\phi}(\mathbf{k}) = \hat{G}(\mathbf{k})\hat{\rho}(\mathbf{k})$: solve Poisson's equation by multiplication
   with optimal influence function $\hat{G}(\mathbf{k})$
   (in continuum: product of Green's function $\frac{4\pi}{k^2}$ and
   Fourier transform of Gaussians $e^{-k^2/4\alpha^2}$)
4. $i\mathbf{k}\hat{\phi}(\mathbf{k}) \rightarrow \hat{\mathbf{E}}(\mathbf{k})$: obtain field by Fourier space differentiation
4. $\widehat{\mathbf{E}}(\mathbf{k}) \rightarrow \mathbf{E}(\mathbf{r})$: Fourier transform field back
5. $\mathbf{E}(\mathbf{r}) \rightarrow \{\mathbf{r}_i, \mathbf{F}_i\}$: interpolate field at position of charges
   to obtain forces $\mathbf{F}_i = q_i\mathbf{E}_i$

Instead of ik-differentiation (4.) I can also use finite difference or differenciate the pullback function of $\nabla\phi$. This saves two FFT's

Charge Assignment





- interpolate charges onto *h*-spaced grid

$$\rho_{\mathbb{M}}(\mathbf{r}_p) = \frac{1}{h^3} \sum_{i=1}^{N} q_i W^{(p)}(\mathbf{r}_p - \mathbf{r}_i)$$

- $W^{(p)}(\mathbf{r})$ cardinal B-splines in P^3M / SPME

Optimal Influence Function

- minimize the rms error functional

$$Q[G] := \int_{h^3} d\mathbf{r}_1 \int_V d\mathbf{r} \left[\phi(G;\mathbf{r},\mathbf{r}_1) - \phi(\mathbf{r})\right]^2$$

with the analytic reference potential

$$\hat{\phi}(\mathbf{k}) = \frac{4\pi}{k^2} e^{-k^2/4\alpha^2}$$

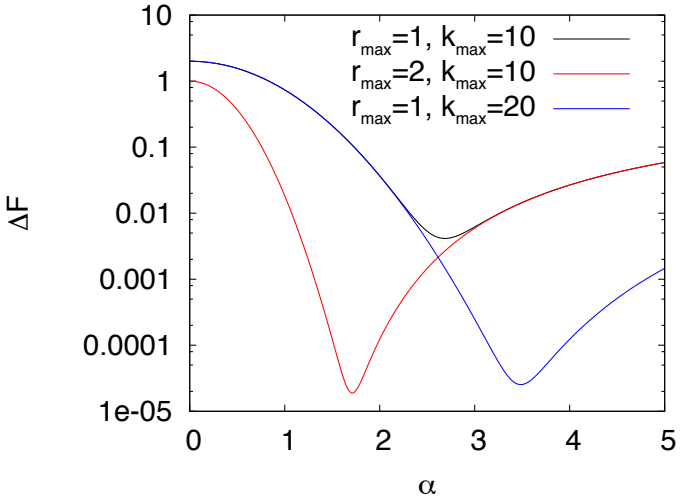
- leads to

$$\hat{G}^{\text{opt}}(\mathbf{k}) = \frac{\sum_{\mathbf{l}\in\mathbb{Z}^3} \hat{\varphi}^2(\mathbf{k}+m\mathbf{l})\hat{G}(\mathbf{k}+m\mathbf{l})}{\left[\sum_{\mathbf{l}\in\mathbb{Z}^3} \hat{\varphi}^2(\mathbf{k}+m\mathbf{l})\right]^2}$$

