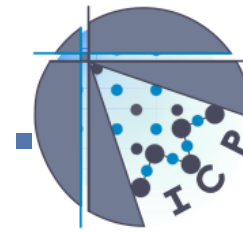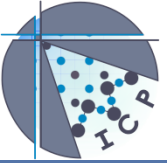**University of Stuttgart**

Germany

INSTITUTE FOR
COMPUTATIONAL
PHYSICS

Polyelectrolytes and Long Range Interactions

Christian Holm

Institut für Computerphysik, Universität Stuttgart
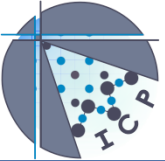Stuttgart, Germany

Outline of the 2 Talks

- **Tuesday Talk 1:**

Intro to Charged Soft Matter, Algorithms for computing long range interactions
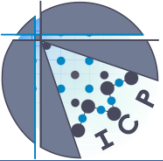
- **Wednesday Talk 2:**

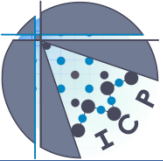Applications mainly towards the dynamics of Charged Soft Matter

Motivation Lecture 1

- Introduction to Charged Soft Matter taking Polyelectrolytes as example

- Theoretical descriptions (blobology, PB)

- Simple Test Systems and Comparisons to Mean-Field Results

- Methods for Treating Long Range Interactions under Various Conditions

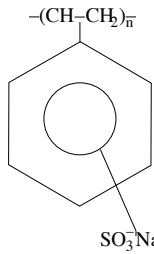# Overview Part 1: Polyelectrolytes

- charged polymers $\simeq$ Polyelectrolytes

- general considerations

- Poisson-Boltzmann (PB) and Debye-Hückel (DH) mean field theory

- counterion distributions

- condensation criteria

What are Polyelectrolytes?

Charged macromolecules which dissociate charges in solution
($\Rightarrow$ water soluble **!**)

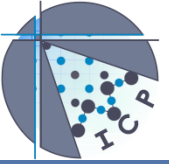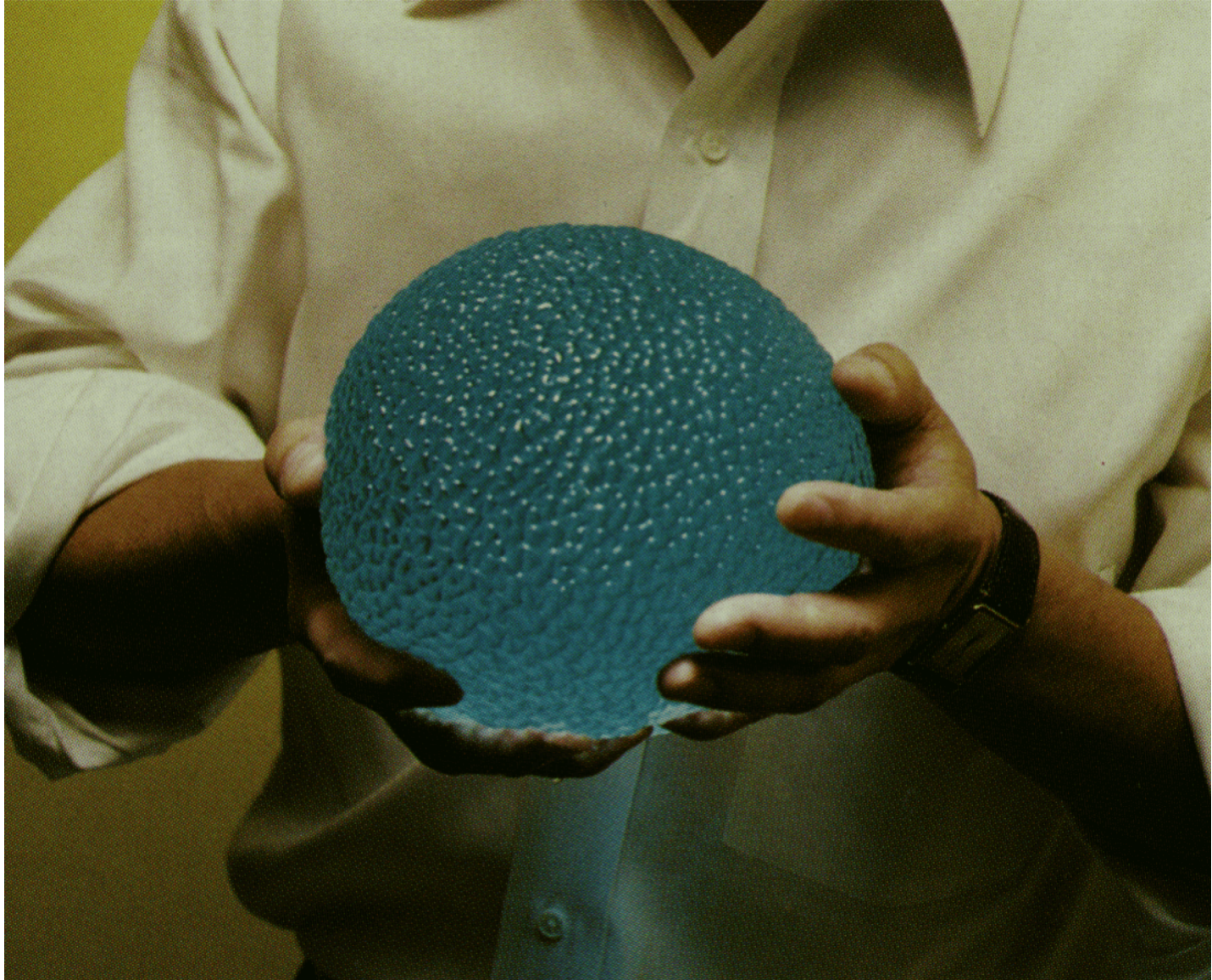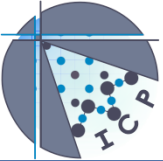| synthetic examples:	biological examples:
$-(CH-CH_2)_{\overline{n}}$ $SO_3^-Na^+$ poly-acrylic acid sulfonated polystyrene	cell membranes DNA, RNA, proteins
Applications:	Useful for:
super-absorber viscosity modifiers, additives to detergents paper industry, waste management	gene transfer mechanisms understanding biological functions, DNA packing

Large tendency to self-assemble in nanostructures !!

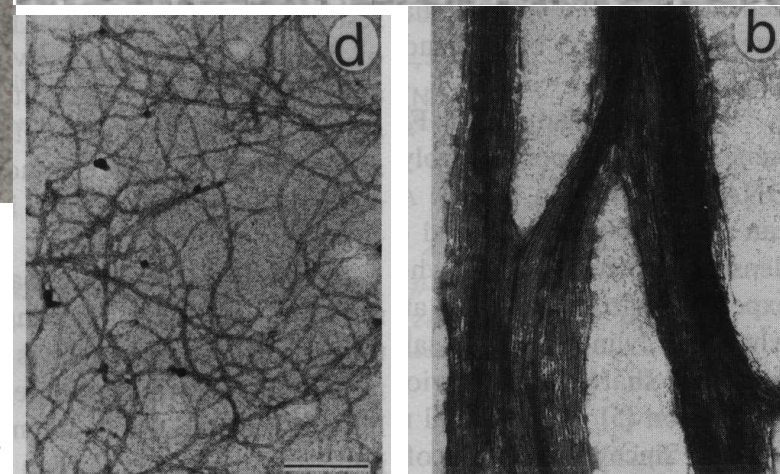# 1. Example Hydrogel

Structure formations of charged semi-flexible polymers
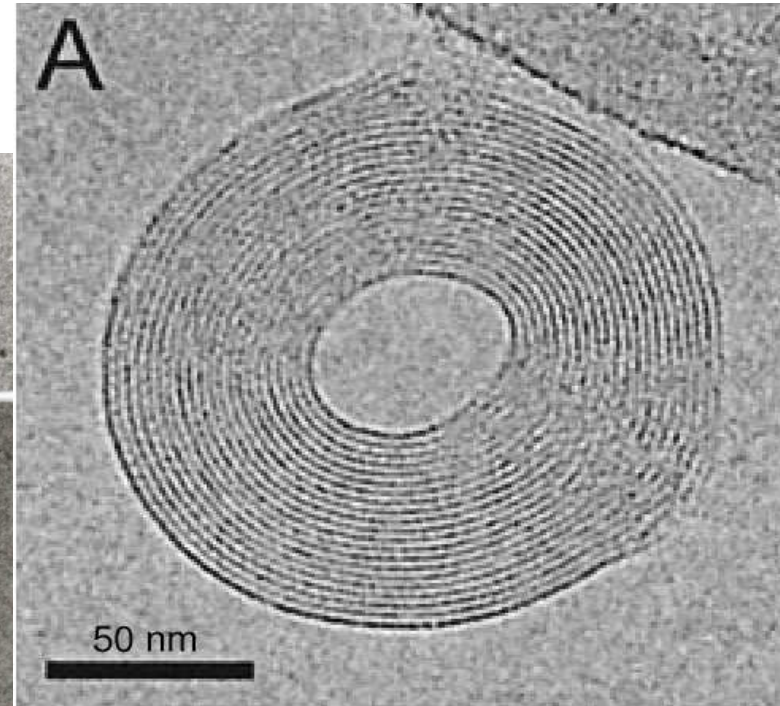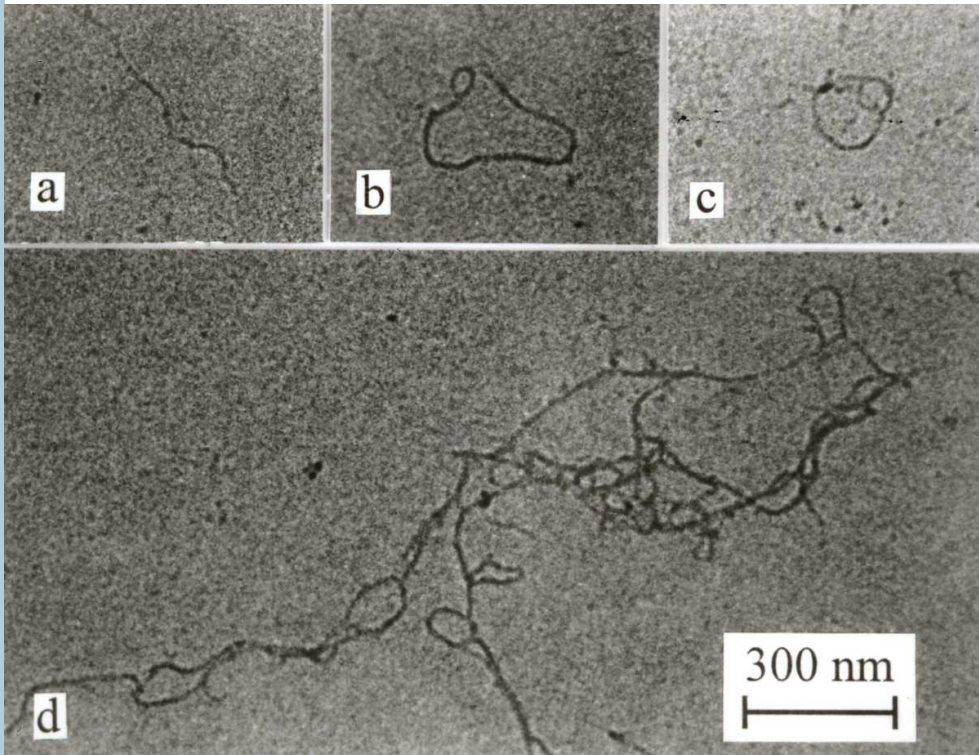
synthetic (PPPs) vs. biological semi-flexible PEs (fd, DNA)

morphologies, thermodynamics vs kinetics
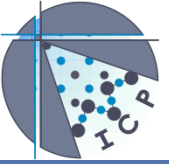
Polyelectrolyte (PE) Theory
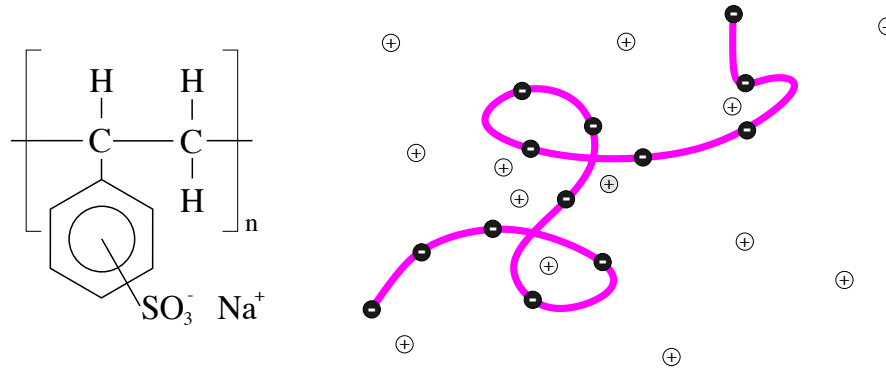
PEs possess many length scales: R_e, ξ, L_p, λ_D, ℓ_B . . .

Implicit solvent model
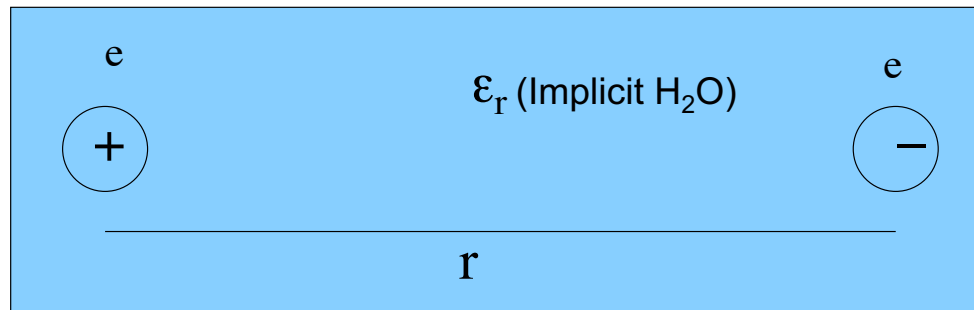
e: unit electronic charge, ϵ_r: relative dielectric permittivity. Electrostatic interaction energy: $\frac{e^2}{4\pi\epsilon_0\epsilon_r r}$.

