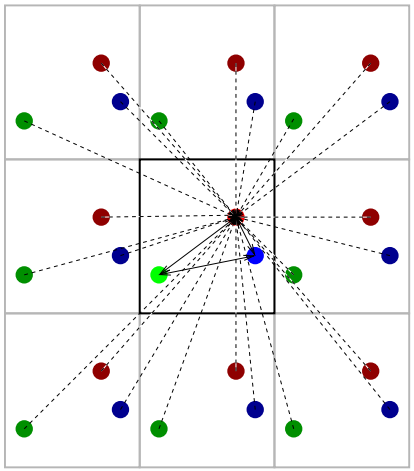
Electrostatics under periodic boundary conditions

- Periodic boundary conditions (pbc) eliminate boundary effects in bulk simulations



- Minimum image convention for short ranged potentials
- Coulomb potential $\approx 1/r$ is long ranged, many images contribute significantly
- Sum is only conditionally convergent
- For fully periodic boundary conditions (pbc) many efficient methods exist:
  Ewald ($N^{3/2}$), P^{3}M ($N \log N$), FMM (N)
- Simulation of surface effects: both periodic and nonperiodic coordinates (2d+h / 1d+2h geometries)

Conditional convergence: Why the summation order does matter

Example: The alternating harmonic series:

$$\sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k} = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \cdots = \ln 2$$

but look at this...

$$(1 - \frac{1}{2}) - \frac{1}{4} + (\frac{1}{3} - \frac{1}{6}) - \frac{1}{8} + (\frac{1}{5} - \frac{1}{10}) - \frac{1}{12} + (\frac{1}{7} - \frac{1}{14}) - \frac{1}{16} - \cdots$$

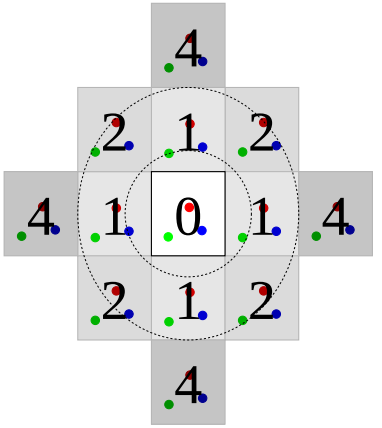
$$= \frac{1}{2} - \frac{1}{4} + \frac{1}{6} - \frac{1}{8} + \frac{1}{10} - \frac{1}{14} - \cdots$$

$$= \frac{1}{2}\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \ldots\right] = \frac{1}{2}\ln 2$$

Order of summation

- Value of the Coulomb sum depends on the order of summation
- Ewald sum corresponds to a spherical summation order
- Alternative: Slabwise summation order
  Difference to the spherical sum:

$$E_{\text{slabwise}} = E_{\text{radial}} + 2\pi M_z^2 - \frac{2\pi M^2}{3}$$



- Alternative: Screening convergence factor approach:

$$\tilde{E} = \frac{1}{2} \lim_{\beta \to 0} \sum_{i,j=1}^{N} {\sum_{\boldsymbol{n} \in \mathbb{Z}^3}}' \frac{q_i q_j e^{-\beta |\boldsymbol{r}_{ij} + \boldsymbol{n}L|}}{|\boldsymbol{r}_{ij} + \boldsymbol{n}L|}$$

Methods to sum up the Coulomb sum in 3D

periodicity	3	2	1
+MC	Ewald $(N^{3/2})$	Ewald (N^2)	Ewald (N^2)
+MC	MMM3D $(N \log N)$	MMM2D $(N^{5/3})$	MMM1D (N^2)
-	Lekner (N^2)	Lekner (N^2)	Lekner (N^2)
+MD	P^{3}M $(N \log N)$	P^{3}MLC $(N \log N)$	?
	Tree codes $(N \log N)$	possible	possible
	FMM (N)	possible	possible
+MD	Multigrid $(N \log N)$	possible	possible
+MC, ?	Maggswellian (N)	possible	possible

- Use the method most applicable to your problem
- MD or MC, N, density, desired accuracy, method familiarity
- know which parameters need to be tuned
- Check accuracy

