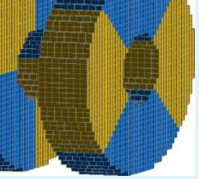
Constrained electrodynamics- numerics and interactions

A.C. Maggs, Samuela Pasquali

CNRS and ESPCI, Paris



Summary

Algorithms

Faster/simpler codes for electrostatics

Thermodynamics of Electric fields

Partition function of electric field

Fluctuations and interactions

Classical fluctuations in dielectrics- numerical methods

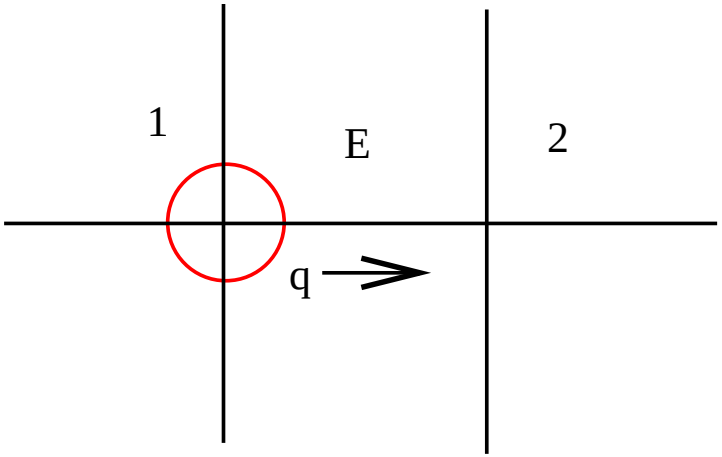
Quantum formulation

non-retarded
retarded

Local Algorithm

Vincent Rossetto (Grenoble), Joerg Rottler (UBC)

- The charges q live on the vertices
- E_{ij} field on the links of a cubic lattice.



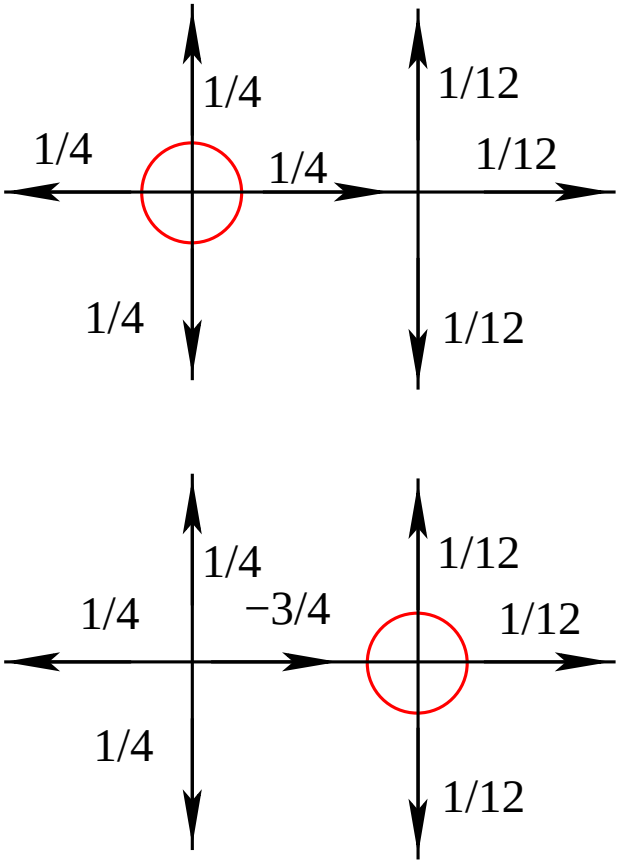
- When a particle, moves from 1 to 2 then $E_{12} \rightarrow E_{12} - q$
- Metropolis rule

$$U = \frac{1}{2} \sum_{<ij>} E_{ij}^2$$

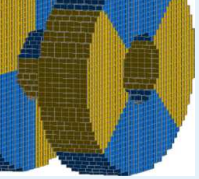
Never calculate the potential

Constrained Monte-Carlo: Particle Motion

Flux interpretation of Gauss' law $\int \mathbf{E} \cdot d\mathbf{S} = q$



Gauss constraint is satisfied dynamically (conserved)



Constrained Minimization of Energy

$$U = \frac{\epsilon_0}{2} \int \mathbf{E}^2 \, \mathrm{d}^3\mathbf{r}$$

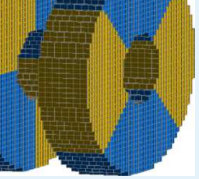
with $\mathrm{div}\, \mathbf{E} = \rho/\epsilon_0$

