Long-range interactions: P^{3}M, MMMxD, ELC, MEMD and ICC*

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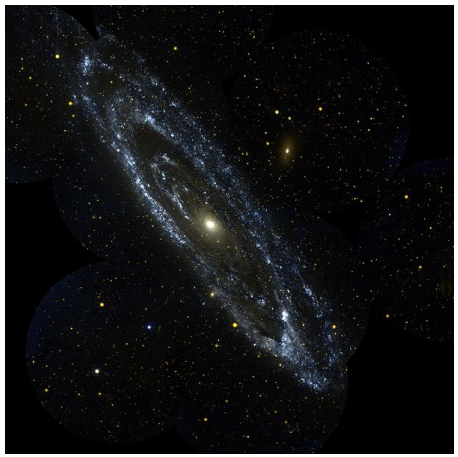
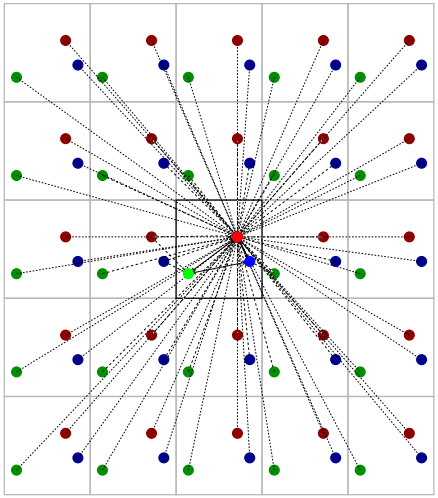
October 10, 2012

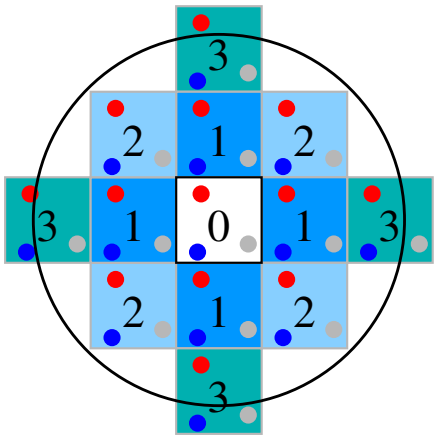
Long-range interactions



- gravity
- **Coulomb interaction**
- dipolar interaction
- hydrodynamic interaction

Electrostatics in periodic boundary conditions



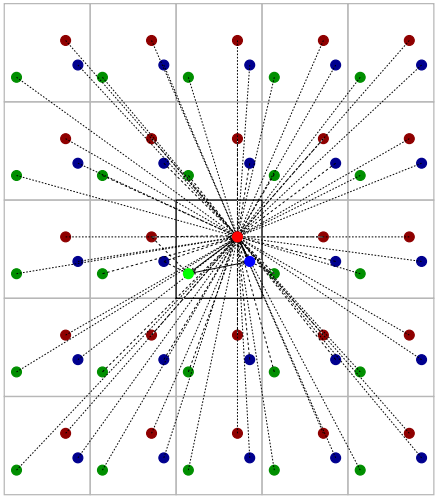


Coulomb potential

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

- Bjerrum length $l_B = \frac{e^2}{4\pi\epsilon_0 k_B T}$ measures Coulomb interaction strength against thermal fluctuations
- sum conditionally convergent — summation order important
- ... and numerical summation difficult
- spherical summation order “physical”
- spherical U *not* periodic in coordinates $\mathbf{r}_i$

Electrostatics in periodic boundary conditions



Alternatively from potential

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

- Poisson's equation:

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

  imposing periodic boundary conditions
- *intrinsic* solution
- difference to spherical sum known
- intrinsic U *is* periodic in coordinates $\mathbf{r}_i$

Electrostatics in ESPResSo

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

```
inter coulomb <l_B> <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

- assigning charges to particles

```
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

- adding a charged rod

```
constraint rod center <c_x> <c_y> lambda <λ>
```

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

The Ewald method

P. P. Ewald, 1888 — 1985

Coulomb potential has 2 problems

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

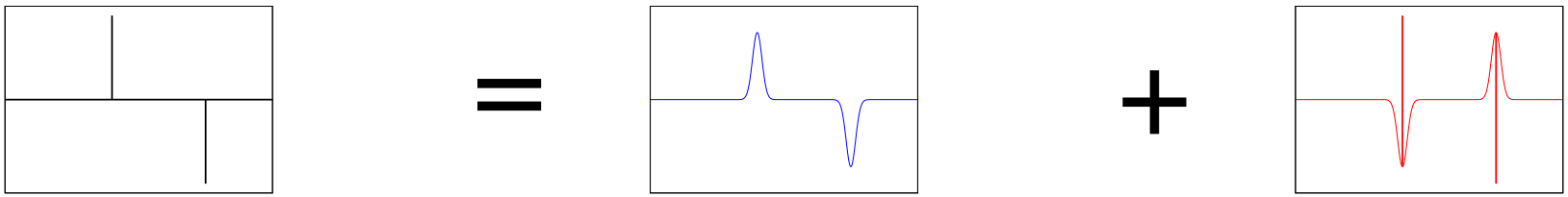
Idea: separate the two problems!