The Bjerrum length ℓ_B is defined via $k_B T = \frac{e^2}{4\pi\epsilon_0\epsilon_r\ell_B}$

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

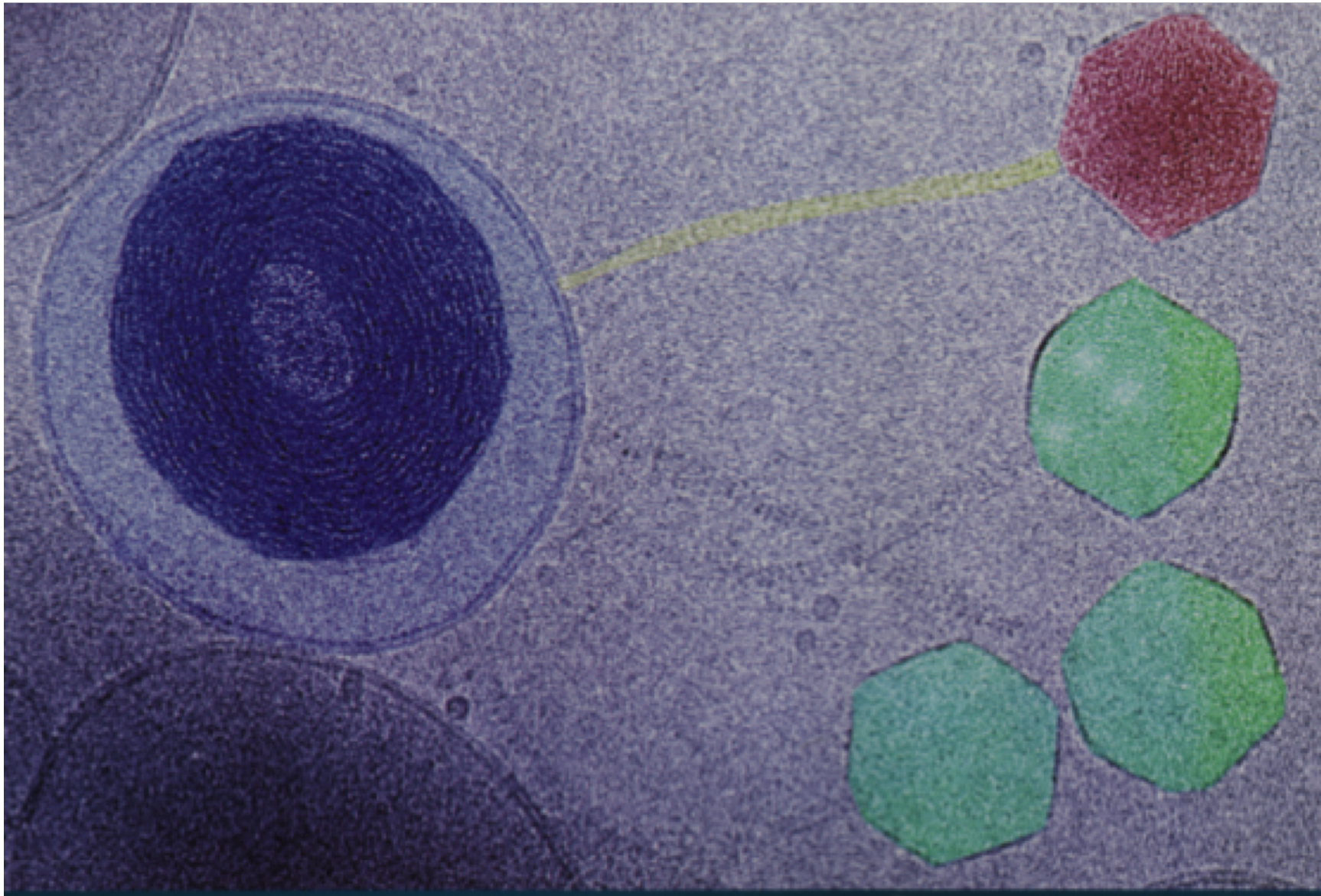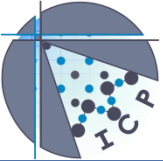For water at room temperature we find

$$\ell_B = \frac{(1.6 \cdot 10^{-19}C)^2}{4\pi \cdot 8.85 \cdot 10^{-12}\frac{C}{Vm} \cdot 78.5 \cdot 1.38 \cdot 10^{-23}\frac{J}{K} \cdot 298K} \approx 7.13\mathring{A}$$

The electrostatic interaction of two charges Q_1 and Q_2 separated by r is

$$E/k_B T = \ell_B \frac{Q_1 Q_2}{r}.$$

The electrostatic energy of a homogeneously charged (Q) sphere of radius R is

$$E/k_B T = \ell_B \frac{Q^2}{2R} \approx \ell_B \frac{Q^2}{R}.$$

Validity of Implicit Water Model

look at the NaCl (aq) pair potentials using an explicit water simulation containing 1000 SPC water molecules

B. Hess, C.H., N.vdV., PRL (2006)
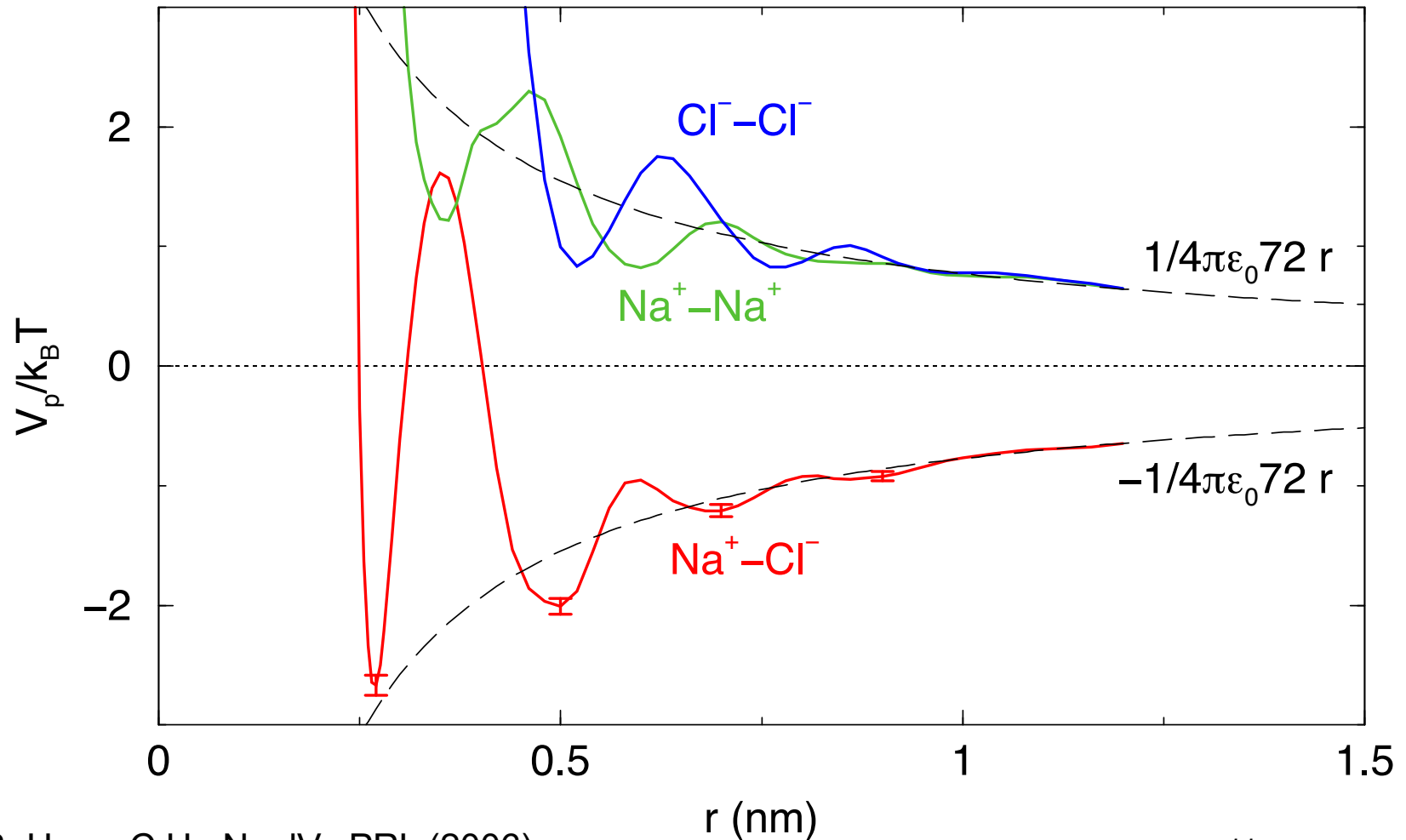
The Hamiltonian of a Gaussian chain is given by

$$H_0 = \frac{3k_B T}{2b^2} \sum_{i=1}^{N} (\vec{r}_{i+1} - \vec{r}_i)^2$$

$\implies R = b\sqrt{N}$ (RW), N monomers of size b, f: fraction of charged monomers. The Flory energy of a PE chain is

$$E_F = k_B T \left(\frac{R^2}{Nb^2} + \frac{(Nf)^2 \ell_B}{R} \right)$$

$$\frac{\partial E_F}{\partial R} = 0 \implies \frac{2R}{Nb^2} - \frac{(Nf)^2 \ell_B}{R^2} = 0$$

$$\implies R \sim N \ell_B^{1/3} f^{2/3} b^{2/3}$$

Chain growth linear in N, electrostatic interactions swell the chain $R \propto N^\nu$, PE has $\nu = 1$, as opposed to RW ($\nu = 0.5$) or SAW ($\nu = 3/5$)
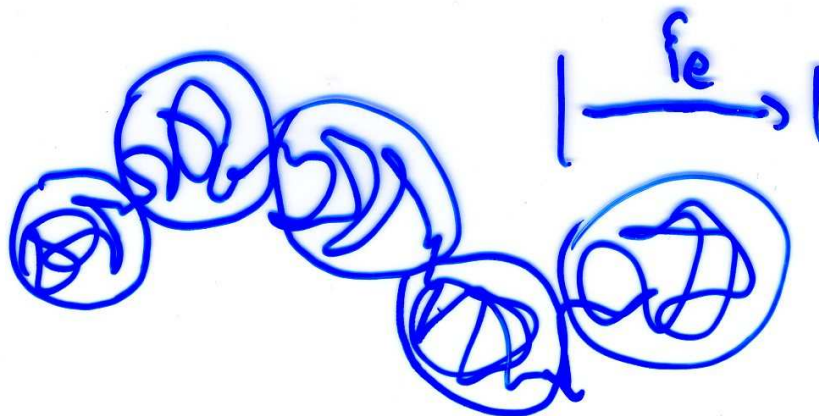
g: number of monomers within a blob

ξ_e: electrostatic correlation length (size of the blob)

Two Assumptions:

• chain inside electrostatic blob behaves Gaussian $\xi_e^2 \cong b^2 g$

• electrostatic interaction inside blob $\frac{(fg)^2 \ell_B}{\xi_e} \cong 1$

$\Longrightarrow$ the electrostatic blob parameters $\xi_e = (\frac{b^4}{f^2 \ell_B})^{1/3}$, $g = (\frac{b}{f^2 \ell_B})^{2/3}$

The chain length is given by a blob pole $\frac{N}{g} \xi_e$

$\Longrightarrow R = N(\frac{f^2 \ell_B}{b})^{2/3}(\frac{b^4}{f^2 \ell_B})^{1/3} = N\ell_B^{1/3} f^{2/3} b^{2/3} \equiv$ Flory argument

Neglected: • counterions, • solvent quality
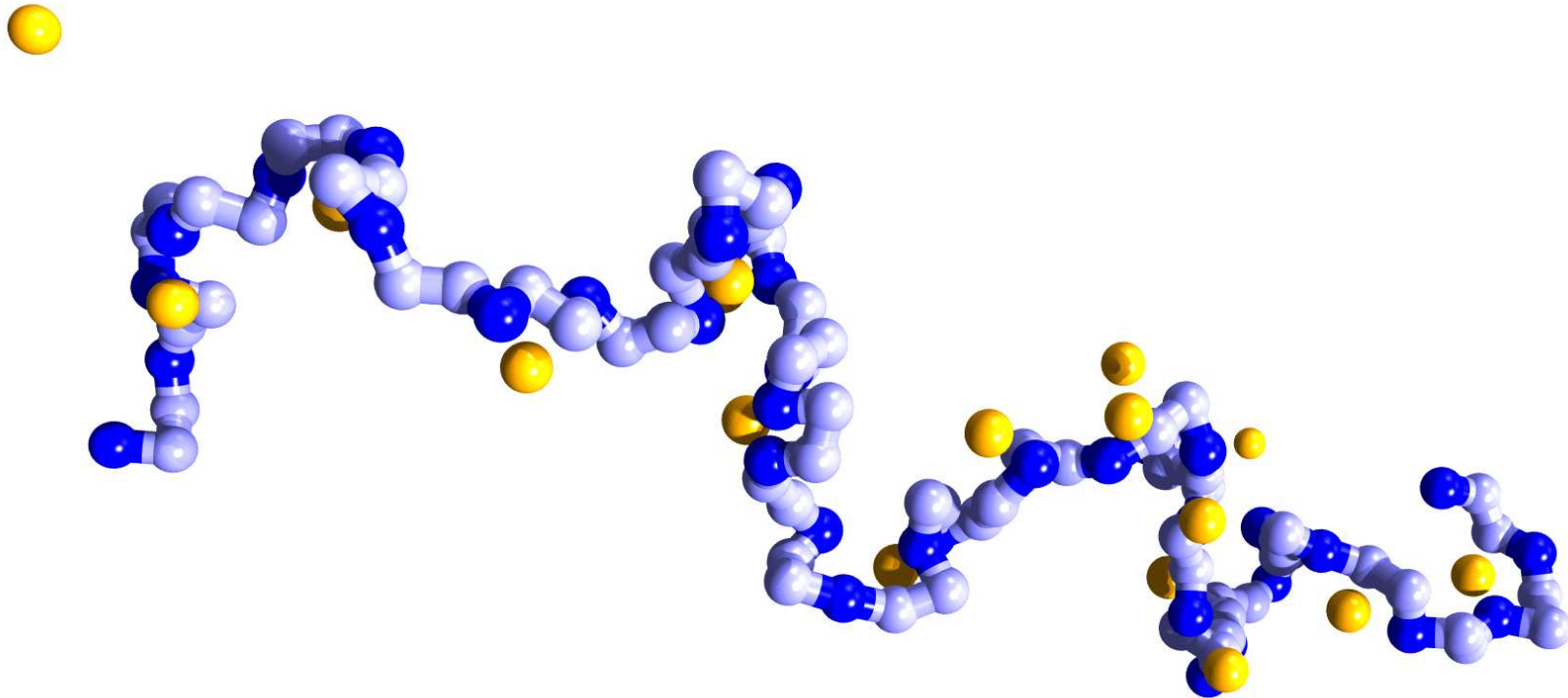
complex interaction: ion distribution $\leftrightarrow$ polymer conformation

stiff, stretched polymer conformation $\longrightarrow$ uniformly charged rod.
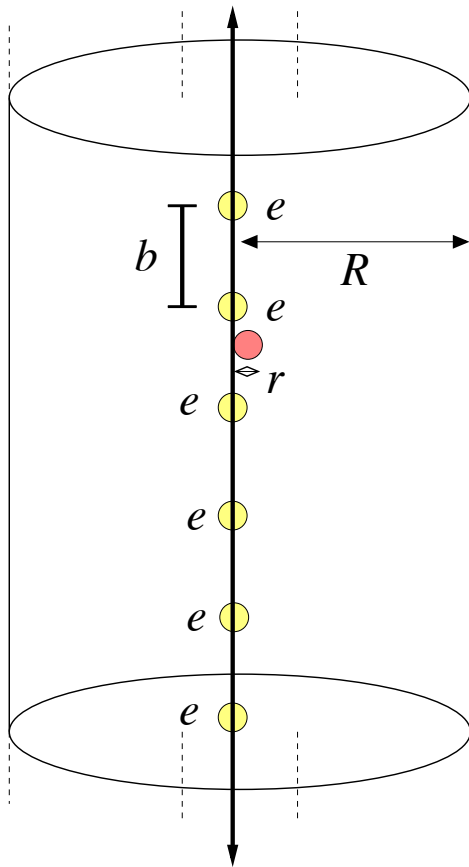
$$\lambda = e_0/b \qquad \ell_{\mathrm{B}} := e_0^2/4\pi\varepsilon k_{\mathrm{B}}T$$

$$\phi(r) \approx \frac{\lambda}{2\pi\varepsilon}\ln(r)$$

question: $\Delta F = \Delta E - k_{\mathrm{B}}T\Delta S$?