Lagrange multiplier to minimize:

$$\mathcal{A} = \int \frac{\epsilon_0}{2}\mathbf{E}^2 - \phi(\epsilon_0 \mathrm{div}\, \mathbf{E} - \rho) \, \mathrm{d}^3\mathbf{r}$$

leading to

$$\delta\mathbf{E}: \quad \mathbf{E} = -\nabla\phi_p$$
$$\nabla^2\phi_p = -\rho/\epsilon_0$$



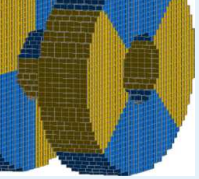
Constrained Statistical Mechanics

Define:

$$Z(\mathbf{r}) = \int \delta(\mathrm{div}\ \mathbf{E} - \rho/\epsilon_0)\ \mathcal{D}\mathbf{E}\ \exp\left(-\beta\frac{\epsilon_0}{2}\int \mathbf{E}^2\ \mathrm{d}^3\mathbf{r}\right)$$

Gaussian, but constrained, sample with two MC moves.

Lattice Boltzmann hydrodynamics
Dirac quantization in field theory



Inhomogeneous Media

The basic trick generalizes using the electric displacement

$$\begin{aligned} \operatorname{div} \mathbf{D} &= \rho \\ U &= \int \frac{\mathbf{D}^2}{2\epsilon(\mathbf{r})}\, \mathrm{d}^3\mathbf{r} \end{aligned}$$

Minimize:- generalized Poisson equation is

$$\operatorname{div}\left(\epsilon(\mathbf{r})\nabla\phi\right) = -\rho$$

Statistical mechanics when $\rho = 0$

$$Z_{fluct} = \int \mathcal{D}\mathbf{D}\ \delta(\operatorname{div}\mathbf{D}) \exp\left(-\beta \int \frac{\mathbf{D^2}}{2\epsilon(\mathbf{r})}\, \mathrm{d}^3\mathbf{r}\right)$$

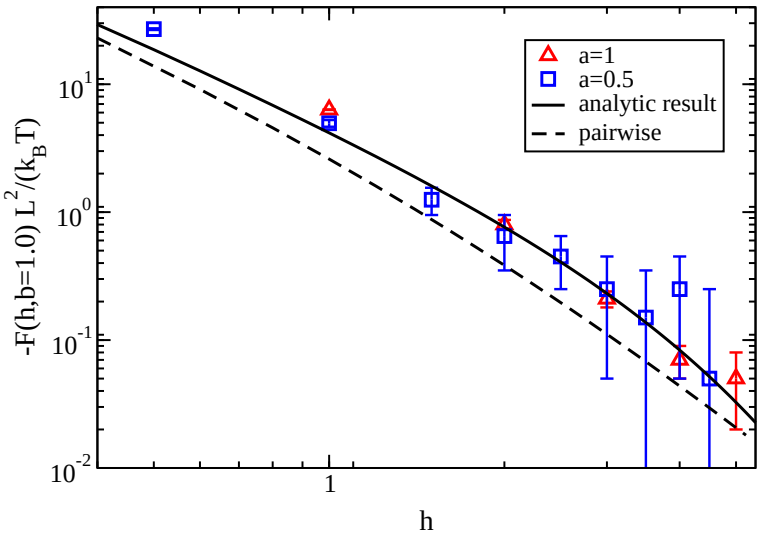
Partition function for electromagnetic field

Fluctuation potentials

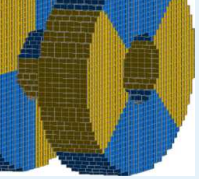
A pair of dipoles $\mathbf{p}$

$$V_{fluct} \sim -\frac{\mathbf{p}^4}{kTr^6}$$

NOT quantum: Keesom/Debye potential
Algorithm sums these potentials, classical Lifshitz
Interaction between two plates



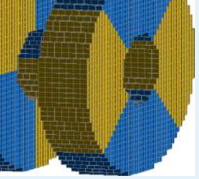
Measured with thermodynamic integration



Numerical Modeling

Typical atomistic code

- Lennard-Jones, Coulomb
- Neglect collective multibody interactions
- Neglects screening of Keesom
- Quantum chemistry usually neglects all long range interactions

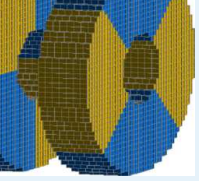


Numerical methods

Large amounts of analytic work in special geometries

- MC algorithm includes fluctuation potentials
- measuring them is difficult- statistics, asymptotics
- would like tool to evaluate interaction in general geometry
- importance of multi-body interactions
- “difficult geometries”- points, rough surfaces where perturbation theory might not work

Parallel work by Steven Johnson et al. MIT.