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

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

$$U^{(r)} = \frac{1}{2} \sum_{\mathbf{m}\in\mathbb{Z}^3} \sum_{i,j}{}' q_i q_j \frac{\operatorname{erfc}(\alpha|\mathbf{r}_{ij} + \mathbf{m}L|)}{|\mathbf{r}_{ij} + \mathbf{m}L|}$$

real space correction

$$U^{(k)} = \frac{1}{2L^3} \sum_{\mathbf{k}\neq\mathbf{0}} \frac{4\pi}{k^2} e^{-k^2/4\alpha^2} |\widehat{\rho}(\mathbf{k})|^2$$

Gaussians in k-space

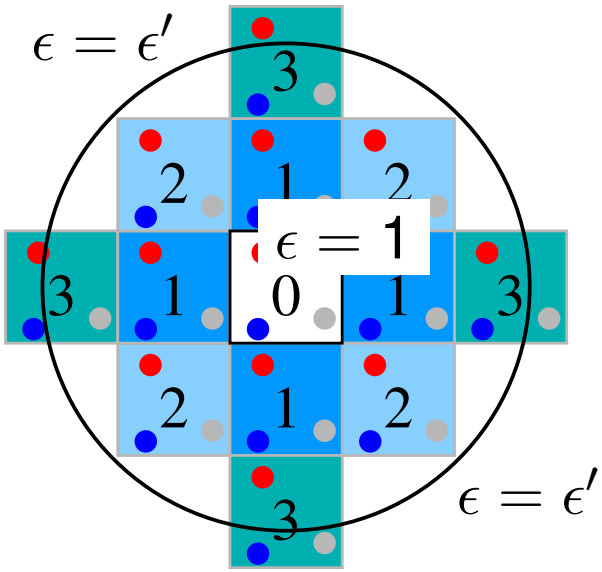
$$U^{(s)} = -\frac{\alpha}{\sqrt{\pi}} \sum_i q_i^2$$

Gaussian self interaction

forces from differentiation

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

The dipole term



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

- Ewald sum derived from Poisson's formula $\Rightarrow$ intrinsic potential
- spherical summation leads to additional term $U^{(d)}$
- polarizable material of dielectric constant ϵ' outside sphere
- $\epsilon' = 1$ corresponds to mathematical sum
- $\epsilon' = \infty$ (metallic boundary conditions) $\Leftrightarrow$ intrinsic potential

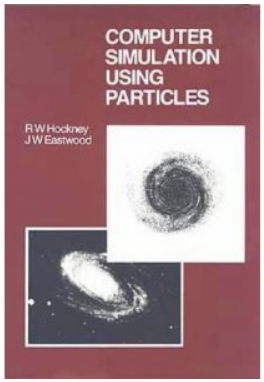
Non-neutral systems

$$U^{(d)} = \frac{2\pi}{(1+2\epsilon')L^3}\left[\sum_i q_i\left(\mathbf{r}_i - \frac{L}{2}\mathbf{e}\right)\right]^2$$

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

- Ewald can handle systems with net charge
- assuming a homogeneous, neutralizing background in $[0, L]^3$
- contributes dipole moment and constant energy
- energy constant is *important* since it depends on non-physical α

Mesh-based Ewald methods



R. W. Hockney
J. W. Eastwood

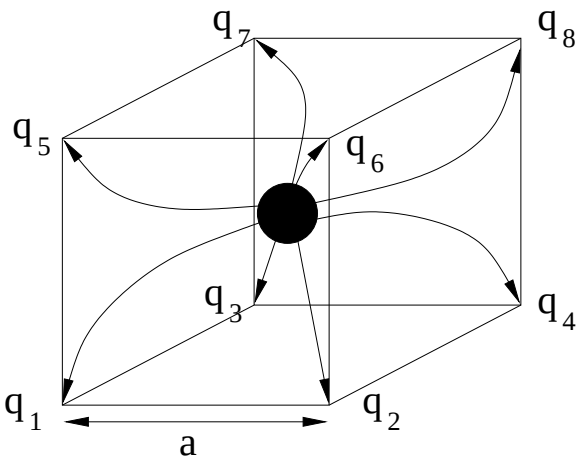
- replace k-space Fourier sum by discrete FFT
- discrete FT is exact — constant real space cutoff
- computational order $\mathcal{O}(N \log N)$
- most frequently used methods:
  - **P^{3}M**: optimal method
  - PME
  - SPME

