Study of the microscopic structure of concentrated electrolyte solutions through neutron diffraction and EPSR simulation

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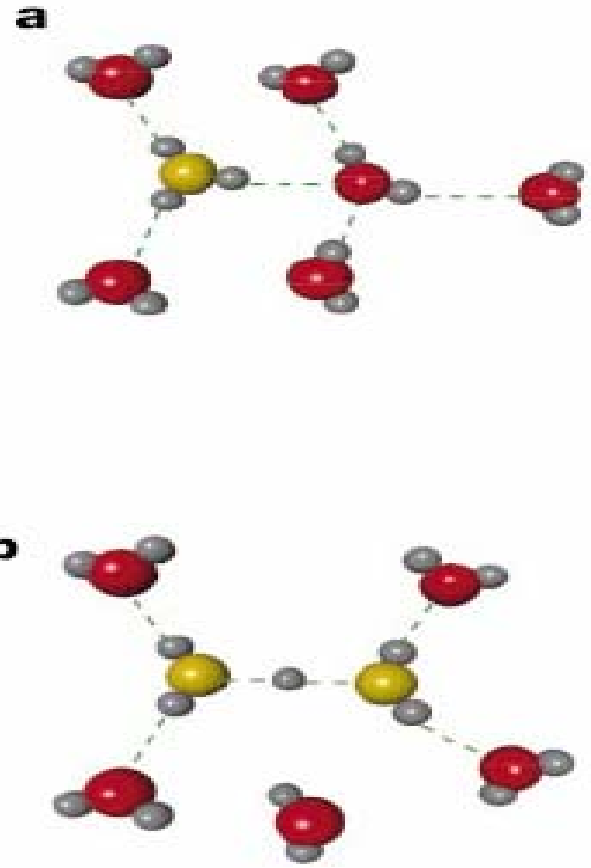
Water ions mobility

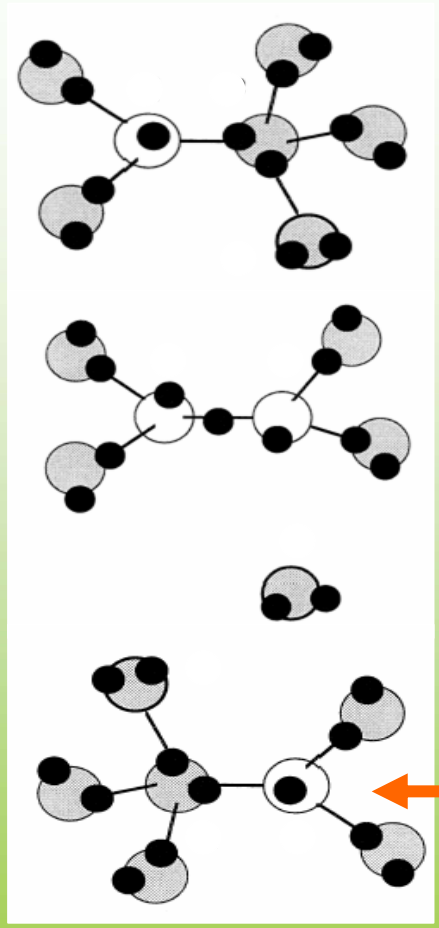
	Λ_0^m	$-\Delta H_h$
	cm^2/Ω mol	kJ/mol
Li^+	*38.7*	*559*
Na^+	*50.1*	*444*
K^+	*73.5*	*360*
H^+	*350*	*1129*
OH^-	*192*	*423*
F^-	*55*	*474*

Ab initio MD:
D.Marx,
M.E.Tuckermann,
J.Hutter,
M.Parrinello, *Nature*
397 (1999) 601



- **Mechanism of structural diffusion** with effective charge transport (**proton transfer**)
- Breaking of an HB, reorientation of one or more water molecules, re-forming of an HB

OH- : two schools of thought



Proton *hole* transfer

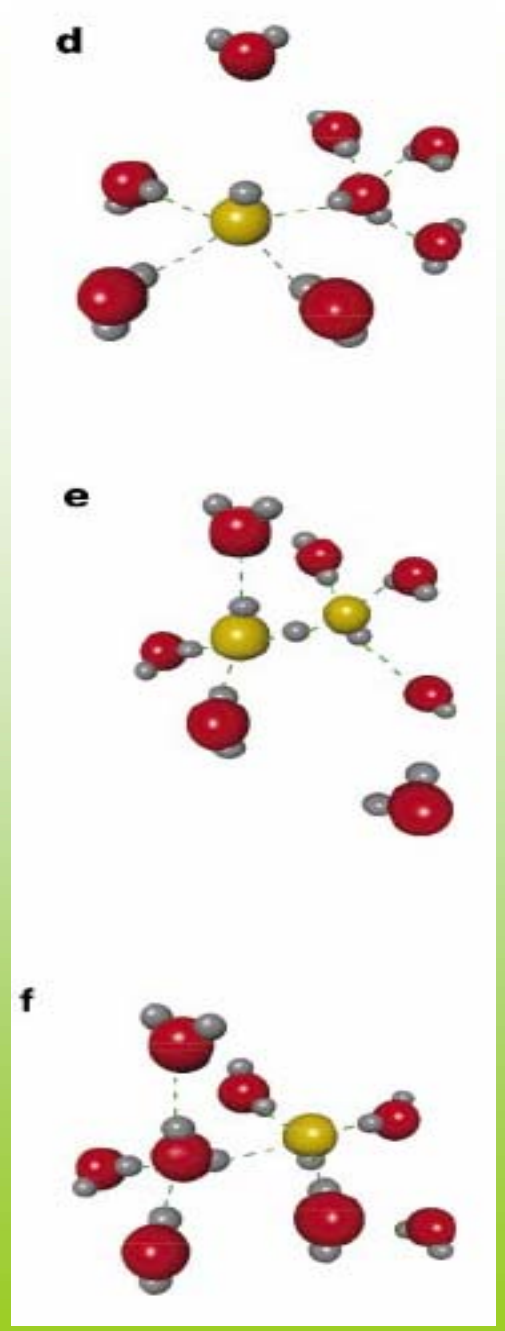
- Derived through symmetry arguments from the H^+ case
- from the structural point of view implies the presence of three water molecules around OH-

J.J.Novoa et al., J.Phys.Chem. A 101 (1997) 7842-7853
N.Agmon, Chem.Phys.Lett. 319 (2000) 247-252

