Description of electrolyte solution properties

using integral equation theory and MD simulations

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Integral equation machinery (OZ + HNC)

Ornstein-Zernike equation defines the direct correlation function **c**

$$\begin{aligned} h_{ij} &= c_{ij} + \sum_k \rho_k \int c_{ik} h_{kj} dr_k \\ h_{ij} &= g_{ij} - 1 \end{aligned}$$

splitting the total interaction **h** between 2 particles to direct and indirect parts. HyperNetted Chain closure relates the direct correlation function to the total correlation function

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

u is pair potential and **Γ** is indirect correlation function

$$\Gamma_{ij}(r) = h_{ij} - c_{ij}$$

These equations have to be solved iteratively.

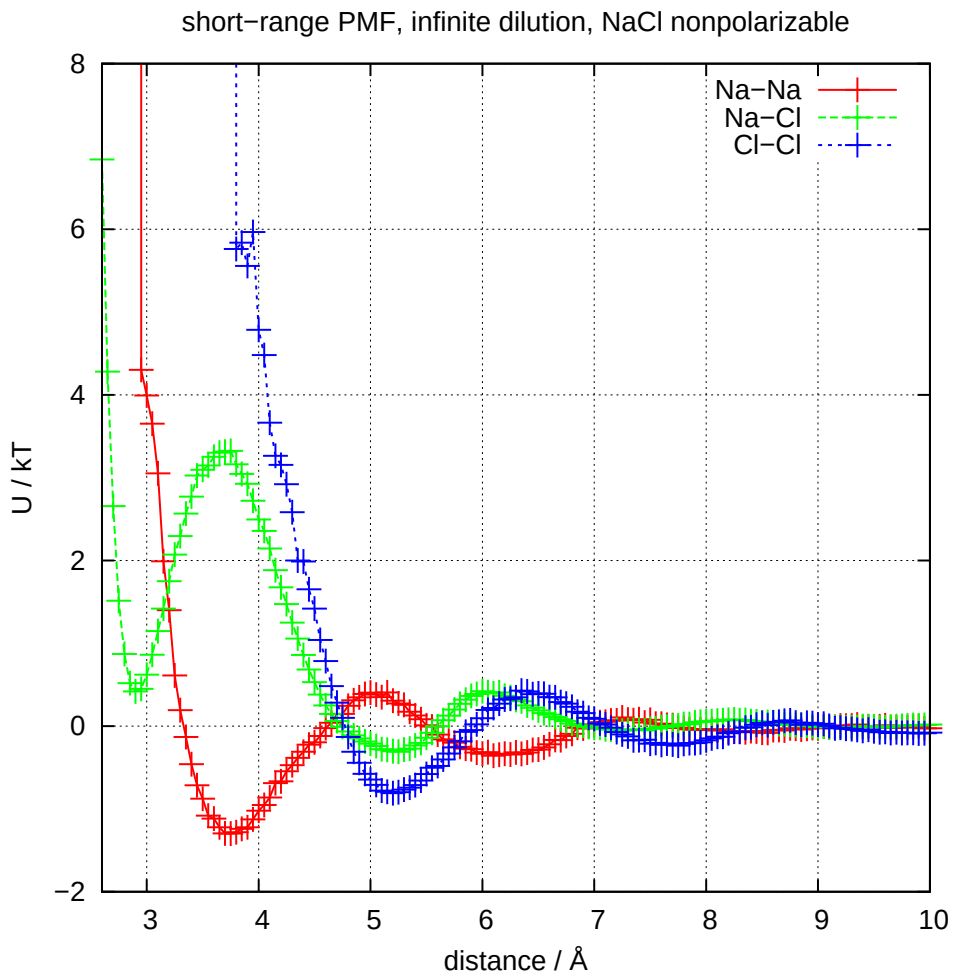
Goal of the work

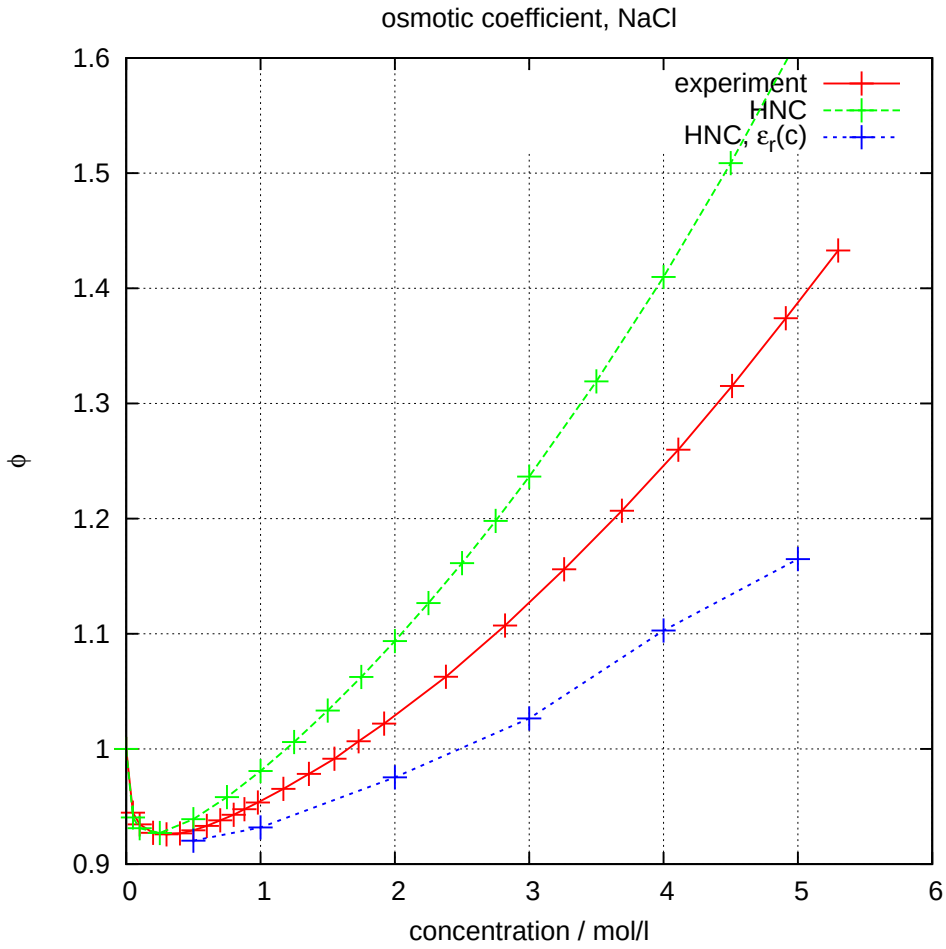
- ... to use potentials of mean force (PMF) of NaCl at infinite dilution from molecular dynamics (MD) simulation in OZ/HNC, aiming at description of thermodynamic properties at wide range of concentrations, and thus linking experiments, statistical thermodynamics, and MD
- PMFs using nonpolarizable forcefield (SPC/E water model) *J. Dzubiella and I. Kalcher*
- PMFs using polarizable forcefield (POL3 water model) *D. Horinek*
- osmotic coefficients Φ (measure of activity of solvent in a solution) are property of interest