Transformation of partition function

Impose constraint using multiplier,

$$A = \frac{\mathbf{D^2}}{2\epsilon(\mathbf{r})} - i\phi(\mathrm{div}\ \mathbf{D})$$

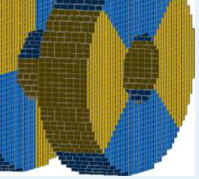
Integrate over $\mathbf{D}$, being careful with zero modes:

$$Z(\epsilon) = \int \mathcal{D}\phi\ \exp\left(-\beta \int \epsilon(\mathbf{r}) \frac{(\nabla\phi)^2}{2}\ \mathrm{d}^3\mathbf{r}\right)$$

avoiding integral over $q = 0$.

$$F \sim k_B T\ \mathrm{Tr}'\ \log\left(-\mathrm{div}\ \epsilon\,\mathrm{grad}\ \right)$$

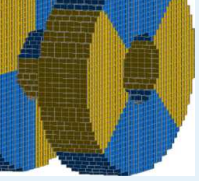
How can we study this determinant numerically?



Evaluating the determinant

Discretize- finite difference $(\text{grad } \phi) \rightarrow \phi_i - \phi_j$

- Direct methods
- Iterative methods:- Lanczos
- Factorization
- Reordering+Factorization



Failures

Direct Methods

- In 3D $V = L^3$ sites
- V^3 operations required to diagonalize
- Effort L^9
- $L = 10$ in about 1 second, $L = 20$ takes 20 minutes
- Memory requirements L^6, hit wall again at $L = 20$, ($500MB$)

Lanczos

widely used in physics
Good for a few EV, gives spurious results if one looks for all EV