$$\Delta E \sim e_o\frac{\lambda}{2\pi\varepsilon}\ln\frac{R}{r} \quad \Delta S \sim \ln\frac{V_R}{V_r} \sim 2\ln\frac{R}{r}$$

$$\implies \Delta F = \left(\frac{\ell_{\mathrm{B}}}{b} - 1\right)2k_{\mathrm{B}}T\ln\frac{R}{r}$$

$\xi := \frac{\ell_{\mathrm{B}}}{b} < 1$, entropy dominated, $\xi := \frac{\ell_{\mathrm{B}}}{b} > 1$, energy dominated

$\implies$ The charged plane is energy dominated

$\implies$ The charged sphere is entropy dominated

Cell Model

a)   b)   c)   d)
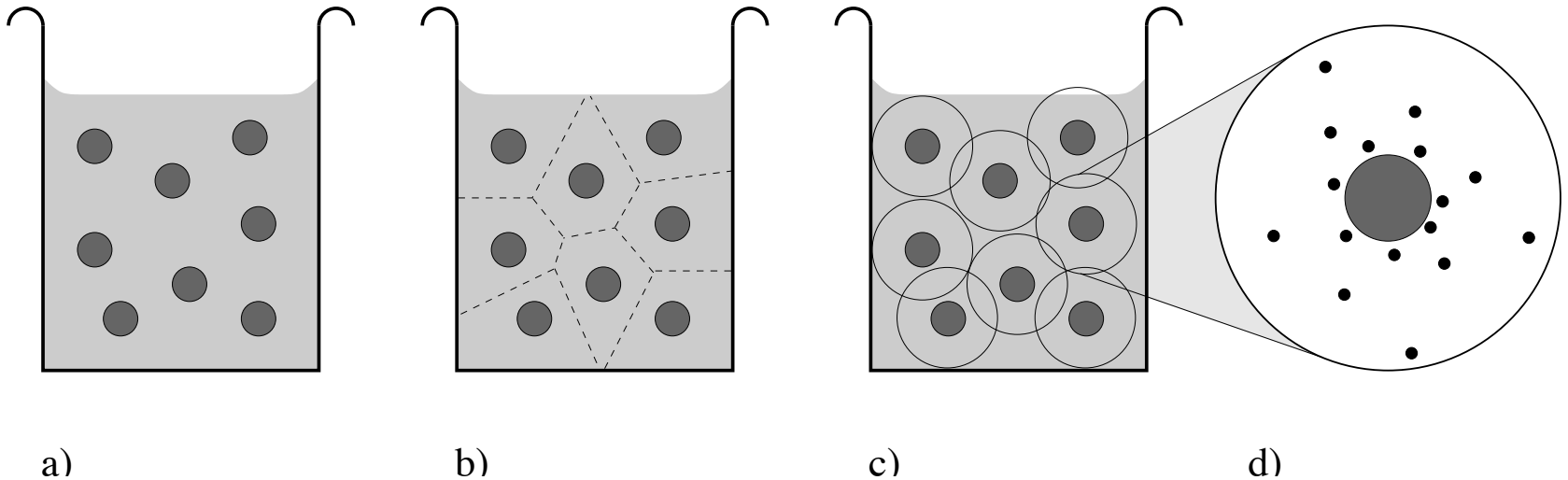
Successive approximation stages to go from a solution of many macromolecules to a cell model of **one** macromolecule

Factorization of the many-body partition function into a product of one-particle partition functions

Poisson Boltzmann Equation

Poisson Eq: $\nabla^2 \psi(\vec{r}) = -\dfrac{e}{\epsilon}(v^{(+)}n^{(+)}(\vec{r}) + v^{(-)}n^{(-)}(\vec{r}))$

The electrochemical potential of each ion is $\mu^{(i)} = ev^{(i)}\psi + k_B T \ln n^{(i)} \Rightarrow$
Boltzmann populations $n^{(i)} = n_0^{(i)} e^{-ev^{(i)}\psi/k_B T} \Rightarrow$

<div style="text-align:center">Poisson-Boltzmann Equation</div>

$$\nabla^2 \psi(\vec{r}) = -\tfrac{e}{\epsilon}(v^{(+)}n_0^{(+)} e^{-ev^{(+)}\psi/k_B T} + v^{(+)}n_0^{(-)} e^{-ev^{(-)}\psi/k_B T})$$

For an 1:1 electrolyte

$$n_0 = n_0^{(+)} = n_0^{(-)}$$

$$\nabla^2 \psi(\vec{r}) = \tfrac{2e}{\epsilon} n_0 \sinh(e\psi/k_B T)$$

the linearized equation is called the Debye-Hückel approximation:

Debye-Hückel Theory

$$\nabla^2 \psi(\vec{r}) = 8\pi \ell_B n_0 \psi(\vec{r}) = \lambda_D^{-2} \psi(\vec{r}) = \kappa^2 \psi(\vec{r})$$

with an exponentially screened solution

$$\psi(r) = A e^{-\kappa r}$$

where κ is called screening parameter, and $\kappa^{-1} = \lambda_D = (8\pi \ell_B n_0)^{-1/2}$ λ_D is called Debye-Hückel screening length ($\approx$ range of the electrostatic interaction). Its value has a $1/\sqrt{n_0}$ salt dependence:

- 3 Å for 1 Mol NaCl

- 10 Å for 100 mMol (1:1) salt (physiological conditions)

- 1 μm for pure water ($n_0 \approx 10^{-7}$ Mol due to autoionization of water into H^+ and OH^-).

Let us look at the Poisson-Boltzmann theory for the infinite plane with surface charge density $\sigma > 0$ and neutralizing counterions of valence v in one half-space (Gouy and Chapman):

$$\psi''(x) \;=\; \frac{v e_0}{\epsilon}\, n(0)\, \mathrm{e}^{\beta e_0 v \psi(x)} \quad ; \quad \psi'(0) \;=\; -\frac{\sigma}{\epsilon} \quad , \quad \lim_{x \to \infty} \psi'(x) \;=\; 0. \quad (5)$$

It is straightforward to verify that the solution to Eqns. (5) is

$$y(x) \;=\; \beta e_0 v \psi(x) \;=\; -2 \ln\left(1 + \frac{x}{\lambda_{GC}}\right) \qquad \text{with} \quad \lambda_{GC} := \frac{e_0}{2 \pi \ell_{\mathrm{B}} v \sigma}.$$

λ_{GC} is referred to as the *Gouy-Chapman length*. Ion density $n(x)$ and integrated ion distribution $P(x)$ are given by

$$n(x) = \frac{(2\pi \ell_{\mathrm{B}} v^2)^{-1}}{(x + \lambda_{GC})^2} \quad \text{and} \quad P(x) \;=\; \frac{v e_0}{\sigma} \int_0^x \mathrm{d}\bar{x}\, n(\bar{x}) \;=\; 1 - \left(1 + \frac{x}{\lambda_{GC}}\right)^{-1}. \quad (6)$$

Note that $P(\lambda_{GC}) = \frac{1}{2}$, strong ion localization !

In linearized Poisson-Boltzmann approximation Eqn. (5) becomes a linear second order differential equation with constant coefficients. Its solution is
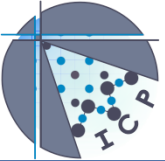
$$y(x) = e^{-2x/\lambda_{GC}} - 1. \qquad (7)$$

The ion distribution in the linear case is given by

$$n(x) = \frac{1}{\pi \ell_{\mathrm{B}} v^2 \lambda_{GC}^2} e^{-2x/\lambda_{GC}}. \qquad (8)$$

The ionic density in Eqn. (8) shows an exponential rather than algebraic decay, as in Eqn. (6). The contact density $n(0)$ is overestimated by a factor of 2 independent of the surface charge density σ. Hence, linearized PB theory fails already at arbitrarily small σ.

Ex: For $\sigma = \frac{e}{100 \mathring{A}^2}$, $\ell_B = 7.1 \mathring{A} \Rightarrow \lambda_{GC} \approx 2 \mathring{A}$ very small! Important for membranes, large colloids etc.
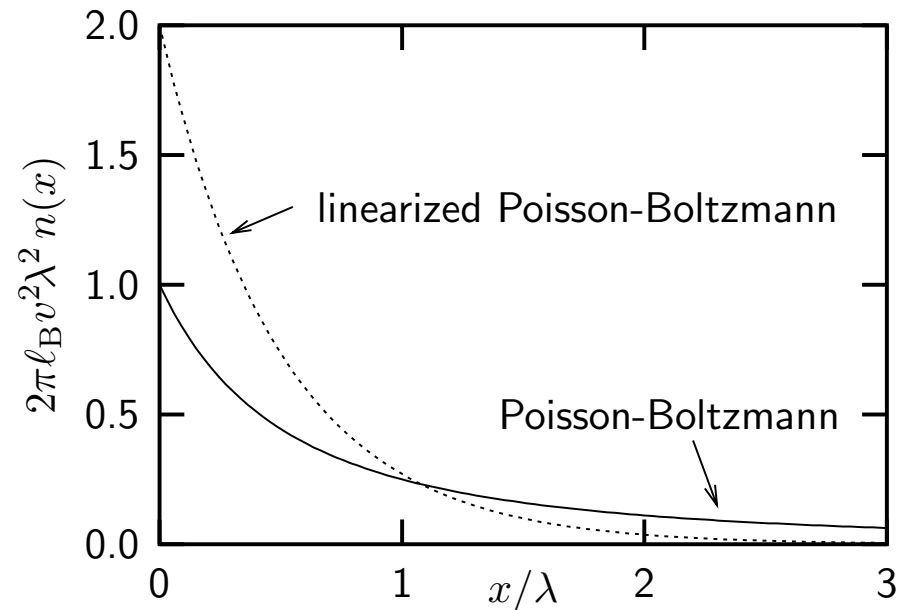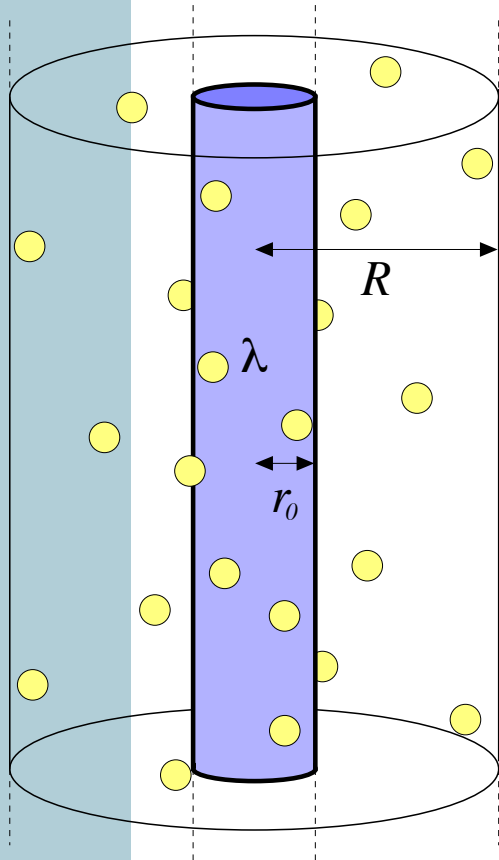
Bjerrum length: $\qquad \ell_{\mathrm{B}} := e_0^2 / 4\pi\varepsilon k_{\mathrm{B}}T$

Manning parameter: $\qquad \xi := \lambda \ell_{\mathrm{B}} / e_0$

potential: $\qquad y(r) := e_0 \psi(r) / k_{\mathrm{B}}T$

$$y'' + \frac{1}{r}\, y' = 4\pi\ell_{\mathrm{B}}\, n(r) \qquad\qquad y'(r_0) = -2\xi/r_0$$
$$; \qquad$$
$$n(r) = n(R)\, \mathrm{e}^{y(r)} \qquad\qquad y'(R) = 0$$

$$y(r) = -2\ln\left\{ \frac{r}{R}\sqrt{1 + \gamma^{-2}}\cos\left(\gamma\ln\frac{r}{R_{\mathrm{M}}}\right) \right\}$$

