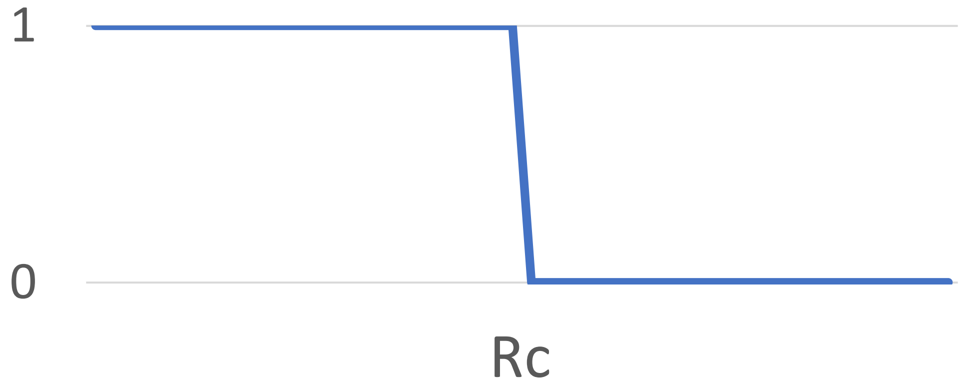
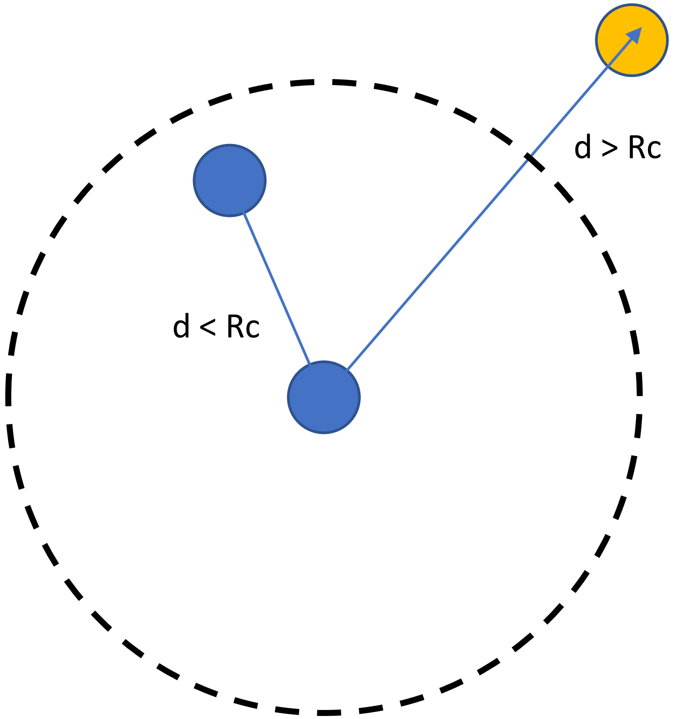
Cutoff truncation methods for long-range interactions

Simple truncation

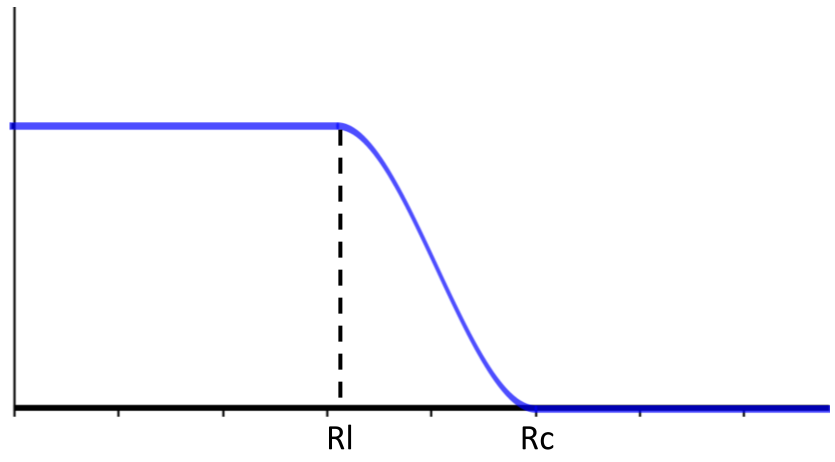
- If distance between particles > cutoff radius (Rc), interaction is neglected.
- Artificial discontinuity in the potential
- Leads to heating of the molecules at Rc

