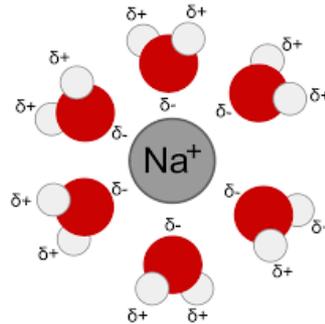


Solvation of ions and ion-ion interaction in polar liquids

Jörg Rottler

The University of British Columbia, Vancouver, Canada



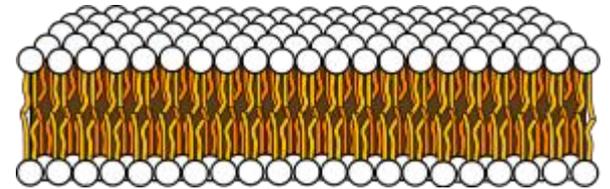
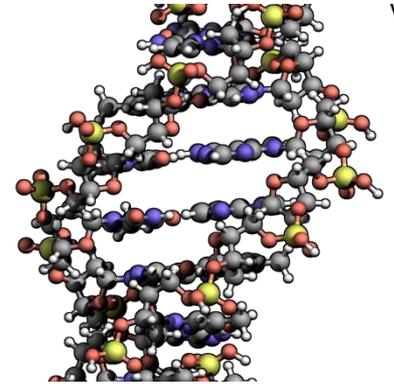
Solvation, non-uniform polarizability, and local field effects in solids, liquids, life, and devices

Quantum Matter Institute, UBC Vancouver

April 11-14, 2016

Electrostatics for biomolecules

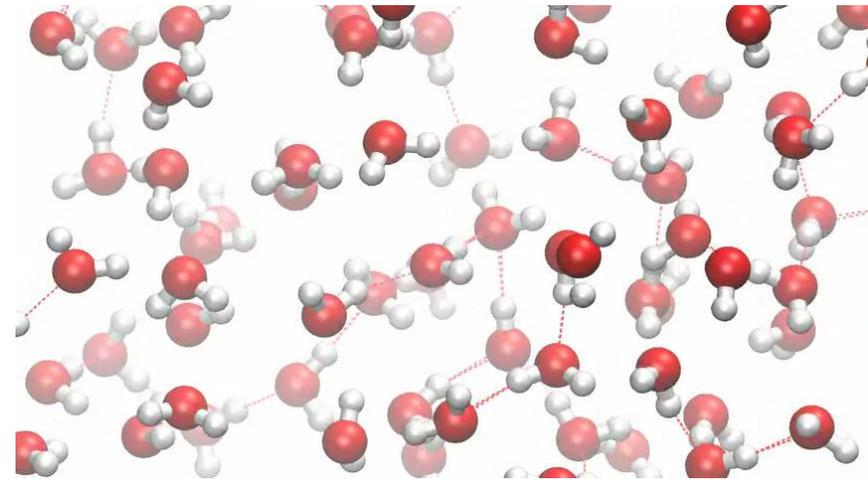
- dominates many static and dynamical properties
- DNA is highly negatively charged: $\lambda=2e^-/0.34\text{ nm}$
→ counterions mediate DNA-DNA interactions
- Proteins: 4 out of 20 amino acids are charged
- Phospholipid membranes can carry surface charge density.
→ electric double layer
- Motion of ions (Na, K, Cl) through membrane channels regulate action potential → biological electricity



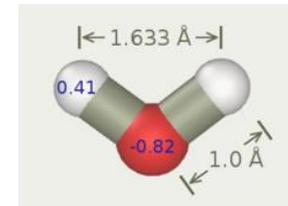
Potential of mean force of ion pair (NaCl)

- Classical molecular dynamics at $T=300\text{K}$ for a single ion pair solvated in water
- Model ions:

$$V_{ij}(r_{ij}) = V_{ij}^{\text{el}}(r_{ij}) + V_{ij}^{\text{LJ}}(r_{ij})$$
$$= \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$



- SPC/E water model
(rigid molecule, dipole moment 2.35 D, $\epsilon = 72 \epsilon_0$)

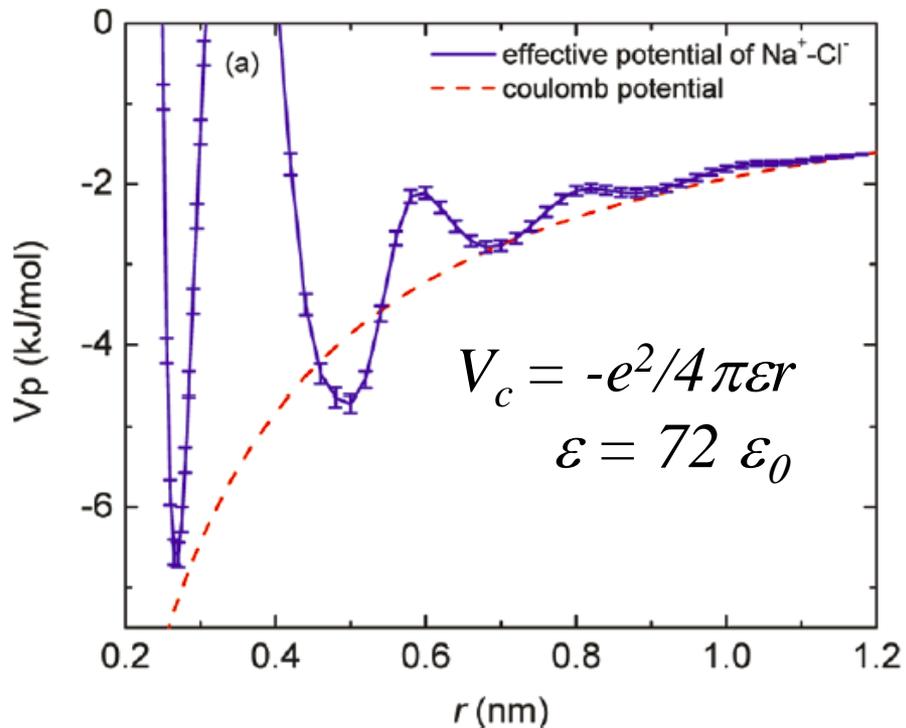


- Insert ion pair, compute radial distribution function $g(r)$
Boltzmann invert to obtain PMF