The integration constants γ and R_{M} follow from the boundary conditions

the fraction of counterions within a distance $r \in [r_0, R]$ is given

$$f(r) \;=\; 1 - \frac{1}{\xi} + \frac{\gamma}{\xi}\,\tan\left(\gamma \ln \frac{r}{R_{\mathrm{M}}}\right)$$
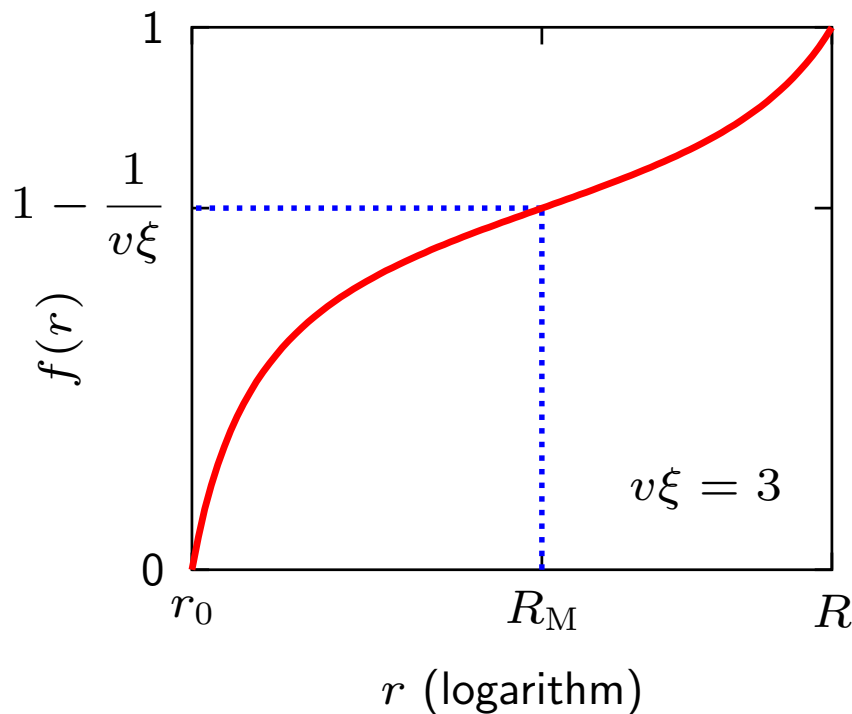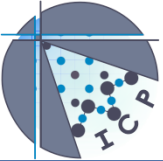

Manning condensation at $\xi > 1$:

$$f < 1 - \frac{1}{\xi} \;\Longleftrightarrow\; \lim_{R\to\infty} r(f) < \infty$$

Inflection point criterium:

$$\left.\frac{\mathrm{d}^2 f}{\mathrm{d}(\ln r)^2}\right|_{r=R_{\mathrm{M}}} \;=\; 0 \quad \Rightarrow \quad R_{\mathrm{M}}$$

Manning Condensation

The (Manning–) fraction $f(R_{\mathrm{M}}) = 1 - 1/\xi$ is a critical limit, because (for $\xi > 1$) we find:

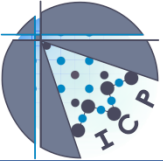$$\lim_{R \to \infty} f(r) \;<\; 1 - \frac{1}{\xi} \qquad \Longrightarrow \qquad r < \infty$$

$$\lim_{R \to \infty} f(r) \;=\; 1 - \frac{1}{\xi} \qquad \Longrightarrow \qquad r = R_{\mathrm{M}} \sim \sqrt{R} \to \infty$$

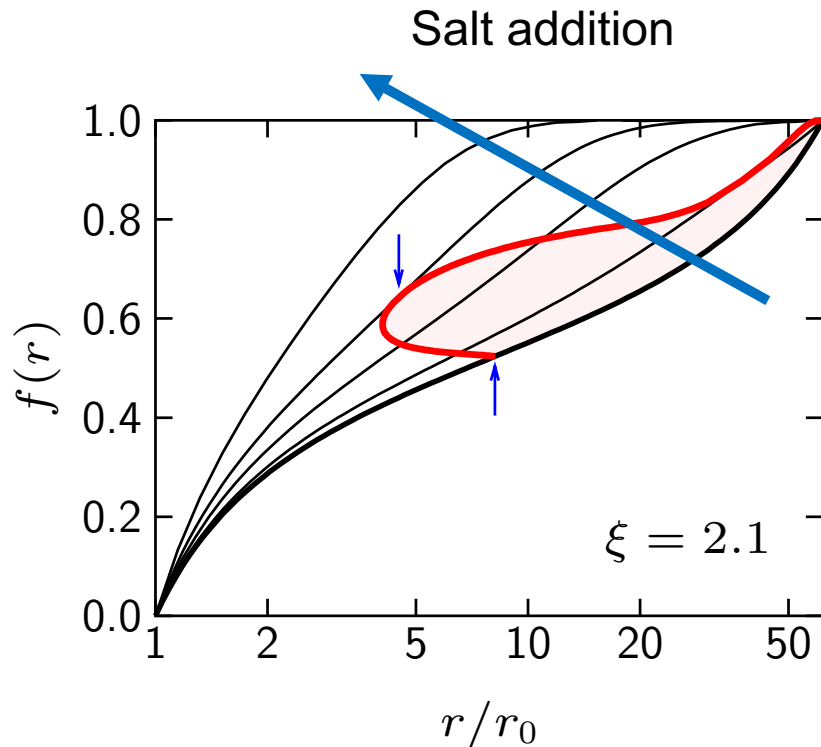$$\lim_{R \to \infty} f(r) \;>\; 1 - \frac{1}{\xi} \qquad \Longrightarrow \qquad r \sim R \to \infty$$

$$y(r) - y(r_0) = -2 \ln(r/r_0) + \mathcal{O}(\ln \ln \frac{r}{r_0})$$

Rod with charge parameter $\xi = 1$

$$\lim_{R \to \infty} \frac{n(R)}{n(r)} = \lim_{R \to \infty} \frac{1 + \gamma^2}{2\xi} = \frac{1}{2\xi} = \frac{P}{P_{ig}} = \hat{p}$$

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Salt addition

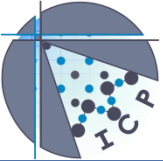Ion fraction $\rightarrow$ charge fraction

more salt $\rightarrow$ more screening
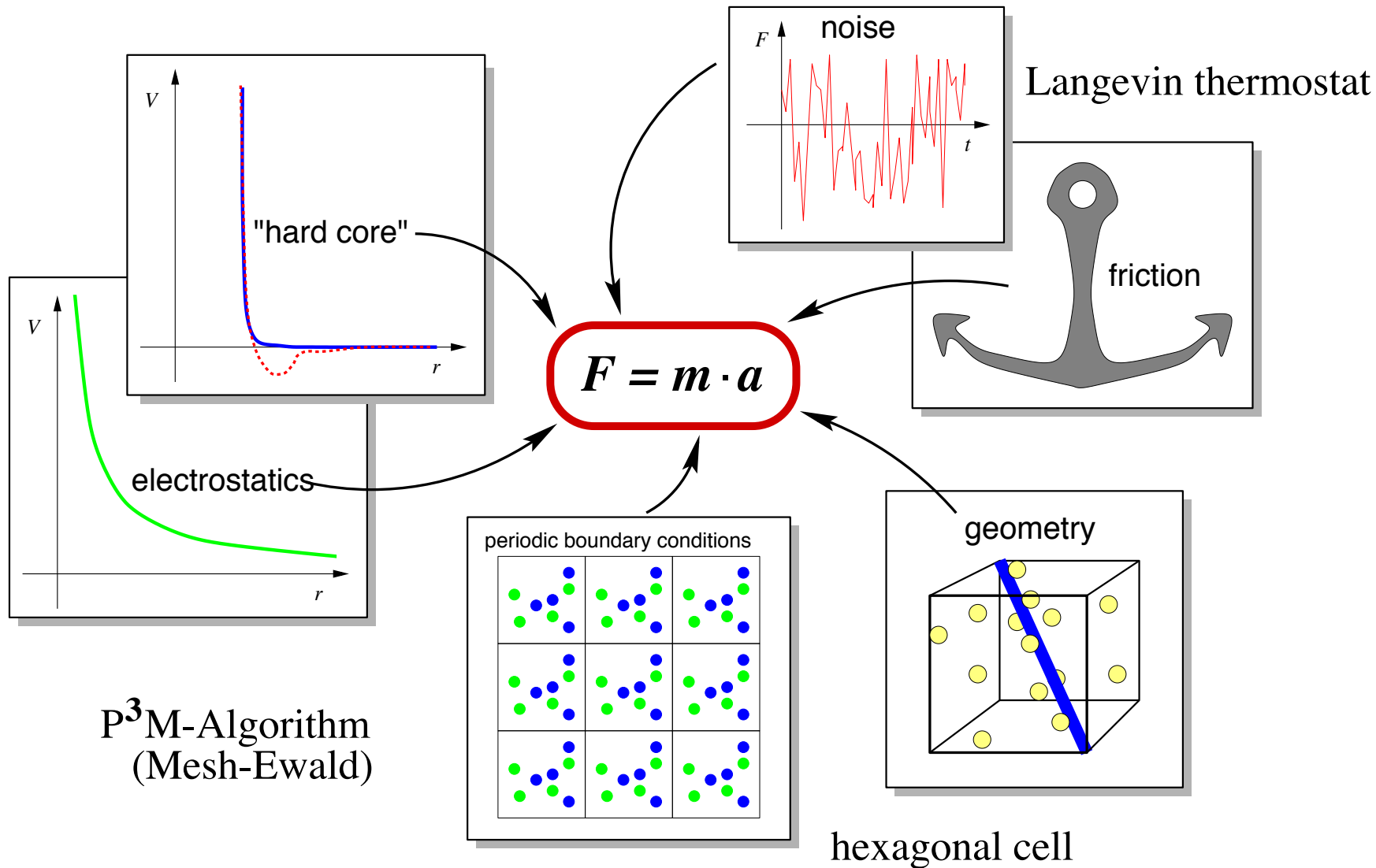
condensed layer contracts

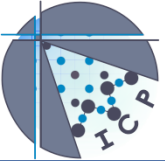$\lambda_D \lesssim R \quad \Rightarrow$ new inflection points

$\lambda_D \lesssim R_M \Rightarrow$ no inflection points

addition of salt causes an exchange of the relevant length scales: $R_M \longrightarrow \lambda_D$. The crossover can be quantified through the inflection point criterion. At $\lambda_D \lesssim R_M$ condensation looses it meaning!
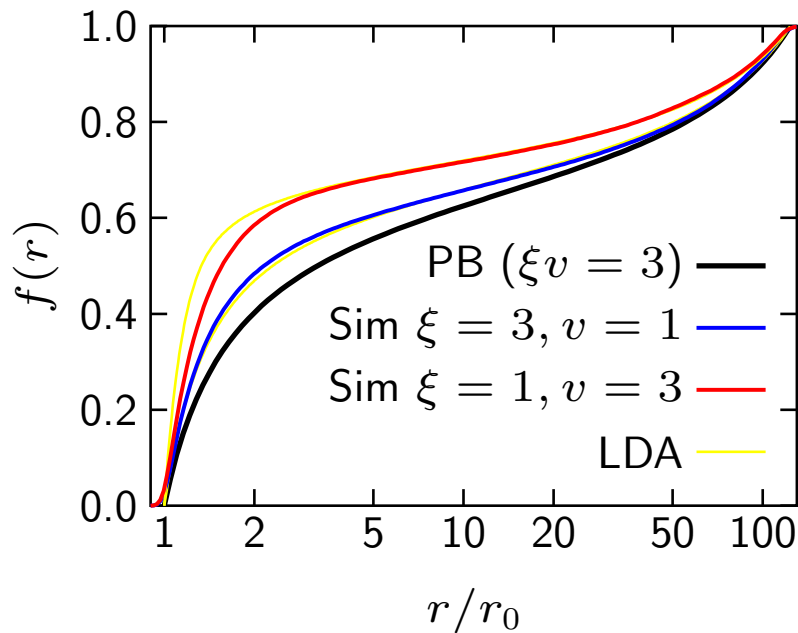
noise

Langevin thermostat

V

"hard core"

r

friction

V

electrostatics

r

$$F = m \cdot a$$

P^3M-Algorithm
(Mesh-Ewald)

periodic boundary conditions

geometry

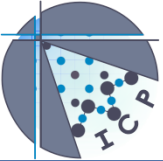hexagonal cell

Manning Parameter versus Valence

counterion condensation is stronger than in the Poisson-Boltzmann theory
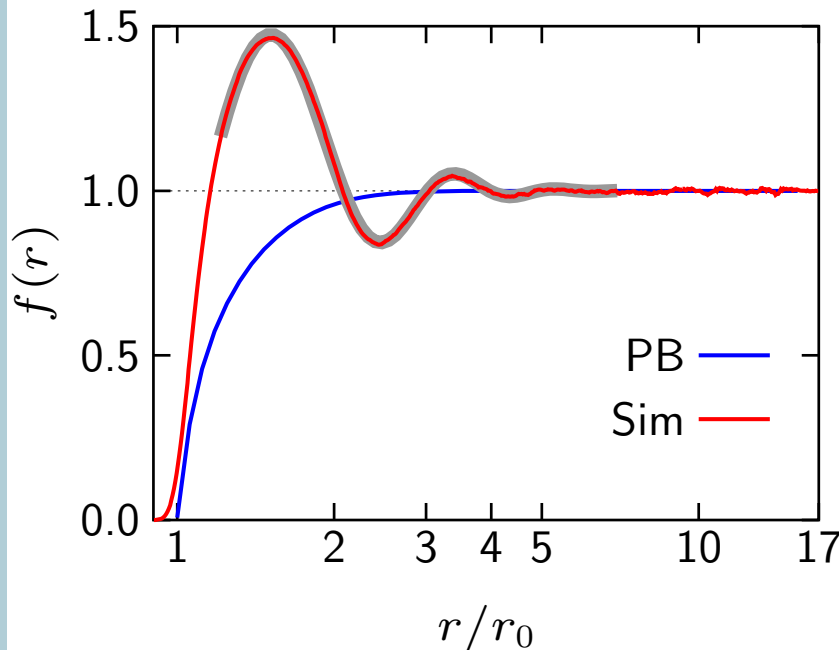
product ξv no longer universal.

discrepancy increases with valence.

theoretical description through a local correction to the PB free energy functional possible.

Poisson-Boltzmann neglects correlations. These enhance counterion condensation, especially for multivalent counterions.

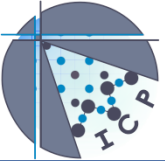$\xi = 4$; 2:2-Salt; $\bar{n} = 2.1 \times 10^{-2}\sigma^{-3}$.

the charge of the rods gets repeatedly over-compensated.

reversed charged layers.
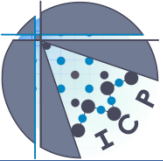
charge oscillations are exponentially damped.

