Salty water under pressure:

polyamorphism, crystallization and *l-l* transition

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dépasser les frontières

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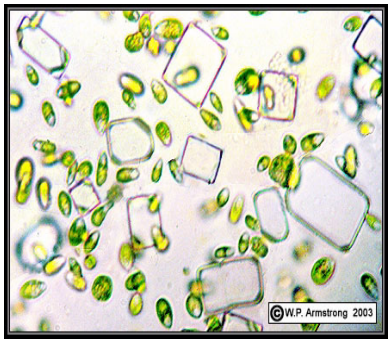
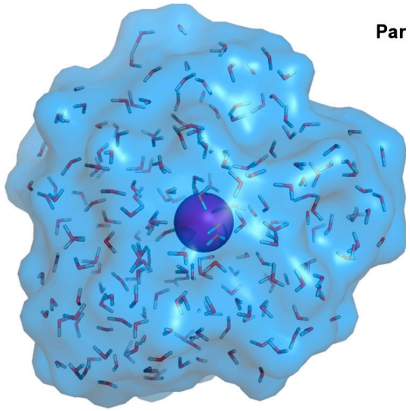
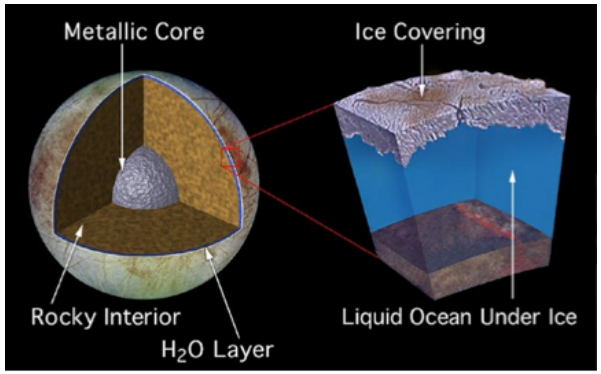
Why salty water?



Most of the chemical reactions occurring in water, including various biological phenomena, are mediated by the presence of ions.



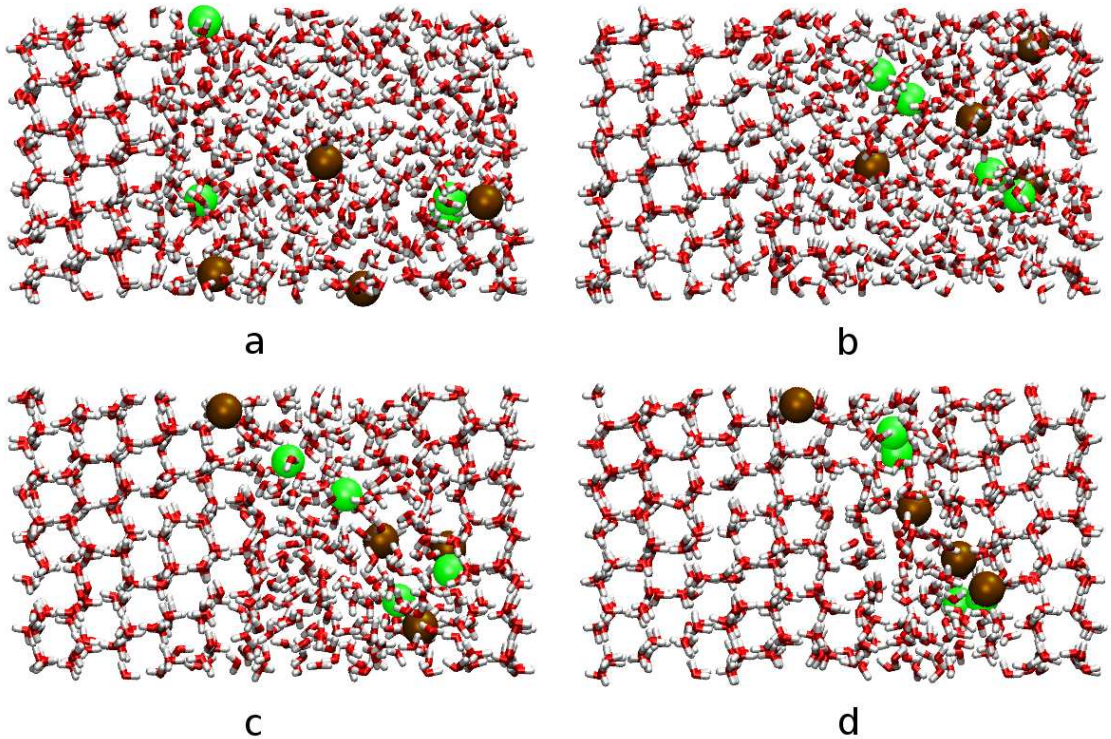
The interaction between water and ions modifies the local structure and promotes disordered phases of water

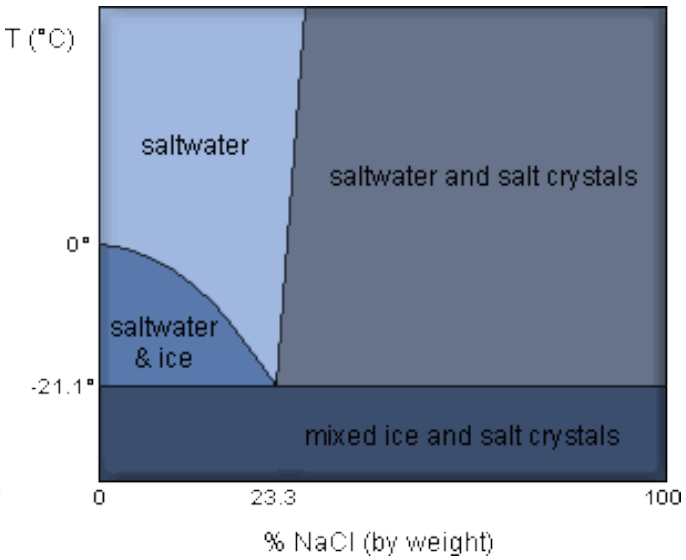


Salty water under pressure could have different properties with respect to pure water: relevant for ice bodies

Why salty ice has never been studied?

The common belief was that freezing, expels the salt ions to form a mixture of pure ice and some salt hydrate….





L. Vrbka, et al. *PRL 95, 148501 (2006)*

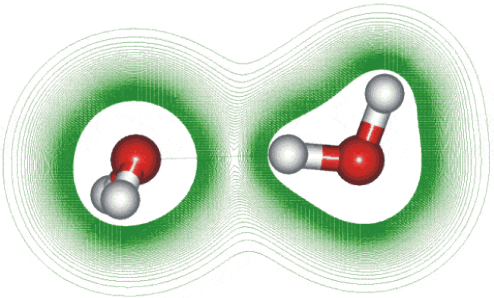
Observation→ salts excluded from the "*open*" structures of ice (Ih, Ic, LDA)

The presence of salts dissolved in water was considered irrelevant for ices

Outline

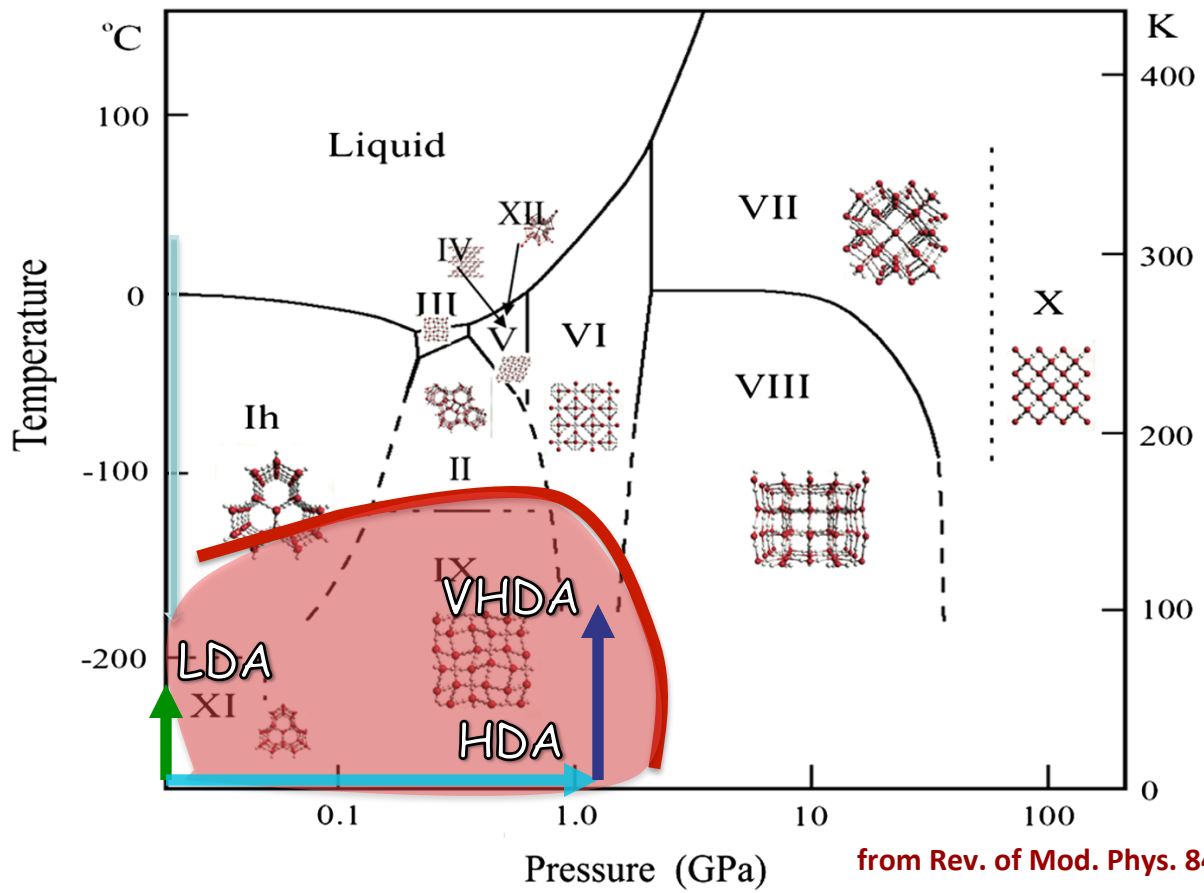
- ❑ Hints on poly-amorphism in ice
- ❑ Observation of poly-amorphism in salty ice
- ❑ The making of salty ice VII under pressure
- ❑ Consequences and prospective