$$\Phi = -\frac{n_w}{\nu_s n_s} \ln a_w = -\frac{\ln a_w}{\nu_s m_s M_w}$$

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

Nonpolarizable PMFs





- quite good agreement with experiments, g(r)s agree with MD
- usage of concentration dependent dielectric constant $\varepsilon_r(c)$? *Adelmann, Hess*

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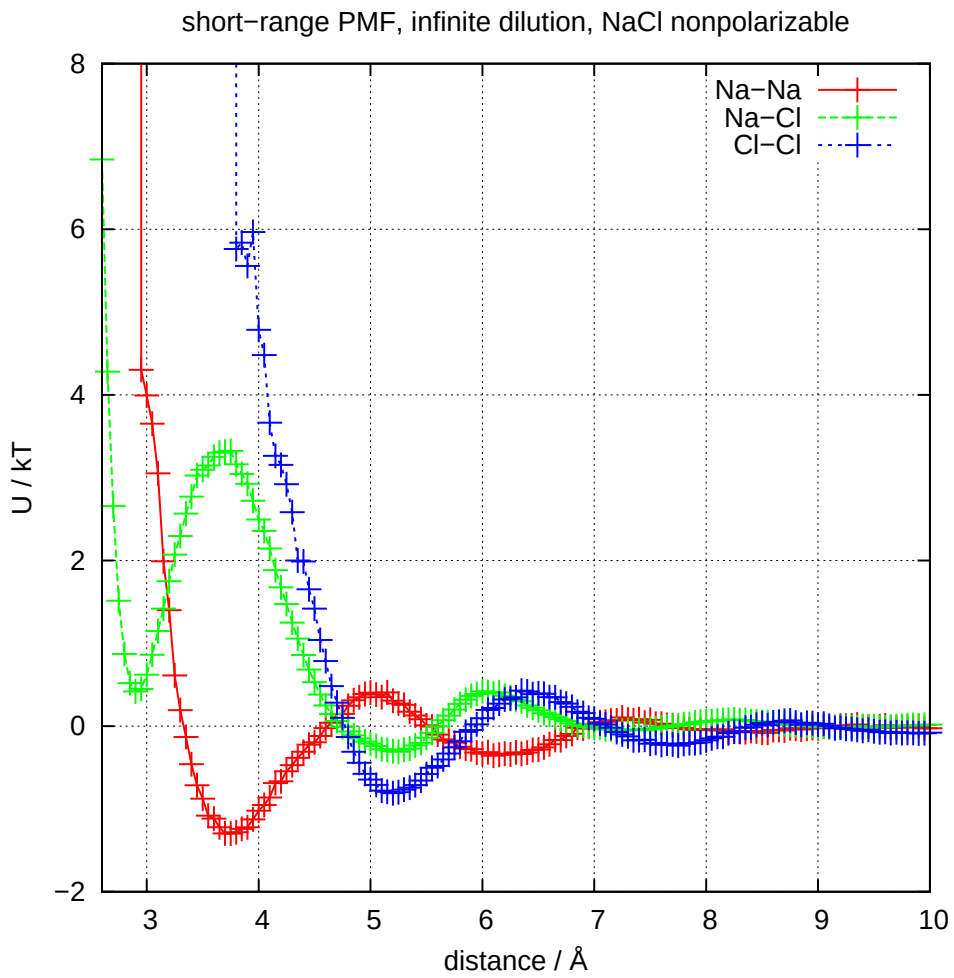