Pre-solvation rule

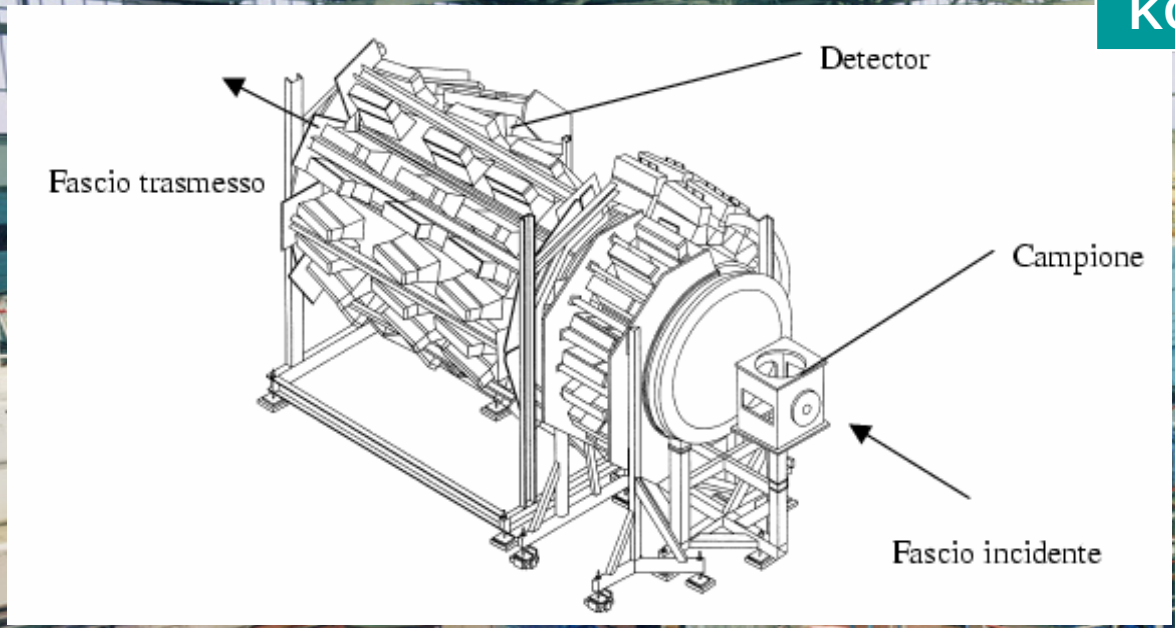
- from the structural point of view implies the presence of four water molecules around OH-

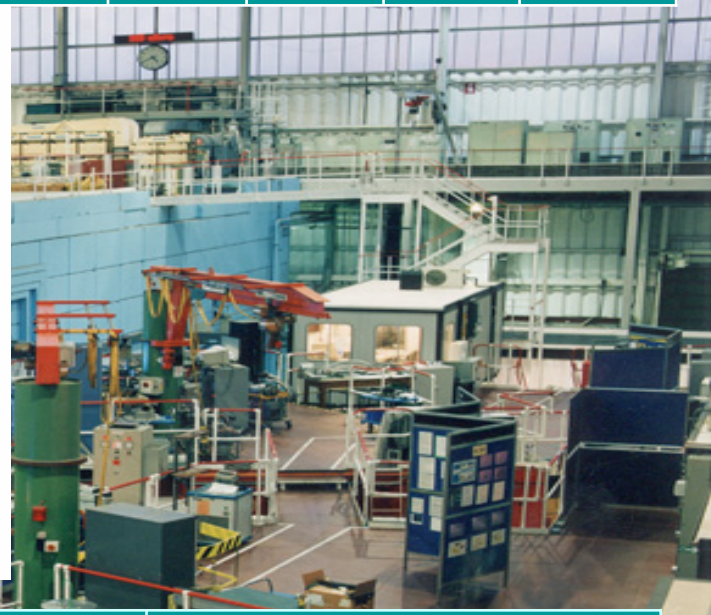
***Ab initio* MD**:
D.Marx, M.E.Tuckermann, J.Hutter, M.Parrinello, Nature 397 (1999) 601
D.Marx, M.E.Tuckermann, J.Hutter, M.Parrinello, Nature 417 (2002) 925

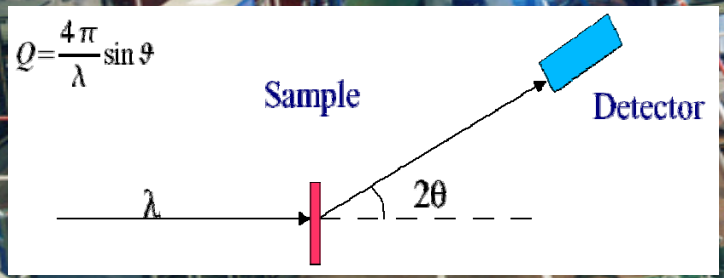


Neutron Diffraction with Isotopic Substitution

LiOH	1:12			
NaOH	1:12	1:9	1:6	1:3
KOH	1:12		1:6	1:4





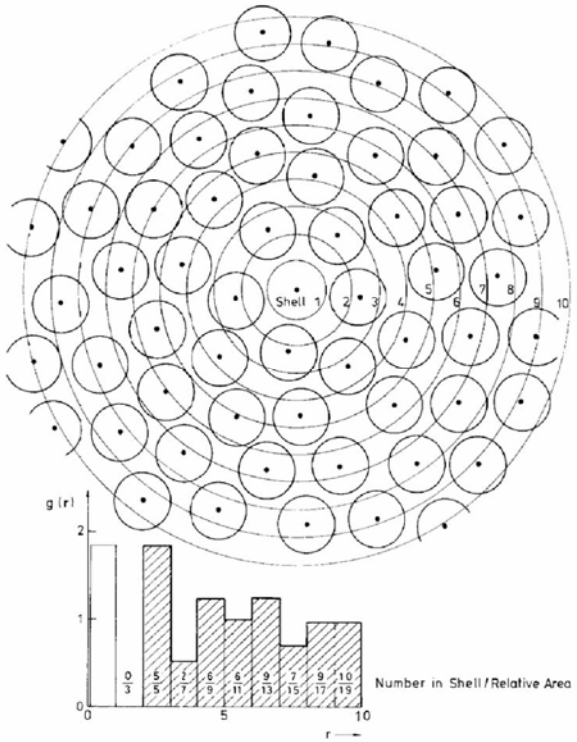


Incident scattering length:	0.05 - 4.5 Å
Q range:	0.05 - 50 Å
Moderator:	Liquid methane at 110K
Incident flight path:	11 m
Final flight path:	0.75 - 4.0 m
Detectors:	1070 ZnS
Angular range:	3.8° – 39°

$$\frac{d\sigma}{d\Omega} = N[\frac{\sigma_{inc}}{4\pi} + \frac{\sigma_{coh}}{4\pi}S(q)] \qquad b_{inc}^2 = \frac{\sigma_{inc}}{4\pi} = [\langle b^2\rangle - \langle b\rangle^2] \qquad b_{coe}^2 = \frac{\sigma_{coe}}{4\pi} = \langle b\rangle^2$$

•In the static approximation

$$S(\mathbf{q}) = \int_{-\infty}^{\infty} S(q,\omega)d\omega = 1 + \int \exp(i\mathbf{q}\cdot\mathbf{r})[g(\mathbf{r}) - 1]d\mathbf{r}$$