Poisson-Boltzmann fails *qualitatively* for strongly charged systems

better: integral equations, i.e. "'hypernetted-chain"' (HNC).
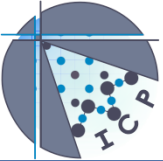
Efficient Algorithms for Long Range Interactions

(... All I say will in principle also be valid for dipolar interactions)

Electrostatics under pbc

- 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)
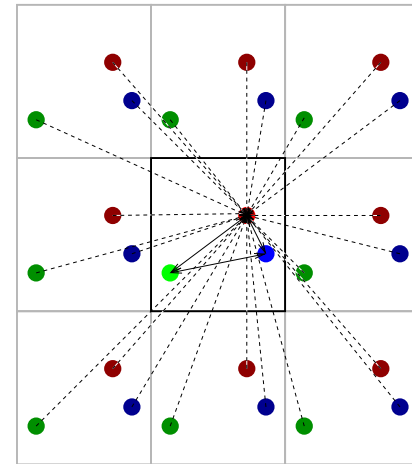
Example: The alternating harmonic series:

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

Conditionally Convergence

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...

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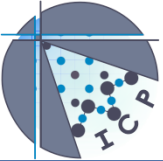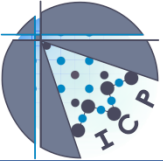
Conditionally Convergence

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...

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

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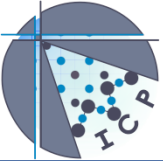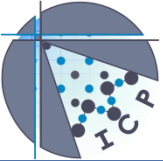
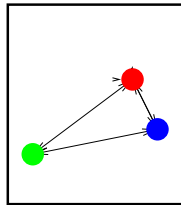# Conditionally Convergence

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...

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

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

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

Electrostatics

Coulomb energy

Pair energy summation

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

- 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:
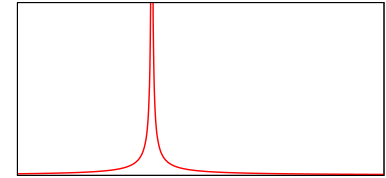
$1k_BT$

$1l_B$
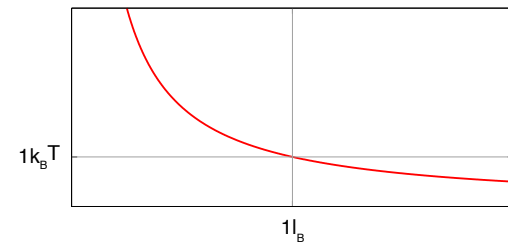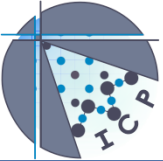
Electrostatics

Coulomb energy

Pair energy summation

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

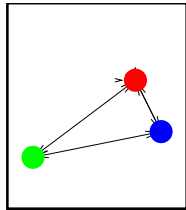- summing up $1/r$ Coulomb pair potential
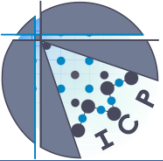- Bjerrum length l_B

Potential summation

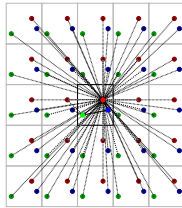$$U = \frac{1}{2} \sum_{i=1}^{N} q_i \phi(\mathbf{r}_i)$$

- 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 BC

Coulomb energy
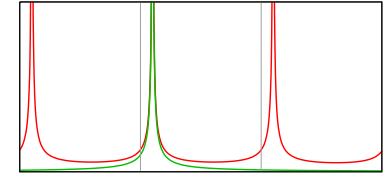
Pair energy summation

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

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

Potential summation

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

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

these two calculate something different!

The Dipole Term

- assume summation in periodic shells
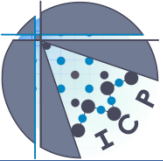- surrounded by polarizable material of dielectric constant ϵ_∞
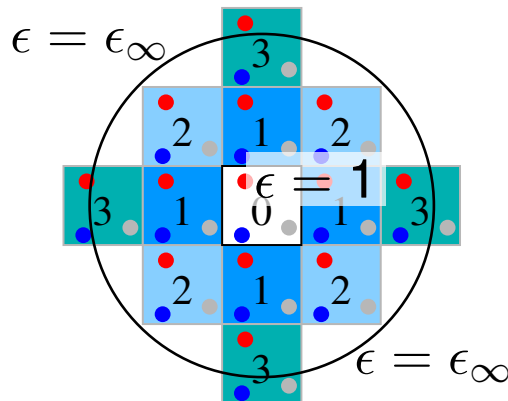
Pair energy summation
vacuum around: $\epsilon_\infty = 1$

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

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

Splitting the Potential

charge distribution

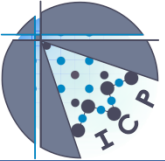$$\rho = \sum_{\mathbf{n} \in L\mathbb{Z}^3} \sum_{i=1}^{N} q_i \delta(\mathbf{r} - \mathbf{r}_i - \mathbf{n})$$
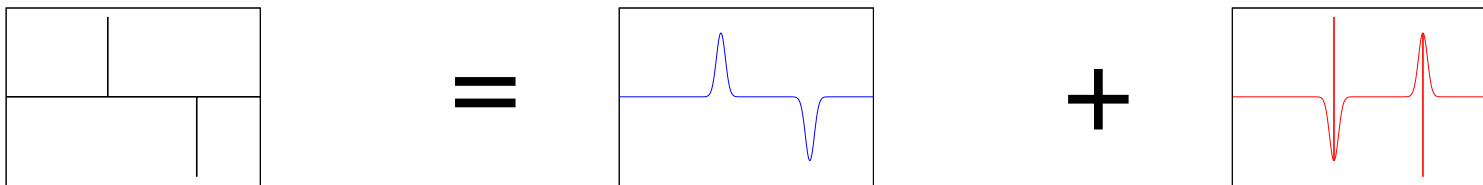
replace δ by Gaussians of width α^{-1}:

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

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

The Standard Ewald Sum

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

with

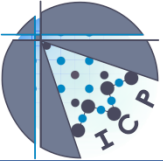$$U^{(r)} = \frac{l_B}{2} \sum_{\mathbf{m} \in \mathbb{Z}^3} \sideset{}{'}\sum_{i,j} q_i q_j \frac{\text{erfc}(\alpha|\mathbf{r}_{ij} + \mathbf{m}L|)}{|\mathbf{r}_{ij} + \mathbf{m}L|}$$ real space correction

$$U^{(k)} = \frac{l_B}{2L^3} \sum_{\mathbf{k} \neq \mathbf{0}} \frac{4\pi}{k^2} e^{-k^2/4\alpha^2} |\widehat{\rho}(\mathbf{k})|^2$$ Gaussians in *k*-space
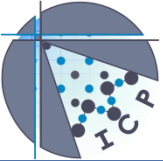
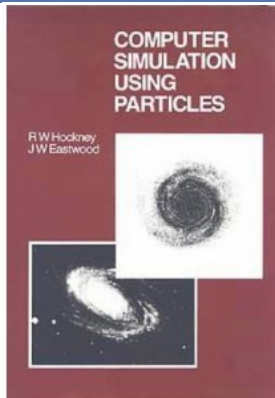$$U^{(s)} = -\frac{\alpha l_B}{\sqrt{\pi}} \sum_i q_i^2$$ Gaussian self interaction

forces from differentiation

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

Particle Mesh Ewald Methods

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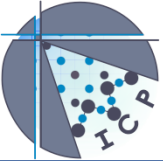written by the evangelists
R.W. Hockney, J.W. Eastwood, 1988

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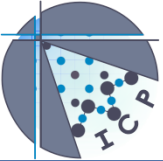
**Particle-Particle-Particle-Mesh ♪♭ Simply the best.....**

Steps of the P³M

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. $\mathbf{i}\mathbf{k}\hat{\phi}(\mathbf{k}) \rightarrow \hat{\mathbf{E}}(\mathbf{k})$:   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
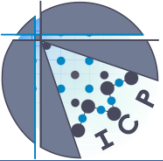
Charge Assignment Function
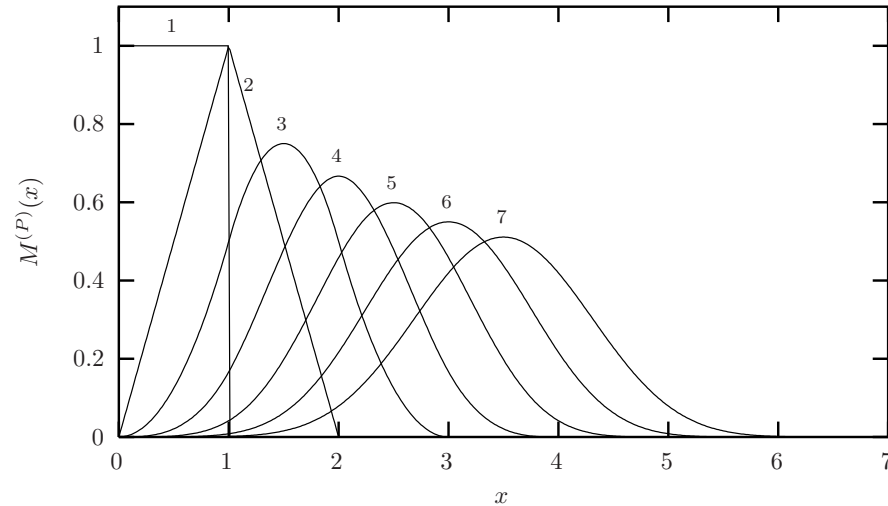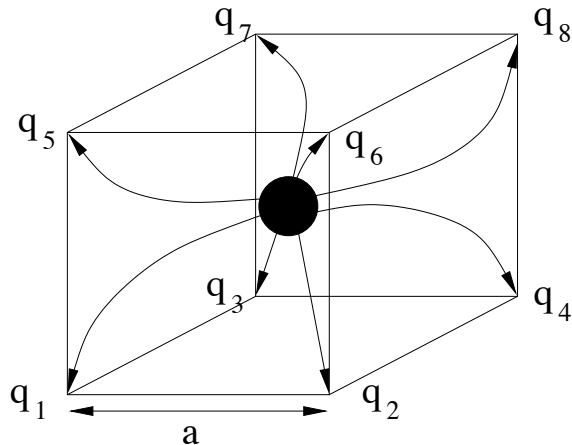
- interpolate charges onto h-spaced grid

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

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

Optimal Influence Function

■ minimize the rms error functional

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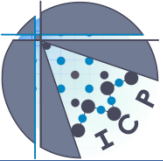
with the analytic reference potential

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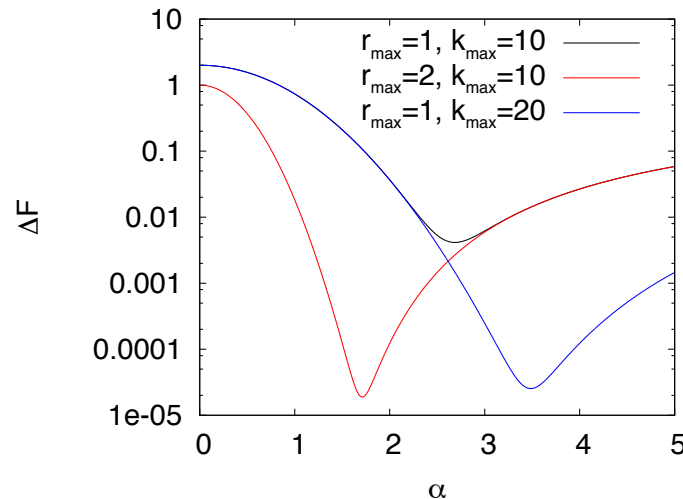
■ leads to

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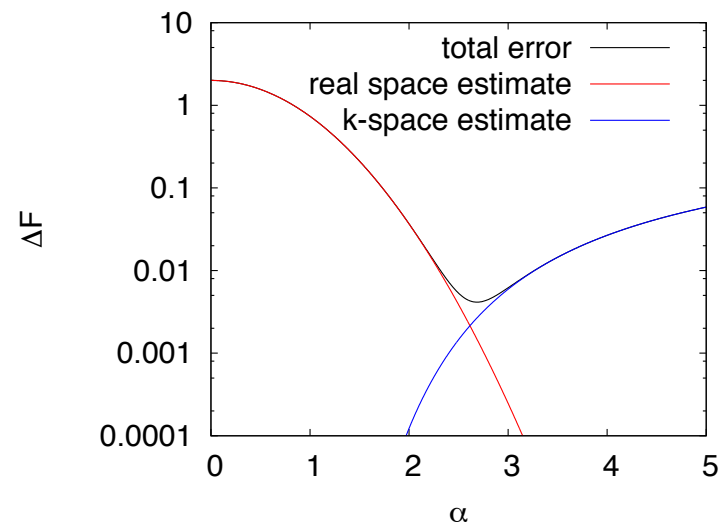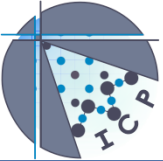
with $m = L/h$

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
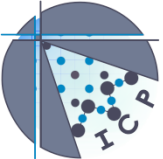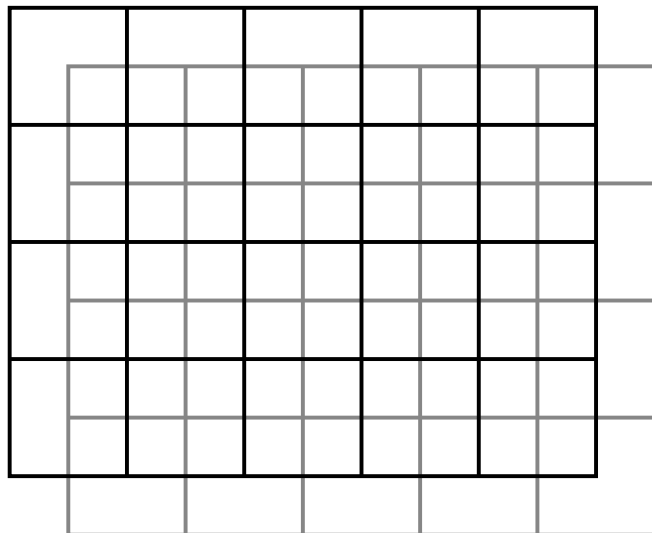
How to Control Errors

Kolafa and Perram:

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

Hockney and Eastwood:

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

Interlaced P³M:

$$\mathbf{F}_i^{(int)} = \frac{1}{2}\left(\mathbf{F}_i + \mathbf{F}_i^{\mathbf{p}}\right)$$

- force $\mathbf{F}_i$ is average of P³M force and P³M force with grid shifted by $\mathbf{p} = (h/2)\mathbf{e}$
- doubles the effort, gains order of magnitude in accuracy
- effort can be reduced by using complex-to-complex FFT

Interlacing plus analytical differentiation seems to be the fastest method currently !