$$V_p(r) = -k_B T \ln(g(r))$$

Potential of mean force from simulations

- Classical molecular dynamics at T=300K for a single ion pair

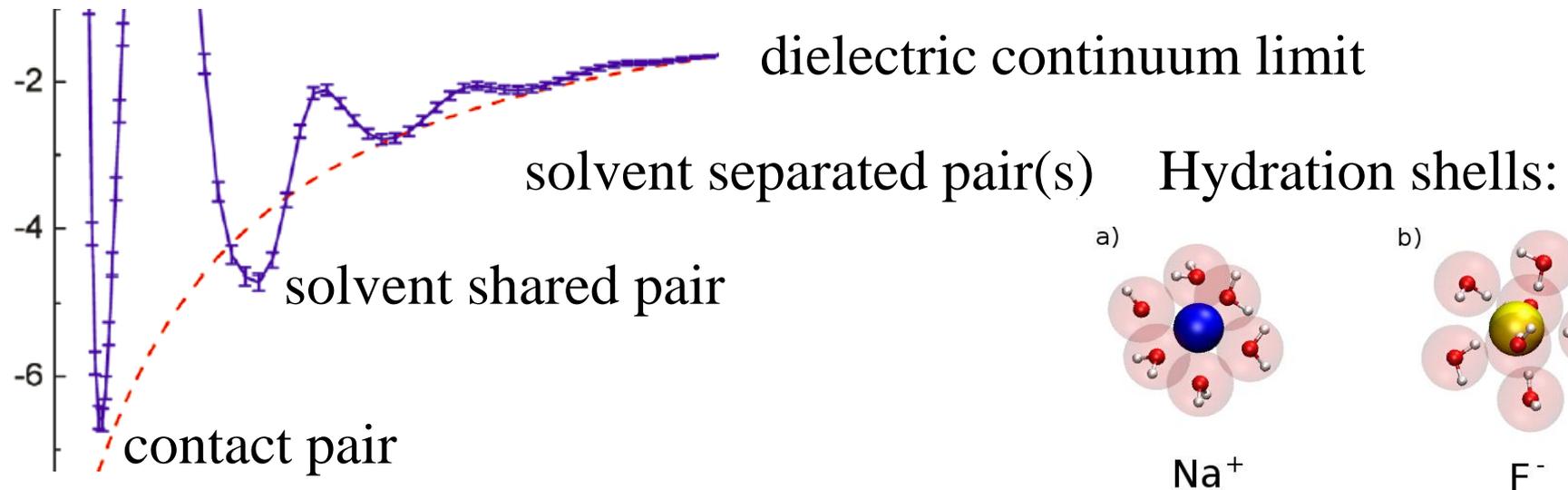


Shen et al, JCTC (2011)

Observations

- Strong deviations from continuum electrostatics at the nanoscale
- Oscillatory short range potential, interaction even reverses sign (for some ion separations)
- Granularity of the solvent clearly becomes important

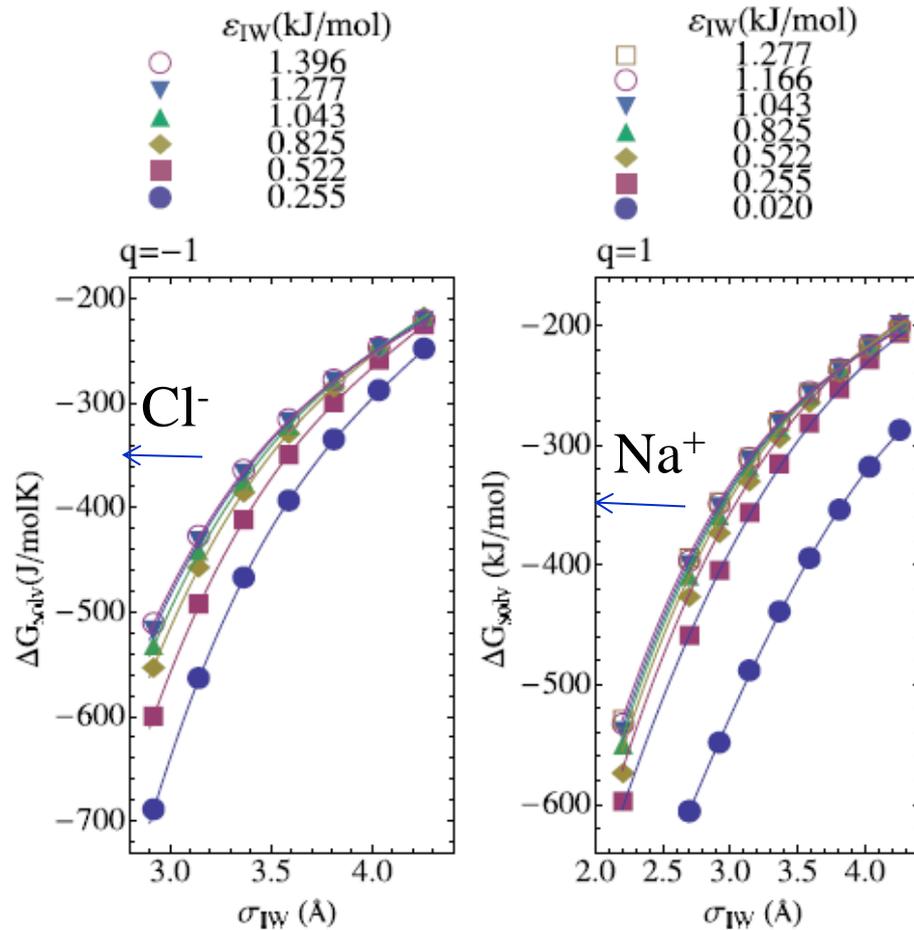
How could we think about this?