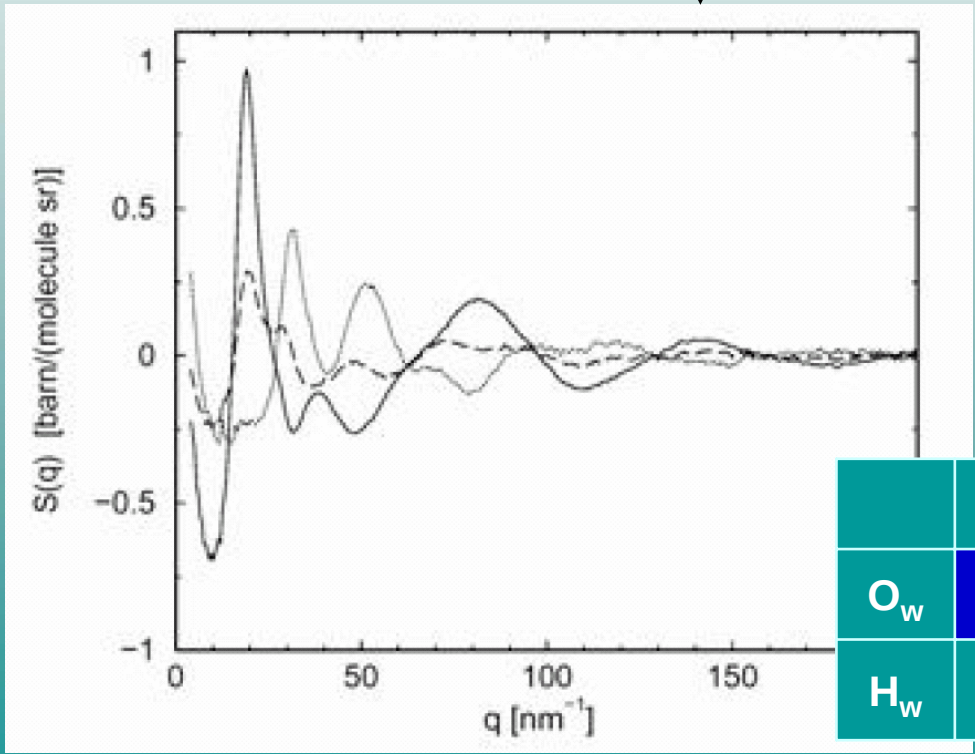
• For a multi-component system

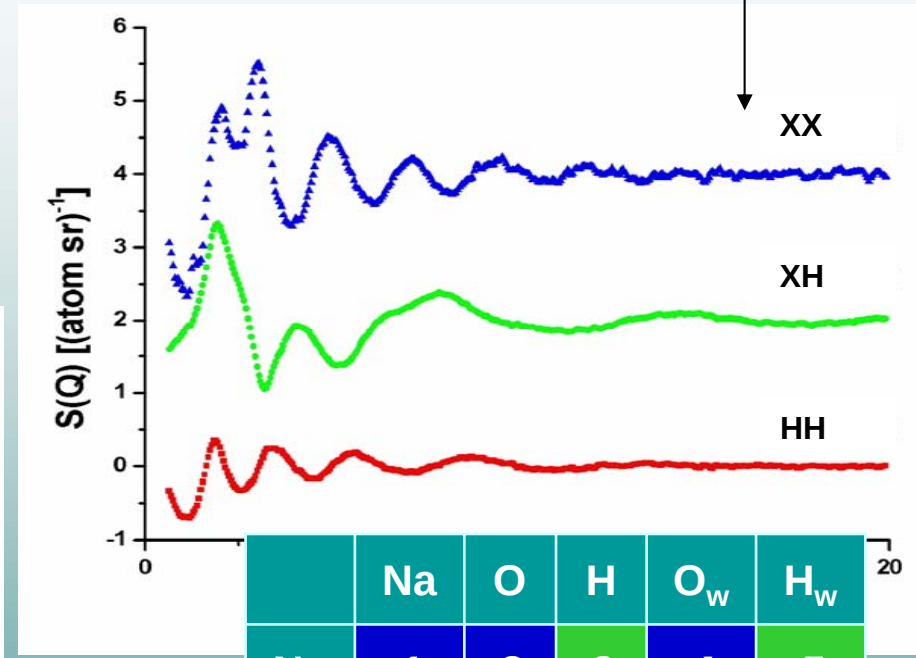
$$\frac{d\sigma}{d\Omega} = \sum_{\alpha} c_\alpha \frac{\sigma_{sc}^{\alpha}}{4\pi} + \underbrace{\sum_{\alpha\beta} c_\alpha c_\beta b_\alpha b_\beta S_{\alpha\beta}(q)}_{F(q)}$$

$$S_{\alpha\beta}(q) - 1 = 4\pi\rho \int r^2 \, (g_{\alpha\beta}(r) - 1) \, \frac{\sin qr}{qr} \, dr$$

- **H/D Isotopic Substitution**
- Based on the assumption that the structure doesn't change

$$\begin{pmatrix} F_{H_2O}(q) \\ F_{D_2O}(q) \\ F_{mix}(q) \end{pmatrix} = \begin{bmatrix} c_X^2 b_X^2 & 2c_X b_X c_H b_H & c_H^2 b_H^2 \\ c_X^2 b_X^2 & 2c_X b_X c_D b_D & c_D^2 b_D^2 \\ c_X^2 b_X^2 & 2c_X b_X c_{mix} b_{mix} & c_D^2 b_D^2 \end{bmatrix} \begin{pmatrix} S_{XX} \\ S_{XH} \\ S_{HH} \end{pmatrix}$$

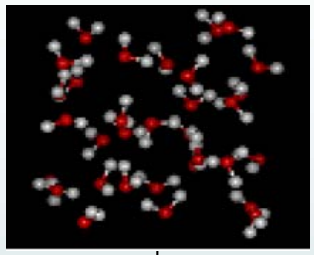




	O_w	H_w
O_w	1	2
H_w		3

	Na	O	H	O_w	H_w
Na	1	2	3	4	5
O		6	7	8	9
H			10	11	12
O_w				13	14
H_w					15

The Empirical Potential Structure Refinement



CONSTRAINTS:

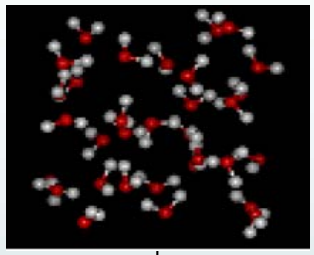
- Density
- Intramolecular structure

Reference potential

$$U_{ref} = U_{Intra} + U_{Inter}$$

Monte Carlo with molecular roto-translations

The Empirical Potential Structure Refinement



CONSTRAINTS:

- Density
- Intramolecular structure

Reference potential

$$U_{ref} = U_{Intra} + U_{Inter}$$

Monte Carlo with molecular roto-translations

Structure factors calculation

$$S^{cal}_{XX}(Q) \qquad S^{cal}_{XH}(Q) \qquad S^{cal}_{HH}(Q)$$

Difference between calculated and experimental structure factors

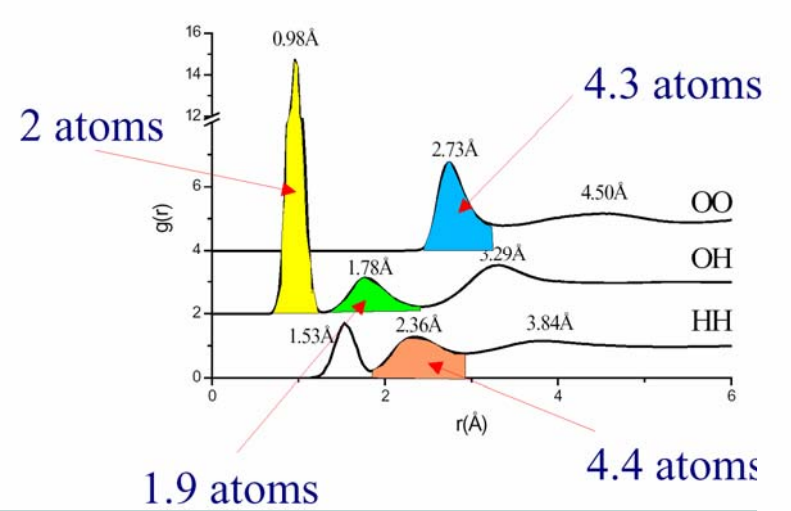
$$\Delta S_{AB} = S^{exp}_{AB} - S^{cal}_{AB}$$

$$U^{N}_{\alpha\beta} = U^{O}_{\alpha\beta} + kT\left(\ln\left(\frac{g_{\alpha\beta}(r)}{g^{D}_{\alpha\beta}(r)}\right)\right)$$

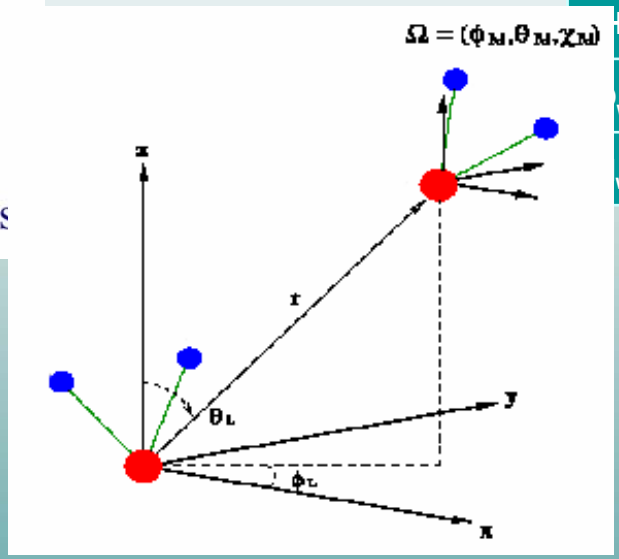
Allows to define an Empirical correction to the reference potential