with $m = L/h$

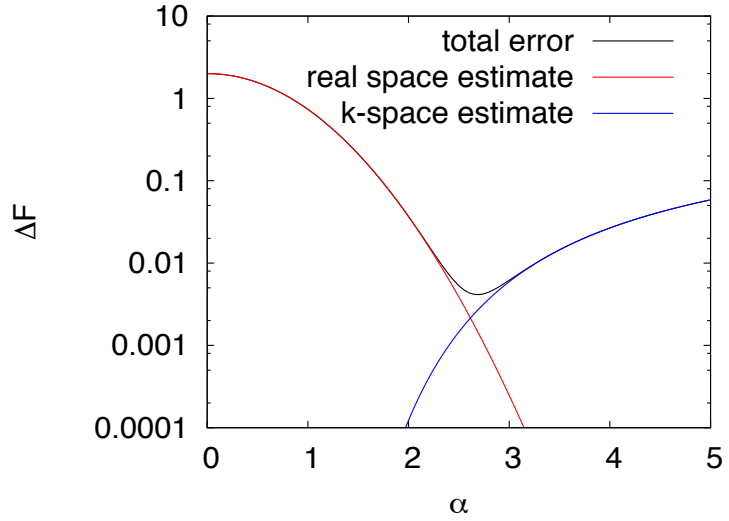
Why Control Errors ?

rms force error $\Delta F = \sqrt{\left\langle (\mathbf{F}^{\text{exact}} - \mathbf{F}^{\text{Ewald}})^2 \right\rangle} = \sqrt{\frac{1}{N}\sum_{i=1}^{N} \Delta F_i^2}$



- optimal α brings orders of magnitude of accuracy
- at given required accuracy, find fastest cutoffs
- compare algorithms at the same accuracy

How to Control Errors



Kolafa and Perram:

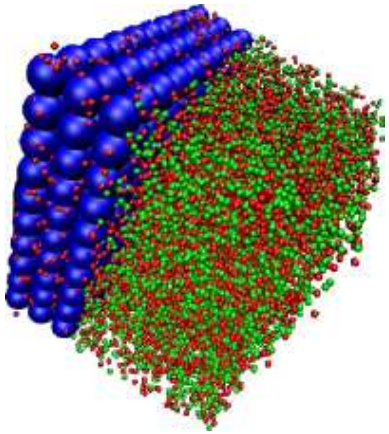
$$\Delta F_{\text{real}} \approx \frac{\sum q_i^2}{\sqrt{N}} \frac{2}{\sqrt{r_{\max} L^3}} \exp\left(-\alpha^2 r_{\max}^2\right)$$

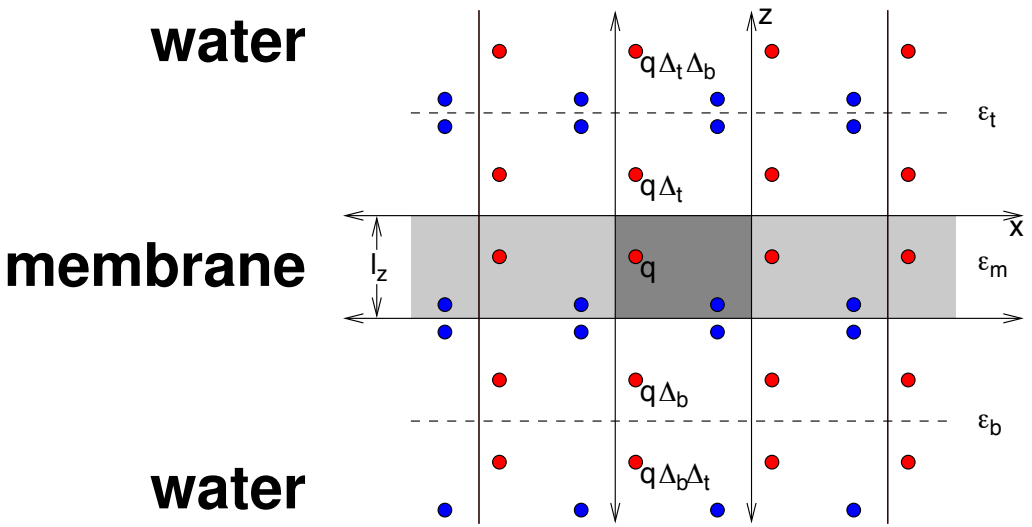
Hockney and Eastwood:

$$\Delta F_{\text{Fourier}} \approx \frac{\sum q_i^2}{\sqrt{N}} \sqrt{\frac{Q[\hat{G}_{\text{opt}}(\mathbf{k})]}{L^3}}$$

