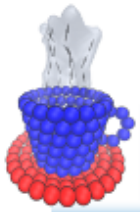

Coulomb interactions: P^{3}M, MMMxD, ELC and ICC*

Axel Arnold

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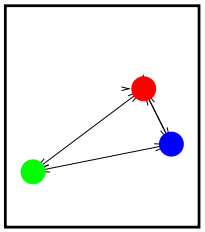
Universität Stuttgart

October 10, 2012

Electrostatics



Coulomb energy

Pair energy summation

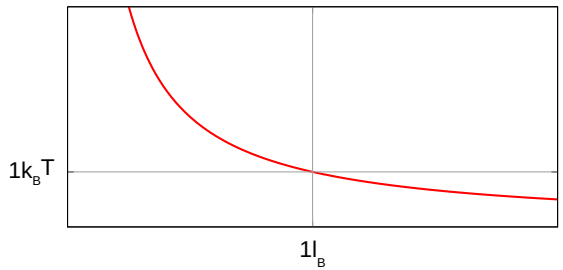
$$U = \frac{l_B}{2} \sum_{i,j=1}^{N}{}' \frac{q_i q_j}{|\mathbf{r}_{ij}|}$$

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

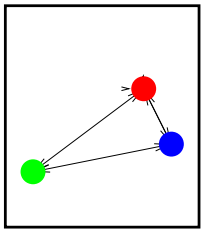
Bjerrum length

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

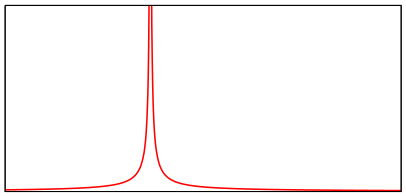
- electrostatic prefactor $\propto$ inverse temperature
- for two unit charges:



Electrostatics



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

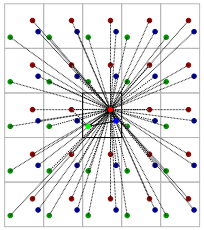
$$U = \frac{1}{2} \sum_{i=1}^{N} q_i \phi(\mathbf{r}_i)$$

- potential from solving Poisson's equation

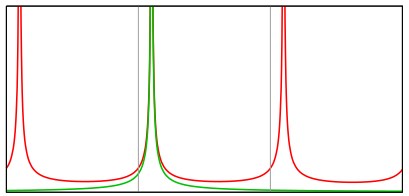
$$\nabla^2 \phi(\mathbf{r}) = -4\pi l_B \sum_{j=1}^{N} q_j \delta(\mathbf{r}_j - \mathbf{r})$$

equivalent approaches

Electrostatics *in periodic boundary conditions*



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

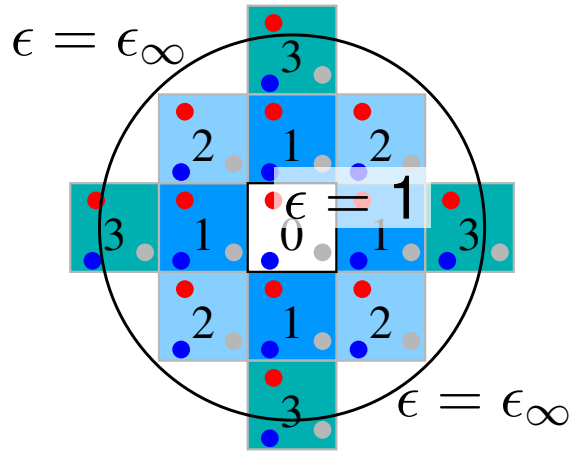
$$U = \frac{1}{2} \sum_{i=1}^{N} q_i \phi_{\text{per}}(\mathbf{r}_i)$$

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

these two calculate something different!

