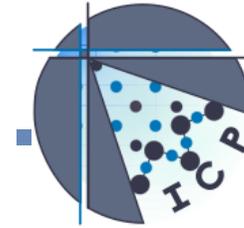


**University of Stuttgart**  
Germany



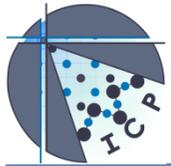
**INSTITUTE FOR  
COMPUTATIONAL  
PHYSICS**

# Ionic Liquids studied across different Scales

---

<sup>1)</sup>Christian Holm, <sup>1)</sup>F. Dommert, <sup>2)</sup>K. Wendler, <sup>3)</sup>L. Delle Site, <sup>4)</sup>R. Berger

- 1) Institut für Computerphysik, Universität Stuttgart, Germany
- 2) Max-Planck-Institut für Polymerforschung, Mainz, Germany
- 3) Institut für Mathematik, FU Berlin, Germany
- 4) Clemens-Schöpf-Institut, Technische Universität Darmstadt, Germany



# Collaborators

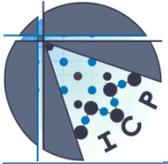


R. Berger (TU Darmstadt), L. Delle Site (FU Berlin), K. Wendler (MPIP-Mainz), B. Kirchner (Leipzig), F. Dommert (ICP)

S. Balasubramanian for correspondence on CPMD data

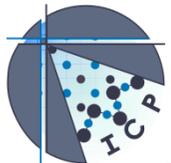
B. Qiao, C. Krekeler, J. Schmidt, Y.Y. Zhao

€€: DFG- SPP 1191, HLRS for Computer time, GROMACS



# What are Ionic Liquids?

- Molten salts with a melting point below 373 K (NaCl has 1074 K)
- Green solvent: vanishing vapor pressure, environmental friendly, non-flammable
- Applications: catalysis, battery solvents, solar cells,...
- Designer solvents ...



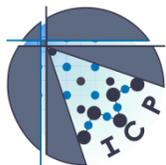
# Design Principles...

To produce an ionic liquid one has many choices:

- Variation of cation
- Variation of side chains for imidazolium
- Variation of anions
- Mixtures, chiral solvents, ILCs

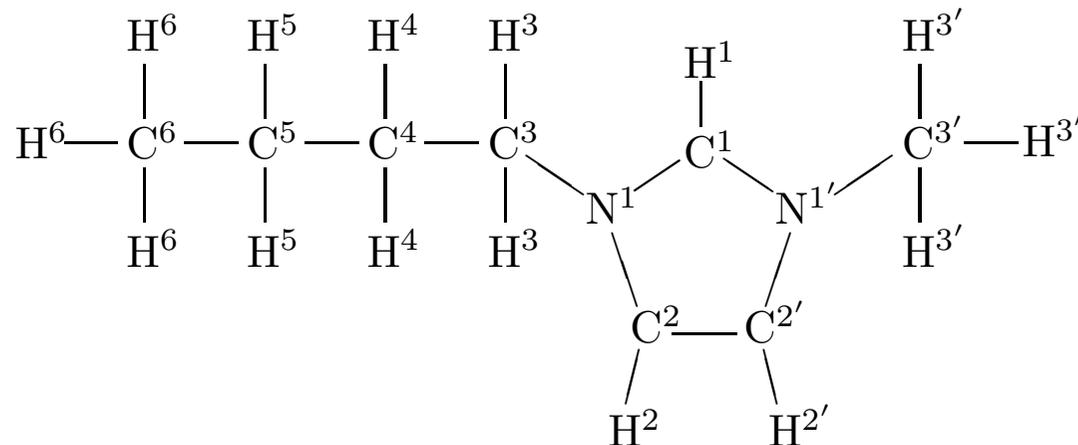
Normally one *a posteriori* measures the properties

Desire for rational design, i.e. predicting properties before synthesis: Can one model ILs *a priori*?



# Investigated Systems

imidazolium based cations:  $[C_nMIM]^-$  with  $n=1,2,4$



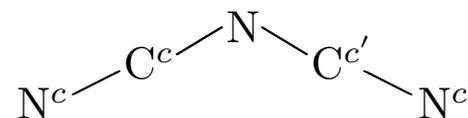
thiocyanate

chloride

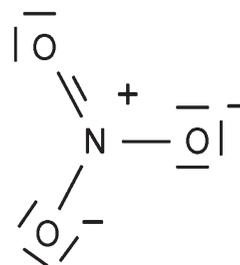
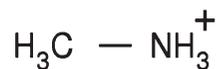
dicyanamide

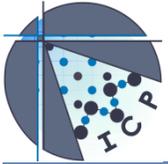


(d)

