

Discovery of Water Structural Transitions near Interfaces of Polarizable Solutes

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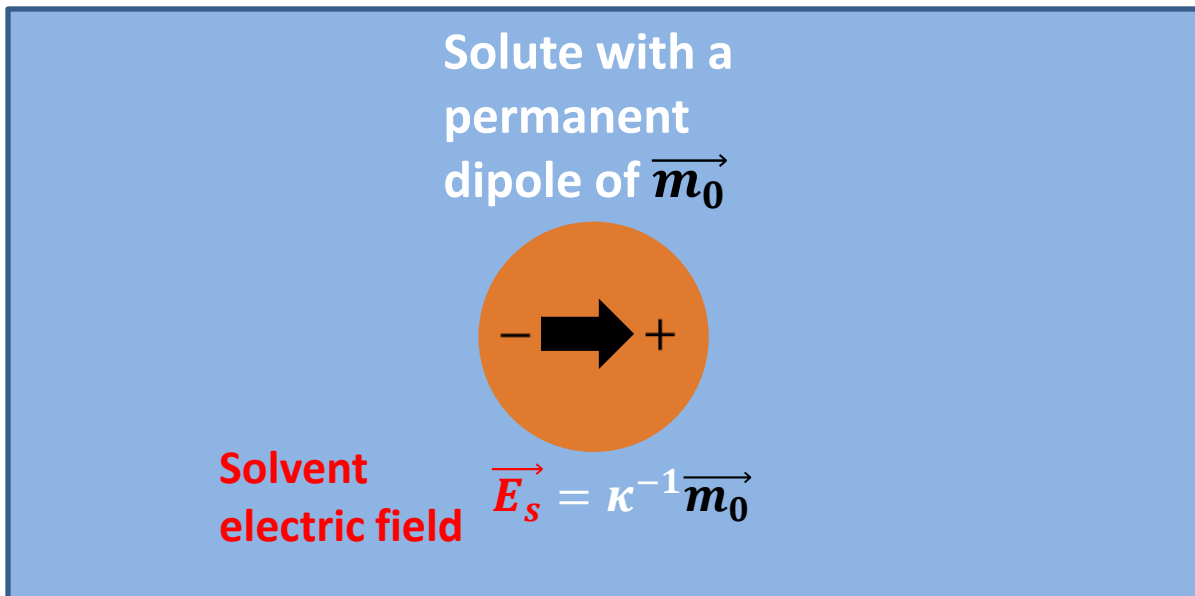
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Solvent Response



Solvent response is mostly linear

Linear response
(Gaussian approximation)

$$F[\vec{E}_s] = -\vec{m}_0 \cdot \vec{E}_s - \frac{\alpha}{2} \vec{E}_s^2 + \frac{\kappa}{2} \vec{E}_s^2$$

free energy of dipole moment in the solvent field

polarizing the solute
 α : polarizability of the solute

fluctuations of solvent \vec{E}_s
 $\kappa = \langle \delta E_s^2 \rangle^{-1}$

What happens in the non-harmonic limit?

$$F[\vec{E}_s] = -\vec{m}_0 \cdot \vec{E}_s - \frac{\alpha}{2} \vec{E}_s^2 + \frac{\kappa}{2} \vec{E}_s^2 + G[\vec{E}_s]$$

$$\alpha = \kappa$$

α : polarizability of the solute

Higher order terms

- The **harmonic truncation** becomes **inadequate**
- How **solvent response** is different from standard harmonic (Gaussian) models?
- What are the microscopic changes in the **structure of the interface**?