See also: M. Deserno, C. Holm, J. Chem. Phys. **109**, 7694-7701 (1998)

Partially Periodic Systems



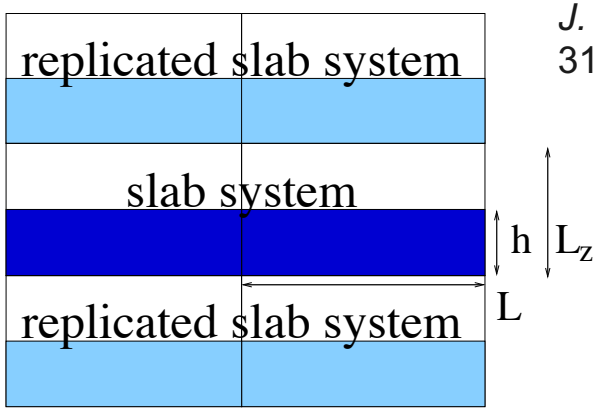


- 2D periodic: slablike systems, surfaces, thin films, membranes, air-water interfaces
- 1D periodic: needles, rods, nanopores,
- 0D periodic boundaries = open systems

- P^3M cannot be employed straightforwardly
- P2NFFT can be formulated to work

2D PBC approx. with 3D PBC

The Yeh and Berkowitz correction



J. Chem. Phys. 111, 3155–3162 (1999)

- potential of a charge and its periodic images similar to plate
- plates cancel due to charge neutrality

$$2\pi q_i \sum_{j=1}^{N} \sigma_j (|z_{ji} + mL_z| + |z_{ji} - mL_z|) = 4\pi q_i \, nL_z \sum_{j=1}^{N} \sigma_j = 0$$

- leave a gap and hope artificial replicas cancel
- requires changed dipole term $U^{(d)} = \frac{2\pi}{L^3} \left(\sum_i q_i z_i \right)^2$

Changes the summation order

The ELC Method

$$U_{lc} = \frac{\pi}{L^2} \sum_{\substack{\mathbf{k} \in \frac{2\pi}{L}\mathbb{Z}^2 \\ \mathbf{k}^2 > 0}} \sum_{i,j=1}^{N} q_i q_j \frac{e^{|\mathbf{k}|z_{ij}} + e^{-|\mathbf{k}|z_{ij}}}{f_{pq}(e^{f_{pq}L_z} - 1)} e^{\mathrm{i}(k_x x_{ij} + k_y y_{ij})}$$

- Calculate contribution of image layers exactly
- Subtract numerically => smaller gap size
- Change summation order with dipole term
- 2-4x faster than plain Yeh-Berkowitz plus full error control

A. Arnold, J. de Joannis, C.H., J. Chem. Phys. **117**, 2496 (2002)

ScaFaCoS Library

- ScaFaCoS currently provides 11 method implementations: DIRECT, EWALD, P3M, P2NFFT, VMG, PP3MG, PEPC, FMM, MEMD, MMM1D, MMM2D
- Features:
  - For reference purposes (not competitive): DIRECT, EWALD
  - 3d-periodic boundaries: P3M, P2NFFT, VMG, PP3MG, PEPC, FMM(, EWALD)
  - Open boundaries: P2NFFT, FMM, PEPC(, DIRECT)
  - Partially periodic boundaries: P2NFFT, FMM, PEPC, MMM*D
  - General triclinic boundaries: P3M, P2NFFT
- Distinguish *Splitting Methods*, *Hierarchical Methods* and *Local Methods* (*i.e.* MEMD)