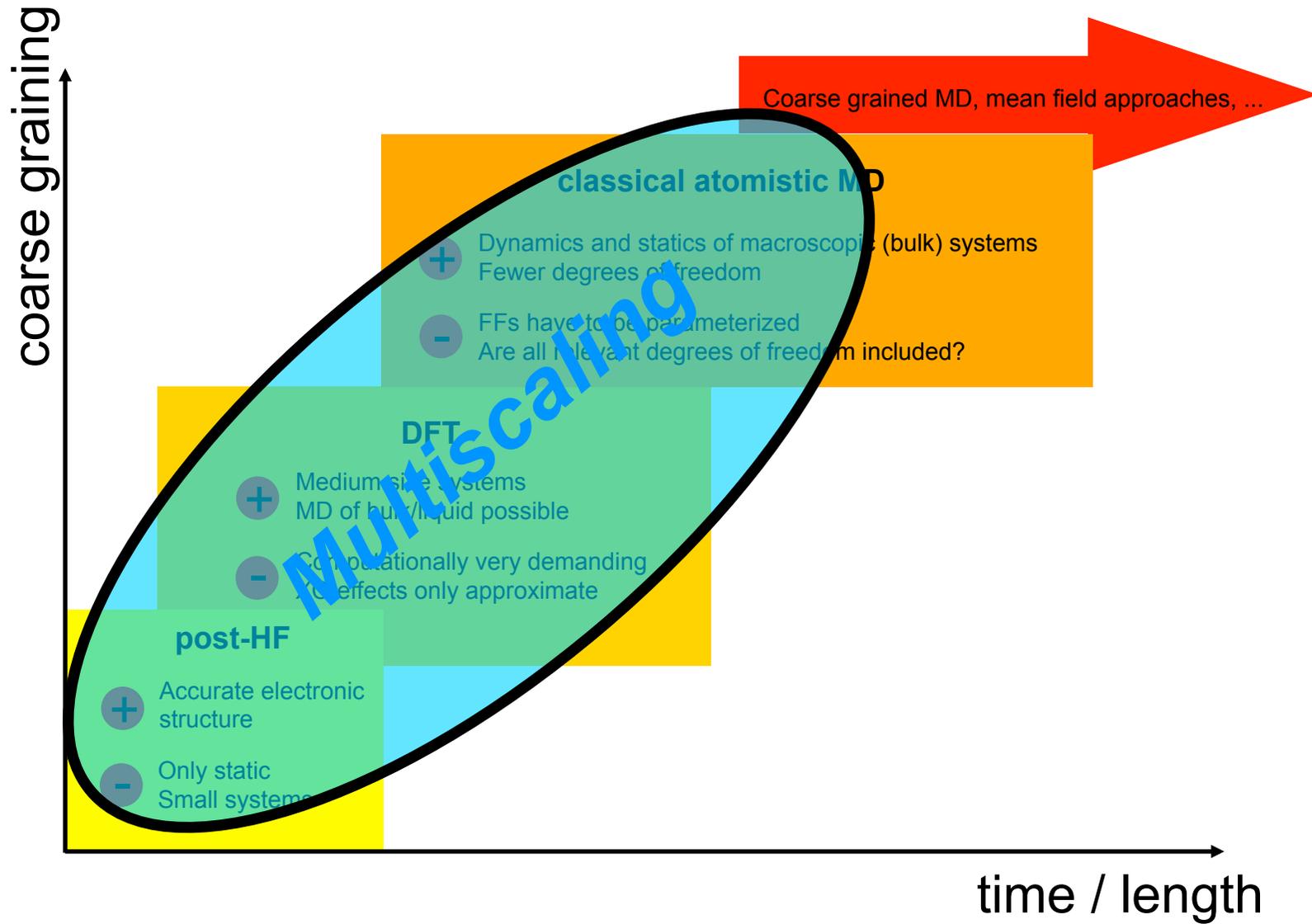


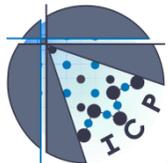
Protic IL:  
monomethyl  
ammonium  
nitrate (MMAN)





# The Multiscaling Idea

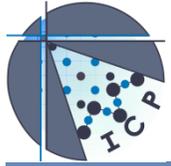




# Problems with Current IL Classical FFs

- Dynamics an order of magnitude to slow
- Dielectric properties questionable
- Missing transferability
- Slow dynamics makes it time consuming to parametrize them
- Polarizability often not taken into account
- *StandardFF* CLaP: C. Lopez and A. Padua, J. Phys. Chem. B **110**, 19586 (2006)

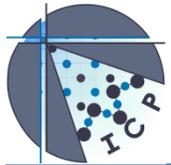
F. Dommert et al., *Force Fields for Studying the Structure and Dynamics of Ionic Liquids: A Critical Review of Recent Developments*, ChemPhysChem 2012, <http://dx.doi.org/10.1002/cphc.201100997>.



# Previous Charge Scaling Approaches

**Conventional Solution:** semi-empirical approach (“engineering”):

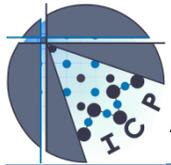
- Global scaling of ionic charges to  $q < \pm 1$ :
- Müller-Plathe et al. (1996), Morrow and Maginn (2002), Bühl et al. (2005), Bhargava and Balasubramanian (2007), Youngs and Hardacre (2008); may need additional refinement to reproduce the density correctly
- Drawback: **many** parameters, little physical guidance



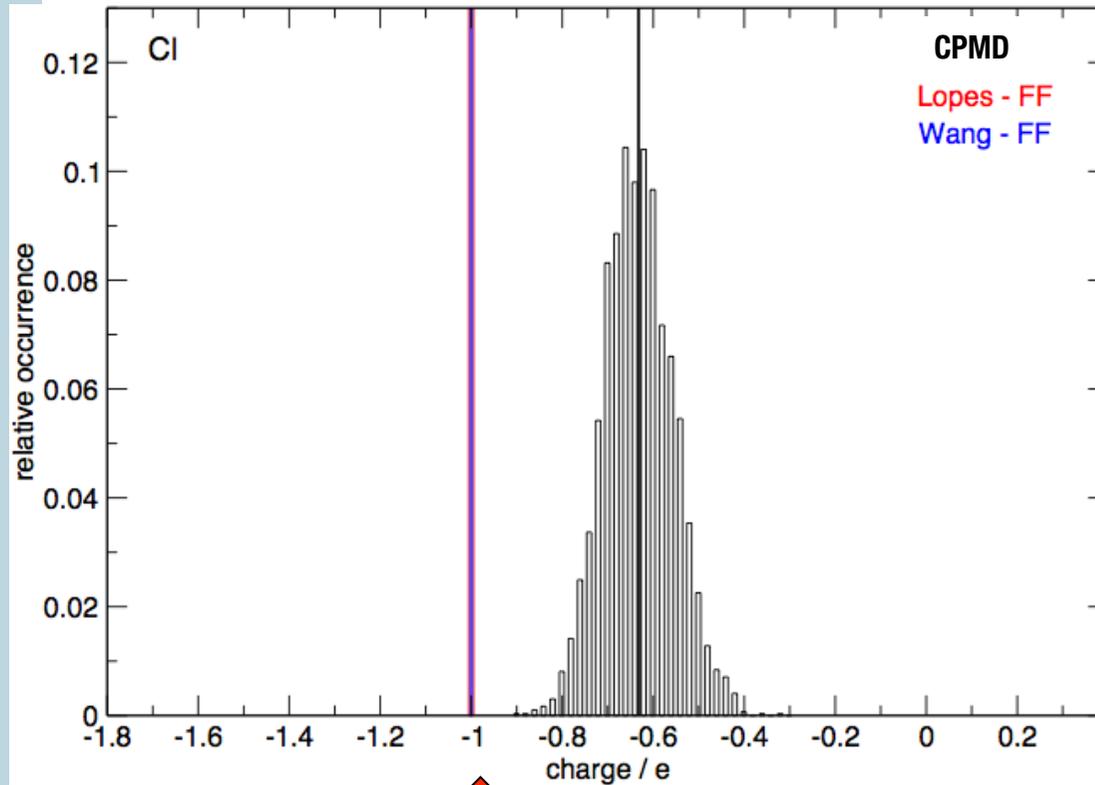
# Previous Charge Scaling Approaches

Conventional Solution: semi-empirical approach (“engineering”):

- Global scaling of ionic charges to  $q < \pm 1$ :
- Müller-Plathe et al. (1996), Morrow and Maginn (2002), Bühl et al. (2005), Bhargava and Balasubramanian (2007), Youngs and Hardacre (2008); may need additional refinement to reproduce the density correctly
- Drawback: **many** parameters, little physical guidance
- **Our approach**: fitting the electron density of a **bulk** system using the Blöchl method
- Partial charges derived from *ab initio* results...