ScaFaCoS Library

Scalable **Fa**st **Co**ulomb **So**lver

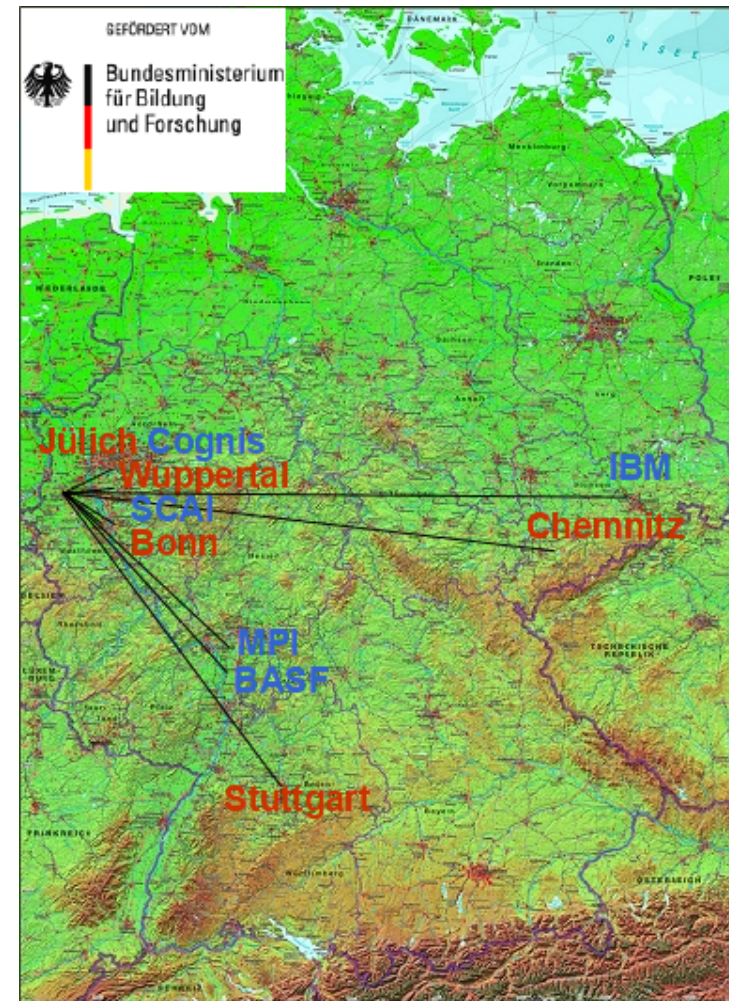`http://www.scafacos.de`

Library of different Coulomb solvers

"Highly scalable", MPI-parallelized
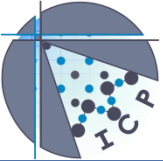
Common interface for all methods

Developed by groups from Jülich, Wuppertal, Chemnitz, Bonn and Stuttgart

Project by the German Research Ministry (BMBF), officially ended 2011

Open source: Source code on github


http://www.scafacos.de/
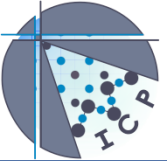
Implemented Algorithms

- 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).
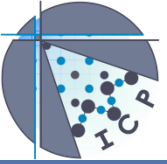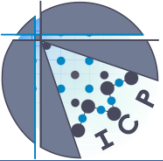
P2NFFT

- Particle-Particle Nonequidistant FFT
- Simplified P³M is a special case of P2NFFT
- Same structure = same performance
- Minor mathematical details, simpler approach
- Advantage: can be formulated in 3D, 2D,1D, 0D

Multigrid

- Solve Poisson equation in far field with multigrid PDE solver
  - use different levels of successively coarser meshes
  - solve poisson equation on these meshes by recursively improving the solution of the coarser mesh
- Complexity $\mathcal{O}(N)$
- Can be extended to handle periodic BC
- In SCAFACOS: PP3MG (Wuppertal), VMG (Bonn)

$l = 4$

$l = 3$

$l = 2$

$l = 1$

Restriction

Prologation

◦ Smoothing/Solving

51
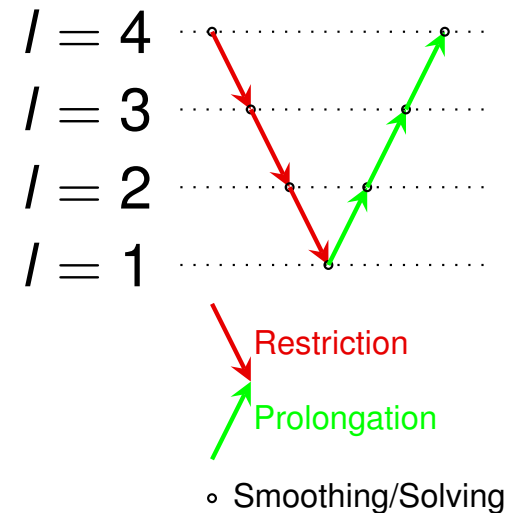
Barnes-Hut Tree code
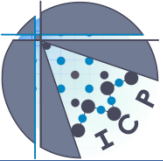
- Hierarchically cluster charges
- Multipole expand these clusters
- Compute interaction with far away cluster multipole moments instead of single particle charges
- Complexity $\mathcal{O}(N \log N)$
- Can be extended to handle periodic BC
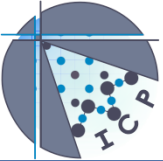- In SCAFACOS: PEPC (Jülich)
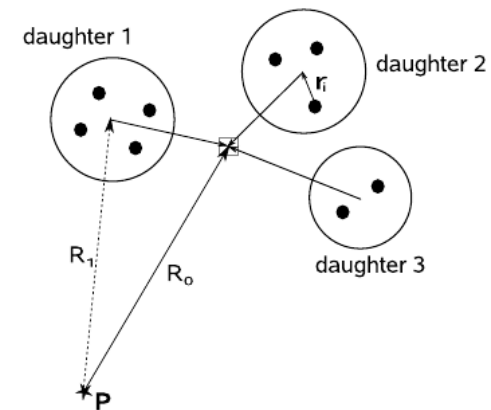
Fast Multipole Method

- Expand Treecode: let clusters interact with each other

- Put everything on a grid

- Complexity $\mathcal{O}(N)$

- Can be extended to handle periodic BC

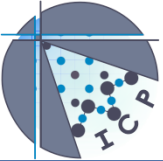- In SCAFACOS: FMM (Jülich)
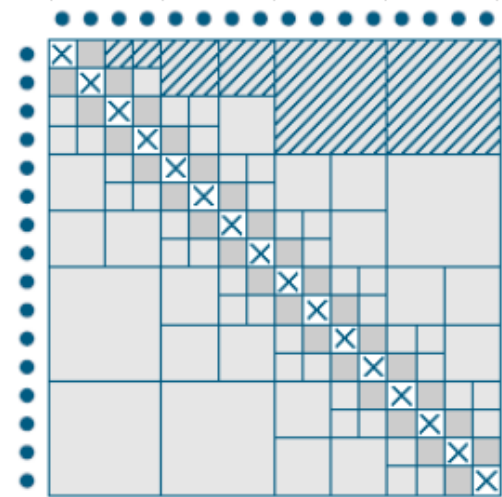
FMM Interaction

MEMD for Molecular Dynamics

- MEMD (Maggs/Rosetto 2002, Pasichnyk/Dünweg 2004)

  - *In principle, Maxwell's equations are local*

  - *Problem is the large speed of light*

  - *Simply assume that the speed of light is small*

  - *Statistics is still correct!*

- Method

  - *Simulate the propagation of E, j, H, on a cubic lattice (plaquettes)*

  - *Use same time steps as MD*

- Can handle dielectric variations

- $O(N)$

- Parallelization: Algorithm is fully local!

- ScaFaCoS: MEMD (Stuttgart)
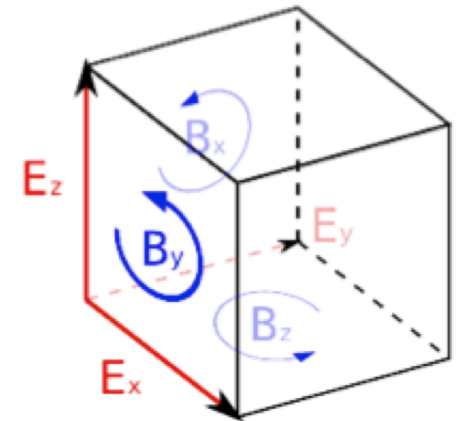
- A. C. Maggs and V. Rosetto, PRL 88:196402, 2002

- I. Pasichnyk and B. Dünweg, JPCM 16:3999, 2004

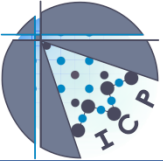F. Fahrenberger, CH, Phys. Rev. E **90**, 063304 (2014)

Benchmarks Complexity

- P2NFFT, P^{3}M and FMM are fastest
- MEMD and Multigrid $\approx \times 10$ slower
- All algorithms show (close-to-)linear behavior
- log N-term of P2NFFT and P^{3}M is invisible
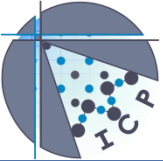- No cross-over with FMM
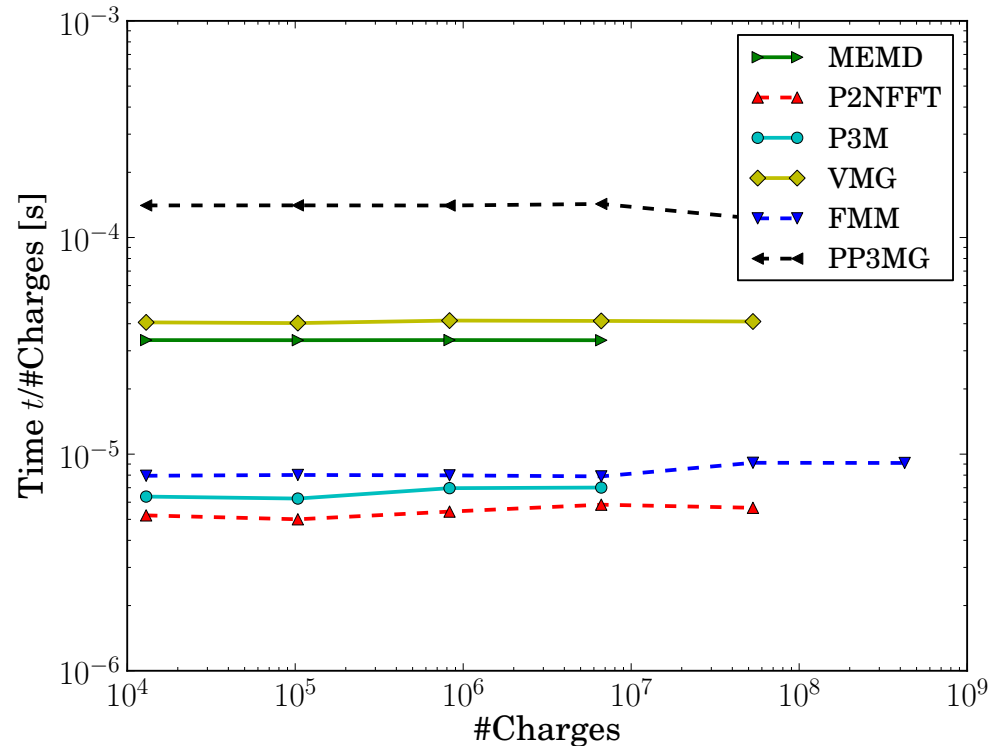
Silica melt, $\varepsilon_{\text{pot}} \leq 10^{-3}$, $P = 1$ (JUROPA)

ScaFaCoS Conclusions

- Performance depends heavily on architecture, compiler and implementation

- . . . and tuning!

- $\times 2$ differences between algorithms are "normal"

- Within these limits, FMM, P^{3}M and P2NFFT perform equally good

- MEMD slightly worse ($\approx \times 4$), but performs better with larger systems

- Multigrid methods seem to be worse ($\approx \times 10$)

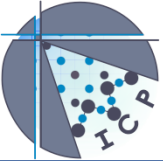- . . . apparently due to large variation in the potential

Some Coulomb Solvers

N = Number of charges

Year	Method	Complexity	Reference
1820	Direct Summation	N^2	Laplace
1921	Ewald Summation	$N^{\frac{3}{2}}$	Ewald
1974	Particle-Particle Particle-Mesh	$N \log N$	Hockney, Eastwood
1977	Multigrid Summation	N	Brandt
1986	Barnes-Hut Treecode	$N \log N$	Barnes, Hut
1987	Fast Multipole Method	N	Greengard, Rokhlin
2002	Maxwell Equation Molecular Dynamics	N	Maggs, Rossetto

- Methods often complex
- They do not parallelize easily
- Prefactors and scaling are highly platform and implementation dependent
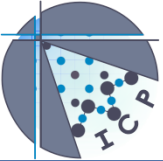- MC and MD performance differs, check accuracy 57

