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Dynamics of Charged Soft Matter

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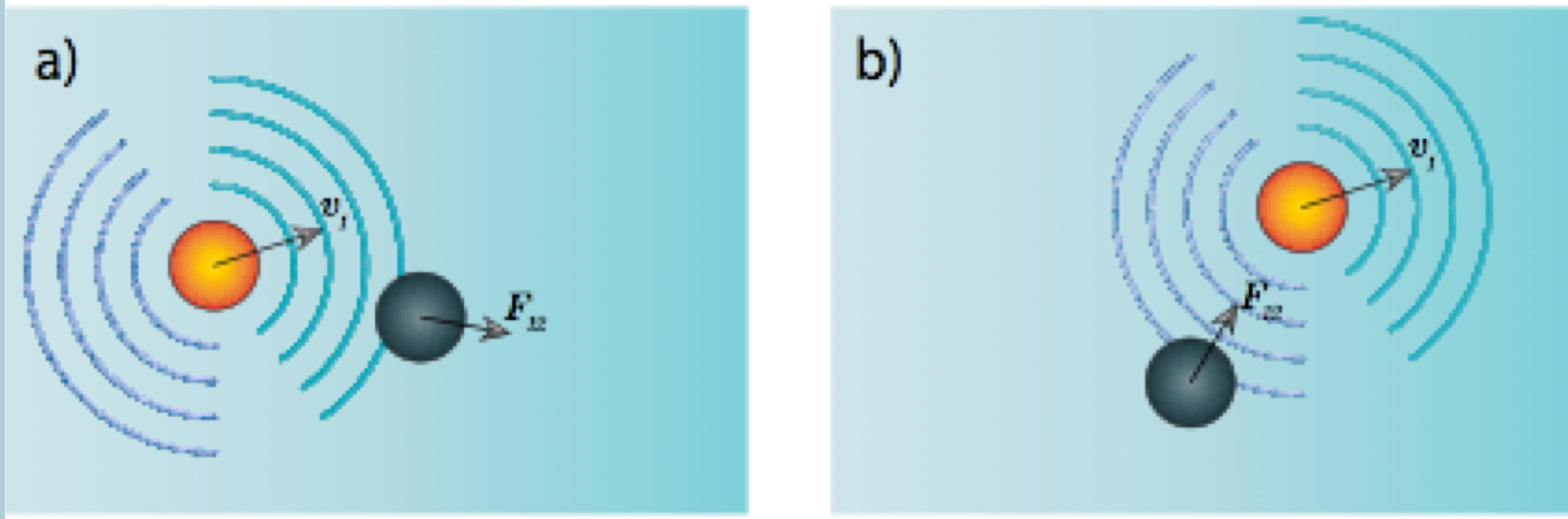
Outline Lecture 2

- The Lattice-Boltzmann method coupled to MD particles
- Applications:
  - Colloidal electrophoresis
  - Polymer electrophoresis
  - Electrophoresis on “Hairy” Colloids
  - Ion transport through nanopores (with and without a DNA being present)
  - Ionic conductivity of a polyelectrolyte solution

Intro to Dynamics

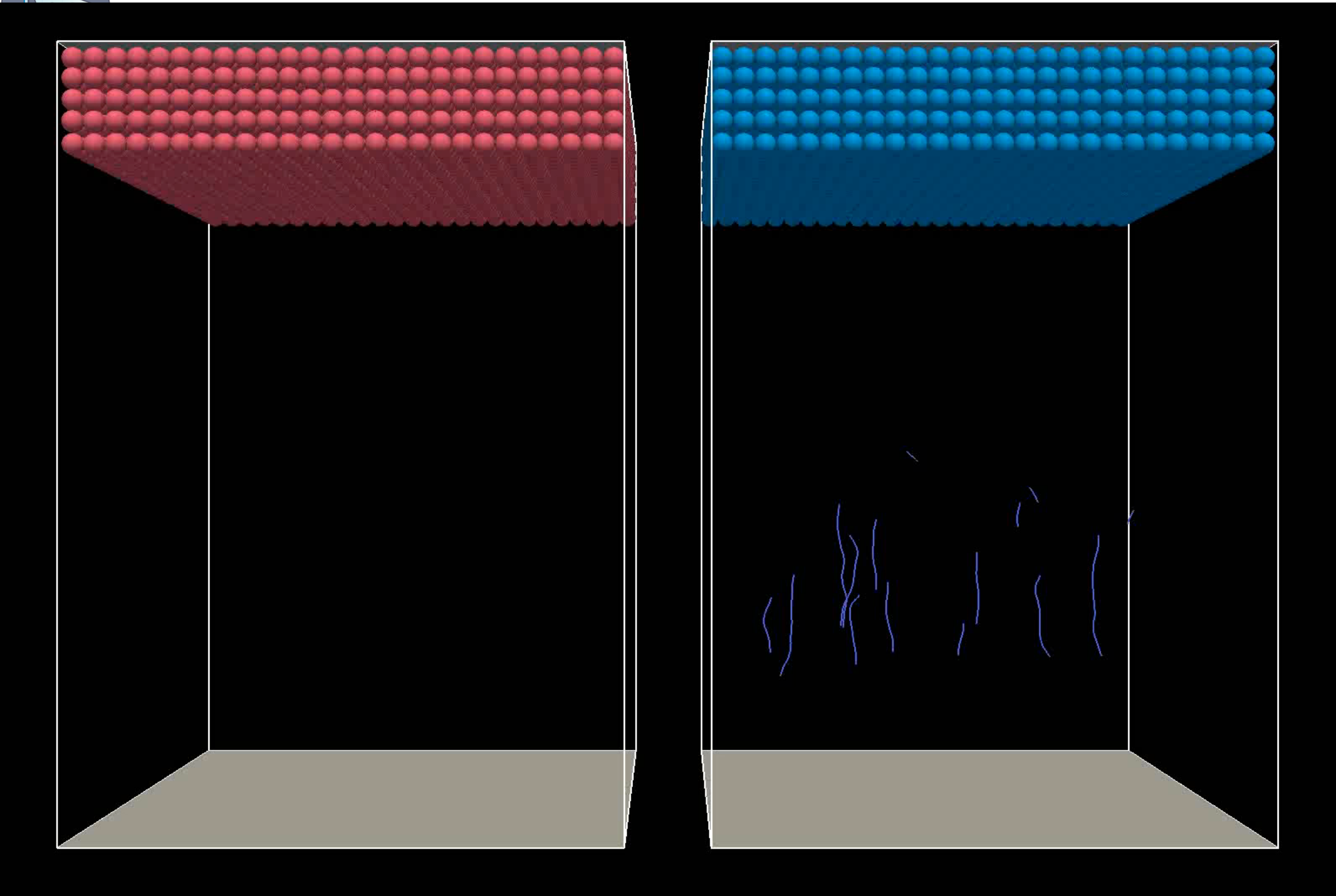
Hydrodynamic Interactions for two Colloids



The yellow particle has a velocity v, whereas the dark particle is at rest.

a) When the yellow particle moves towards the darker one, it induces a repulsive force F_{12} on the darker particle due to the bow waves

a) when the darker particle is behind the yellow one, then the induced force F_{12} is attractive since the stern waves follow the brighter particles thus pulling the darker particle behind



The Lattice-Boltzmann Method

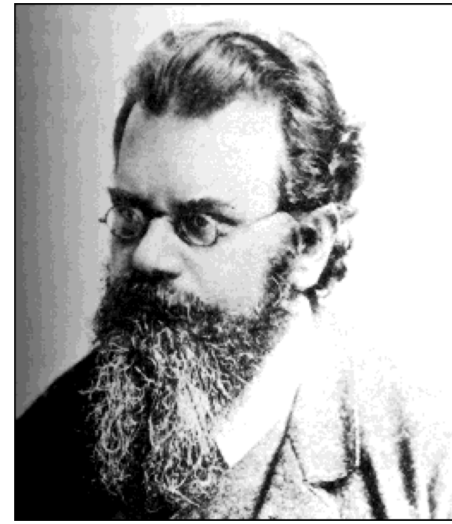
Particle distribution function

$$f(\vec{x},\vec{p},t)$$

$$\frac{d}{dt}f=\nabla_{\vec{x}}f\cdot\dot{\vec{x}}+\nabla_{\vec{p}}f\cdot\dot{\vec{p}}+\partial_t f$$

$$=\nabla_{\vec{x}}f\cdot\frac{\vec{p}}{m}+\nabla_{\vec{p}}f\cdot\vec{F}+\partial_t f$$

Boltzmann equation for kinetic theorie of gases



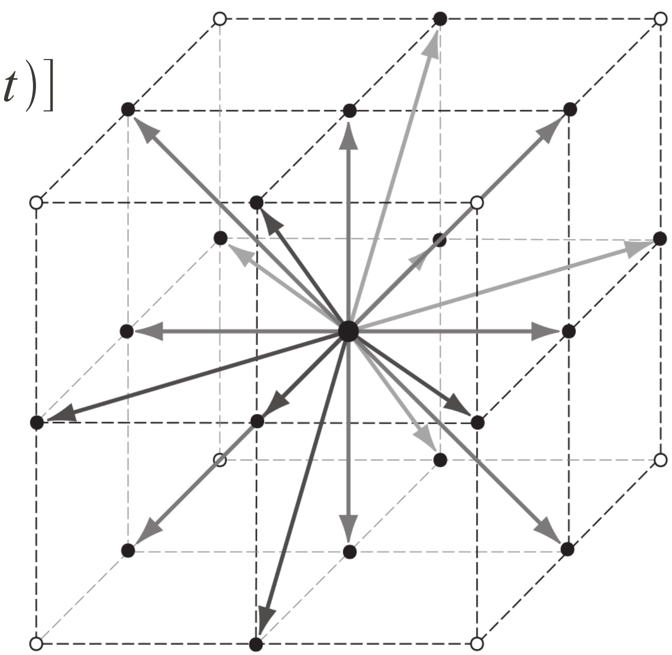
Discretisation of time and drive towards local equilibrium

BGK

$$f(x,t+\Delta t)=f(x,t)+\frac{1}{\tau}\cdot[f^{eq}(x)-f(x,t)]$$

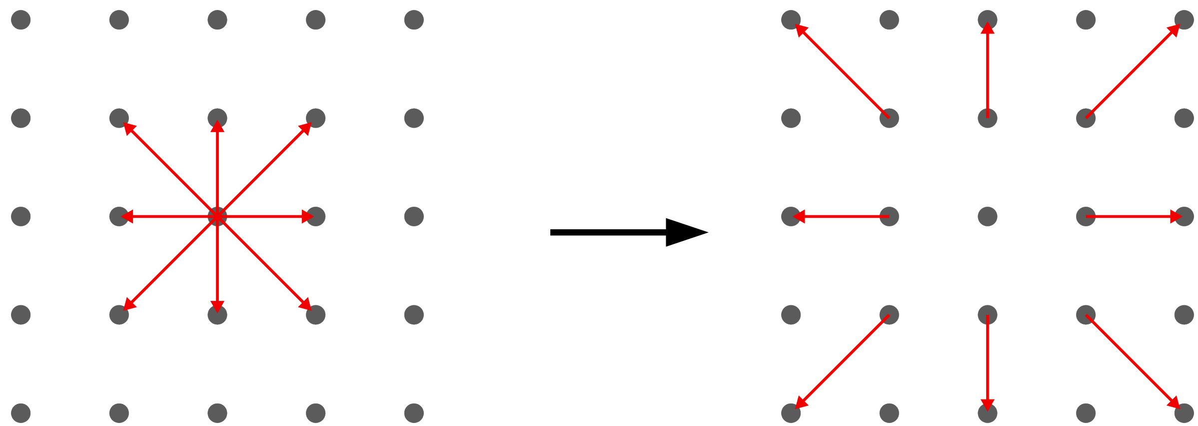
Full discretisation of time, space and velocities

D3Q19 lattice



The Lattice-Boltzmann Method

Streaming



Collision (multimode version)

$$\rho = \sum_{i=0}^{18} n_i$$

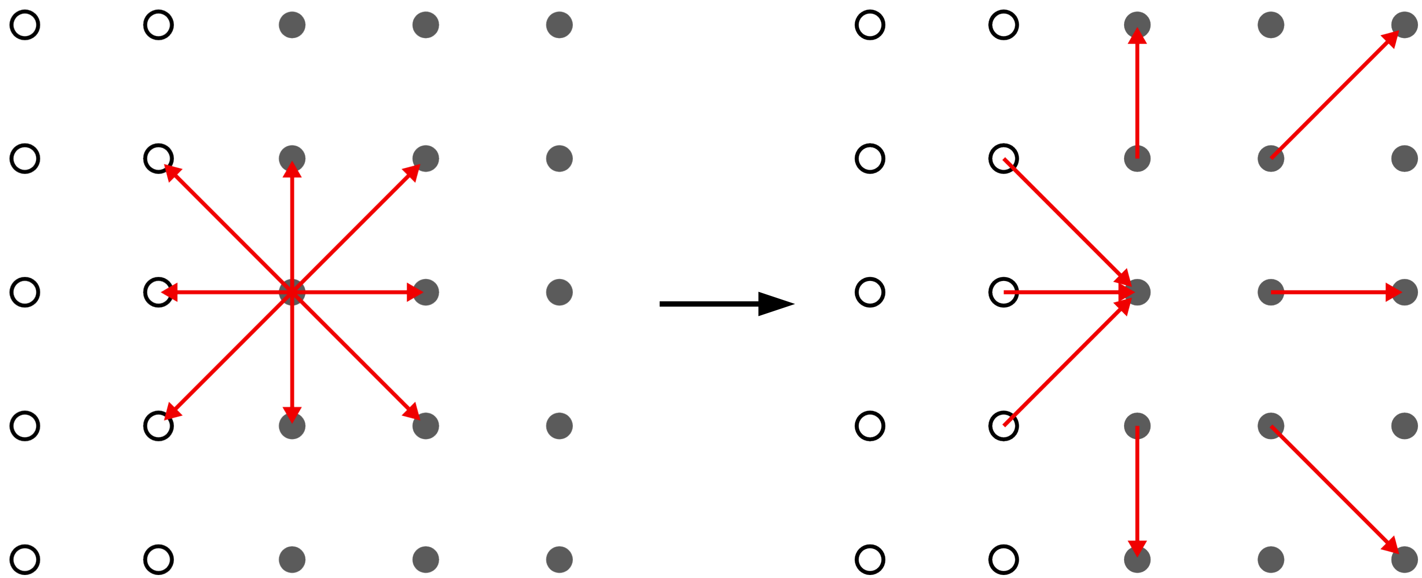
$$\vec{j} = \sum_{i=0}^{18} n_i \cdot \vec{c}_i$$

$$\dots$$

mode	meaning	relaxation parameter
0	density	0
1-3	momentum	0
4-6	bulk stress	finite
7-12	sheer stress	finite
13-18	none	0

B. Dünweg, U. Schiller, and A. J. C. Ladd, Statistical mechanics of the fluctuating Lattice-Boltzmann equation, Phys. Rev. E, 76, 36704, 2007.

Walls in LB via bounce-back rules



Particle Coupling to LB

- Frictional coupling of MD particles to Lattice Boltzmann fluid [1]
  - Modified Langevin equation:

$$\boxed{m \frac{\vec{v}_i}{dt} = \vec{F}_i - \Gamma(\vec{v}_i - \vec{u}_{\mathrm{LB}}) + \vec{F}_r(t)}$$

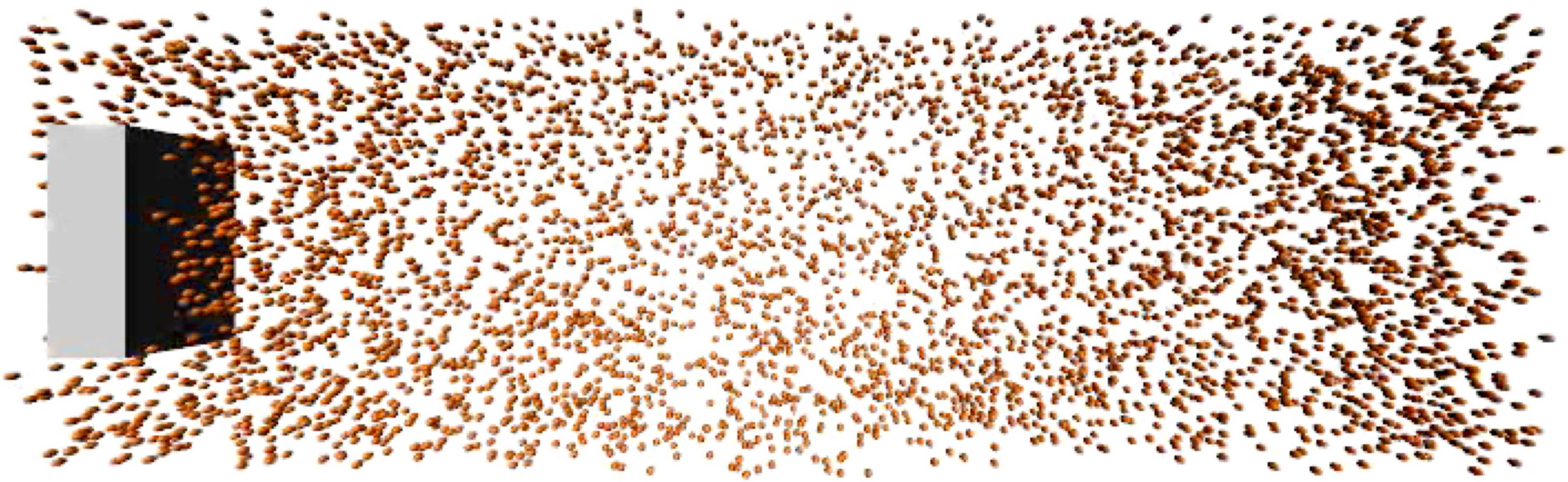
  - Momentum exchange between immersed particles and fluid
  - Total momentum conservation

Hydrodynamic interactions

[1] P. Ahlrichs and B. Dünweg. *International Journal of Modern Physics C*, 9:1429-1438, 1998.

Current D3Q19 Version with correct fluctuation spectrum due to Schiller, Duenweg implemented in **ESPResSo**

Particles Coupled to Fluid Flow

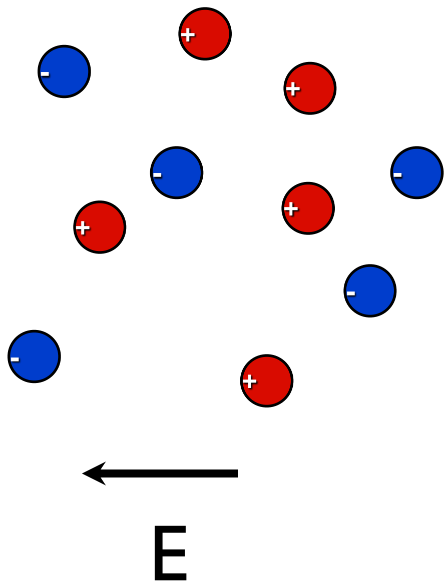


Electrostatics basic Abbreviations

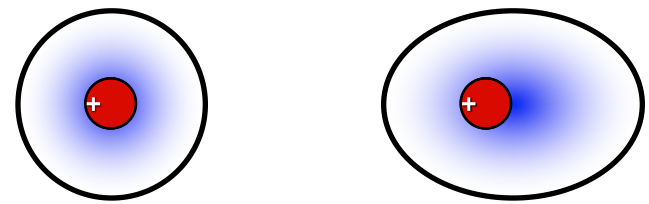
- Bjerrum length $$\ell_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}$$

- Debye length $$\lambda_{\mathrm{D}} = \left(4\pi l_{\mathrm{B}} N_{\mathrm{A}} \sum_i z_i^2 c_i^\infty\right)^{-1/2}$$

Electrolyte Conductivity



Relaxation Effect



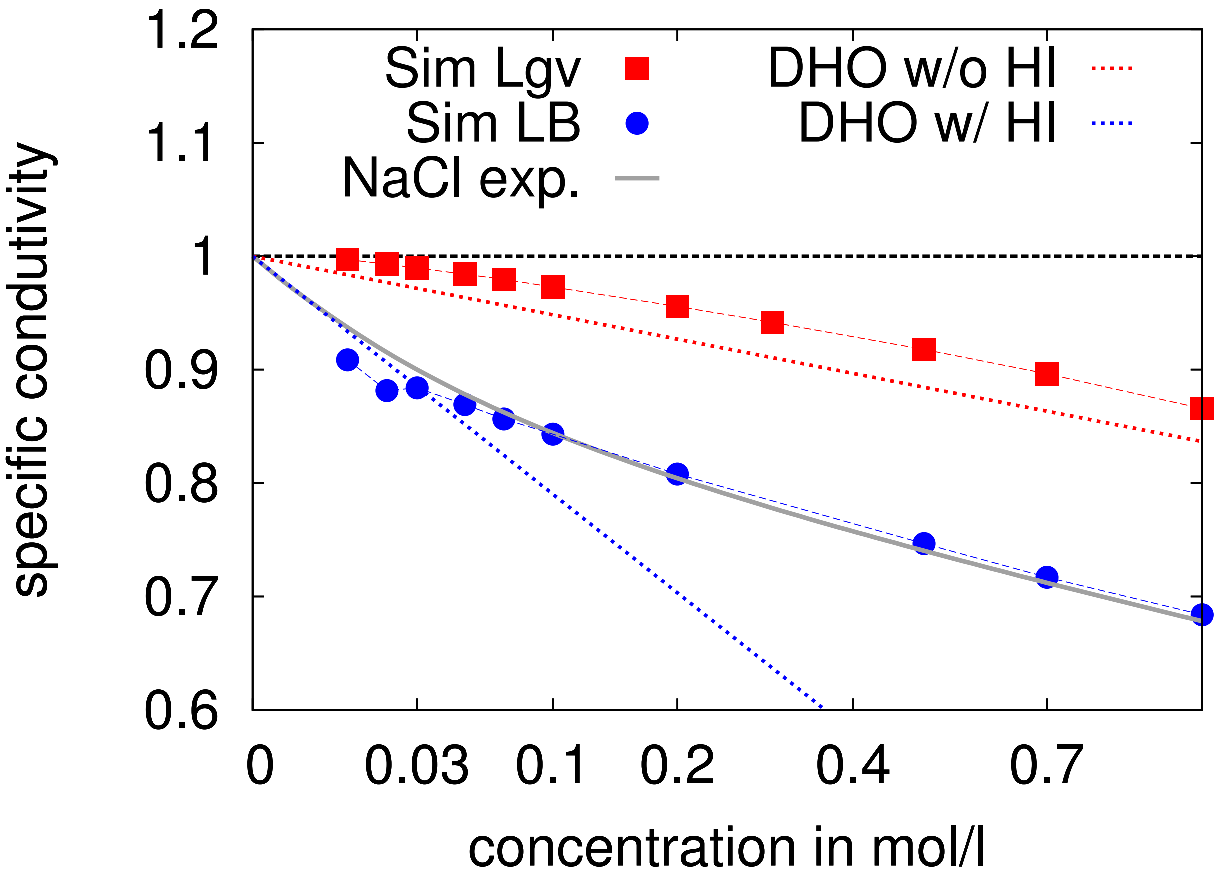
Electrophoretic Effect

Onsager 1927

$$\lambda = \lambda^{\infty}\left[1 - 0.07\frac{l_B}{l_D} - \frac{r_{\text{ion}}}{l_D}\right]$$

Specific conductivity

Specific Conductivity depends on c



- Debye-Hückel-Onsager (DHO) works for low concentrations (w HI)
- Experimental results of NaCl for different concentrations are well reproduced by primitive model MD/LB simulations!!

Applications

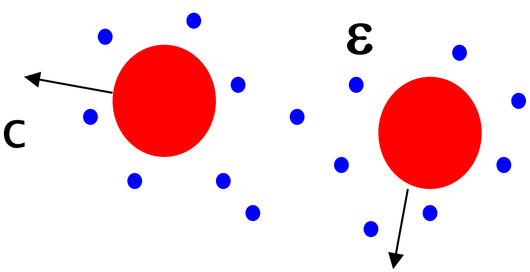
Charge stabilized Colloids

The analytical description of charged colloidal suspensions is problematic:

- Long ranged interactions: electrostatics/hydrodynamics
- Inhomogeneous/asymmetrical systems
- Many-body interactions

Alternative: the relevant microscopic degrees of freedom are simulated via Molecular Dynamics!

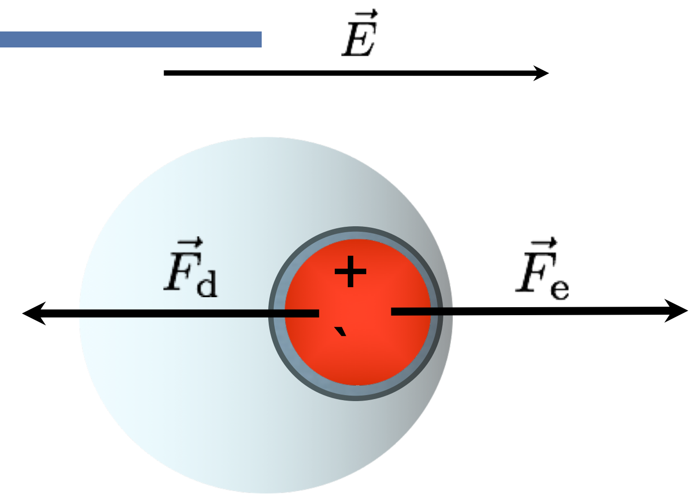
- Explicit particles (ions) with charges
- Implicit solvent approach, but hydrodynamic interactions of the solvent are included via a Lattice-Boltzmann algorithm



Colloidal Electrophoresis

$\vec{F}_\mathrm{e}$: electric force

$\vec{F}_\mathrm{d}$: hydrodynamic drag force



Steady State: $\vec{F}_\mathrm{tot} = \vec{0}$

$$\boxed{\mu = \frac{|\vec{v}_\mathrm{d}|}{|\vec{E}|}}$$

Electric Double Layer (EDL):

i) Stern layer (strongly bound counterions)

ii) Diffuse layer characterized by the Debye length

Electro-osmotic Flow (EOF):

Fluid flow generated by the excess charge in the EDL.

Counterpart of the electrophoretic flow.

Electrokinetic Equations

Stokes equation:

$$\eta \nabla^2 \vec{u} - \vec{\nabla} P - \sum_{j=1}^{N} n_j z_j e \vec{\nabla} \psi = \vec{0}$$

Nernst-Planck equation:

$$\lambda_j (\vec{u} - \vec{v}_j) - z_j e \vec{\nabla} \psi - k_{\mathrm{B}} T \vec{\nabla} \log n_j = \vec{0}$$

Incompressibility:

$$\vec{\nabla} \cdot \vec{u} = \vec{0}$$

Important boundary condition:

ζ : Potential at the slip plane relative to the bulk

Electrokinetic Equations: Limits

Hückel limit of no salt ($\kappa R \ll 1$): $\kappa = \lambda_D^{-1}$

$$\mu = \frac{Q}{6\pi\eta R} = \frac{2\epsilon}{3\eta}\zeta \qquad \left(\zeta = \frac{Q}{4\pi\epsilon R}\right)$$

Helmholtz-Smoluchowski limit of high salt ($\kappa R \gg 1$):

$$\mu = \epsilon\zeta/\eta$$

Planar geometry.
Valid only for small ζ.

$$\mu_{red} = 6\pi\eta\ell_B\mu$$

$$\zeta_{red} = e\zeta/k_BT$$

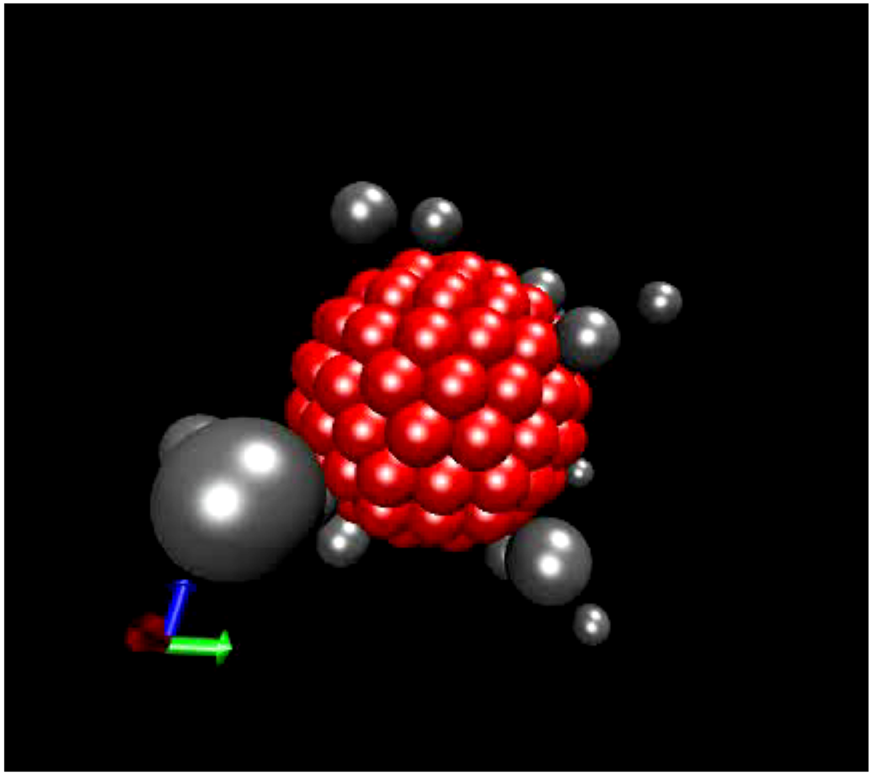
Numerical Solutions:

Standard Electrokinetic Model (SEM)*,**
Poisson-Boltzmann description of the electrostatics
First-order linearization and decoupling of the EK equations.

* Wiersema *et al.*, J. Col. Int. Sci. 22, 78-99 (1966).
** O' Brien *et al.*, J. Chem. Soc. Faraday Trans. II 74, 1607-1626 (1978).