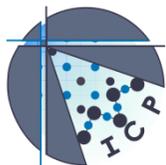
# Ab initio CPMD Results for the Bulk



- Charge fitting for 100 snapshots from the 30 IP CPMD simulation
- Using Blöchl method
- Corresponds to 3000 IPs

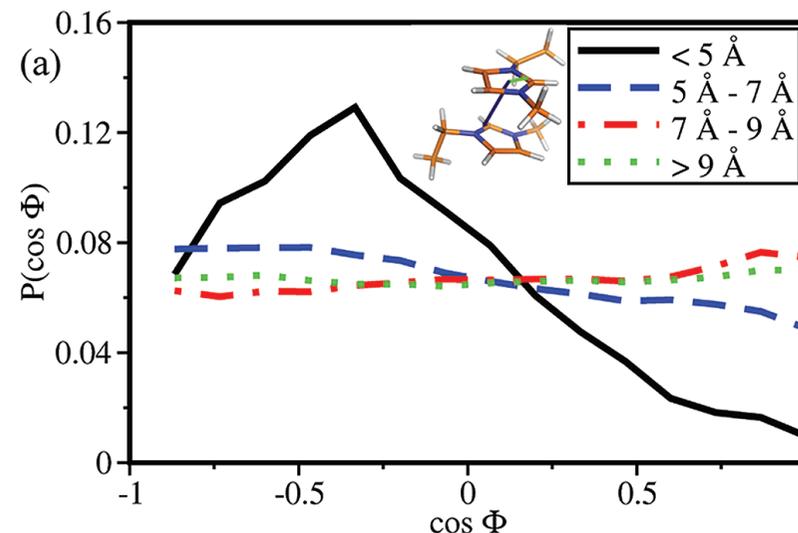
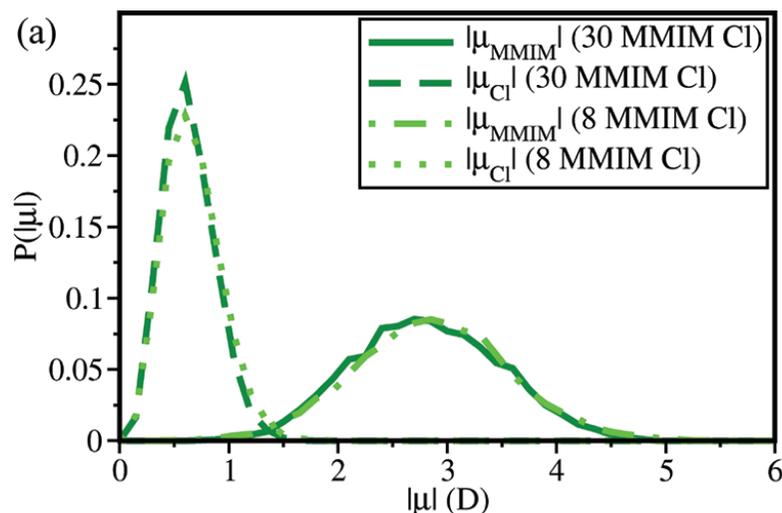
CLaP- FF

Charge screening  
reduces charge to  
 $\pm 0.63$

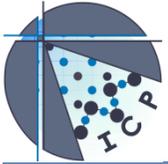


# Charge Scaling is general in ILs:

system	MMIM Cl	EMIM SCN	EMIM DCA	MMAN
$\geq 30$	$0.63 \pm 0.15$	$0.56 \pm 0.25$	$0.67 \pm 0.21$	$0.55 \pm 0.29$
8	$0.64 \pm 0.16$	$0.56 \pm 0.25$	$0.70 \pm 0.19$	$0.56 \pm 0.27$



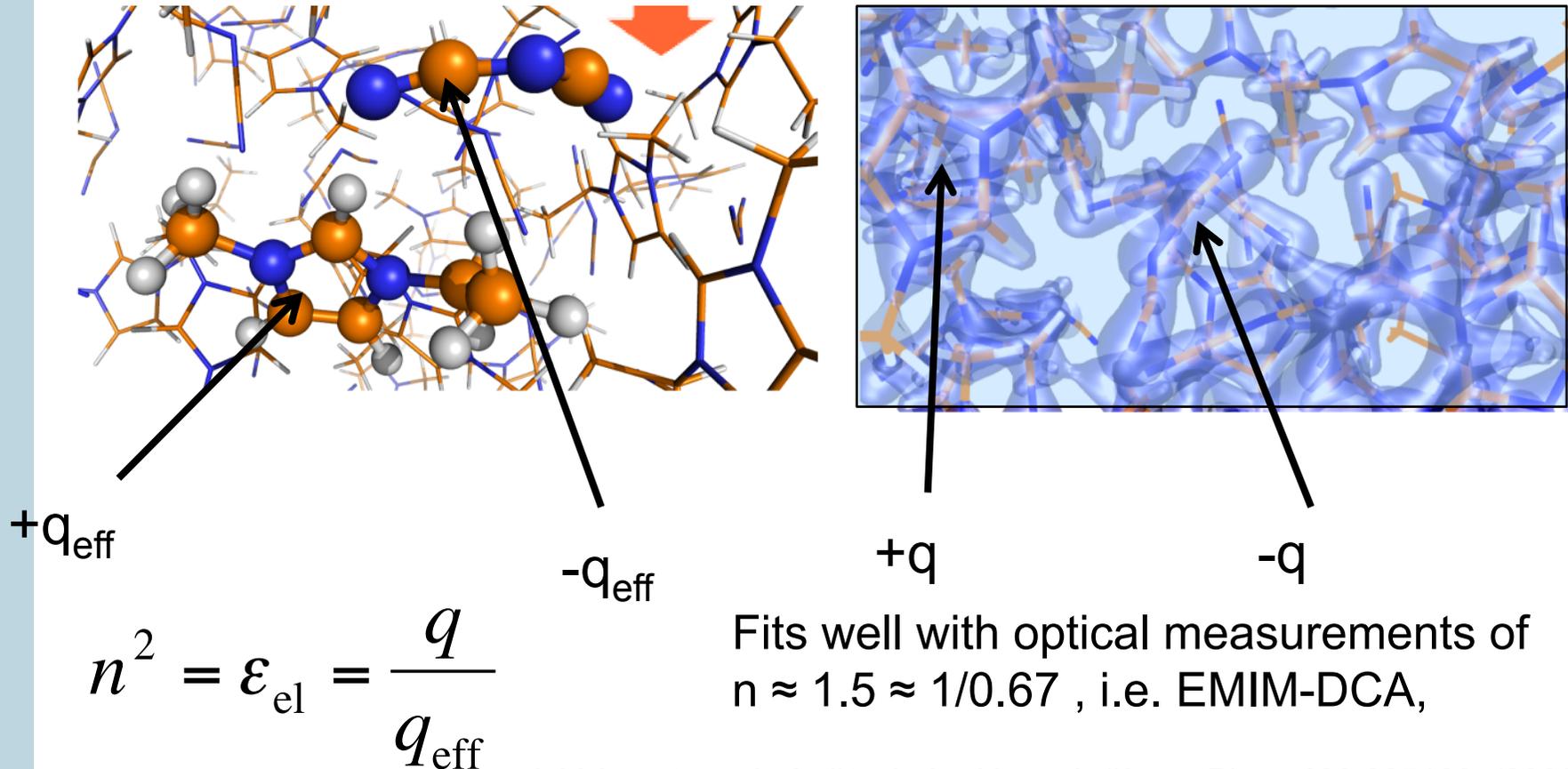
Charge correlations are local, but highly fluctuating  
 The reduced charges originate from *averaging*  
 polarization effects

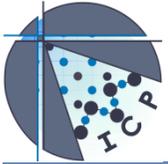


# Continuum Electrostatics MF Picture

$$E^{\text{Coulomb}} \approx \frac{q^2}{\epsilon_{\text{el}} r} = \frac{q_{\text{eff}}^2}{r}$$

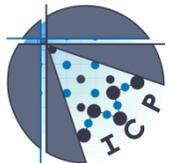
$$\epsilon_{\text{el}} = \left( \frac{q}{q_{\text{eff}}} \right)^2$$