$$U_{new} = U_{ref} + U_{Ep}(r)$$

The Empirical Potential Structure Refinement



	Na	O	H	O_w	H_w
Na	1	2	3	4	5
O		6	7	8	9
H			10	11	12
O_w				13	14
H_w					15

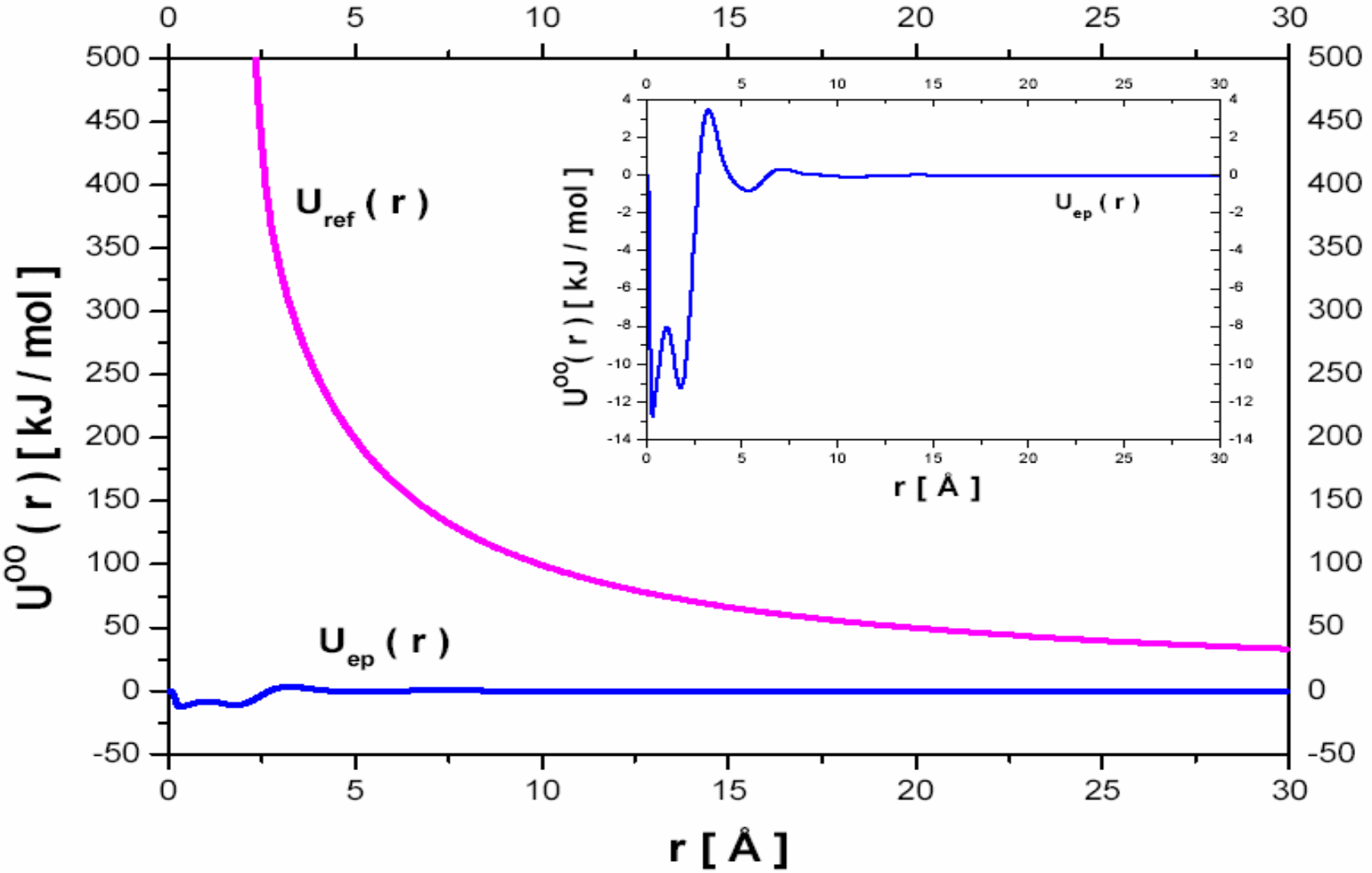


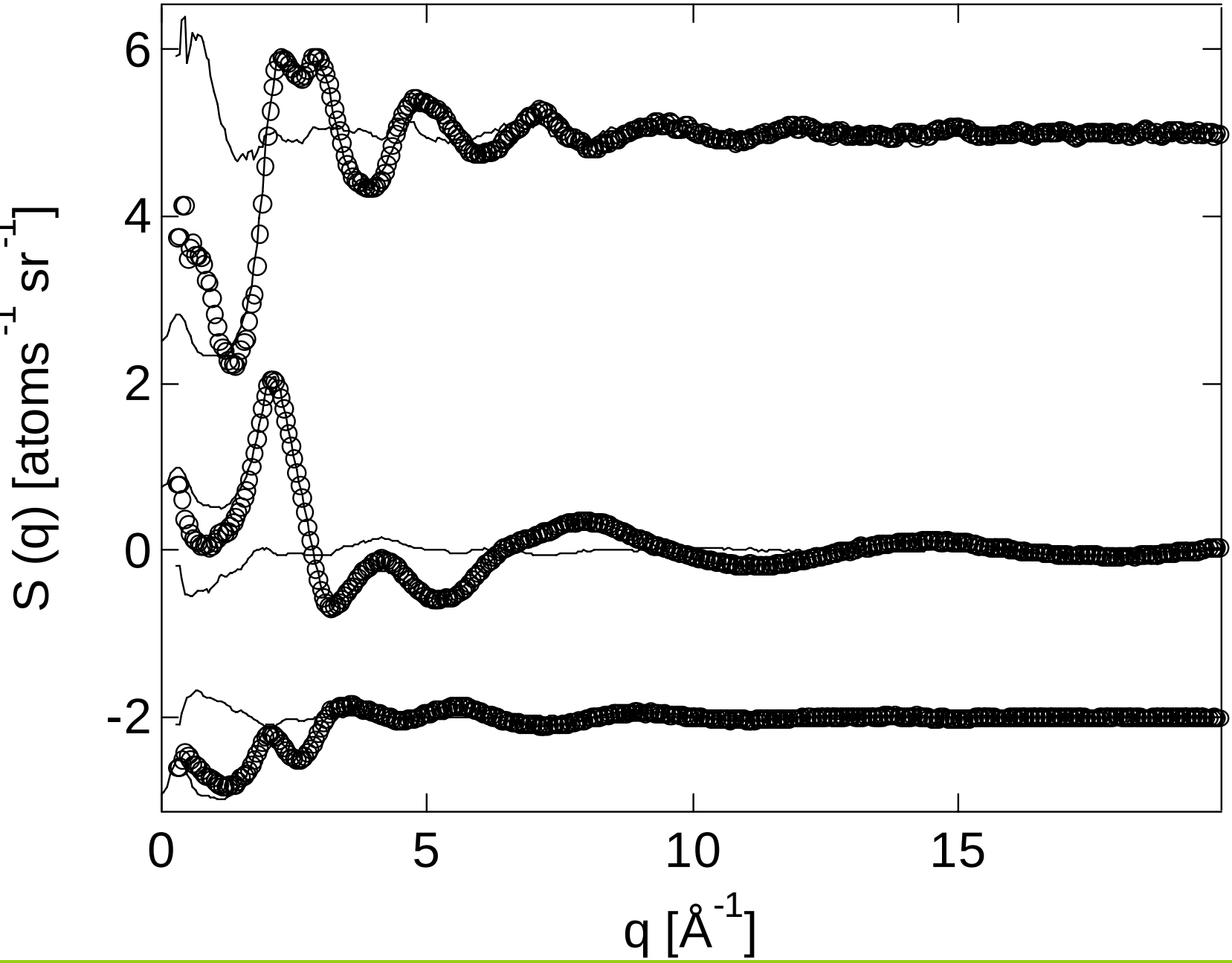
G(r)s averaged over hundreds of configurations

Monte Carlo with molecular roto-translations

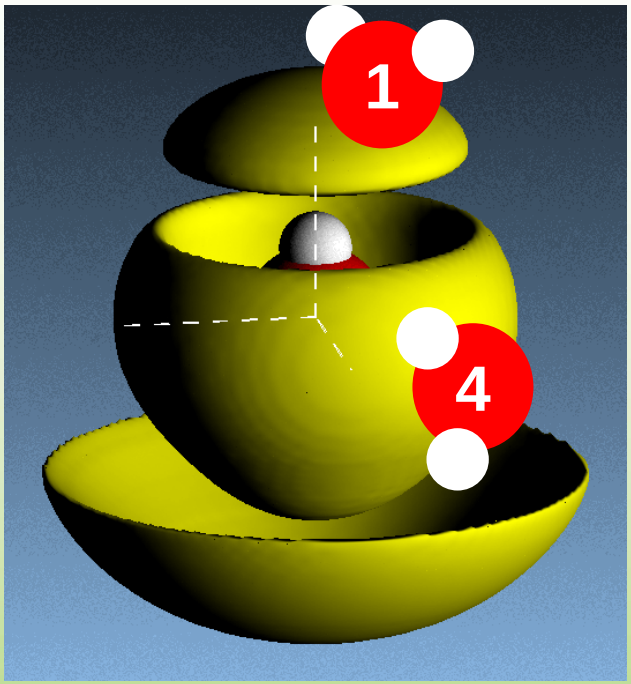
Allows to define an Empirical correction to the reference potential