… or simply solve the equations with, i.e. COMSOL

Electro-Hydrodynamical Model



charged colloid

- **driven system**

(external constant E –field)

- **1 central Lennard-Jones (LJ) bead**
- **100 LJ monomers on the surface, connected to a network via FENE bonds**
- **counterions: LJ beads**

simulation=> lattice (implicit) hydrodynamics

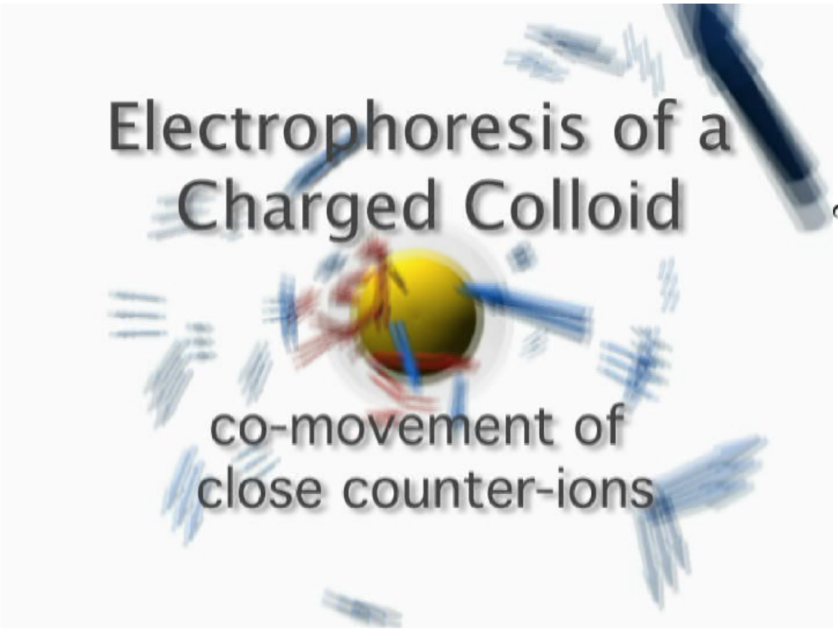
Langevin MD + Lattice-Boltzmann algorithm

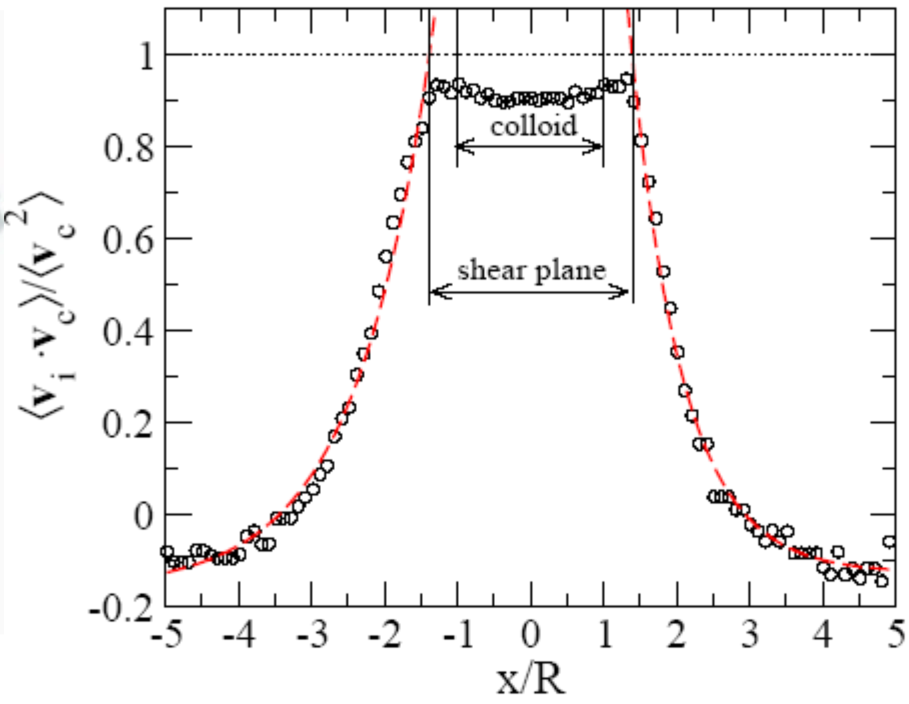
periodic boundary conditions

Ewald sum: P^3M

V. Lobaskin, B. Dünweg, CH J. Phys.: Condens. Matter **16**, S4063-S4073 (2004)

Ionic Distribution around the Colloid

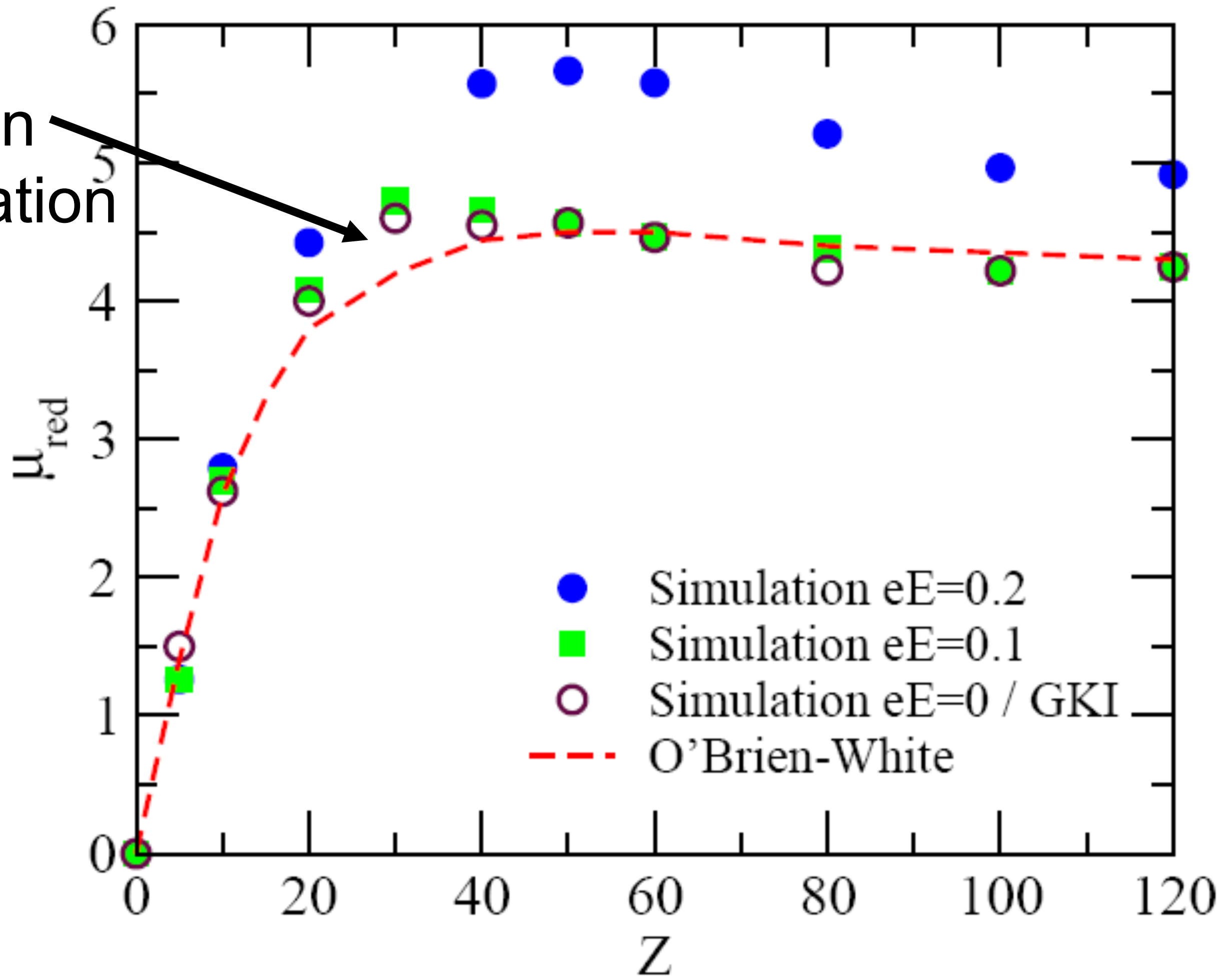




the ions within the shear plane renormalize the charge Z to Z_{eff}

Mobility as a Function of Charge Z

counterion condensation

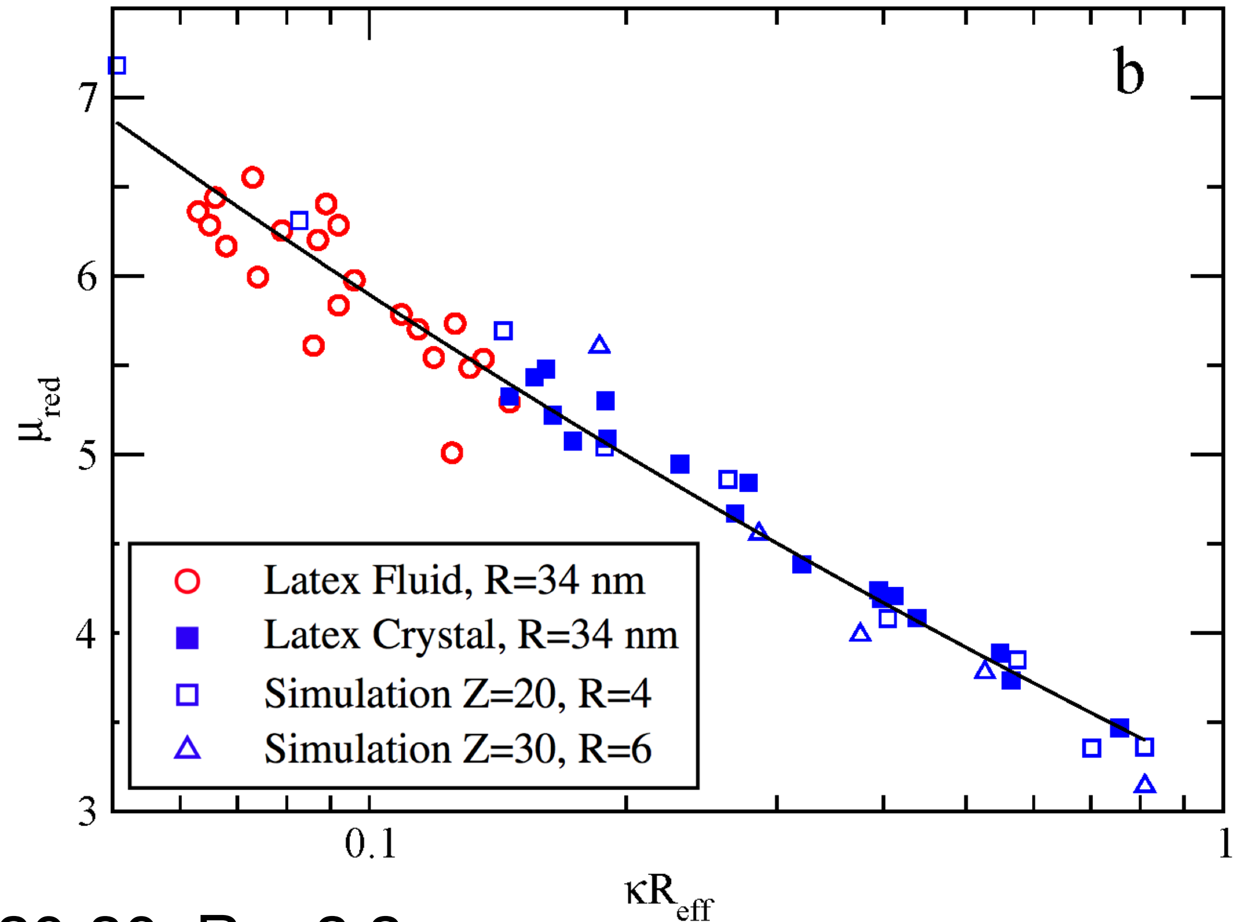


influence of comoving counterions

Mobility is calculated at zero field with the Green-Kubo integral: linear regime

$$\mu = \frac{1}{3k_B T} \sum_i Z_i \int_0^\infty dt \, \langle \vec{v}_c(t) \cdot \vec{v}_i(0) \rangle$$

Comparison to Experiments

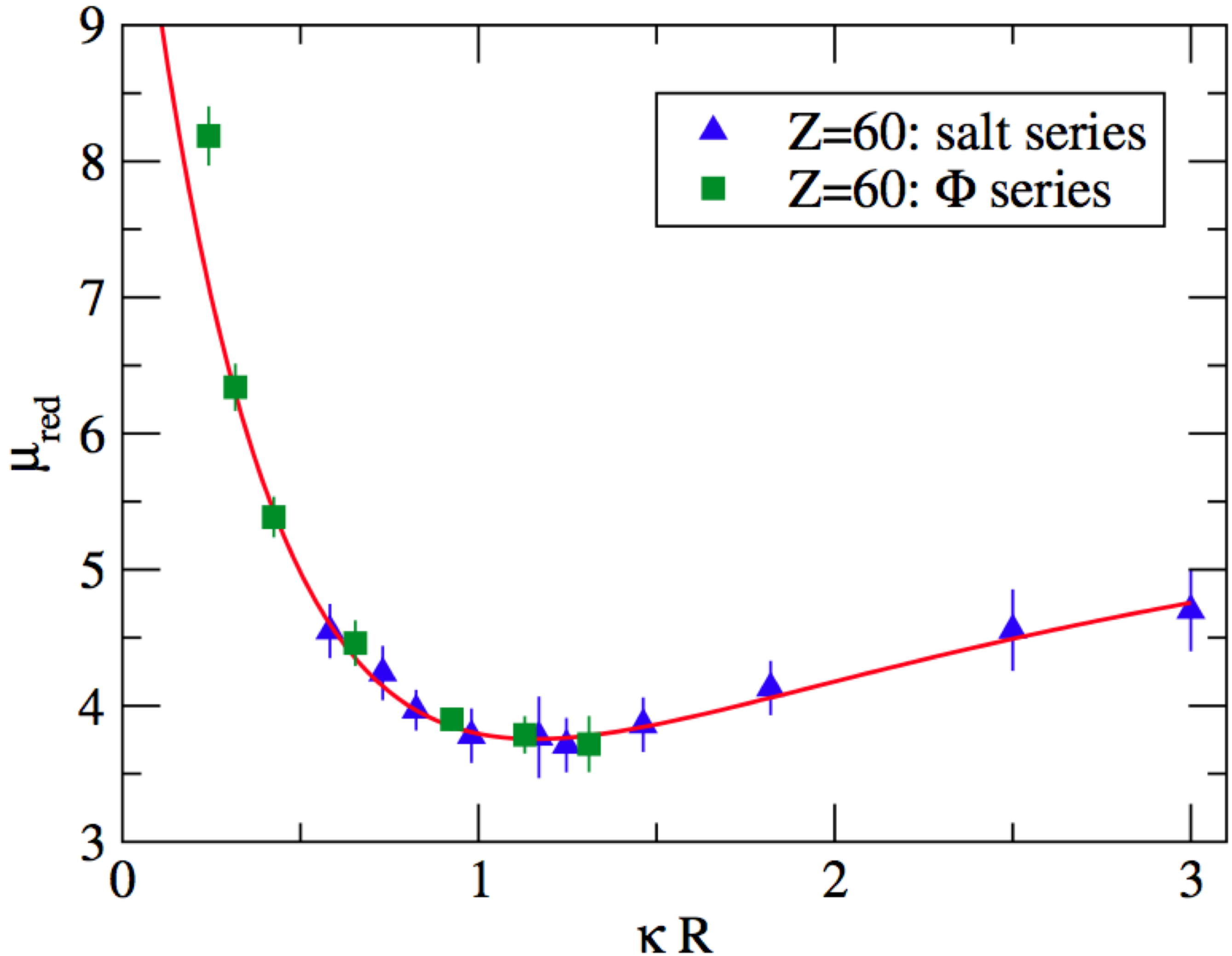


Z_{Eff}=20-30, R = 2.2 nm

$$\kappa^2 = 4\pi\ell_B(n_{salt} + n_M Z_{eff} + n_{H,OH})$$

V. Lobaskin, B. Dünweg, M. Medebach, T. Palberg, CH, PRL **98,** 176105 (2007)

Salt and Concentration Effects



Salt-free simulations at finite Φ can be mapped to simulations including salt

Conclusions

•Successful mapping of simulations of charged colloidal electrophoresis onto experimental values

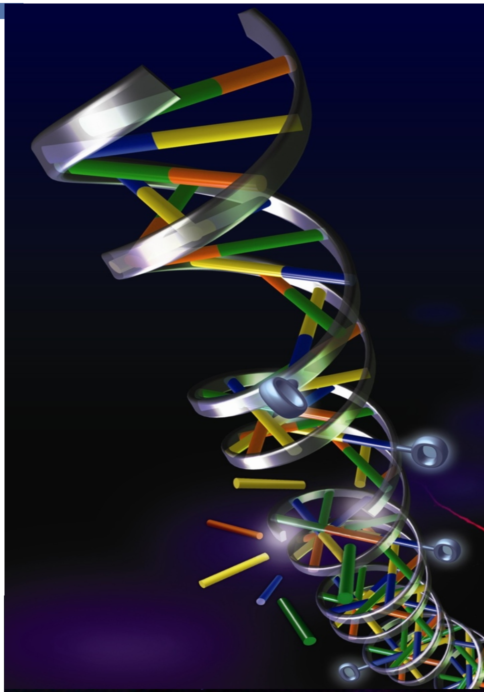
•Colloidal concentration can be mapped on salt concentration

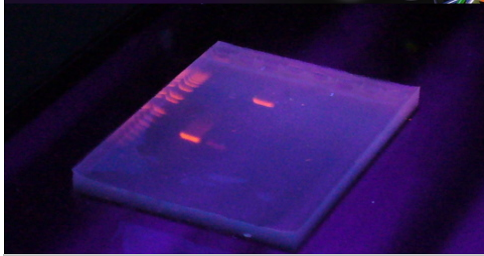
•Intriguing minimum observed in μ_{red} as function of κR

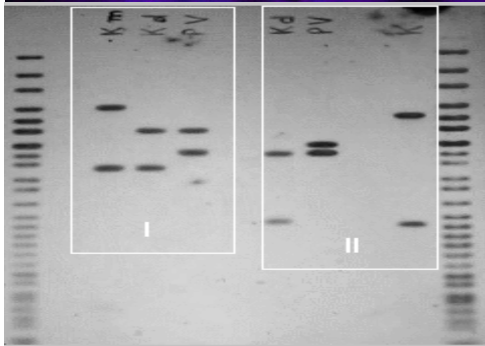
Why care about electrophoresis?

- Electrophoretic separation of DNA
  - Crucial step is gene analysis
  - Yields characteristic genetic finger prints
- Today: Gel Electrophoresis based on entanglement
  - Widely applicable and reliable
  - Slowed down dynamics leads to long elution times
- Future: Novel separation techniques based on hydrodynamic and chemical interactions
  - Micro-fluidic devices with structured surfaces
  - On-going design and development process

First Goal: Understand free-flow Electrophoresis

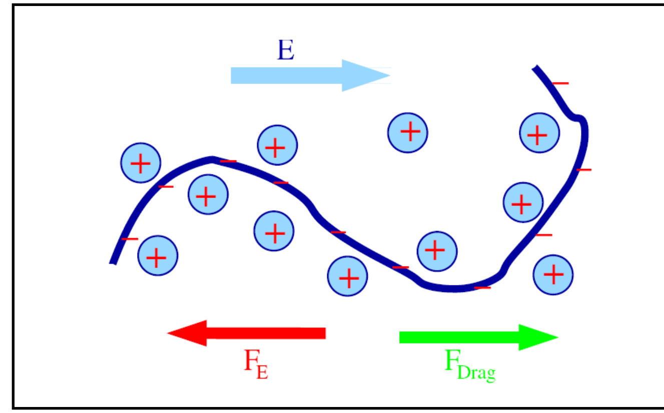






Free-Flow Electrophoresis

- Charged polymers move in solution under the influence of an external electric field



- Local force balance leads to constant velocity
  - Electrical driving force
  - Solvent friction force

$$F_E = Q_{\text{eff}} E$$
$$F_{\text{Drag}} = \Gamma_{\text{eff}} v$$

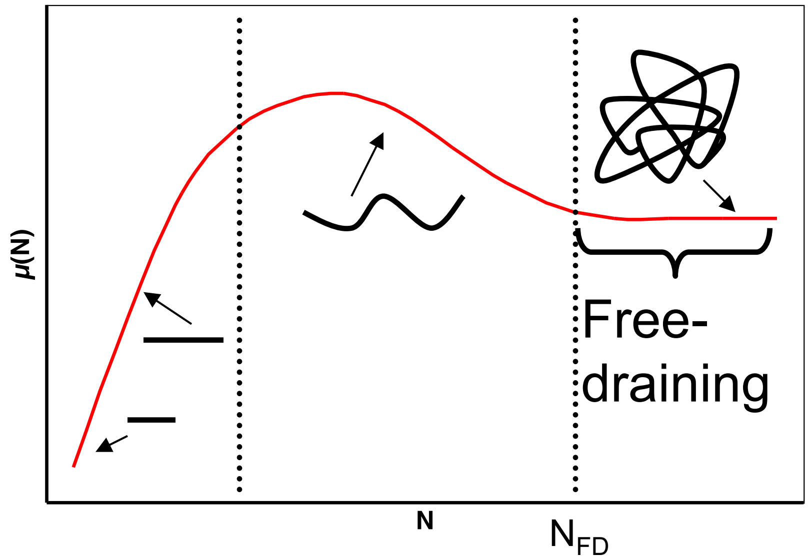
- Electrophoretic mobility μ
  - Size dependence of μ (N) determines separation process

$$\mu = \frac{v}{E} = \frac{Q_{\text{eff}}(N)}{\Gamma_{\text{eff}}(N)}$$

Short and long polyelectrolytes

- Short PE chains:
  - Extended rod-like conformation
  - Length dependent mobility
- Long PE chains:
  - Random coil conformations
  - Screening of long range hydrodynamic interactions
  - Length independent mobility (free-draining)

Experimental observations:



Crossover:

- DNA: N_{FD} ~ 170 bp
- PSS: N_{FD} ~ 100 units

Short and long polyelectrolytes

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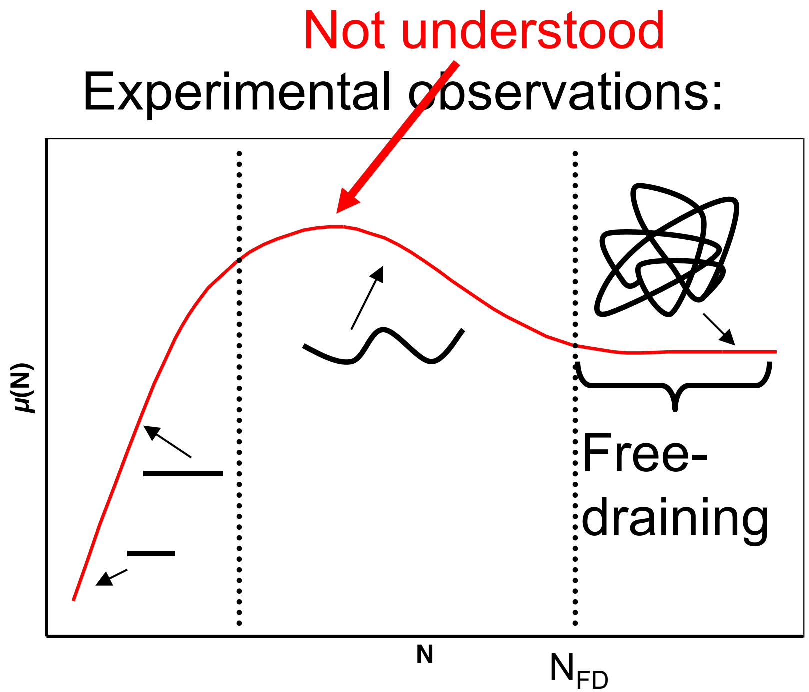
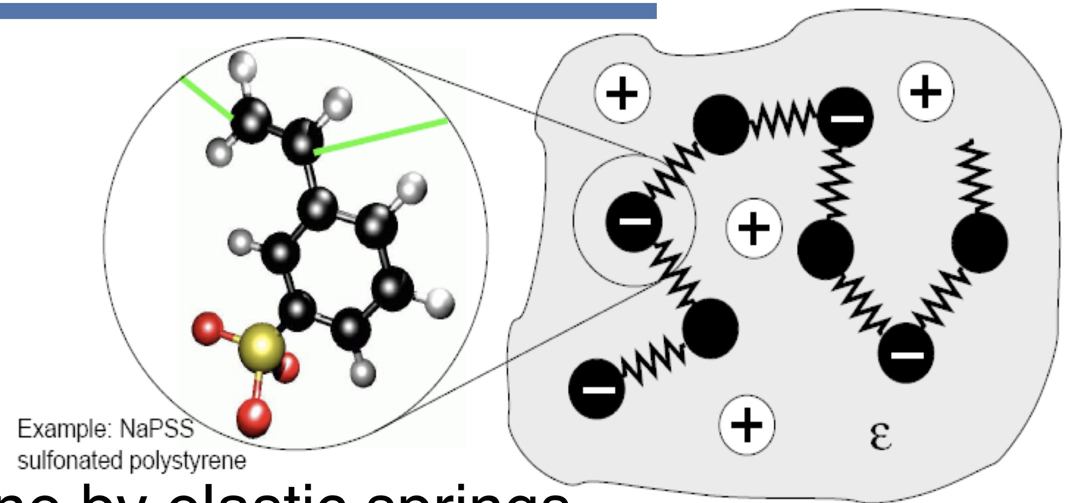


Crossover:

- DNA: N_{FD} ~ 170 bp
- PSS: N_{FD} ~ 100 units

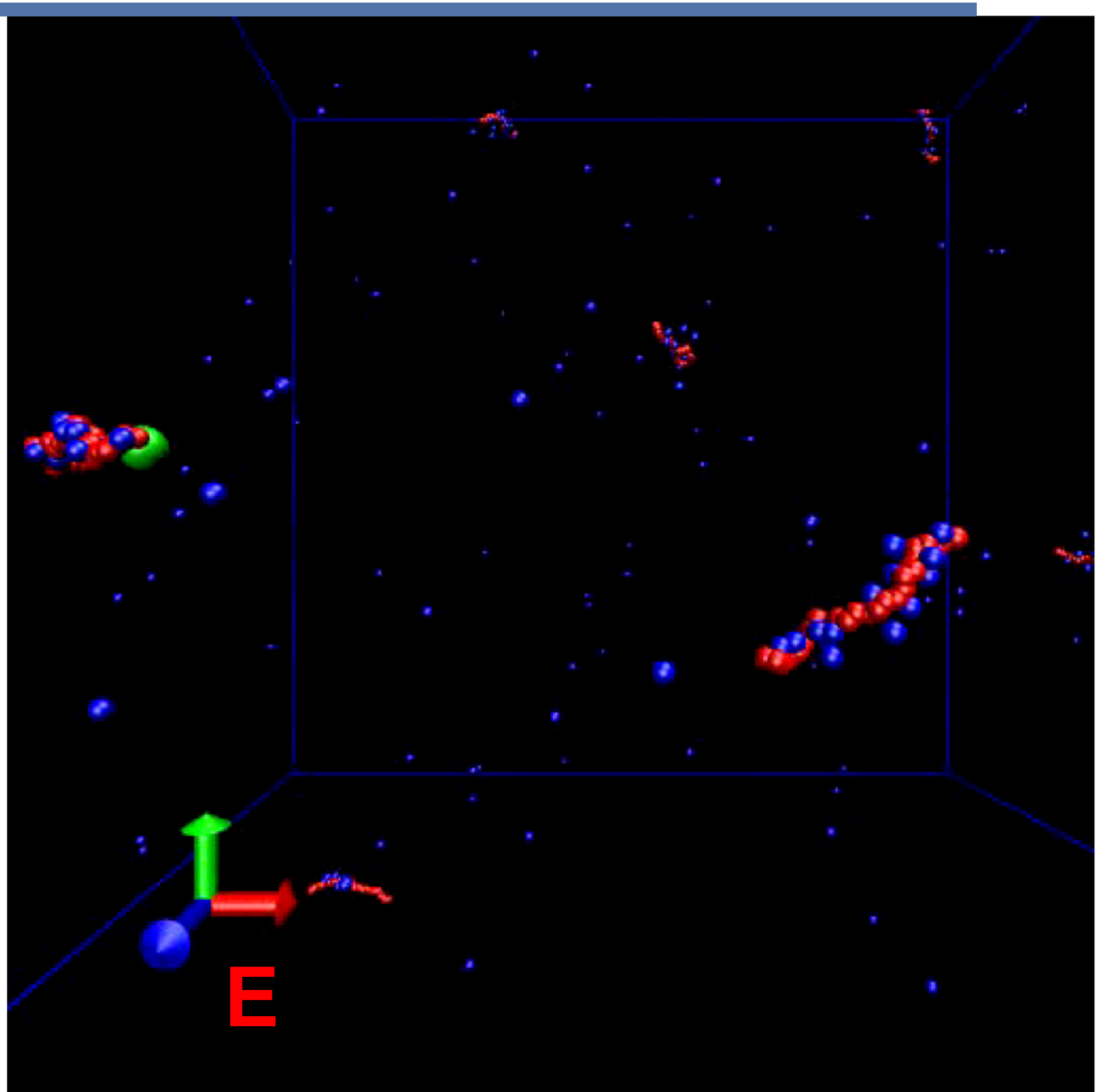
Model

- No chemical details
  - Charged subgroups connected along a backbone by elastic springs



  - Ions modeled as free mobile charges
- Implicit solvent model
  - continuous dielectric background
  - Explicit charges treated with full electrostatics via P3M in p.b.c.
  - Explicit hydrodynamics by frictionally coupling the beads to a Lattice-Boltzmann fluid
  - Can simulate with HI and without HI (Langevin)