Factorization

Cholesky for positive definite matrix

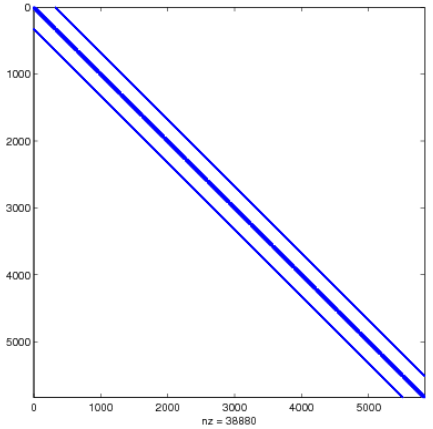
$$M = AA^T$$

A lower triangular

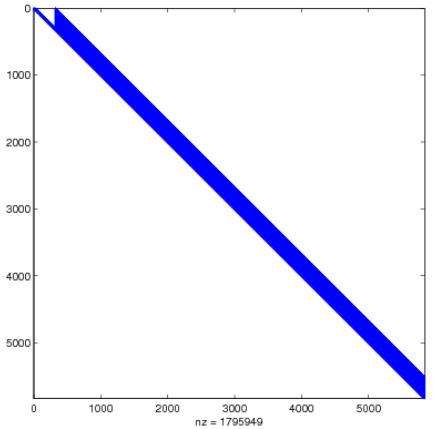
Determinant from diagonal elements of A

Remarkably A remains sparse

Laplacian, $L = 20$



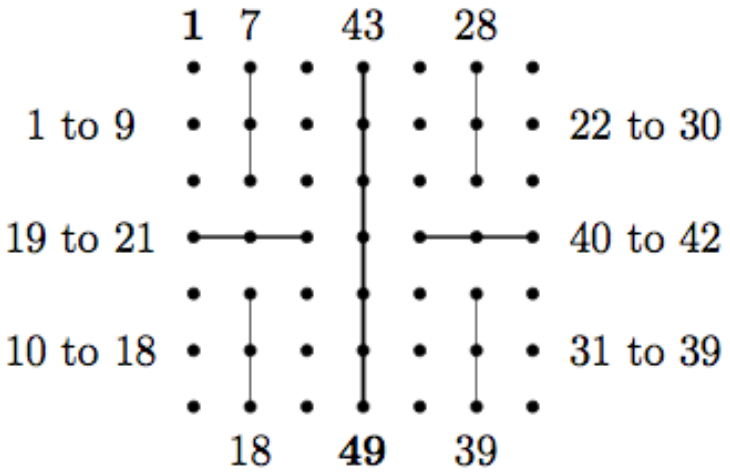
A^T



Reordering

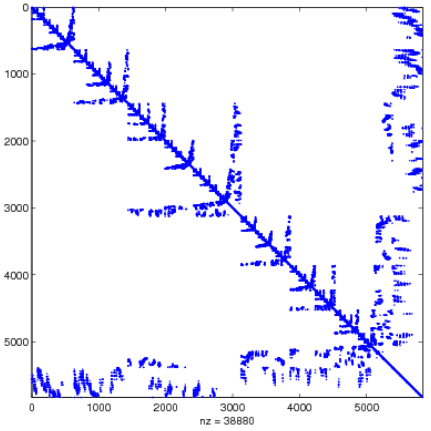
Nested dissection, (George 1973): better Cholesky factors

- $S = L^4$, $t = L^6$ in 3D
- $S = L^2 \log L$, $t = L^3$ in 2D

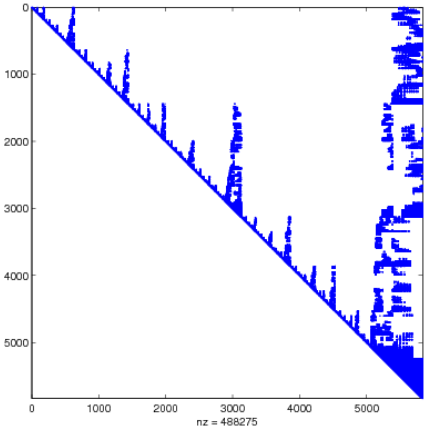


Up to $L = 120$ on a workstation in about 15 minutes. Limited by main memory.