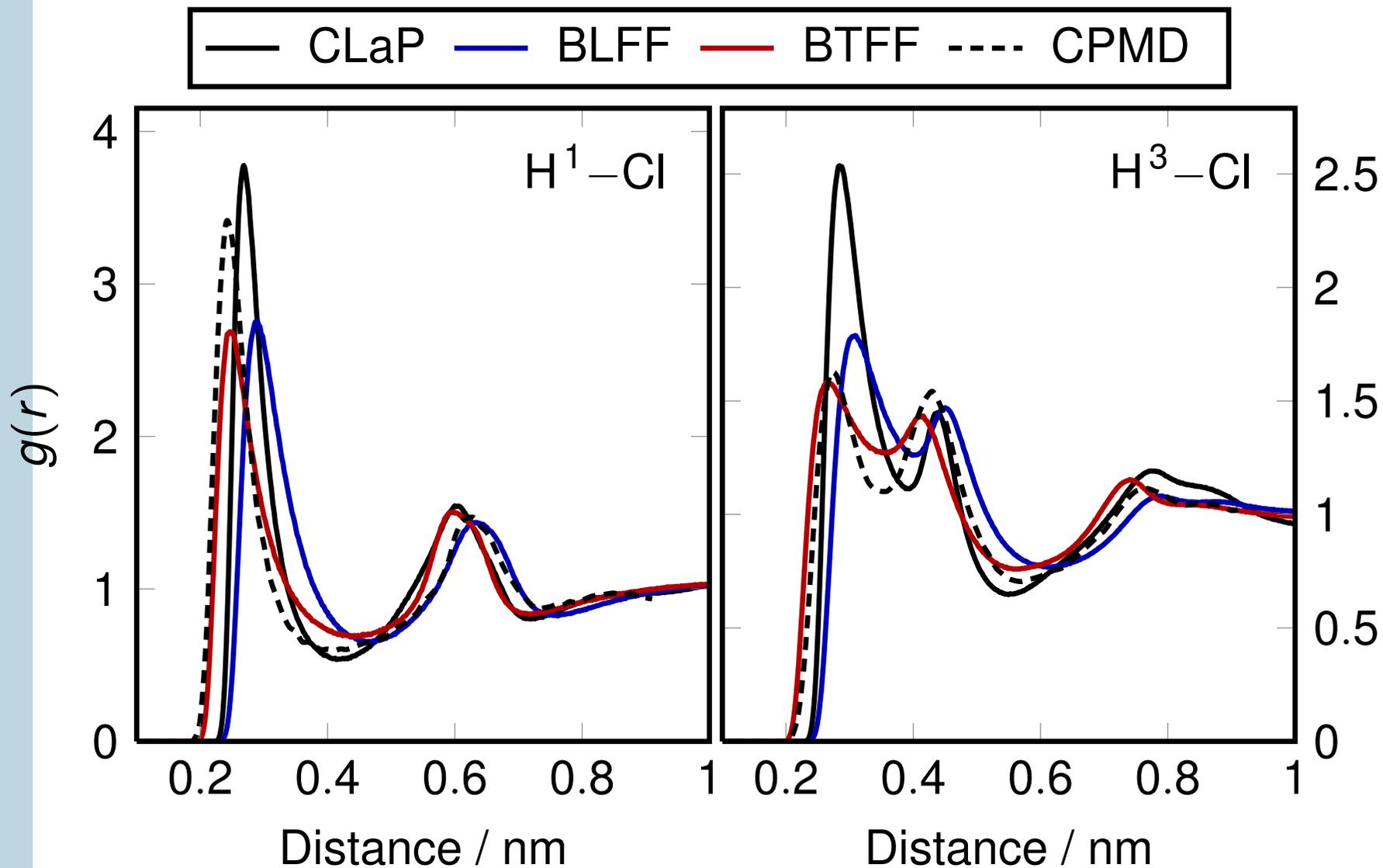


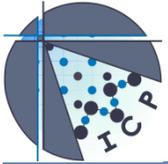
# The Blöchl Tuned Force-Field BTFF

- Changing partial charges in the Lopez (CLaP) FF will first invalidate it, yielding wrong densities, dihedral angles, etc.
- First step is to correct the dihedral angles by fitting to reference QM potential
- Second step: fit partial  $g(r)$  and densities over a range of temperatures
- Use automated iterative fitting procedure to specified target functions (F. Dommert, paper in preparation)
- All Results so far only for [MMIM][Cl]