Polyelectrolyte-ion-complex



Observables

- (Self-)Diffusion D

$$D = k_B T/\gamma_{\text{eff}} \qquad D = \frac{1}{3}\int_0^\infty d\tau \langle \vec{v}(\tau)\vec{v}(0)\rangle$$

- Electrophoretic mobility μ

$$\mu = v/E = q_{\text{eff}}/\gamma_{\text{eff}} \qquad \mu = \langle v_{PE}\rangle/E$$

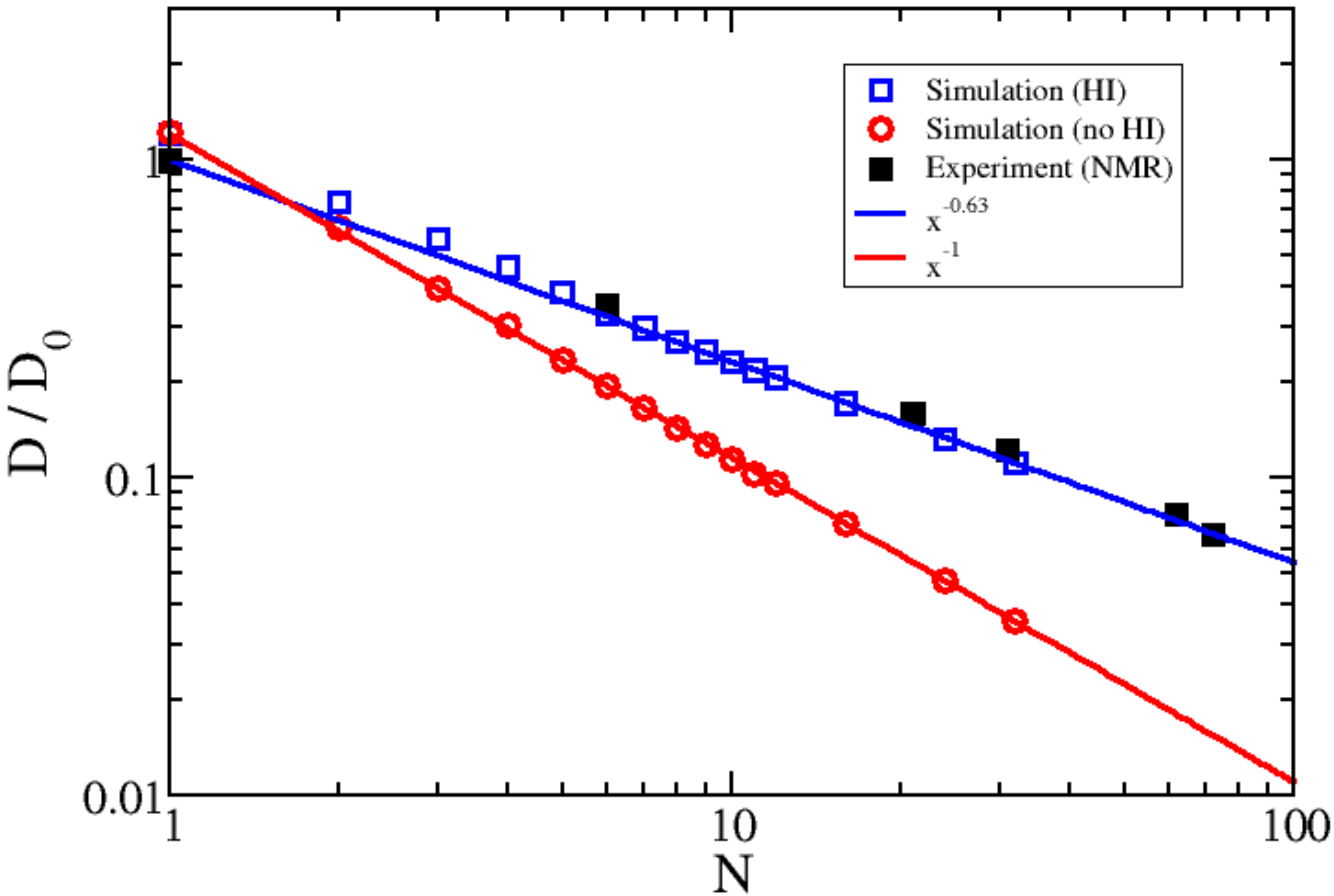
- Zero-field mobility (Green-Kubo):

$$\mu = \frac{1}{3k_BT}\sum_i q_i \int_0^\infty \langle \vec{v}_i(0)\cdot\vec{v}_{PE}(\tau)\rangle d\tau$$

Simulation parameters

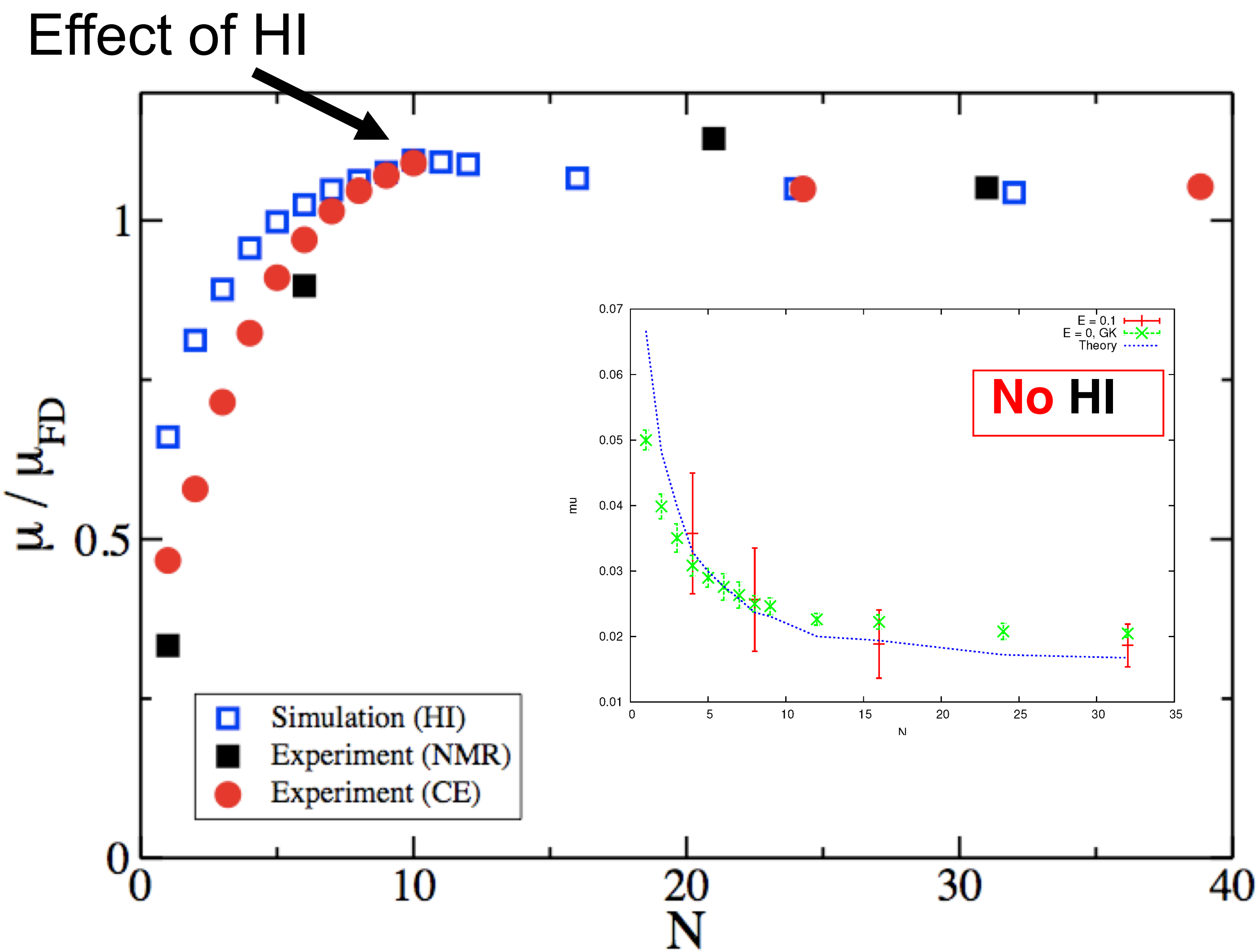
- Mapping on **sulfonated polystyrene** (PSS)
- All beads have diameter of 2.5 Ångström
- Chain length N=1 …64
- l_b = 7.1 Ångström (H_2O at 20° C)
- Monomer concentration 100 mMol
- No added salt
- Experimental conditions:
  - Böhme, Scheler, IPF Dresden, PFG-NMR
  - H. Cottet, CNRS Montpellier, Cap. Elec.

Results 1: Diffusion



K. Grass, U Böhme, U. Scheler, H. Cottet, and C. Holm, Phys. Rev. Lett. **100**, 096104 (2008)

Electrophoretic mobility

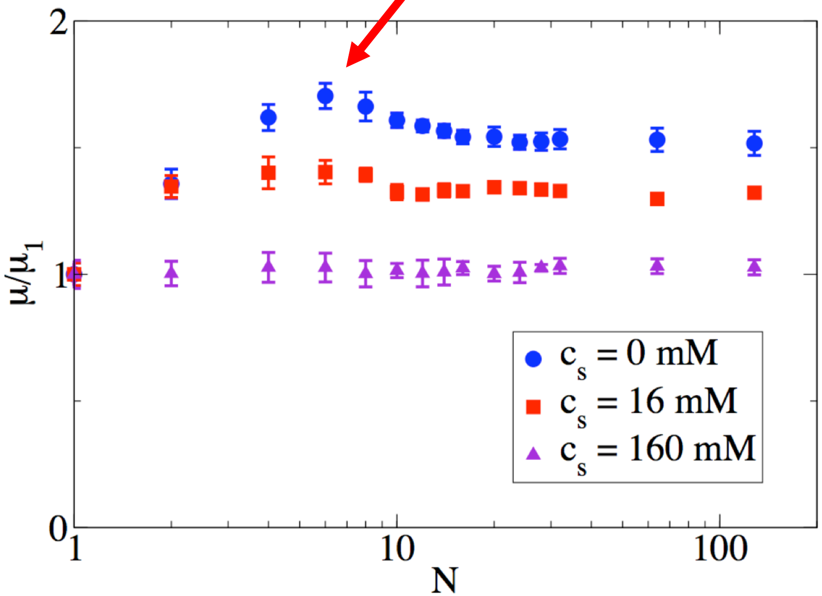


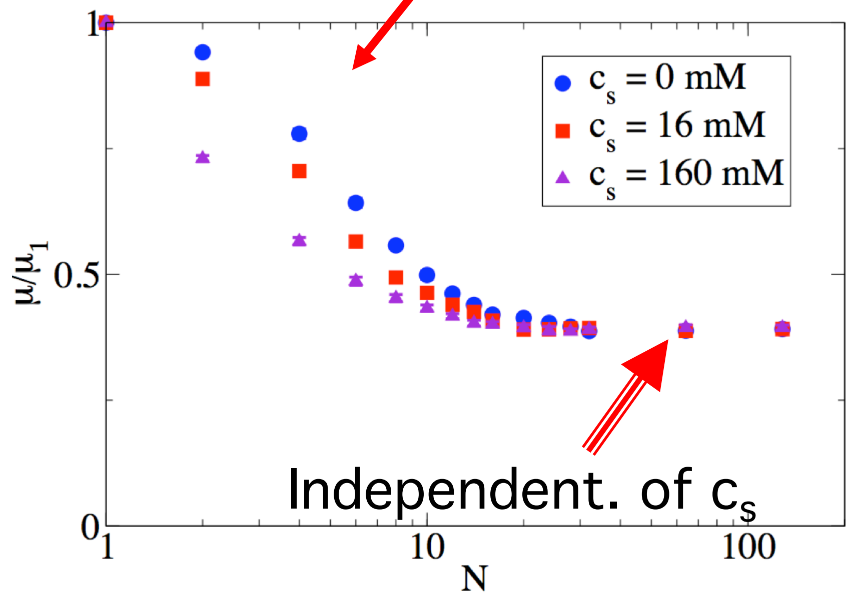
K. Grass, U Böhme, U. Scheler, H. Cottet, and C. Holm, Phys. Rev. Lett. **100**, 096104 (2008)

Salt dependence c_s of Mobility

Maximum reproduced

No maximum





with

without

hydrodynamical interactions (HI)

Conclusion on FSE

- Coarse-grained MD with full electrostatic and explicit hydrodynamic interactions reproduce experimental results on bulk electrophoresis of polyelectrolytes, with and without salt
- Also the self-diffusion coefficient of the PE chain is reproduced if we include HI
- Mobility maximum due to hydrodynamic shielding
- Hydrodynamic shielding for short N, constant friction per monomer for long chains due to hydrodynamic screening

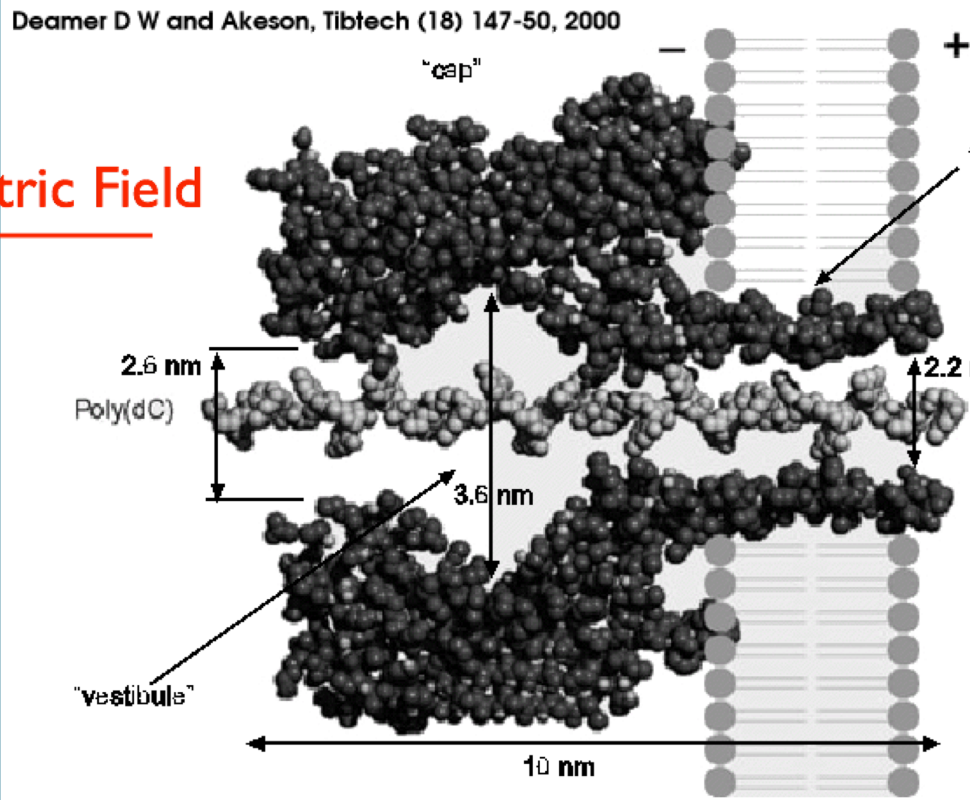
•K. Grass, U. Böhme, U. Scheler, H. Cottet, C. Holm, Phys. Rev. Lett., **100**, 096104 (2008).

•K. Grass, C. Holm, J. Phys.: Condens. Matter **20**, 494217 (2008).

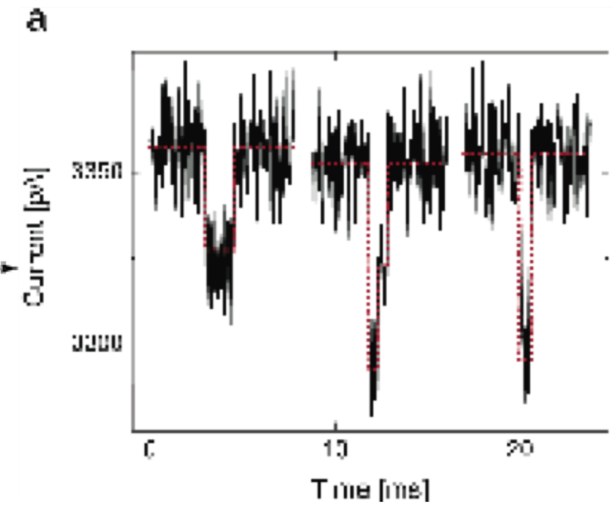
•K. Grass, C. Holm, Soft Matter **5**, 2079 (2009).

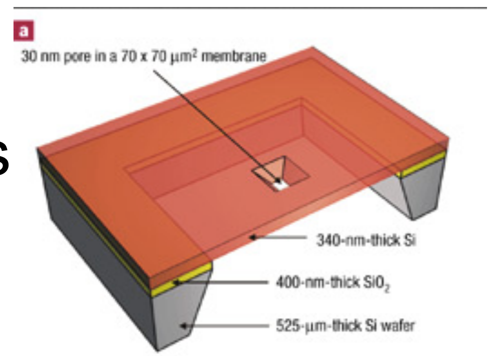
Nanopore Examples

Electric Field



Electric Current

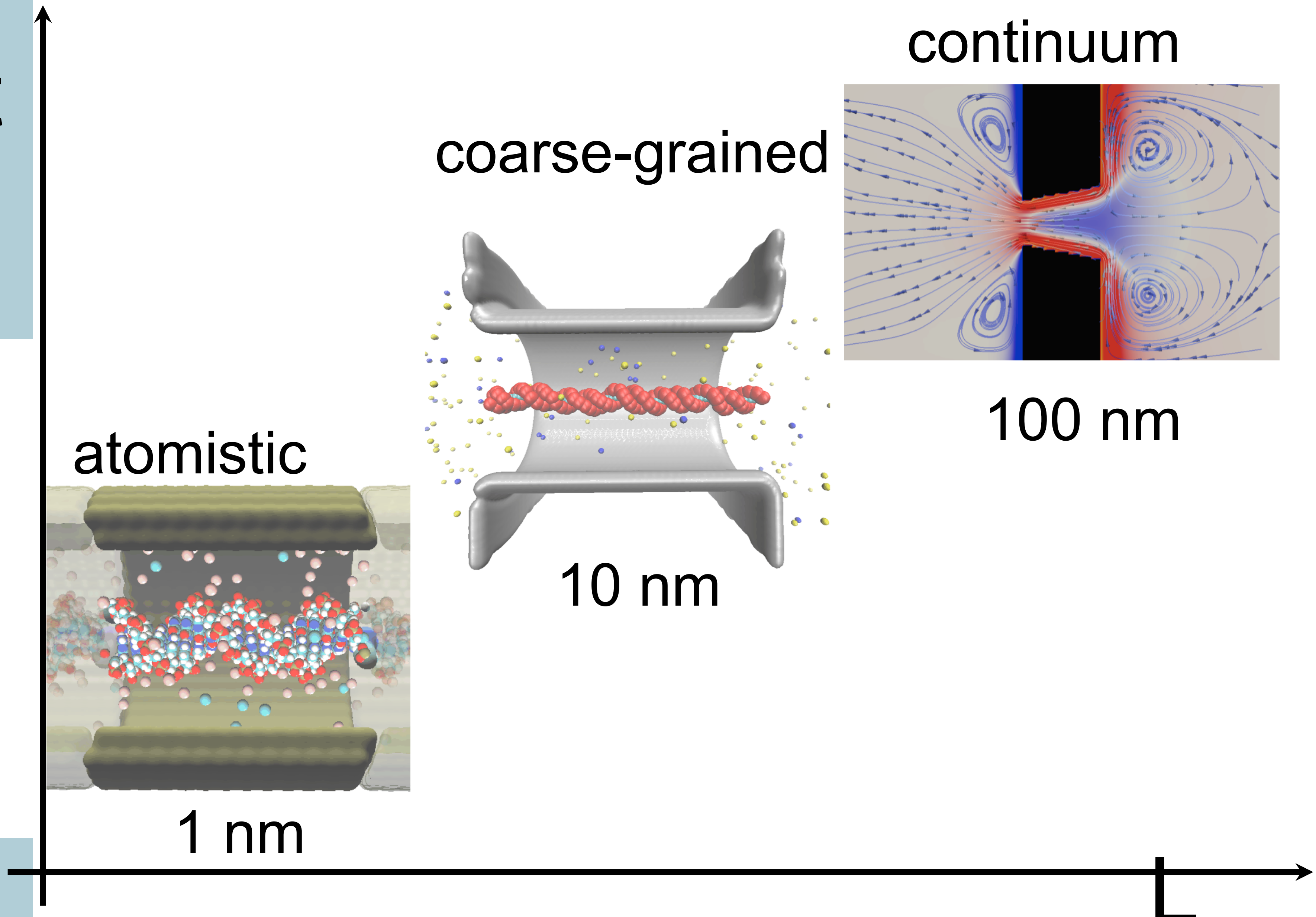




solid state nanopores
Cees Dekker, Delft,
many others here…

- conductivity measurements can reveal bp translocation of ssDNA
- Recognition of binding sites of proteins to DNA

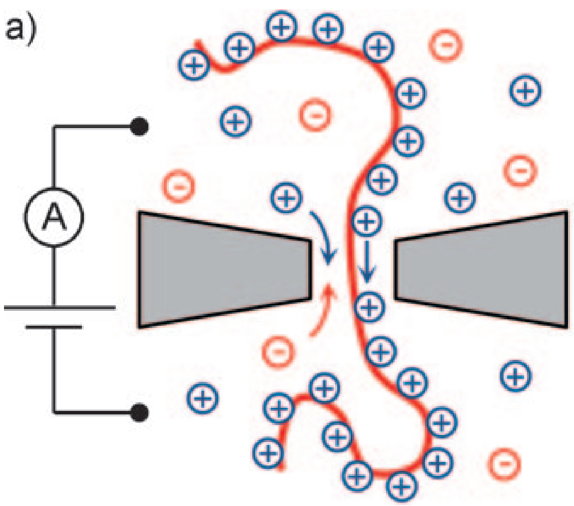
Scale Bridging Modelling Strategy

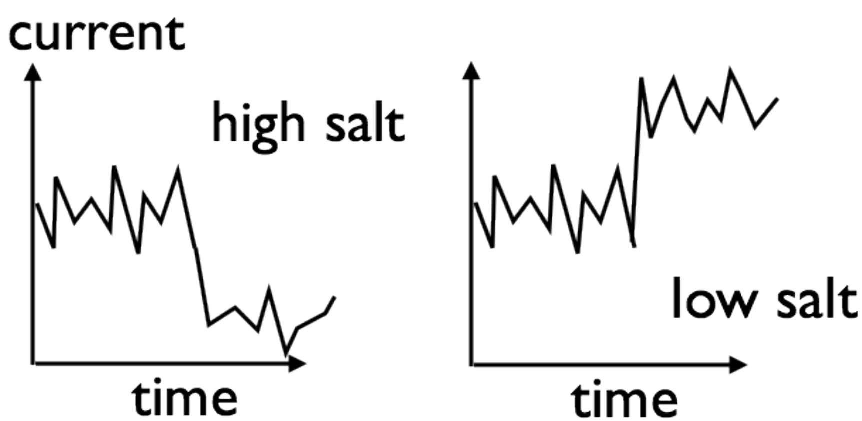


The Smeets et al. Experiment

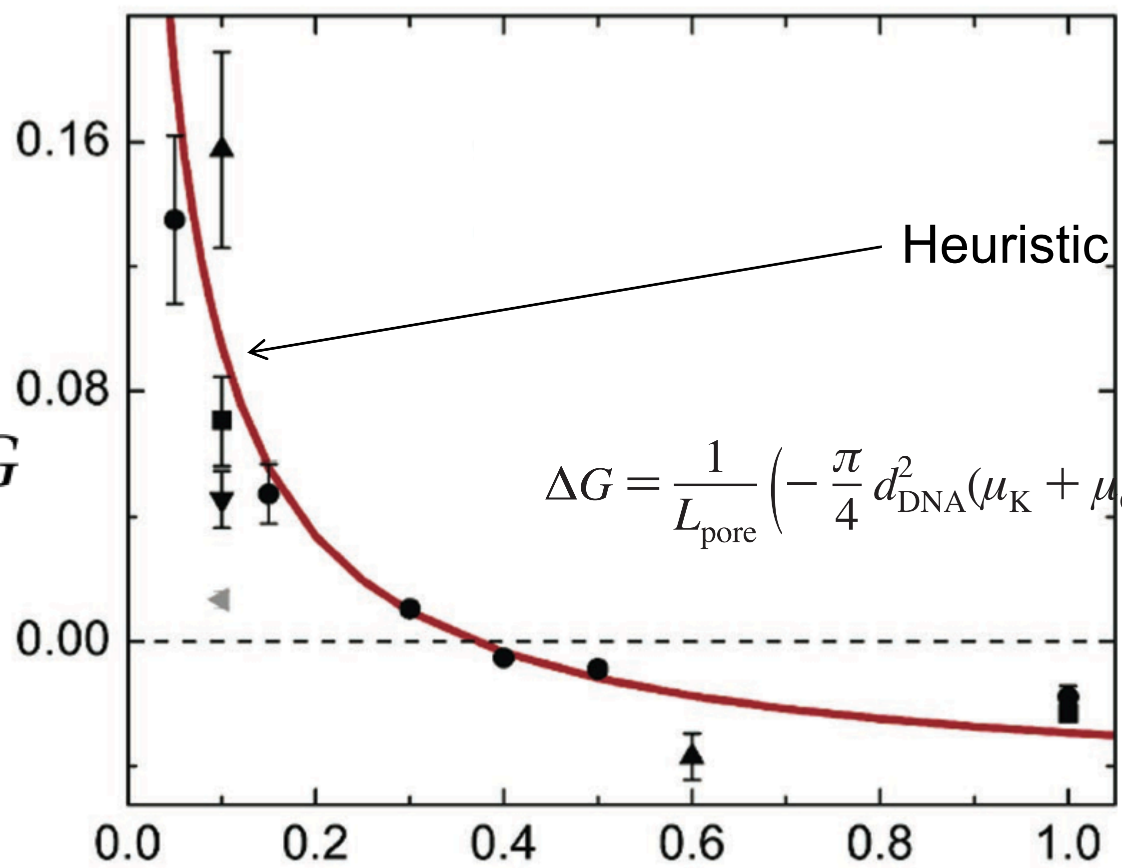
Translocation of 16.5-μm-long dsDNA through a 10-nm-diameter and 34-nm-long cylindrical pore

ΔG, depends on the length of the nanopore. Therefore the *relative* change in conductance, $\Delta G/G$ is measured, because its value no longer depends on the length of the nanopore but only on its diameter,





Smeets experimental Results



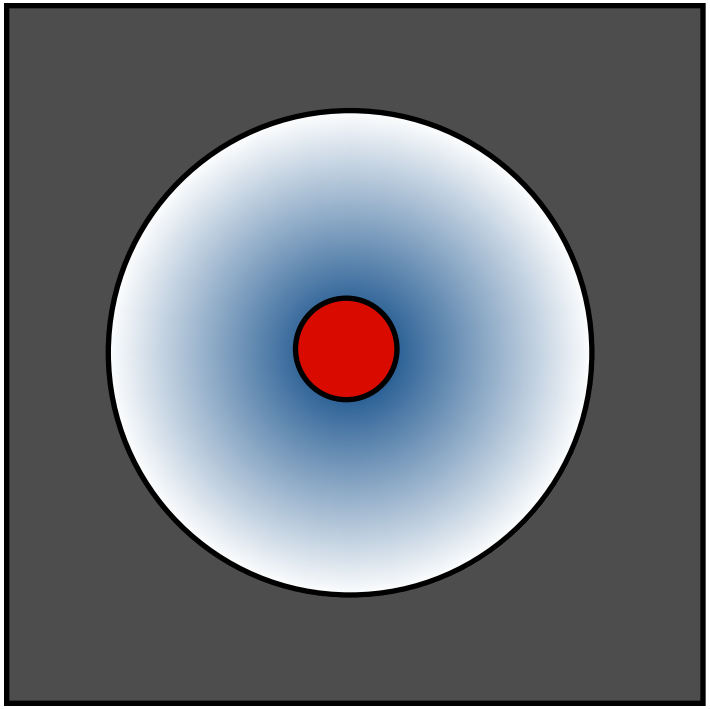
$$\Delta G/G$$

$$\Delta G = \frac{1}{L_{\mathrm{pore}}}\left(-\frac{\pi}{4}\, d_{\mathrm{DNA}}^2(\mu_{\mathrm{K}} + \mu_{\mathrm{Cl}})n_{\mathrm{KCl}}\, e + \mu_{\mathrm{K}}^* q_{l,\mathrm{DNA}}^*\right)$$

c in mol/l

Ralph M. M. Smeets, Ulrich F. Keyser, Diego Krapf, Meng-Yue Wu, Nynke H. Dekker, and Cees Dekker. Nano Lett. **6**, 89–95 (2006).