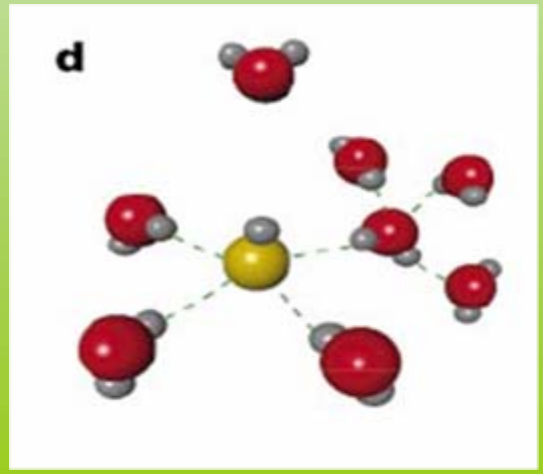
$$U_{new} = U_{ref} + U_{Ep}(r)$$

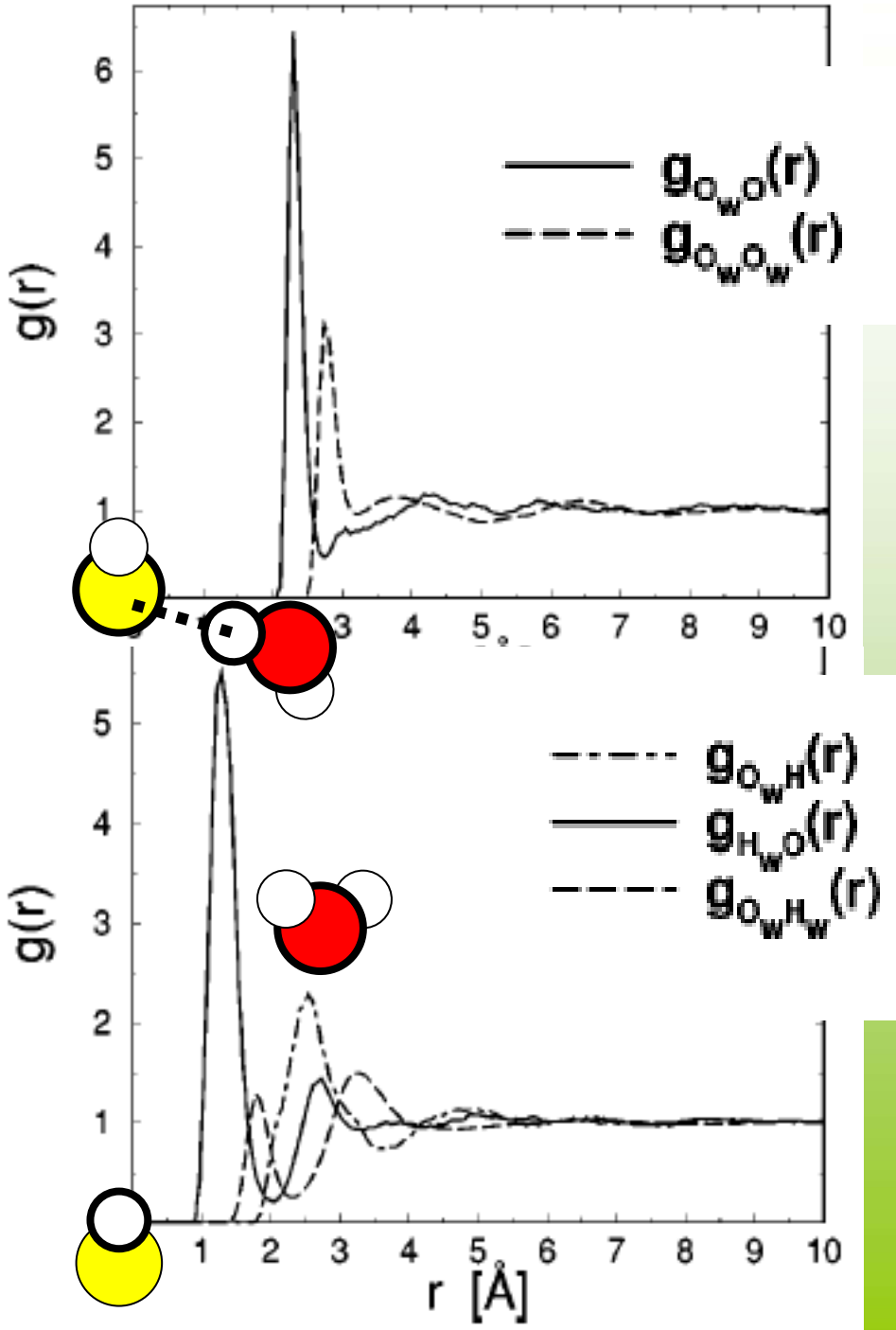

U_ref (r)
U_ep (r)
U^OO (r) [kJ / mol]
r [Å]
U_ep (r)
U^OO (r) [kJ / mol]
r [Å]


6
4
2
0
-2
0
5
10
15
S (q) [atoms-1 sr-1]
q [Å-1]

Hydroxyl ion solvation shell



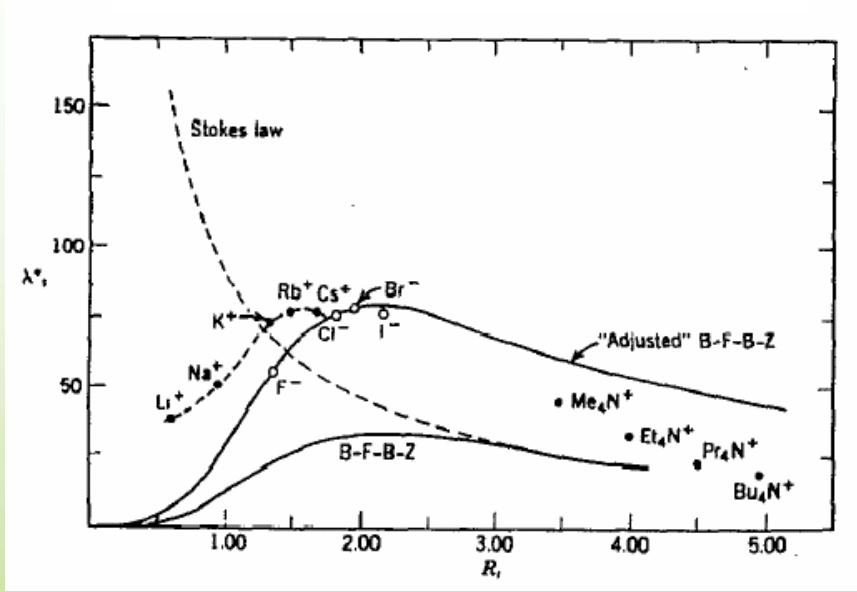




Ionic mobility

	r	Λ_0^m	$-\Delta H_h$
	Å	cm^2/Ω mol	kJ/mol
Li^+	*1.95*	*38.7*	*559*
Na^+	*2.45*	*50.1*	*444*
K^+	*2.80*	*73.5*	*360*

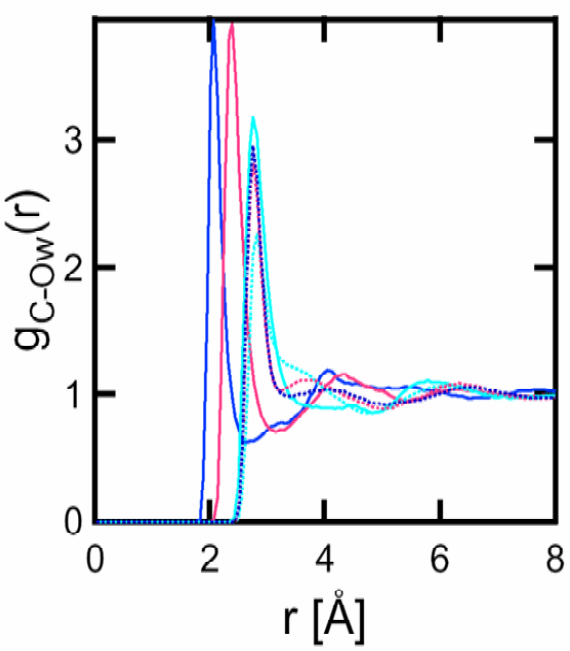
Debye-Huckel-Stokes of a ion in a continuous medium