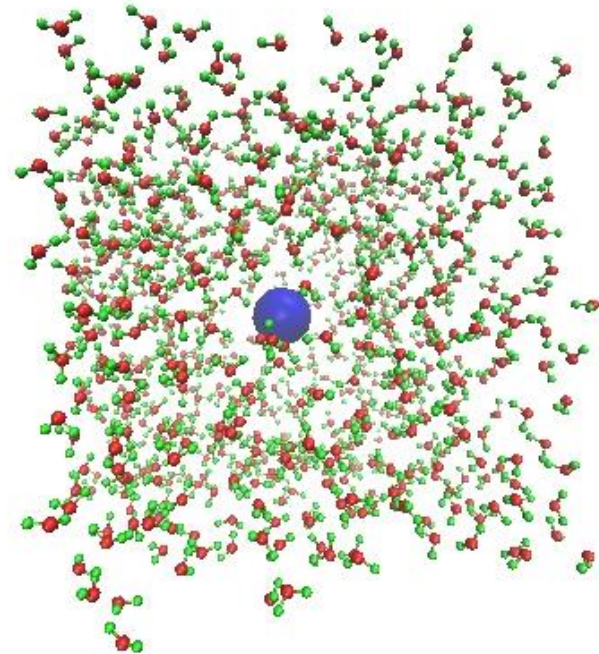
Monte Carlo Simulations

Electrostatic potential energy used in the **Monte Carlo** simulations of a polar polarizable solute in TIP3P **water**

$$U = -\vec{m}_0 \cdot \vec{E} - \frac{\vec{a} \cdot \vec{E}^2}{2} - \frac{1}{2} \sum_{j,k} \vec{m}_j \overleftrightarrow{T}_{jk} \vec{m}_k$$

$$\vec{m}_0 = 5 \text{ D}$$

solvent electric field at the center of solute



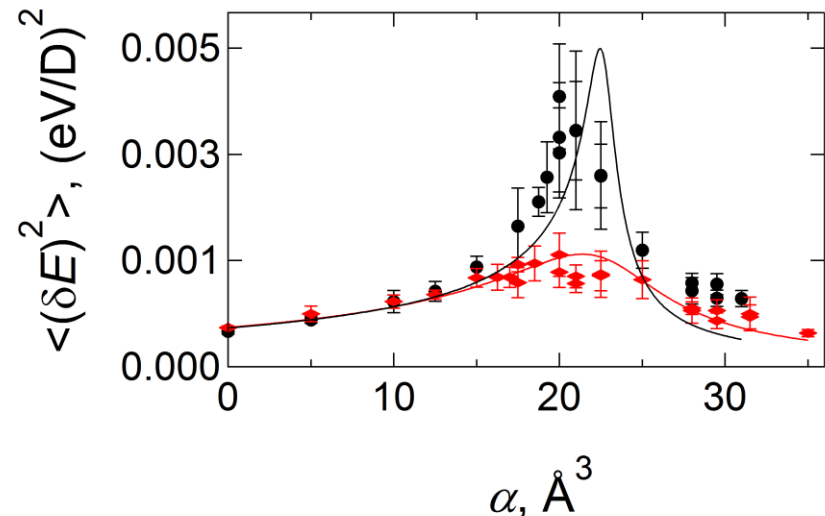
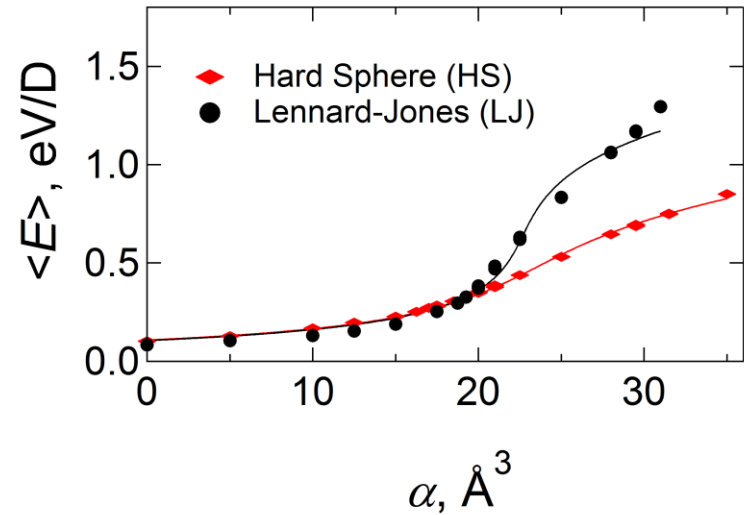
**Van der Waals Interactions:
Solute-Solvent**