Solvation free energy ΔG_{solv}

“free energy change due to transferring single ion from vacuum into water”

MD calculations for model ions:



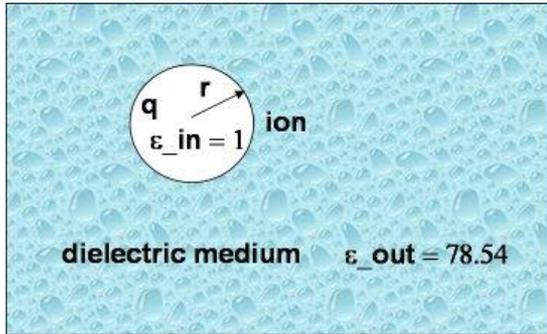
$$V_{ij}(r_{ij}) = V_{ij}^{\text{el}}(r_{ij}) + V_{ij}^{\text{LJ}}(r_{ij})$$

$$= \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

Horinek et al, J. Chem. Phys. (2009)

Continuum electrostatics picture

Consider spatially dependent dielectric function $\epsilon(r)$:



Born solvation free energy for one ion:

$$\Delta G_{Born} = \frac{q^2}{8\pi a} \left[\frac{1}{\epsilon_{out}} - \frac{1}{\epsilon_{in}} \right]$$

effective ion radius

Can be **generalized** to $N > 1$ ions:

$$\Delta G_{GB} = \left[\frac{1}{\epsilon_{out}} - \frac{1}{\epsilon_{in}} \right] \sum_{i,j} \frac{q_i q_j}{4\pi \epsilon_{out} r_{ij}} + \left[\frac{1}{\epsilon_{out}} - \frac{1}{\epsilon_{in}} \right] \sum_i \frac{q_i q_i}{8\pi a_i}$$

(a popular implicit solvent model)

Approximates the **Poisson-Boltzmann** (mean-field) equation:

$$-\nabla D(r) = \nabla[\epsilon(r)\nabla\phi(r)] = -\rho_{macro} - \sum_{ions} q_i n_i e^{-q_i\phi(r)/k_B T}$$

Limitations

- Generalized Born approximation: success strongly dependent on choice of (empirical) Born radii
 - Poisson-Boltzmann theory: more accurate than GB, but challenging to solve numerically, difficult to use for dynamics
 - Neither model takes into account structure of solvent medium at the nanoscale
-

Can we do better?

- **Integral equation theory (IET)** of liquids:
3D – reference interaction site model (RISM) theory
solve for solvent structure (radial distribution function) using
stat. mech. and integral equations (Ornstein-Zernike) from which
PMFs, free energies etc can be calculated
→ Andriy Kovalenko (Tuesday am)
- **Nonlocal continuum electrostatics:**
generalize $\mathbf{D}(\mathbf{r}) = \epsilon(\mathbf{r})\mathbf{E}(\mathbf{r})$
to include correlations (orientation of dipole moment of a water
molecule depends on configuration in neighborhood)”:

$$\mathbf{D}(\mathbf{r}) = \int d\mathbf{r}' \epsilon(\mathbf{r}, \mathbf{r}') \mathbf{E}(\mathbf{r}'). \quad \rightarrow \text{Jay Bardhan (Monday pm)}$$

Nonlocal electrostatics (linear response)

Displacement:

$$D(r) = \int dr' \epsilon(r, r') E(r')$$

Polarization:

$$P(r) = \int dr' \chi(r, r') D(r')$$

nonlocal susceptibility

Translational invariance (homogeneous isotropic medium):

$$D(r) = \int dr' \epsilon(|r - r'|) E(r')$$

$$\rightarrow \hat{D}(k) = \epsilon(k) \hat{E}(k)$$

$$\hat{P}(k) = \chi(k) \hat{D}(k)$$

length-scale dependent
static dielectric function
(longitudinal part)

Measuring dielectric response

using fluctuation-dissipation theorems at finite T:

- $k=0$: $\varepsilon = 1 + \frac{1}{3\varepsilon_0 k_B T V} (\langle P^2 \rangle - \langle P \rangle^2)$

(P total dipole moment)

- $k>0$: $\varepsilon(k) = 1 / (1 - \chi(k))$

$$\chi(k) = \frac{1}{k_B T} S(k) = \frac{1}{k_B T} \frac{\langle \rho(k) \rho(-k) \rangle}{\varepsilon_0 V k^2}$$

($S(k)$ bound charge structure factor)

Nonlocal static dielectric function of liquid water

Measure $S(k)$ from thermal fluctuations of water molecules (no ions)
from molecular dynamics simulation