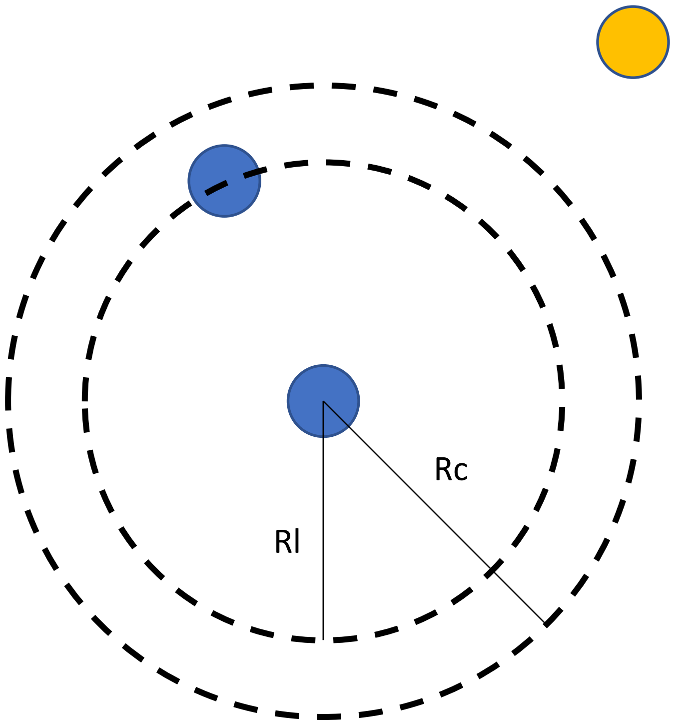




Switching procedure

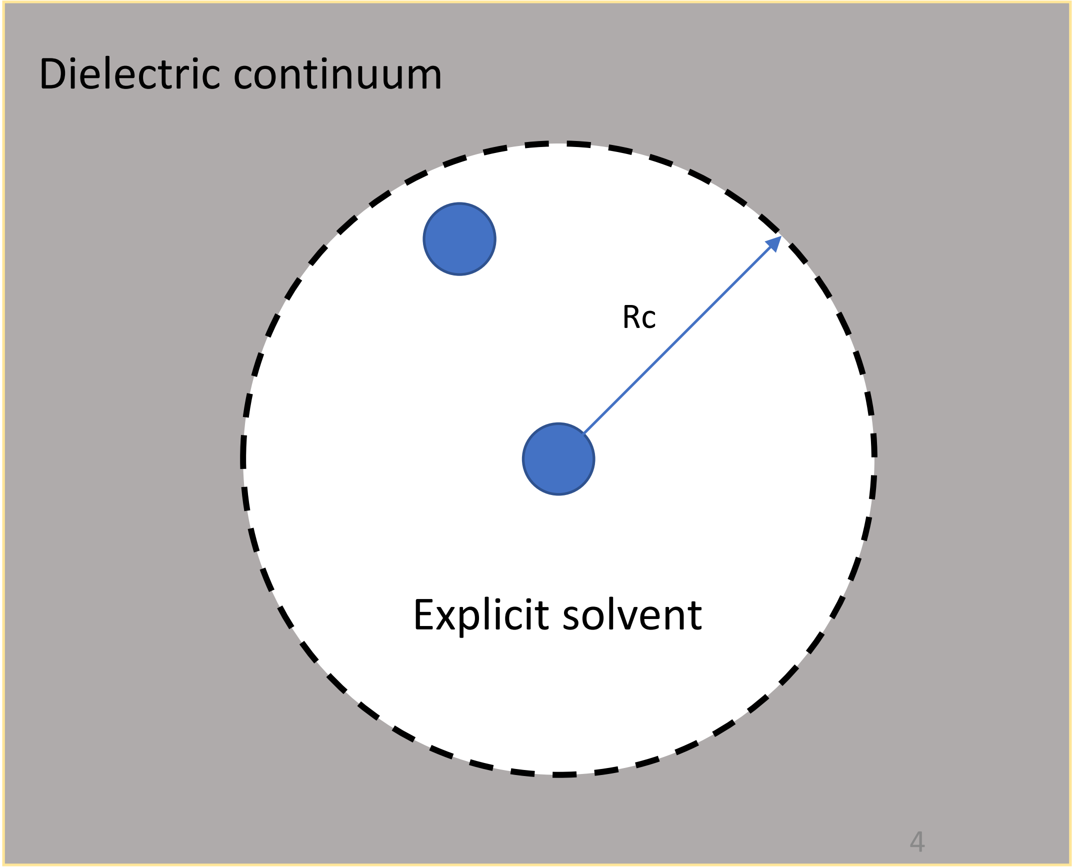
- Switching function to avoid discontinuity and heating.
- Starts at distance Rl until Rc.
- Creation of sudden changes in the force.