Ice: a very rich phase diagram



Ice has an open structure and H-bonds are very flexible → 16 crystalline phases

Poly-amorphism: 3 phases differing for density and local structure



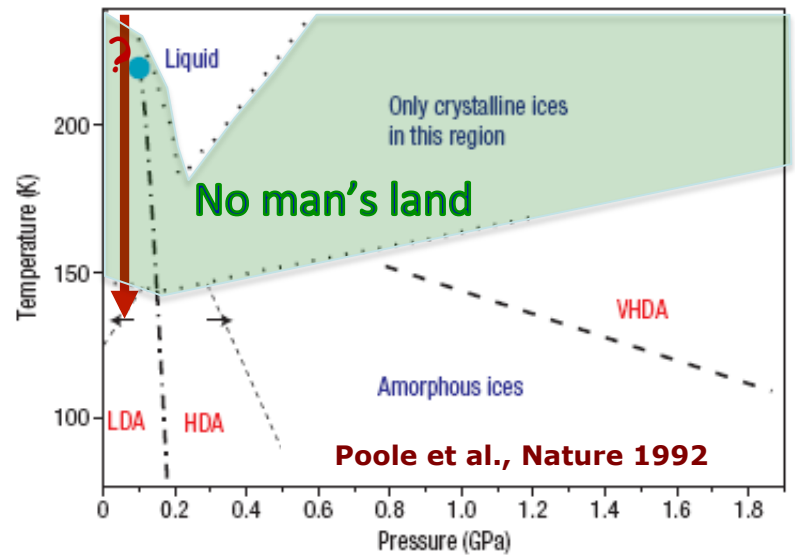
from Rev. of Mod. Phys. 84, 2012

- **HDA**: obtained by low-T compression of ordinary ice, can be recovered at AP
- **LDA**: annealing of HDA at low-P (115 K) or hyperquenching at AP
- **VHDA**: high-P annealing of HDA, can be recovered at AP

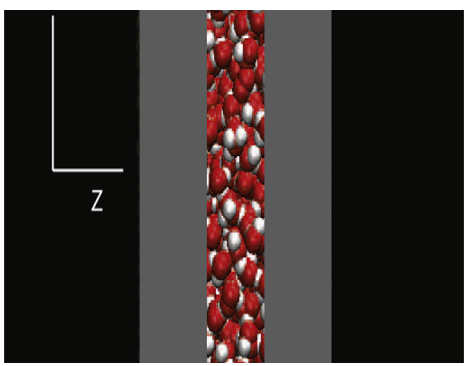
Polyamorphism @ liquid/liquid transition

No man's land→ second critical point?
…not accessible to experiments!!!

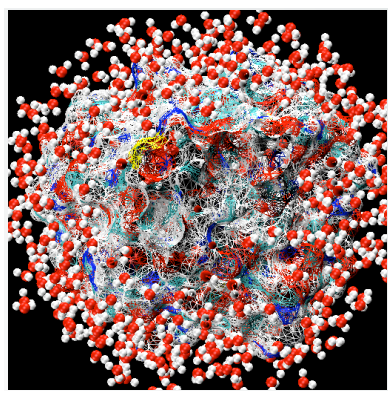
Are LDA and HDA the amorphous proxies of LDL and HDL?



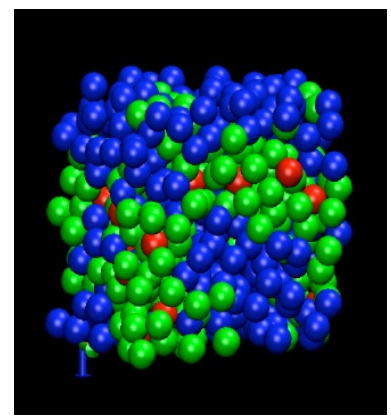
Alternative methods to undercool water
Confinement, Hydration, Solvation



liquid water confined between two surfaces separated by 1.1 nm.

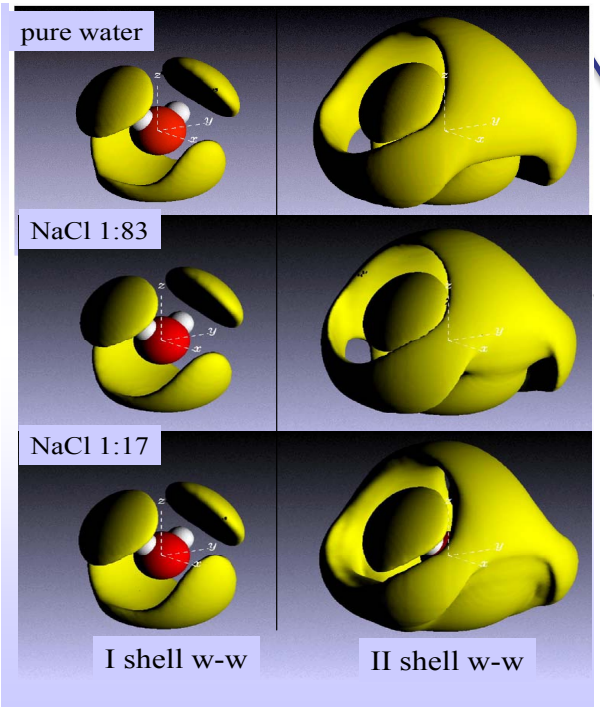


Hydration water of lysozyme

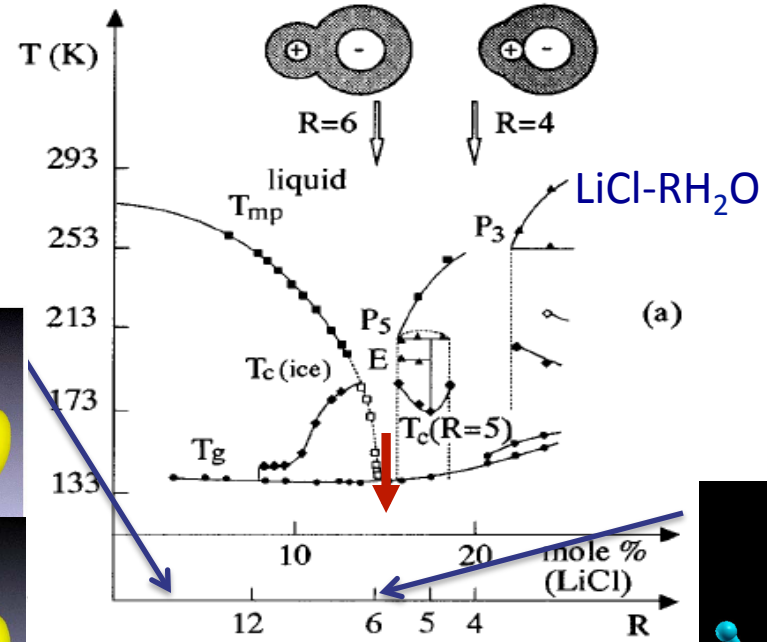


Solvation water around a polar solute

Salty aqueous solutions

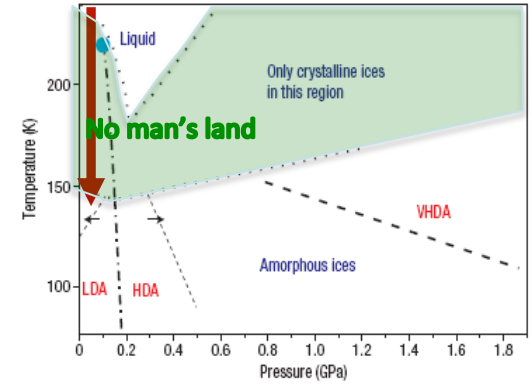


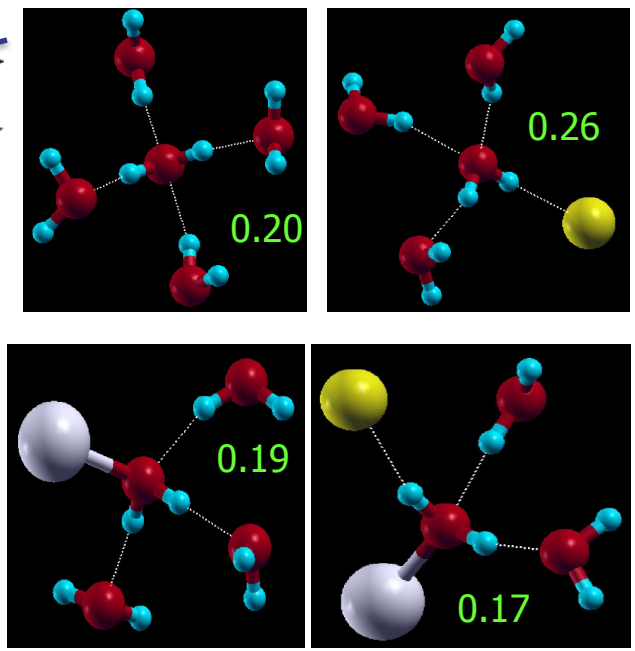
R. Mancinelli et al., PCCP 07 (2007).



LiCl-RH$_2$O

Prevel et al., JCP 103 (1995).





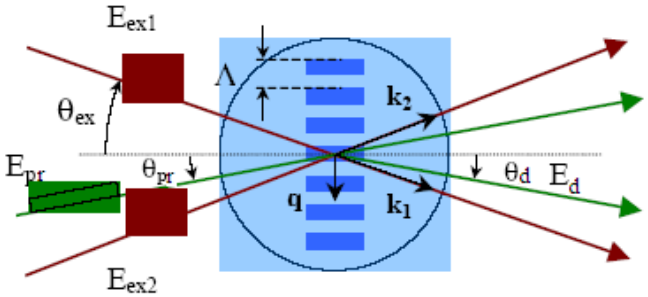
Salty aqueous solutions: a long history!