Hard Sphere (HS)

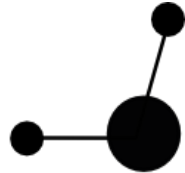
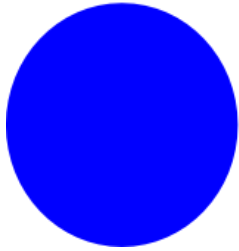
Lennard-Jones (LJ)

Solvent Electric Field

- An **inflection** of the average field at $\alpha^* \simeq 20\text{--}22 \text{ \AA}^3$
- A **spike** in the field variance at $\alpha^* \simeq 20\text{--}22 \text{ \AA}^3$
- The field variance is proportional to the **dipolar susceptibility**



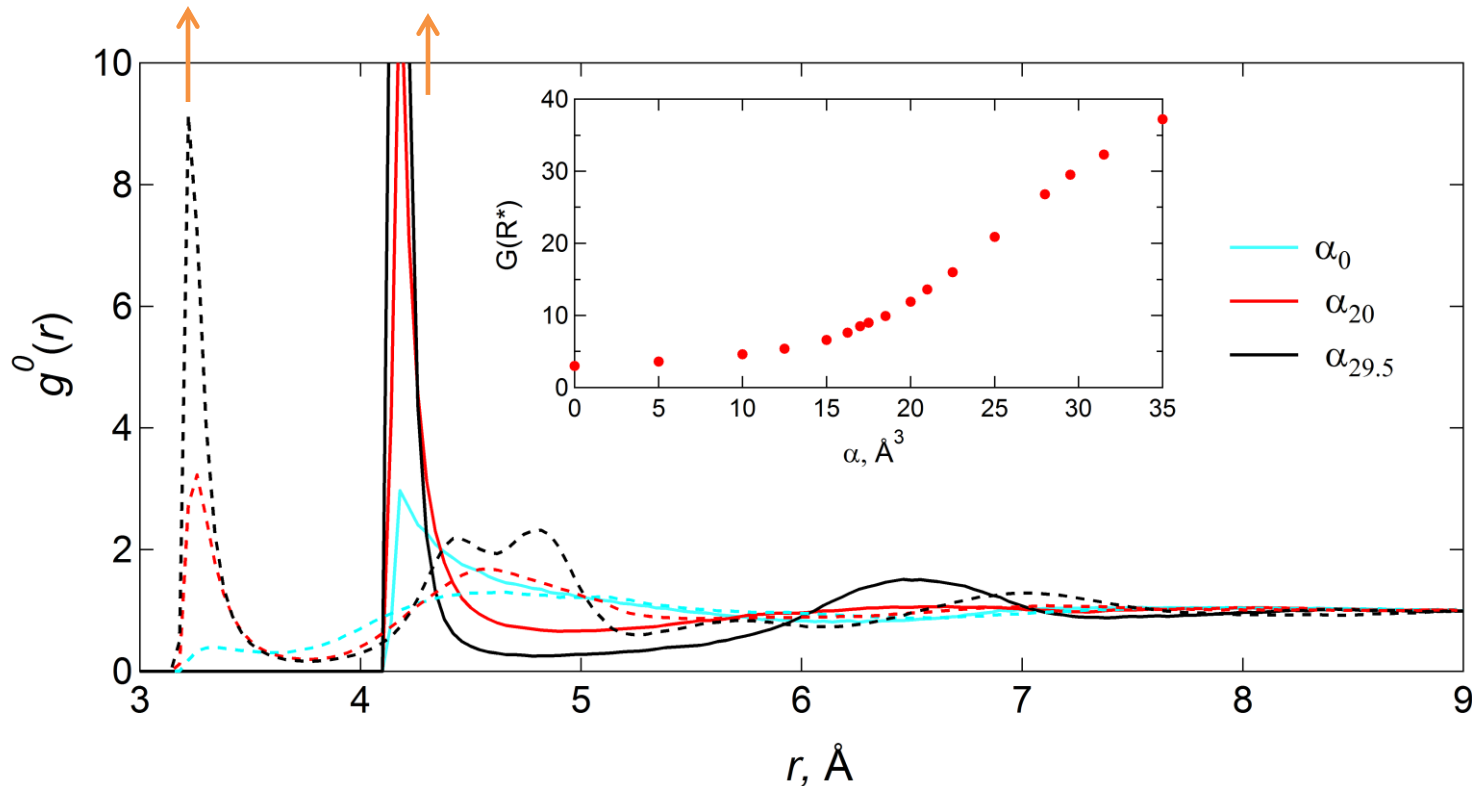
RDF: Hard Sphere Solute



- Near the critical polarizability α^* , a **layering transition** occurs separating the first and the second hydration layers

Hydrogen-Solute

Oxygen-Solute

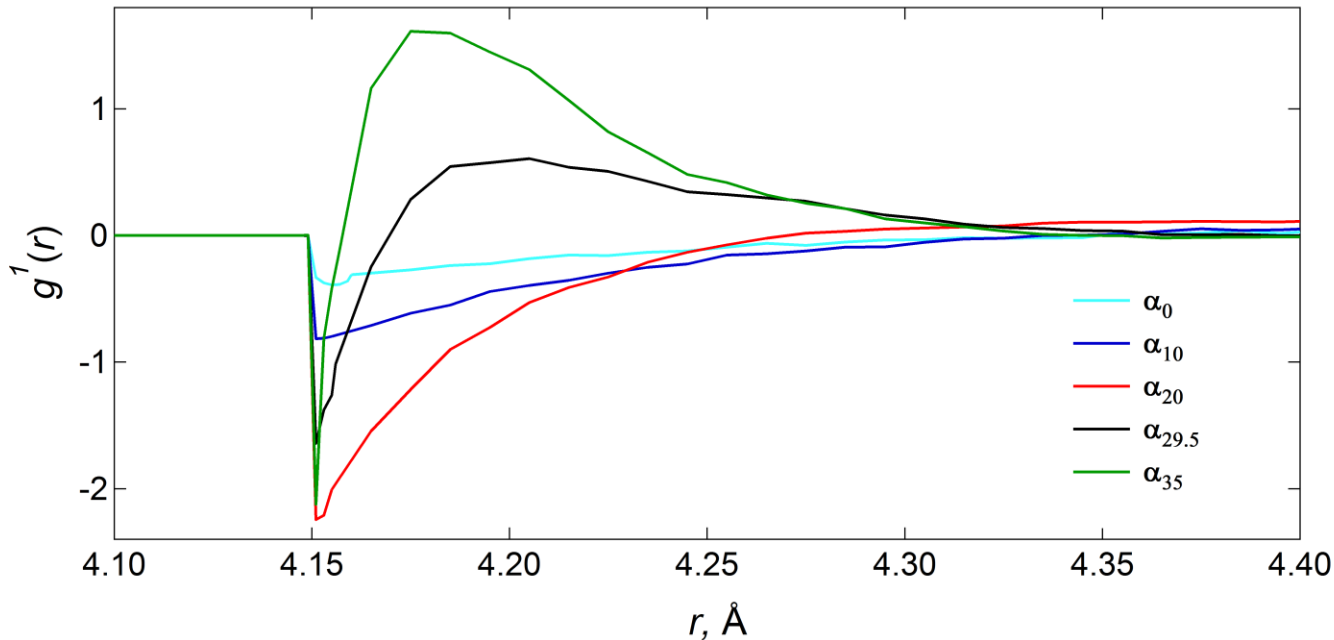
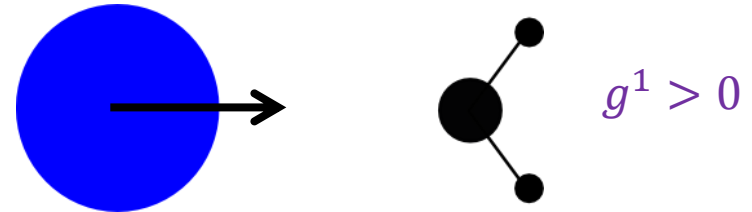
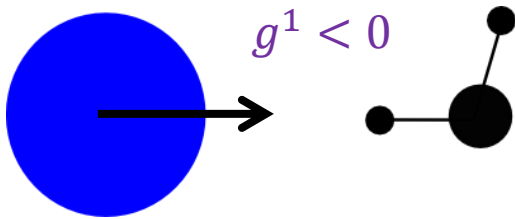