Reaction field

- If distance < Rc molecules interact
- Particles outside Rc are represented by a dielectric continuum

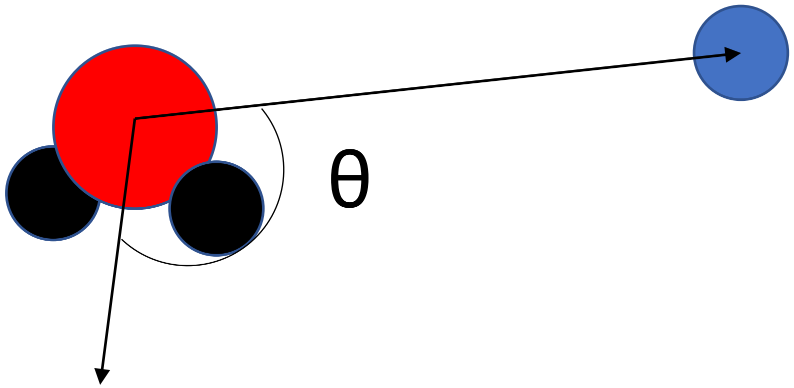


Dielectric continuum

Explicit solvent

Ion mobility

- Buildup of water before Rl
- Preferential orientation of water dipoles
- Caused by a sudden increase in the Coulomb force near Rl



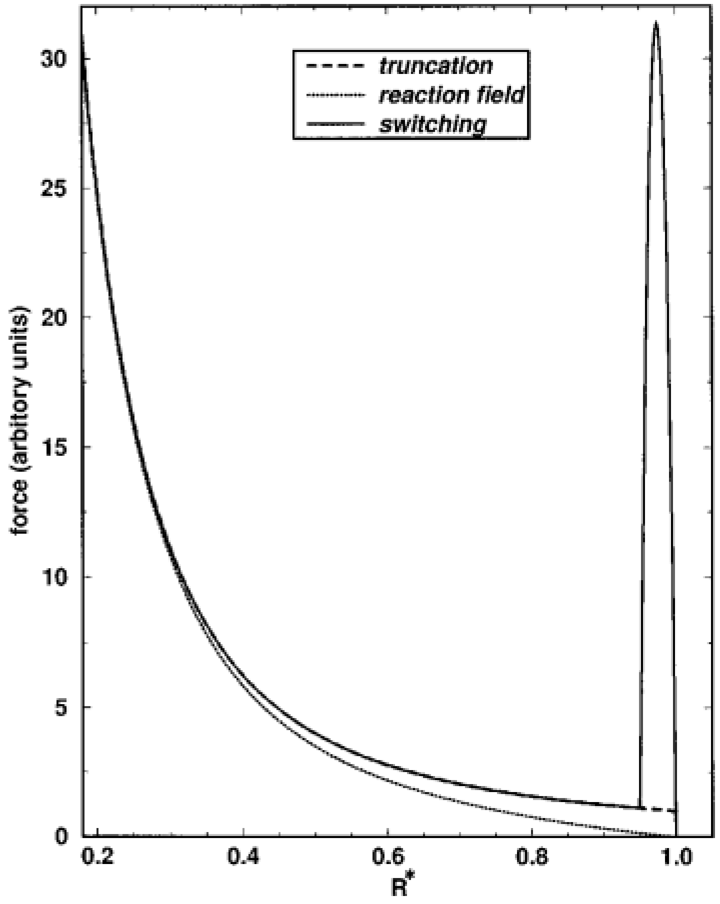


FIG. 7. The force between two charges as a function of $R^*(=R/R_c$ under different cutoff schemes. The switching of the force begins at 0.95 R_c.