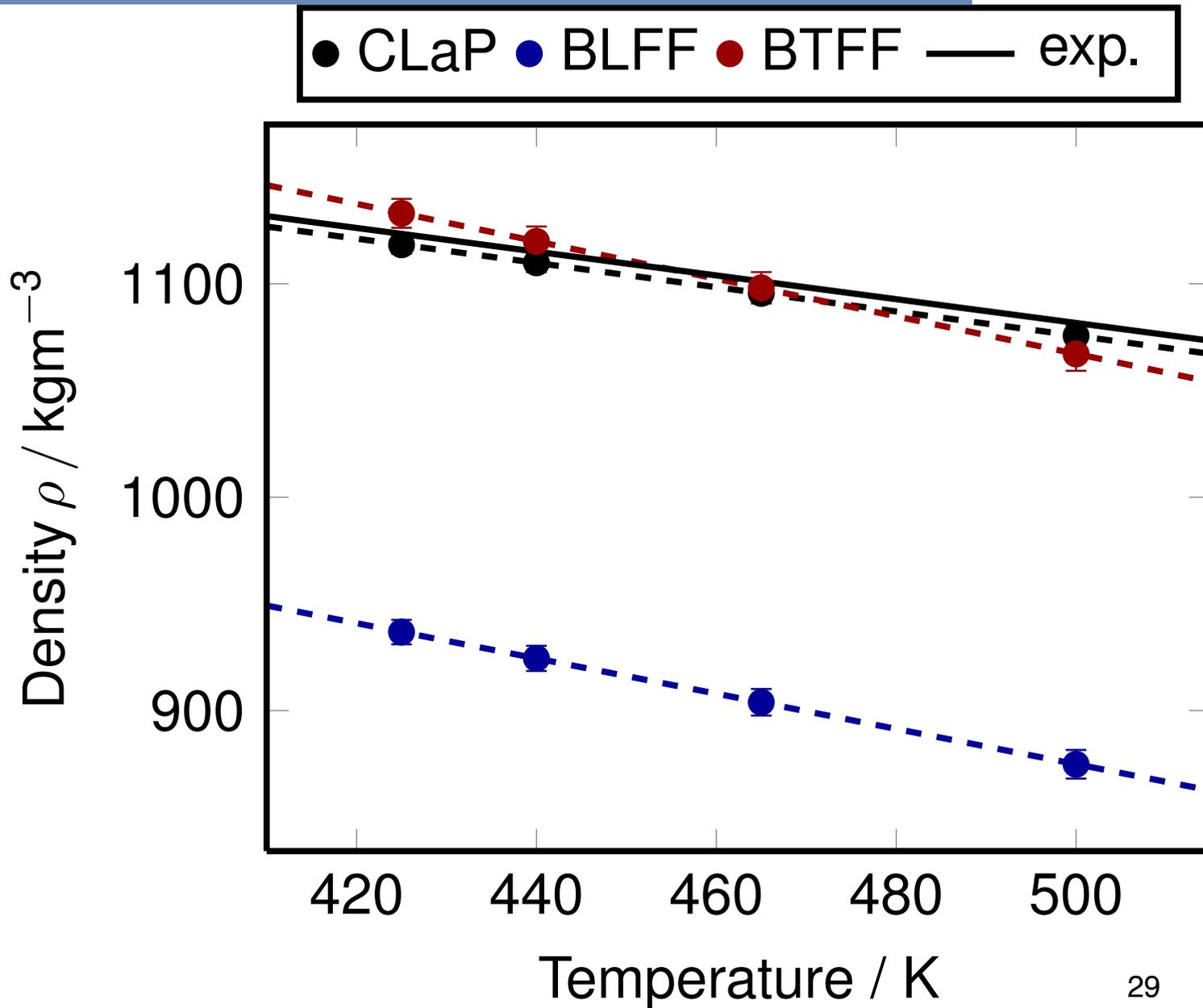


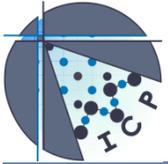
# Inclusion of RDFs into FF Fits



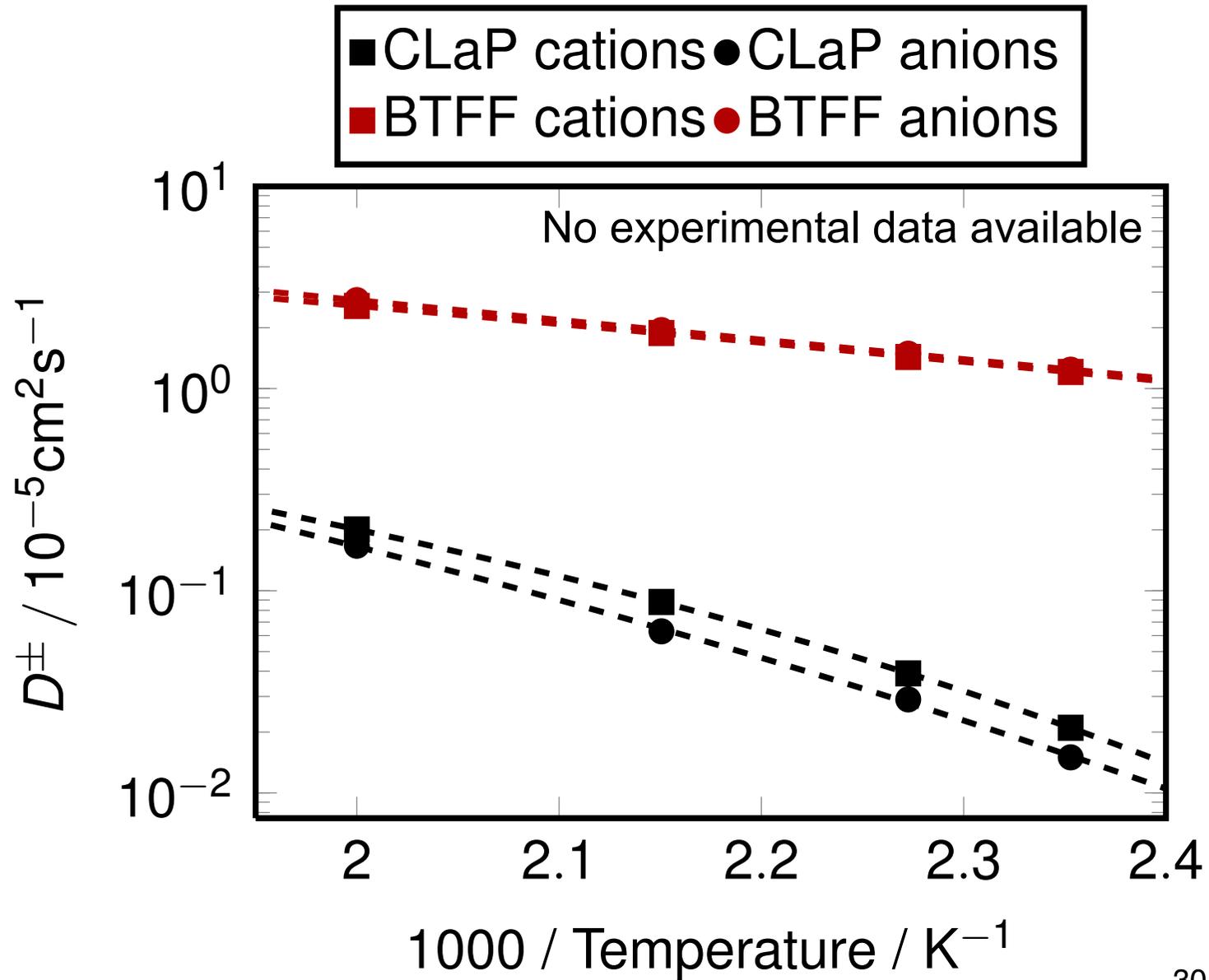


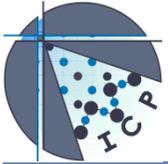
# Results: Density Fits





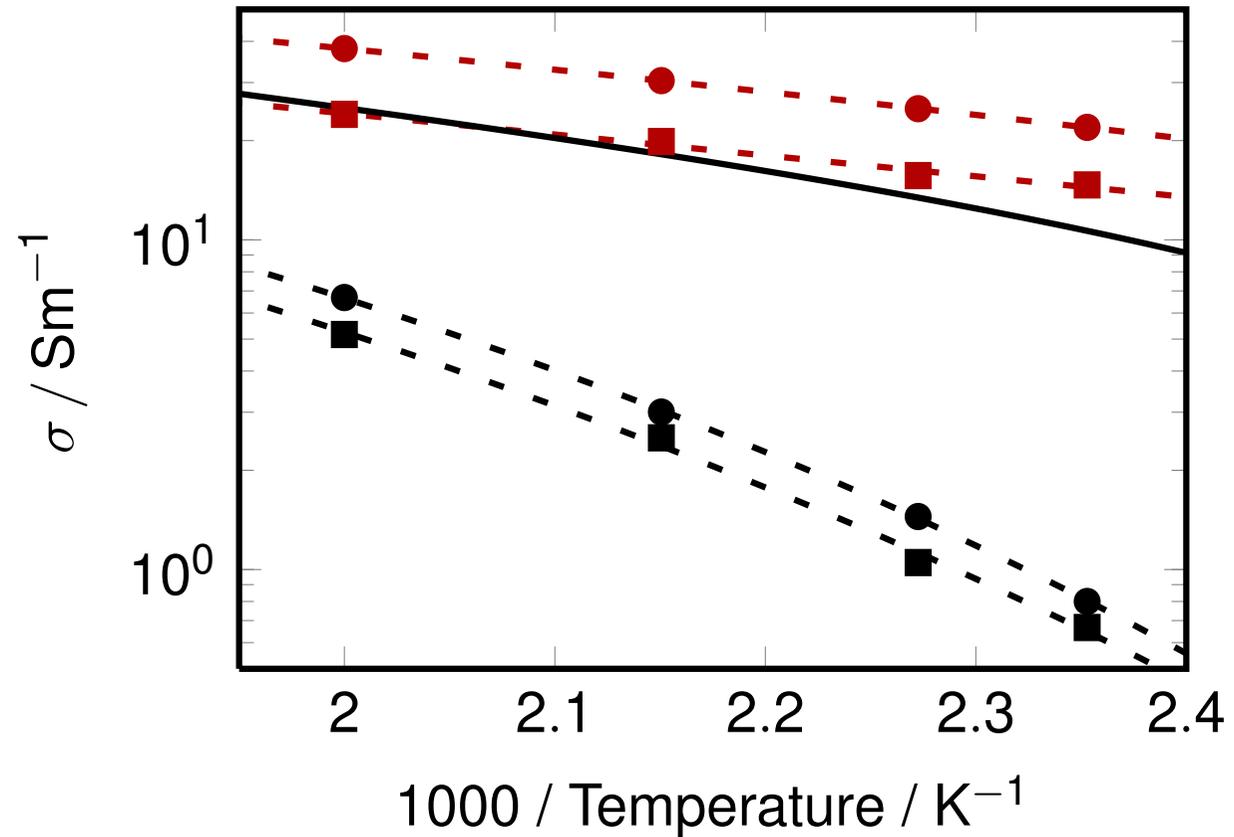
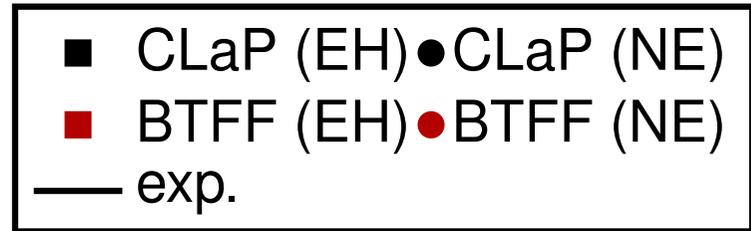
# Results of BTFF