Ewald summation in a nutshell

$E = \frac{1}{2}\sum_{i,j=1}^{N}\sum_{\boldsymbol{n}\in\mathbb{Z}^3}{}' \frac{q_i q_j}{|\boldsymbol{r}_{ij}+\boldsymbol{n}L|}$ **Trick:** $\frac{1}{r} = \frac{\mathrm{erfc}(\alpha,r))}{r} + \frac{1-\mathrm{erfc}(\alpha,r)}{r}$

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

$$\begin{aligned} E^{(r)} &= \frac{1}{2}\sum_{i,j}\sum_{\mathbf{m}\in\mathbb{Z}^3}{}' q_i q_j \frac{\mathrm{erfc}(\alpha|\boldsymbol{r}_{ij}+\mathbf{m}L|)}{|\boldsymbol{r}_{ij}+\mathbf{m}L|} \\ E^{(k)} &= \frac{1}{2}\frac{1}{L^3}\sum_{\mathbf{k}\neq 0}\frac{4\pi}{k^2}e^{-k^2/4\alpha^2}|\tilde{\rho}(\mathbf{k})|^2 \end{aligned}$$

$$E^{(s)} = -\frac{\alpha}{\sqrt{\pi}}\sum_i q_i^2, \qquad E^{(d)} = \frac{2\pi}{(1+2\epsilon')L^3}\left(\sum_i q_i \boldsymbol{r}_i\right)^2$$

$\tilde{\rho}(\mathbf{k}) = \int_{V_b} \mathrm{d}^3 r\ \rho(\boldsymbol{r}) e^{-i\,\mathbf{k}\cdot\boldsymbol{r}} = \sum_{j=1}^{N} q_j\ e^{-i\,\mathbf{k}\cdot\boldsymbol{r}_j}$ is the Fourier transformed charge density.

Suitably truncate $\mathbf{m}$ and $\mathbf{k}$ in the exponentially convergent sums

Particle-Particle-Particle-Mesh idea

Central idea: Use a **F**ast **F**ourier **T**ransformation (FFT)

$$N^{3/2} \longrightarrow N \log N$$

1. Assign charges to a mesh
   Discretization error in coordinates!

2. Solve Poisson equation on that mesh
   Aliasing problems!

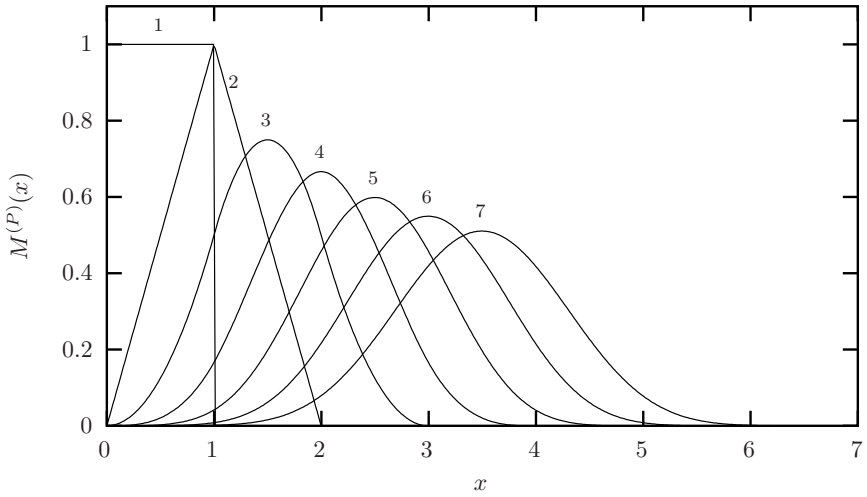
3. Calculate lattice forces from energies
   Discretization error in derivative or three extra FFTs

4. Backinterpolation of forces to particles
   Interpolation errors!

Goal: at fixed CPU work minimize total error

Charge assignment:

- Lagrange interpolation: $W_p^{(P)}(x_q) = \delta_{p,q}$
- Spline interpolation: $W^{(P)}(x) = \left(\chi_{[-\frac{1}{2},\frac{1}{2}]}\right)^{\star P}(x)$