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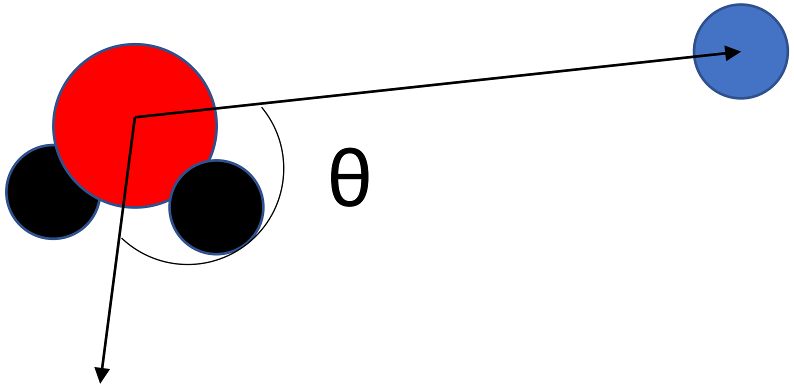


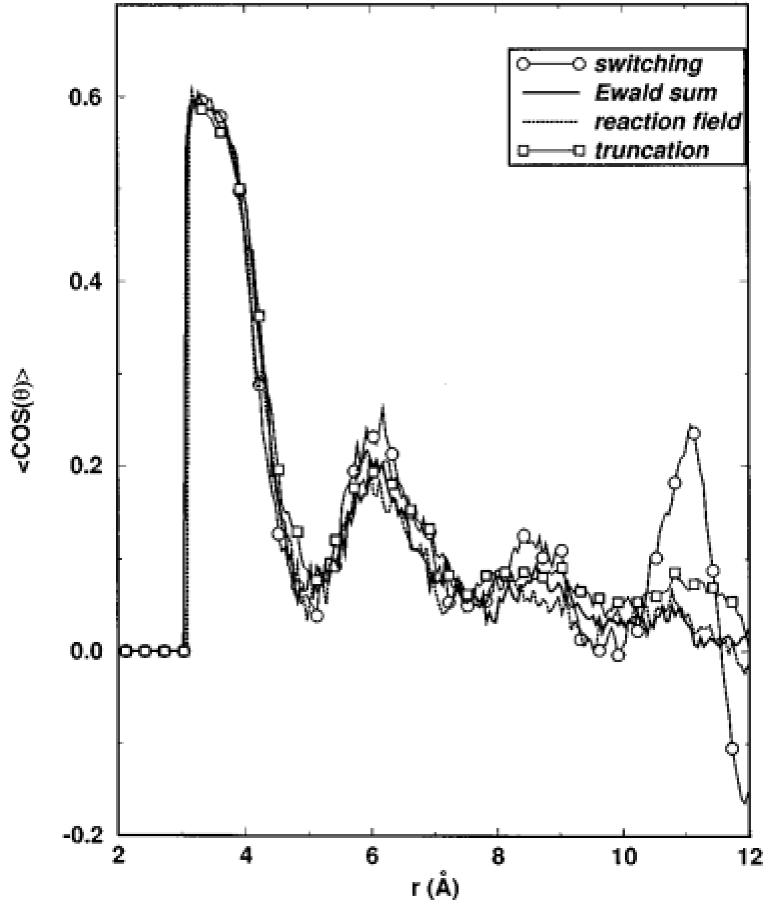


FIG. 6. Distributions of the cosine of the angle between the line joining the bromide ion and the water oxygen and the dipole vector as a function of distance from the ion.

