Characterization of Amorphous Ice Structures

via the Microscopic Structure and Dynamics and via the Kinetics of the Transformation Processes

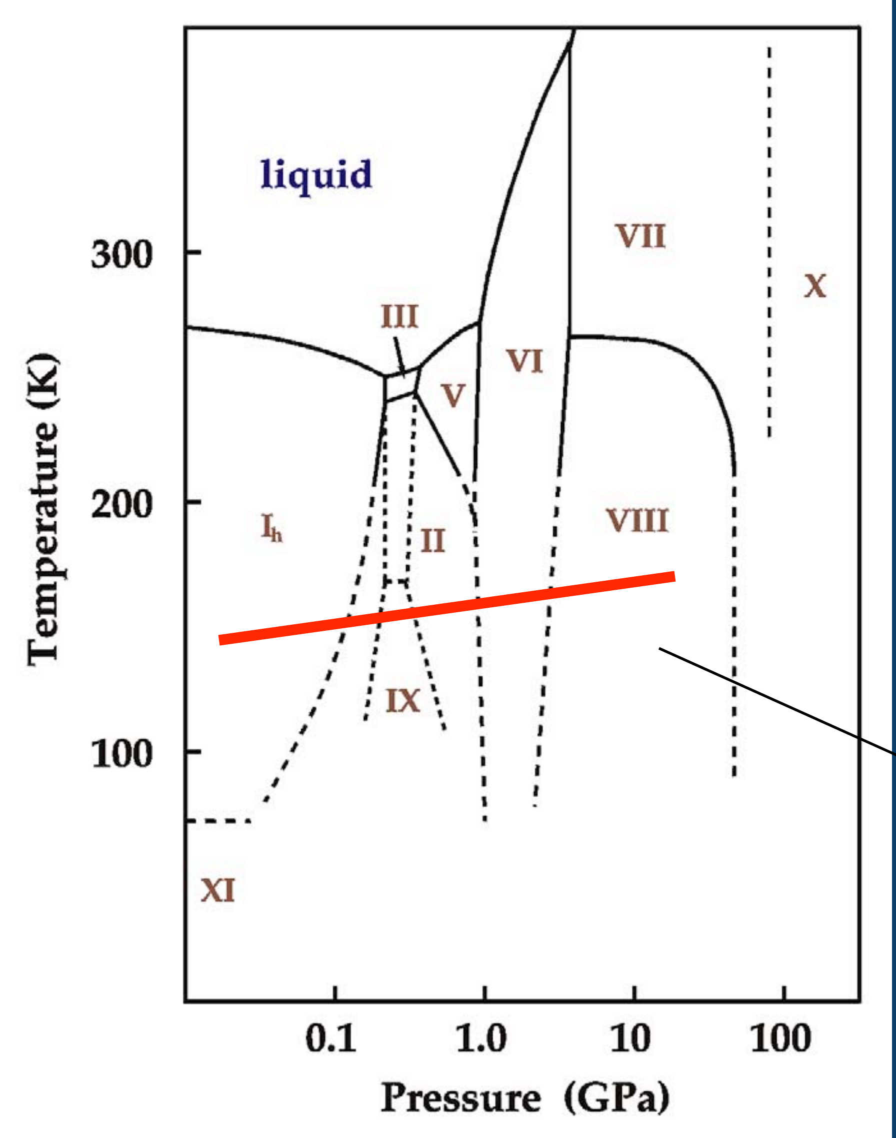
Helmut Schober
Michael Marek Koza

Institut Laue Langevin, Grenoble, France

Thomas Hansen
Roland May

Objective:
Shed some light on the mysterious world of amorphous water

The complex world of solid water

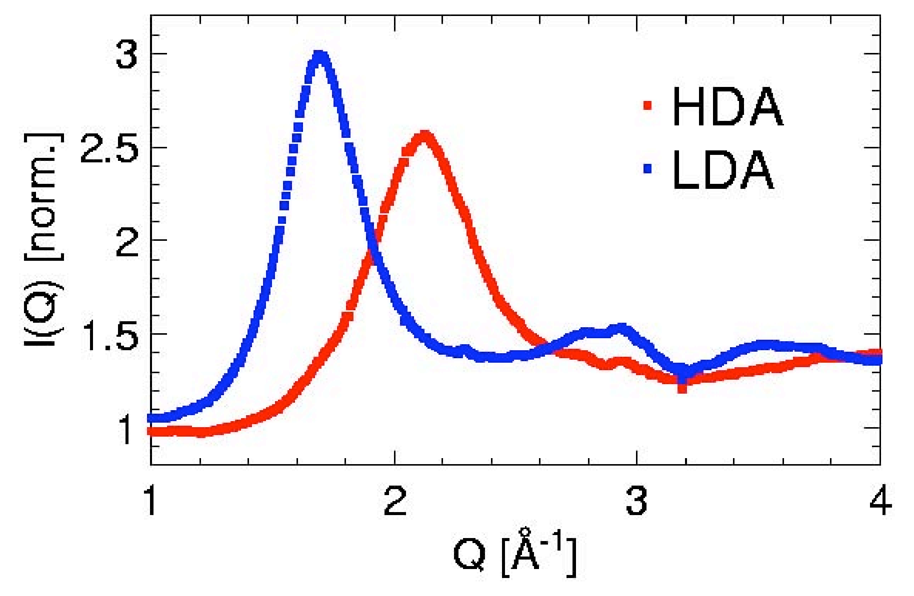


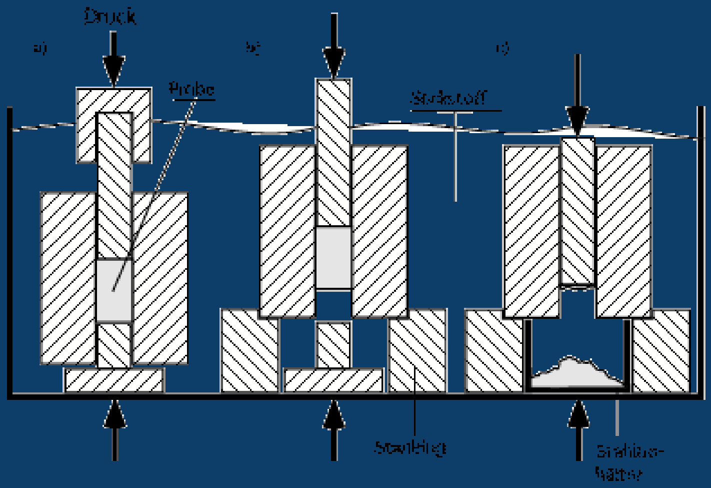
Room for many structural arrangements in a rather narrow (T,P)-range

Polymorphism of amorphous structures

Historically LDA and HDA are the main amorphous players

O. Mishima, L.D. Calvert, and E. Whalley, Nature 310, 393, (1984)





D20 / ILL

Koza et al. JPCM 15, 321, (2003)

High Density Amorphous structure - 39 molec./nm^3

Low Density Amorphous structure - 31 molec./nm^3

The riddle

Nature of amorphous ice phases

How many are there?
What distinguishes them?
How do they transform into each other?