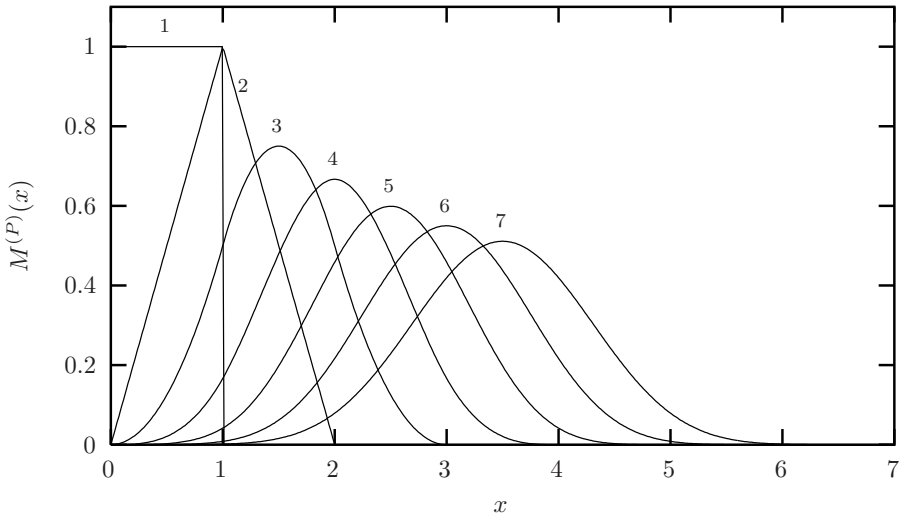
R. W. Hockney and J. W. Eastwood, *Computer Simulation Using Particles*, 1988
M. Deserno and C. Holm, JCP 109:7678, 1998

Steps of P^{3}M

1. $\{\mathbf{r}_i, q_i\} \rightarrow \rho(\mathbf{r})$: 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 $\mathbf{F}_i = q_i\mathbf{E}_i$

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

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

- aliasing of continuum force

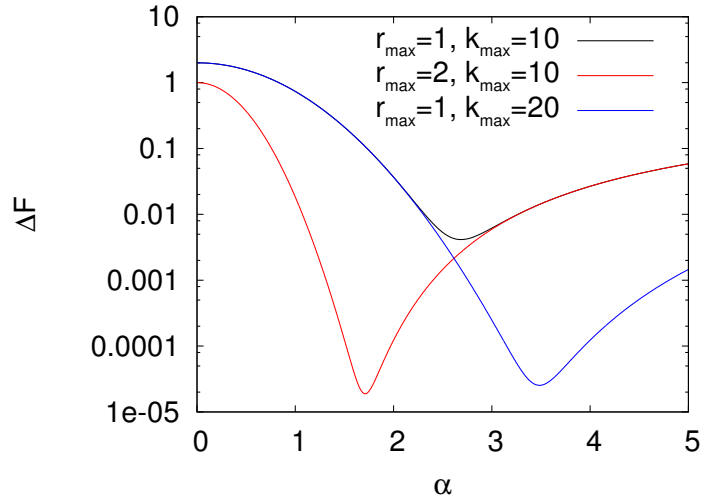
$$\widehat{\mathbf{R}}(\mathbf{k}) = -\mathrm{i}\mathbf{k}\frac{4\pi}{k^2}e^{-k^2/4\alpha^2}$$