Where the difference comes from: the dipole term

- 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

Electrostatics in ESPResSo

- requires myconfig.h-switch ELECTROSTATICS
- switching on:

```
inter coulomb <lB> <method> <parameters>
```

- methods and their parameters: next 2 hours
- switching off:

```
inter coulomb 0
```

- getting l_B, method and parameters:

```
inter coulomb
```

returns e. g.

```
{coulomb 1.0 p3m 7.75 8 5 0.1138 0.0}
{coulomb epsilon 80.0 n_interpol 32768 mesh_off 0.5 0.5 0.5}
```

Assigning charges

```
part 0 pos 0 0 0 q 1
part 1 pos 0.5 0 0 q -1.5
```

Adding a charged plate

```
constraint plate height <h> sigma <σ>
```

- plate parallel to xy-plane at $z = h$, charge density σ
- requires 2D periodicity (nonperiodic in z)

Adding a charged rod

```
constraint rod center <cx> <cy> lambda <λ>
```

- rod parallel to z-axis at $(x, y) = (c_x, c_y)$, line charge density λ
- requires 1D periodicity (periodic in z)

The Ewald method

P. P. Ewald, 1888 — 1985

Coulomb potential has 2 problems

1. singular at each particle position
2. very slowly decaying

Idea: separate the two problems!

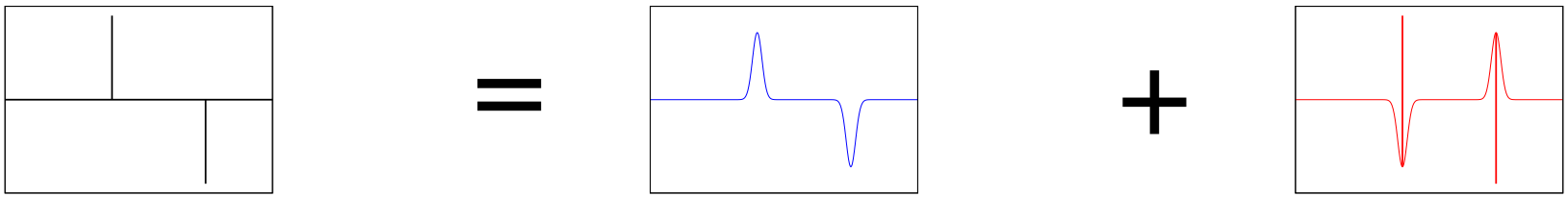
- one smooth potential — Fourier space
- one short-ranged potential — real space

P. P. Ewald, *Die Berechnung optischer und elektrostatischer Gitterpotentiale*, Ann. Phys. 369(3):253, 1921

Ewald: 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

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

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

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

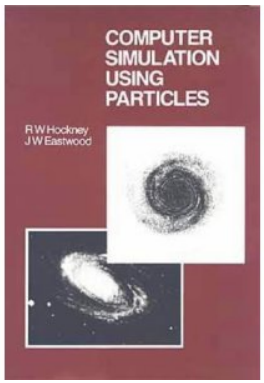
Gaussian self interaction

forces from differentiation

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

... coming soon to ESPResSo (on GPU)

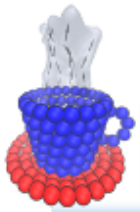
Mesh-based Ewald methods



R. W. Hockney
J. W. Eastwood

- replace k-space Fourier sum by discrete FFT
- discrete FT is exact — constant real space cutoff
- computational order $\mathcal{O}(N \log N)$
- most frequently used methods:
  - **P^{3}M**: optimal method
  - PME
  - SPME

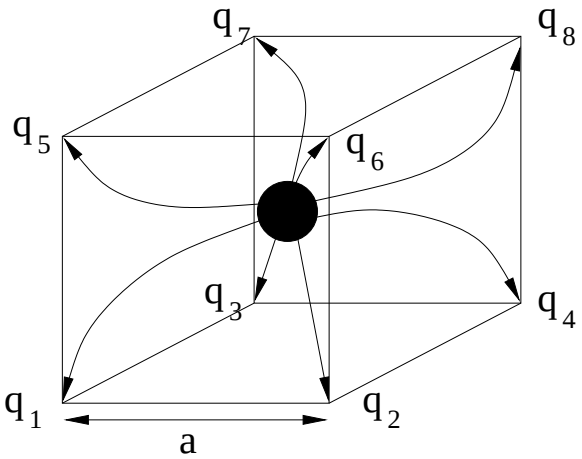
R. W. Hockney and J. W. Eastwood, *Computer Simulation Using Particles*, 1988
M. Deserno and C. Holm, JCP 109:7678, 1998