1. Poisson-Nernst-Planck



Poisson 's Equation

$$\Delta\Phi = -e\left(z_+ c_+ + z_- c_-\right)/\varepsilon$$

Diffusion Equation

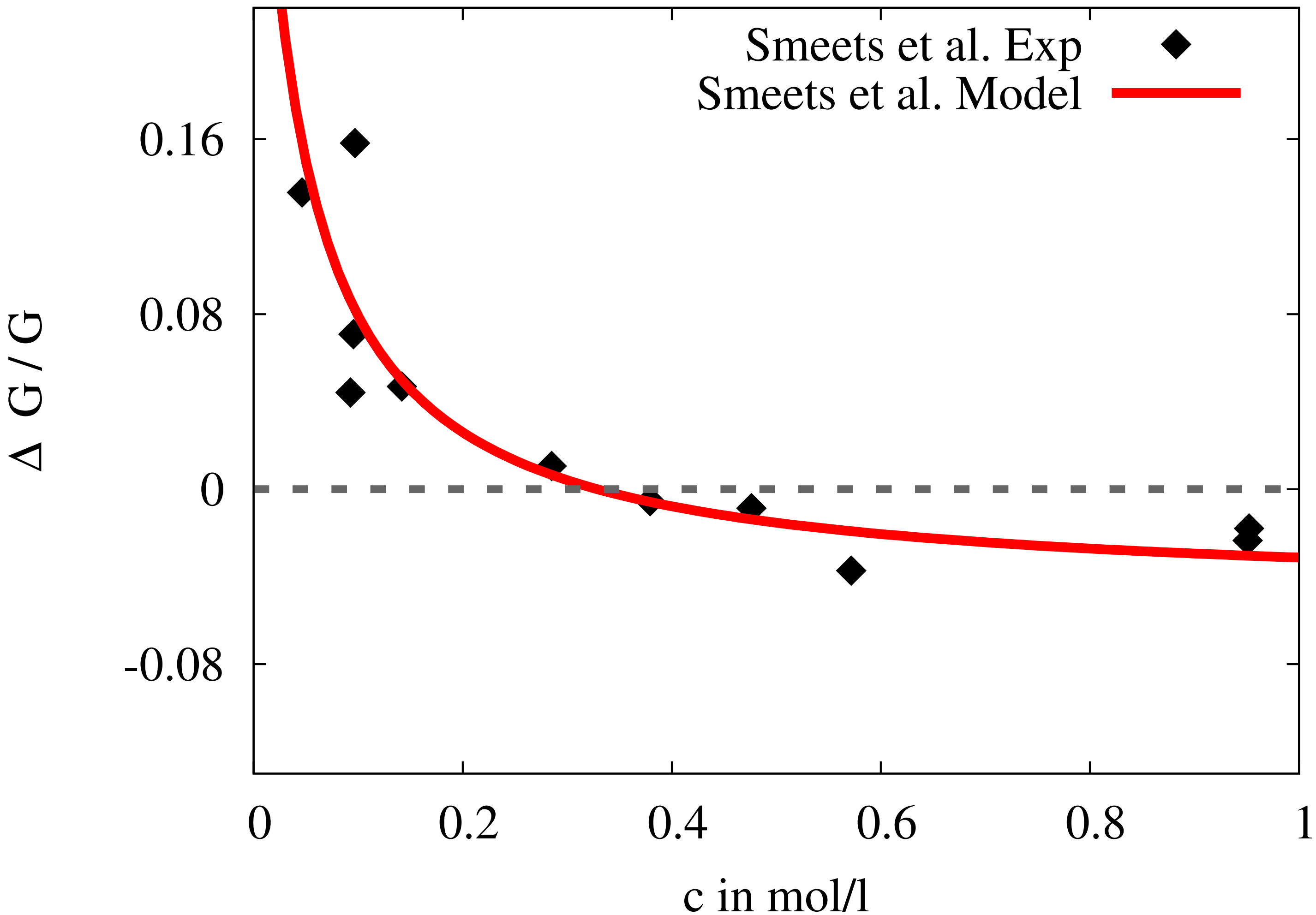
$$\vec{j}_\pm = -D\left(\vec{\nabla} c_\pm - \vec{\nabla}\Phi c_\pm\right)$$

$$\nabla \cdot \vec{j}_\pm = 0$$

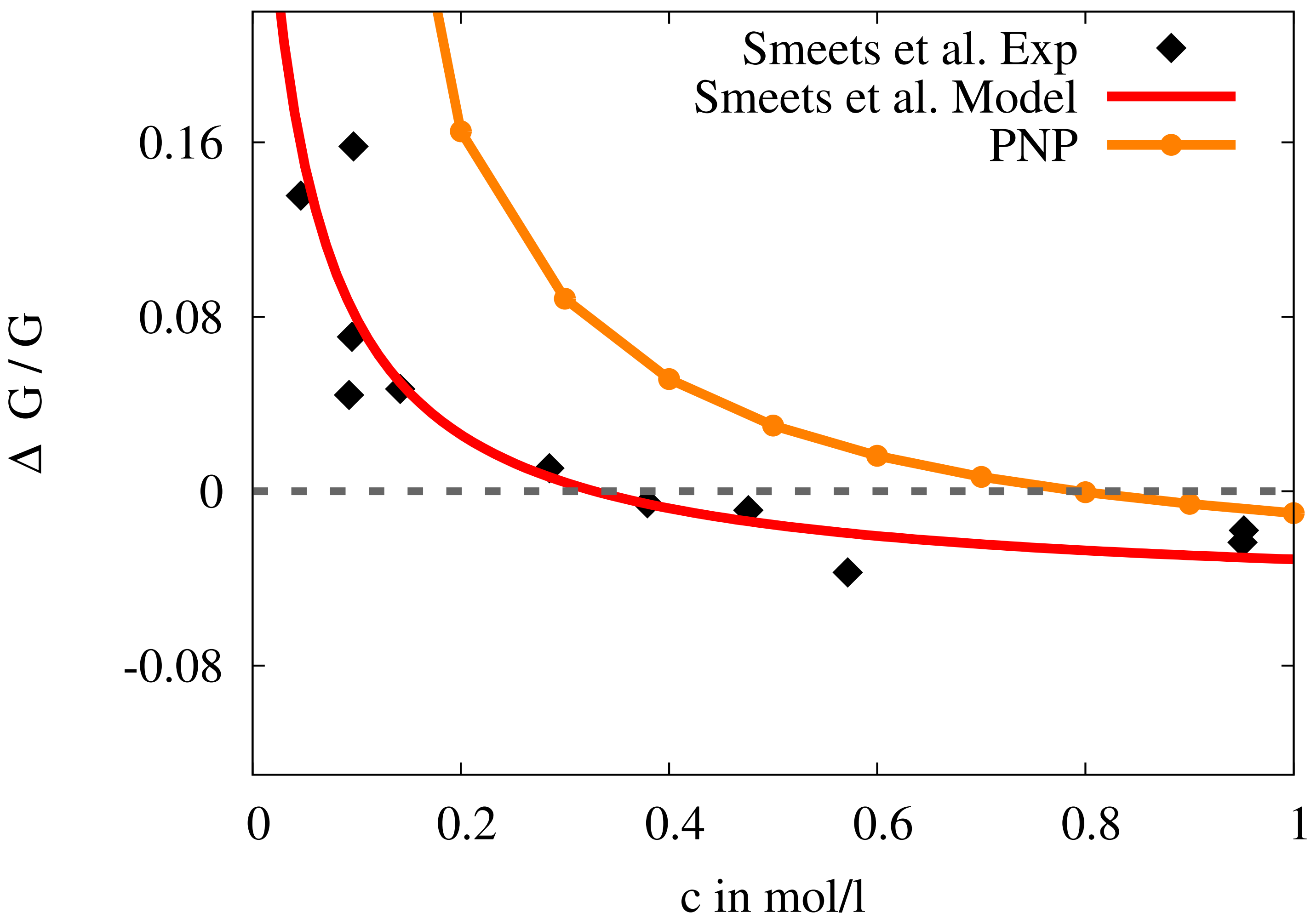
Numerical solution is easy for an infinite cylinder:

- Poisson-Boltzmann equation in radial direction
- Current proportional to number of ions
- DNA charged rod model with bare DNA line charge density

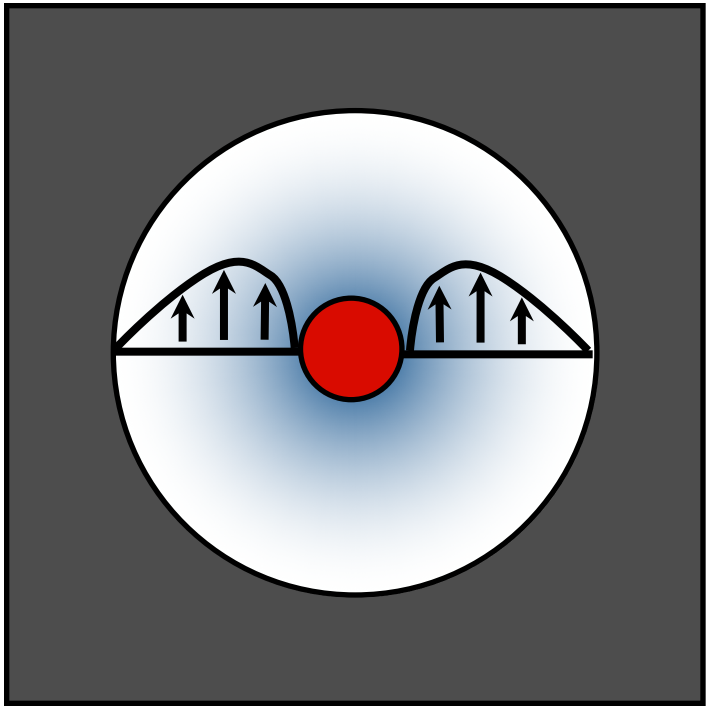
1. Poisson-Nernst-Planck



1. Poisson-Nernst-Planck



2. Standard Electrokinetic Model



Poisson 's Equation

$$\Delta\Phi = -e\,(z_+ c_+ + z_- c_-)\,/\,\varepsilon$$

Diffusion-Convection Equation

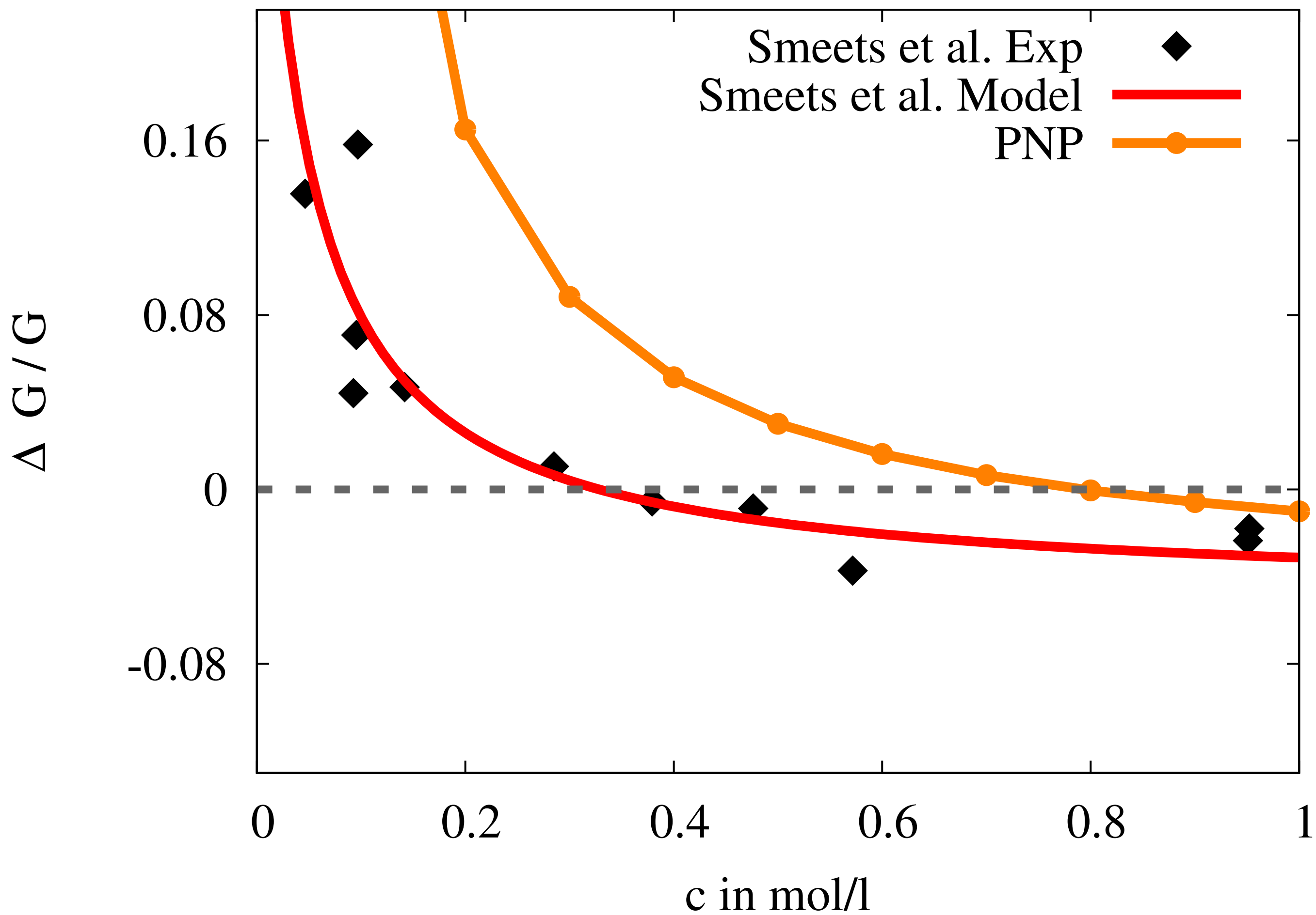
$$\vec{j}_\pm = -D\left(\vec{\nabla} c_\pm - \vec{\nabla}\Phi c_\pm\right) + c_\pm \vec{u}$$

$$\nabla \cdot \vec{j}_\pm = 0$$

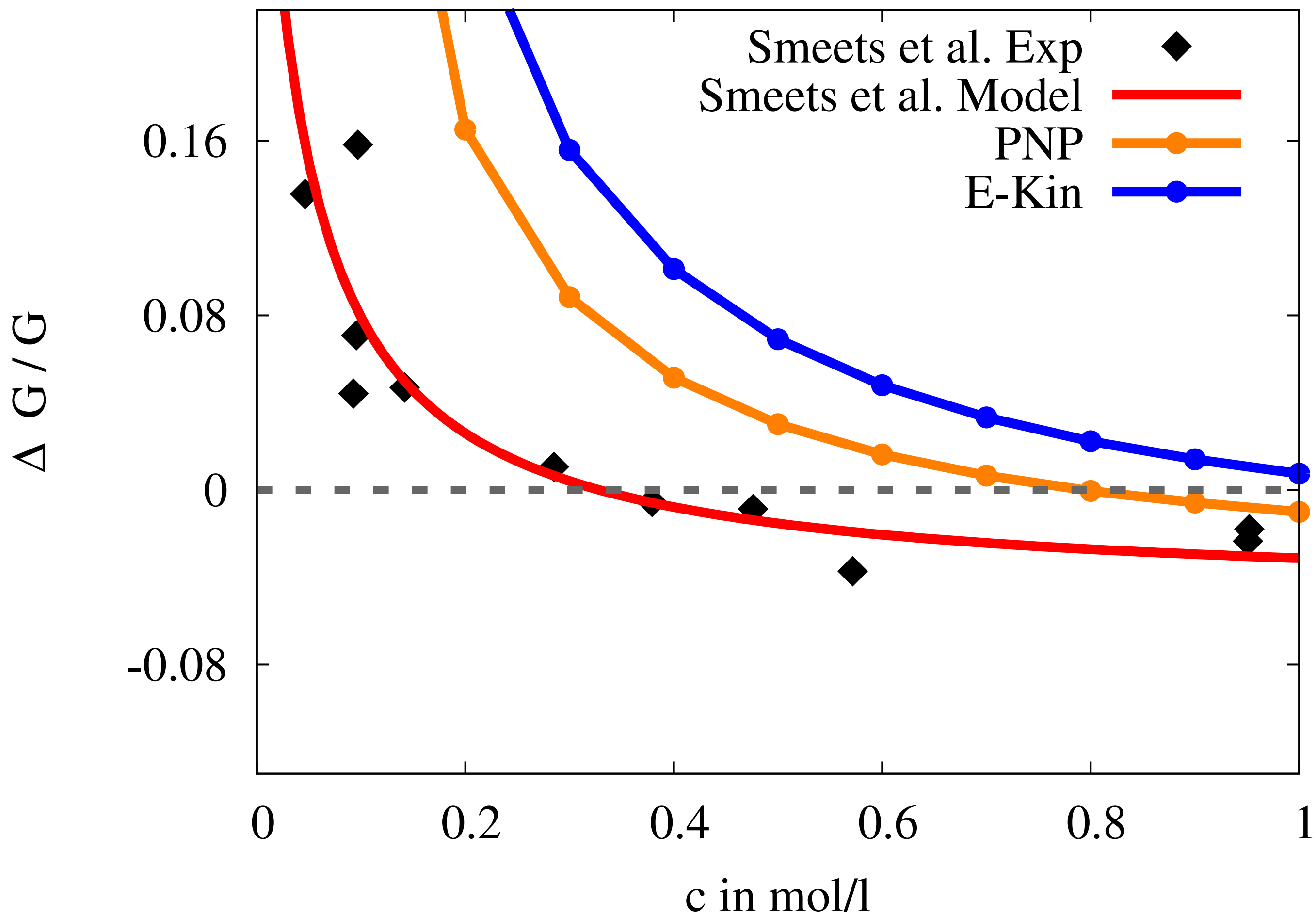
Stokes ' Equation

$$\eta\Delta\vec{u} = -e\,(z_+ c_+ + z_- c_-)\,\vec{\nabla}\Phi + \vec{\nabla} p \qquad \nabla \cdot \vec{u} = 0$$

2. Standard Electrokinetic Model



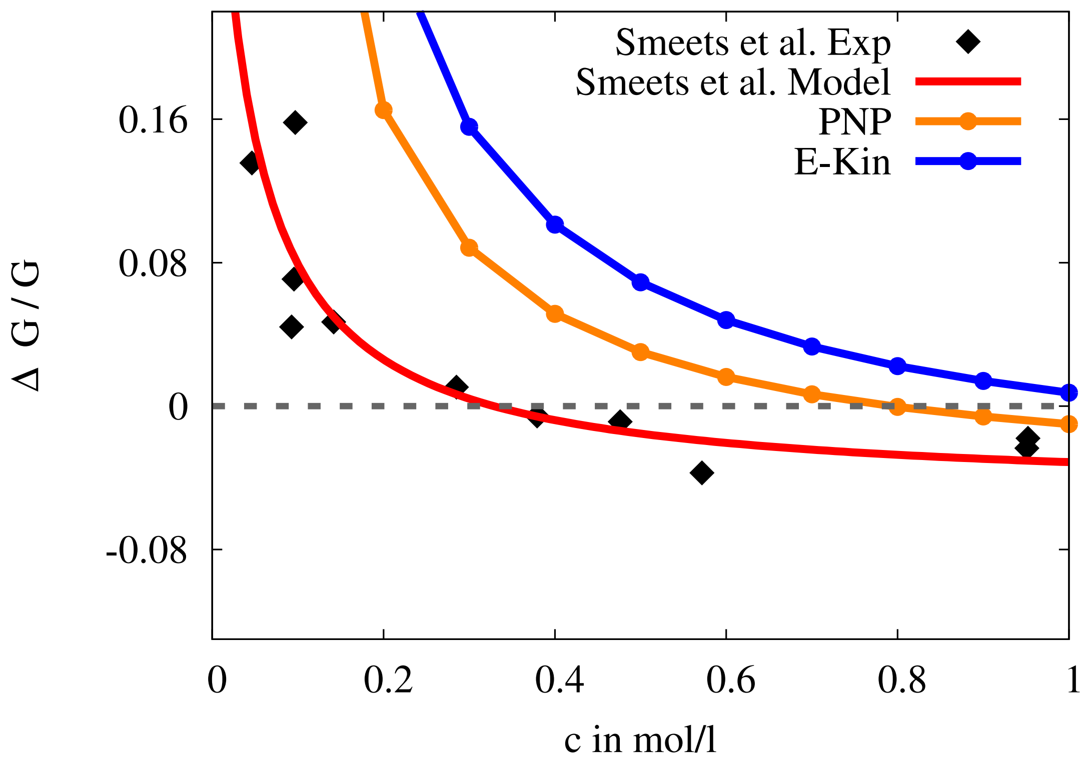
2. Standard Electrokinetic Model



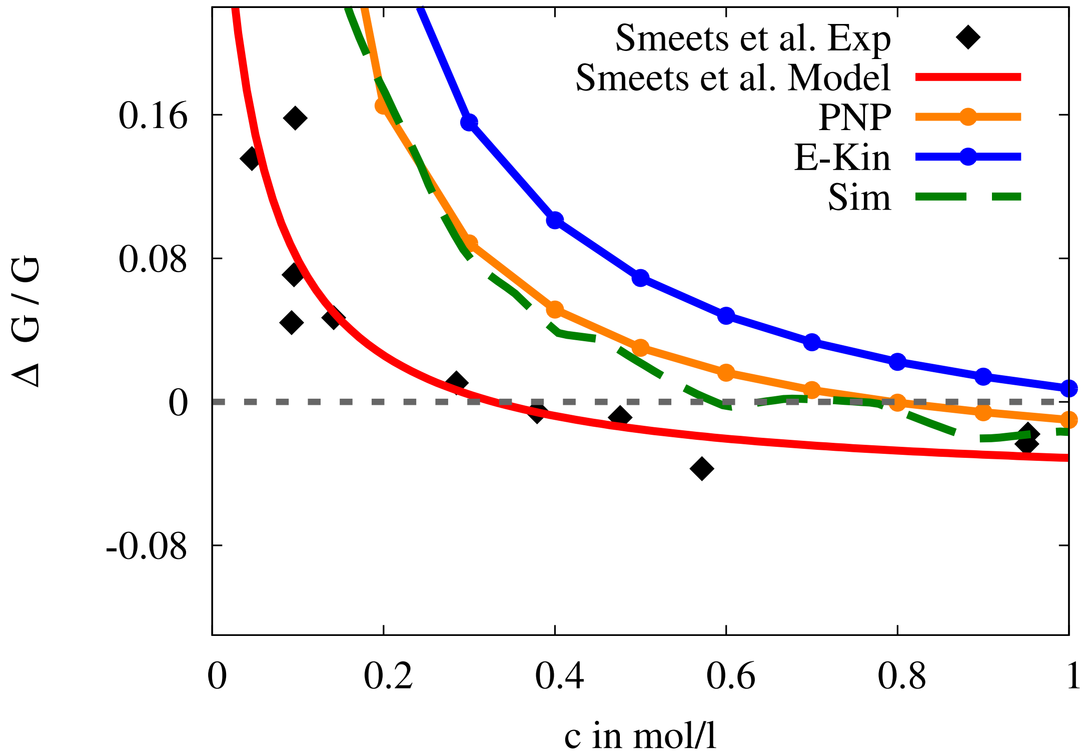
E-Kin shows larger ΔG/G

Reason: EOF enhances current!

3. LB/MD Simulation



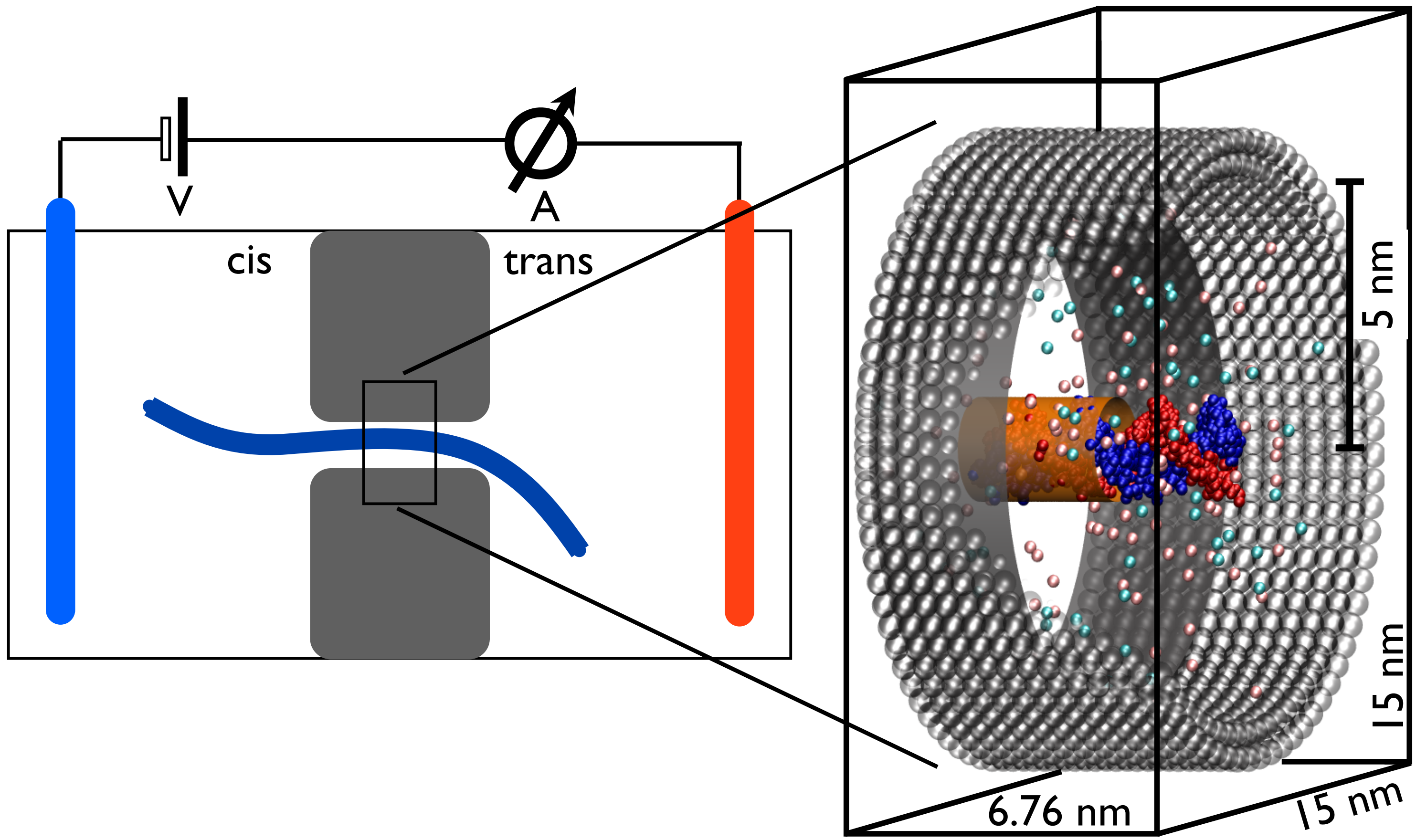
3. LB/MD Simulation



Lattice-Boltzmann MD does not agree with E-Kin!