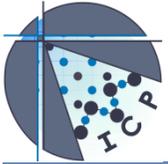


# Comparison of Conductivities

$$\sigma_{NE} = \frac{Nq^2}{Vk_B T} (D^+ + D^-)$$

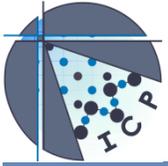


Exp: A. A. Fannin et al, J. Phys. Chem. **88**, 2609 (1984)

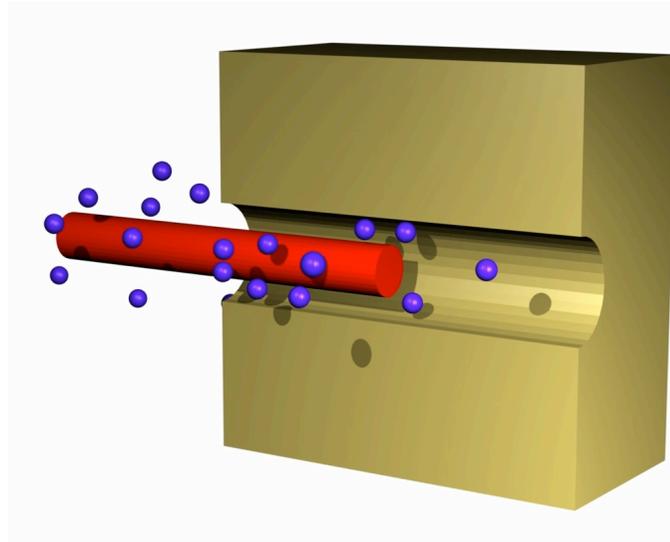


# Conclusions

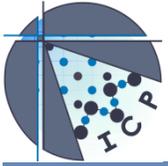
- Standard classical FF can reproduce structure but not dynamics
- Consistent mapping of geometric and electronic structure information from pHF to classical scale
- Charge scaling is a universal feature in IIs, electronic structure information can be used for partial charge reparametrization
- Large fluctuation on atomic site charges and dipole moments, however effects are very local
- A refined BTFF with reduced charges does give correct structure and much better dynamics than the CLaP
- Promising approach to parametrize a classical (non-polarizable) FF for ILs from ab-initio dat (contains average polarizability )
- Transferability?



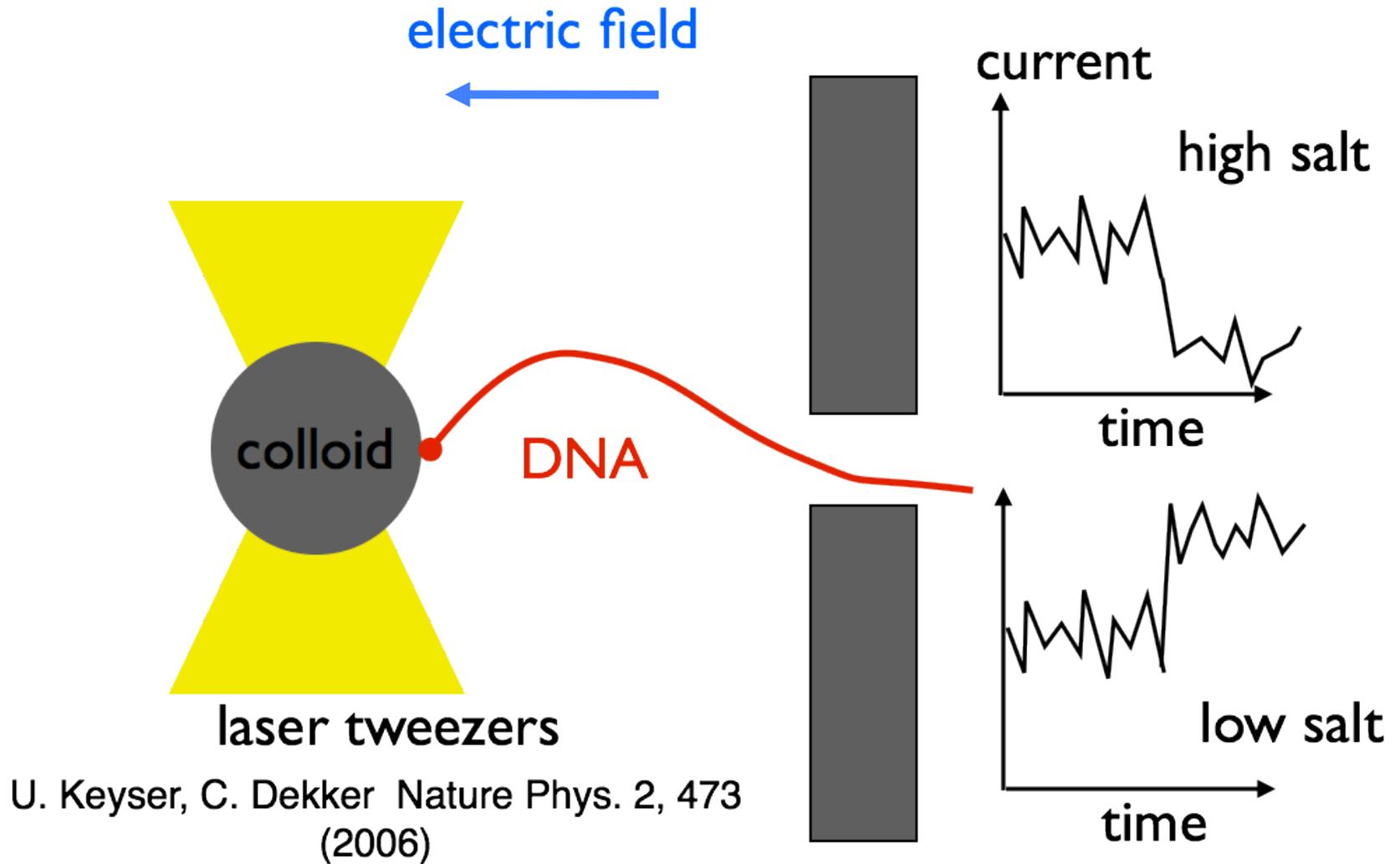
# Understanding electrical currents in DNA translocation experiments