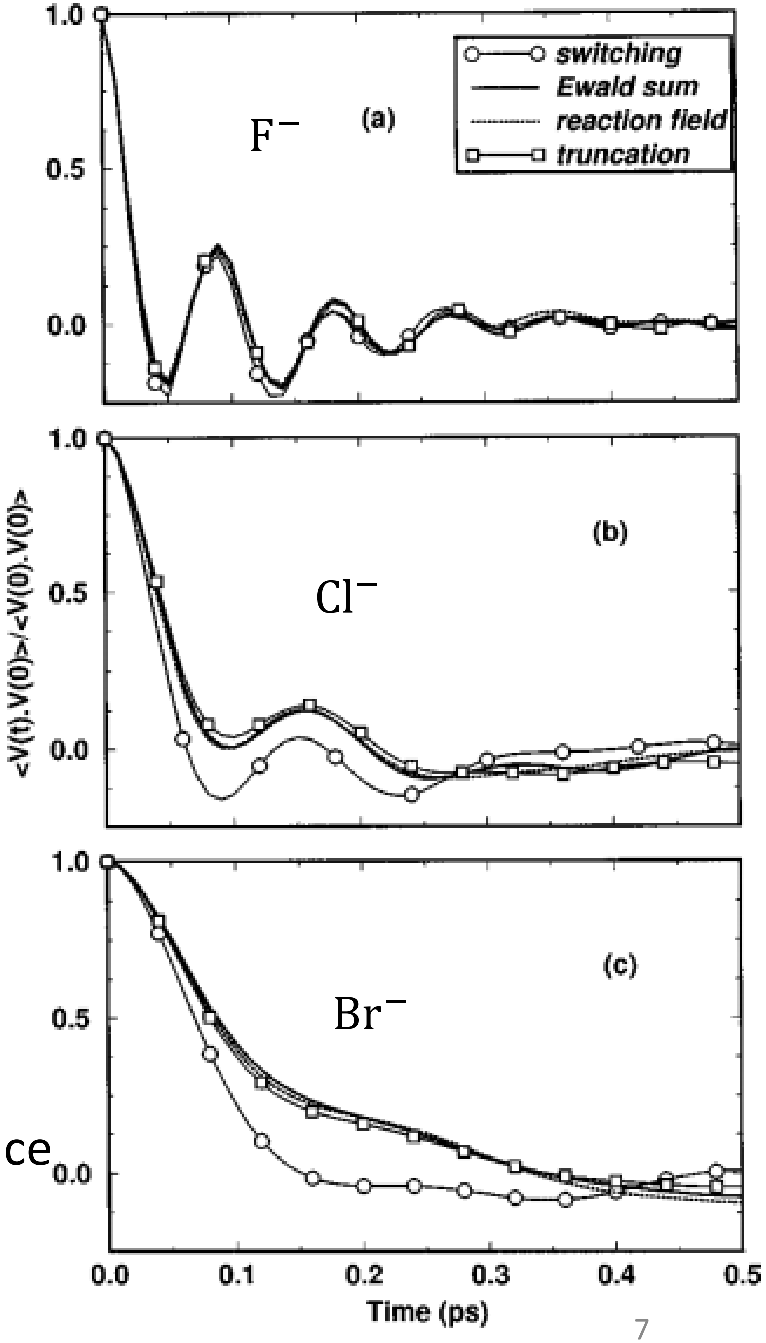
Ion mobility

- Velocity autocorrelation functions
- Simulations with switching function have more oscillations
- Initial decay enhanced