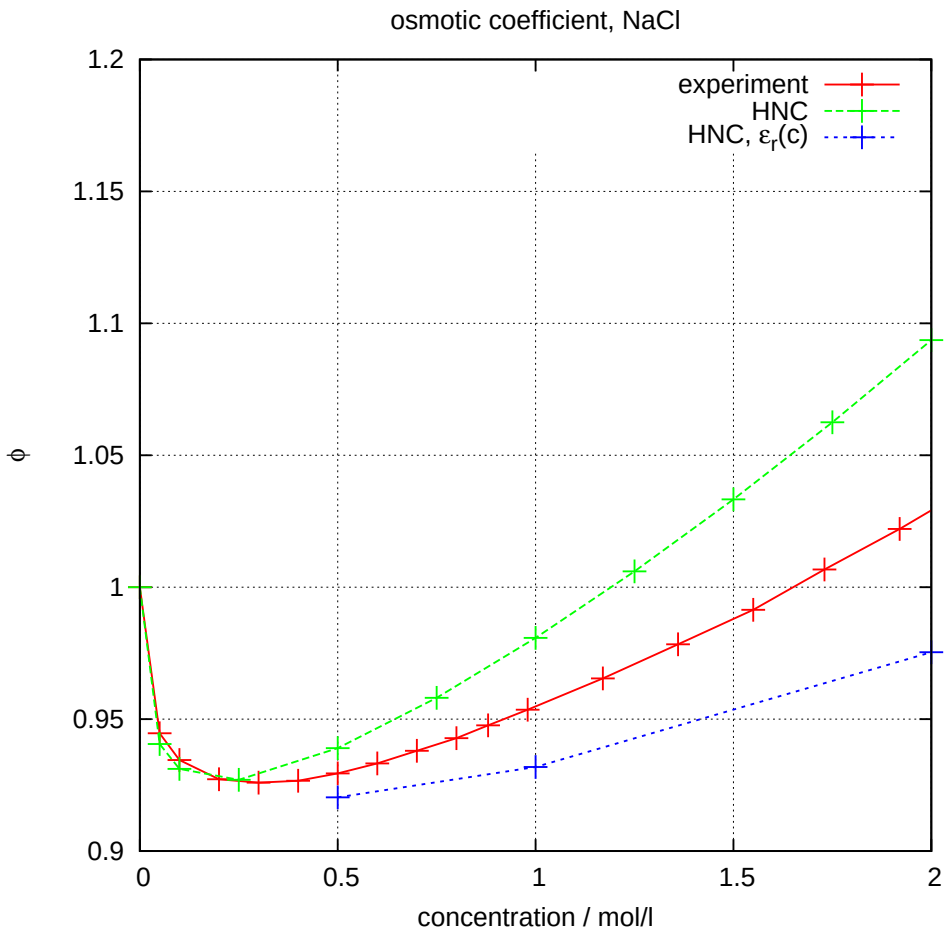

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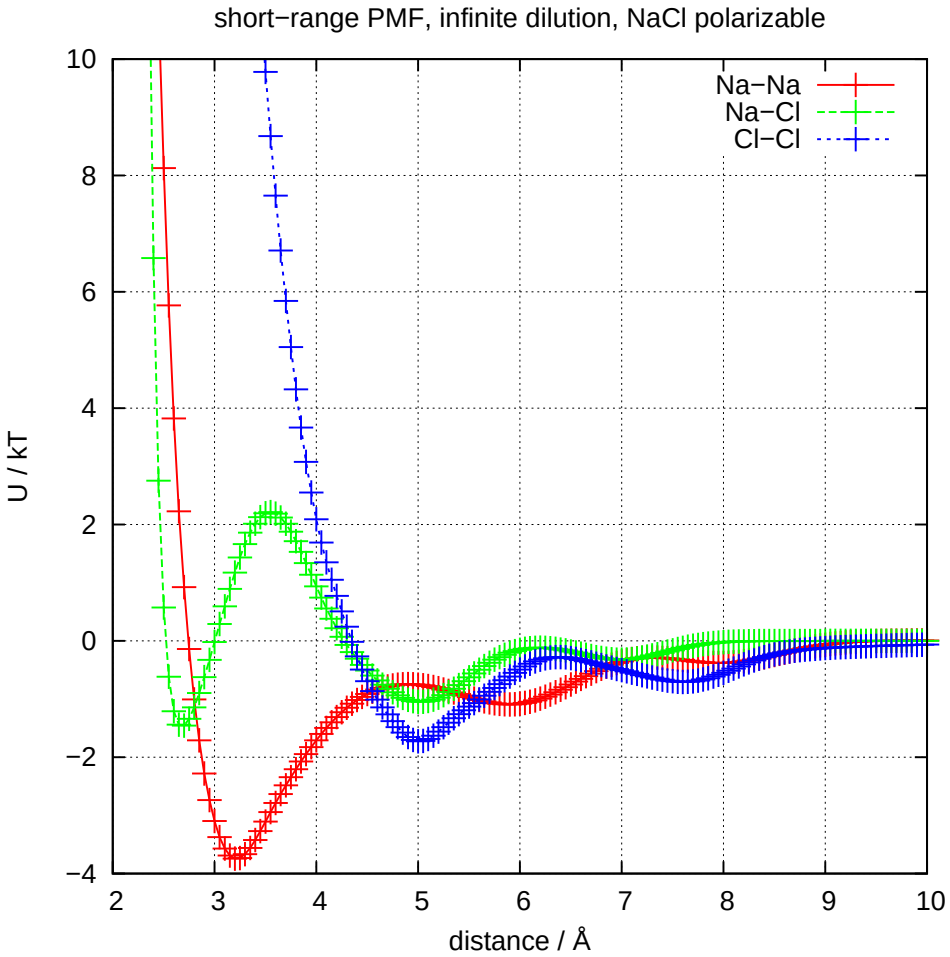
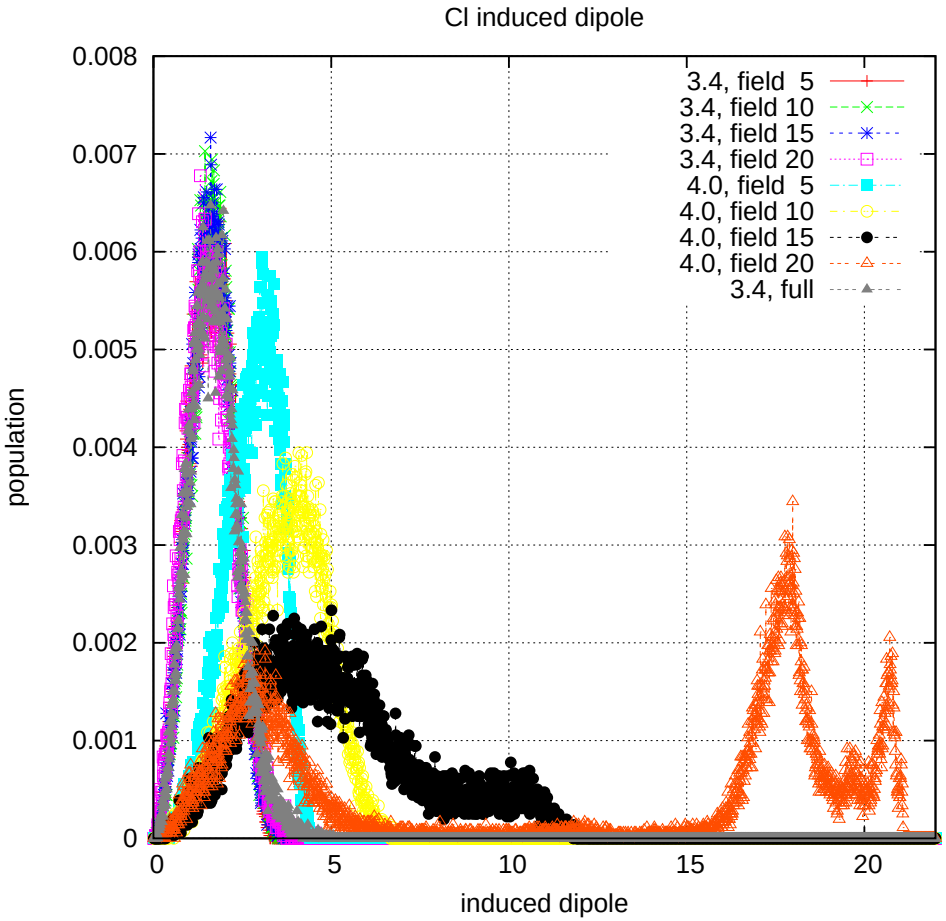
Polarizable PMFs