A. Arnold, F. Fahrenberger, C. Holm, O. Lenz, M. Bolten, H. Dachsel, R. Halver, I. Kabadshow, F. Gähler, F. Heber, J. Iseringhausen, M. Hofmann, M. Pippig, D. Potts, G. Sutmann, *Comparison of scalable fast methods for long-range interactions*, Phys. Rev. E **88,** 063308 (2013). www.scafacos.de

Dipolar Interactions

- There is also a dipolar P^3M available in ESPResSo
- Also a 2D+h Version as DLC

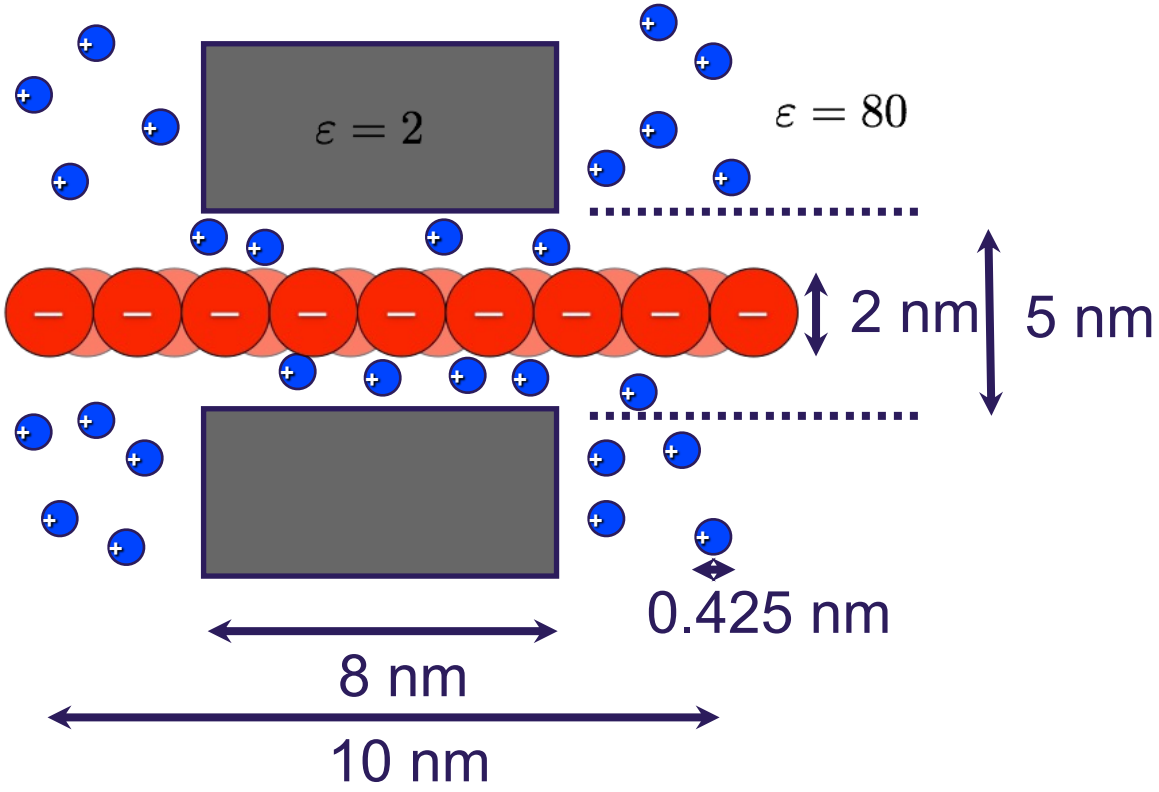
J. J. Cerdà ,V. Ballenegger, O. Lenz, Ch. Holm, *P3M algorithm for dipolar interactions*, J. Chem. Phys, **129**, 234104 (2008)

Include Dielectric Interfaces

Where does this matter?