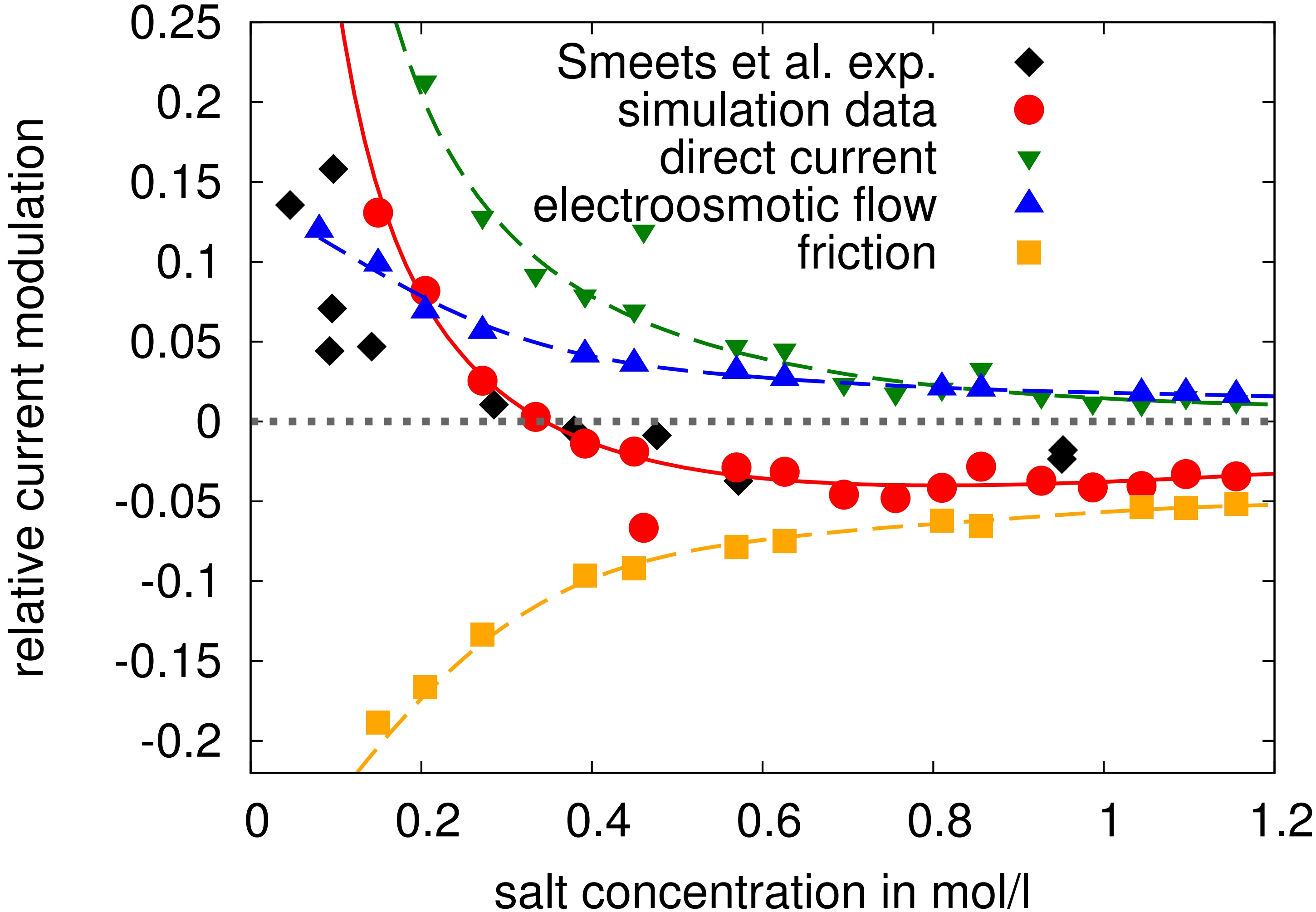
- Conductivity depends on ionic concentration (HI and Coulomb)
- Friction effects near walls

Investigations via AA Simulations



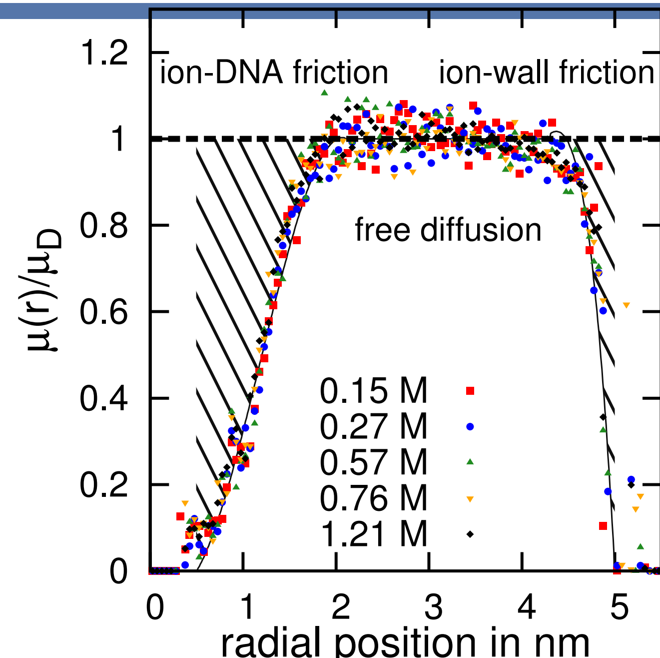
Force Field: AMBER03, Water: SPC/E
double-stranded DNA closed over PBC,consisting of 20 GC bps, P-Atoms fixed in space, generic pore atoms
Electric field 0.2 V/nm applied along pore

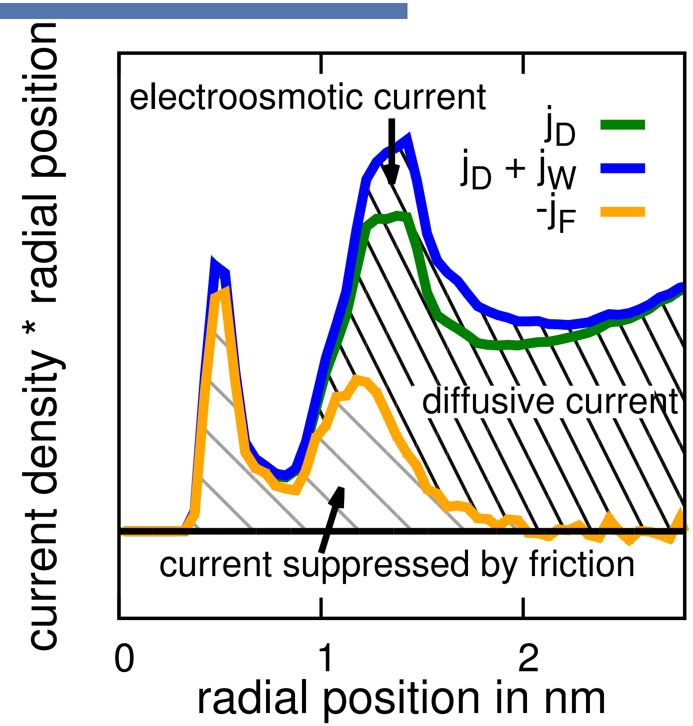
Atomistic Simulation

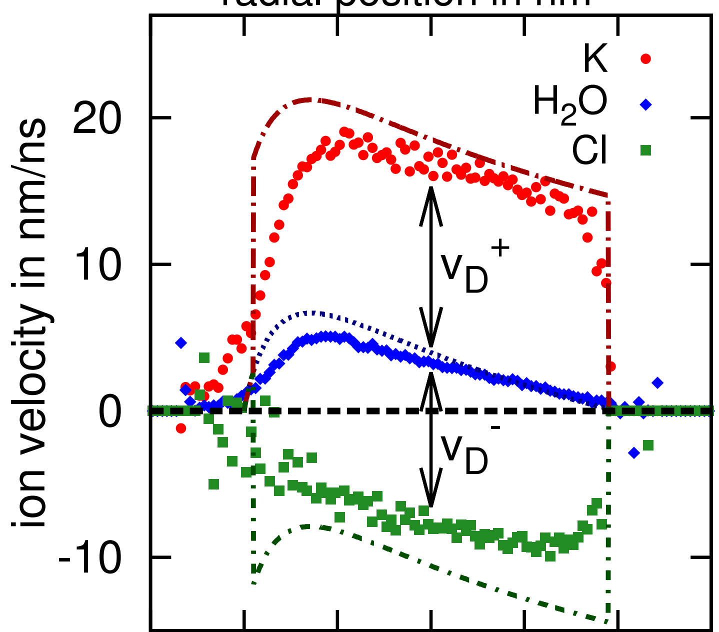


Direct current always larger with DNA inside

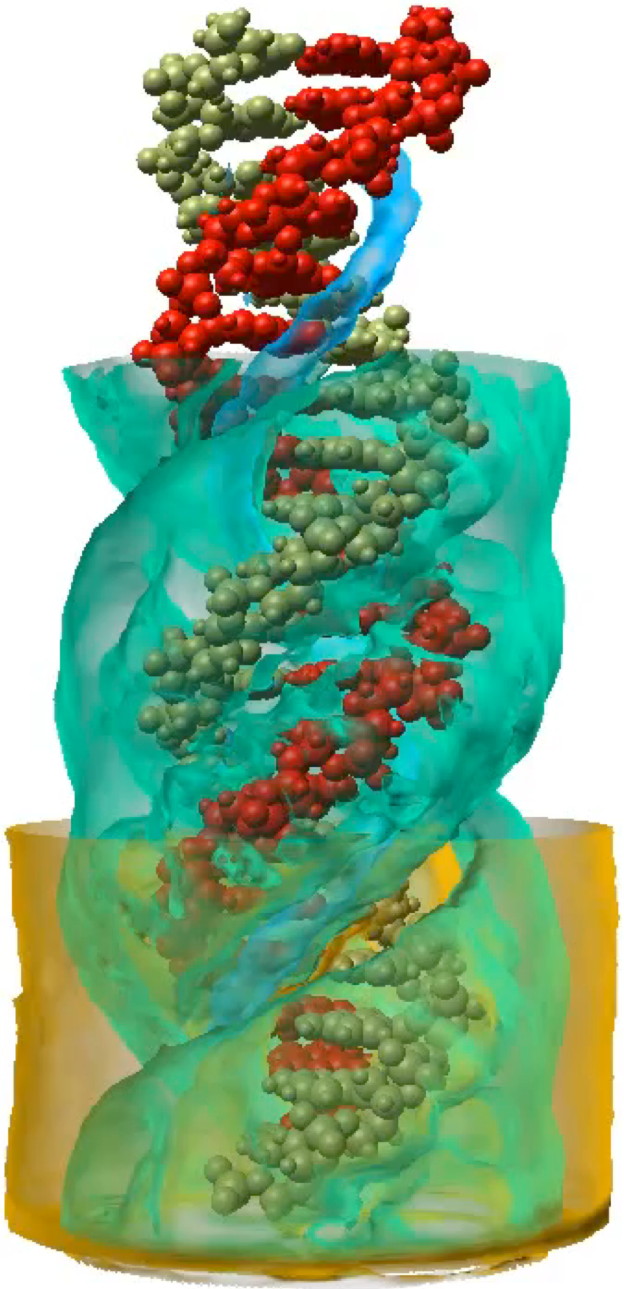
Results from AA Simulations



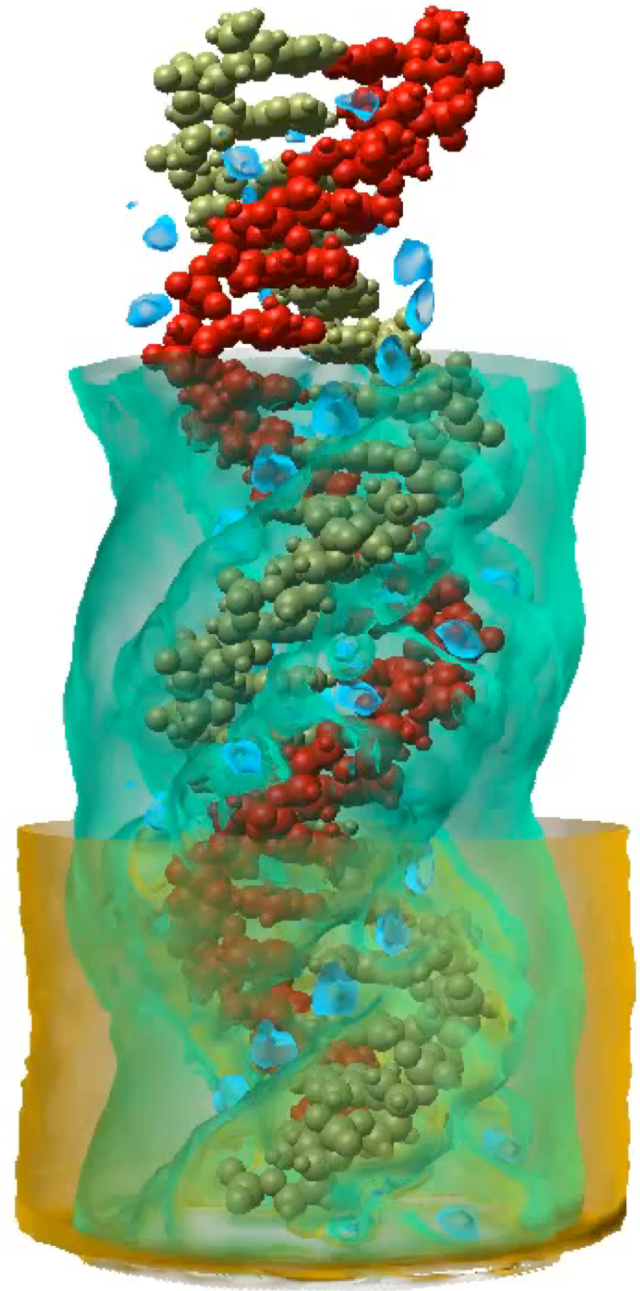




- Ion mobility not constant near the DNA surface
- Electrokinetic model quite accurate for flows

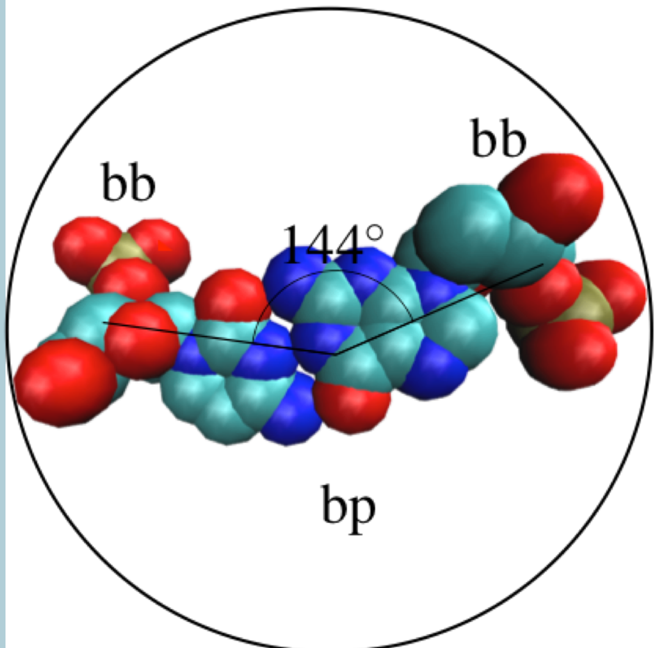


Poly-CG-DNA



Poly-AT-DNA

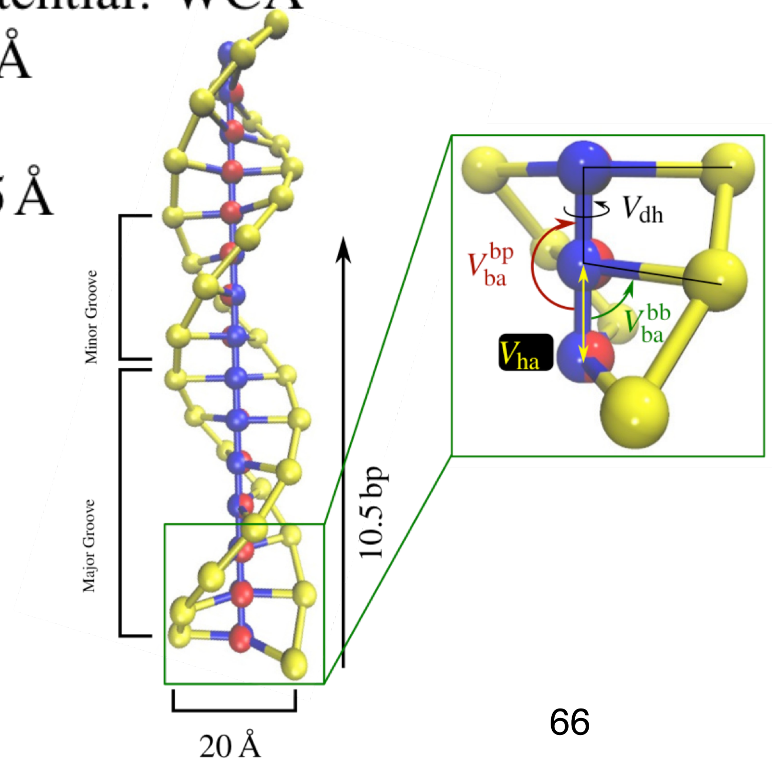
Semi-flexible CG dsDNA Model



ion-bb potential: WCA
$\sigma = 4.25\,\text{Å}$
$\varepsilon = k_B T$

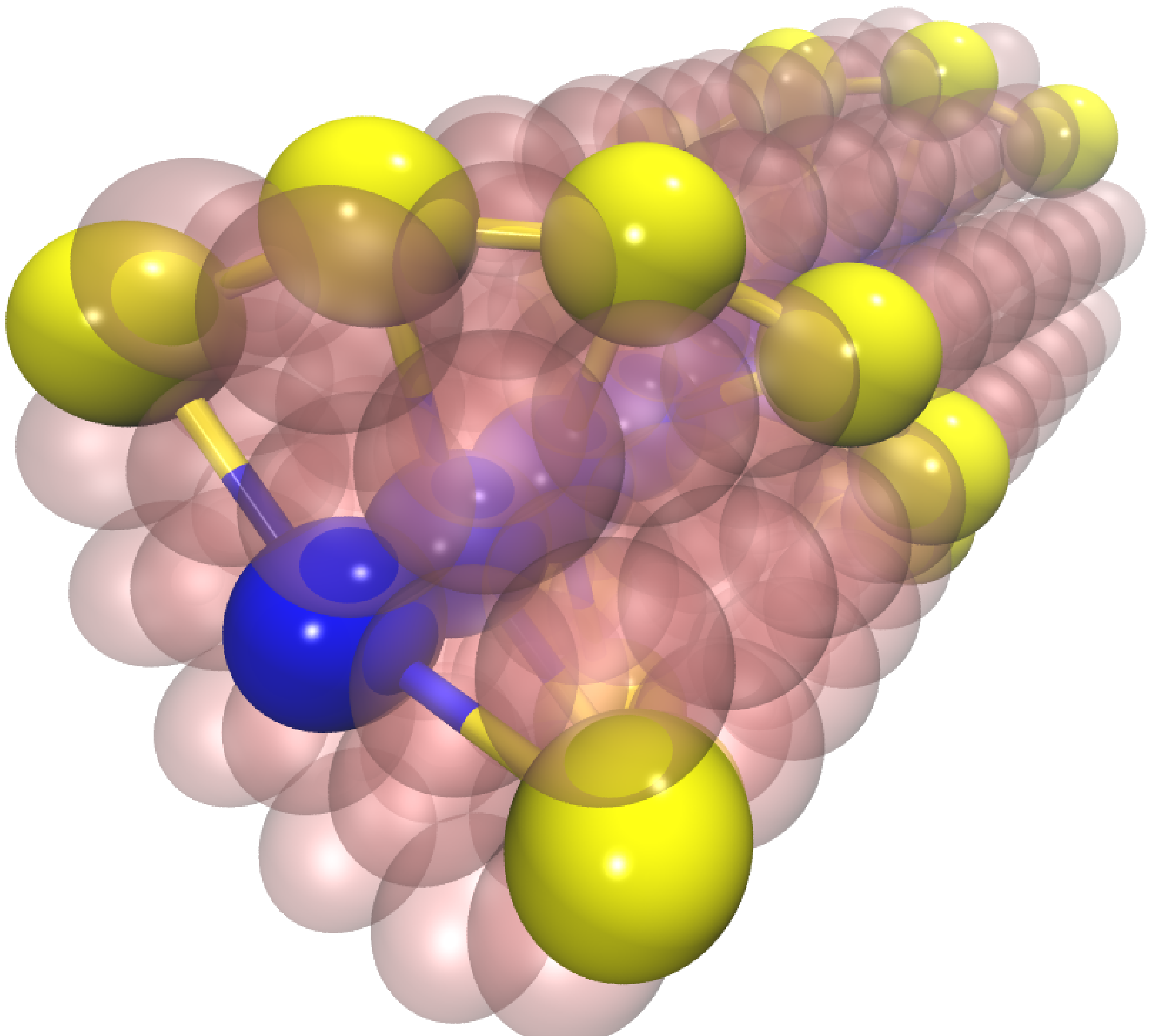
ion-ion potential: WCA
$\sigma = 4.25\,\text{Å}$
$\varepsilon = k_B T$

ion-bp potential: WCA
$\sigma = 4.25\,\text{Å}$
$\varepsilon = k_B T$
$r_{sh} = 0.75\,\text{Å}$