- cannot be used directly in HNC due to depth of the first Na-Cl minimum
- interaction too strong, unreasonable osmotic coefficients (too low, always decreasing)
- how to make it better?

Polarization interaction

Iterative algorithms are used for evaluation of polarization interaction in MD.



- $\vec{p} = \alpha \vec{E}$
- problems – polarization catastrophe
- decreasing polarizability size
- dipole limiting schemes (limiting maximal electric field)
- effect on induced dipole distribution and on g(r)s

Work to do

- finding 'correct' potential for description of both bulk and surface properties
- further comparison of HNC, Poisson-Boltzmann, MD, and experiment
- calculation of chemical activities
- calculation of pH in buffers
- ... and much more

Acknowledgements

- Werner Kunz
- Joachim Dzubiella, Immanuel Kalcher
- Dominik Horinek, Roland Netz

- Alexander von Humboldt Foundation

Thank You for Your Attention

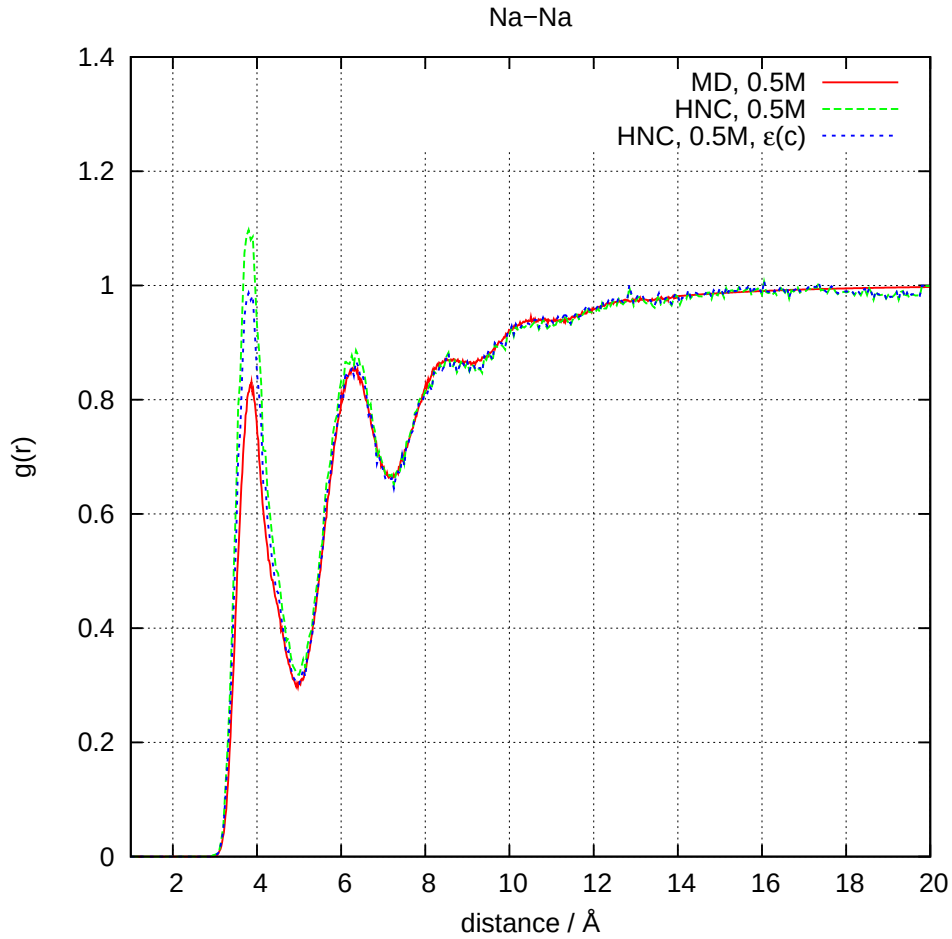
pyOZ solver

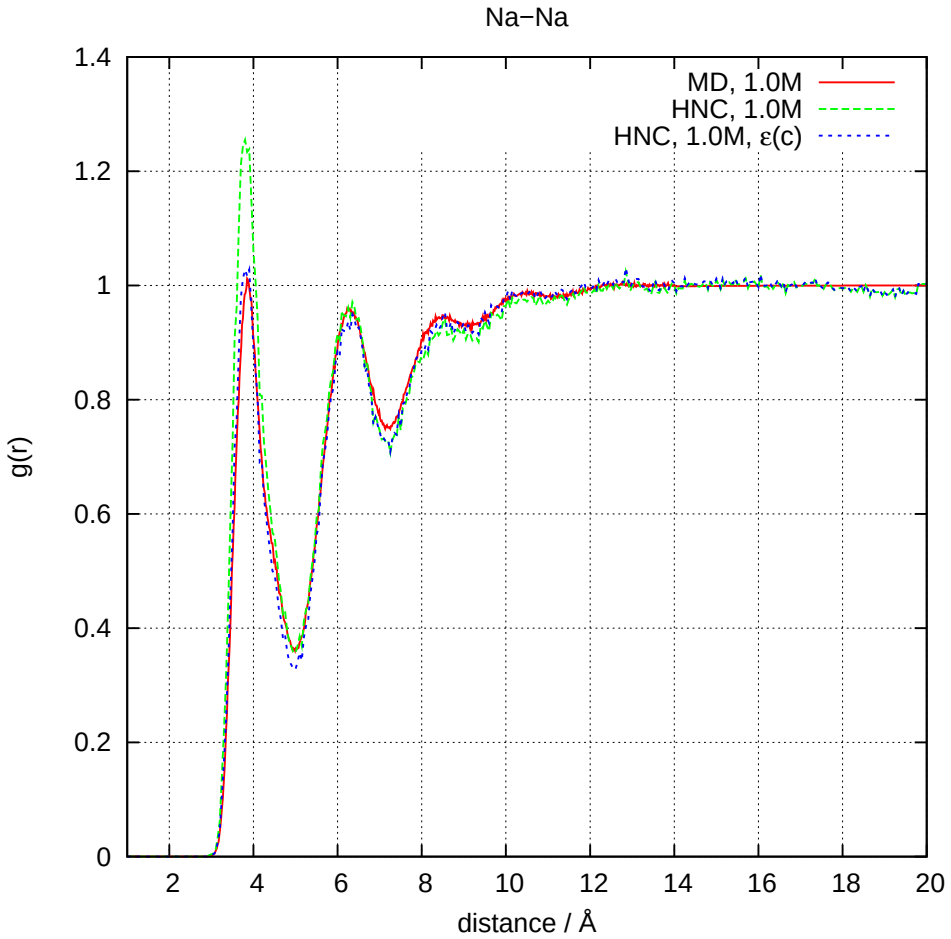
- `http://pyoz.vrbka.net`

- numerical solver of the Ornstein-Zernike equation
- support for HNC, PY
- various pair potentials (HS, Coulomb, LJ, PMF)
- currently only osmotic coefficients calculated

- multiplatform and easily extensible (Python)
- open source

Nonpolarizable PMFs - g(r)





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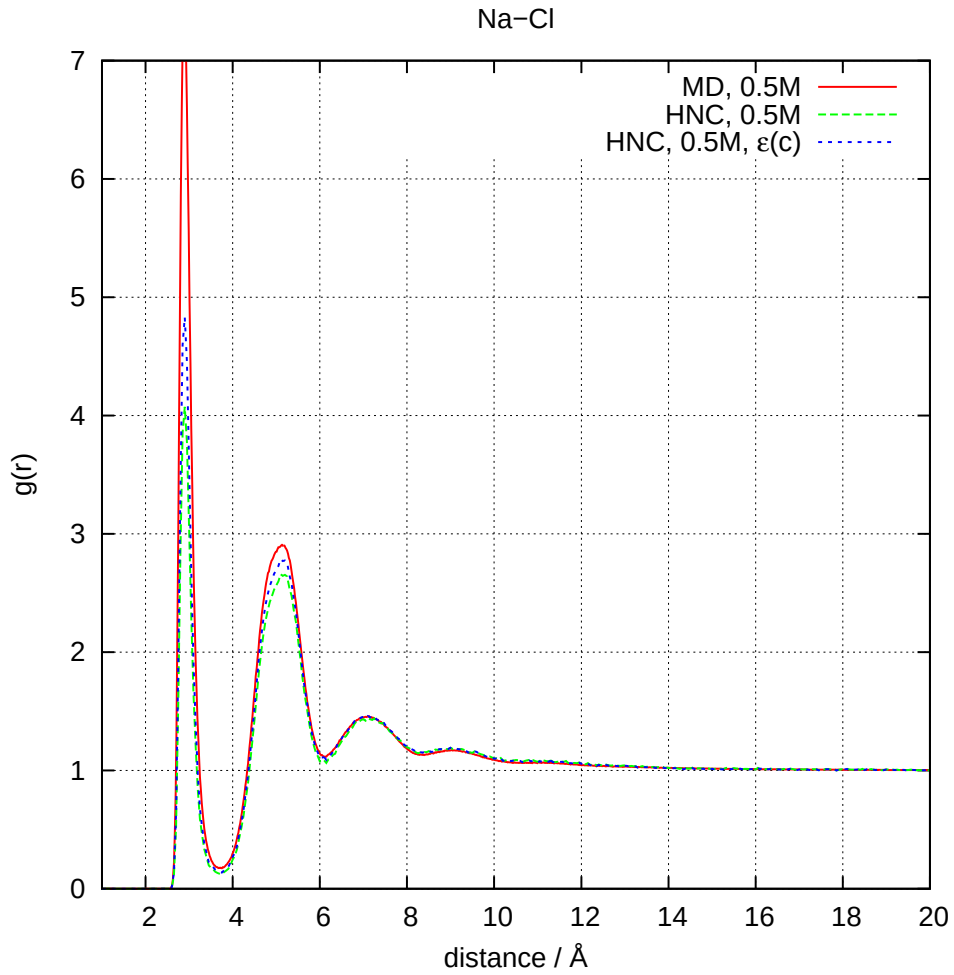