Sketch of the first 7 cardinal-B-splines $M^{(P)}(x)$, parameterized by P. Note that the charge assignment functions $W^{(P)}(x)$ for the P^{3}M algorithm are just the "centered" B-splines

Differentiation:

- Multiplication in Fourier space by $i\mathbf{k}$.

$$\begin{aligned}\mathbf{E}(\boldsymbol{r}_p) &= -\frac{\partial}{\partial \boldsymbol{r}_p}\phi^{(k)}(\boldsymbol{r}_p) = -\frac{\partial}{\partial \boldsymbol{r}_p}\big[\rho_{\mathsf{M}} \star G\big](\boldsymbol{r}_p) \\ &= -\overleftarrow{\mathsf{FFT}}\left[i\mathbf{k} \times \hat{\rho}_{\mathsf{M}} \times \hat{G}\right](\boldsymbol{r}_p)\end{aligned}$$

- Convex sum of finite difference operators on the mesh.

$$D_j(x) := \frac{\delta(x+jh) - \delta(x-jh)}{2jh}$$

- Analytic differentiation of $W^{(P)}$.

$$\mathbf{F}_i \approx -h^3 \sum_{\boldsymbol{r}_p \in \mathbb{M}} \frac{\partial \rho_{\mathsf{M}}}{\partial \boldsymbol{r}_i}(\boldsymbol{r}_p)\big[\rho_{\mathsf{M}} \star G\big](\boldsymbol{r}_p)$$

Particle Mesh ingredients #2:(Smeared) Green function

- from continuum:

$$\frac{4\pi}{k^2}\, e^{-k^2/4\alpha^2}$$

- from Euler exponential spline interpolation:

$$\frac{4\pi}{k^2}\, e^{-k^2/4\alpha^2} \left| \frac{e^{ik_x Ph}}{\sum_{l=1}^{P-1} W^{(P)}(lh)\, e^{ik_x lh}} \cdot \overset{y}{\bullet} \cdot \overset{z}{\bullet} \right|^2$$

- from rms force error minimization:

$$\frac{\tilde{\mathbf{D}}(\mathbf{k}) \cdot \sum_{\mathbf{m}\in\mathbb{Z}^3} \tilde{U}^2(\mathbf{k}+\frac{2\pi}{h}\mathbf{m})\tilde{\mathbf{R}}(\mathbf{k}+\frac{2\pi}{h}\mathbf{m})}{|\tilde{\mathbf{D}}(\mathbf{k})|^2 \left[\sum_{\mathbf{m}\in\mathbb{Z}^3} \tilde{U}^2(\mathbf{k}+\frac{2\pi}{h}\mathbf{m})\right]^2}$$

$\tilde{\mathbf{R}}(\mathbf{k}) = -i\mathbf{k}\frac{4\pi}{k^2}\, e^{-k^2/4\alpha^2}$, $\tilde{U}(\mathbf{k}) = \tilde{W}^{(P)}(\mathbf{k})/h^3$, $\tilde{\mathbf{D}}(\mathbf{k})$: Fourier transformed differentiation operator.

Some (in)famous mesh combinations

	Charge Assignment	Green function	Differentiation
PME [2]	Lagrange	continuum	$i\mathbf{k}$
SPME [3]	Spline	Euler	analytic
P^3M [1]	Spline	error-optimized	finite difference

[1] R.W. Hockney und J. W. Eastwood, *Computer Simulation Using Particles*, IOP 1988.

[2] T. Darden, D. York und L. Pedersen, J. Chem. Phys **98**, 10089 (1993).

[3] U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee und L. Pedersen, J. Chem. Phys. **103**, 8577 (1995)

The Optimal Influence Function

Define the following measure for the error in k-space:

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

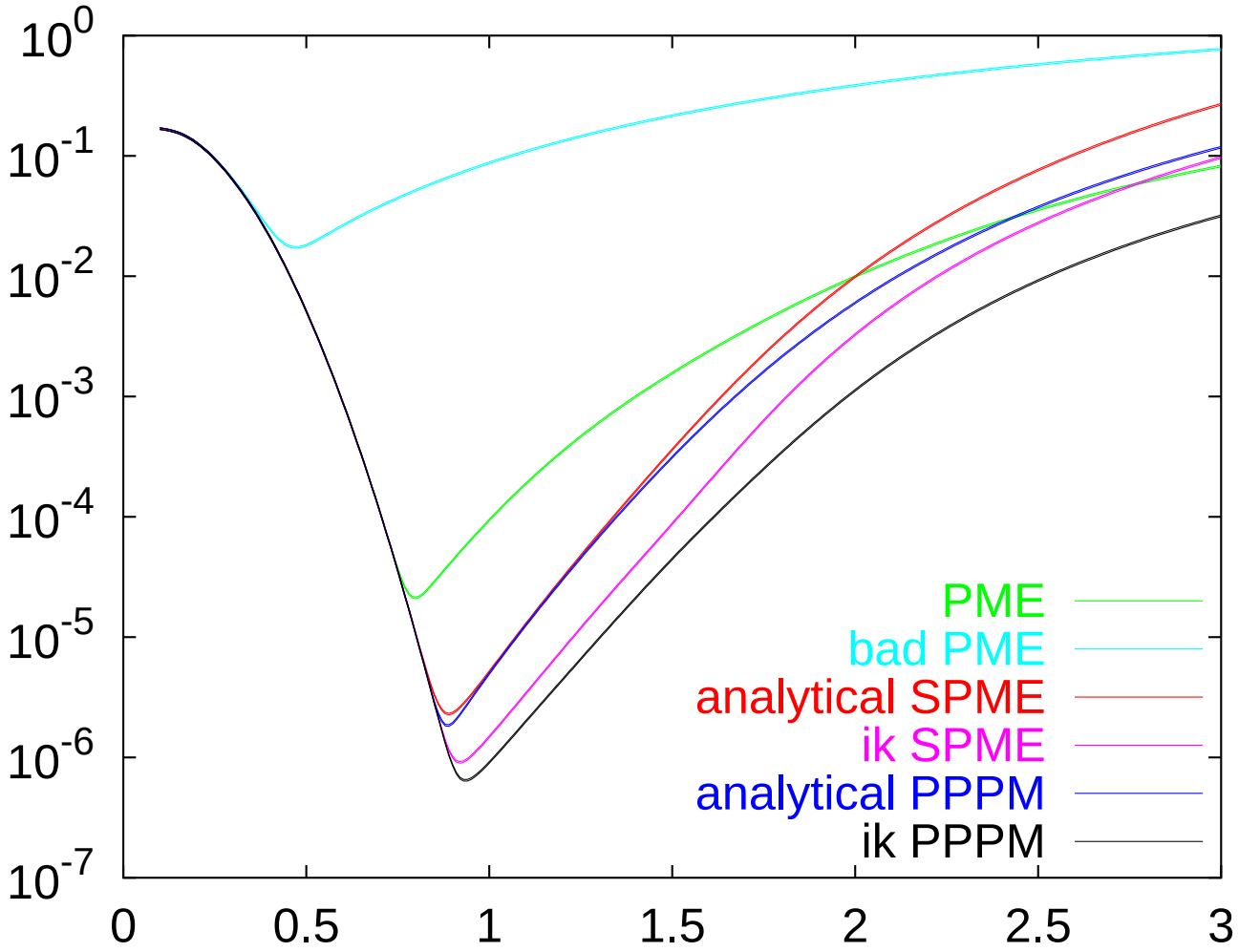
$\mathbf{F}^{(k)}(\boldsymbol{r};\boldsymbol{r}_1)$ is the force between 2 particles at $\boldsymbol{r}_1$ and $\boldsymbol{r}_1+\boldsymbol{r}$ and $\mathbf{R}^{(k)}(\boldsymbol{r})$ is the reference force that depends only on $\boldsymbol{r}$, with $\tilde{\mathbf{R}}(\mathbf{k}) = -i\mathbf{k}\frac{4\pi}{k^2}\tilde{\gamma}(\mathbf{k})$

$\left.\frac{\delta Q[\hat{G}]}{\delta \hat{G}}\right|_{\hat{G}=\hat{G}_{opt}} = 0$ yields the optimal influence function:

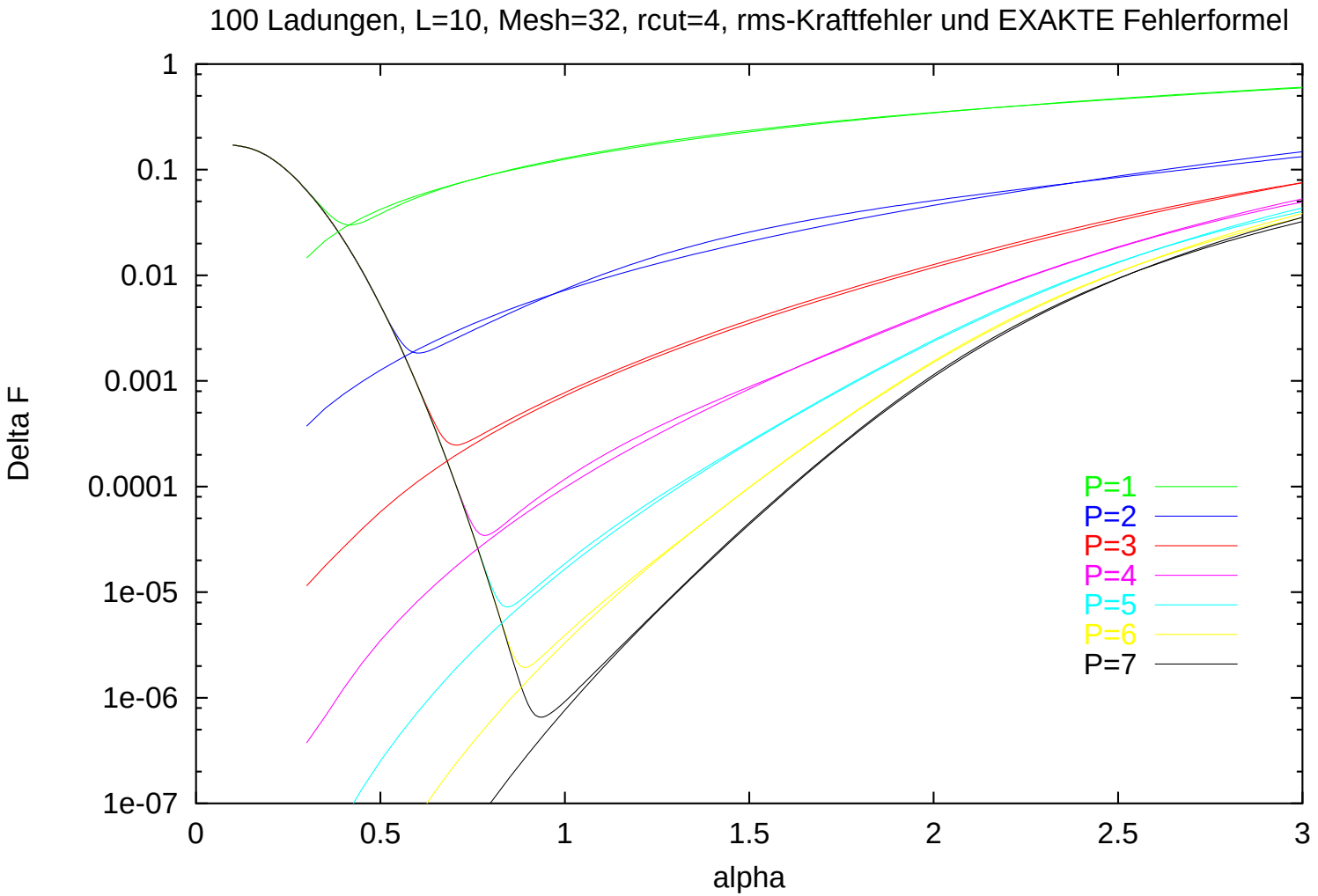
$$\hat{G}_{opt}(\mathbf{k}) = \frac{\tilde{\mathbf{D}}(\mathbf{k})\cdot\sum_{\mathbf{m}\in\mathbb{Z}^3}\tilde{U}^2(\mathbf{k}+\frac{2\pi}{h}\mathbf{m})\tilde{\mathbf{R}}(\mathbf{k}+\frac{2\pi}{h}\mathbf{m})}{|\tilde{\mathbf{D}}(\mathbf{k})|^2\left[\sum_{\mathbf{m}\in\mathbb{Z}^3}\tilde{U}^2(\mathbf{k}+\frac{2\pi}{h}\mathbf{m})\right]^2}$$

Here $\tilde{U} = \tilde{W}/h^3$ and $\tilde{\mathbf{D}}$ is the FT differential- or difference operator.