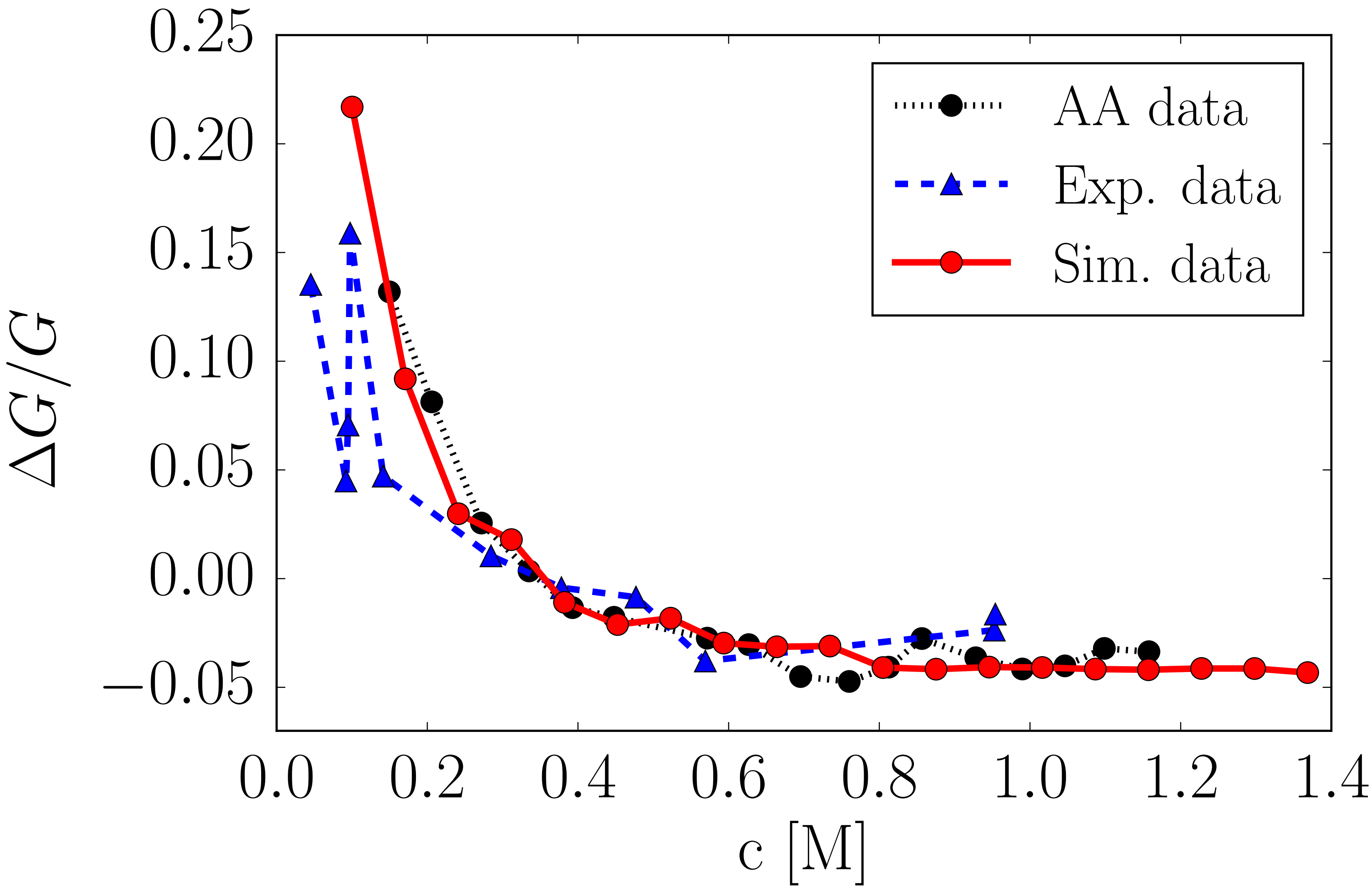


3 beads per bp

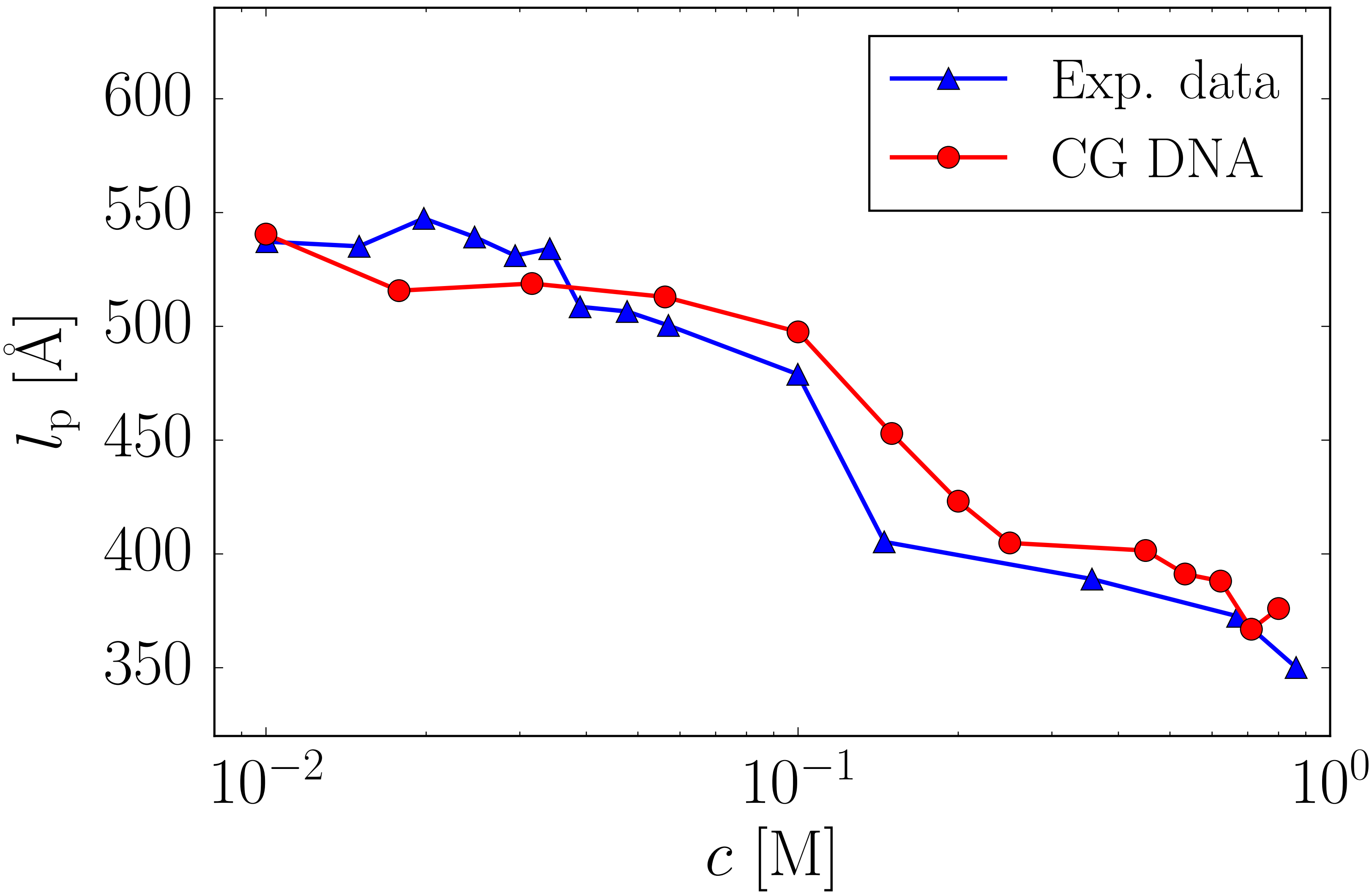
Addition of Frictional Coupling



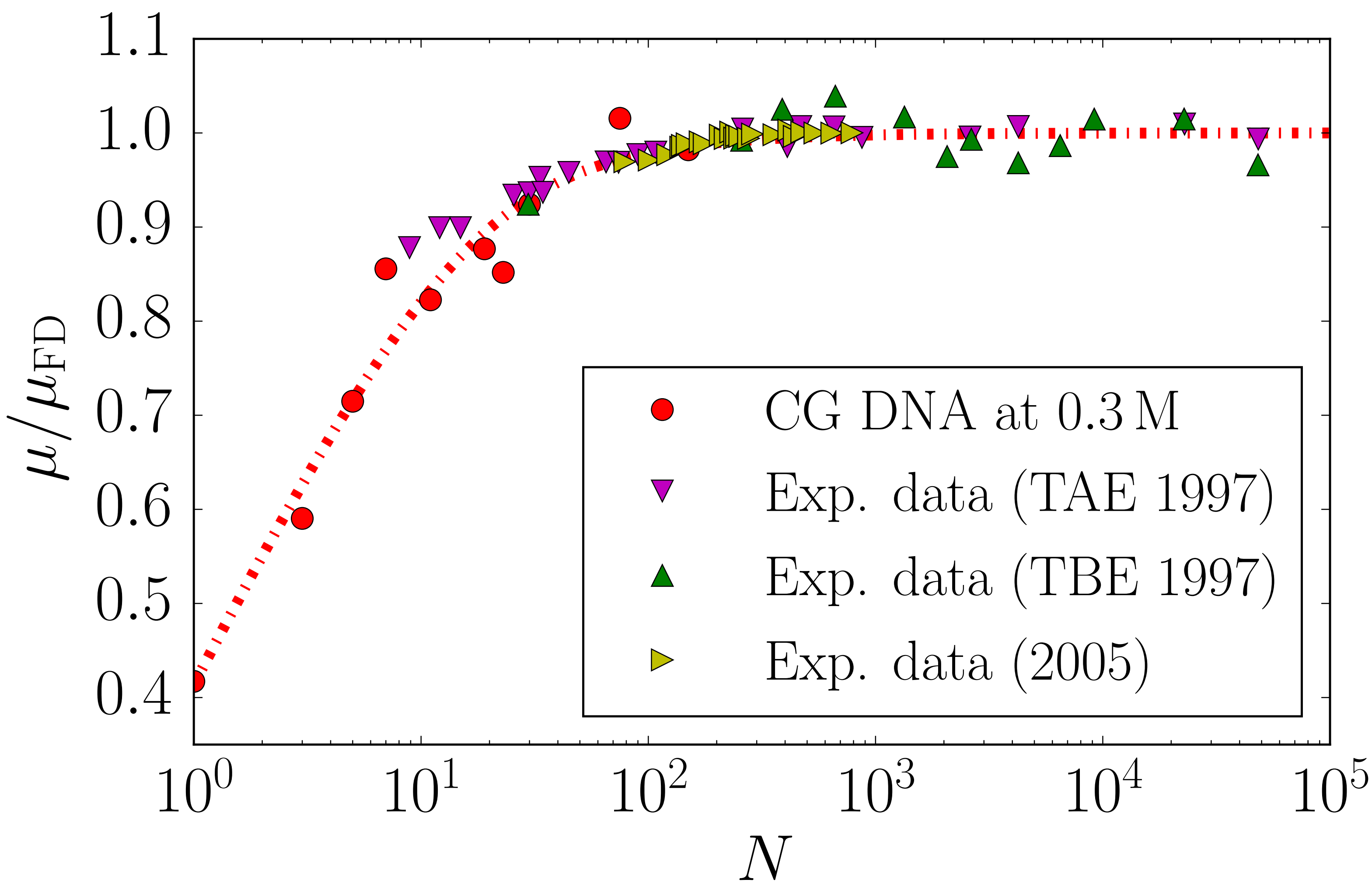
Check of Validity of Model



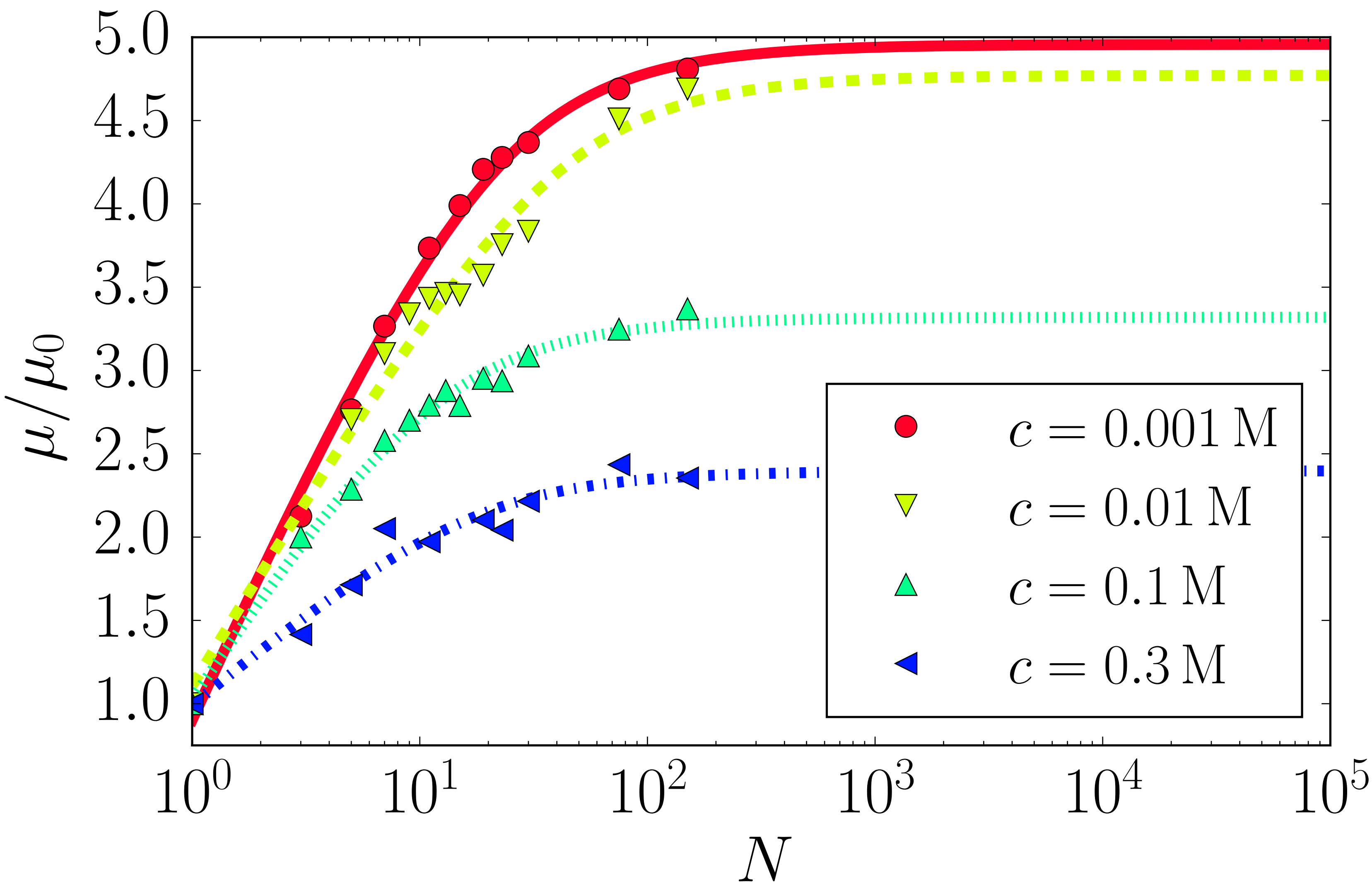
Comparison of l_p to Experiments



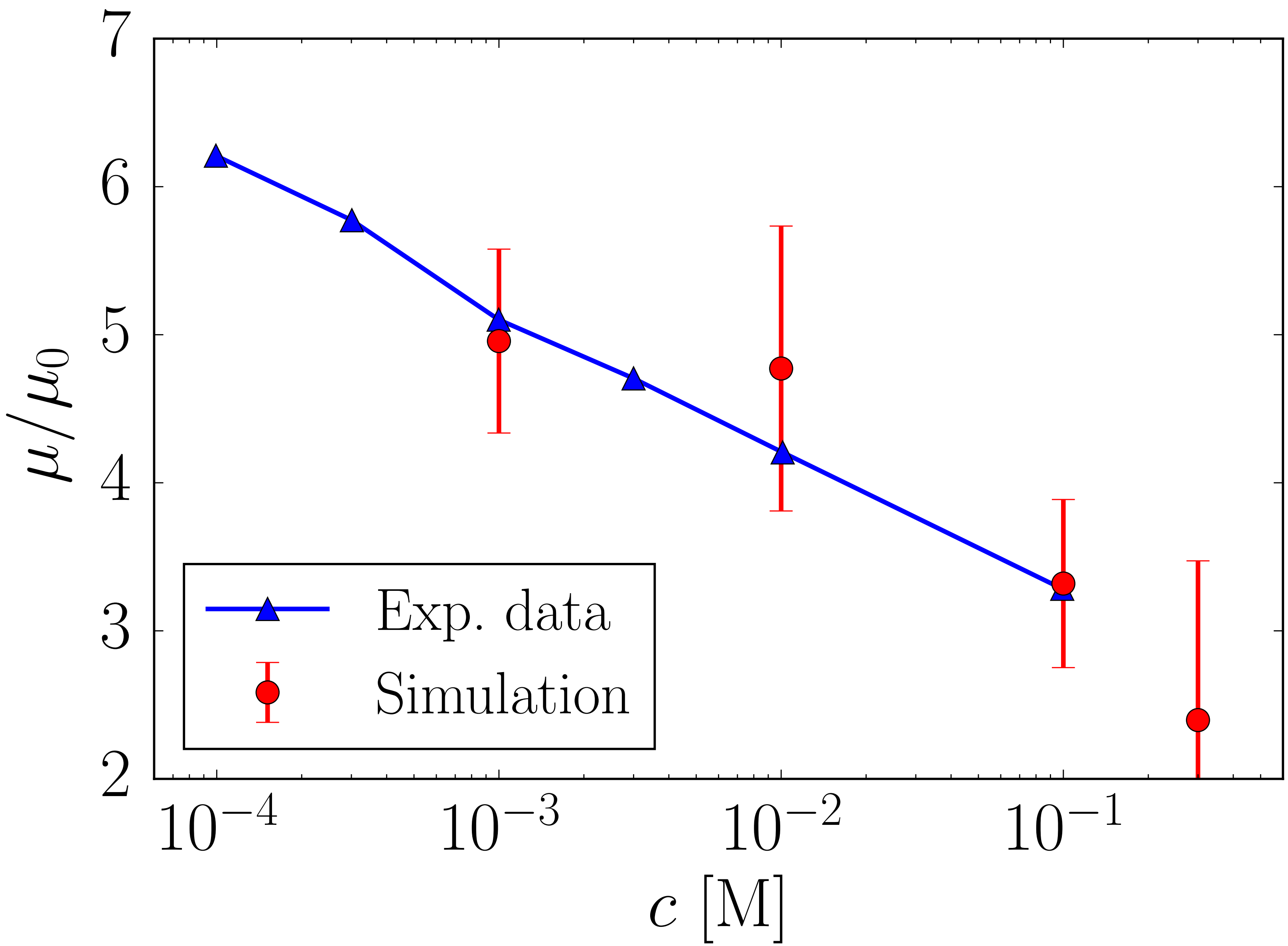
Comparison of μ to Experiments



Mobility as Function of N



Salt Dependence of μ_{FD}



Conclusions on dsDNA Model

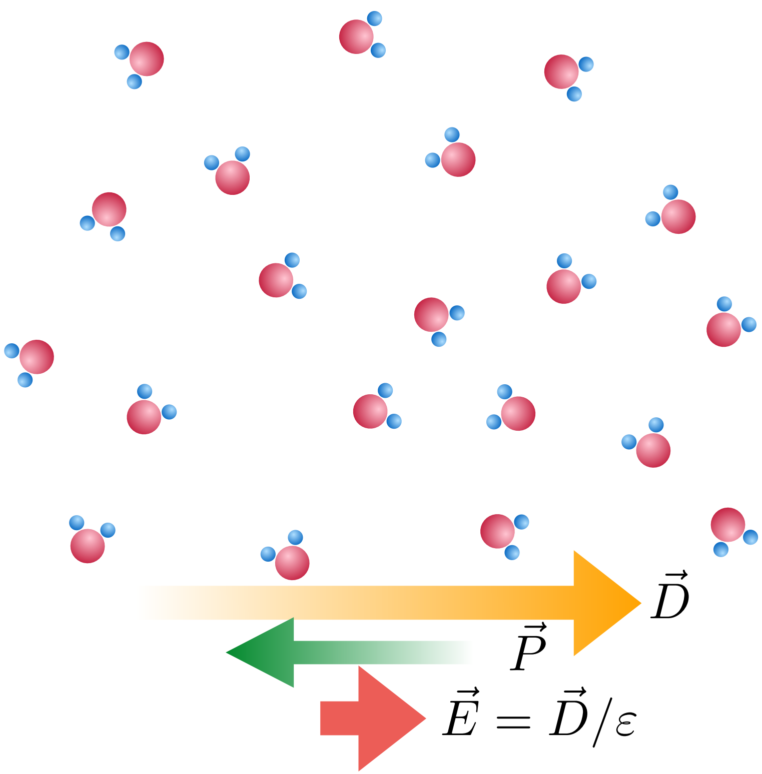
- AA Simulations in excellent agreement with experimental data
- Main cause of the deficiency of the electrokinetic model is the increased interfacial friction caused by the presence of the DNA
- Electrokinetic model works surprisingly well up to a scale ~ 1 nm
- There is a difference in ion distribution between CG and AT,
- We have a well working CG model for elektrokinetic applications
- Further studies on the way….

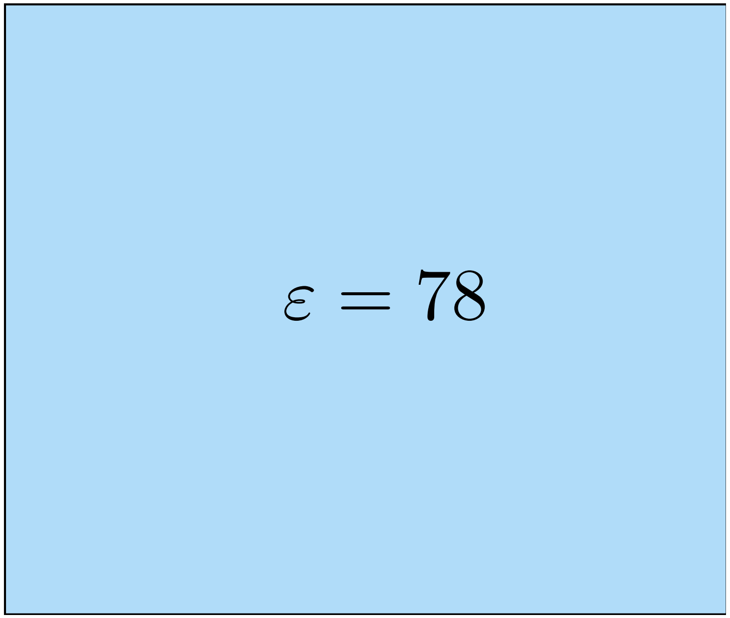
S. Kesselheim, W. Müller, C. Holm, Phys. Rev. Lett. **112**, 018101 (2014);
F. Weik, S. Kesselheim, C. Holm, JCP **145** 194106 (2016);
T. Rau, F. Weik, C. Holm, Soft Matter **13**, 3918 (2017)

Inhomogeneous Dielectrics

The Implicit Solvent Model

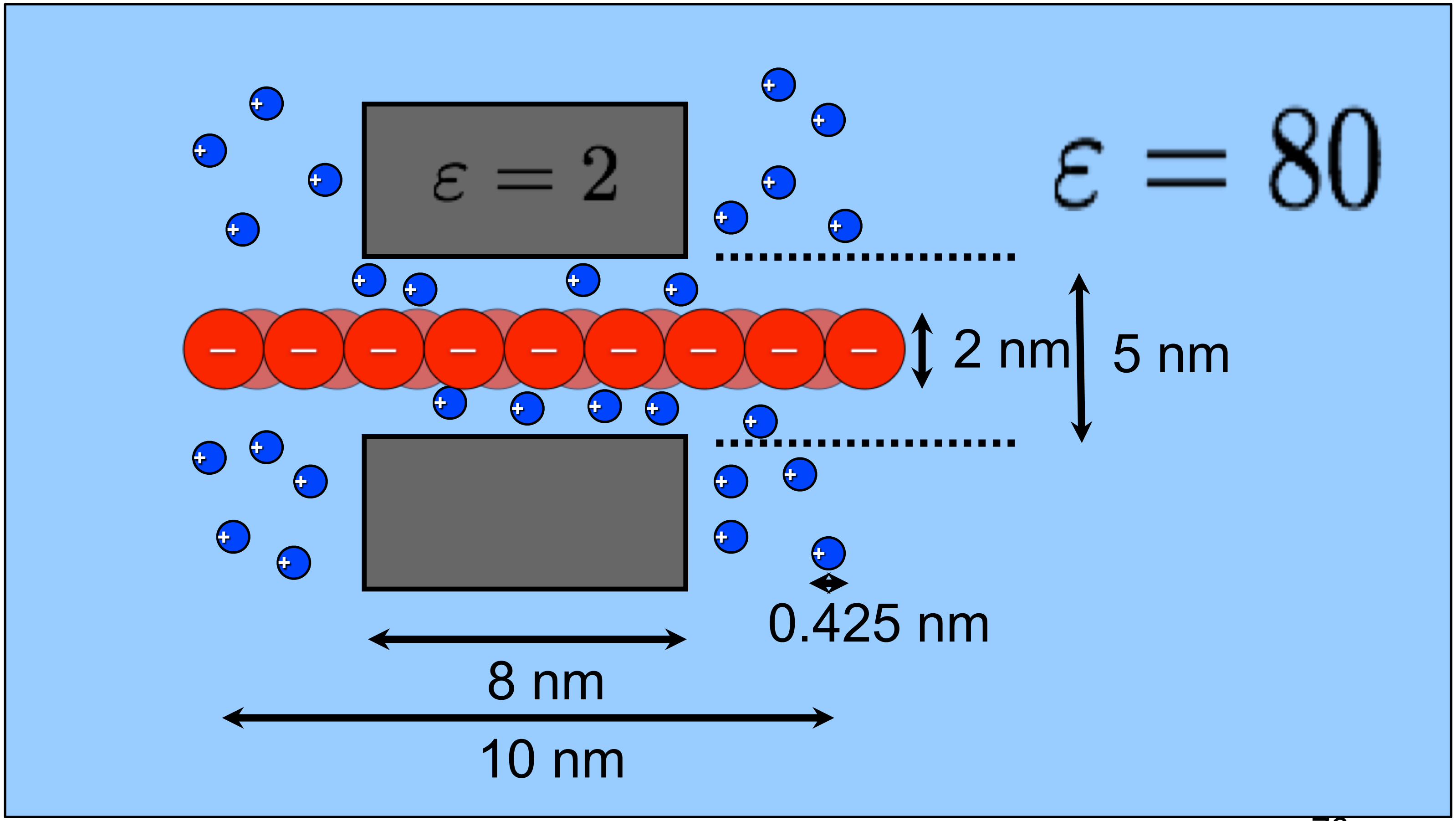
- Water is highly polar, i.e. $\varepsilon_r = 78$
- For dynamics we have to add hydrodynamical interactions, i.e. DPD, LB, MPCD,….





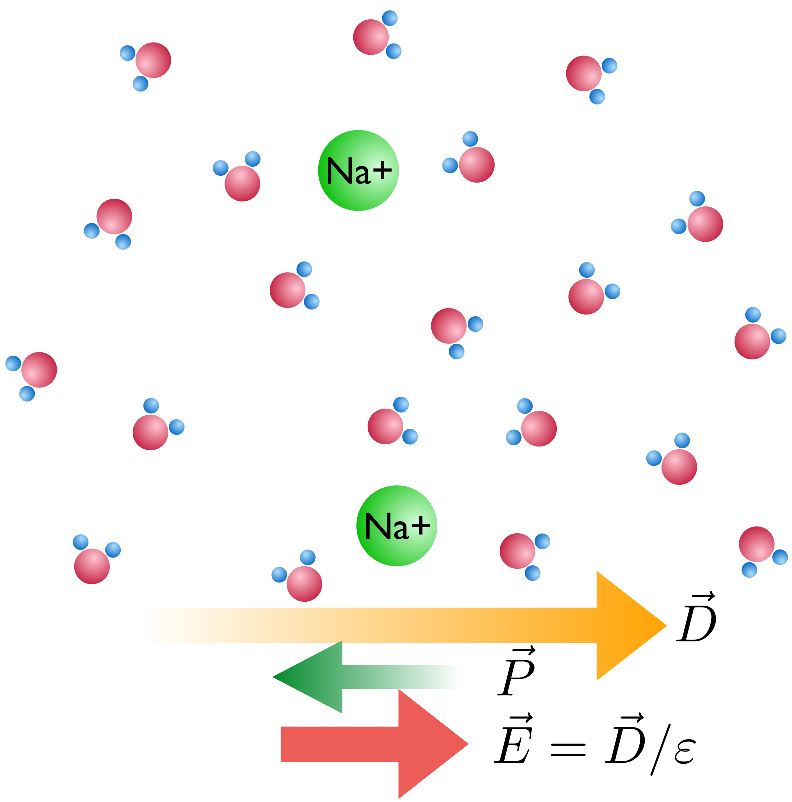
The Implicit Solvent Model

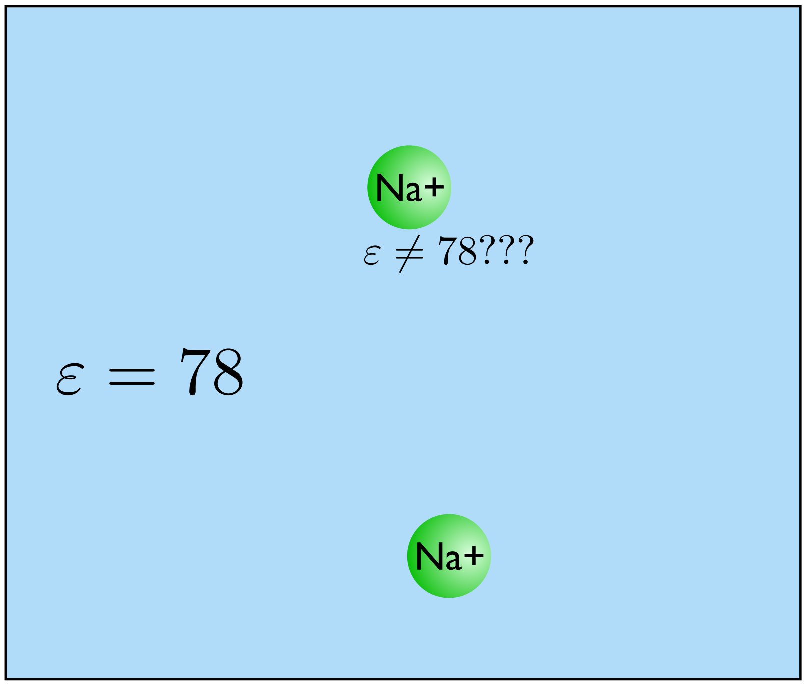
- Dielectric interfaces are basically everywhere where there are interfaces



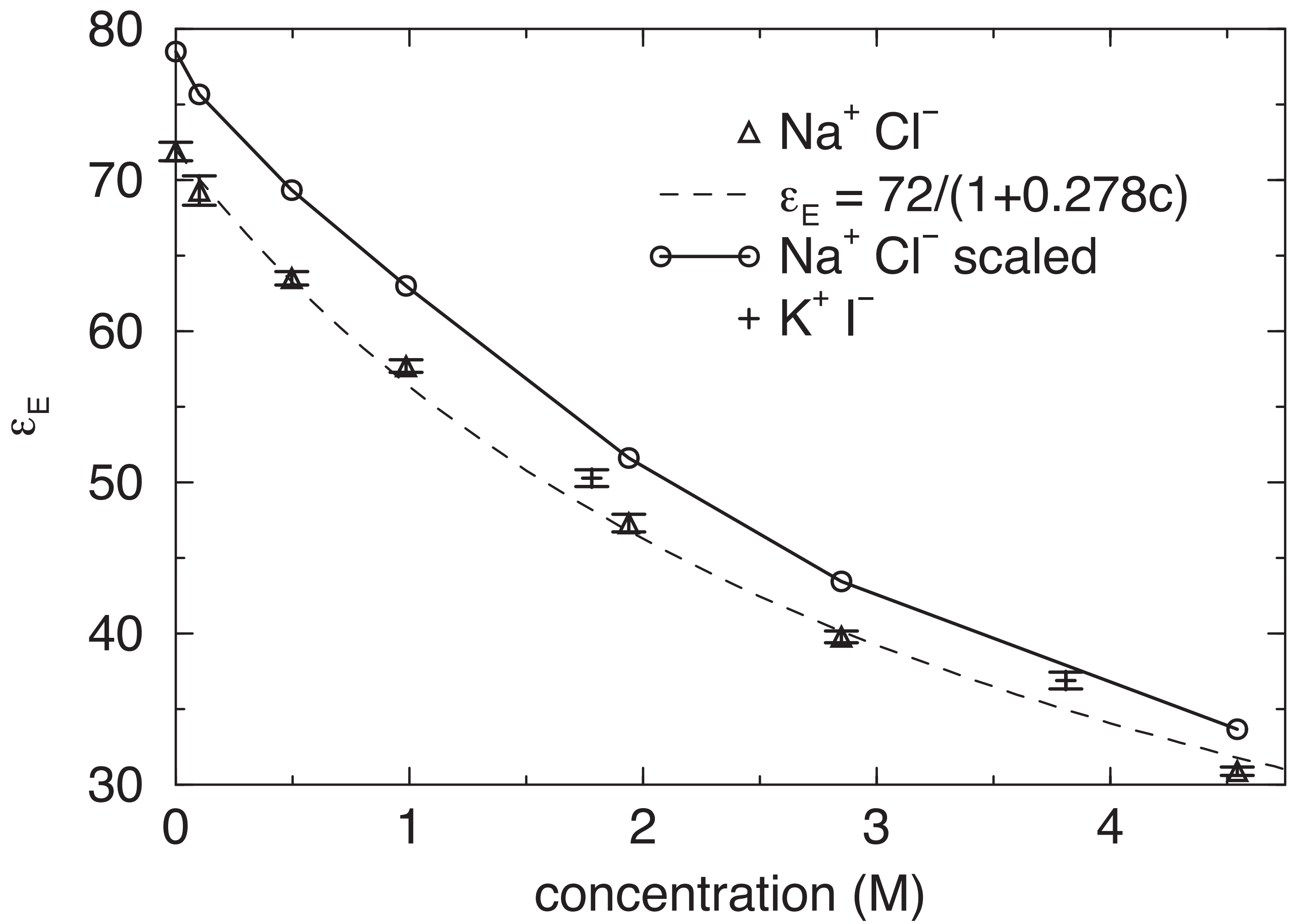
The Implicit Solvent Model

- Permittivity reduced by presence of ions
- Homogeneous dielectric => heterogeneous dielectric





ε_r depends on salt concentration

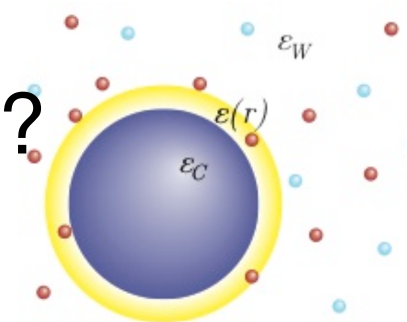


All-Atom MD, SPC/E explicit water

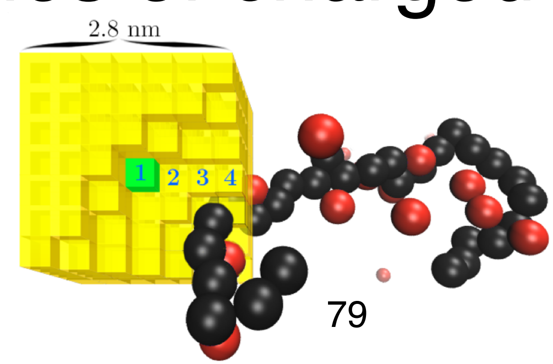
B. Hess, C. Holm, N. van der Vegt: PRL **96,** 147801 (2006)

Outline: Basic Questions

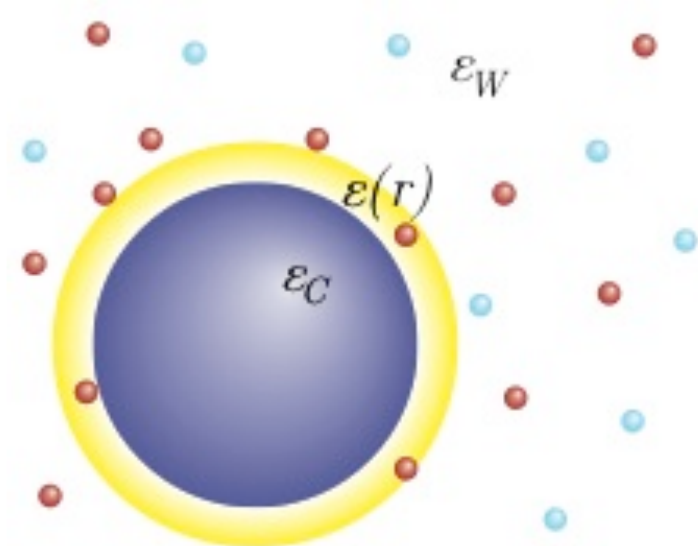
- How does the dielectric permittivity change
- … in close vicinity of highly charged objects?
- … with varying salt concentration?



- How do these features affect the behavior of static and dynamic properties of charged macromolecules?
- How can I model this?



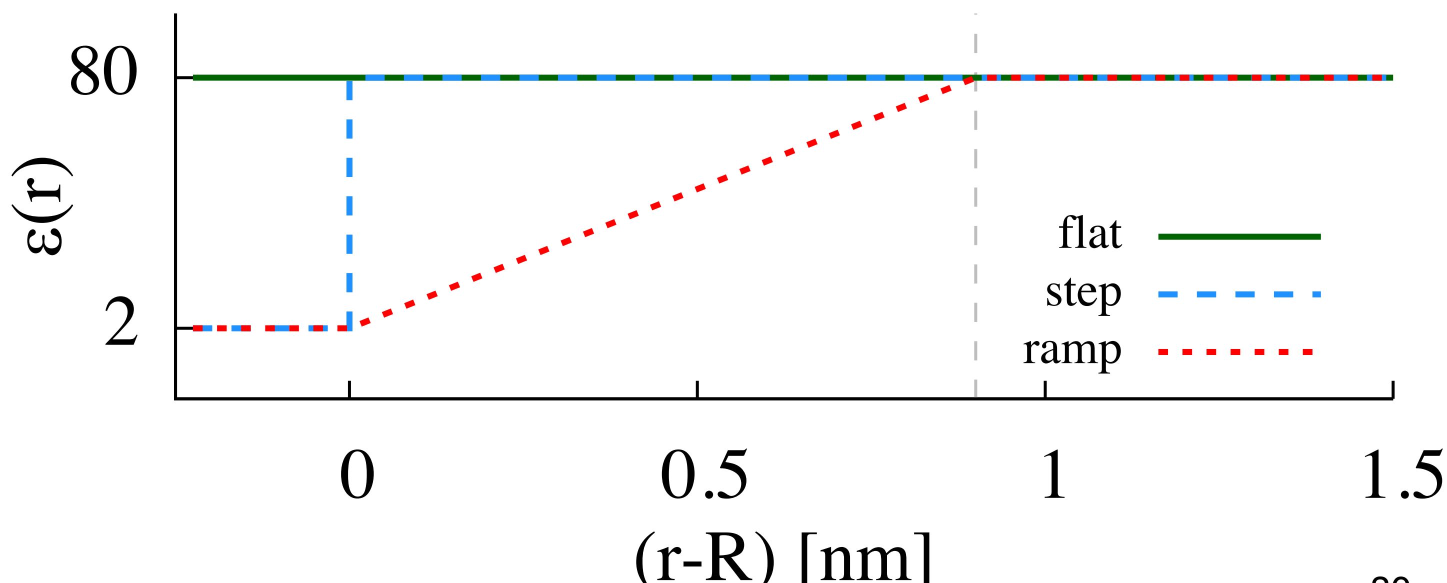
Colloid with different ε-profiles



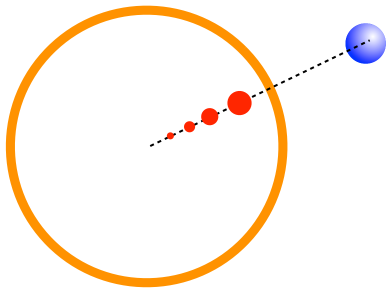
Dielectric, charged colloid (Z = 30e - 90e)

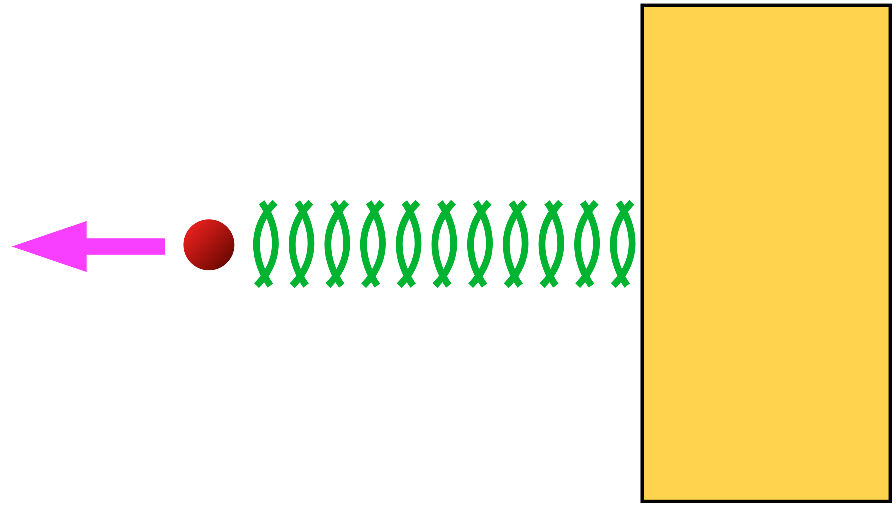
R=4nm and D_{ion} = 0.45 nm

salt solution 20-60 mMol



2 Methods: HIM and MEMD





Harmonic **I**nterpolation **M**ethod

- MC-simulation: energy
- series of mirror charges
- able to deal with piecewise harmonic functions

MD-simulation: force
electric and magnetic fields that propagate
arbitrary permittivity on a lattice link

F. Fahrenberger, Z. Xu, C. Holm, J. Chem. Phys. **141**, 064902 (2014)

Maxwell-like Equations

A. C. Maggs and V. Rosseto, PRL **88**, 196402 (2002).
I. Pasichnyk and B. Dünweg, J. Phys. Cond.Mat. **16**, 3999 (2004).

$$\begin{aligned} \nabla \varepsilon \nabla \phi &= -\rho \\ \Rightarrow \nabla \cdot \mathbf{D} &= \rho \qquad \text{(Gauss law)} \quad \boldsymbol{D} = \varepsilon \boldsymbol{E}, \\ \nabla \times \mathbf{D} &= 0 \end{aligned}$$

- 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.