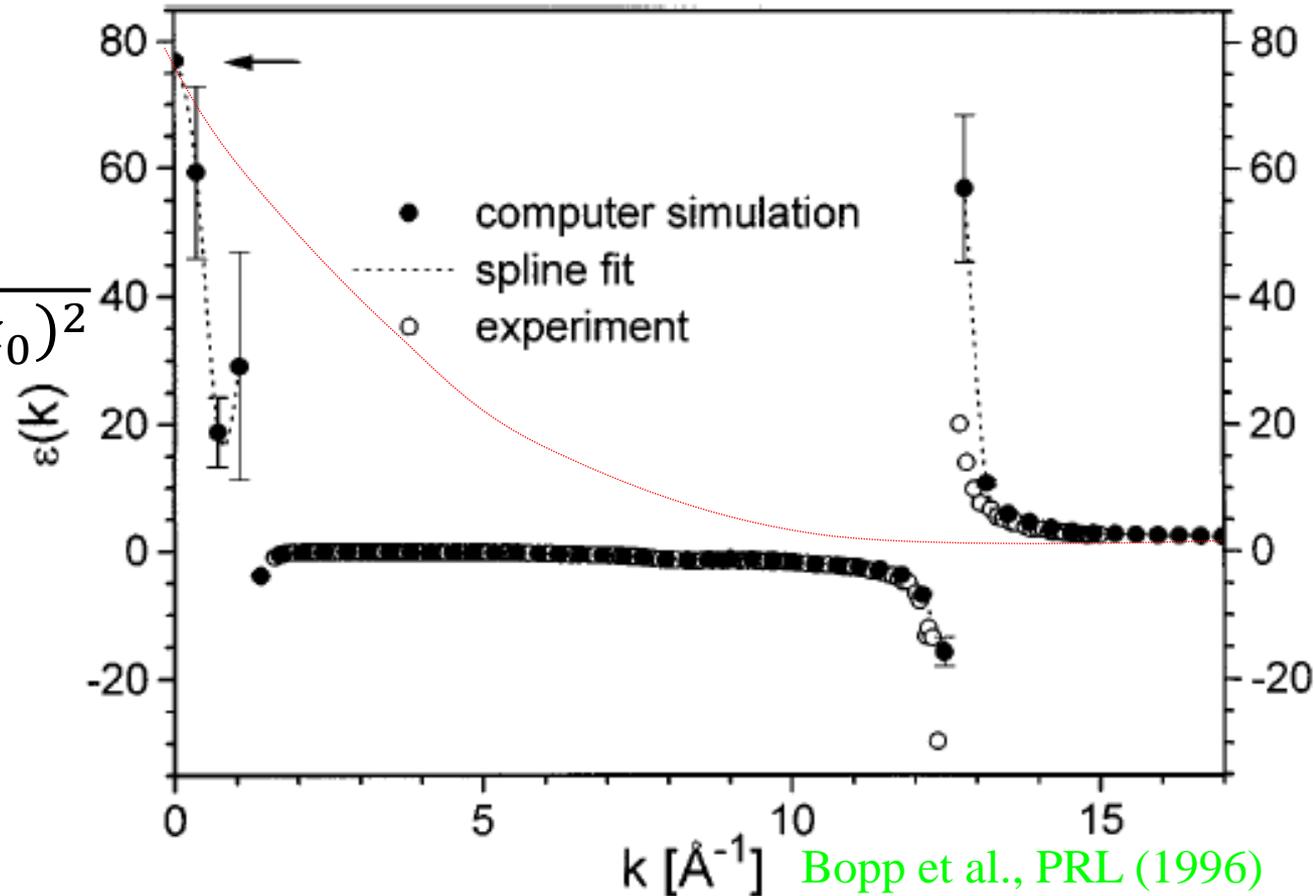
Might expect
“Lorentzian:”

$$\epsilon(k) = 1 + \frac{1}{\kappa + (k/k_0)^2}$$

Interpolates
between

$$\lim_{k \rightarrow 0} \epsilon(k) = 78$$

$$\lim_{k \rightarrow \infty} \epsilon(k) = 1$$



Nonlocal static dielectric function of liquid water

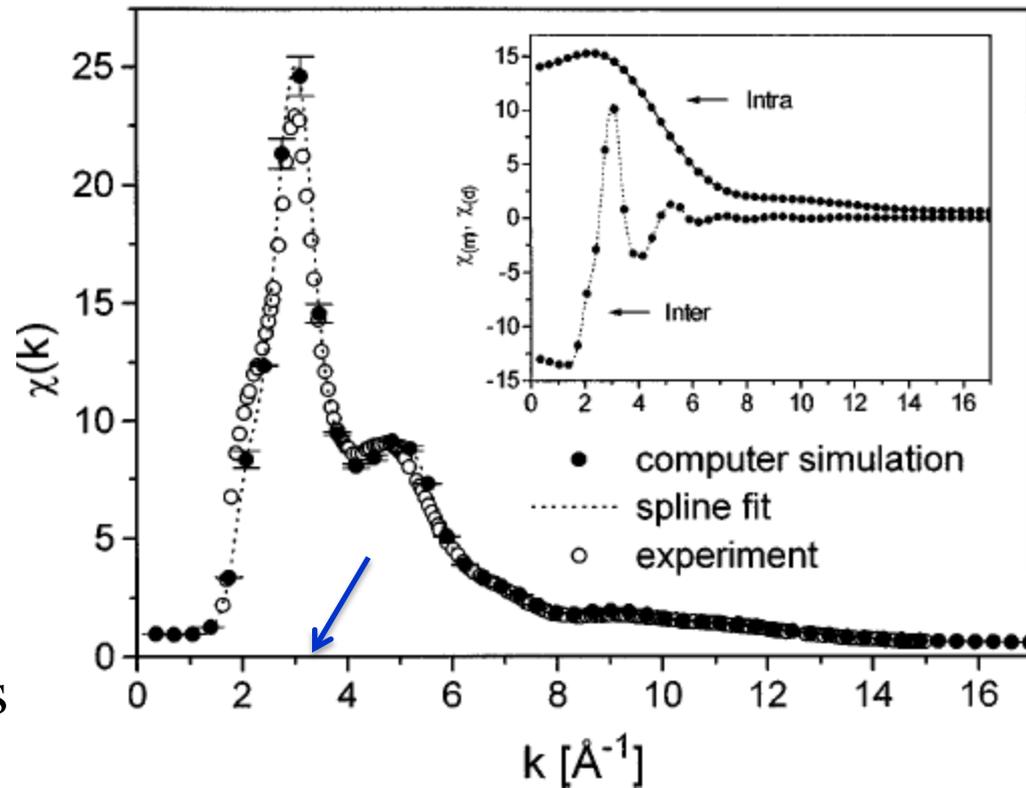
$\epsilon(k) < 0$ or $S(k) > 1$: overscreening