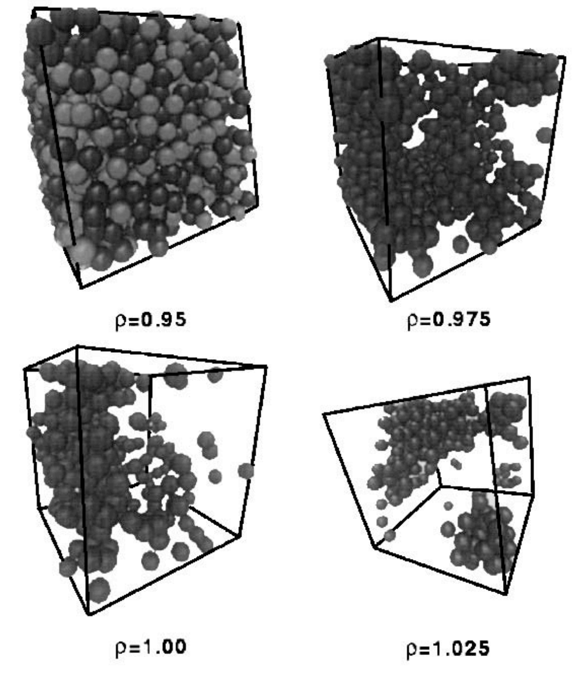
Relation with water's phase diagram

How many are there?
What distinguishes them?
How do they transform into each other?

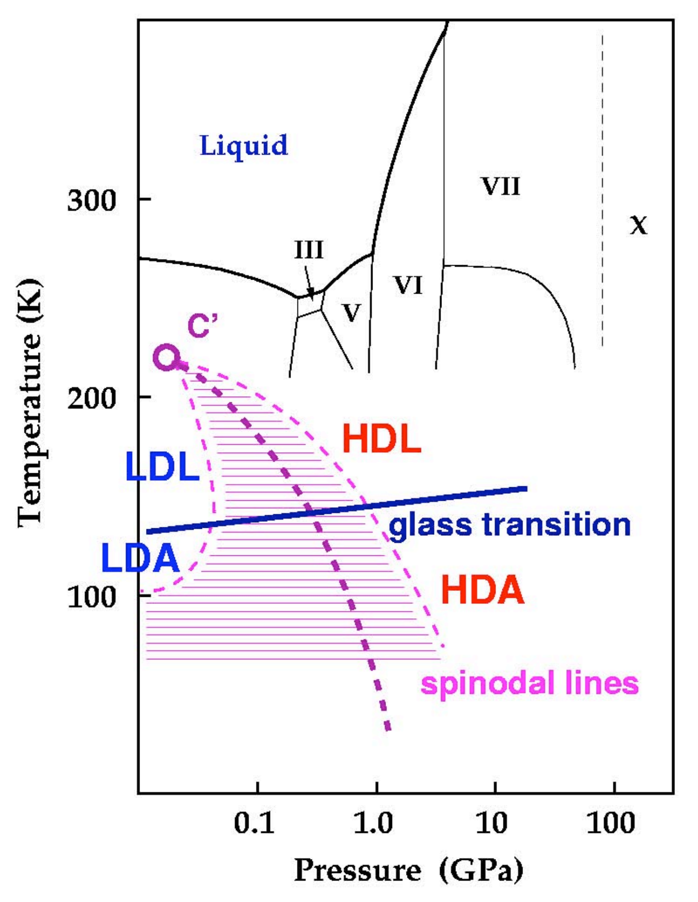
Possible solutions

P.H.Poole et al., PRL, 73, 1632, (1994) :

Two liquid model !



Stephen Harrington et al., PRL (1997)



Real phase transition between HDL and LDL !

A second critical point in water's phase diagram !

A first-order transition separates HDA and LDA !

Still no consensus

Continuous relaxation of an amorphous matrix !

C.A.Tulk et al., Science 297, 1320, (2002)
M.Guthrie et al., PRB 68, 184110, (2003)

A first-order transition between LDA and HDA !

S.Klotz et al. PRL 94, 25506, (2005)

A third amorphous 'state' : vHDA (41 molec./nm^3) !

T.Lörting et al., PCCP 3, 5355, (2001)

Structure of vHDA, HDA and LDA and order parameter found !

J.L.Finney et al., PRL 88, 225503, (2002), PRL 89, 205503, (2002)

Multiple first-order transitions from MD simulations !