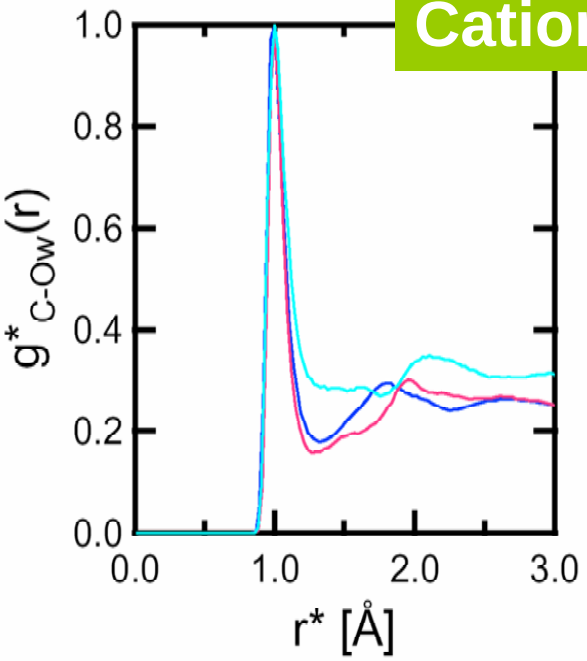


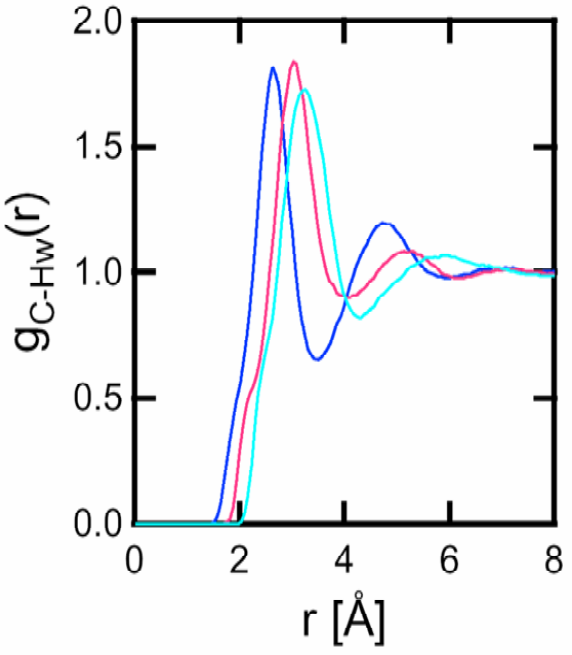
What happens to the solvent?

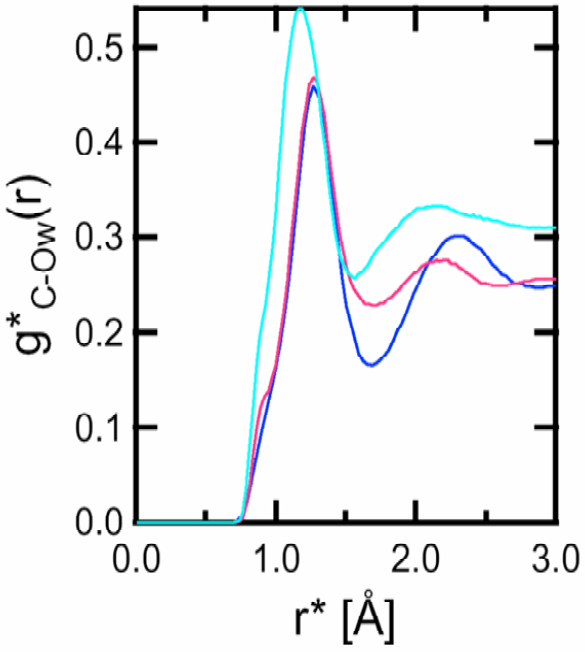
Gurney and Franck model for the ion-solvent interaction