↓

Lower value of the diffusion constant

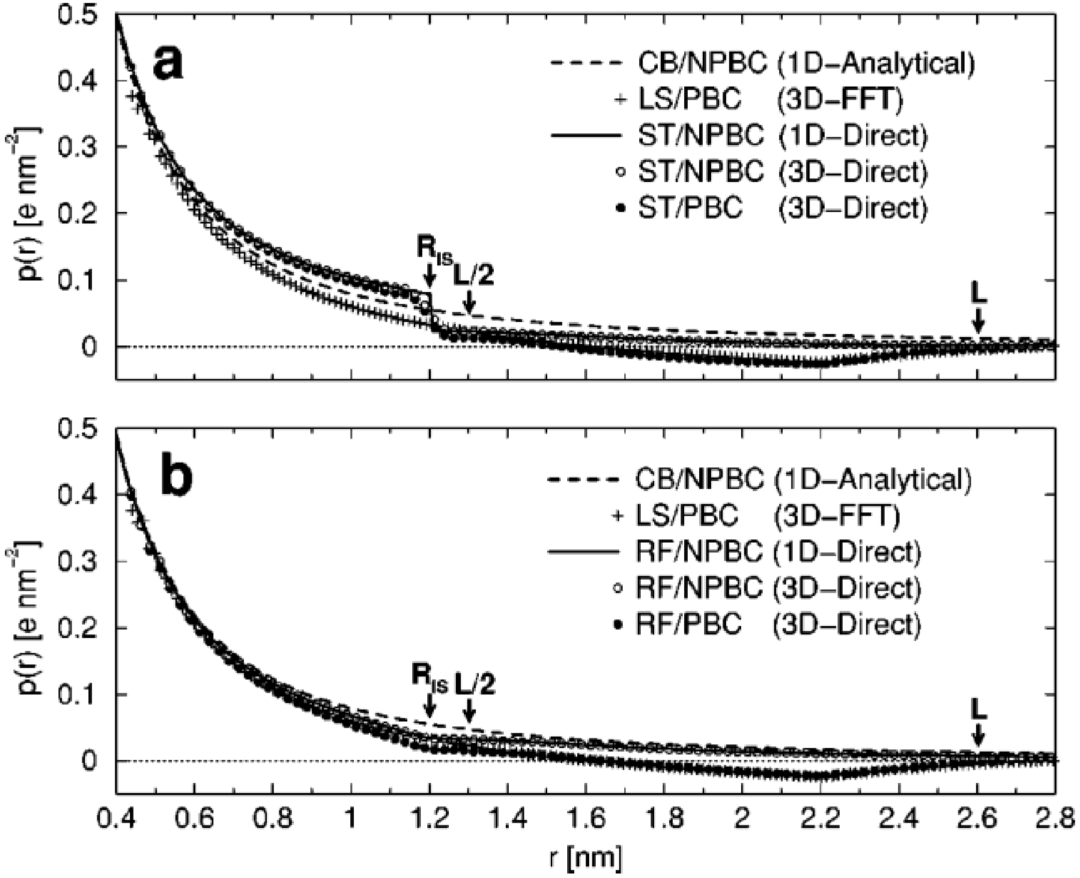
Increasing difference ↓



Polarization and periodic conditions

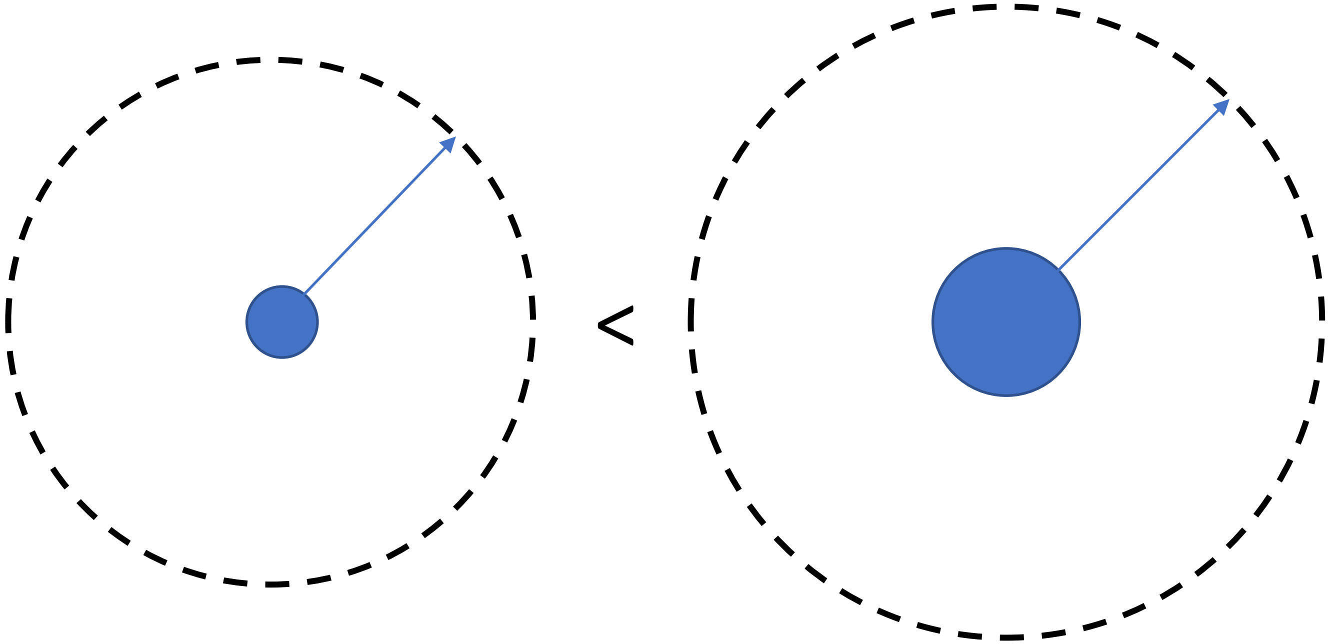
ST: Simple truncation
RF: Reaction field
R_{IS} = Rc