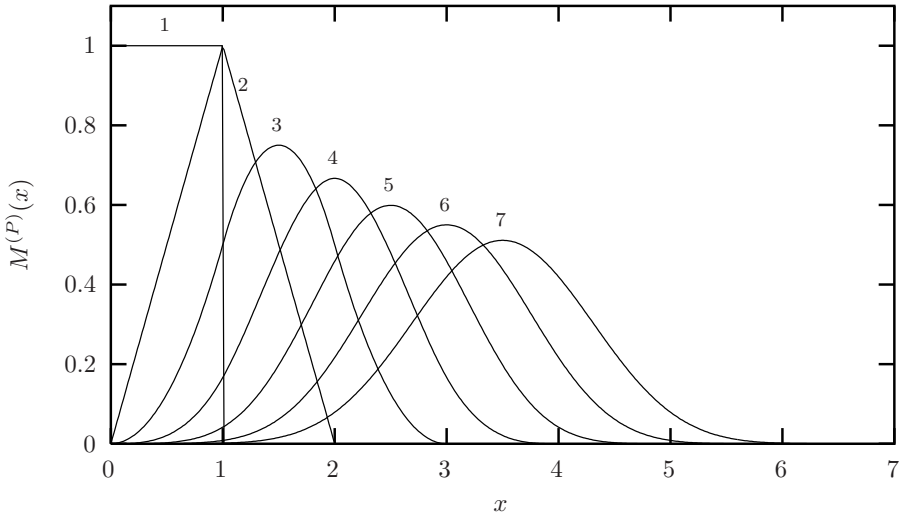


Steps of P^{3}M

1. $\{\mathbf{r}_i, q_i\} \to \rho(\mathbf{r})$: interpolate charges onto a grid
   (window functions: cardinal B-splines)
2. $\rho(\mathbf{r}) \to \hat{\rho}(\mathbf{k})$: 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. $i\mathbf{k}\hat{\phi}(\mathbf{k}) \to \hat{\mathbf{E}}(\mathbf{k})$: obtain field by Fourier space differentiation
4. $\hat{\mathbf{E}}(\mathbf{k}) \to \mathbf{E}(\mathbf{r})$: Fourier transform field back
5. $\mathbf{E}(\mathbf{r}) \to \{\mathbf{r}_i, \mathbf{F}_i\}$: interpolate field at position of charges to obtain forces $\mathbf{F}_i = q_i\mathbf{E}_i$

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^{3}M / SPME

Optimal influence function

$$\hat{G}_{\text{opt}}(\mathbf{k}) = h^6 \frac{i\mathbf{k} \cdot \sum_{\mathbf{m}\in\mathbb{Z}^3} \widehat{W^{(p)}}^2(\mathbf{k}+\frac{2\pi}{h}\mathbf{m})\hat{\mathbf{R}}(\mathbf{k}+\frac{2\pi}{h}\mathbf{m})}{|\mathbf{k}|^2 \left[\sum_{\mathbf{m}\in\mathbb{Z}^3} \widehat{W^{(p)}}^2(\mathbf{k}+\frac{2\pi}{h}\mathbf{m})\right]^2}$$

- aliasing of continuum force

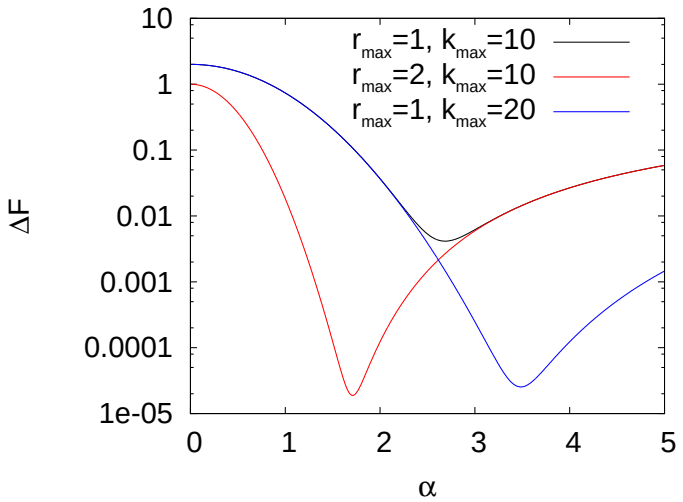
$$\hat{\mathbf{R}}(\mathbf{k}) = -i\mathbf{k}\frac{4\pi}{k^2} e^{-k^2/4\alpha^2}$$

  with differentiation, Green's function and transform of Gaussian
- minimizes the rms force error functional

$$Q[F] := \frac{1}{h^3} \int_{h^3} d^3 r_1 \int_V d^3 r \left[\mathbf{F}(\mathbf{r};\mathbf{r}_1) - \mathbf{R}(\mathbf{r})\right]^2$$