Double Glass Transitions in Aqueous Lithium Chloride Solutions Vitrified at High Pressures: Evidence for a Liquid–Liquid Immiscibility

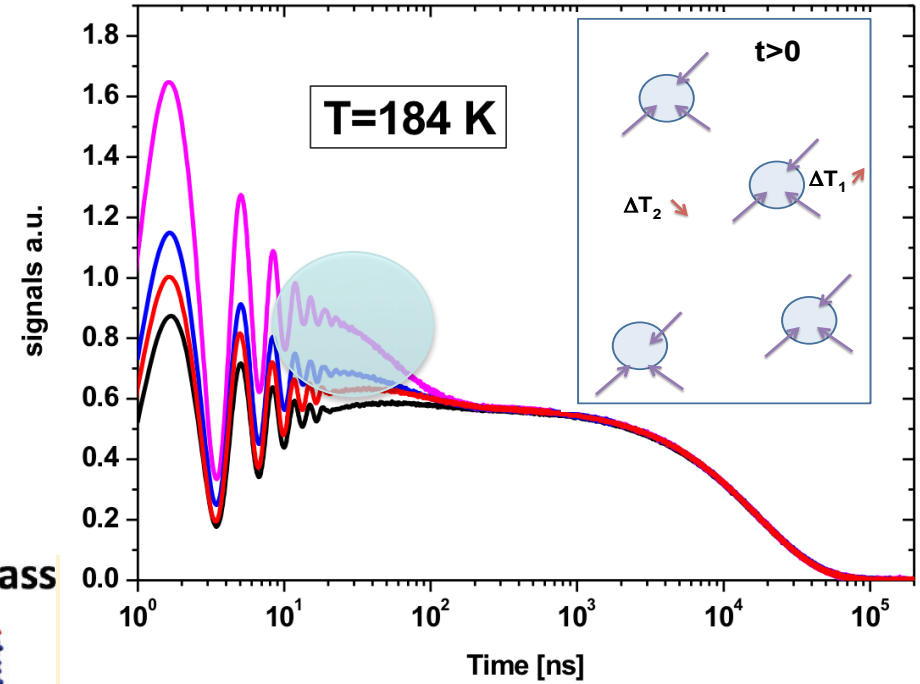
H. Kanno

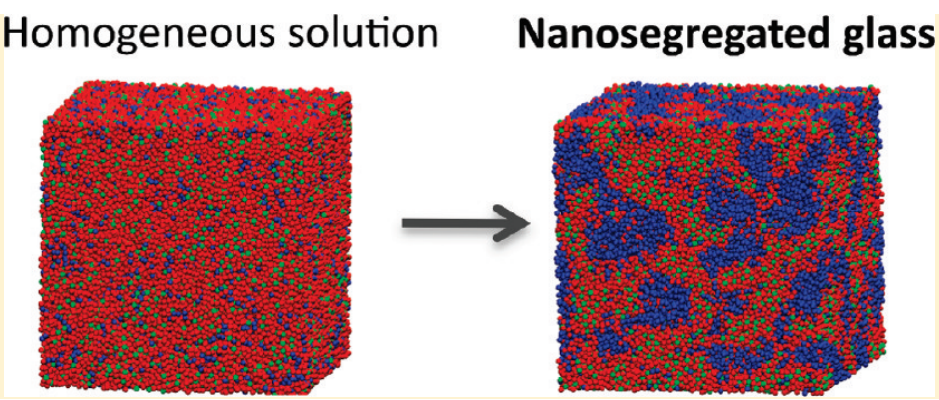
Department of Chemistry, The National Defence Academy, Hashirimizu, Yokosuka, Kanagawa 239, Japan
(Received: September 15, 1986; In Final Form: December 4, 1986)

Transient Grating:



$\Lambda = 10\mu$



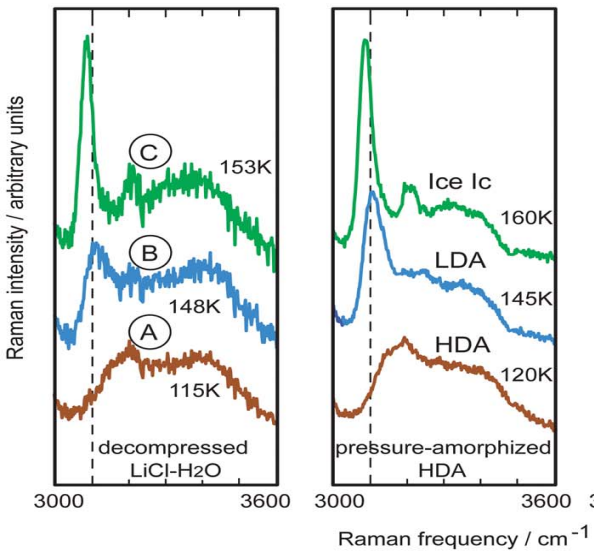


Le and Molinero, JPC A 115 (2011)

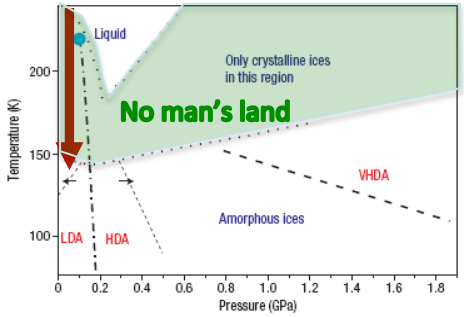
M.E. Gallina, L.E.B, et al. JCP 2009
L.E.B., C. Dreyfus, et al. JCP 2011
L.E.B., C. Dreyfus, et al. JCP subm.

What about polyamorphism?

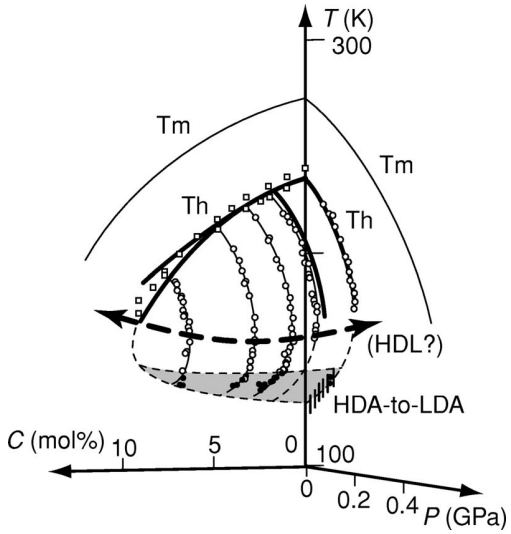
Dilute solutions: emulsions show LDA-HAD poly-amorphism



O. Mishima, J. Chem. Phys 126, (2007)

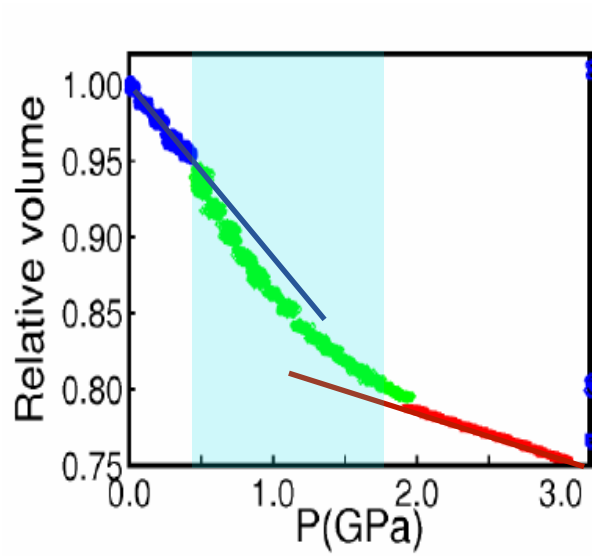


Concentrated solutions: no LDA to HDA poly-amorphism



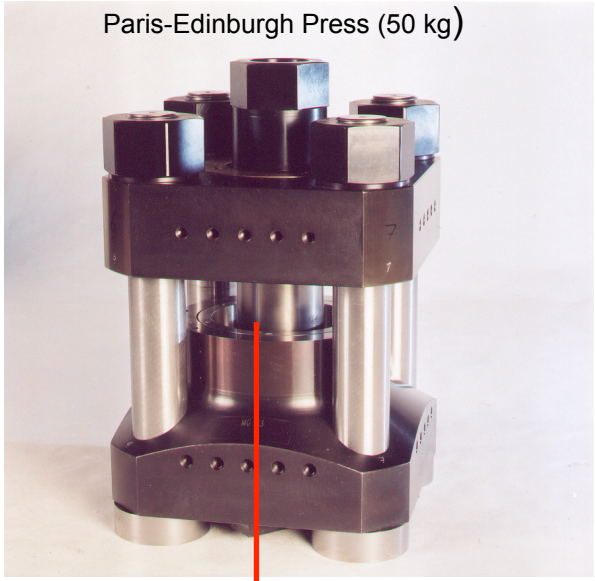
O. Mishima, J. Chem. Phys 128, (2009)

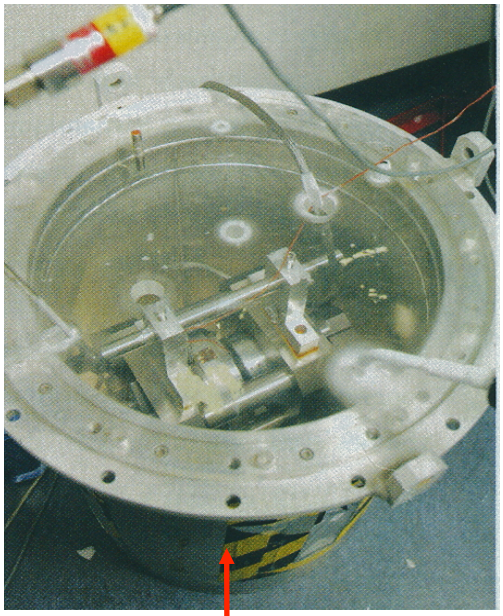
LiCl:6H_2O MD simulations:



A.M. Saitta, et al, unpublished

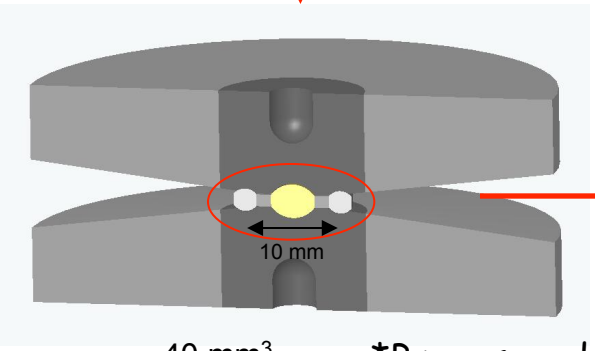
In situ neutron scattering under HP:





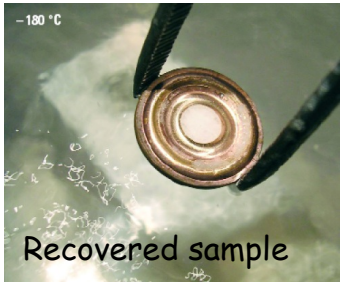
Cool down to liquid nitrogen

Increase load up to 20 GPa

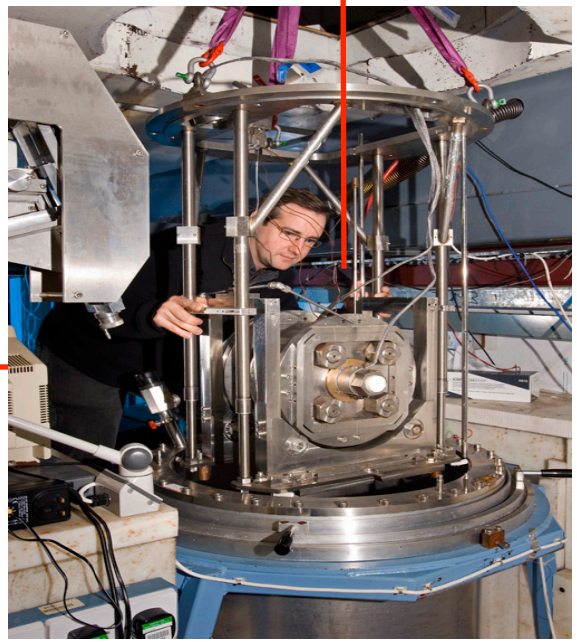


40 mm^3

*P measured by employing a calibrant (Pb)

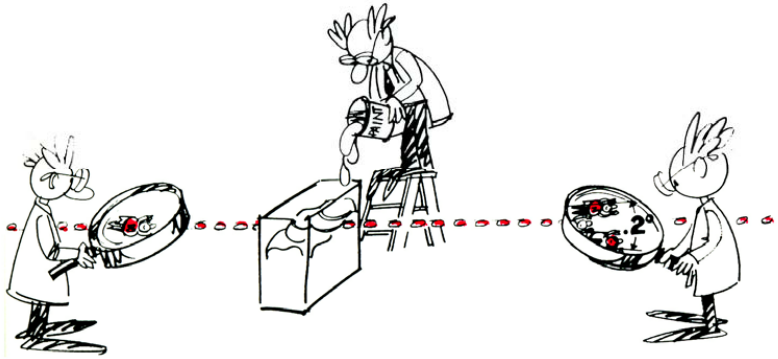


Pearl-Isis



Neutron Diffraction under HP:

Wide Q range

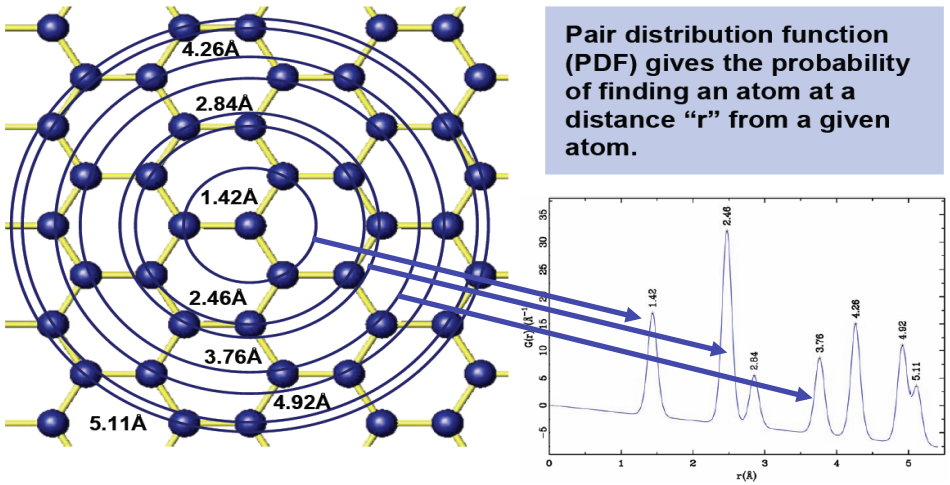


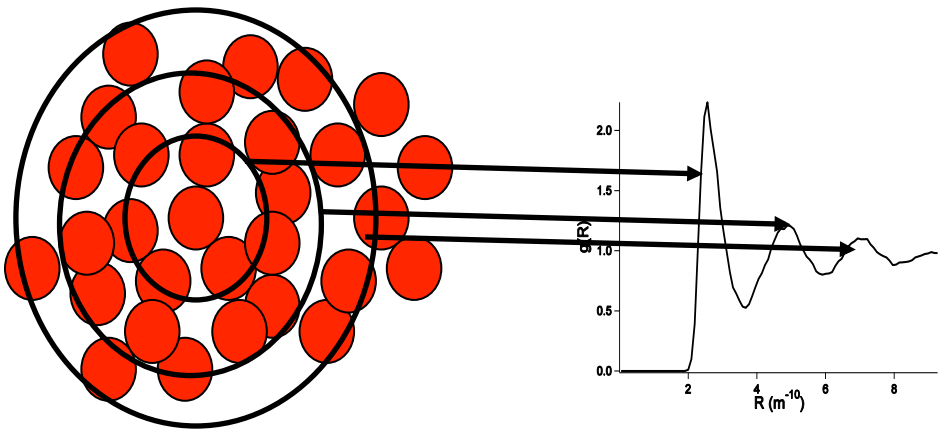
small Q range available

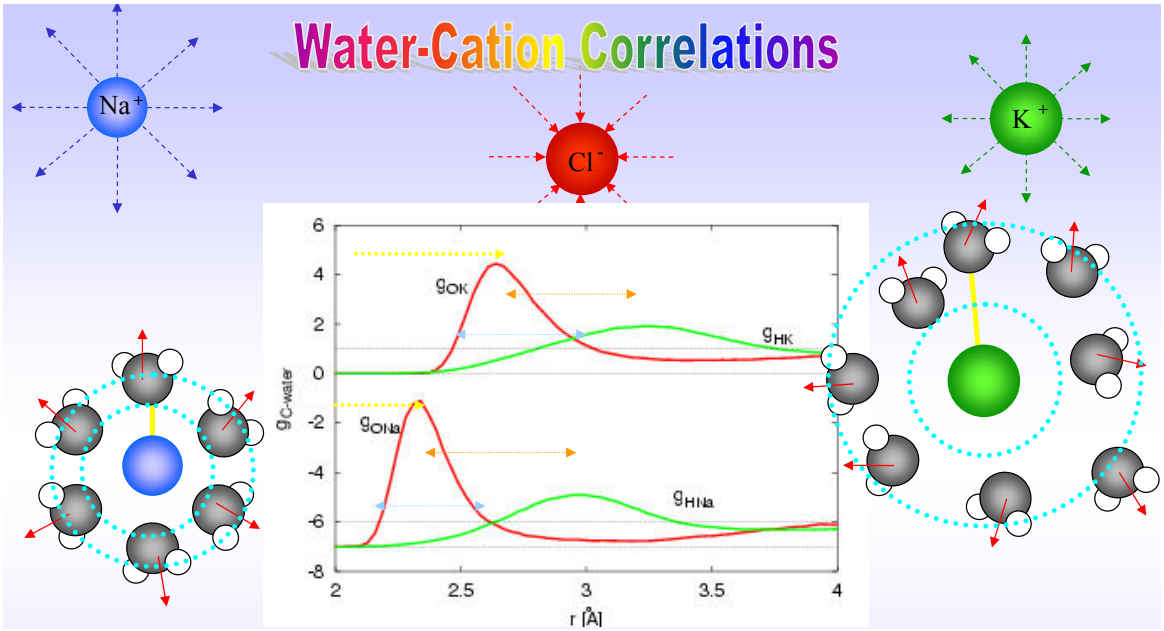
What is a PDF?