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).

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

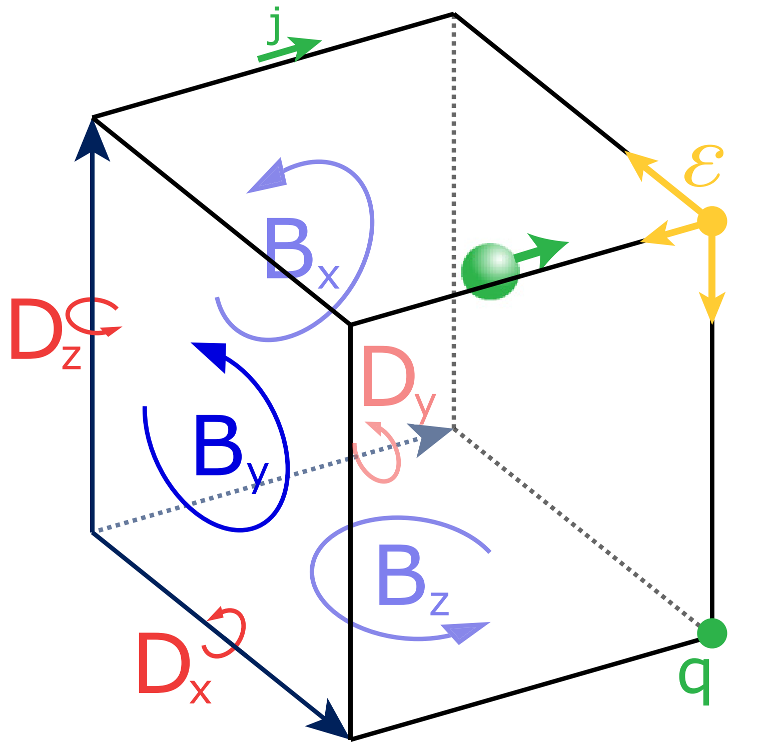
$$\dot{\mathbf{p}}_i = -\frac{\partial U}{\partial \mathbf{r}_i} + \frac{e_i}{\varepsilon}\mathbf{D}(\mathbf{r}_i)$$

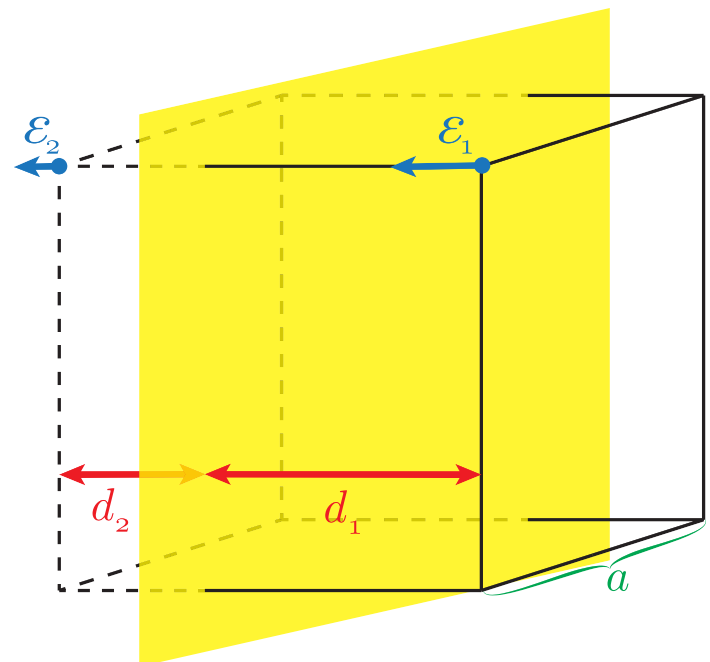
$$\dot{\mathbf{A}} = -\frac{\mathbf{D}}{\varepsilon}$$

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

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

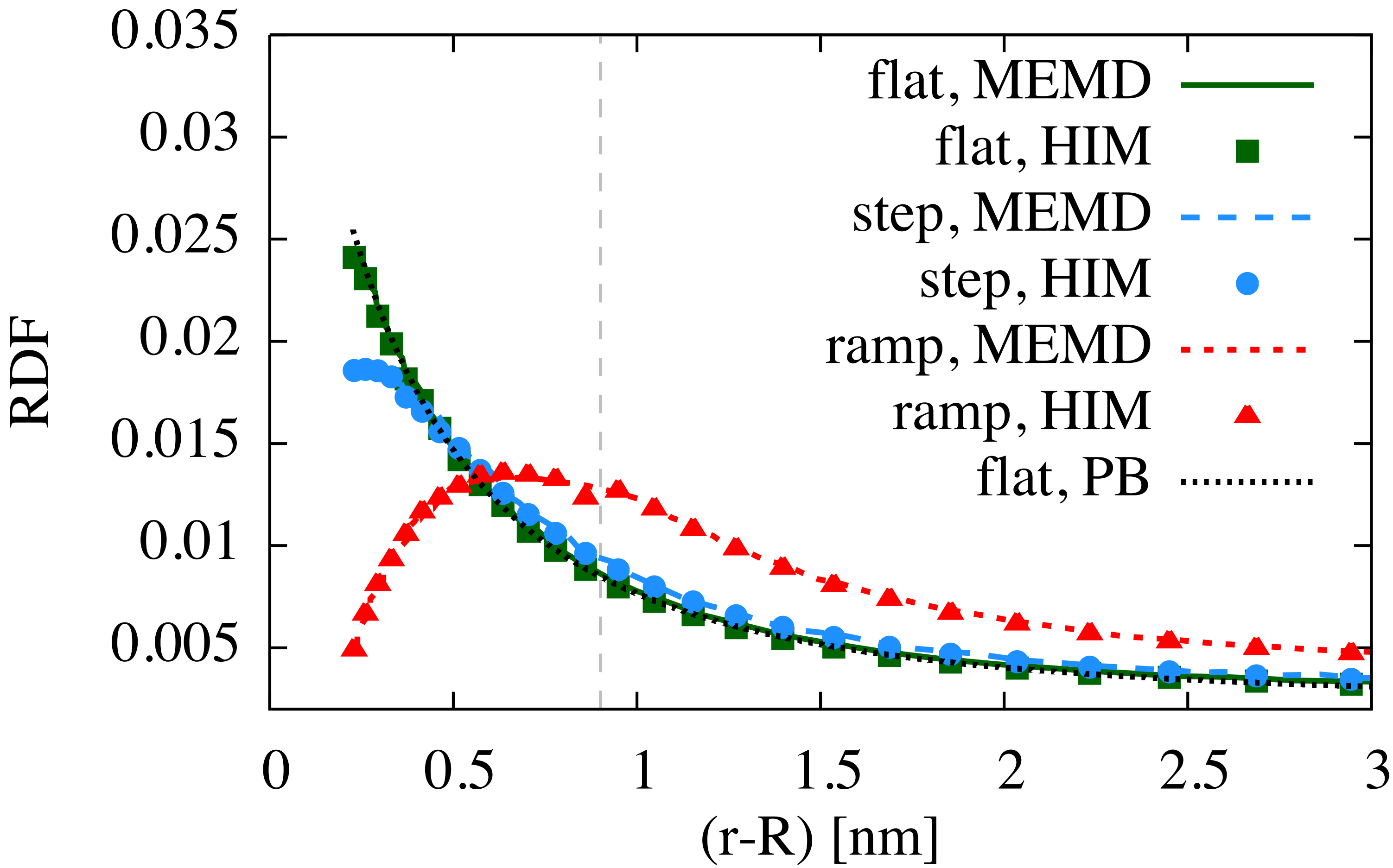
MEMD with Variable Dielectric





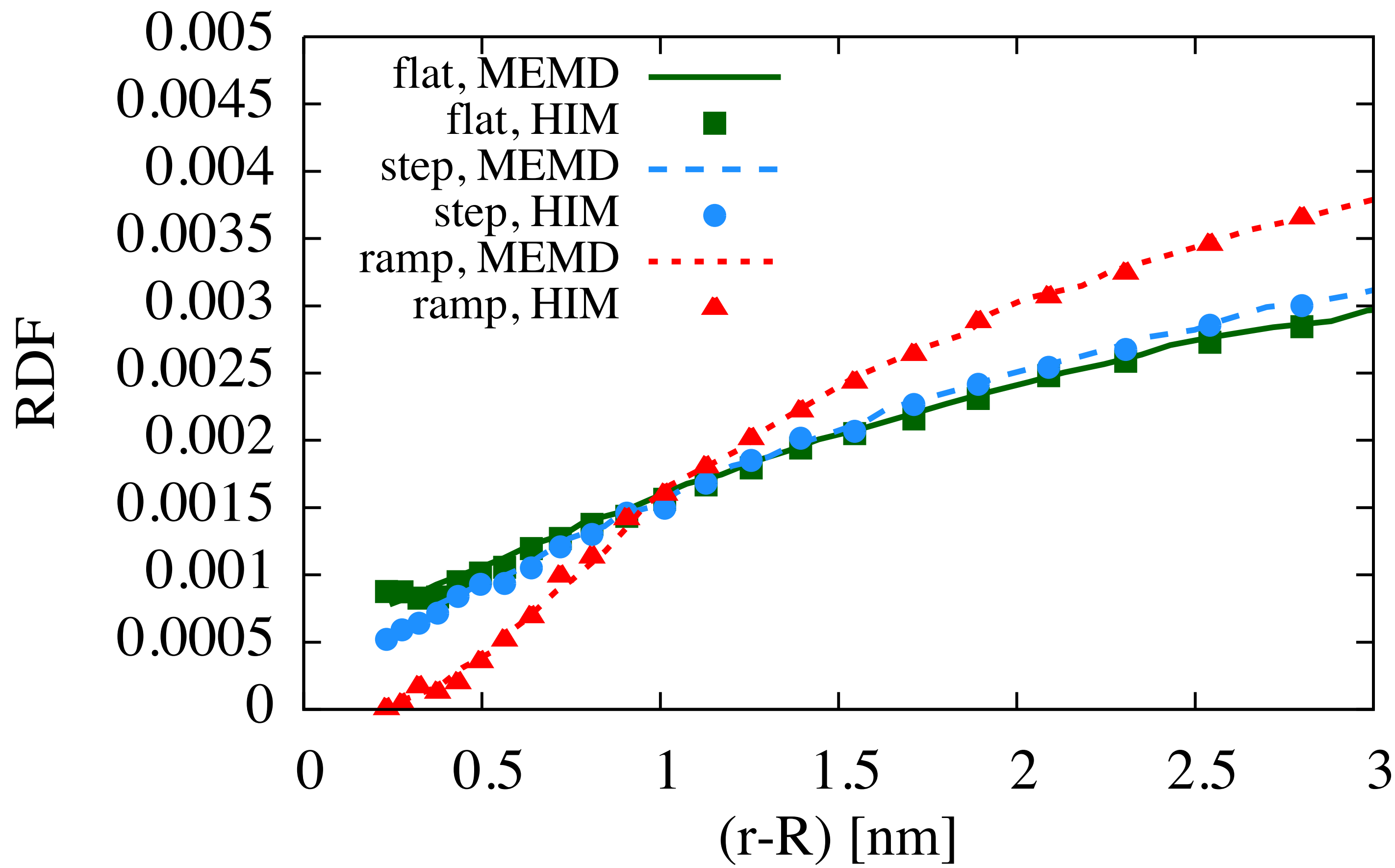
- permittivity as a vector (differential1-form), taken as the difference between adjacent lattice points (harmonic average)

Results for the Counterion RDF



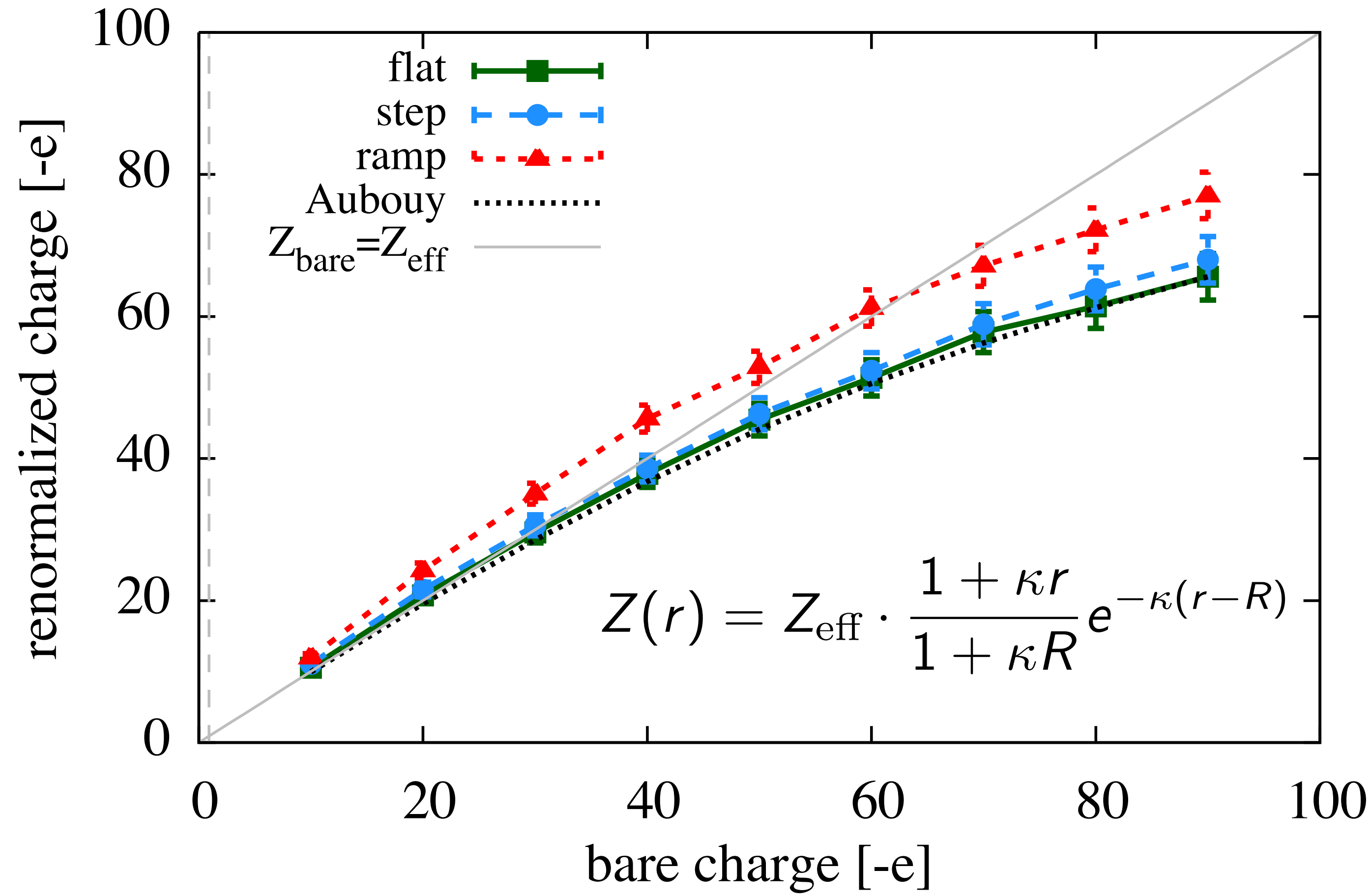
$C_s = 60$ mMol

Coion Depletion (Q=30, c_s=20 mMol)



- Finite coion density at surface for **flat** and **step** model
- Zero coion density at surface for **ramp** model

Far-Field Properties Change



$$Z_{\mathrm{eff}} = \frac{R}{\ell_B}\left[4\kappa R t_Q + 2\left(5 - \frac{t_Q^4+3}{t_Q^2+1}\right)t_Q\right],$$

M. Aubouy at al. , J. Phys. A: Math. Gen. **36**, 5835–5840 (2003)

Intermediate Conclusion

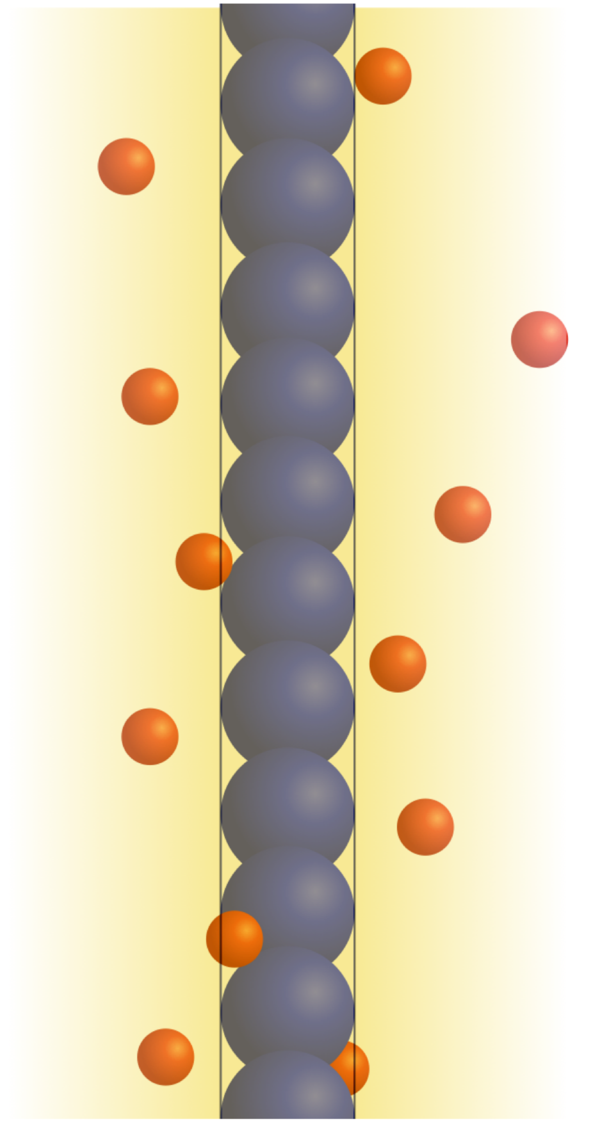
- MEMD has been tested on many other systems
- Both methods, HIM and MEMD, agree very well
- Born self-energy term can get very big
- Dielectric properties around colloids matter, in the near region but also in the far-field!
- The **dielectric gradient** is **important**, not so much the sharp jump!
- MEMD is a completely local algorithm (good for parallelization)
- Almost as fast as P3M (particle-mesh-Ewald)

We now know it works...

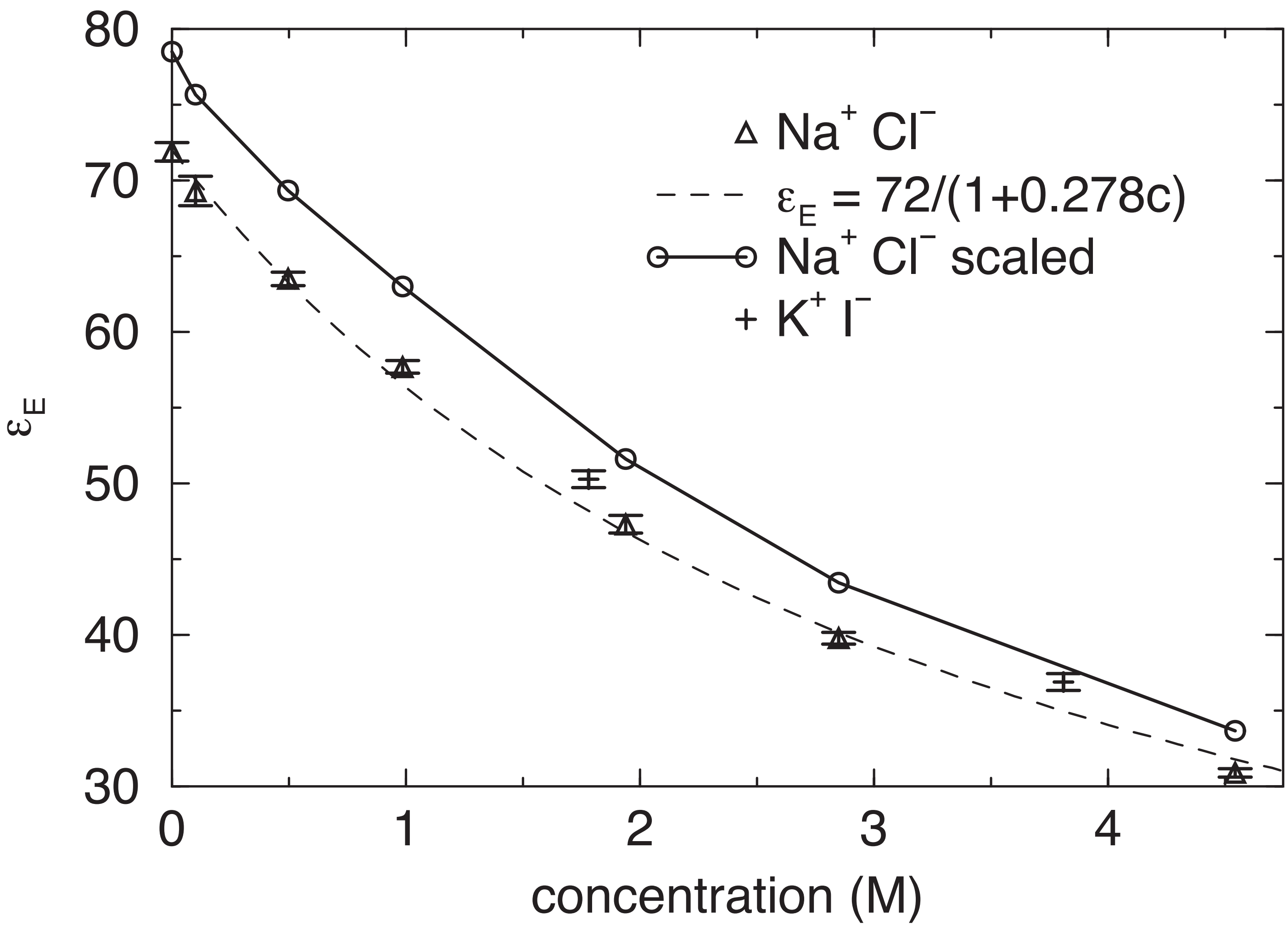
- Apply it to charged macromolecules (polyelectrolytes)
- investigate the influence of heterogeneous dielectric environment on electrokinetic properties

Charged Rod Model

- MD simulations with MEMD
- polyelectrolyte with charge -1
- monomers fixed in space
- no additional salt



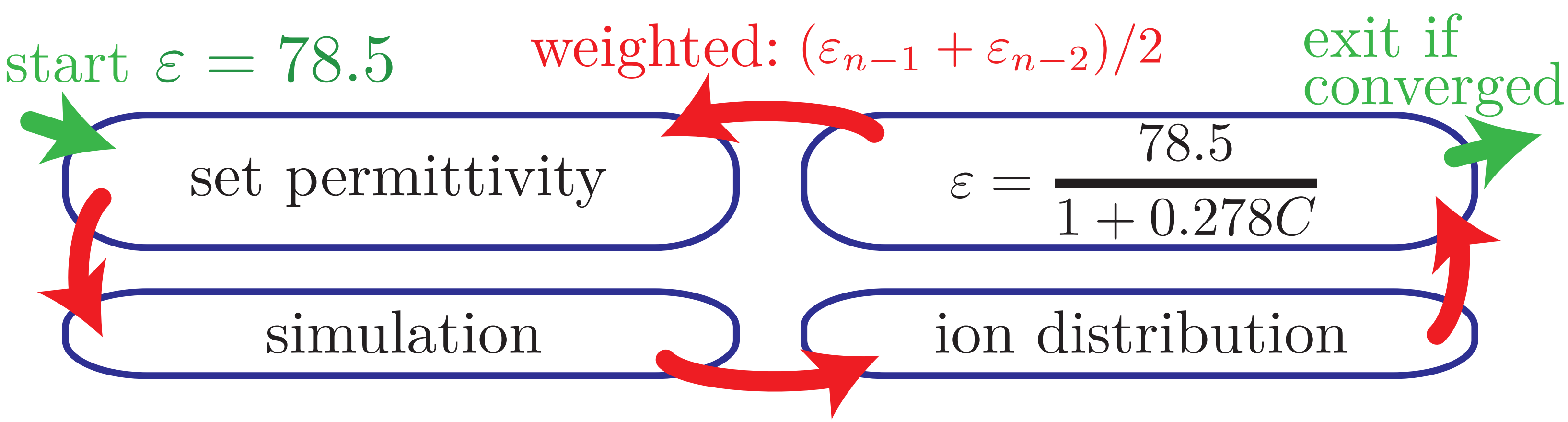
ε_r depends on salt concentration



All-Atom MD, SPC/E explicit water

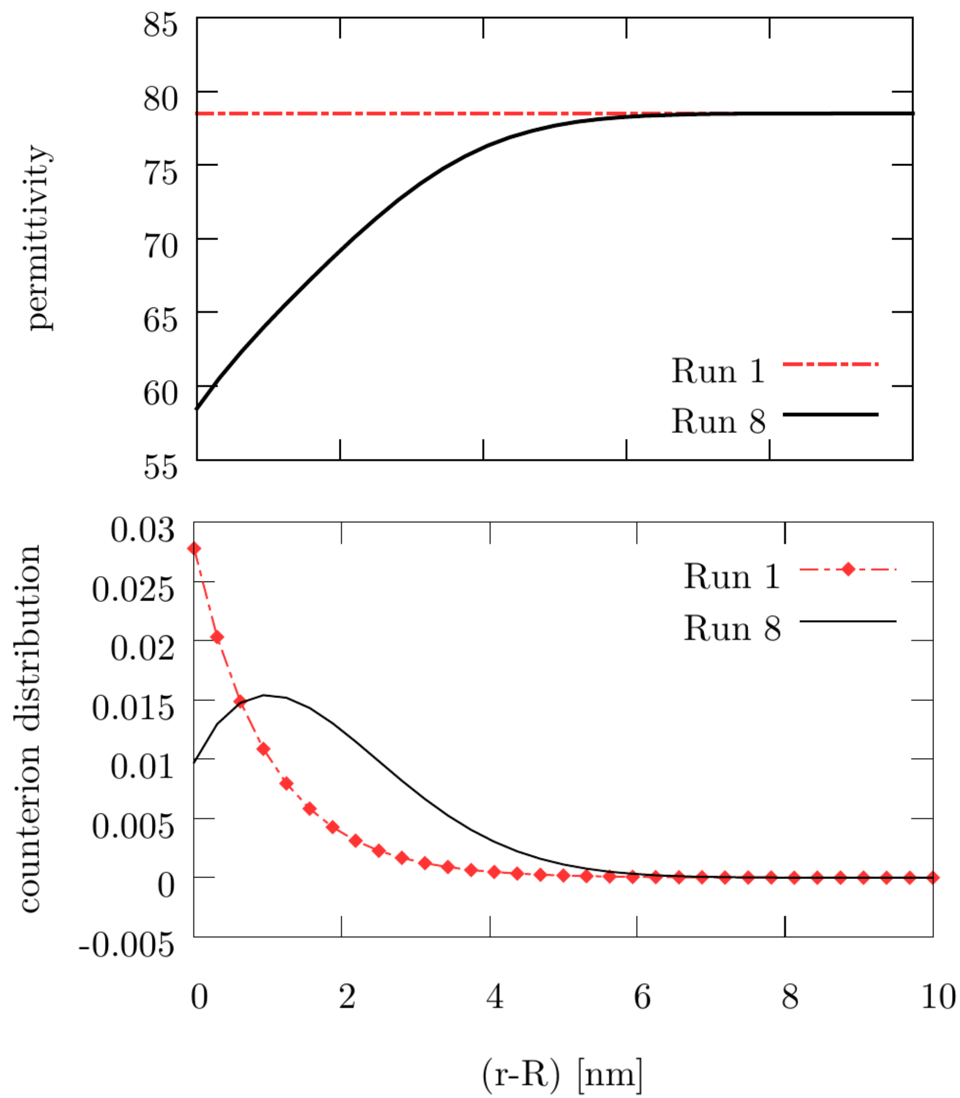
B. Hess, C. Holm, N. van der Vegt: PRL **96,** 147801 (2006)