Partially Periodic Systems

water

membrane

water

$q\Delta_t\Delta_b$

$q\Delta_t$

q

$q\Delta_b$

$q\Delta_b\Delta_t$

ε_t

ε_m

ε_b

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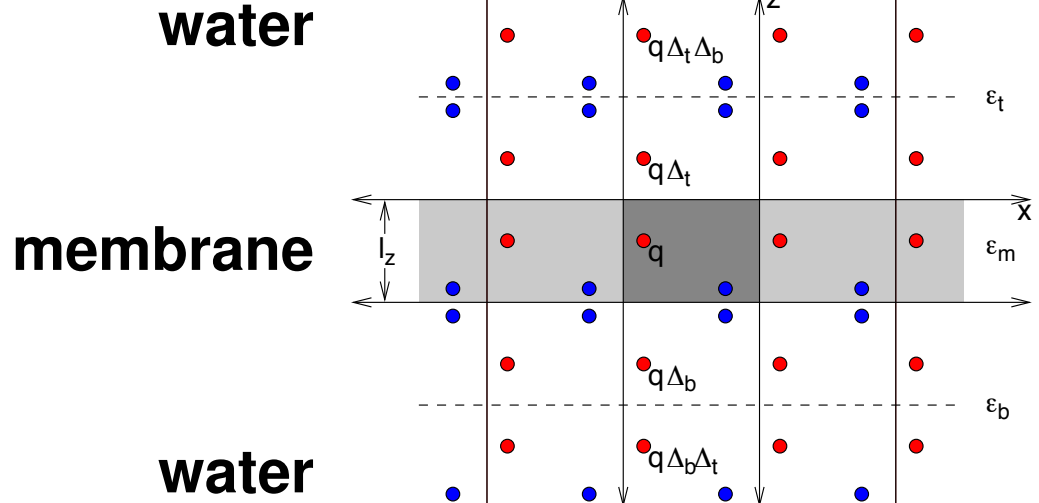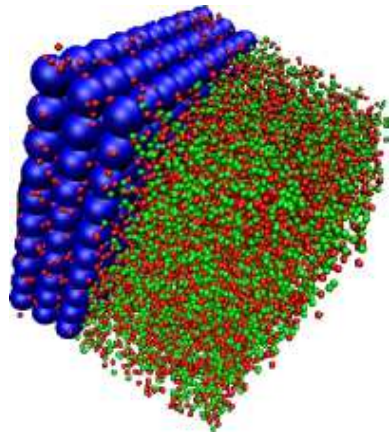
- 2D periodic: slablike systems, surfaces, thin films, membranes, air-water interfaces
- 1D periodic: Needles, rods, nanopores,
- 0D periodic boundaries = open systems

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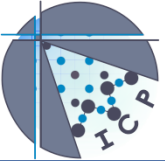- P2NFFT can be formulated to work

MMM2D and MMM1D

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

$$= \frac{2}{L} \sum_{p \in \frac{2\pi}{L}\mathbb{Z}} \left(\sum_{l \in L\mathbb{Z}} K_0\left(\sqrt{\beta^2+p^2}\sqrt{(y+l)^2+z^2}\right) \right) e^{ipx}$$

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

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

- Convergence factor based summation (limit $\beta \to 0$)
- Near formula for $z \approx 0$
- Optimal computation time comparable to Ewald $\mathcal{O}(N^{5/3})$
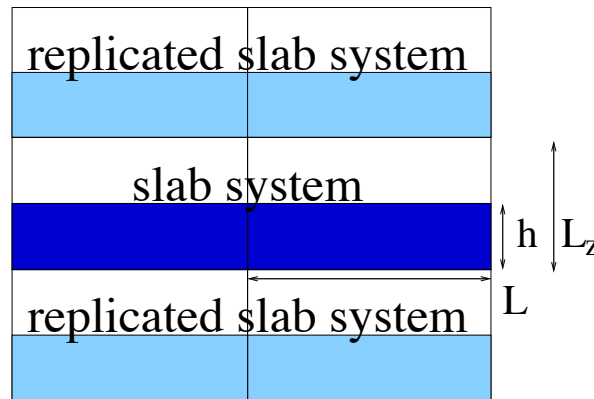- Analogous formulae for 1D, but then $T_{CPU} \approx \mathcal{O}(N^2)$

A. Arnold, C. H., Chem. Phys. Lett. **354,** 324 (2002**);**
A. Arnold, C.H., J. Chem. Phys. **123**, 144103 (2005)

2D PBC approx. with 3D PBC
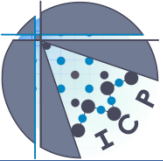
The Yeh and Berkowitz correction

- 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

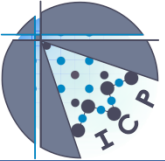- requires changed dipole term $U^{(d)} = \frac{2\pi}{L^3} \left(\sum_i q_i z_i \right)^2$

The ELC Method

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

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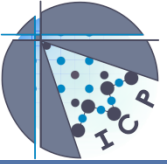- 2-4x faster than plain Yeh-Berkowitz plus full error control

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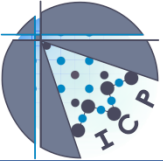
Dipolar Interactions

- There is also a dipolar P^{3}M 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)
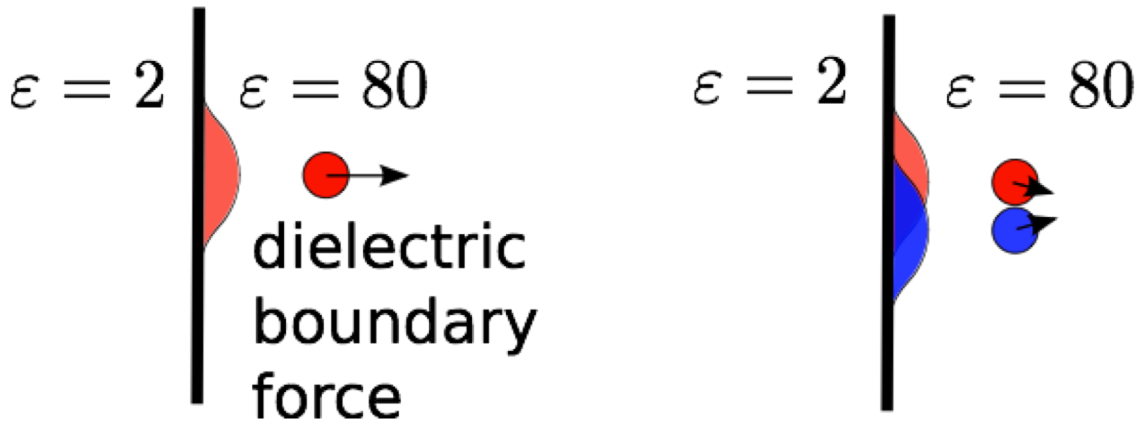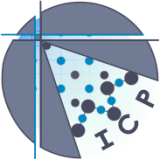
Include Dielectric Interfaces

Where does this matter?

What does Dielectric Contrast do?

$\varepsilon = 2$ | $\varepsilon = 80$
dielectric
boundary
force

$\varepsilon = 2$ | $\varepsilon = 80$

- Water is more polarizable than the solid wall material, leading to an induced charge of the same sign

- Force pushing the charge away from the wall

- For air-water interfaces it is the opposite situation

- How to compute the electrostatic force efficiently?
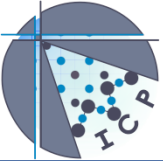
- **Use either Image charges or induced charges….**

Planar Dielectric Interfaces

$\varepsilon = 2$ | $\varepsilon = 80$
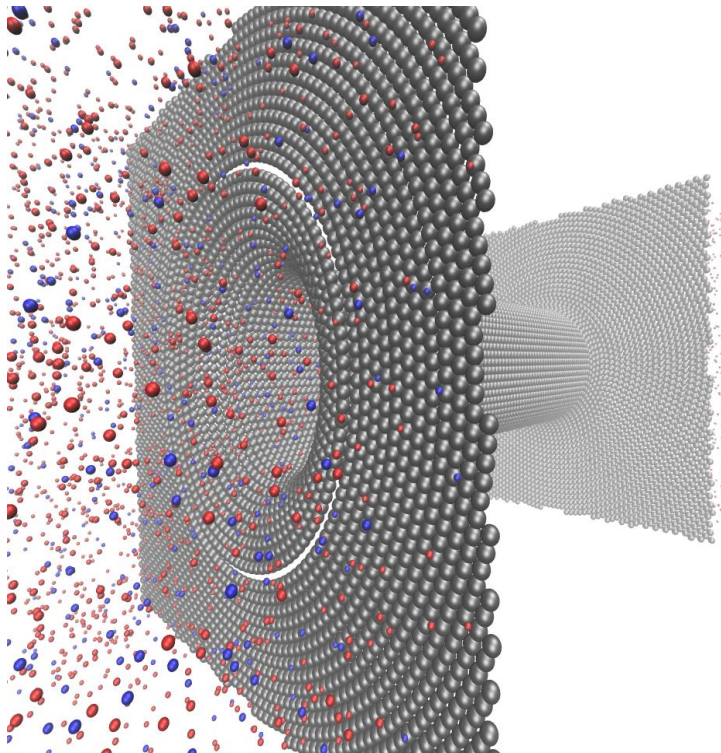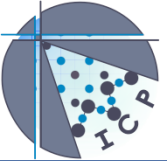
dielectric
boundary
force

$\varepsilon = 2$
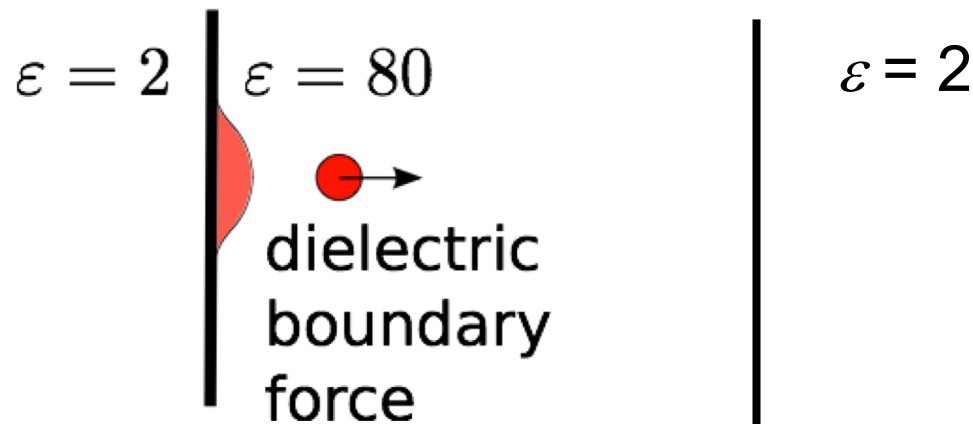
Can be handled by
- ICMMM2D
- ELCIC

- 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)

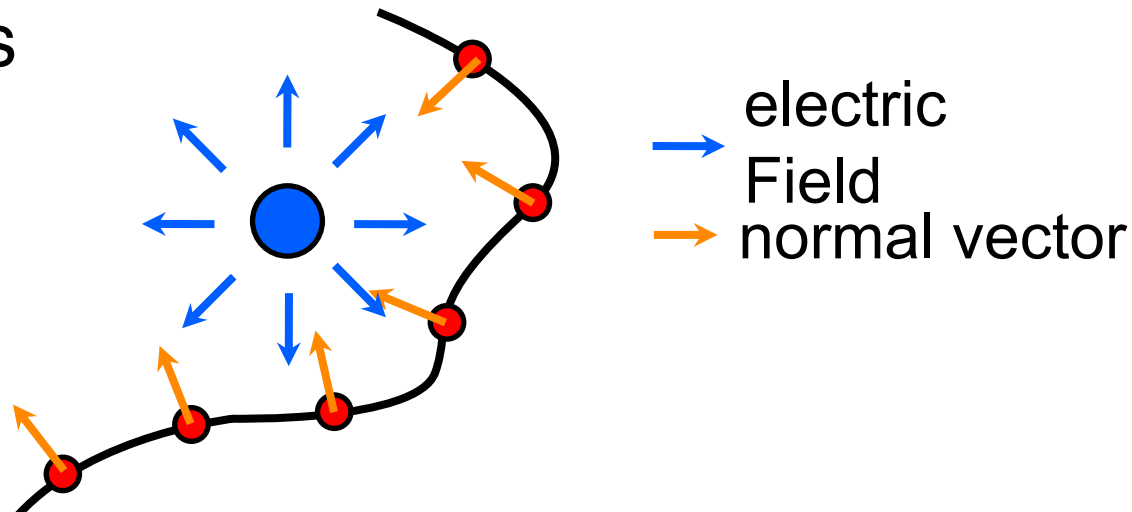# What about arbitrarily curved interfaces like a nanopore?

ICC* Algorithm

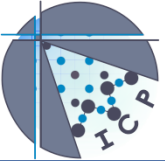■ Boundary condition for the normal component of the electric field:

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

■ 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

electric Field

normal vector

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ICC* Algorithm

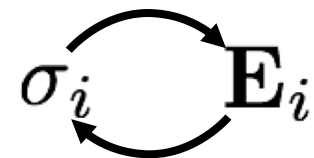- Boundary condition for the normal component of the electric field:

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  - can be fulfilled by introducing a charge density:

$$\sigma = \frac{1}{2\pi} \varepsilon_1 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2} \mathbf{E}$$
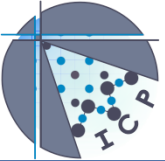
- Discretization of the surface to boundary elements lead to a set of equations