Crystal –long range order

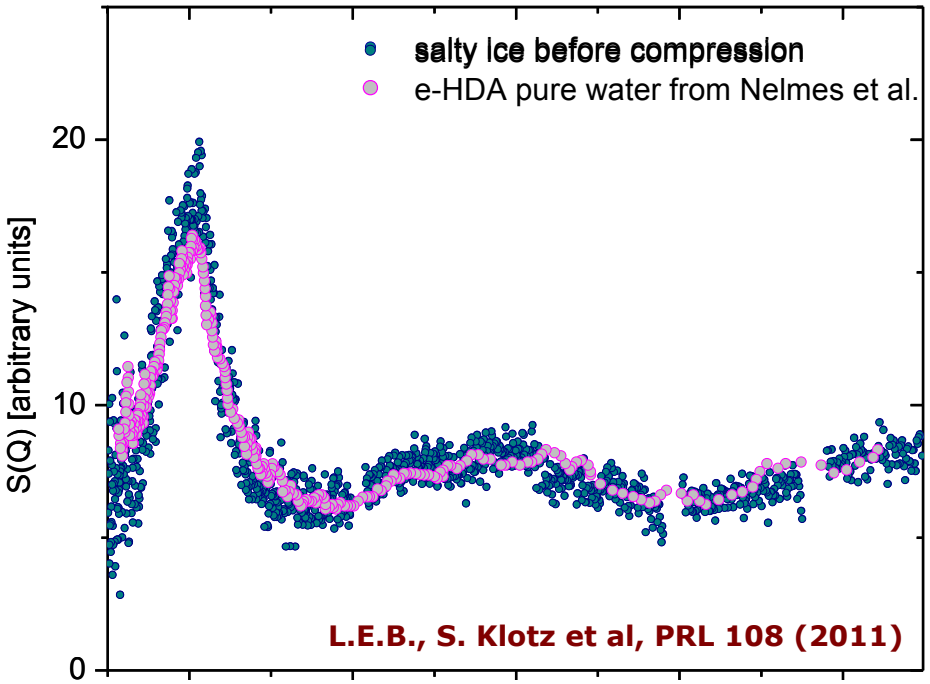
Amorphe –short range order

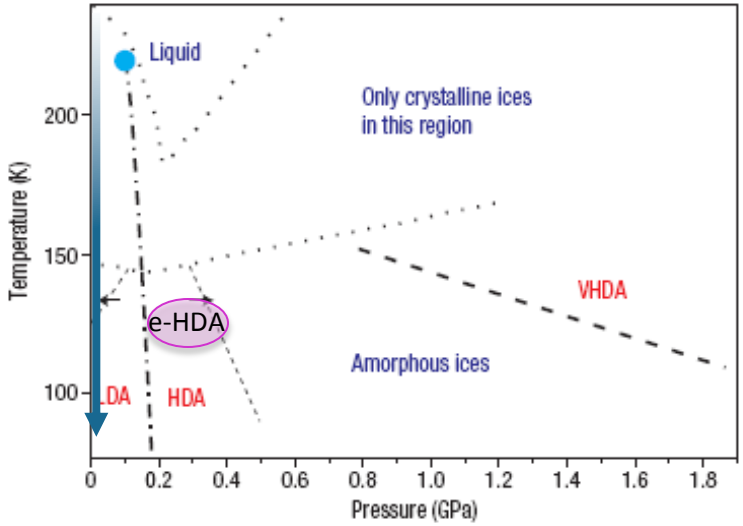


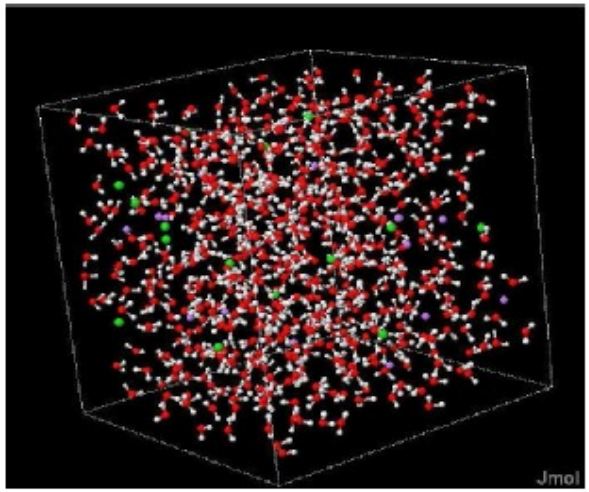


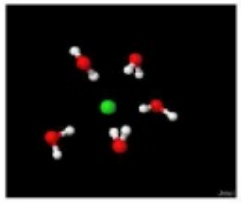


Comparing the salty-glass at HP @ HDA in water









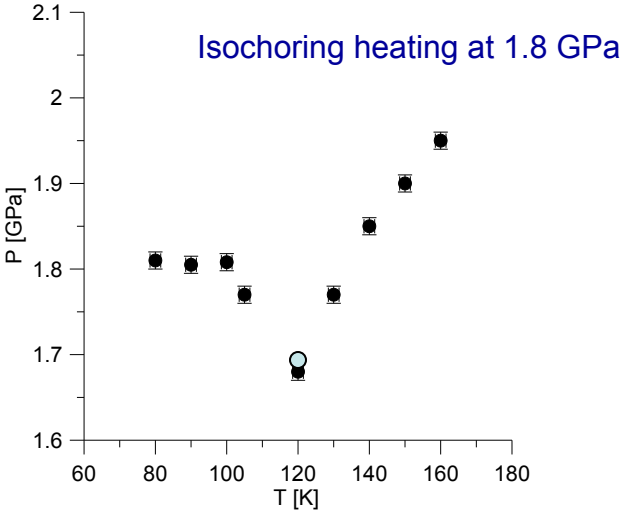
Cooling the salty solution at AP we obtain a relaxed-HDA

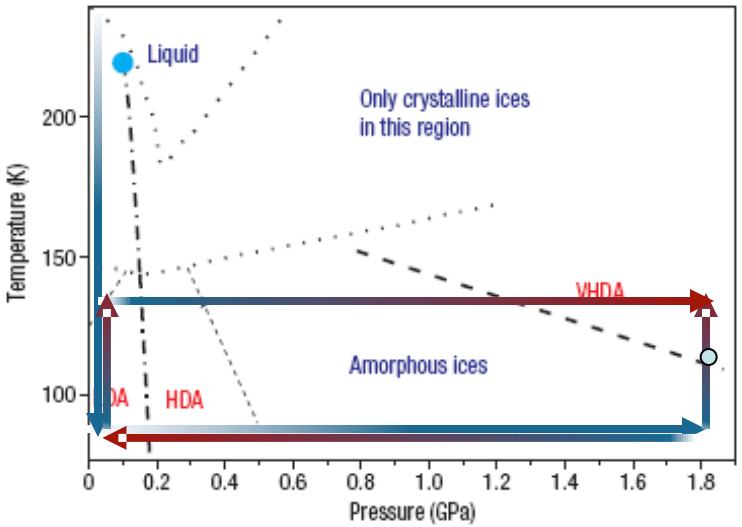
.....how does it work?!!

electrostrictive effect of ions→ equivalent internal pression

Leberman and Soper, Nature 378 1995

HDA-VHDA polyamorphism: annealing under HP



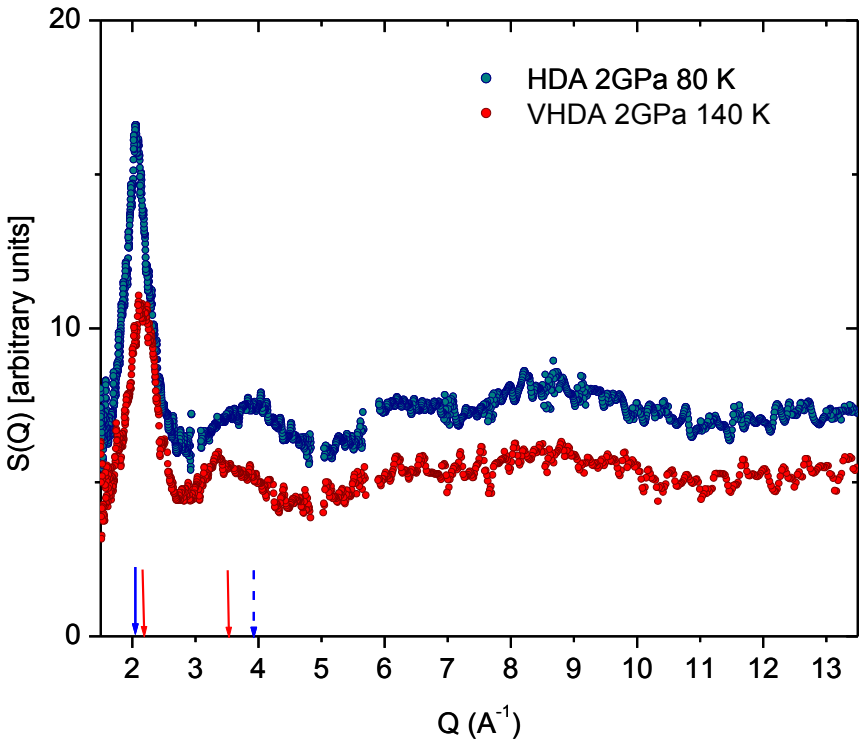


Abrupt change (occurring at at 120K at 1.8 GPa) in the P-T diagram during isochoric annealing under pressure

Density change!

Structural change!

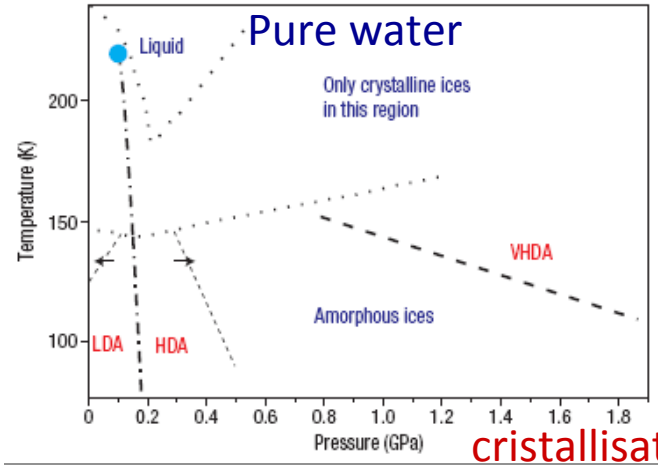
Reversible!



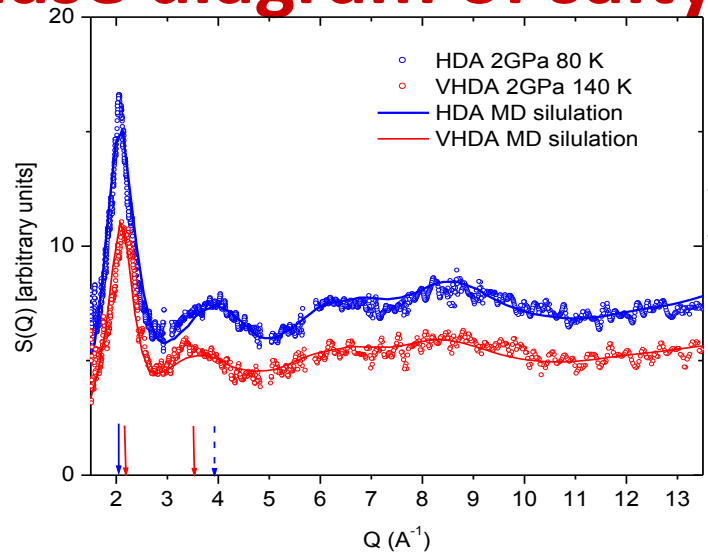
s-HDA@s-VHDA

L.E.B., S. Klotz et al, PRL 108 (2011)