I.Brovchenko et al., JCP 118, 9473, (2003)

Amorphous-amorphous-amorphous transition observed !

T.Lörting et al., PRL 96, 025702, (2006)

Let us first get the vocabulary straight

The concept of a “Phase”

Thermodynamics

- Two states of a system are in the same phase if they can be transformed into each other without abrupt changes
- A phase is a region within the parameter space of thermodynamic variables for which the free energy is analytic

Classification of states according to properties

- Different types of phases are associated with different physical qualities
- Break of symmetry and order parameters

The difficulty arising from the amorphous state

Thermodynamics

Non-ergodic states
Abrupt changes maybe hidden by sluggish kinetics

Classification according to properties

Amorphous, i.e. completely isotropic at long length scales
Change in symmetry will be local

Homogeneity of the states?

A bit of history: Physica B 241-243, (1998), 897-902.

Abstract :

... HDA converts with a strongly temperature-dependent rate towards LDA ice. We have investigated in detail the time evolution of both the static and dynamic response functions at several temperatures. Elastic small-angle signals indicate the presence of strong heterogeneities at the early stages of the conversion process. At least two different time scales are present in the transition. The structural changes are reflected in the frequency distribution. ...

Physica B 241-243, (1998), 897-902.

Conclusions :

... There is strong structural evidence for the existence of amorphous states which might be termed intermediate to HDA and LDA. These states are generated during the transformation process. Transient at the formation temperature they can be frozen into metastable states by fast cooling. The degree of heterogeneity of these states varies with the thermal history and has to be studied in further detail using small-angle scattering. As there is no broken symmetry ...

Therefore the present experiment is unable to discriminate between (i) a continuous transition from high-density towards low-density ice forms crossing a line of compressibility maxima and (ii) a kinetically slowed down first order transition in a two-state coexistence region.

What should we look for?

Kinetics

Wide Angle Diffraction and Dynamics

- Information on changes in Local Structure and nature of the Thermodynamic State