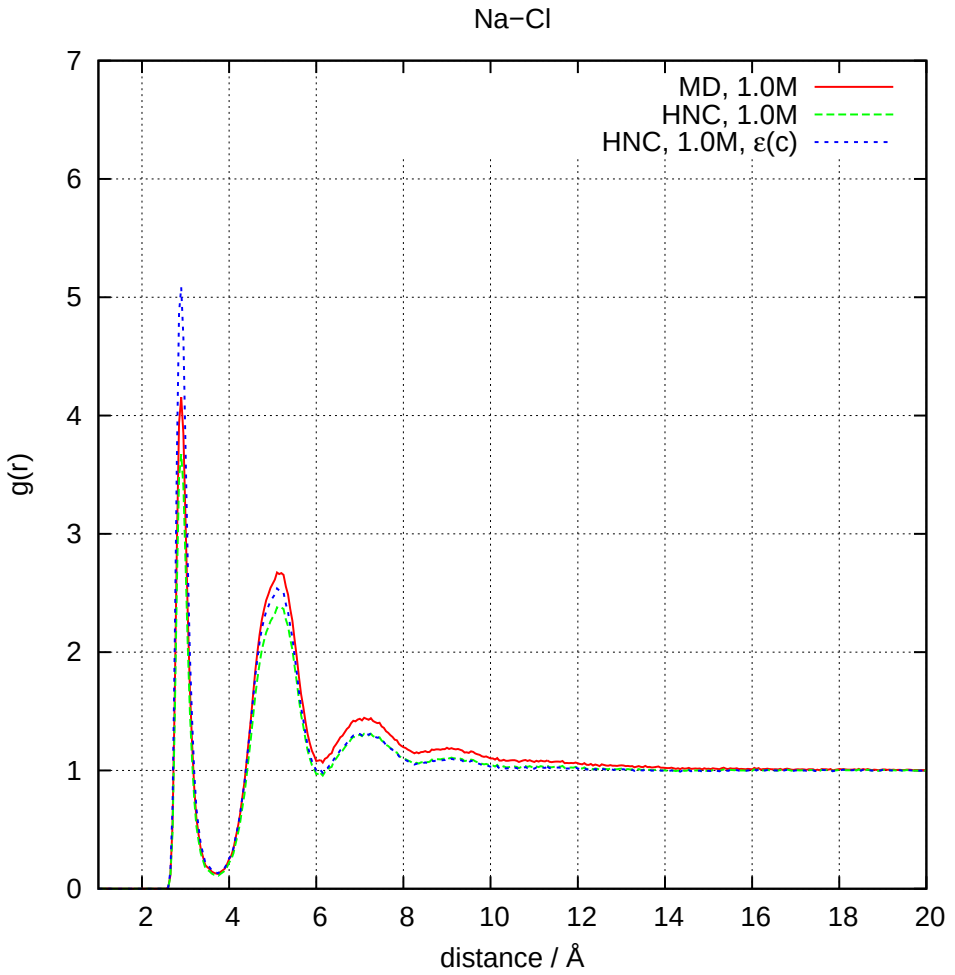

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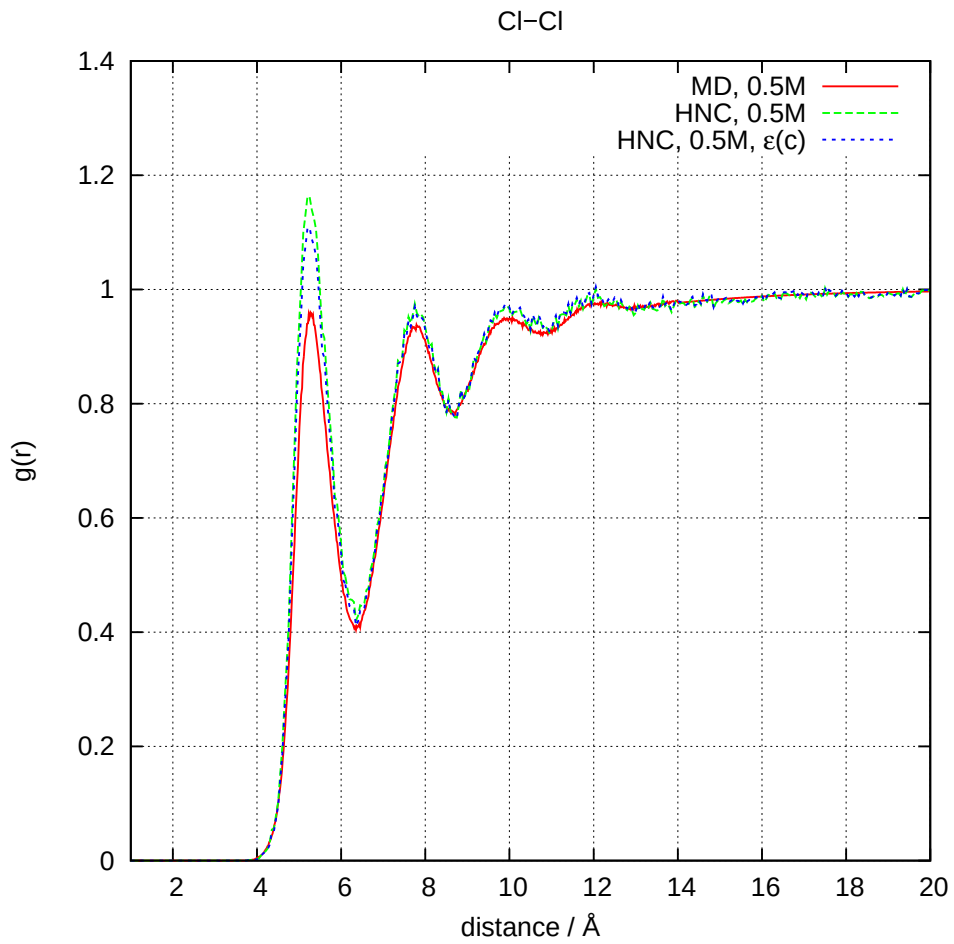