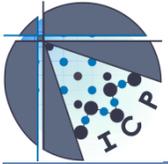
- Stefan Kesselheim, Christian Holm



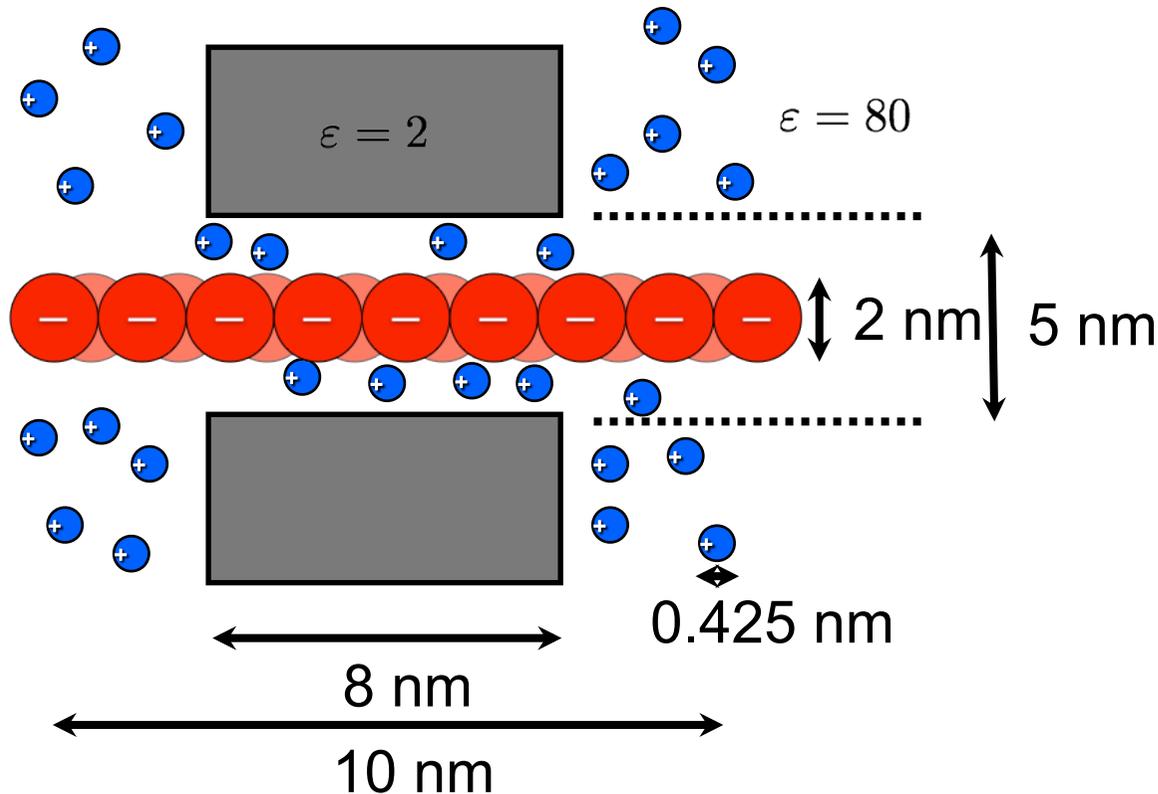
# DNA in a Solid State Nanopore



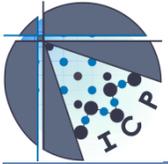
Nanopores of sizes 5 – 20 nm



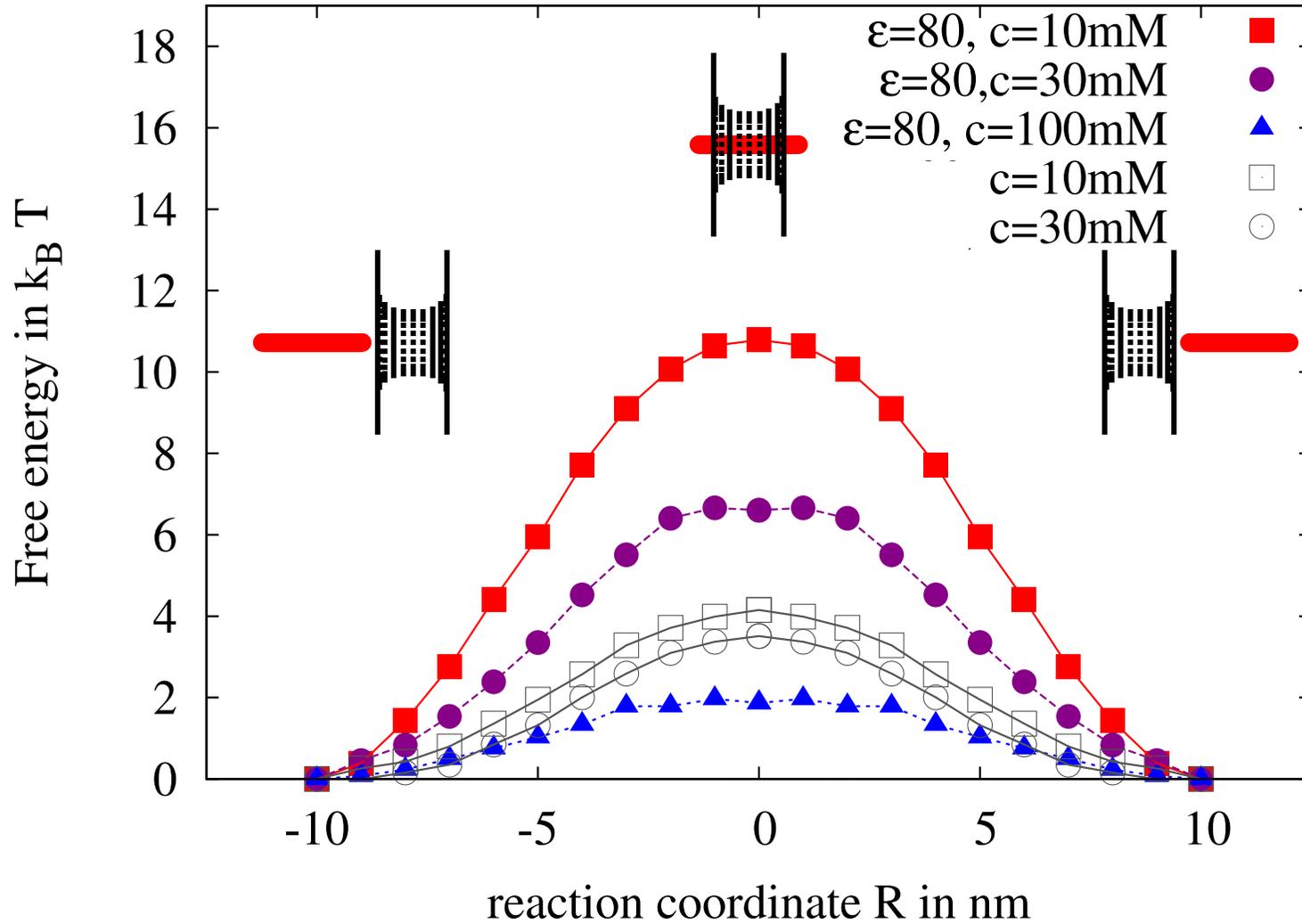
# Coarse Graining the System

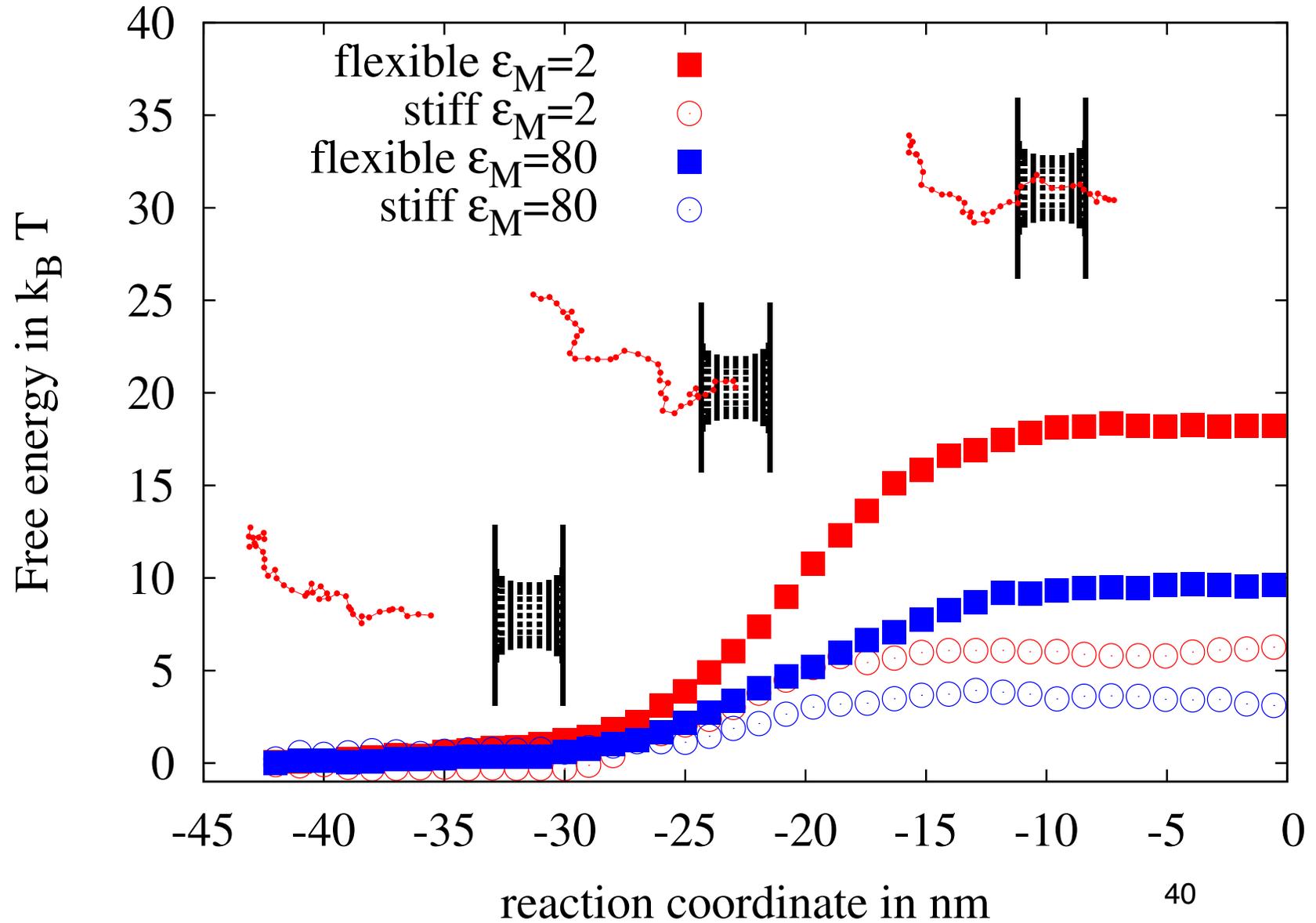
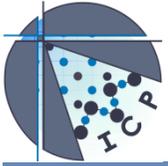


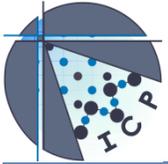
- Implicit solvent model (dielectric continuum) for the solvent and the nanopore, but different  $\epsilon$