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

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

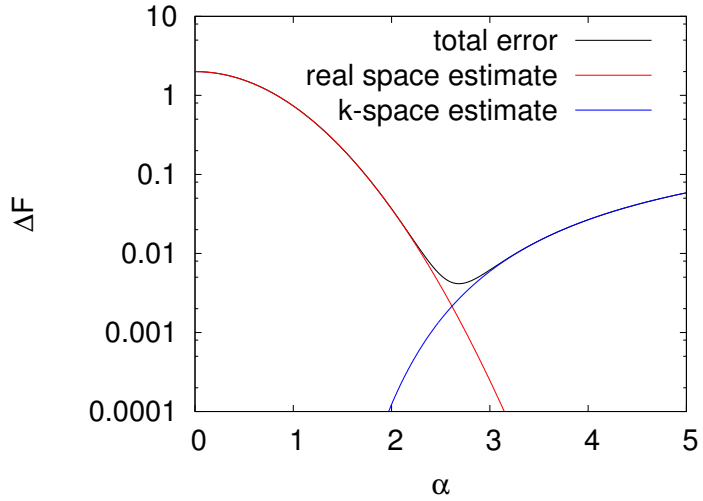
Why to control errors

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



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

How to: 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 (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>] [alpha <α>]
inter coulomb [epsilon ε_∞] [mesh_off o_x o_y o_z]
```

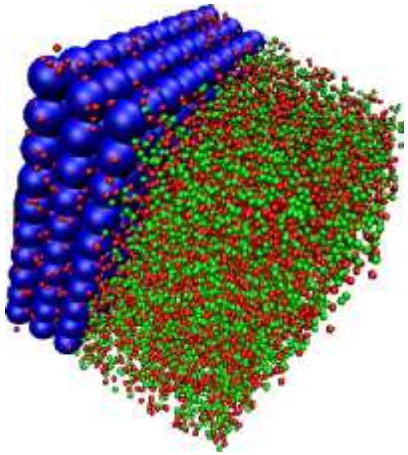
- ϵ_∞ is dielectric constant at infinity (defaults to “metallic”)
- o_x, o_y, o_z shifts the mesh origin (defaults to $(0, 0, 0)$)
- tunable parameters are (can be fixed)

α	Ewald splitting parameter (don’t fix!)
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)

- manually set parameters (dangerous!)

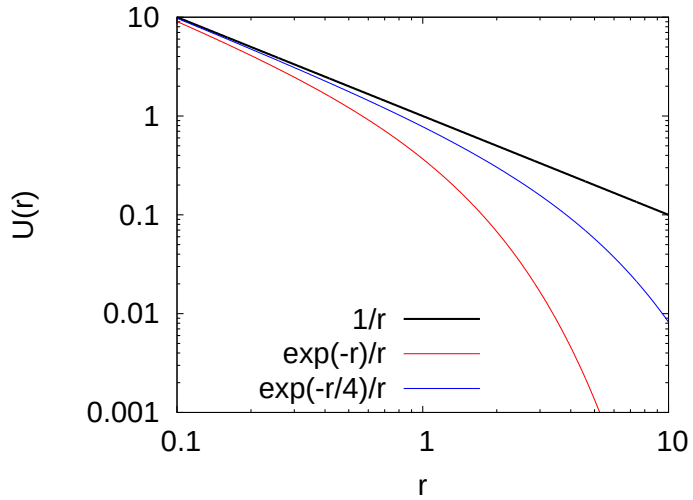
```
inter coulomb <l_B> p3m <r_max> <n_M> <p> <α>
```

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

Alternative approaches: screening



screened Coulomb potential, screening length β^{-1}:

$$U_\beta = \sum_{\mathbf{m}\in\mathbb{Z}^3} \sum_{i,j=1}^{N} q_i q_j \frac{e^{-\beta|\mathbf{r}_{ij}+\mathbf{m}L|}}{|\mathbf{r}_{ij}+\mathbf{m}L|}$$

- $U = \lim_{\beta\to 0} U_\beta$ is periodic $\Rightarrow$ intrinsic solution

Taking the limit: MMM2D far formula

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

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

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

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

- singularity cancels due to charge neutrality
- bad or no convergence for $z \approx 0$

MMM2D near formula

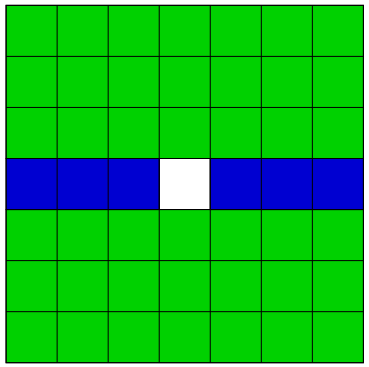
$$\phi_\beta(r) = \frac{4}{L}\sum_{l\in L\mathbb{Z}}\sum_{p\in\frac{2\pi}{L}\mathbb{N}} \mathrm{K}_0\left(p\sqrt{(y+l)^2+z^2}\right)\cos(px)$$

$$-\frac{2}{L}\sum_{n\geq 1}\frac{b_{2n}(2\pi)^{2n}}{2n(2n)!}\Re\left[\left(\frac{z+\mathrm{i}y}{L}\right)^{2n}\right]$$

$$-\frac{1}{L}\sum_{n\geq 0}\binom{-\frac{1}{2}}{n}\frac{\psi^{(2n)}(2+\frac{x}{L})+\psi^{(2n)}(2-\frac{x}{L})}{(2n)!}\left(\frac{y^2+z^2}{L^2}\right)^n$$

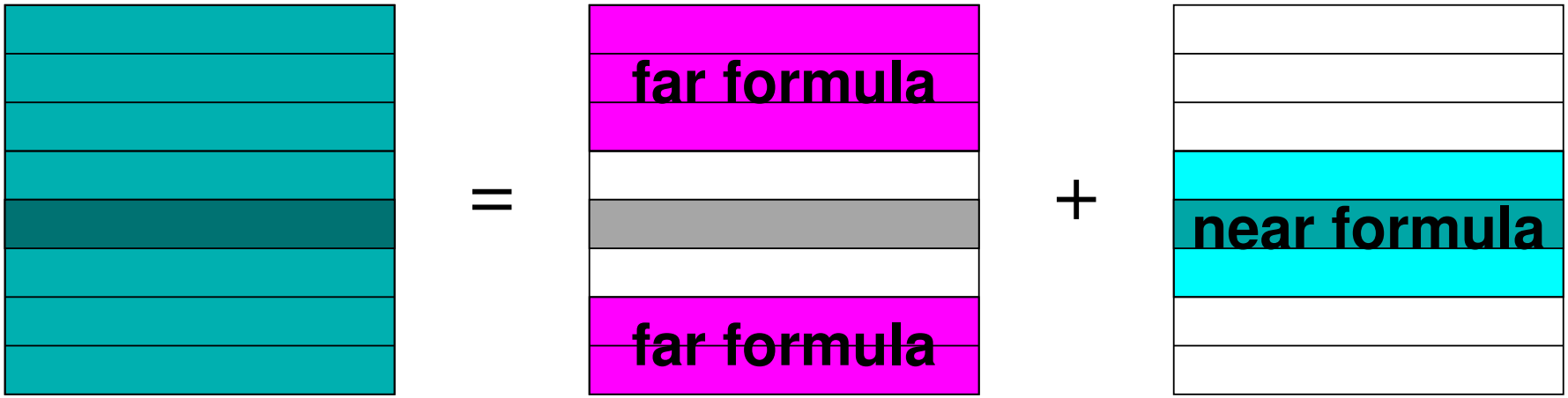
$$+\frac{1}{\sqrt{(x+L)^2+y^2+z^2}}+\frac{1}{\sqrt{(x-L)^2+y^2+z^2}}$$

$$-\frac{2}{L}\log(4\pi)-\frac{2\pi}{L^3}\beta^{-1}+'\frac{1}{|r|}+\mathcal{O}_{\beta\to 0}(\beta)$$



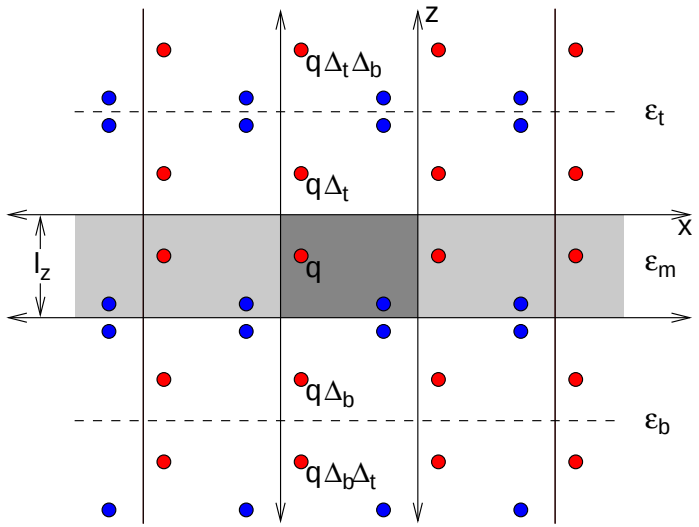
- uses most special functions math offers
- self energy: special case $r = 0$

MMM2D procedure



- split system into slices
- use near formula for adjacent slices, far for the rest
- computation time near formula $\mathcal{O}(N^2/B)$
- far formula $\mathcal{O}(NR_{\text{max}}) = \mathcal{O}(NB^2)$
- optimal $B \sim N^{-1/3}$, computation time $\mathcal{O}(N^{5/3})$

Dielectric contrasts



- thin film of water in air, water at metallic plate
- take into dielectric contrast by image charges
- image charges take form of geometric series
- handle using far formula

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>]
```