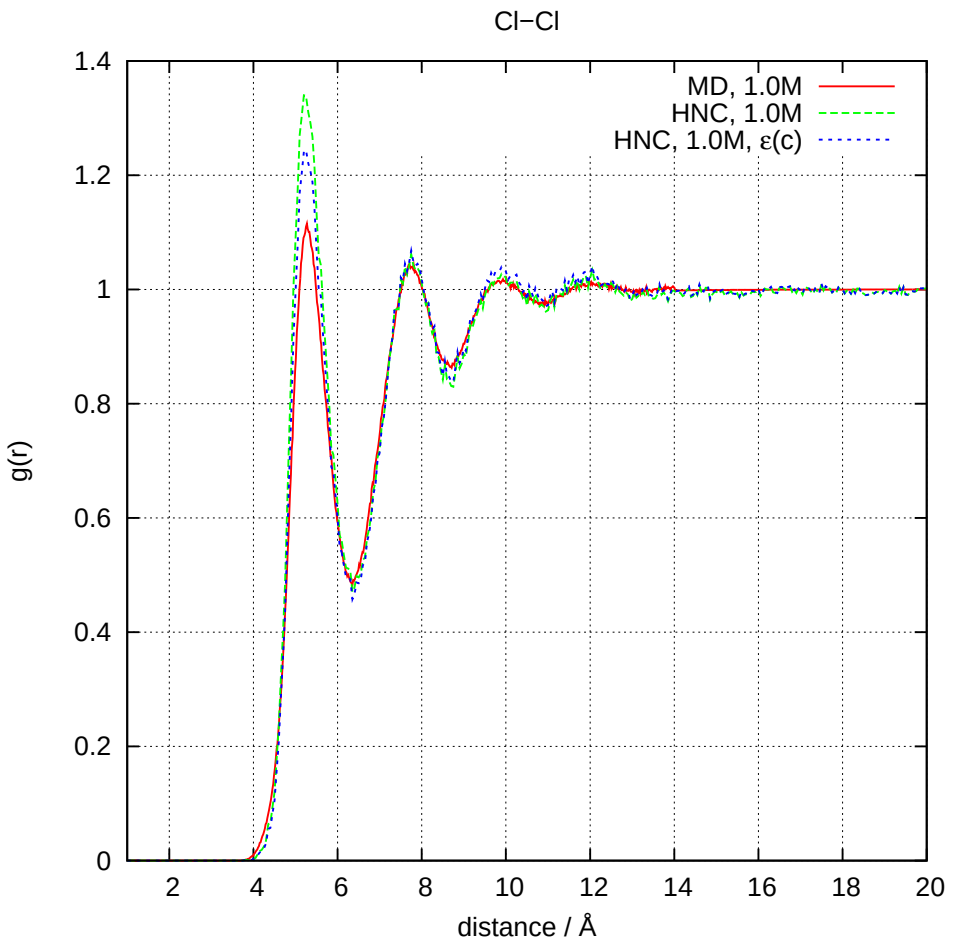

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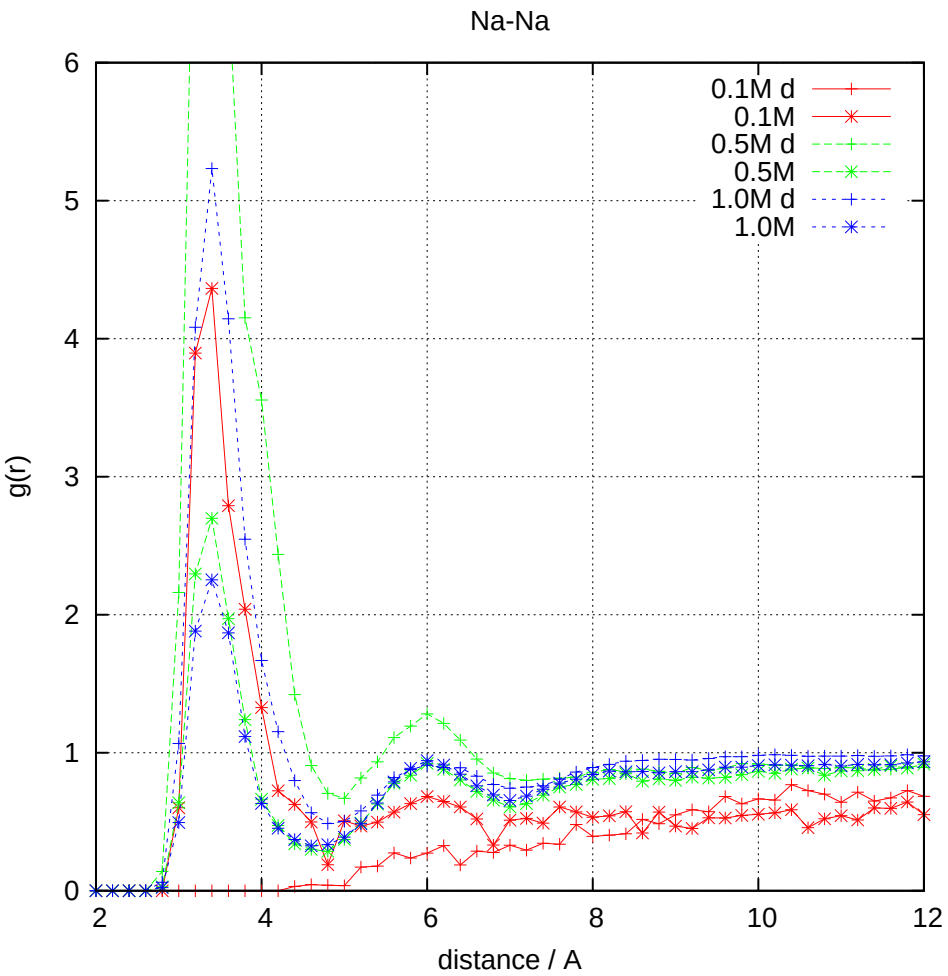
Effect of polarizability on g(r)



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- polarizability size and used dipole limiting scheme influence the structural properties