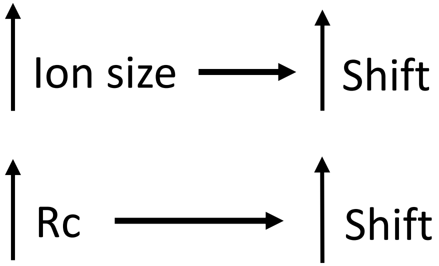
- ST/NPBC: overpolarization for r < Rc; underpolarization for r > Rc
- ST/PBC: polarization is lower in general
- RF/NPBC: deviations around Rc
- RF/PBC: in general lower



Solvation free energy

- Periodicity induced shift in solvation free energy
- PBC induce further reduction of solvation free energy
- If simulation box is big enough there is no difference





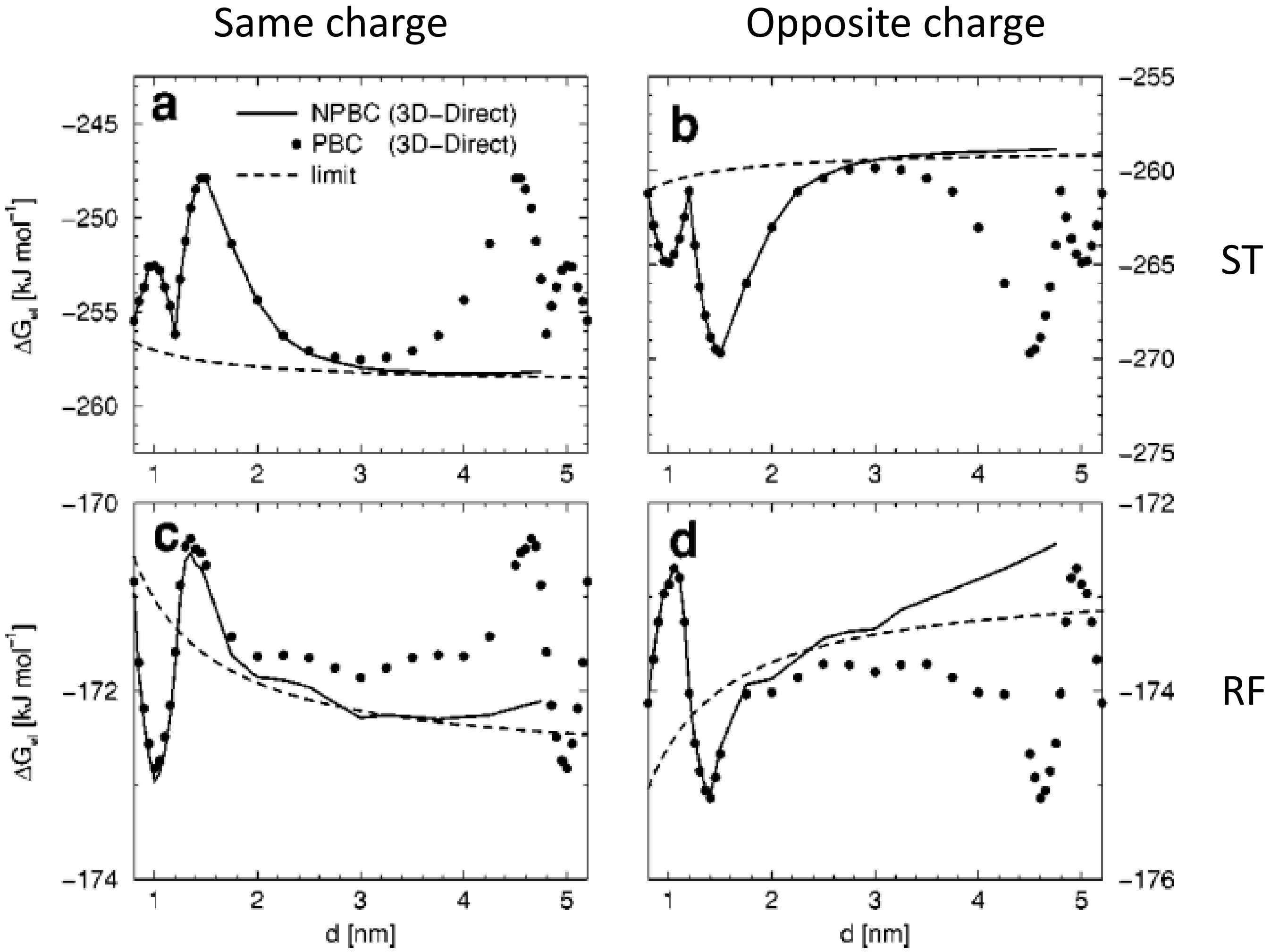
↑ Ion size → ↑ Shift

↑ Rc → ↑ Shift

Reaction field shift > Simple truncation shift

Ion-ion interaction

