

Modeling of ion-specific thermodynamics

using integral equation theory

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Meeting Regensburg, 9. July 2009



Methodology

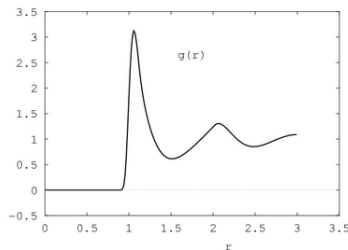


Integral equation machinery (OZ+HNC)

Ornstein-Zernike equation splits the total interaction (\mathbf{h}) between two particles to direct (\mathbf{c}) and indirect ($\mathbf{\Gamma}$) parts.

$$h_{ij} = c_{ij} + \sum_k \rho_k \int c_{ik} h_{kj} dr_k$$

$$h_{ij} = g_{ij} - 1$$



HyperNetted Chain closure relates the correlation function \mathbf{c} and pair potential \mathbf{U} (**infinite dilution**, usually solvent averaged)

$$c_{ij} = \exp(-\beta U_{ij} + \Gamma_{ij}) - \Gamma_{ij} - 1$$

$$\Gamma_{ij} = h_{ij} - c_{ij}$$

The concentration comes in only through the particle densities ρ .
These equations have to be solved iteratively.



- osmotic coefficients Φ

$$\Phi = 1 - \frac{1}{6\rho kT} \sum_i \sum_j \rho_i \rho_j \int_0^\infty r \frac{\partial U_{ij}(r)}{\partial r} g_{ij}(r) 4\pi r^2 dr$$

- excess chemical potentials μ^{ex} (activity coefficients)

$$\beta \mu_i^{\text{ex}} = \sum_j \rho_j \int_0^\infty \left(\frac{h_{ij} \Gamma_{ij}}{2} - c_{ij}^s \right) 4\pi r^2 dr$$

- isothermal compressibilities χ_T

$$(\chi_T^{\text{ex}})^{-1} = \frac{\chi_T^\circ}{\chi_T} = 1 - \sum_i \sum_j \frac{\rho_i \rho_j}{\rho} \int_0^\infty c_{ij}^s 4\pi r^2 dr$$

MD and MC simulations

- interaction potential (force field) – total energy of the system U

$$U = \underbrace{\sum_{\text{BONDS}} E_i^{\text{STRETCH}} + \sum_{\text{ANGLES}} E_i^{\text{BEND}} + \sum_{\text{TORSIONS}} E_i^{\text{TORSION}}}_{\text{BONDED}} + \underbrace{\sum_{i < j} E_{i,j}^{\text{VDW}} + \sum_{i < j} E_{i,j}^{\text{EL}}}_{\text{NONBONDED}} + \dots$$

- molecular dynamics – Newtonian equations of motion

$$\frac{d^2 \vec{r}_i}{dt^2} = \frac{\vec{F}_i(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}{m_i} \quad \vec{F}_i = -\nabla_i U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

- Monte Carlo calculations – probability of a given arrangement

$$P_i \propto \exp(-U_i/kT)$$

- MD full atomic-level details – very expensive (mostly solvent)
- MC solvent averaged – benchmark for HNC