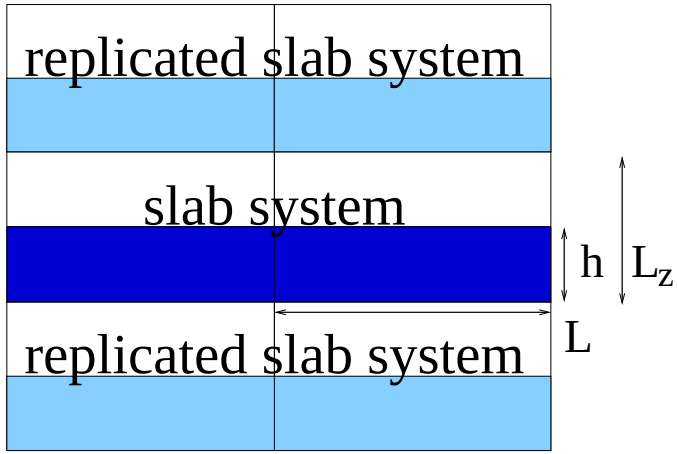
- allows to fix k_{max} (p, q)-space cutoff
  ϵ_t, ϵ_m, ϵ_b dielectric constants *or*
  Δ_t, Δ_b dielectric contrasts
- requires *layered* cell system
- number of layers per CPU $n_{\text{layers}} = B/N_p$ is tuning parameter