M

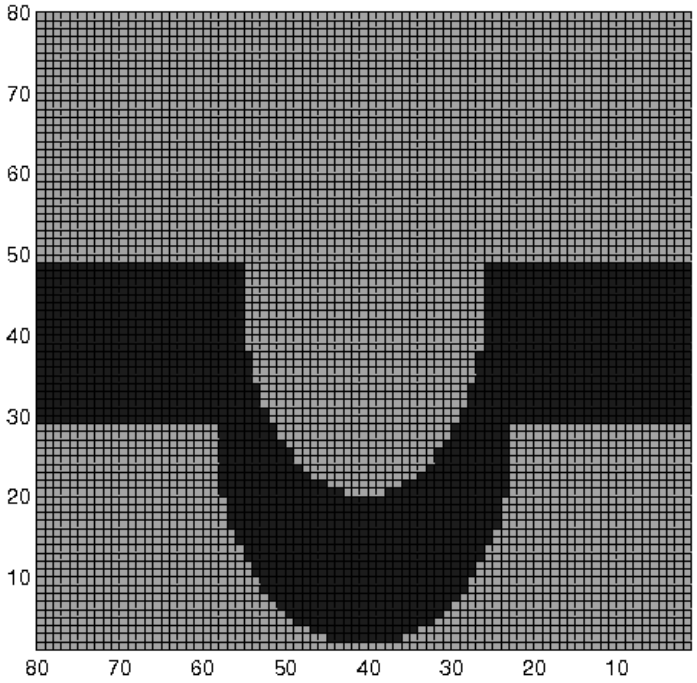


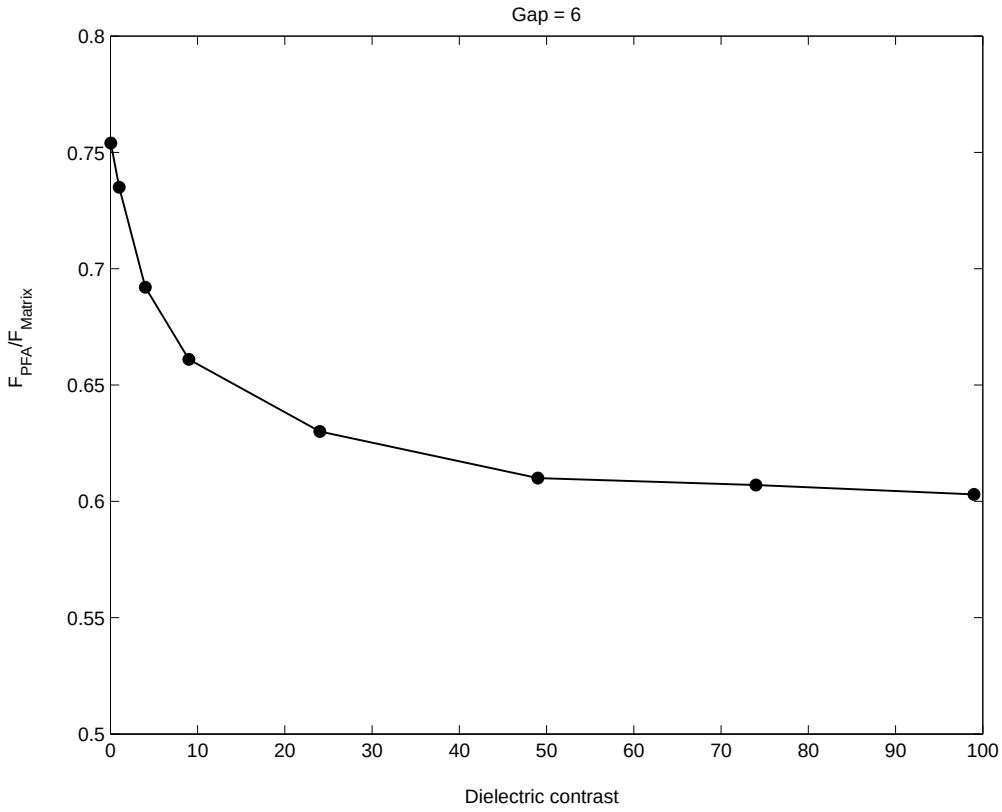
A^T



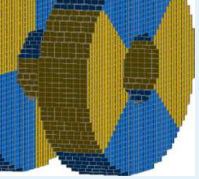
Non-Additivity of Interactions

Thermal interactions in complicated 3D geometry





Compare with proximity force approximation



Quantum, non-retarded

Start with explicit model of dipoles, path integral quantization, $0 < \tau < \beta$

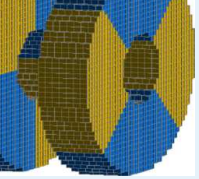
$$\mathcal{L}(i\tau) = \frac{\rho(\mathbf{r})}{2}\left(\frac{d\mathbf{P}}{d\tau}\right)^2 + U_p$$

$$U_p = \frac{(\overbrace{\mathbf{D}-\mathbf{P}}^{\mathbf{E}})^2}{2} + \frac{\mathbf{P}^2}{2\chi}$$

Again (constrained) Gaussian integrals- determinants
Find

$$Z = \prod_n Z(\epsilon(\omega_n))$$

Product over Matsubara frequencies. Need $O(50)$ frequencies for $\epsilon(0) = 5$, $\hbar\omega_0/kT = 10$. $O(15)$ frequencies for $T = 0$.
Valid up to $20nm$



Quantum retarded

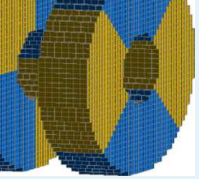
Need to evaluate larger determinants

$$\left| \frac{\omega^2 \epsilon(\mathbf{r}, i\omega)}{\hbar^2 c^2}) + \text{curl curl} \right|$$

$3V \times 3V$ matrix, rather than $V \times V$ Limited to $L < 70$. Comes from the wave equation for the vector potential

$$\left(\frac{-\omega^2 \epsilon \mathbf{A}}{c^2} + \text{curl curl } \mathbf{A} \right) = \mathbf{J}$$

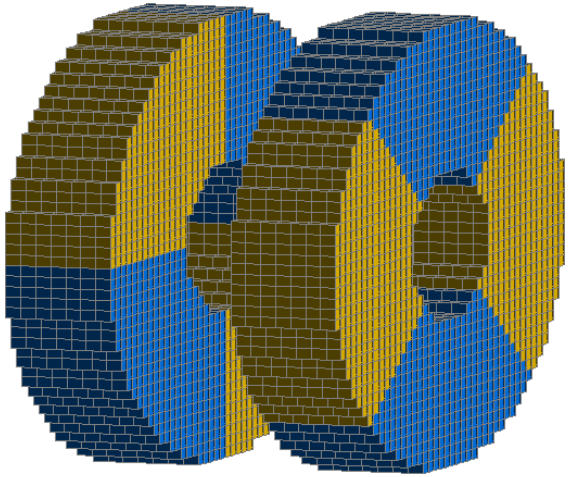
in temporal gauge.