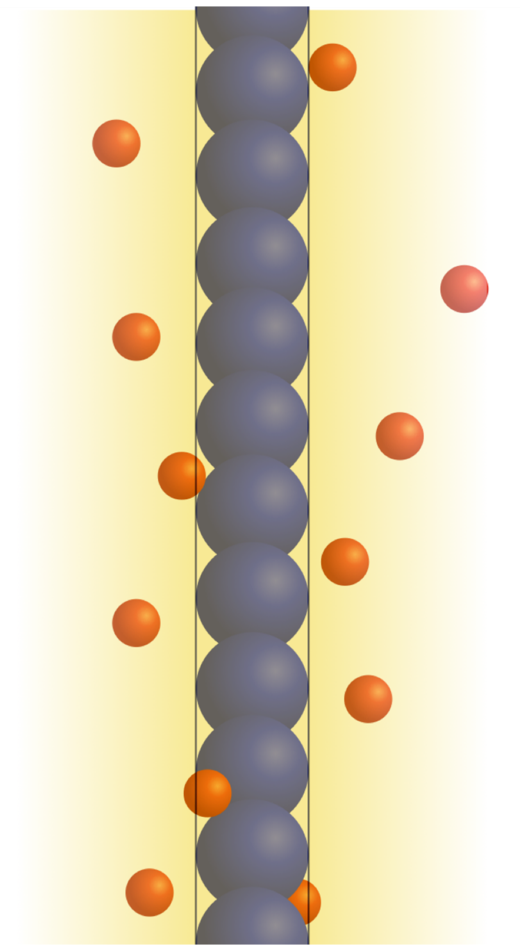
Adapt ε via iterative Procedure



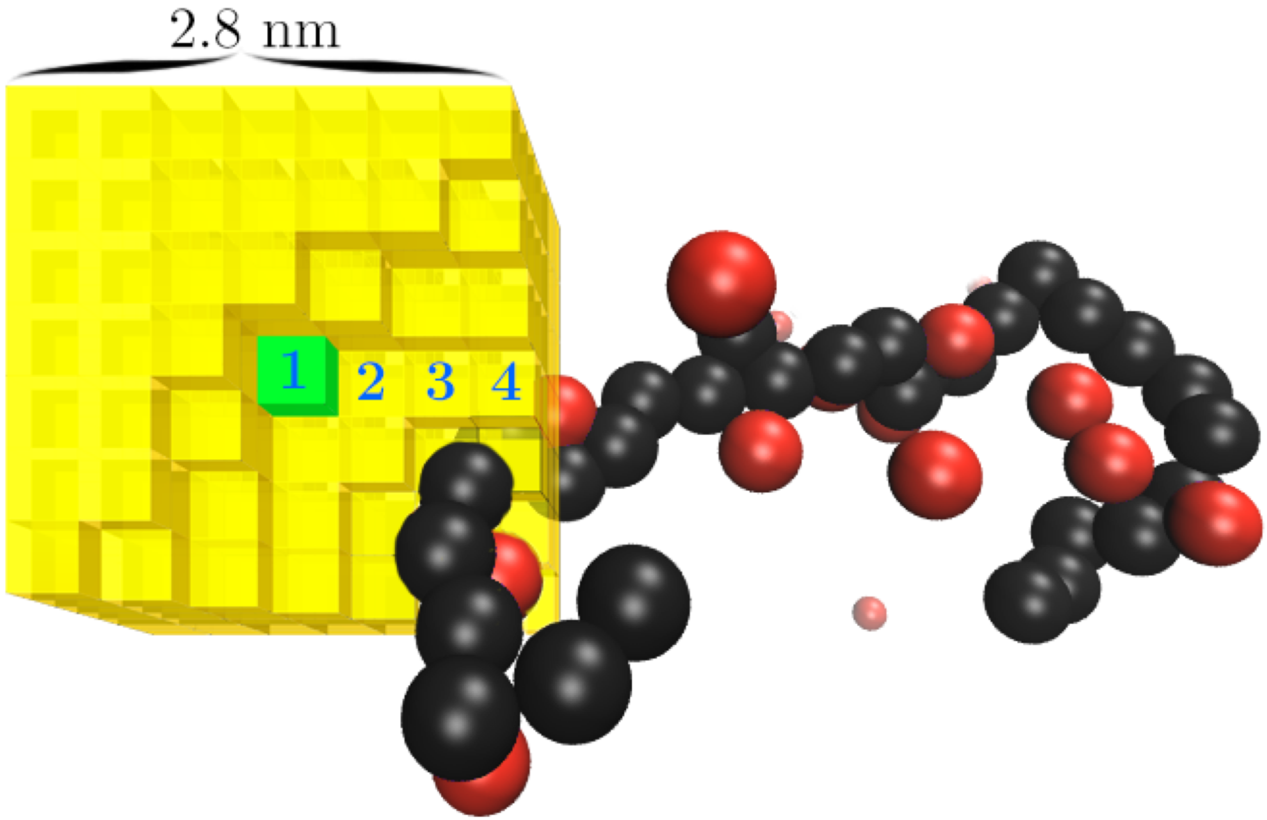
- permittivity 2 „inside“ the rod
- mapped, varying permittivity outside, depending on the radial counterion distribution
- iterative changes in salt concentration

Result: Interfacial Repulsion



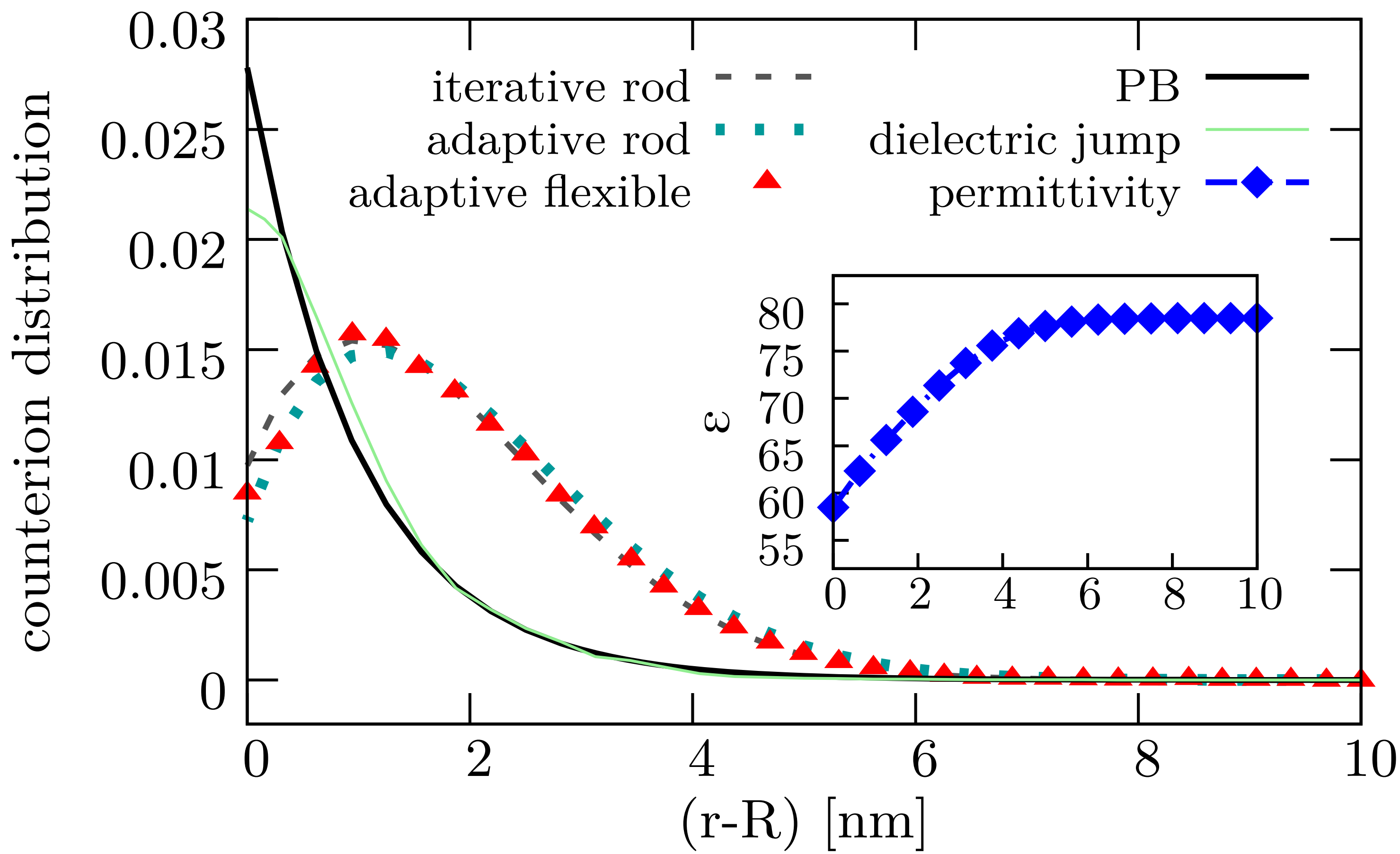


Adaptive Scheme for Flexible PE



- calculate salt concentration „on the fly“
- all charges are taken into account
- surrounding 7^3 cells, weighted
- update every 10 time steps
- overlap results in sufficiently smooth changes

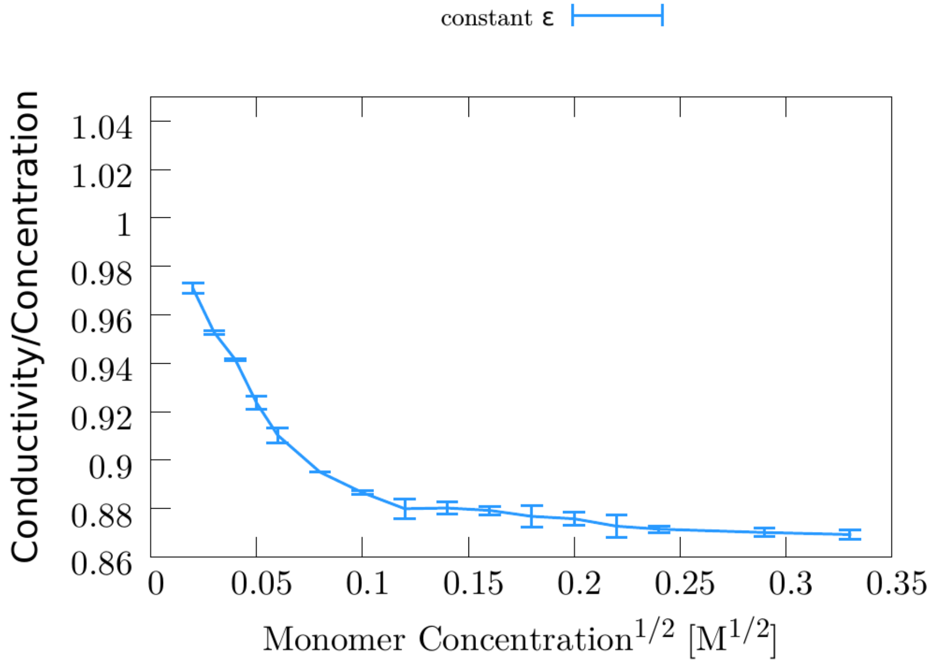
Method Comparison

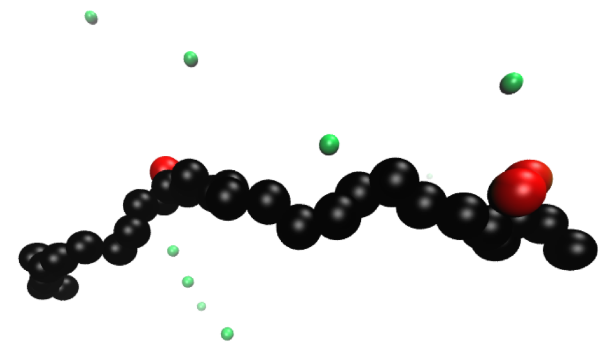


- qualitative changes compared to PB
- Counter ions pushed away from polyelectrolyte, **electrokinetic** properties might be different!
- consistent with all-atom MD

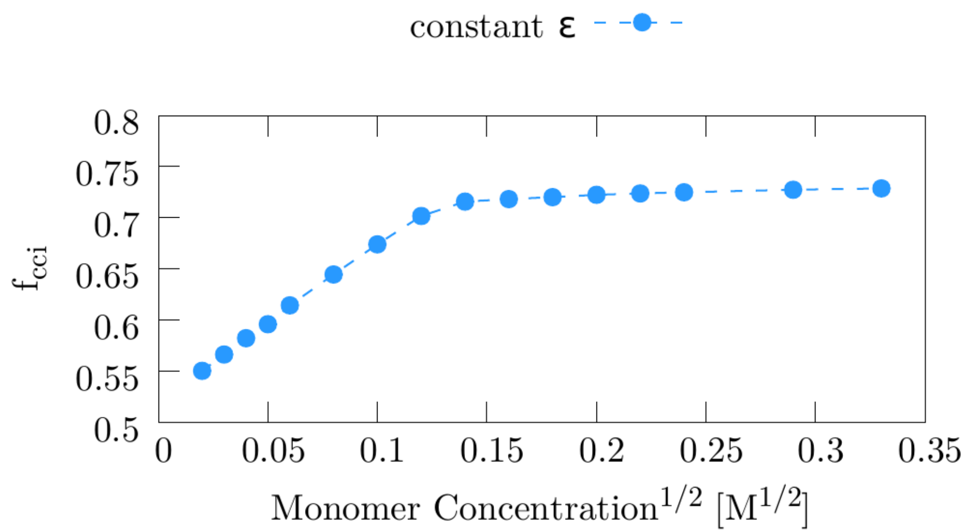
Measure Equivalent Conductivity

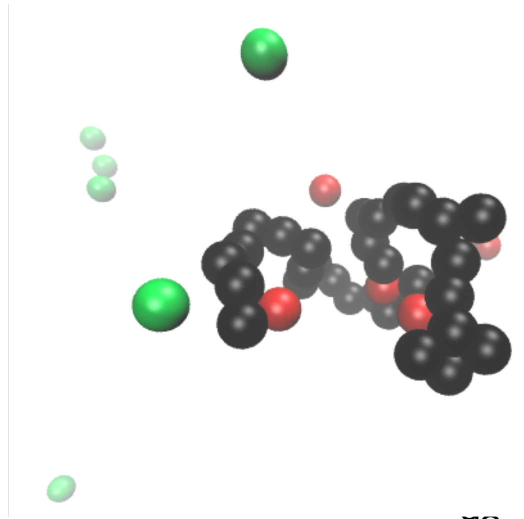
$$\Lambda = \frac{j}{ELC},$$



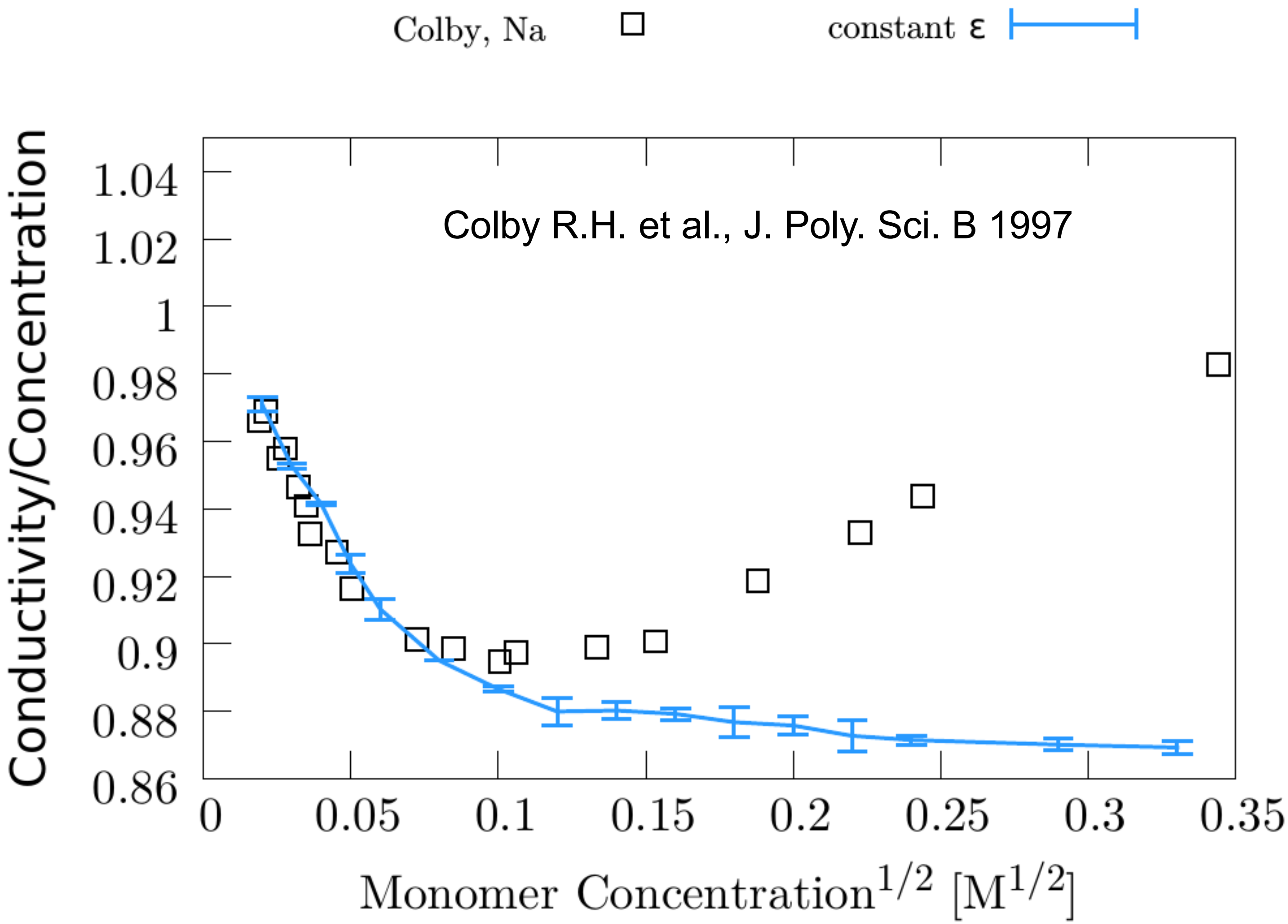


F. Fahrenberger et al., JCP **143**, 243140 (2015)

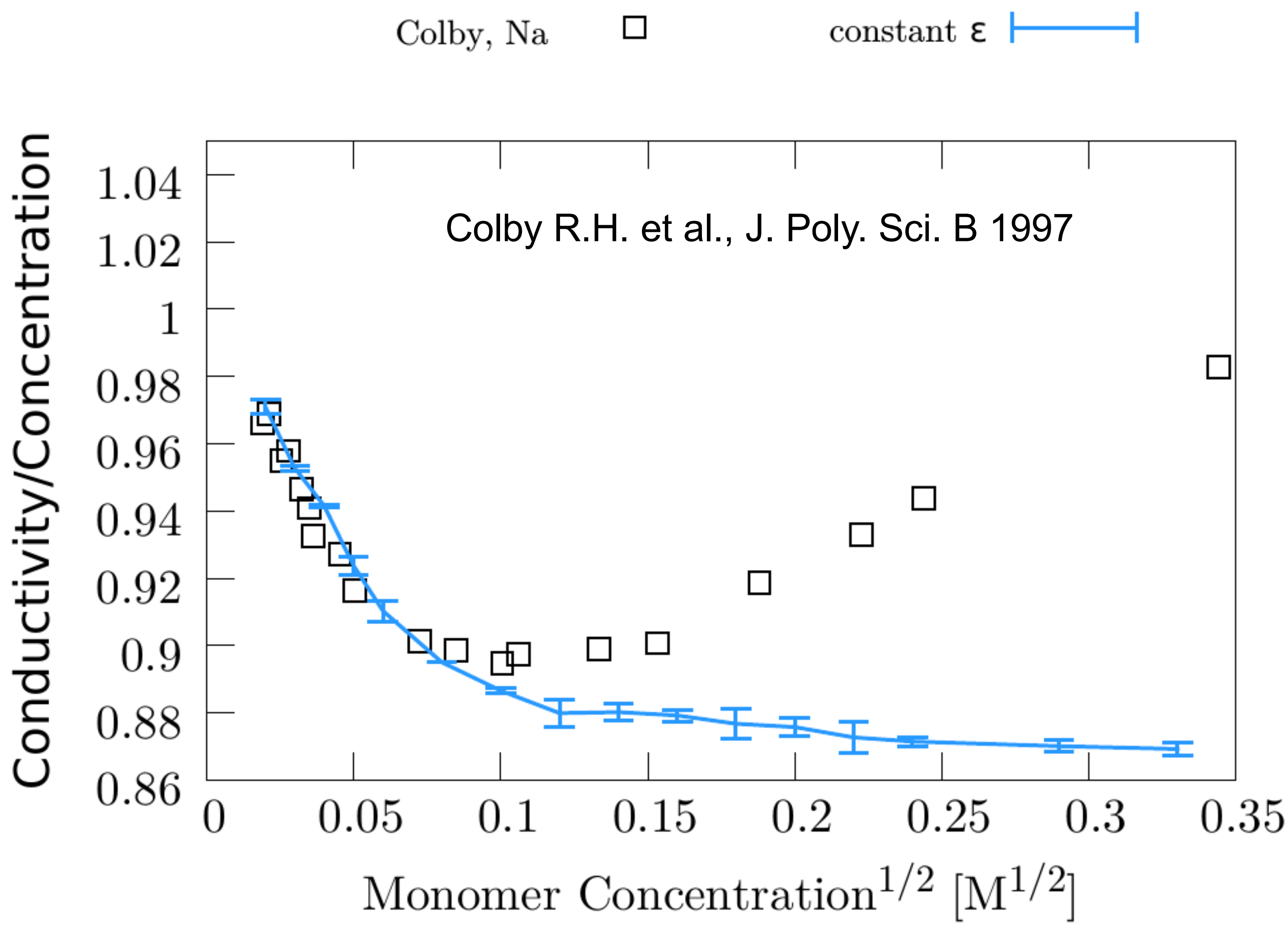




Comparison to Experiments

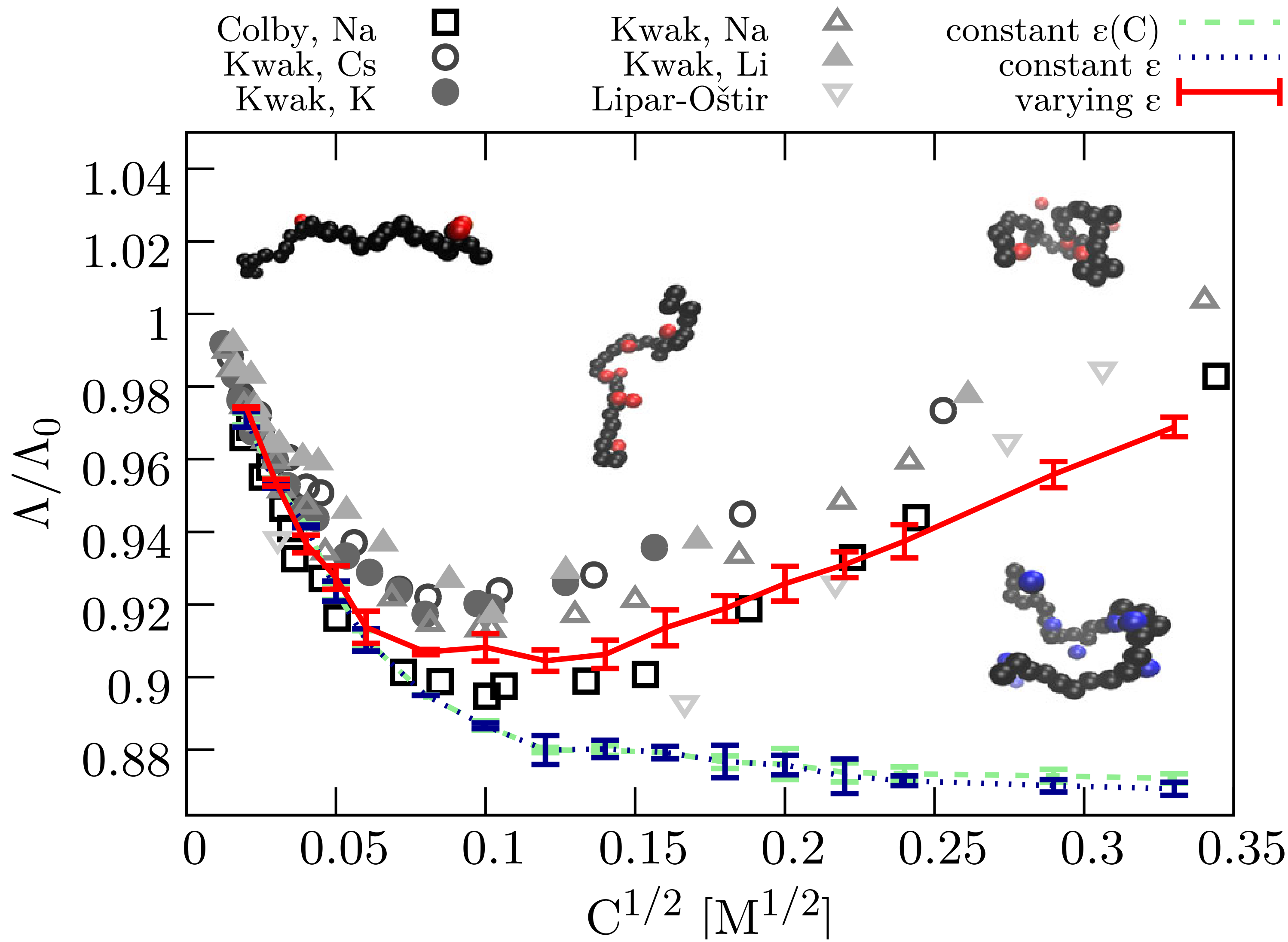


Comparison to Experiments

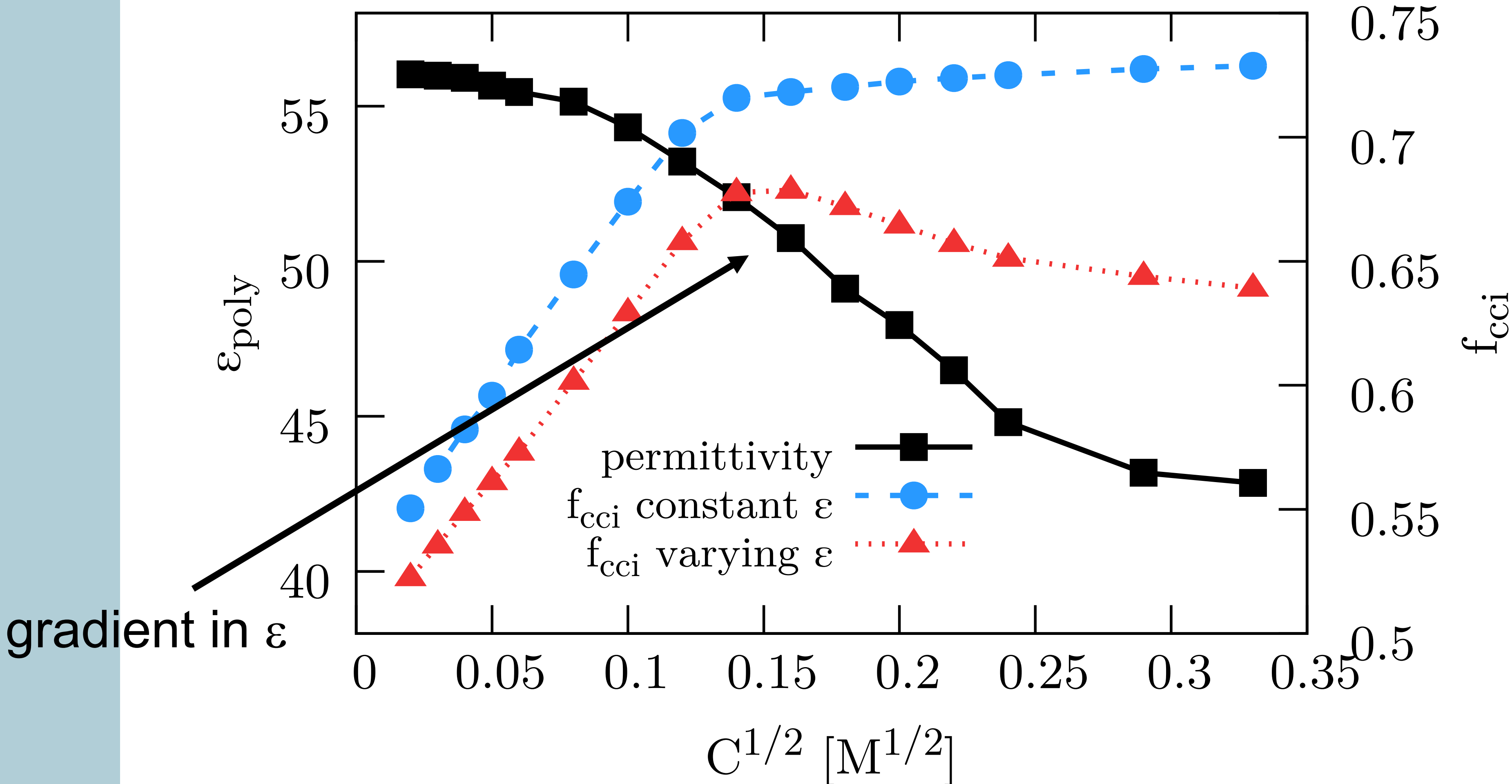


Try Varying ε Method with MEMD…..

Equivalent Conductivity



Local Permittivity around the PE



F. Fahrenberger, O. Hickey, J. Smiatek, C. Holm, Phys. Rev. Lett. **115**, 118301 (2015)

Conclusions on Inhom. Dielectrics

- Influence of dielectric mismatches investigated: Important for coarse-grained models with implicit water
- For permittivity gradients we find a repulsion of counterions at close distances (Born energy)
- Find quantitative changes in far field properties
- Find **qualitative** changes in electrokinetic properties
- Needed for quantitative predictions

Acknowledgements

F. Weik, S. Kesselheim, S. Raafatnia, O.W. Hickey, F. Fahrenberger, G. Rempfer, Z. Xu, K. Grass, B. Dünweg, V. Lobaskin, U. Schiller, T. Palberg, U. Keyser,…

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Dynamische Simulation von Systemen mit großen Teilchenzahlen