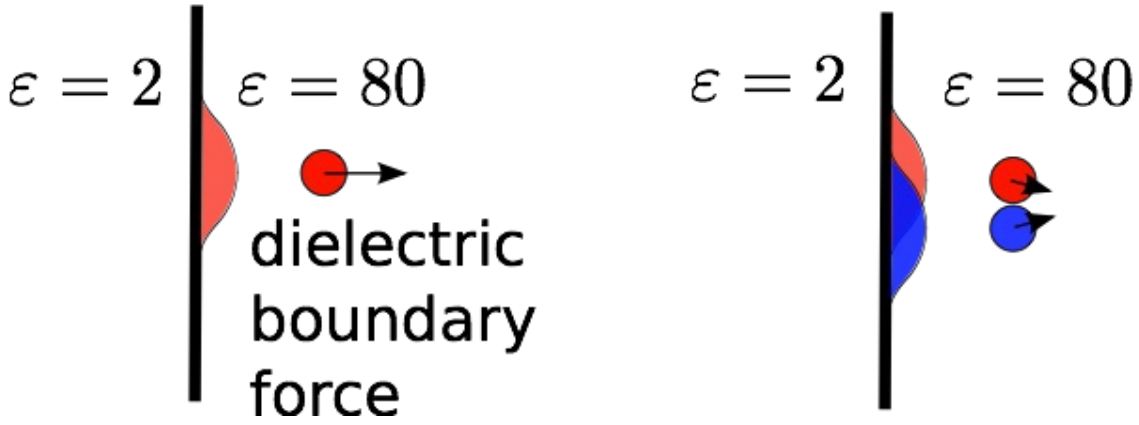
See also: A. Arnold, K. Breitsprecher, F. Fahrenberger, S. Kesselheim, O. Lenz, C. Holm, Efficient algorithms for electrostatic interactions including dielectric contrasts, Entropy **15**, 4569-4588 (2013)

Coarse Grained Modelling



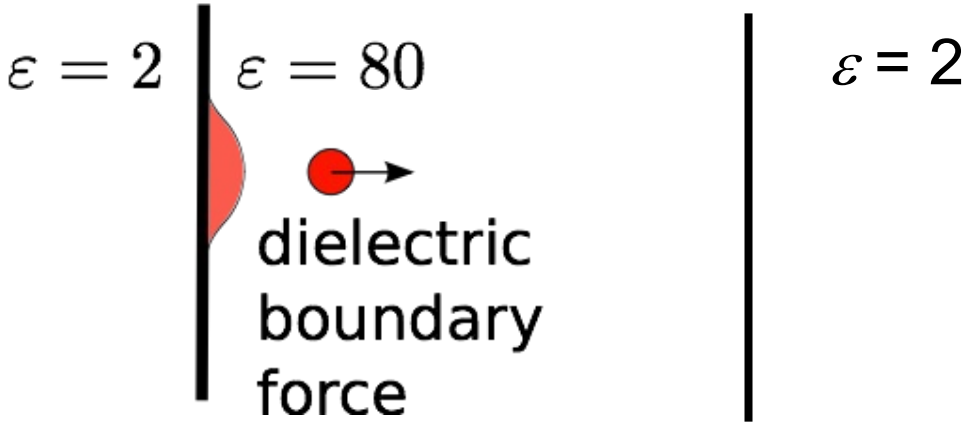
- DNA represented either as a charged rigid rod (l_p = 50 nm, dsDNA) or a fully flexible chain for ssDNA
- Classical MD with Langevin dynamics and explicit ions
- Implicit solvent model (dielectric continuum) for the solvent and the nanopore, but different ε with ICC*

What does Dielectric Contrast do?



- Water is more polarizable than the nanopore material, leading to an induced charge of the same sign
- Force pushing the charge away from the wall
- Inside the pore there is almost no net charge due to strong energetic penalties for charge separation
- How to compute it efficiently?
- Use either Image charges or induced charges….