Correct limits:

$$\lim_{k \rightarrow 0} \epsilon(k) = 78$$

$$\lim_{k \rightarrow \infty} \epsilon(k) = 1$$

Characteristic scale of
polarization fluctuations



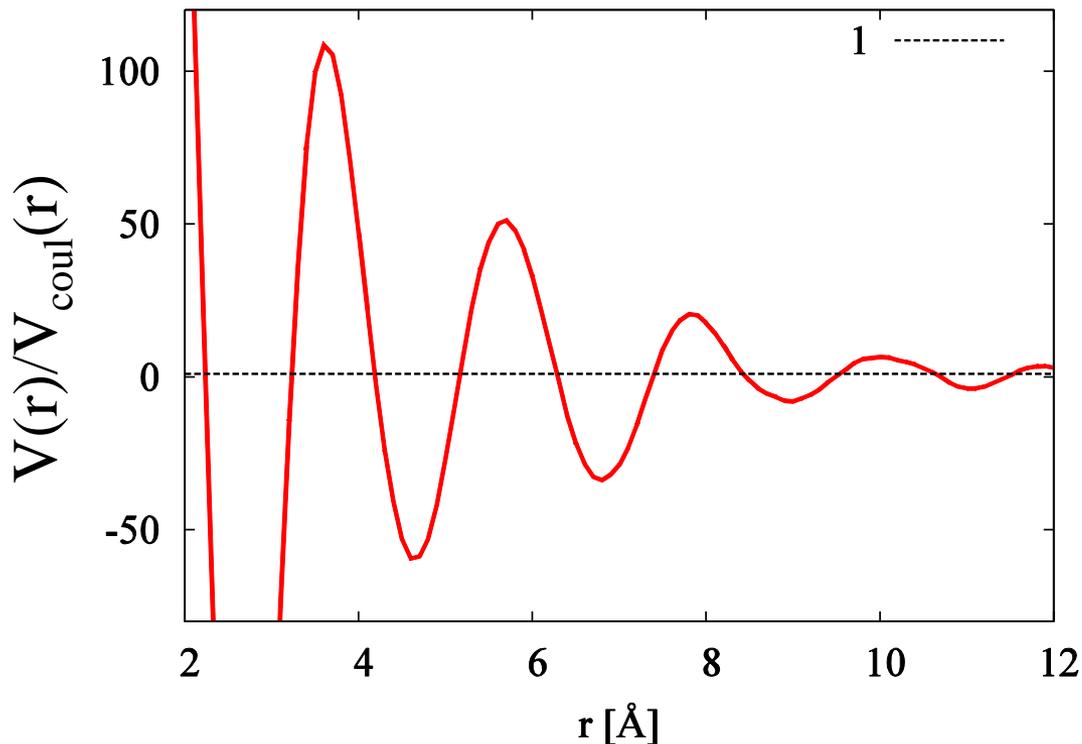
Must have $\chi(k) = 1 - 1/\epsilon(k) > 0$, only forbidden region is $0 < \epsilon(k) < 1$

Potential of a point charge

$$V_E(r) = \frac{q}{2\pi^2\epsilon_0 r} \int_0^\infty dk \frac{\sin(kr)}{k} \frac{1}{\epsilon(k)}$$

($\epsilon(k)=1$ recovers
Coulomb potential)

input $\epsilon(k)$ from simulations and evaluate:



Overscreening effect
implies oscillatory
potential!

Quantitative
agreement with
atomistics?