The metastable phase diagram of salty water

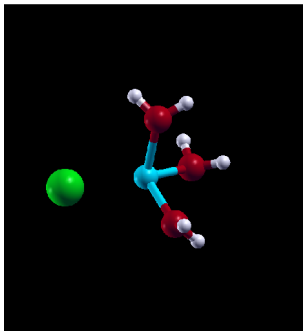


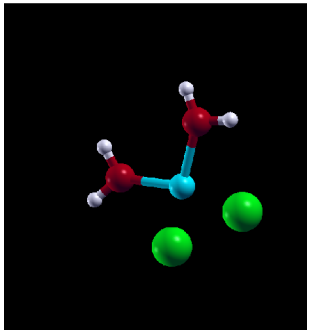
cristallisation

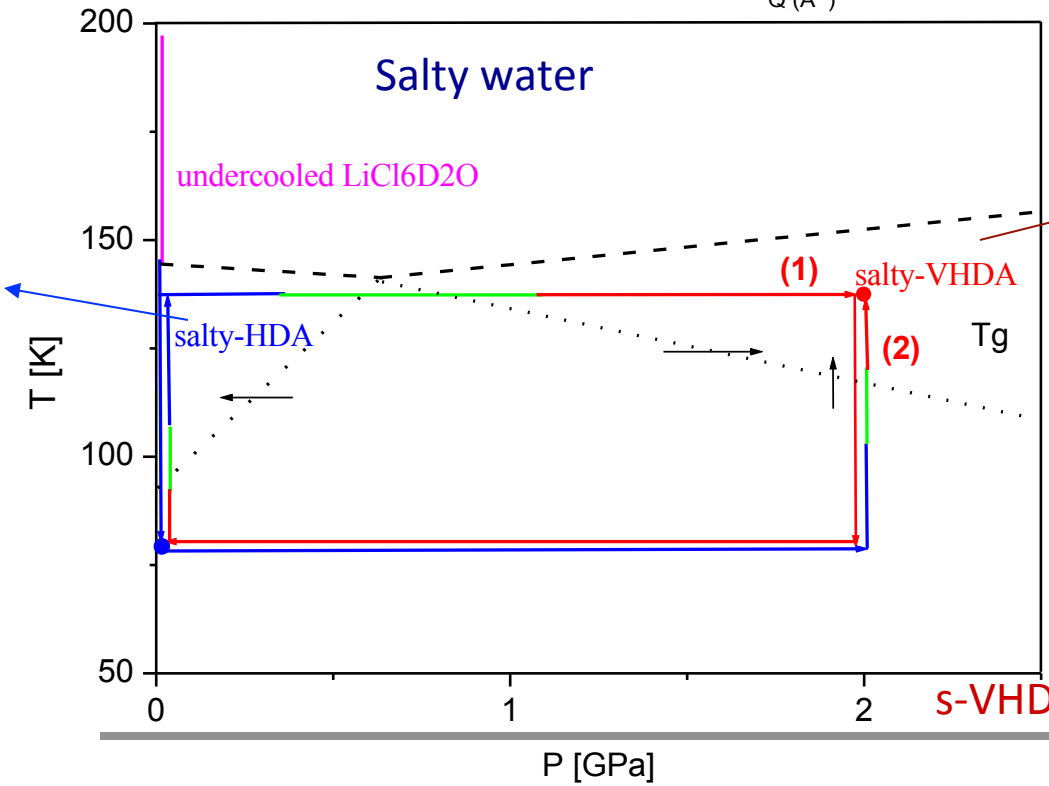


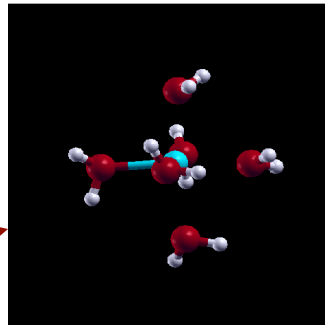
Large MD simulations

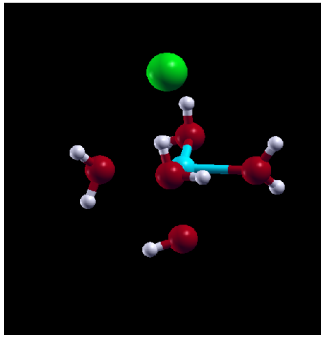
3456 water TIP4P 2005
576 LiCl polarizable pot.





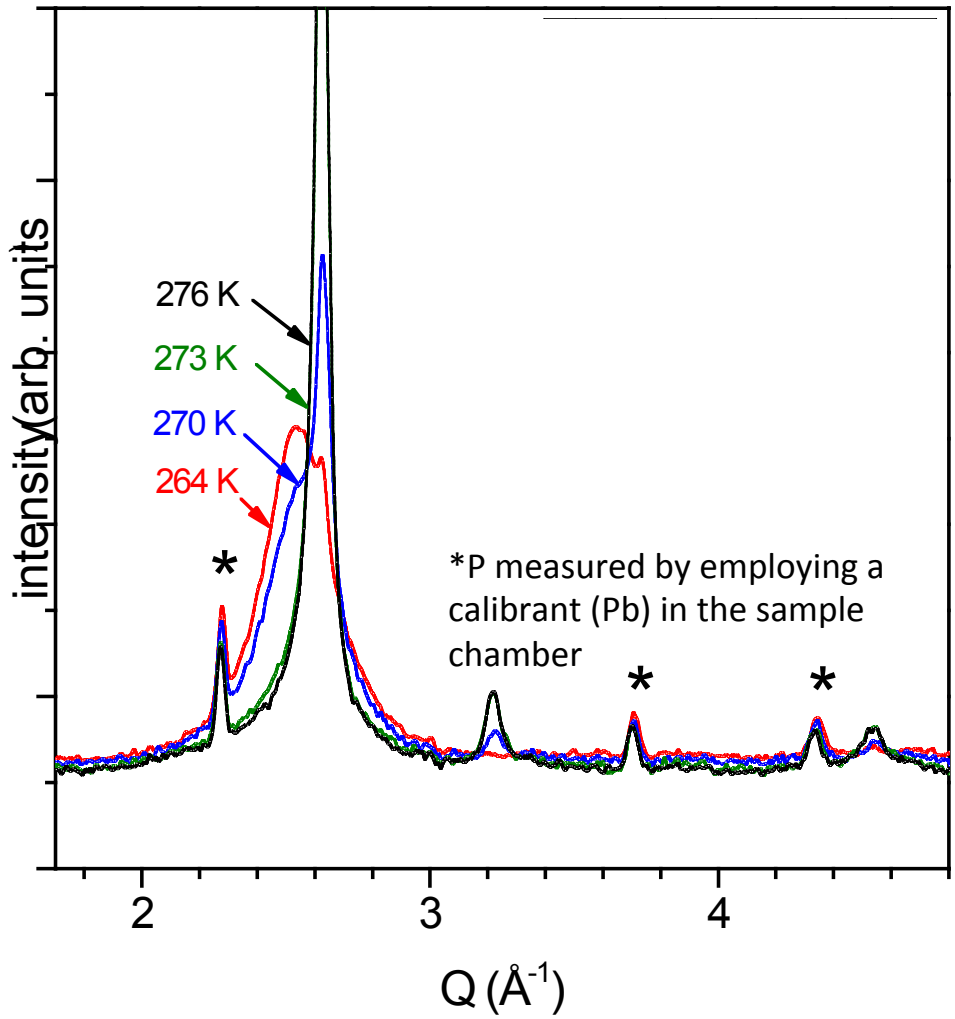


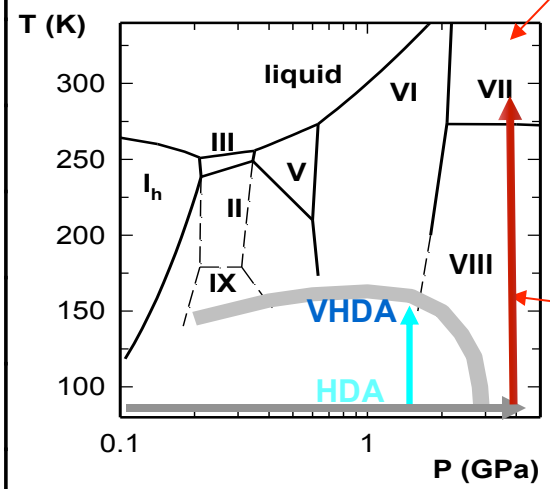


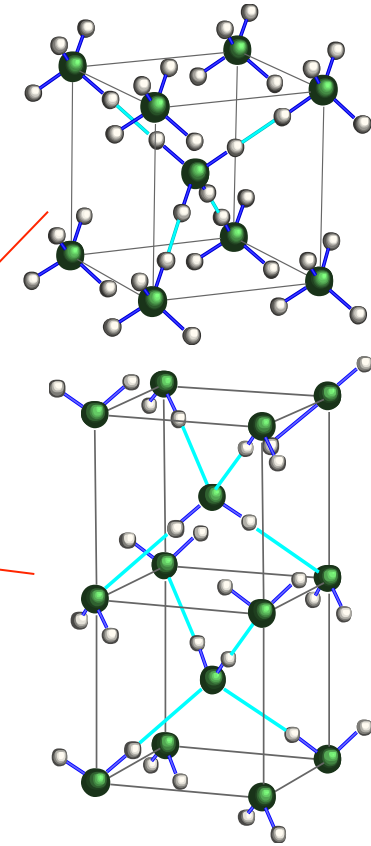


s-VHDA stable at HP!

Annealing salty-VHDA up to RT at 4 GPa







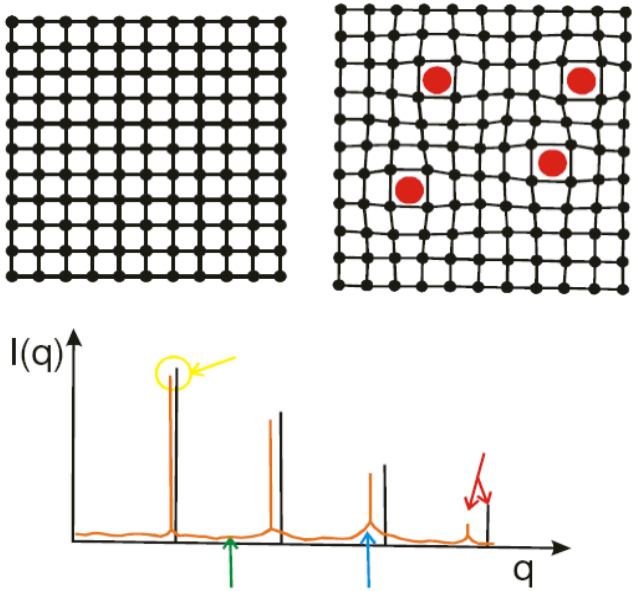
Amorphous-Crystal transformation during annealing under pressure