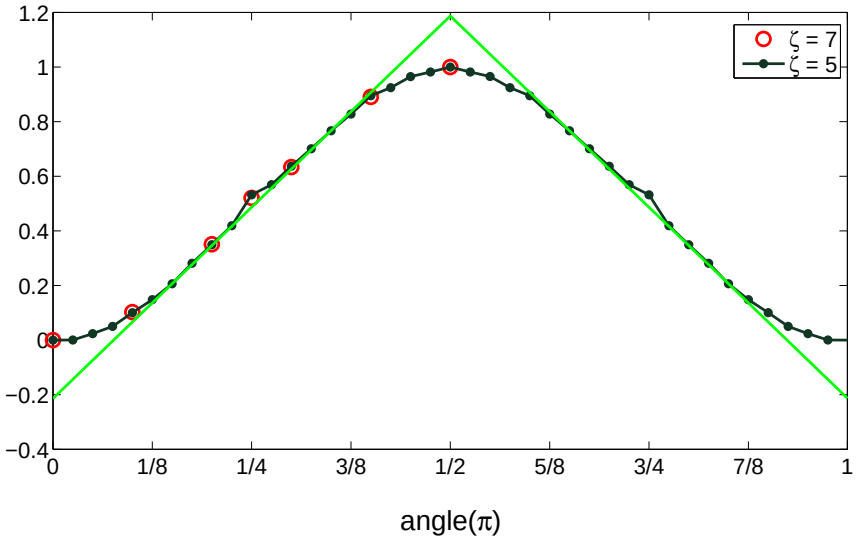
Numerical results

- Exploration of geometries
- Are discretization errors unacceptable?
- How fine a discretization can we evaluate?
- Simple spectra- not limiting
- Simulations with 1 Dell-week.

Torque measurements



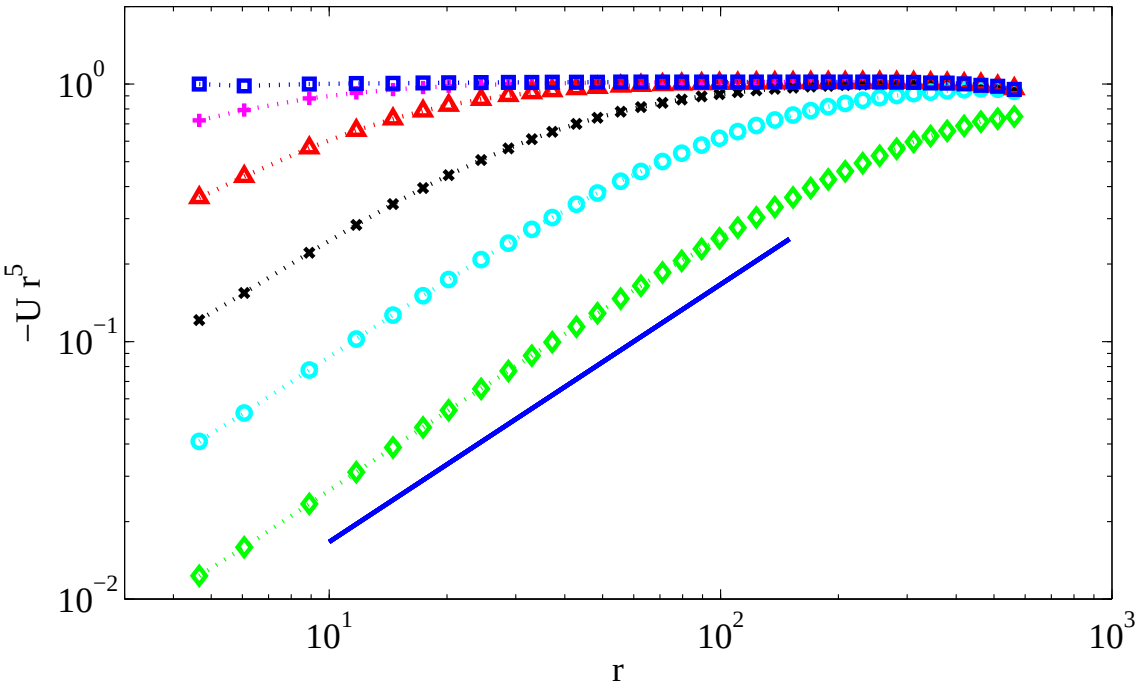
- Interaction between two disks,
- Test of self energy subtractions
- Box size $L = 63$, diameter $D = 42$
- Matrix dimensions 750000^2



Fully retarded regime with $\epsilon(\omega)$=const.