Model electrostatic energy functionals

$$U = \frac{1}{2} \int d^3r [(\mathbf{D} - \mathbf{P})^2 + \kappa(r)\mathbf{P}^2 + \kappa_1(r)(\text{div } \mathbf{P})^2 + \kappa_{\text{tr}}(r)(\text{curl } \mathbf{P})^2 + \alpha(r)(\text{grad div } \mathbf{P})^2]$$

Maggs and Everaers,
PRL (2006)

local electrostatics:

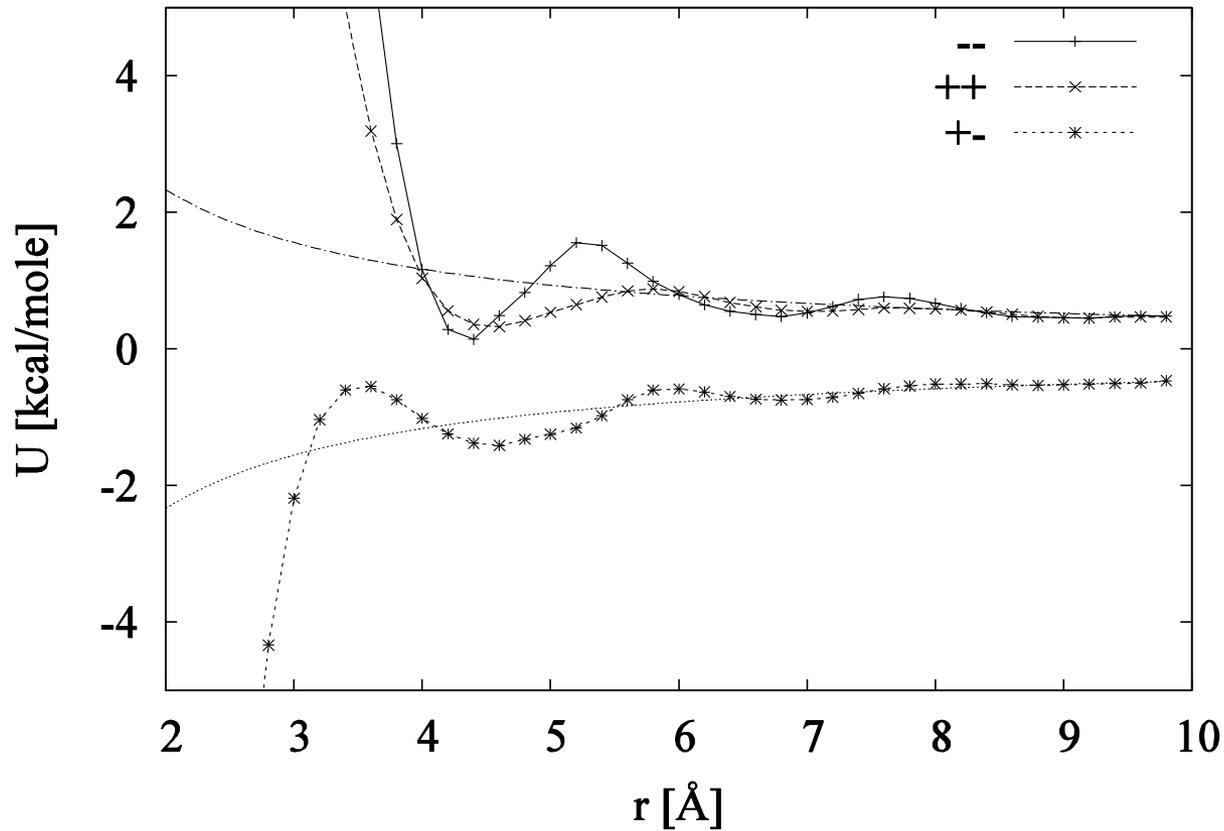
$$\epsilon(\mathbf{r}) = 1 + 1/\kappa(\mathbf{r})$$

nonlocal electrostatics:

$$\epsilon(q) = 1 + 1/(\kappa(\mathbf{r}) + \kappa_1(\mathbf{r})q^2 + \alpha(\mathbf{r})q^4).$$

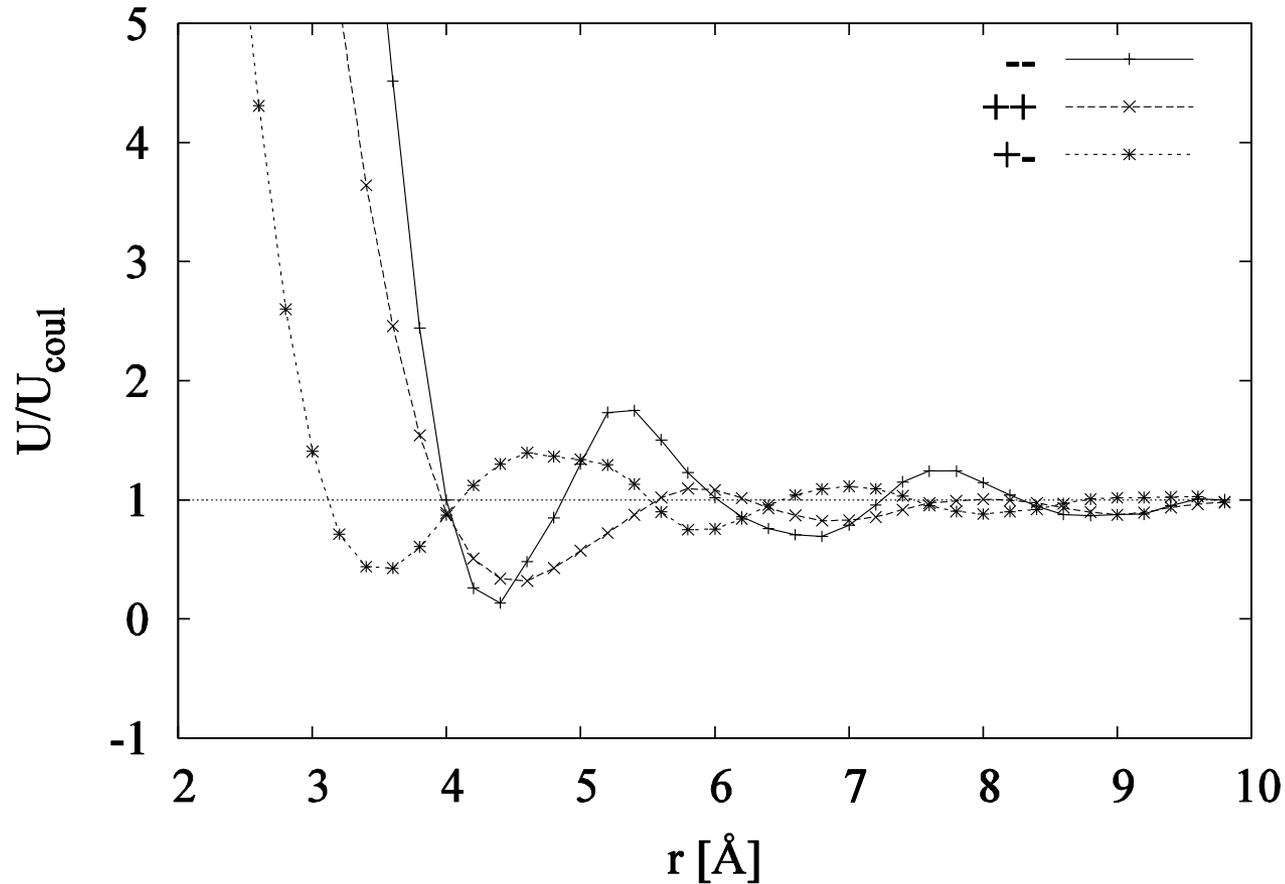
- low order Landau-Ginzburg expansion
- $\kappa_1 < 0$, $\alpha > 0$ gives a region of $\epsilon(\mathbf{k}) < 1$, selects characteristic scale $q_0 = \sqrt{-\kappa_1/2\alpha}$ for spatial modulation of polarization field