Planar Dielectric Interfaces



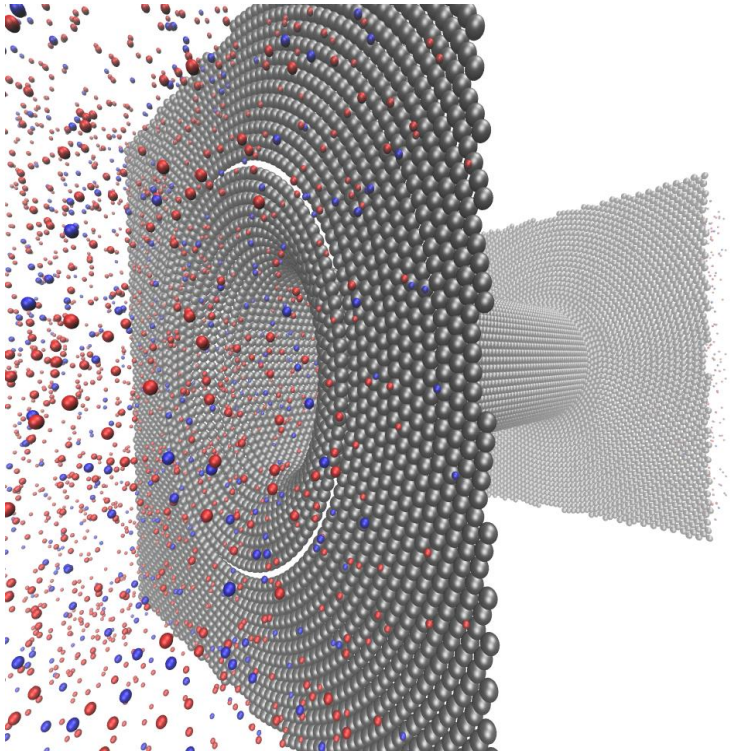
Can be handled by

- ICMMM2D
- ELCIC

- S. Tyagi, A. Arnold, C. H., ICMMM2D: An accurate method to include planar dielectric interfaces via image charge summation, J. Chem. Phys.**127**, 154723 (2007)
- S. Tyagi, A. Arnold C. H., *Electrostatic layer correction with image charges: A linear scaling method to treat slab 2D + h systems with dielectric interfaces*, J. Chem. Phys.**129,** 204102 (2008)

Arbitrary Curved Interfaces

What about arbitrarily curved interfaces like a nanopore?



ICC* Algorithm

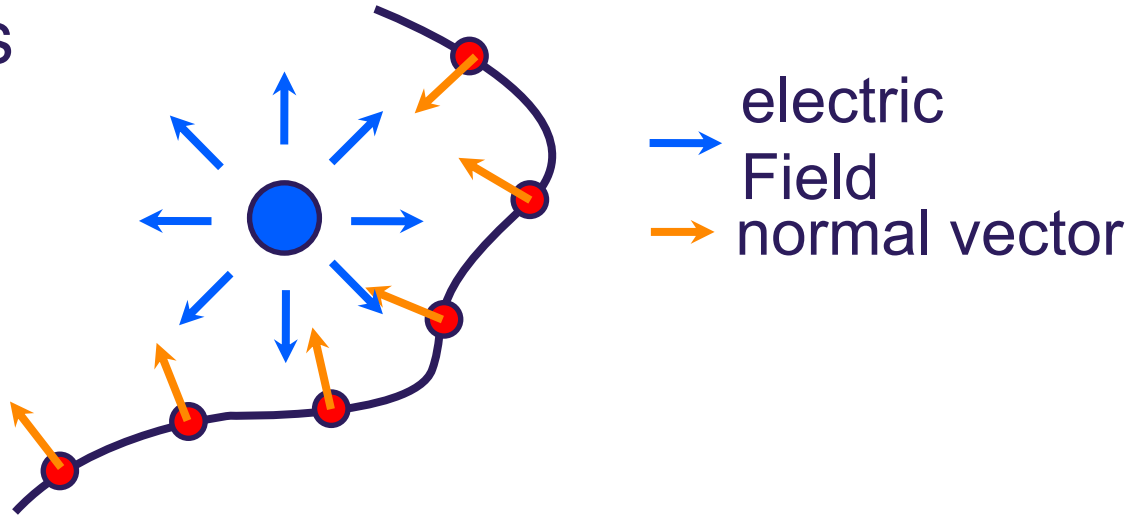
- Boundary condition for the normal component of the electric field:

$$\varepsilon_1 \mathbf{E_1} \cdot \mathbf{n} = \varepsilon_2 \mathbf{E_2} \cdot \mathbf{n}$$