ΔF Error as function of the Ewald parameter α for several mesh methods



Error in comparison with analytical error estimate for P3M



Meshed up Conclusion

- error depends very sensitively on the correct choice of α, hence finding the optimal α is important for accuracy **and** speed
- the old P3M is the most versatile and most accurate (speedy) mesh method (optimal influence function)
- analytical error estimats exist for PME and P3M, but **not** for SPME
- this allows straightforward tuning of the algorithm and knowledge of the error **prior** to the simulation (implemented in ESPResSo)
- why do most programs still work with SPME???

Fast Multipole Method (FMM): I

key to improved scaling of the Ewald method is the product decomposition of the Fourier space sum.

In contrast, multipole methods (Greengard and Rhoklin 1987) are based on a product decomposition in real space with Legendre Polynomials:

$$\frac{1}{|x-y|} = \sum_{n=0}^{\infty} \frac{r'^n}{r^{n+1}} P_n(\cos\gamma)$$

further use of the suface harmonics of the first kind, Y_m^n

$$P_n(\cos\gamma) = \sum_{m=-n}^{n} Y_n^{-m}(\theta',\phi') Y_n^m(\theta,\phi)$$

yields

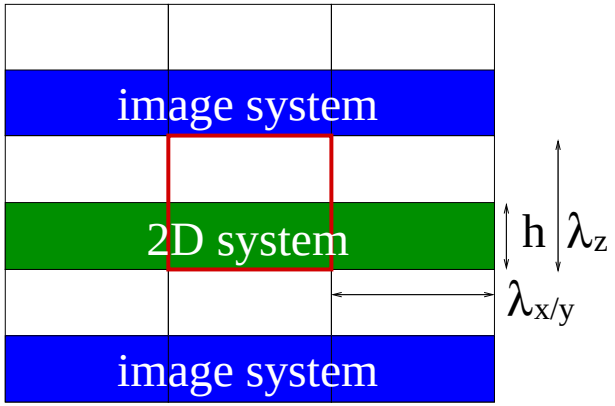
$$\frac{1}{|x-y|} = \sum_{n,m} \left(Y_n^{-m}(\theta',\phi') r'^n \right) \left(\frac{Y_n^m(\theta,\phi)}{r^{n+1}} \right)$$

Fast Multipole Method (FMM): II

- adjacent cells are summed pairwise; all nonadjacent cells use multipole expansion
- complicated bookkeeping for hierarchical breakup, shift of origins,translation and conversion operators, $\mathcal{O}(N)$ scaling
- in original version good for non-periodic geometries, extendable (even more complicated) for pbc
- Barnes-Hut method (1986) (tree-code) uses much simpler, non-hierarchical cell decomposition, $\mathcal{O}(N \log N)$
- faster than P3M for $N \approx> 100\,000$

Using 3D methods for 2D periodic systems

- Yeh und Berkowitz, 1999:
  Apply slabwise summation
  — works, but
  - no a priori error estimates exist
  - Large, asymmetric simulation box



- ELC (**E**lectrostatic **L**ayer **C**orrection):
  Analytic expression for the image contribution

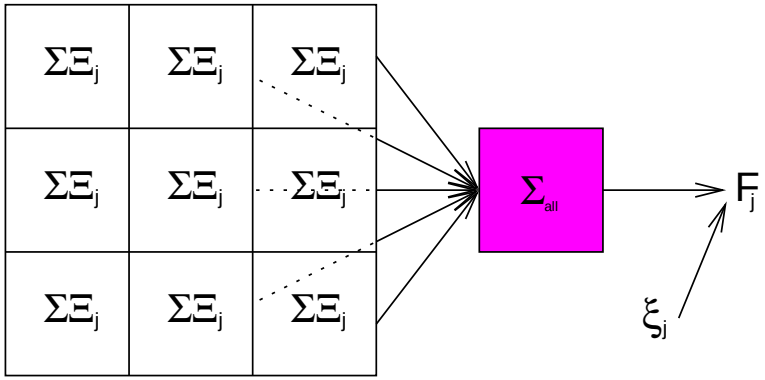
$$E_{ELC} = \frac{2}{\lambda_x \lambda_y} \sum_{i,j} q_i q_j \sum_{p,q>0} \frac{\cosh(2\pi |f_{pq}| z_{ij})}{f_{pq}(e^{2\pi |f_{pq}| \lambda_z} - 1)} e^{\imath f_{pq}^T (x_{ij}, y_{ij})}$$