- DNA represented as a rigid rod ( $l_p = 50$  nm)
- Coarse-Grained dynamics: Classical MD + LB



# Free energy profiles of DNA

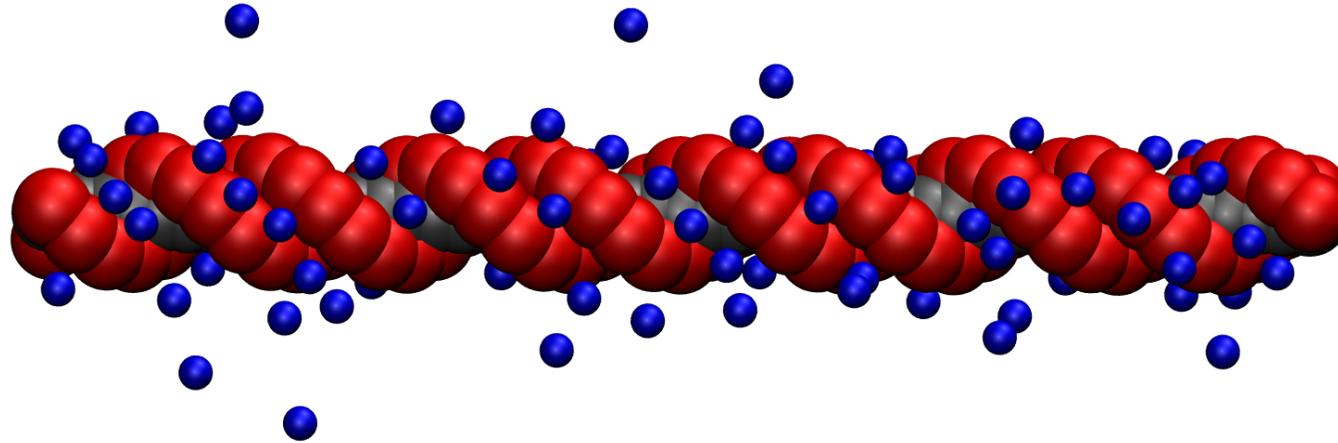






# Atomistic Simulations

- 1 periodic DNA piece in electrolyte



- Which coarse grained model can accurately describe the ion distribution?
- Add a periodic cylindrical pore and check vs. 1-D electrokinetic model
- More difficult: Check hydrodynamic interactions in bulk electrolyte