Charge asymmetry



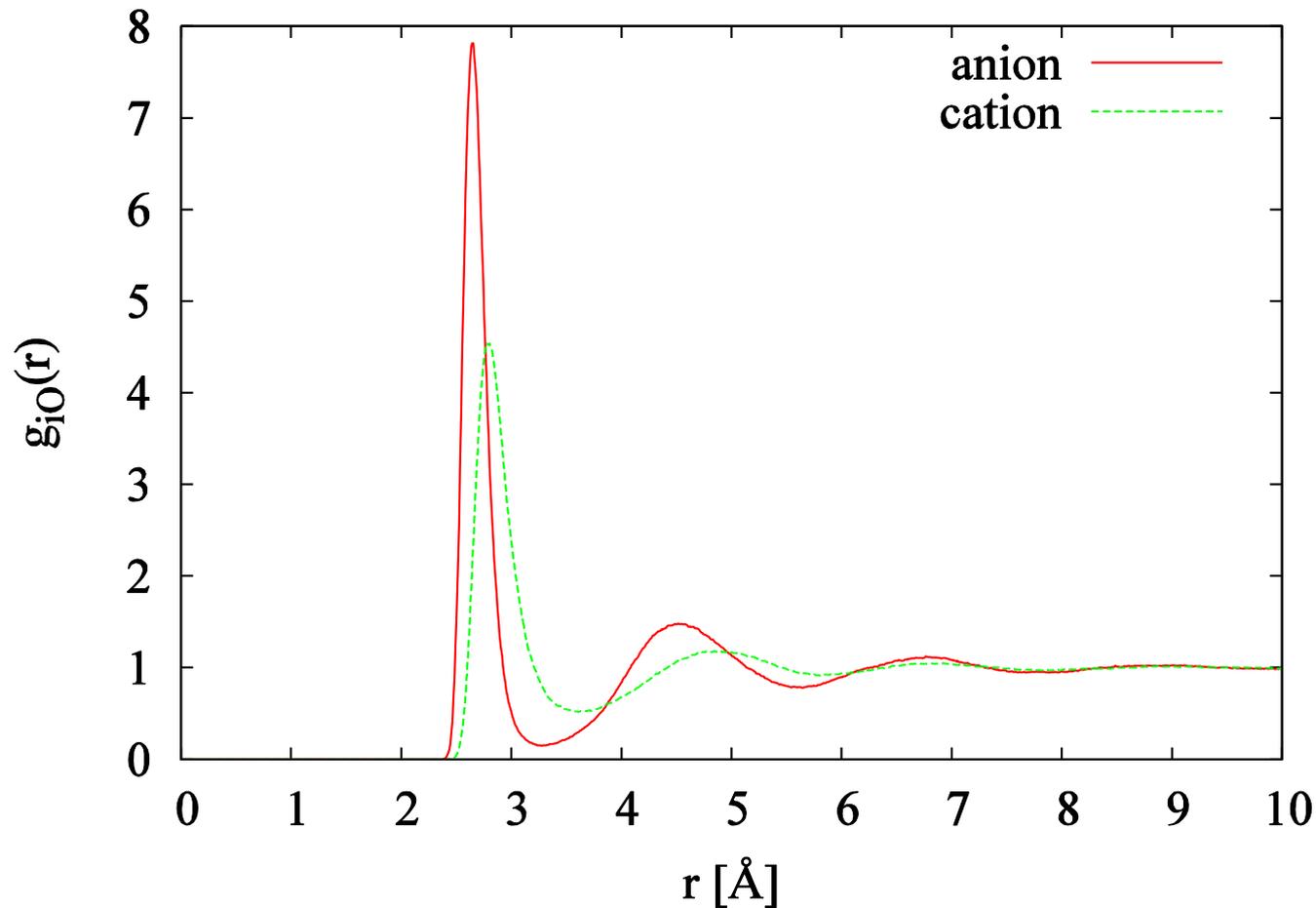
PMF of ion pairs in SPC/E water that differ only by their charge