Orientation Distribution Functions

$$g_{0s}^l = \rho \left\langle \sum_l P_l(\cos \theta_{mj}) \delta(r_j - r) \right\rangle$$

water dipole moment θ_{mj} radial vector

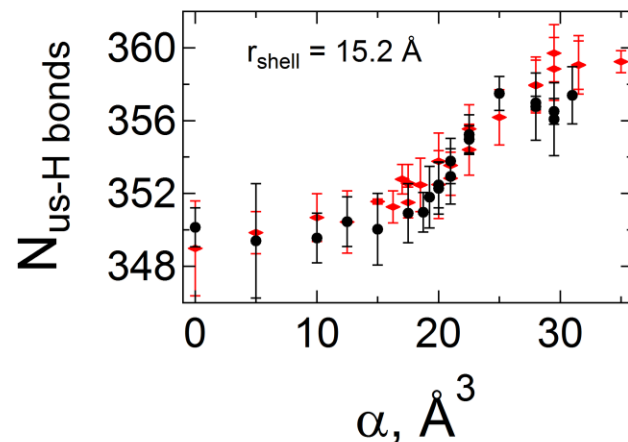
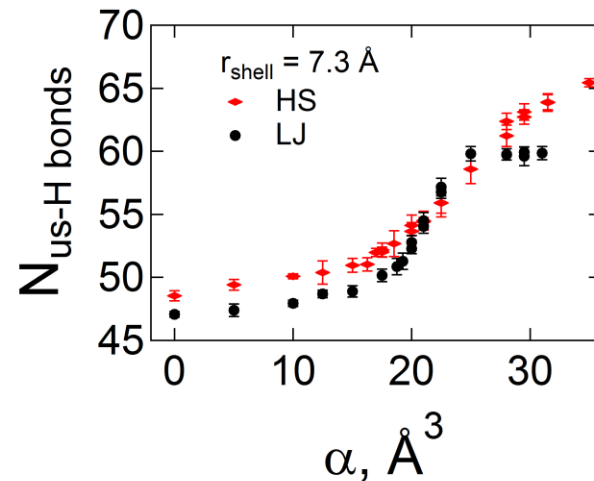
$$P_1(\cos \theta_{mj}) = \cos \theta_{mj}$$



The dipoles **flip** their orientations at the transition to the non-harmonic regime

Unsatisfied Hydrogen (us-H) Bonds

- An **order parameter** of the structural interfacial transition
- Wernet definition of hydrogen bond¹:
 - The O···O distance, R , is bounded by a quadratic function of H—O ··· O angle, θ (degrees):
$$R(\theta) \leq -0.00044\theta^2 + 3.3$$
- The us-H bonds **increase** with α when counted in water layers of different thickness



¹ Ph. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odellius, H. Ogasawara, L. Å. Näslund, T. K. Hirsch, L. Ojamäe, P. Glatzel, L. G. M. Pettersson, and A. Nilsson
Science 14 May 2004: **304**, 995-999