Interaction between 2 particles, 2-dimensions

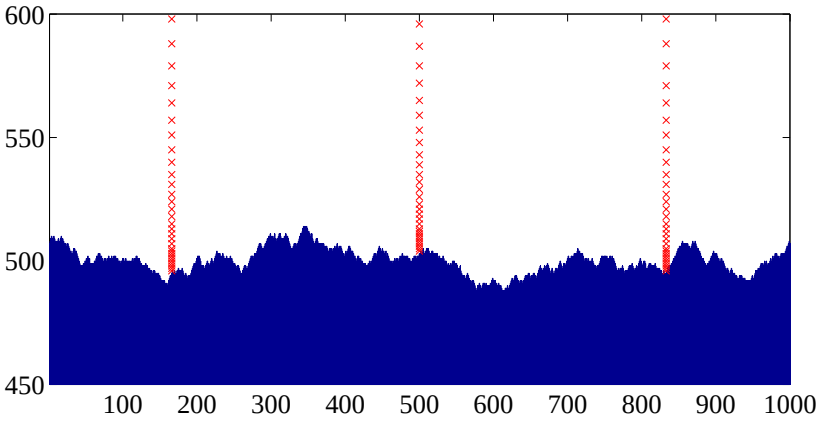
Test of frequency integration, $L = 2000$.



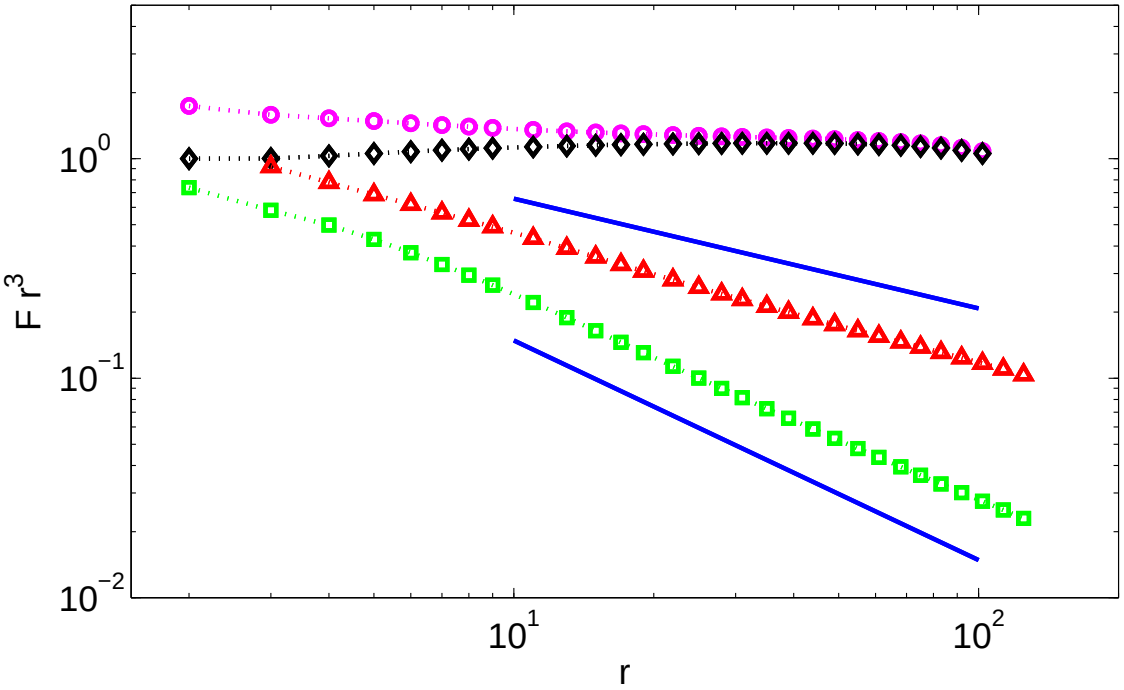
- Non-retarded $U \sim 1/r^4$ (Solid blue line)
- Retarded $U \sim 1/r^5$
- $\epsilon(i\omega) = 1 + \chi/(1 + \omega^2/\Delta^2)$
- Cross-over determined by c/Δ

Rough surface, Retarded

- $L = 1000$, random walk interface. Average over 1000 realizations
- Flat surface $U \sim 1/r^3$.