Cations solvation shell

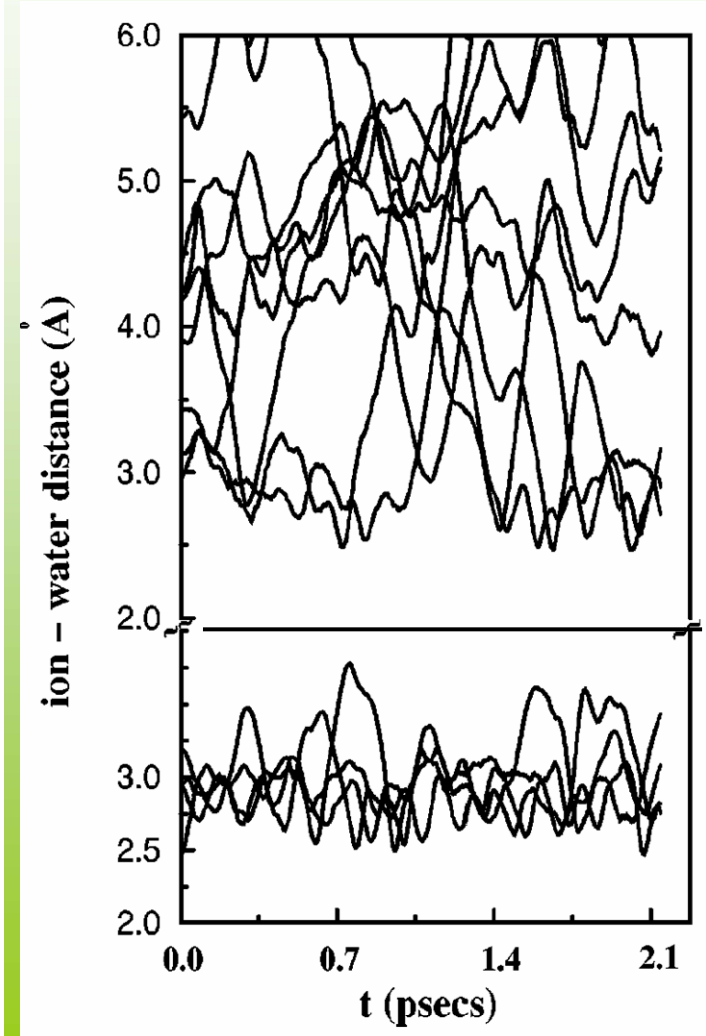




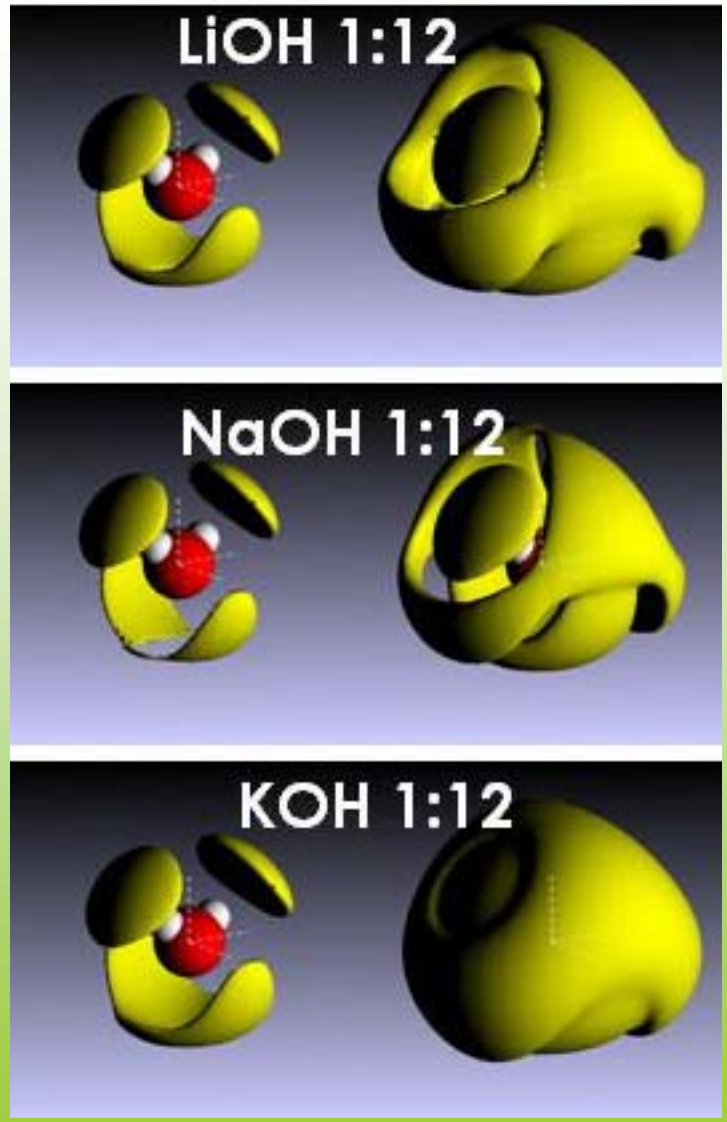




L M Ramaniah, M Bernasconi, M Parrinello, J Chem Phys 111 (1999) 1587

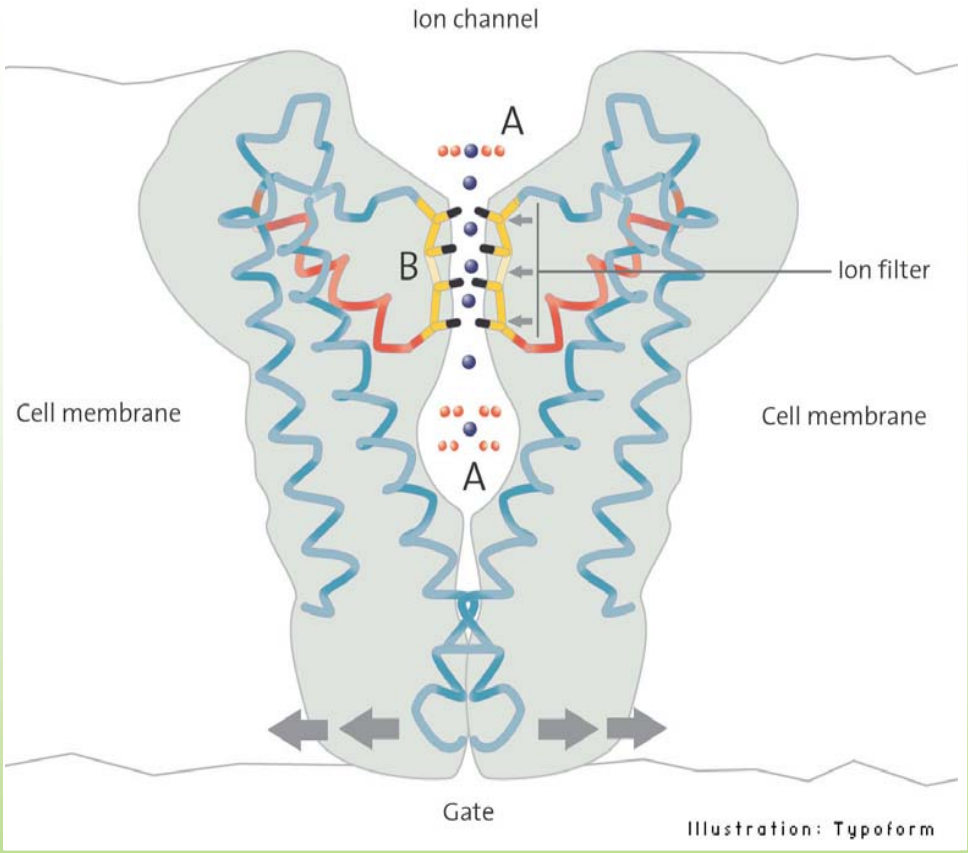


Water –Water correlations



- The same effect can be seen in pure water under external pressure
- Breaking of HBonds
- Lower viscosity

- It's the **combined effect of lower water viscosity and looser bond** with surrounding water molecules which can explain the K+ higher mobility with respect to smaller ions.



Ionic channels through the cell membrane:

K+/Na+ or size selectivity mechanism

It is by looking at the system as whole that we gain an insight in the singular molecular process

Beyond the bulk:

The nano-problem & the liquid scientist:

- Liquids and gases **under confined geometry**
- **Convolution of correlations at different lenghtscales**, from Small to “Wide” angle

Acknowledgments:

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ISIS, RAL, STFC

Alan Soper

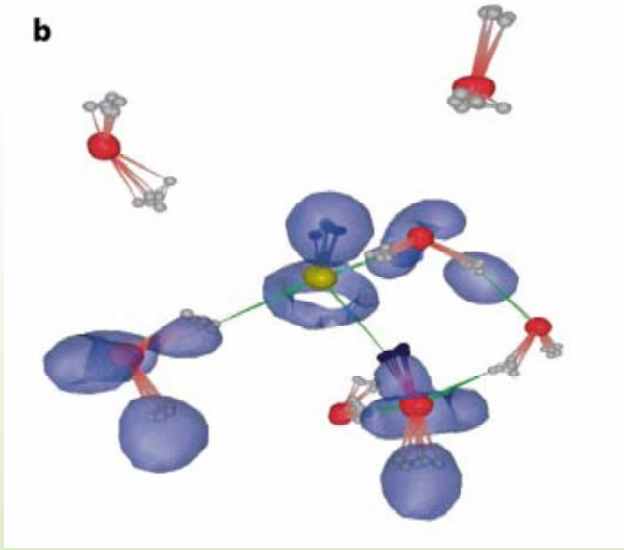
Sylvia McLain

Thanks for your attention!

Hydroxyl ion solvation shell

In full agreement with (newer) ab-initio simulations

in presence of counter-ion and with concentration dependence



D.Marx, M.E.Tuckermann, J.Hutter, M.Parrinello, Nature 397 (1999) 601; D.Marx, M.E.Tuckermann, J.Hutter, M.Parrinello, Nature 417 (2002) 925

B Chen, I Ivanov, J M Park, M Parrinello and M L. Klein *J. Phys. Chem. B* **2002,** *106,* 12006-12016

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