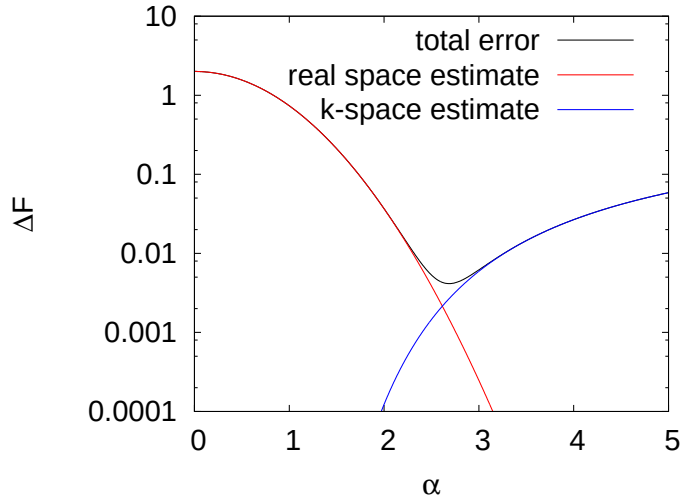
Why to control errors

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



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

How to: error estimates



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:

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

P^{3}M in ESPResSo (F. Weik, H. Limbach, AA)

- tune P^{3}M for rms force error τ

```
inter coulomb <l_B> p3m tune accuracy <τ> \
    [r_cut <r_max>] [mesh <n_M>] [cao <p>]
inter coulomb epsilon ε_∞
```

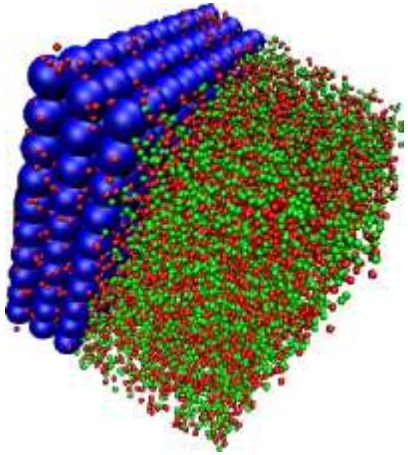
- computes optimal α
- tunes for optimal speed

r_{max}	real space cutoff (0 to retune)
$n_{\mathbb{M}} = L/h$	mesh size (0 to retune)
p	charge assignment spline order p (0 to retune)

- fixing parameters speeds up tuning, if you know the optimal value
- second command to set ϵ_∞ (defaults to ∞ (“metallic”))
- manually set parameters (dangerous!)

```
inter coulomb <l_B> p3m <r_max> <n_M> <p> <α>
```

Partially periodic systems



- partially p. b. c. for slablike systems (surfaces, thin films)
- ... or for cylindrical systems (rods, nanopores)
- dielectric contrasts at interfaces
- P^3M cannot be employed straightforwardly

Another approach: MMM2D far formula

$$\phi_\beta(r) = \sum_{k,l\in L\mathbb{Z}} \frac{e^{-\beta\sqrt{(x+k)^2+(y+l)^2+z^2}}}{\sqrt{(x+k)^2+(y+l)^2+z^2}}$$