  - can be fulfilled by introducing a charge density:

$$\sigma = \frac{1}{2\pi} \varepsilon_1 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2} \mathbf{E}$$

- Discretization of the surface to boundary elements



ICC* Algorithm

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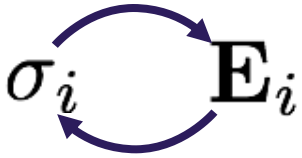
- Discretization of the surface to boundary elements lead to a set of equations

  - Solved by an iterative scheme



  - $\mathbf{E}$ can be obtained by any Coulomb solver
  - Periodic boundary conditions automatically fulfilled

ICC* Algorithm

- Boundary condition for the normal component of the electric field:

$$\varepsilon_1 \mathbf{E_1} \cdot \mathbf{n} = \varepsilon_2 \mathbf{E_2} \cdot \mathbf{n}$$

  - can be fulfilled by introducing a charge density:

$$\sigma = \frac{1}{2\pi} \varepsilon_1 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2} \mathbf{E}$$

- Discretization of the surface to boundary elements lead to a set of equations

ICC* (Induced Charge Computation) Algorithm: S. Tyagi, M. Süzen, M. Sega, M. Barbosa, S. Kantorovich, and C. Holm, Journal of Chemical Physics **132**, 154112, (2010)

Constant Potential Algorithms

MMM2DIC, ELCIC, ICC* work also for const. potential, set $e_r = \infty$

For details refer to: *Efficient algorithms for electrostatic interactions including dielectric contrasts*, A Arnold, K Breitsprecher, F Fahrenberger, S Kesselheim, O Lenz, C. Holm, Entropy **15**, 4569 (2013).
These algorithms model a structureless **continuum metal surface** (no other electrode properties included) with perfect screening. The ions in the solvent are treated as point ions.

Alternative, but physically different method is:

Constant Potential Method (CPM): Electrode atoms possess a Gaussian shaped charge distribution of width a

Siepmann and Sprik, J. Chem. Phys. 102, 511 (1995).
Reed, S. K., Lanning, O. J., & Madden, P. A., J. Chem. Phys., 126, 084704 (2007).

Implementations

- MetalWalls (Al. Marin-Laflèche et al., *MetalWalls: A classical molecular dynamics software dedicated to the simulation of electrochemical systems*, Journal of Open Source Software, Volume 5, Issue 53 (2020)
- Electrodes (L. J. V. Ahrens-Iwers, M. Janssen, S. R. Tee, R. H. Meißner, *ELECTRODE: An electrochemistry package for atomistic simulations*, J. Chem. Phys. 157, 084801 (2022).

Width of Gaussian related to hardness ($\propto (qe)^2$)

Conclusions

- There exist plenty of Coulomb algorithms
- Choose the one with a decent scaling or small prefactor, depending on the # of charges
- Use a method with full error control and preferably use the method you know best
- ESPResSo offers many methods (i.e. ScaFaCoS), but standard horse: P3M, ELC, ICC*, ELCIC
- See next talk for more….

Acknowledgements

- M. Deserno, H.J Limbach, A. Arnold, J. de Joannis, S. Tyagi, V. Ballenegger, J.J. Cerda, O. Lenz, S. Kesselheim, F. Fahrenberger, F. Weik, R. Weeber, current ESPResSo developers and the whole ScaFaCoS team, and many more ….for work on these sometimes cumbersome algorithms….

1. Espresso Workshop 2006, FIAS Frankfurt

- Time for Questions……