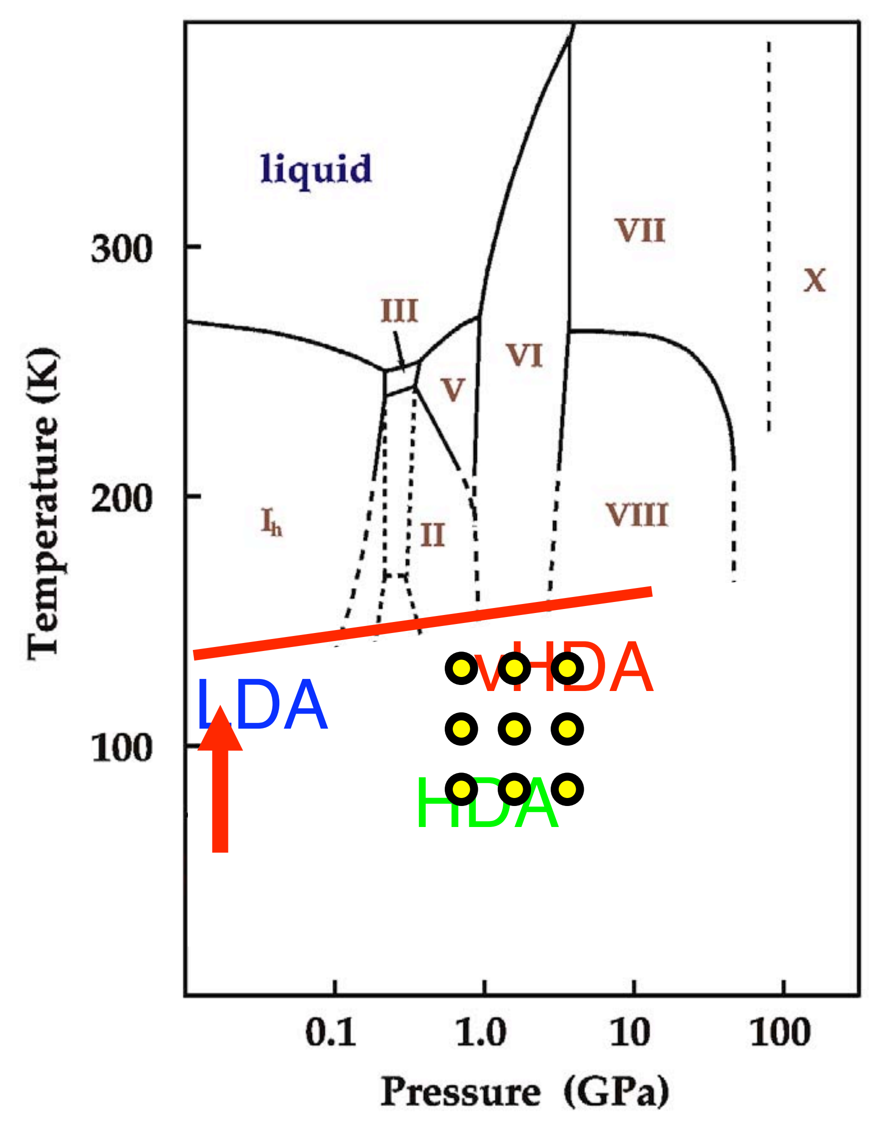
SANS

- Homogeneity of the sample and detection of phase mixtures

This is the outline of the talk

Sample preparation and experimental strategies

Sample Preparation



Prepare (v)HDA samples at different conditions p, T.

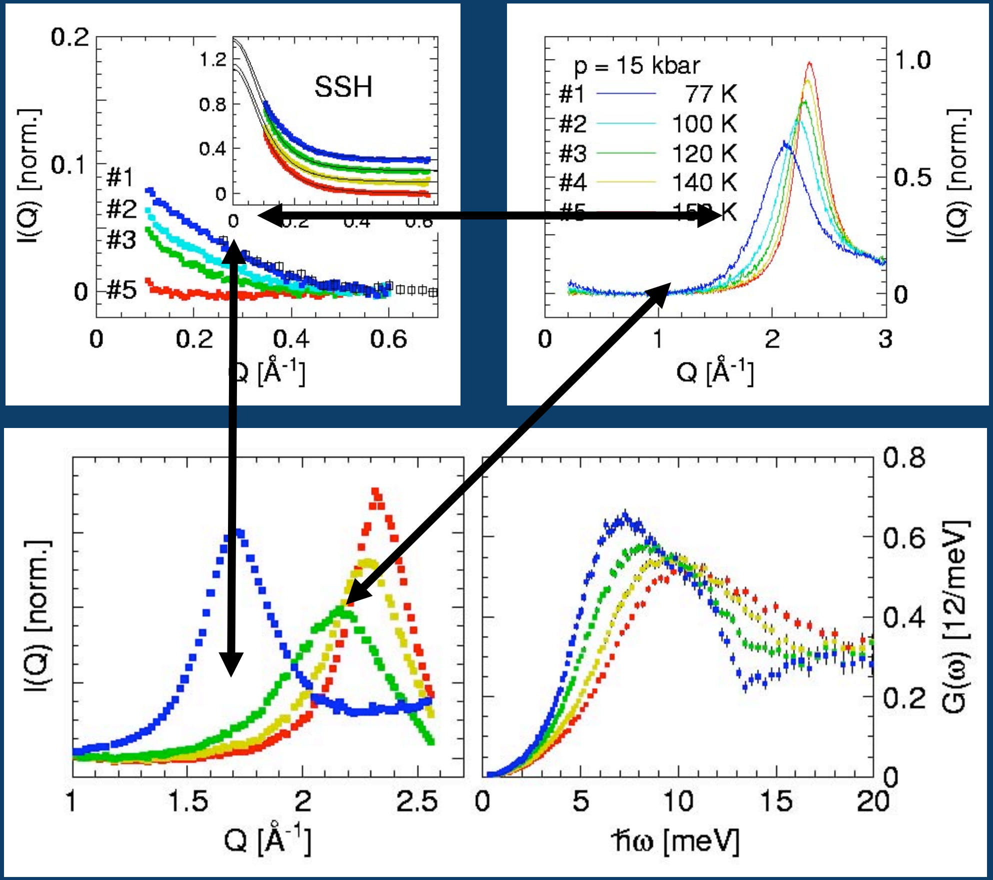
Study of their structure.