  - $\mathcal{O}(N)$ evaluation similar to far formula possible
  - error estimates exist

Implementation and error distribution of ELC

- ELC force formula again has the form $\sum_{p,q} \xi_i^{(p,q)} \sum_j \Xi_j^{(p,q)}$, but this time sum over *all* j.

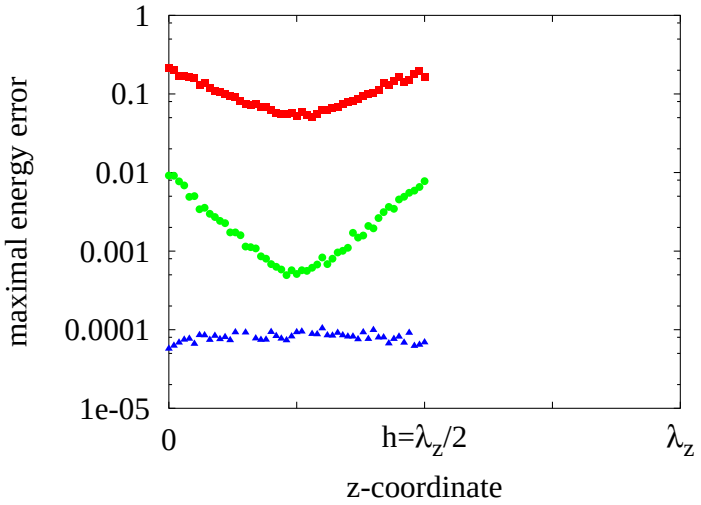
Evaluation:
Simple MPI gather all



error distribution

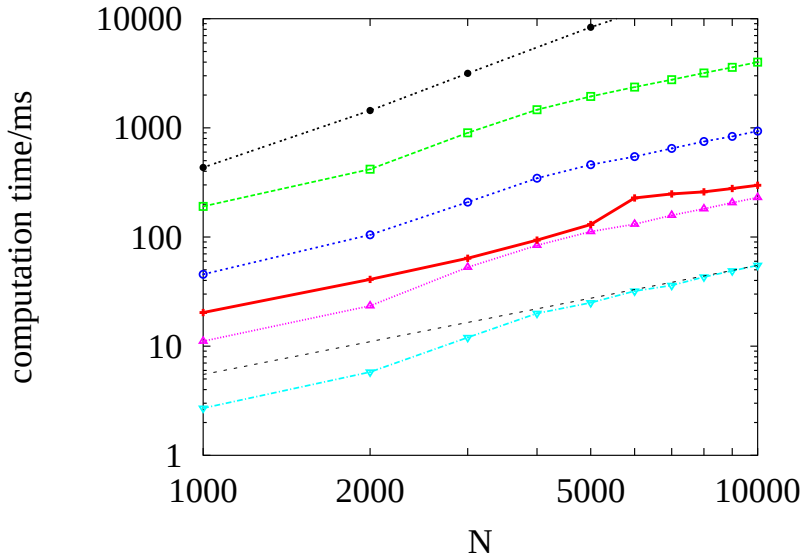
red: P^3M + Y.-B.
green: P^3M + ELC, 10^{-2}
blue: P^3M + ELC, 10^{-4}

$\longrightarrow$ Error accumulation near the surfaces!