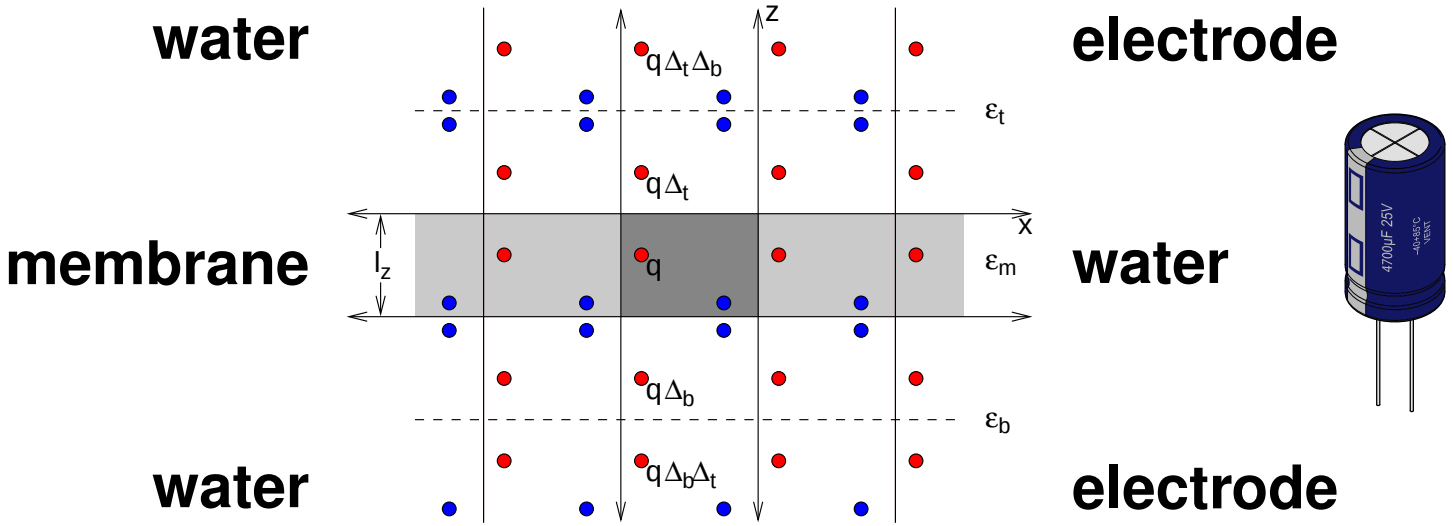
$$= \frac{2}{L} \sum_{p\in\frac{2\pi}{L}\mathbb{Z}} \left(\sum_{l\in L\mathbb{Z}} \mathrm{K}_0\left(\sqrt{\beta^2+p^2}\sqrt{(y+l)^2+z^2}\right)\right) e^{ipx}$$

$$= \frac{2\pi}{L^2} \sum_{p,q\in\frac{2\pi}{L}\mathbb{Z}} \frac{e^{-\sqrt{\beta^2+p^2+q^2}|z|}}{\sqrt{\beta^2+p^2+q^2}} e^{ipx} e^{iqy}$$

$$= \frac{2\pi}{L^2} \left(\sum_{p^2+q^2>0} \frac{e^{f_{pq}|z|}}{f_{pq}} e^{ipx} e^{iqy} + |z| \right) + \frac{\pi}{L^2}\beta^{-1} + \mathcal{O}_{\beta\to 0}(\beta)$$

- screened Coulomb interaction in limit of screening length ∞
- other formula for $z \approx 0$
- optimal computation time $\mathcal{O}(N^{5/3})$, comparable to Ewald
- analogously for 1d, but then $\mathcal{O}(N^2)$

Dielectric contrasts



- typical two dimensional systems: thin films, slit pores
- material boundaries $\Longrightarrow$ dielectric contrast
- take into account polarization by image charges
- can be handled by MMM2D

MMM2D and MMM1D in ESPResSo (AA)

- using MMM2D tuned for maximal pairwise error τ

```
cellsystem layered <n_layers>
inter coulomb <l_B> mmm2d <τ> [<k_max>] \
   [dielectric <ε_t> <ε_m> <ε_b> | dielectric-contrasts <Δ_t> <Δ_b>]
```