- 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)

- error not known *a priori* — required gap size?
- idea: calculate contribution of image layers

Layer correction term

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

- cut off $k^2 < R_{\max}$: computational effort $\mathcal{O}(NR_{\max})$
- subtract numerically the ELC term $\Rightarrow$ 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

Maxwell Equation Molecular Dynamics

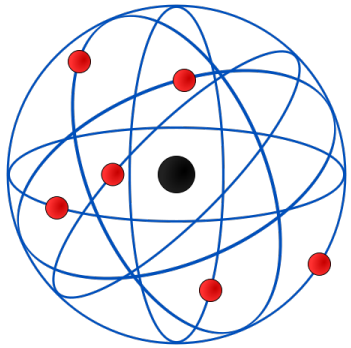
J. C. Maxwell,
1831 — 1879

A. C. Maggs
I. Pasichnyk
B. Dünweg

- Electrostatics is *quasi–static limit* of electrodynamics
- Maxwell equations are intrinsically local
- dielectric constant can vary spatially
- naturally include boundary conditions
- $\Rightarrow$ linear scaling, easy parallelization
- problem: speed of light

A. C. Maggs and V. Rosetto, PRL 88:196402, 2002
I. Pasichnyk and B. Dünweg, JPCM 16:3999, 2004

Car–Parrinello Molecular Dynamics



- Electron dynamics in the nuclear potential is quasi–static limit of coupled electron–nuclei dynamics
- problem: speed of electrons
- Car–Parrinello: heavy electrons to avoid mismatch of time scales
- statistics are still correct

A. C. Maggs: electrostatics from electrodynamics with reduced speed of light

Maxwell equations

Electrostatics

$$\nabla \cdot \mathbf{E} = \frac{1}{\epsilon_0}\rho \qquad \text{and} \qquad \nabla \times \mathbf{E} = 0, \quad \mathbf{F} = qe\,\mathbf{E}$$

is $c \to \infty$ limit of

$$\nabla \cdot \mathbf{E} = \frac{1}{\epsilon_0}\rho \qquad \nabla \times \mathbf{E} = -\frac{1}{\epsilon_0 c^2}\frac{\partial \mathbf{H}}{\partial t}$$

$$\nabla \cdot \mathbf{H} = 0 \qquad \nabla \times \mathbf{H} = \mathbf{j} + \epsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$

$$\mathbf{F} = qe\left(\mathbf{E} + \frac{1}{\epsilon_0 c^2}\mathbf{v} \times \mathbf{H}\right) \qquad \frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0$$

What if $c \ll \infty$?

Electrostatics as a constraint problem

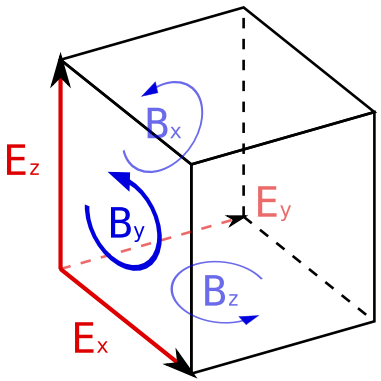
Electrostatic Gauss' law as constraint

$$\nabla \cdot \mathbf{E} = \frac{1}{\epsilon_0}\rho \quad \Rightarrow$$

$$\nabla \cdot \frac{\partial}{\partial t}\mathbf{E} = \frac{1}{\epsilon_0}\frac{\partial}{\partial t}\rho \quad \Rightarrow \quad \frac{\partial}{\partial t}\mathbf{E} + \frac{1}{\epsilon_0}\mathbf{j} - \nabla \times \dot{\mathbf{\Theta}} = 0$$

- solve as constrained dynamics with Lagrange multiplier
- $\dot{\mathbf{\Theta}}$ transversal component
- equivalent to electrodynamics with $\dot{\mathbf{\Theta}} \equiv c^2\mathbf{H}$
- but c freely choosable