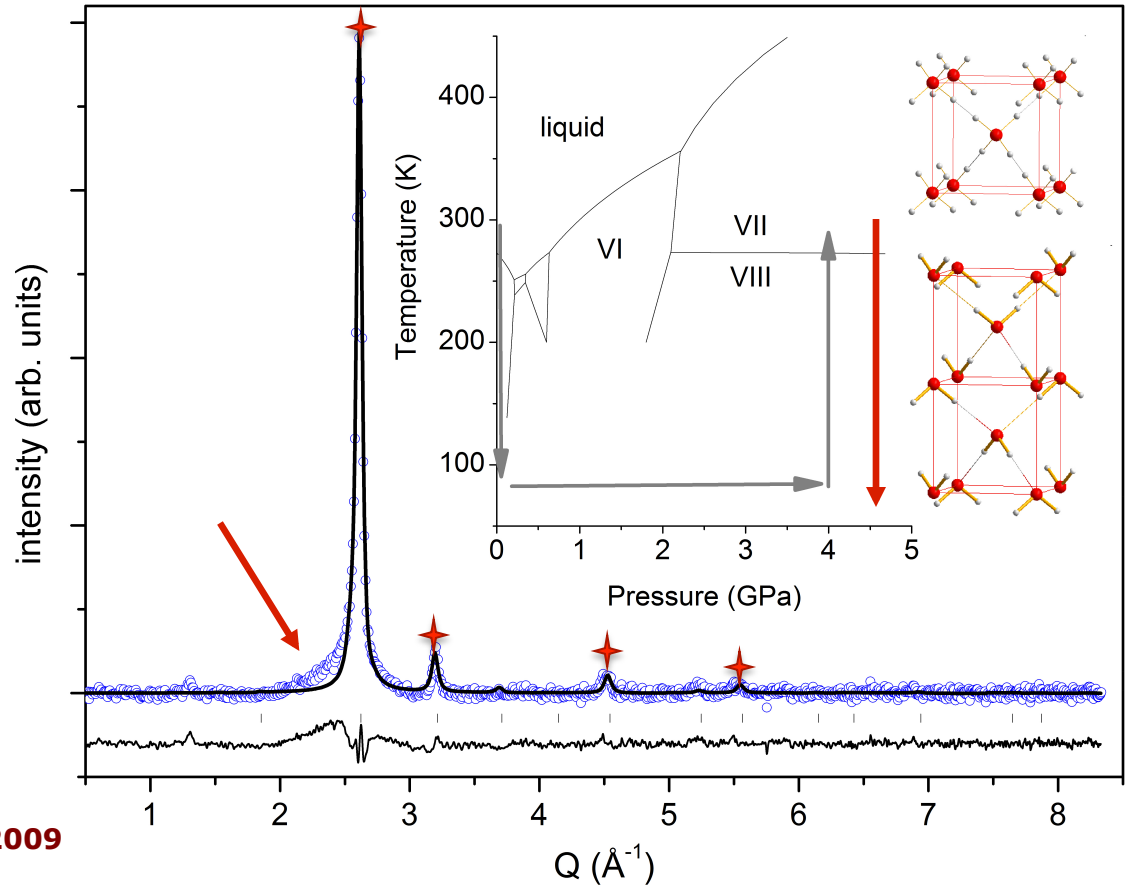
Abrupt pressure variation during crystallization

A new phase crystallizes at 273K!

S. Klotz, L.E.B. et al, Nature Materials (2009)

The making of salty ice VII under pressure





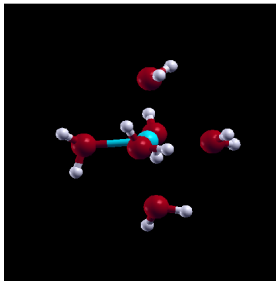
S. Klotz, L.E.B. et al., Nature Materials 2009

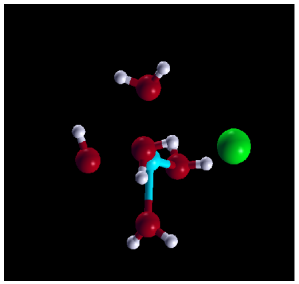
- Diffraction pattern: fitted with ice VII structure with 2.8% larger lattice parameter
- Presence of `tails' at the strongest (110) reflection: Huang scattering
- Large Debye Waller factor: large positional disorder
- No transition to H-ordered ice VIII on cooling

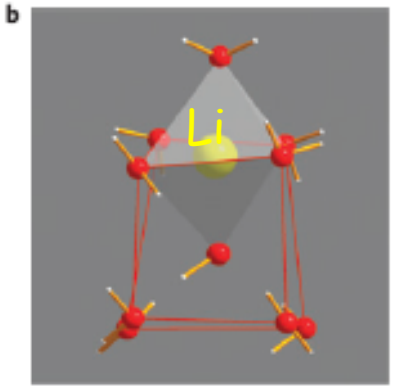
Salt included in ice lattice!

How Li and Cl are included in ice structure?

- Li is in an octahedral coordination in s-VHDA and in all known hydrates

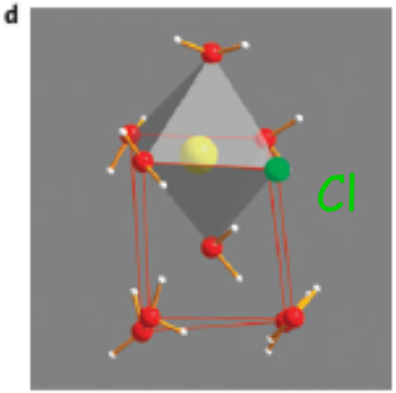






- Centre of the unit cell face→ can be occupied by Li

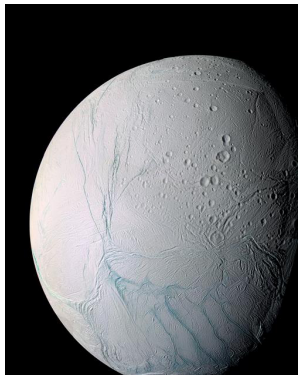
- Cl ion has the same molar volume as H_2O → Substitution of O by Cl on bcc lattice sites



Incorporation of Li and Cl in the ice VII structure
→ local distortions of ~0.35 Å (exp 0.34 Å)

Volume expansion 8%!

Water orientational disorder

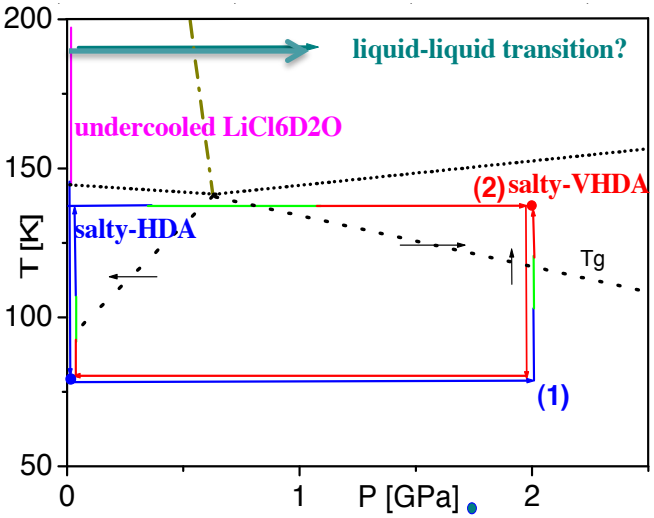


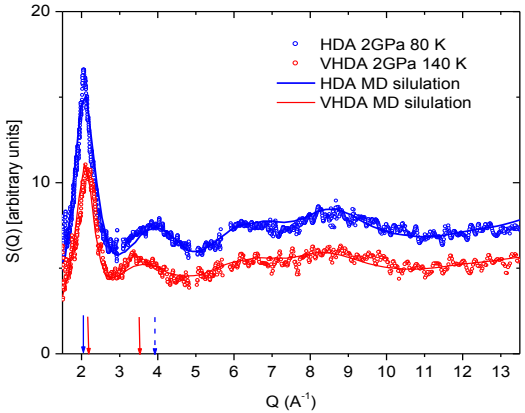
Tested by ab-initio simulations!

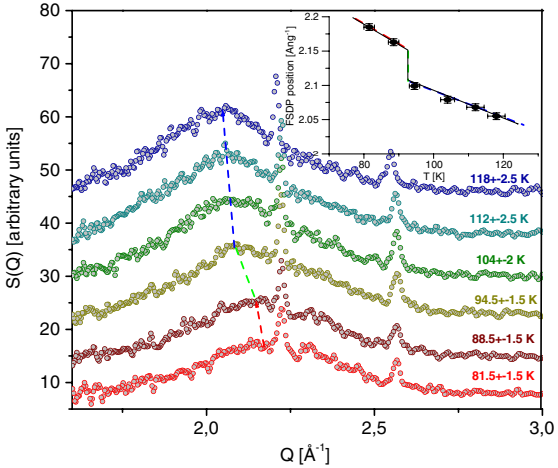
Conclusions and on-going work

- **Existence of polyamorphism in salty ice**

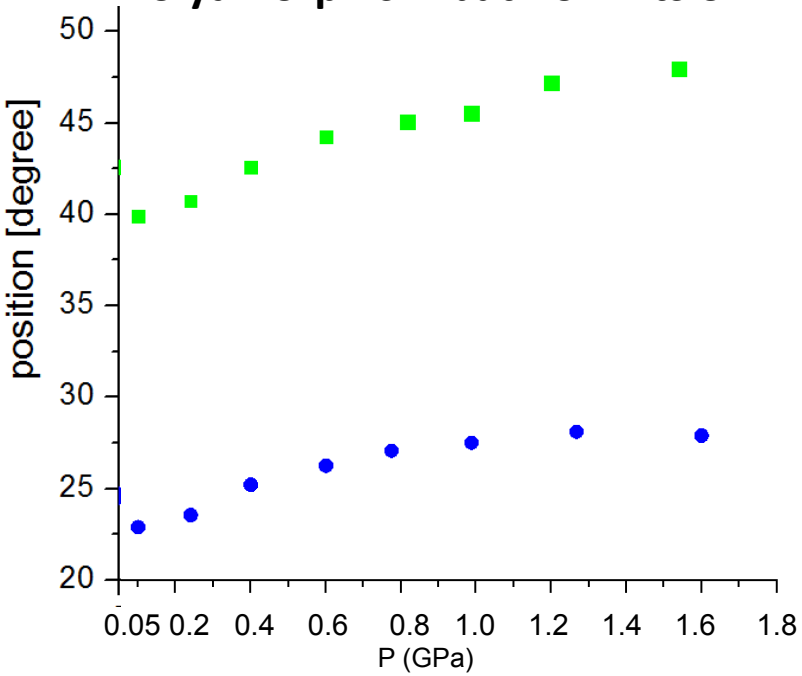
ℓ-ℓ transition in salty water?