Computation time of ELC + P^{3}M

Computation time for a cubic system using ESPResSo on AMD Athlon64 3000+



MMM2D ●
P3M only ●

ELC only 5% of box empty ● 20% empty ●
ELC only 10% of box empty ● 50% empty ●

- P^{3}M + Y.-B., 75% empty $\rightarrow T_{\text{P}^3\text{M,Y.-B.}} \approx 4T_{\text{P}^3\text{M}}$
- P^{3}M + ELC, 33% empty $\rightarrow T_{\text{P}^3\text{M,ELC}} \approx 2.1T_{\text{P}^3\text{M}}$

MEMD - Maxwell Equations Molecular Dynamics: Dünweg, Pasichnyk (basic idea due to A.C. Maggs)

- Electrostatics is the **quasi–static limit** of electrodynamics
- Car–Parrinello: Go back to the coupled dynamics, **but** use heavy electrons to avoid mismatch of time scales, obey constraints on average
- **Here:** Charges + fields coupled via Maxwell equations and Lorentz force, **but** with strongly reduced speed of light
- $\longrightarrow$ **Intrinsically local**
- $\longrightarrow$ **Linear scaling, easy parallelization**

Reformulation of Electrostatics

$\vec{\nabla} \cdot \vec{E} = \frac{1}{\epsilon_0}\rho$	&	$\vec{\nabla} \times \vec{E} = 0$
	$\Leftrightarrow$	
$\vec{\nabla} \cdot \vec{E} = \frac{1}{\epsilon_0}\rho$	&	$\mathcal{H}_{EF} = \frac{\epsilon_0}{2} \int d^3\vec{r}\, \vec{E}^2 = \text{Min.}$

- Longitudinal component determined by charge density
- Transversal component minimized away
- Constraint surface, Born–Oppenheimer surface

Statistical Physics in Equilibrium

Arbitrary c admitted!

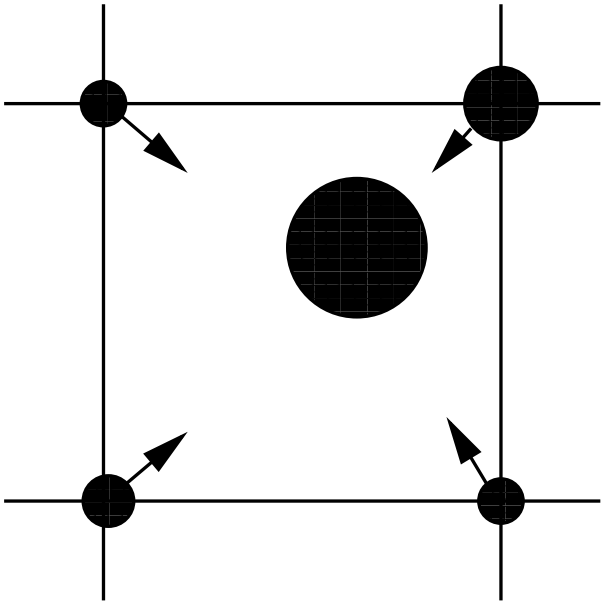
$$\begin{aligned}\mathcal{H} &= \frac{\epsilon_0}{2}\int d^3\vec{r}\,\vec{E}^2 = \frac{\epsilon_0}{2}\int d^3\vec{k}\,\left|\tilde{\vec{E}}\right|^2 \\ &= \frac{\epsilon_0}{2}\int d^3\vec{k}\,\left|\tilde{E}_{\parallel}\right|^2 + \frac{\epsilon_0}{2}\int d^3\vec{k}\,\left|\tilde{E}_{\perp}\right|^2 = \mathcal{H}_{\parallel} + \mathcal{H}_{\perp}\end{aligned}$$

$$\exp(-\beta\mathcal{H}) = \exp(-\beta\mathcal{H}_{\parallel})\exp(-\beta\mathcal{H}_{\perp})$$

$\mathcal{H}_{\parallel} \equiv$ conventional Coulomb interaction

Discretization and Self–Energy

ρ: sites
$\vec{E}$: links
$\vec{H}$: plaquettes



Interpolated charges on the sites drive the particle into the center

$\longrightarrow$ Exact subtraction via lattice Green's function or Yukawa coupling

MEMD has basically 3 tuning parameter (grid spacing,Yukawa coupling, speed of light) – algorithm 1 - 2 times faster than our implemented P3M Advantage: suited ideally for MC, local changing dielectric constant should be easily implementable . . .

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