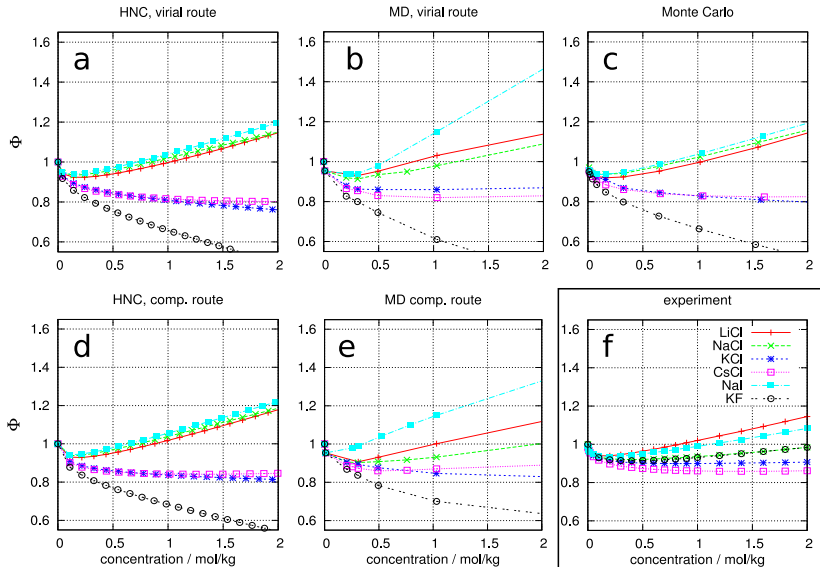
Hybrid HNC/MD scheme with MC validation

Goals of the work

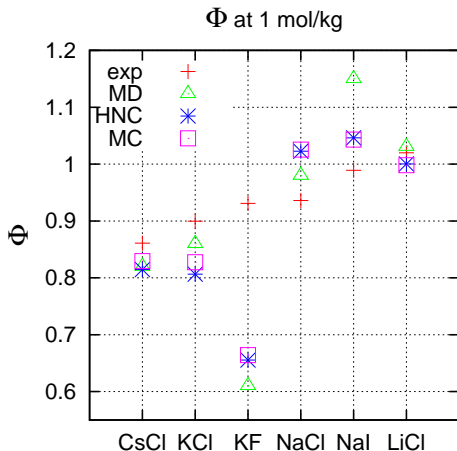
- solvent-averaged PMF from single MD simulation (inf. dilution) as a pair potential in OZ/HNC
- no explicit solvent or atomic details – very fast
- validation using MC using the same pair potentials
- description of thermodynamic properties at wide range of concentrations, and thus linking experiments, statistical thermodynamics, and MD
- no fit-parameters involved



Osmotic coefficients

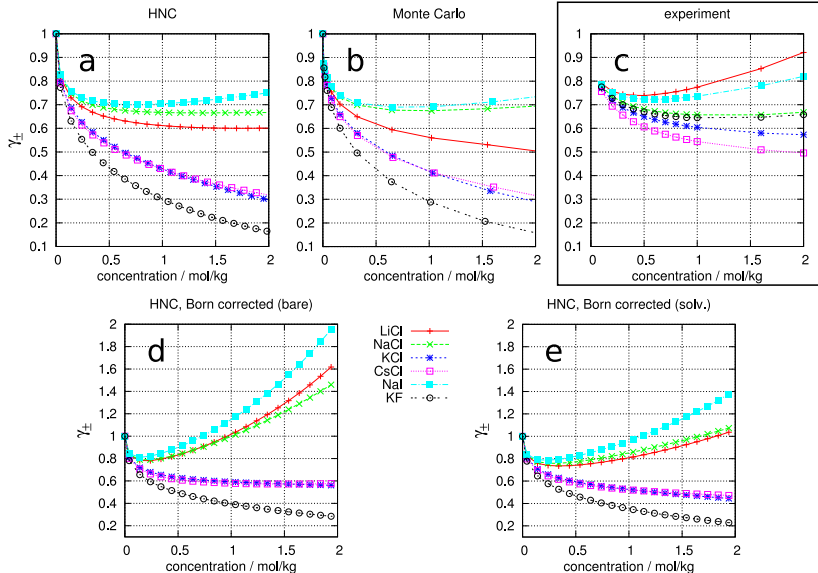


Osmotic coefficients



- structural properties – $g(r)$ – well described (not shown)
- thermodynamic properties (Φ) – MD (explicit solvent) agrees well with HNC and MC (both solvent averaged)
- agreement with experiment for correct force fields (problems with KF, NaI)