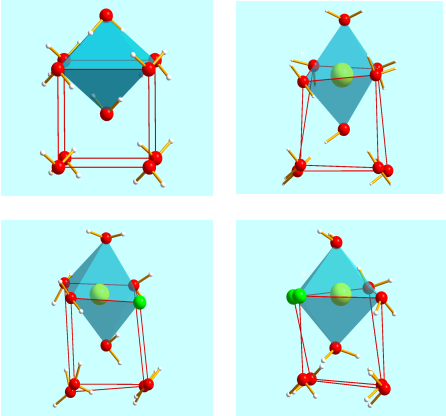
Polyamorphism but no hints of ℓ-ℓ transition!



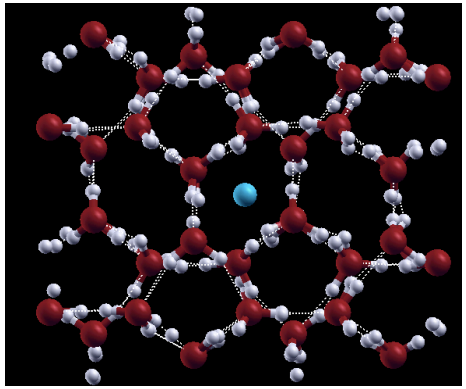
ILL, March 2013

Conclusions and on-going work

- **Existence of salty ice VII (salt incorporation in ice!) under P**

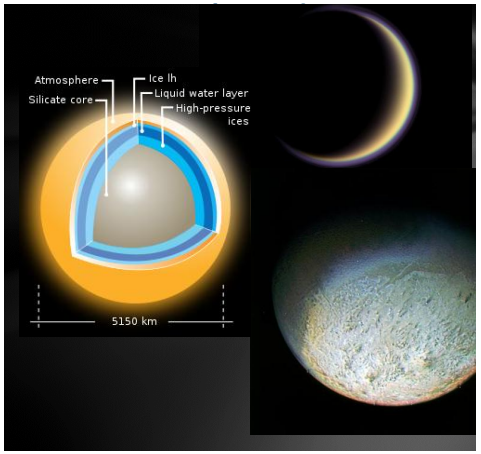


Existence of other LiCl-HP ice phases?



Ice VI

Existence of salty ices relevant for planet interiors: NaCl, KCl…



Long term Perspectives:

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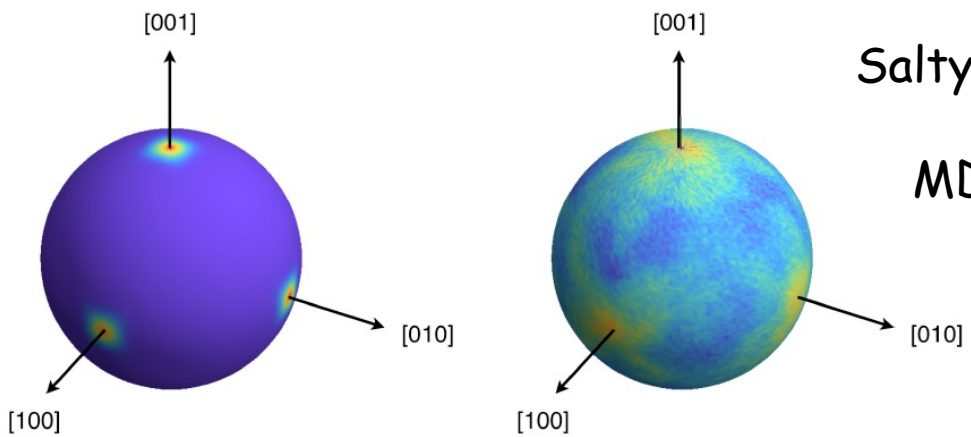
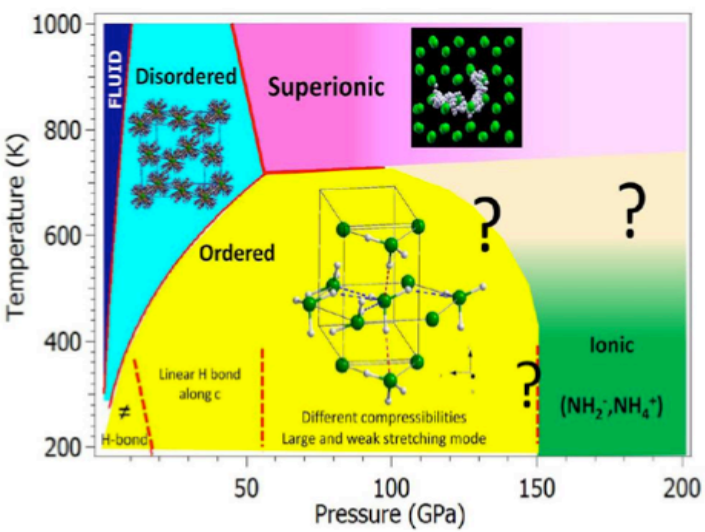
- **Characterize new dynamic properties in salty ices: plasticity, superionicity……**

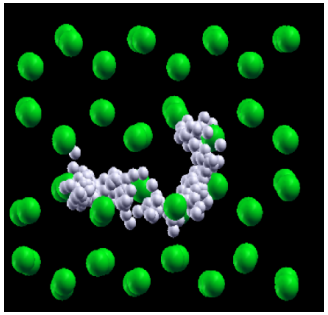


Salty ice VII 4 GPa 300K

MD: plastic at 400 K!

probe Hydrogen dynamics under HP-HT!

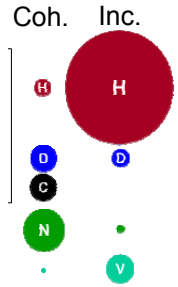




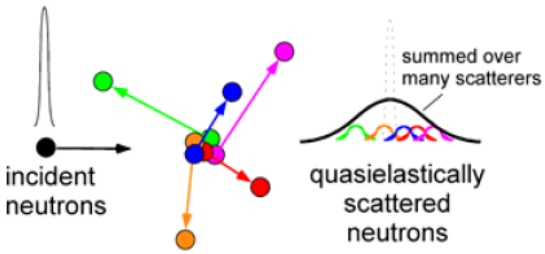
MD: Salty ice VII could become superionic at 800 K, 10 GPa

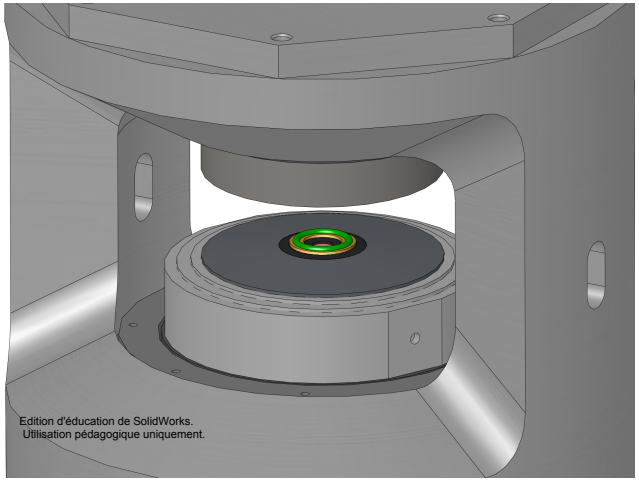
Long term Perspectives:

NEUTRONS FOR SCIENCE



QENS under HP: H dynamics





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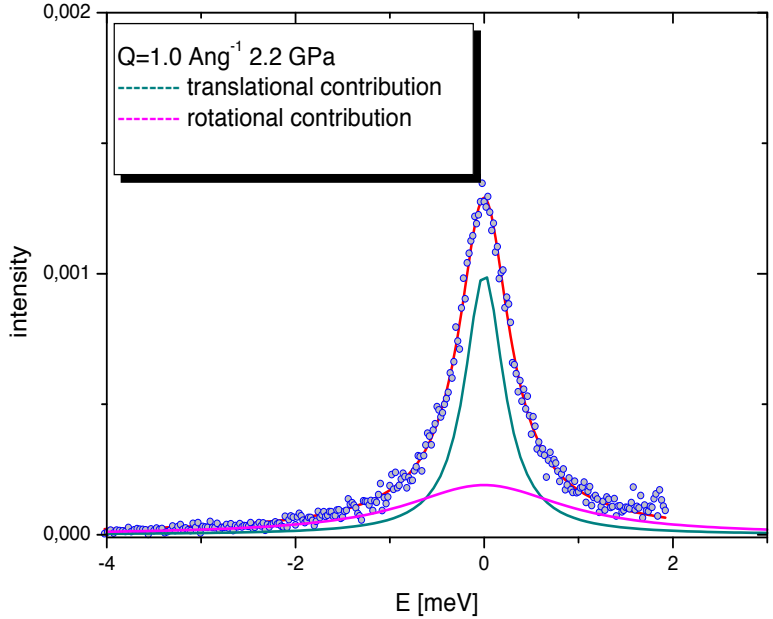
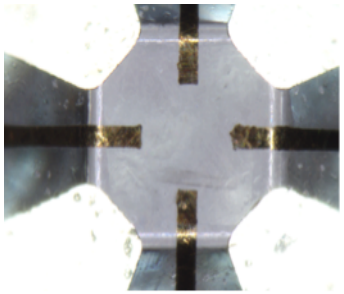
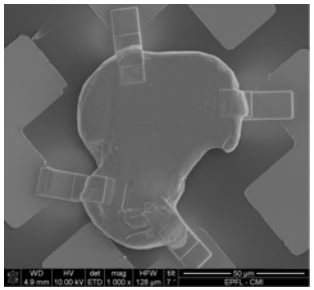
ANR JCJC HP-QENS 0135: HP-QENS up to 5 GPa, 600 K



HP-conductivity measurements: H^+ conductivity





FNS project 25123

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ANR 2009 JCJC 0135

LTP 57686

THANKS!

Some publications on the topic:

S. Klotz, L.E.B., et al. Nature Materials 8, 405 (2009)

L.E.B., S. Klotz, et al., Phys. Rev. Lett 106, 125701 (2011)

L.E.B. et al., Phys. Rev. Lett 101, 125701 (2009)

M. E. Gallina et al., J. Chem. Phys. 131, 124504 (2009)

K. Winkler et al., J. Chem. Phys. 134, 024515 (2011)

L.E.B. et al., J. Chem. Phys. 134, 034514 (2011)

L.E.B. et al., J. Chem. Phys., under review (2013)