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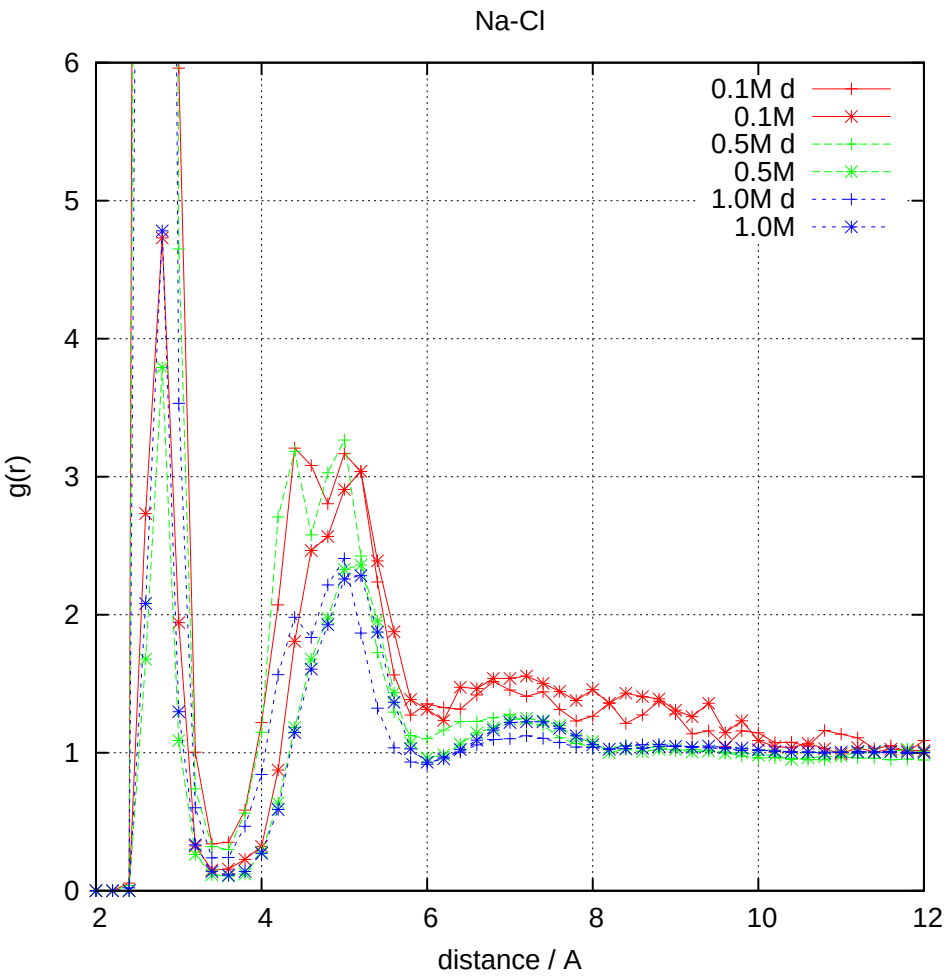

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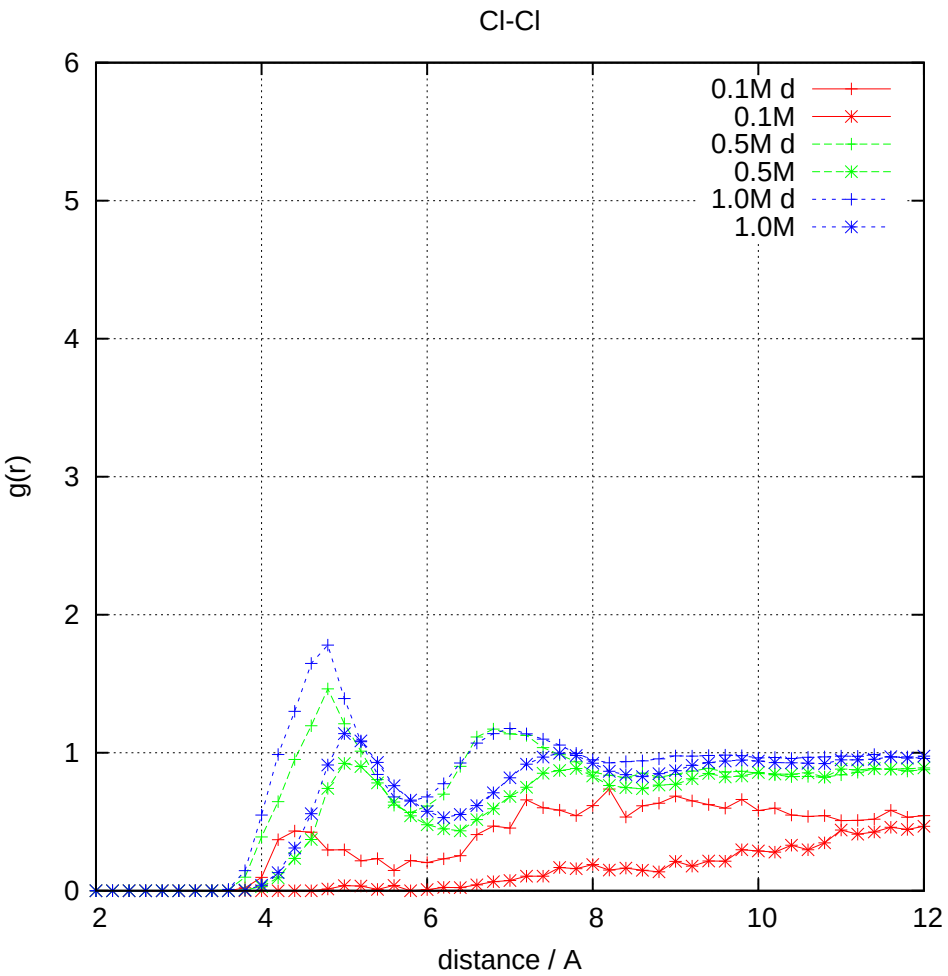

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