  ▶ Solved by an iterative scheme $\sigma_i \circlearrowright \mathbf{E}_i$

  • $\mathbf{E}$ can be obtained by any Coulomb solver

  ▶ Periodic boundary conditions automatically fulfilled

ICC* Algorithm

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

$$\varepsilon_1 \mathbf{E_1} \cdot \mathbf{n} = \varepsilon_2 \mathbf{E_2} \cdot \mathbf{n}$$
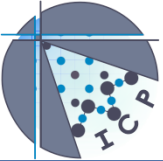
  - can be fulfilled by introducing a charge density:

$$\sigma = \frac{1}{2\pi} \varepsilon_1 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2} \mathbf{E}$$
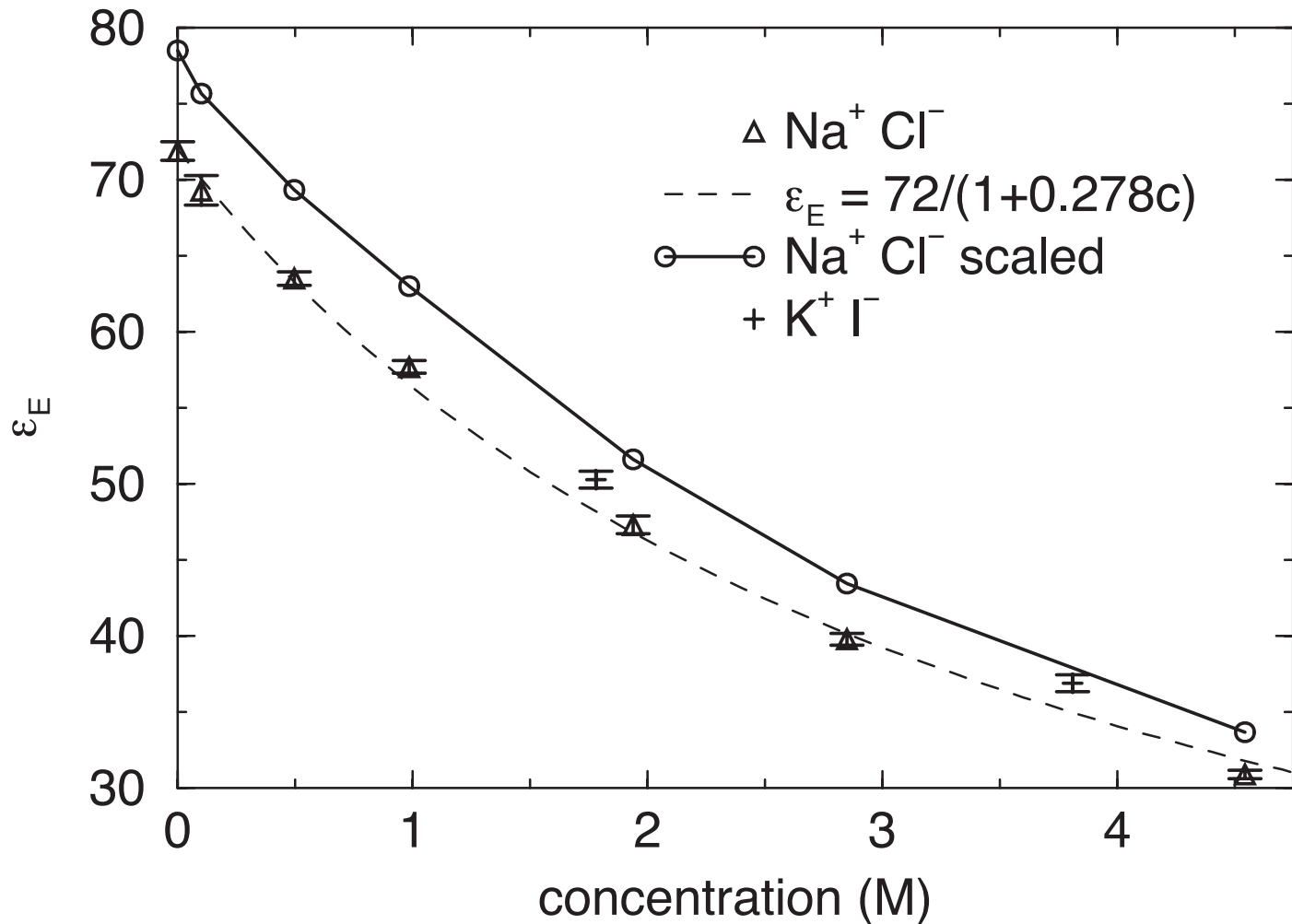
- Discretization of the surface to boundary elements lead to a set of equations

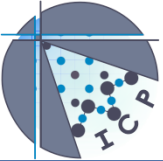ICC* (Induced Charge Computation) Algorithm:
S. Tyagi, M. Süzen, M. Sega, M. Barbosa, S. Kantorovich, and C. Holm, Journal of Chemical Physics **132**, 154112 (2010)
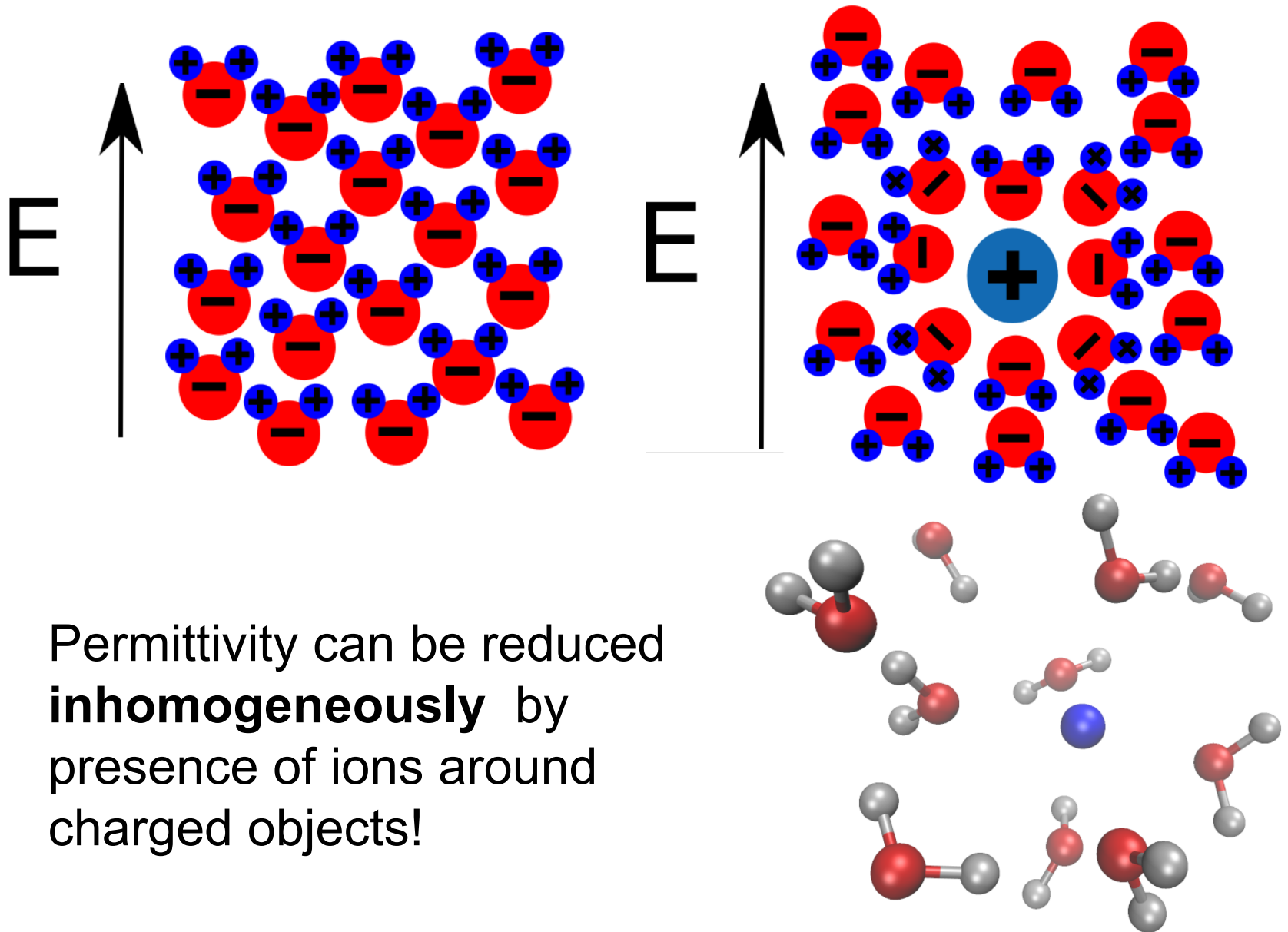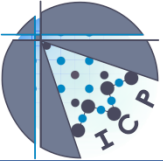
Salt can Reduce the Dielectric ε_r

Legend:
- △ Na$^+$ Cl$^-$
- - - - $\varepsilon_E = 72/(1+0.278c)$
- ○—○ Na$^+$ Cl$^-$ scaled
- + K$^+$ I$^-$

Axes: ε_E vs concentration (M)

All-Atom MD, SPC/E explicit water

B. Hess, C. Holm, N. van der Vegt: PRL **96,** 147801 (2006)

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Inhomogeneous Dielectrics

E

E

Permittivity can be reduced **inhomogeneously** by presence of ions around charged objects!
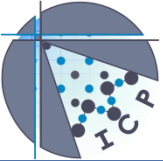
Maxwell-like Equations

$$\nabla \varepsilon \nabla \phi = -\rho$$

$$\Rightarrow \nabla \cdot \mathbf{D} = \rho \qquad (\text{Gauss law}) \qquad \boldsymbol{D} = \varepsilon \boldsymbol{E},$$

$$\nabla \times \mathbf{D} = 0$$

- Varying permittivity
- potentials to fields
- most general form

General constraint

$$\dot{\boldsymbol{D}} + \boldsymbol{j} - \nabla \times \dot{\boldsymbol{\Theta}} = 0 \qquad \boldsymbol{B} = \frac{1}{c^2}\dot{\boldsymbol{\Theta}}.$$

Lagrangian treatment leads to equations of motion for the particles and fields.

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Maggswellian Dynamics with $\varepsilon_r(r)$

- Naturally formulated on a lattice (=>fast and local)
- Changing speed of light (CPMD) (=> tricky)
- Implemented in ESPResSo as **MEMD** (=> useful)

Leads naturally to Maxwell-like equations

A. C. Maggs and V. Rosseto, PRL **88**, 196402 (2002).
J. Rottler and A. C. Maggs, PRL **93,** 170201 (2004).
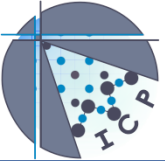
$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = -\frac{\partial U}{\partial \mathbf{r}_i} + \frac{e_i}{\varepsilon}\mathbf{D}(\mathbf{r}_i)$$

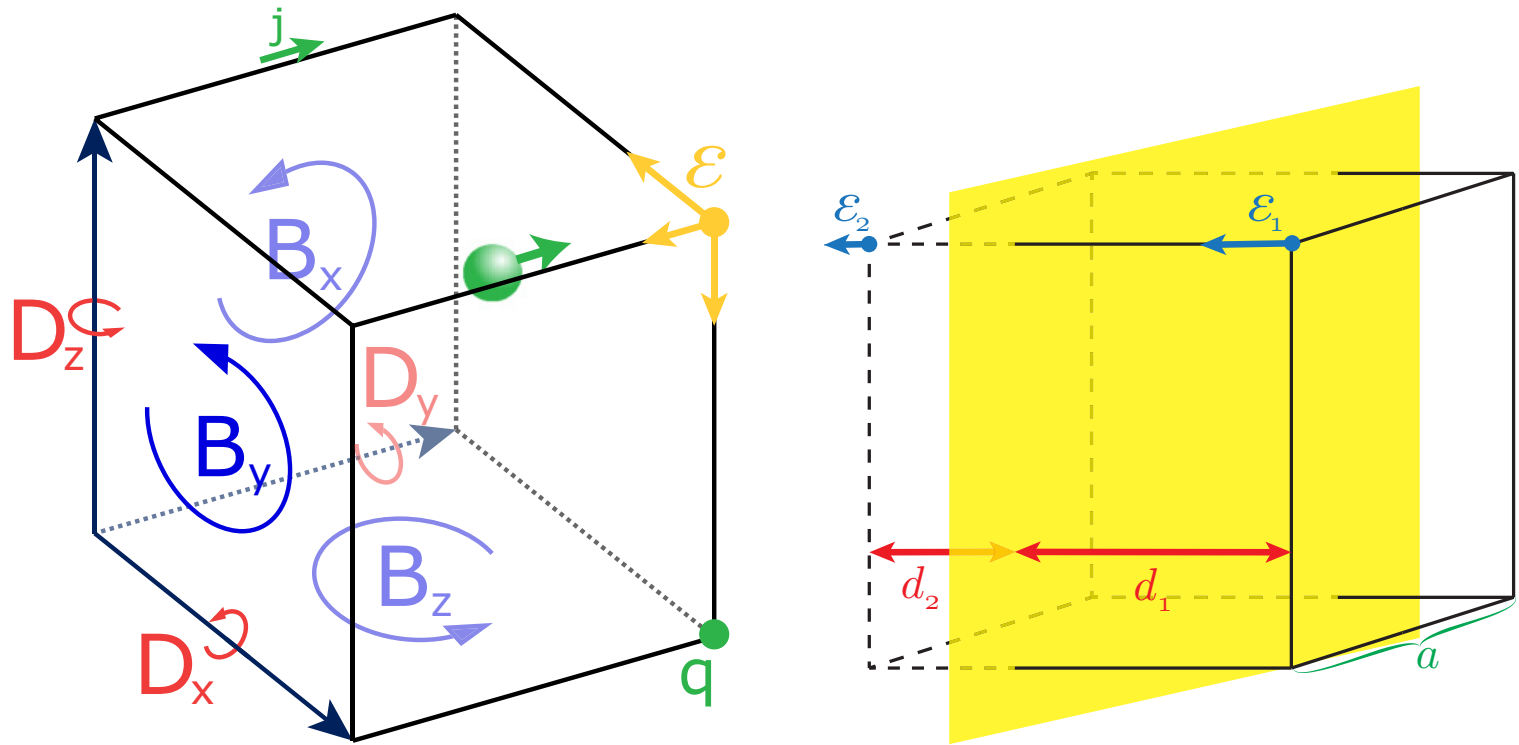I. Pasichnyk and B. Dünweg, J. Phys. Cond.Mat. **16**, 3999 (2004).
F. Fahrenberger, C. Holm, Phys. Rev. E **90,** 063304 (2014)

$$\dot{\mathbf{A}} = -\frac{\mathbf{D}}{\varepsilon}$$
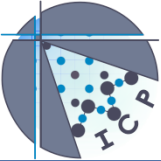
$$\dot{\mathbf{D}} = c^2 \nabla \times (\nabla \times \mathbf{A}) - \frac{\mathbf{j}}{\varepsilon}$$
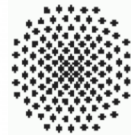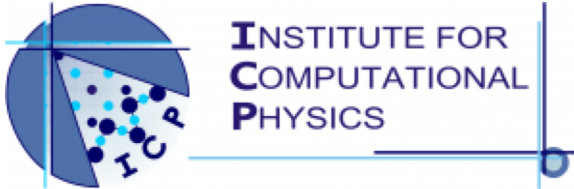
MEMD with Variable Dielectric

- permittivity as a vector (differential1-form), taken as the difference between adjacent lattice points (harmonic average)
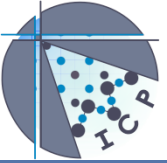
Chance to visit Stuttgart

Tutorial:

„Particle-based Simulations for Hard and Soft Matter"

It takes place at the Institute for Computational Physics, Stuttgart University, **08 - 12 October, 2018**
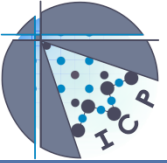
To register look at **www.espressomd.org or https://www.cecam.org/workshop-1605.html**

Wrap up Lecture 1:

- Electrostatic Terminology, Flory arguments, Blobology

- Cell model, Mean-field theories (PB, DH) to describe ionic profiles around charged objects

- Basic simulation methods to describe charged systems

- How to simulate long range interactions with pbc

Any Questions??

Acknowledgements

M. Deserno, A. Arnold, F. Weik, F. Fahrenberger, Z. Xu, J. de Joanis, O. Lenz, S. Tyagi, and many more….

www.espressomd.org

SFB 716

Dynamische Simulation von
Systemen mit großen Teilchenzahlen