Activity coefficients



Summary

- activity coefficients require fit parameter (ion size, correction due to implicit solvent treatment), osmotic coefficients less error-prone
- solvent averaged approaches are (within statistical uncertainty) consistent with explicit solvent simulations, at negligible computational costs
- with correct MD force fields the agreement with experimental data (Φ) is very good
- usable also for mixtures
- quick prediction of thermodynamic properties, optimization of parameter sets



HNC with simple pair potentials

Law of matching water affinities (Collins 2004)

- only ions with similar hydration energies tend to form (strong) ionic pairs
- NaF, CsI strong pairing favorable
- RbF, LiI strong pairing unfavorable
- carboxylate: Na^+ fits better than K^+
- sulfonate (ion exchangers): K^+ fits better than Na^+

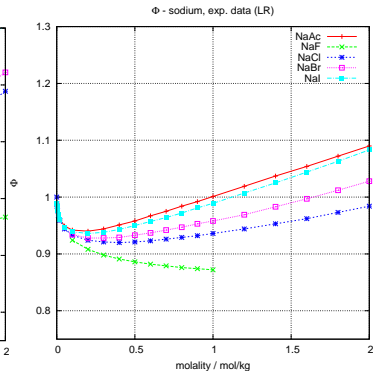
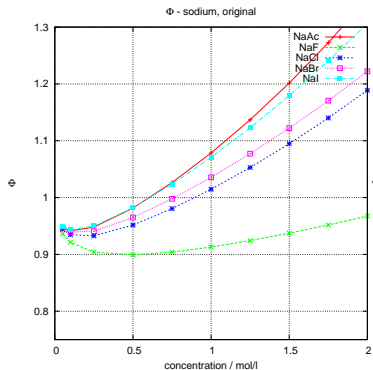


Goals of the work

- charged hard spheres as a pair potential in OZ/HNC
- ionic hard sphere radii coming from ab-initio calculations
- no fit-parameters involved
- taking the law of matching water affinities into account
- aiming at *qualitative* description

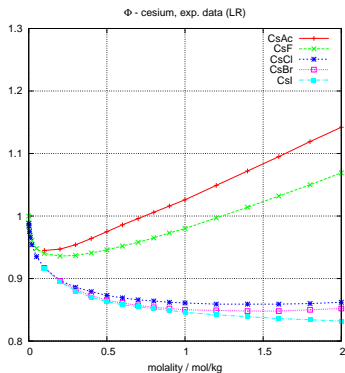
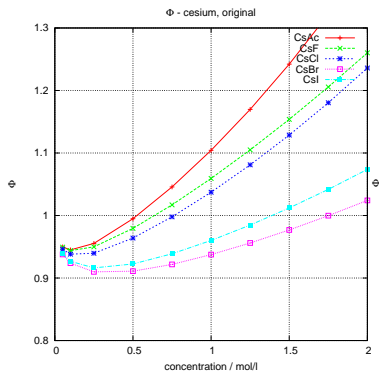
- parameter evaluation – Na-F vs. Li-water-Br
- strongly hydrated Li; Ac, F
- borderline Na, Cl
- weakly hydrated K, Rb, Cs; Br, I

Φ - cationic series



- Li^+ , Na^+ , K^+ series qualitative OK

Φ - cationic series



- Rb^+ , Cs^+ series – Br/I ordering wrong (reason unknown at the moment)

- at the moment no consistent description available
- either strongly or weakly hydrated salts are described qualitatively correctly

Summary

- Collins' concept allows for qualitative description of cationic series within this simple model
- issue of Rb and Cs – Br/I ordering
- concept of counterion-independent ionic parameters is clearly wrong
- for anions, another set of parameters is needed



Acknowledgements

- W. Kunz – Uni Regensburg
- J. Dzubiella, I. Kalcher, D. Horinek, R. Netz – TU München

- M. Lund – Uni Lund



Thank You for Your Attention