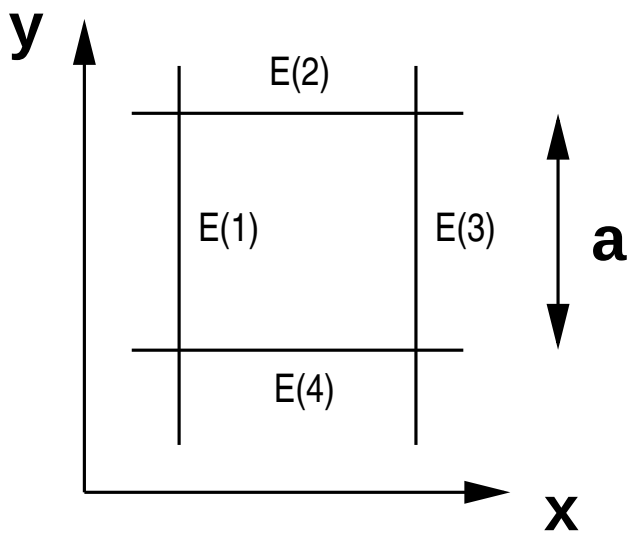
Discretization



- discretize on simple cubic lattice of spacing *a*
- charge on lattice sites
- **j**, **E** on the links
- **Θ**, **H** on plaquettes

Discrete curl

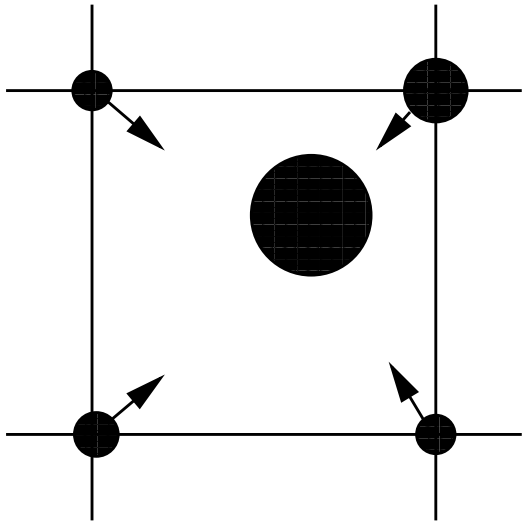
$$(\nabla \times \mathbf{E})_z = \partial_x E_y - \partial_y E_x$$
$$= \frac{1}{a}\left[(E(3) - E(1)) - (E(2) - E(4))\right]$$



MEMD procedure

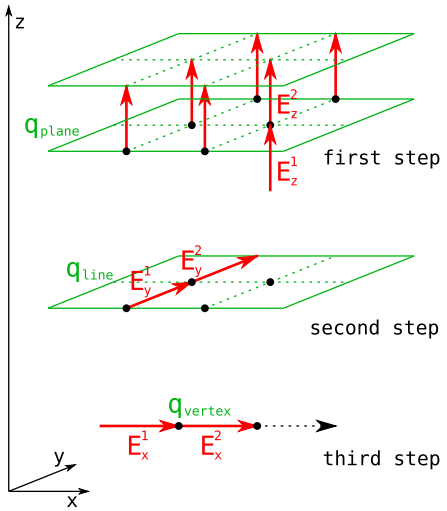
1. calculate current $\mathbf{j}$ from $\int_{\partial V} \mathbf{j}\, d\mathbf{s} = \int_V \dot{\rho}\, dV$
2. calculate $\dot{\mathbf{H}} = -\nabla \times \mathbf{E}$
3. propagate $\mathbf{H}$
4. calculate $\dot{\mathbf{\Theta}} = c^2 \mathbf{H}$
5. calculate $\dot{E} = -\frac{1}{\epsilon_0}\mathbf{j} + \nabla \times \dot{\mathbf{\Theta}}$
6. propagate $\mathbf{E}$
7. backinterpolate $\mathbf{E}$ on particles and calculate force

Self energy correction



- a charge “sees” its interpolated charge on the lattice
- drives charge to center of mesh cell
- solution: calculate lattice Green’s function and subtract

Initial electric field



- initial **E**-field required for updating
- either use P^3M & Co. for this
- ... or a (slow) global update scheme
- allows for spatial inhomogeneous dielectric constant

MEMD in ESPResSo (F. Fahrenberger)