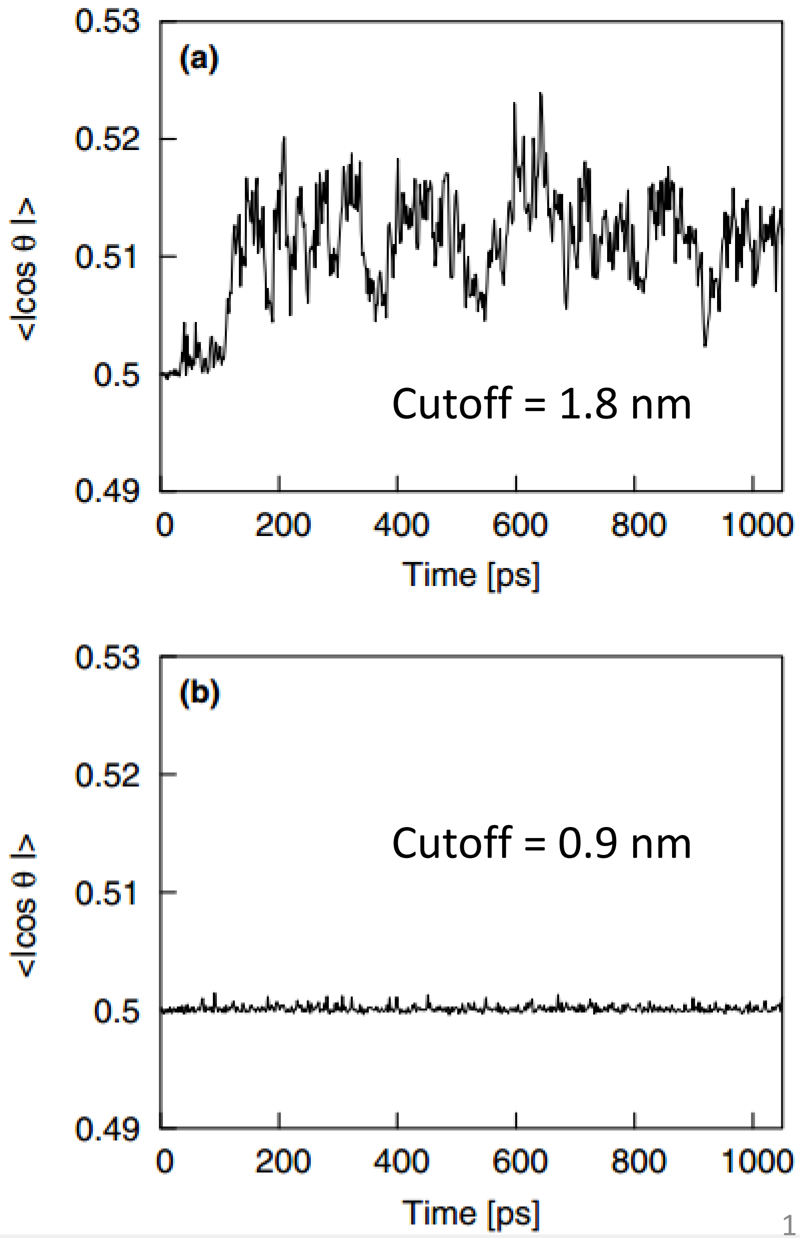
- Artifacts on the electrostatic contribution to the potential of mean force
- Around cutoff distance
- Very small changes when PBC
- RF Works better



Cutoff length

- 0.5 means random oriented water molecules
- Phase transition towards a water structure

(a)



Conclusions

- Standard truncation -> heating and ion-ion interaction artifacts around Rc
- Switching -> sudden force around Rl
- Reaction field and standard truncation -> solvation free energy changes when using PBC
- Increasing the cutoff lenght is not always the solution