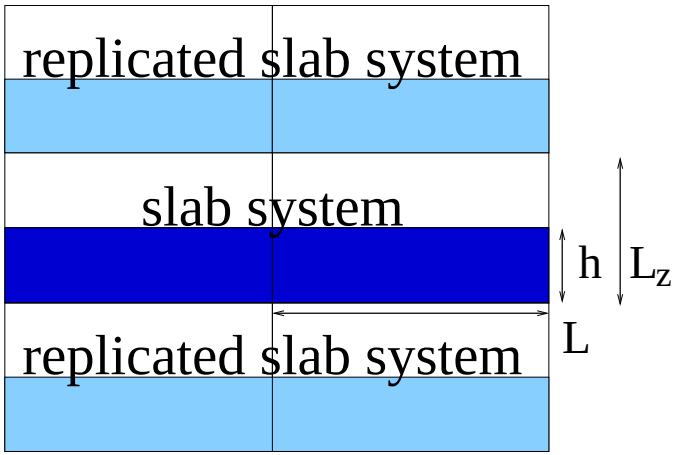
- allows to fix k_{max} (p, q)-space cutoff
  ϵ_t, ϵ_m, ϵ_b dielectric constants *or*
  Δ_t, Δ_b dielectric contrasts
- requires *layered* cell system
- number of layers per CPU $n_{\text{layers}} = B/N_p$ is tuning parameter

- using MMM1D tuned for maximal pairwise error τ

```
cellsystem nsquare
inter coulomb <l_B> mmm1d tune <τ>
```

- requires *all-with-all* cell system

The method of Yeh+Berkowitz



- 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 $U^{(d)} = \frac{2\pi}{L^3} \left(\sum_i q_i z_i \right)^2$

Electrostatic layer correction (ELC)

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

- error not known *a priori* — required gap size?
- calculate contribution of image layers
- subtract numerically $\Rightarrow$ needs smaller gaps
- 2-4x faster than plain Yeh+Berkowitz

AA, J. de Joannis, and C. Holm, JCP 117:2496, 2002

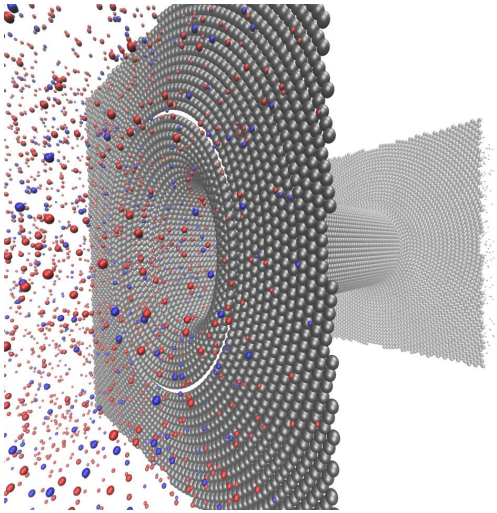
ELC in ESPResSo (AA)

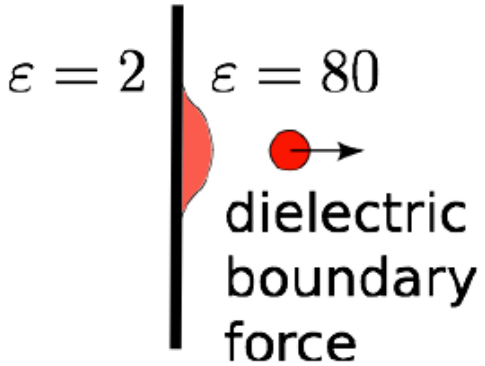
- using ELC for maximal pairwise error τ

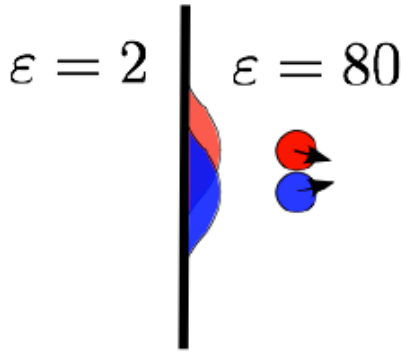
```
inter coulomb <l_B> p3m tune accuracy <τ'> ...
inter coulomb elc <τ> <g> [k_max>] \
   [dielectric <ε_t> <ε_m> <ε_b> | dielectric-contrasts <Δ_t> <Δ_b>]
```

- gap size $g = L_z - h$ has to be specified
- user is responsible to keep a gap (by walls or fixed particles)
- gap location unimportant
- requires P^3M to be switched on first
- allows to fix k_{max} (p, q)-space cutoff (otherwise tuned)
  ϵ_t, ϵ_m, ϵ_b dielectric constants *or*
  Δ_t, Δ_b dielectric contrasts