Corrections to interaction $\delta U \sim 1/r^4$.



cf. Li and Kardar (1991)

Exotic dielectric media, water $\epsilon(q)$

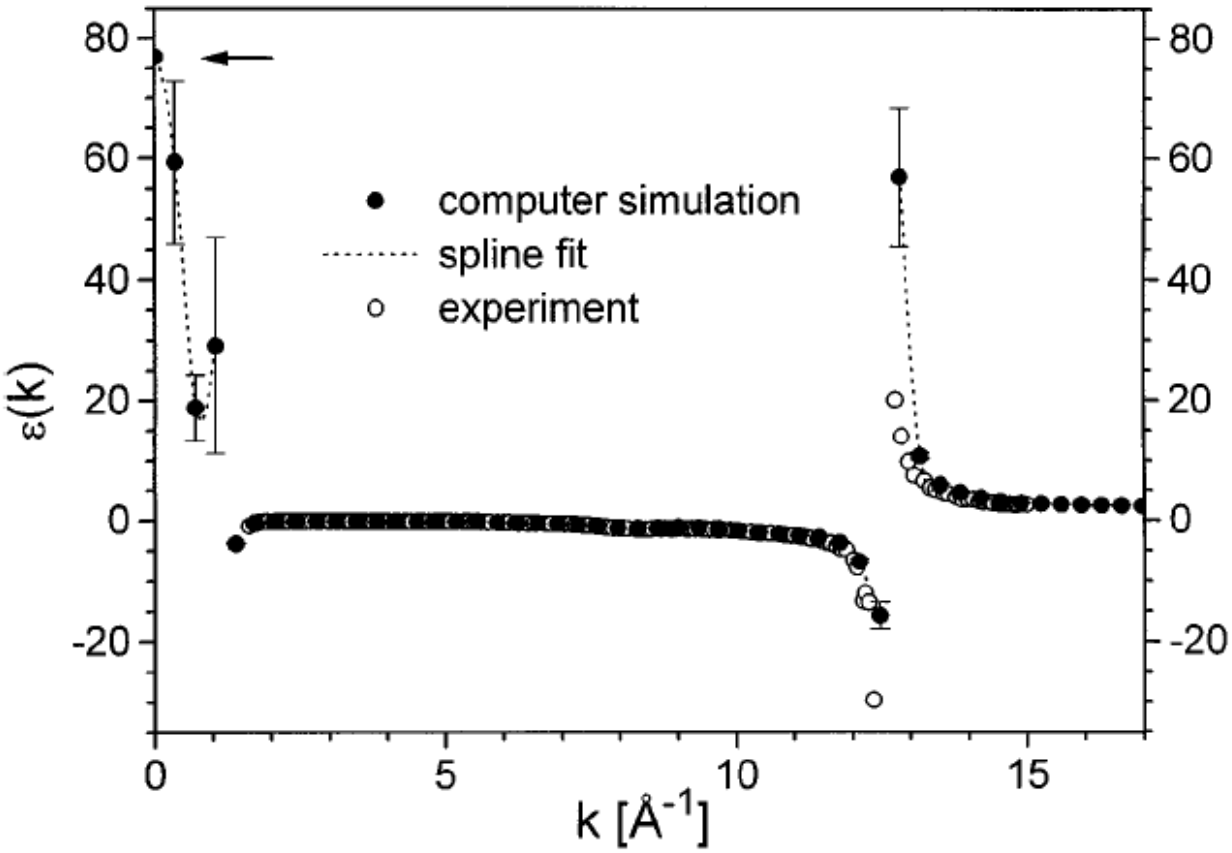
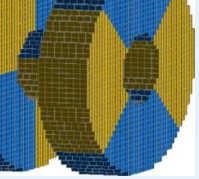


Figure 1: MD- Bopp, Kornyshev, Sutmann, 1995



Non-local dielectrics

How to produce $\epsilon(k)$

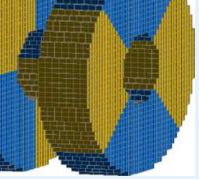
- Constraint

$$\operatorname{div} \mathbf{D} = 0$$

- Field energy, (Landau-Ginzburg) for polarization $\mathbf{P}$

$$U = \frac{(\overbrace{\mathbf{D}-\mathbf{P}}^{\mathbf{E}})^2}{2} + \frac{\mathbf{P}^2}{2\chi} + \frac{\kappa_p}{2}(\operatorname{div} \mathbf{P})^2$$

Water requires $\kappa_p < 0$ (Cf. Ice models)
“Hydrophobic” interactions in nano length scales



Conclusions

- $O(N)$ Monte-Carlo algorithm for Coulomb interactions
- Inhomogeneous $\epsilon(\mathbf{r})$
- Automatically adds in classical fluctuation interactions
- Molecular dynamics implementations also available
- Sparse matrix methods allow detailed study of complicated geometries
- 200 lines in matlab
- Can also exploit 2+1 dimensions/uniform blocks