Charge asymmetry



Screening factor different for ++, --, or +- pairs, cannot be described by nonlocal electrostatic theory

Ion water radial distribution functions



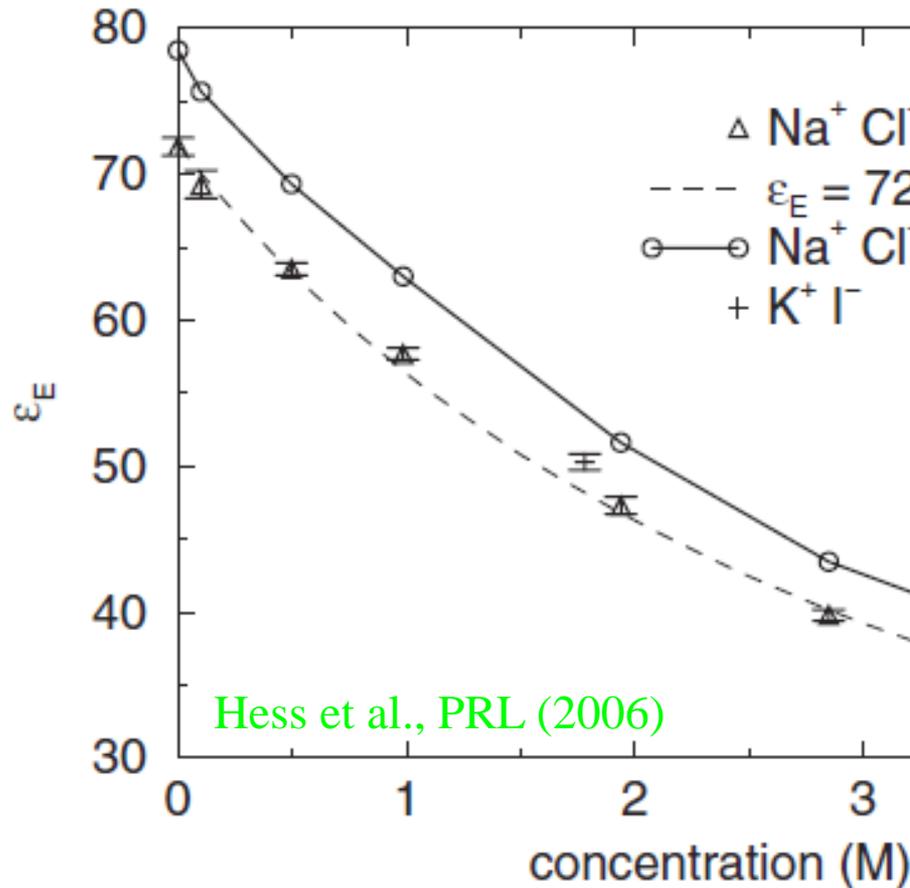
Sign asymmetry of water structure around ion

Issues

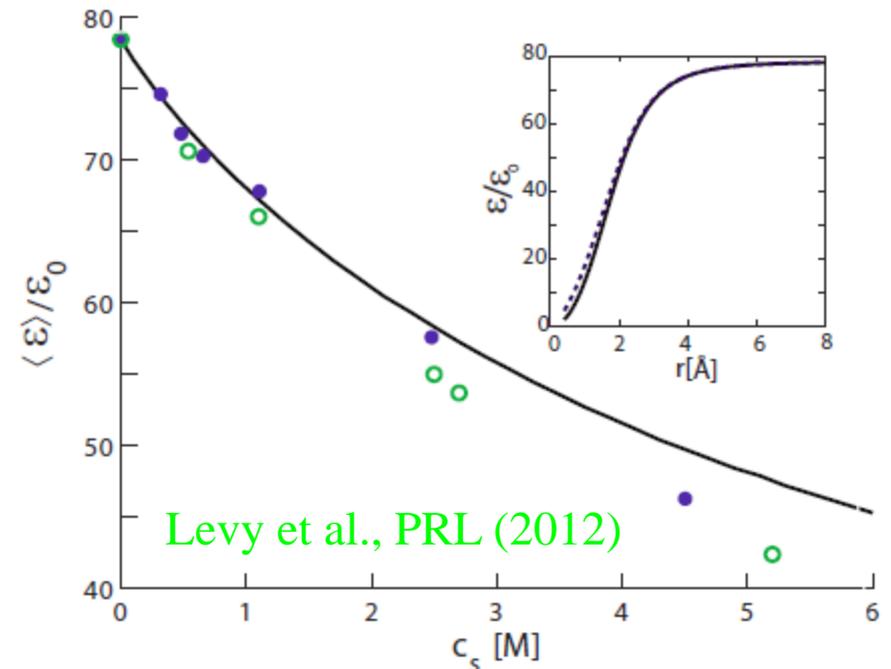
- Sign asymmetry not captured
Nonlinear effects or dielectric saturation
→ no fluctuation dissipation theorem
→ large electric fields of ions cause nonlinearities in water polarization response
- Distortion of solvent structure by finite size of solute

Fedorov and Kornyshev, Mol Phys (2007)
- Assumption of translational invariance too strong:
$$\epsilon(r, r') \neq \epsilon(|r - r'|)$$
- Multibody effects, interfaces?

Beyond infinite dilution: salt dependence of ϵ



Results from MD simulations



Predictions from theory

→ Henri Orland (Tuesday am)

Discussion?