Arbitrarily shaped dielectric surfaces





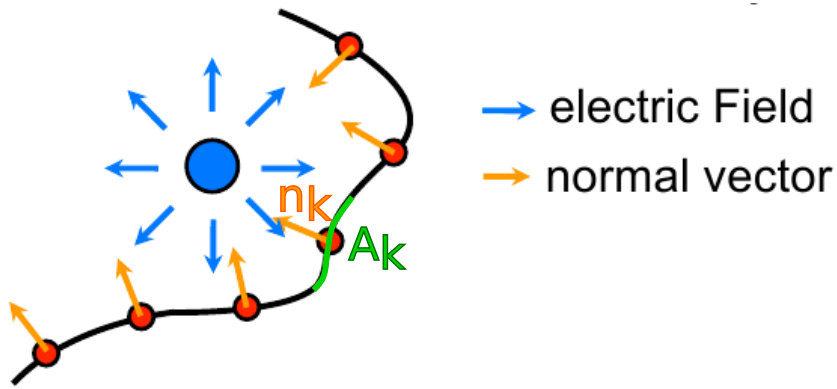


- MMM2D/ELC only handle planar parallel dielectric interfaces
- what about a nanopore? vesicle?
- cannot be handled by image charges
- satisfy boundary constraints for electric field

ICC* algorithm

boundary condition at interface

$$\varepsilon_{\text{in}}\mathbf{E}_{\text{in}} \cdot \mathbf{n} = \varepsilon_{\text{out}}\mathbf{E}_{\text{out}} \cdot \mathbf{n}$$



- can be fulfilled by interface charge density

$$\sigma = \frac{1}{2\pi}\varepsilon_{\text{out}}\frac{\varepsilon_{\text{in}} - \varepsilon_{\text{out}}}{\varepsilon_{\text{in}} + \varepsilon_{\text{out}}}\mathbf{E}(\sigma)$$

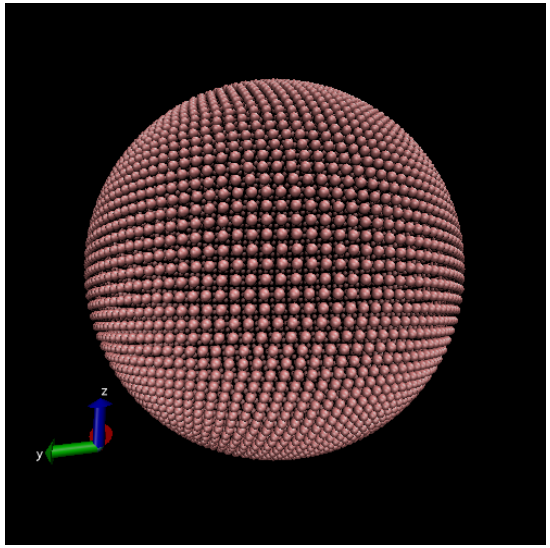
- represent σ as charges q_k at fixed positions at interface
- solve for q_k iteratively, $\mathbf{E}$ from standard Coulomb solver

$$q_k^{l+1} = (1-\omega)\, q_k^l + \omega A_k \frac{\varepsilon_{\text{in}} - \varepsilon_{\text{out}}}{\varepsilon_{\text{in}} + \varepsilon_{\text{out}}}\mathbf{n}_k \cdot \mathbf{E}\left([q_j^l]\right)$$

ICC* in ESPResSo (S. Kesselheim)

- set up the meshed interfaces

```
dielectric sphere center <x y z> \
    radius <r> res <a> eps <ε_in>
```



- *a* is mesh size of the generated mesh
- alternatively wall, pore, cylinder
- creates Tcl variables with properties of the surface points:
  - `n_induced_charges`
  - `icc_epsilons`: list of dielectric constants, can vary per surface point
  - `icc_normals`: list of normal vectors
  - `icc_areas`: list of surface areas
  - `sigmas`: optional list of additional surface charge densities
- surfaces charges are calculated by

```
iccp3m $n_induced_charges epsilons $icc_epsilons \
   normals $icc_normals areas $icc_areas [sigmas $icc_sigmas]
```