- using MEMD

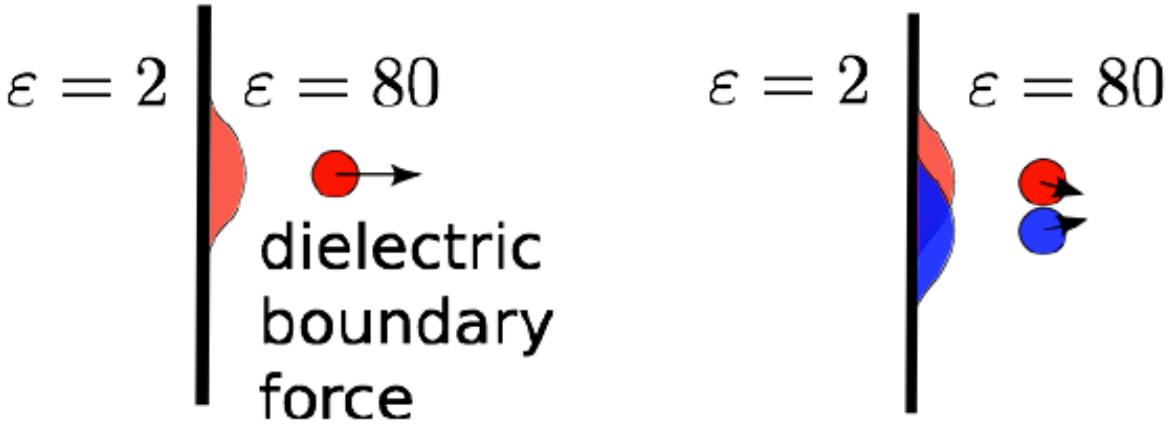
```
cellsystem domain_decomposition -no_verlet_list
inter coulomb <l_B> maggs <f_mass> <n_M> [epsilon ε_∞]
```

- requires the domain decomposition cellsystem, but with exact sorting (which implies not using Verlet lists)
- requires to set

$f_{\text{mass}} = 1/c^2$	mass of the field's degree of freedom
$n_{\mathbb{M}} = L/h$	mesh size
ϵ_∞	dielectric constant at infinity (defaults to "metallic")

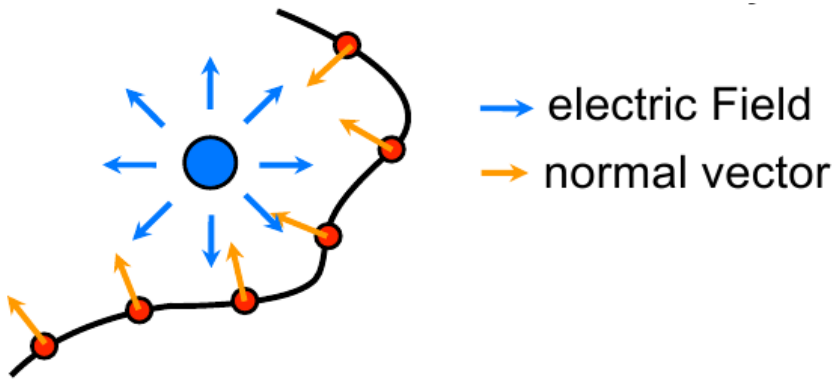
- plain MEMD has artificial dipole term that keeps the *initial* dipole moment constant
- ESPResSo corrects the dipole term similar to P^{3}M

Arbitrary dielectric contrasts



- MMM2D/ELC only handle planar parallel dielectric interfaces
- what about a nanopore? vesicle?
- cannot be handled by image charges

ICC* algorithm



- Maxwell equation in dielectric medium
- 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

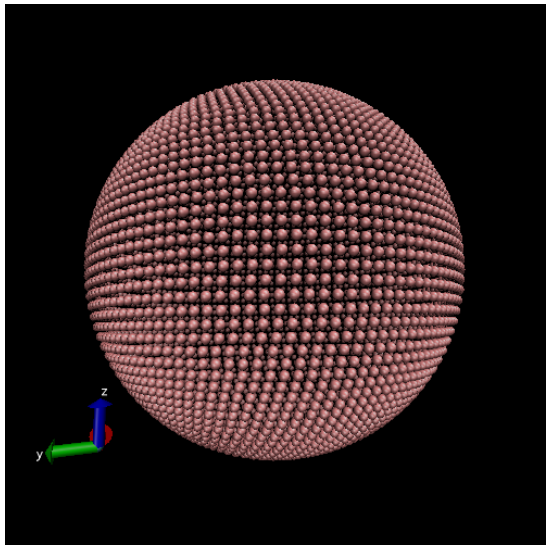
$$\sigma = \frac{1}{2\pi}\varepsilon_{\text{out}}\frac{\varepsilon_{\text{in}} - \varepsilon_{\text{out}}}{\varepsilon_{\text{in}} + \varepsilon_{\text{out}}}\mathbf{E}$$

- solve for σ iteratively, $\mathbf{E}$ from standard Coulomb solver

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]
```