In situ study of structure changes upon transformation into LDA.

Compare structure and dynamics of intermediate transformation stages.

Extract information on the kinetics of transformations.

Full characterization in (Q,ω) on identical samples



Each preparation run results in ~3 ml of sample D_2O volume !

Structural information from local to

mesoscopic length scales

0.1-100 nm !

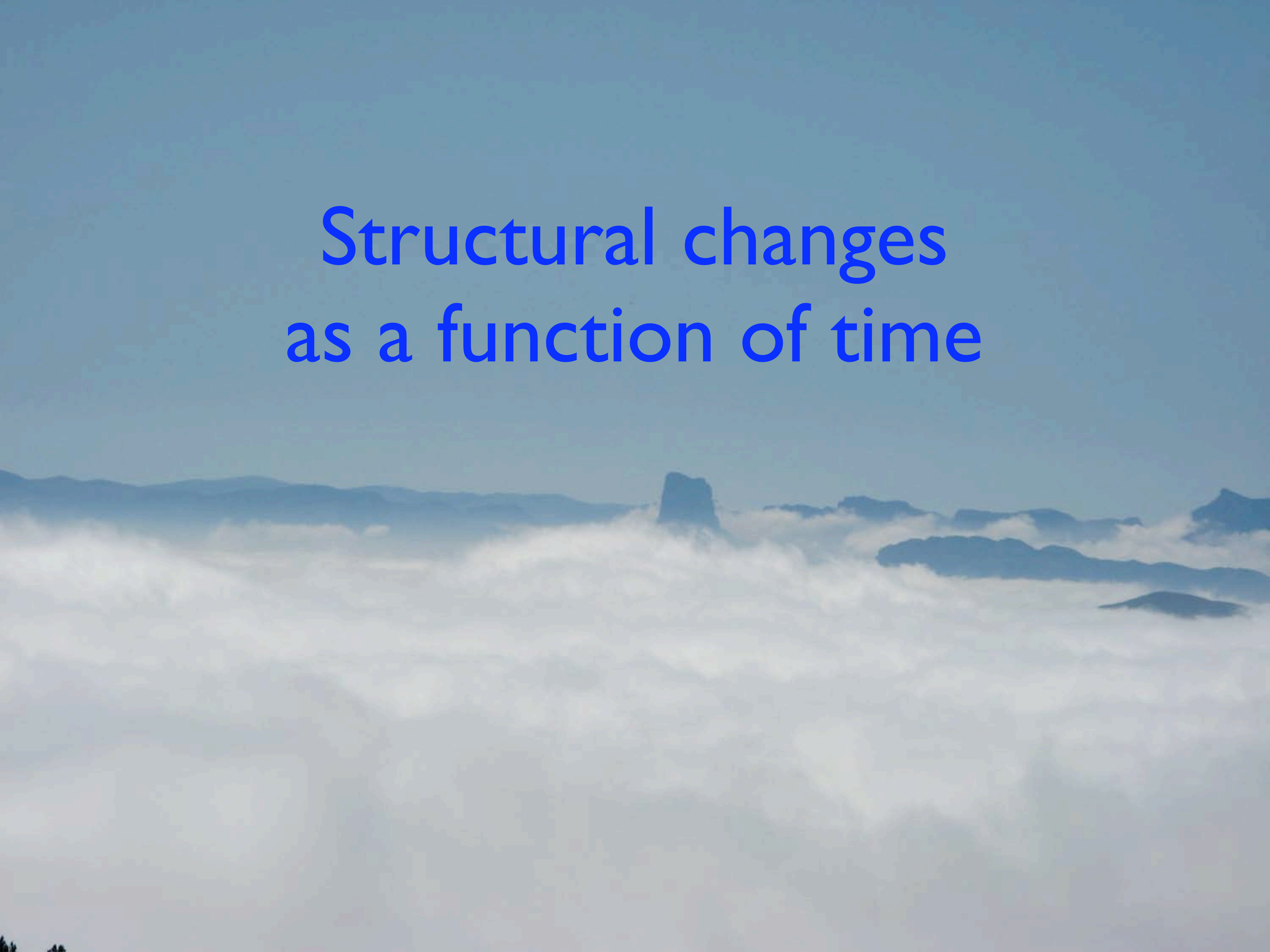
Dynamic response in the range of

vibrational excitations 0.1-100 meV

Complementary, consistent

and cross-checked data !

Structural changes as a function of time

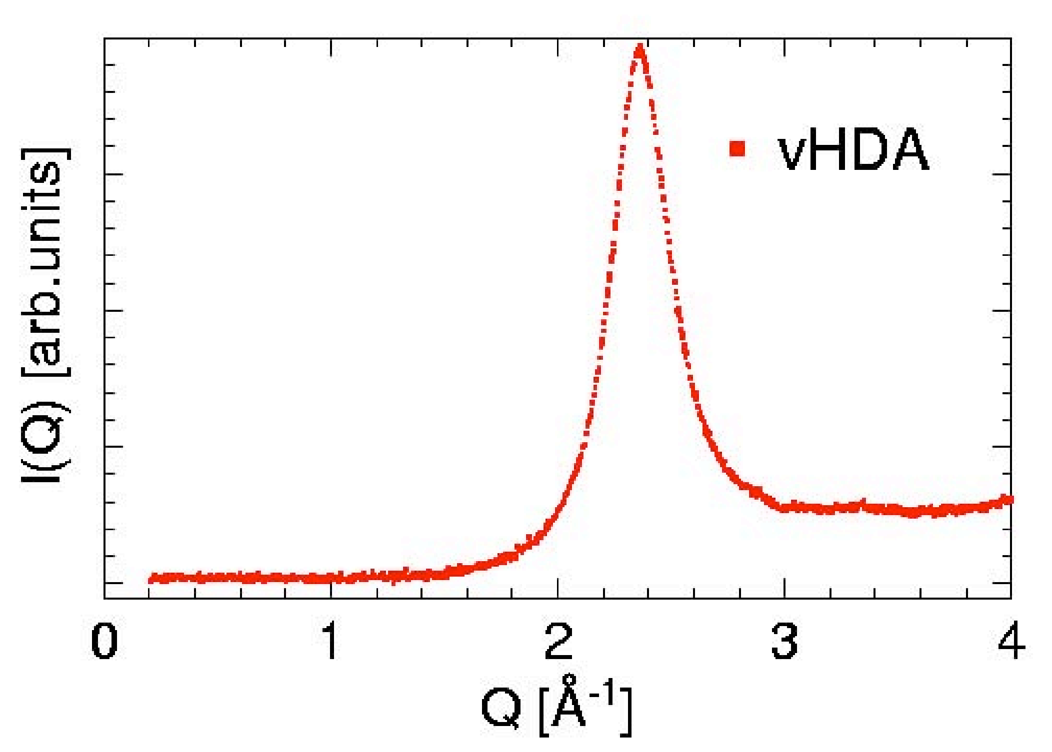


Local Structure via wide angle neutron scattering

In Situ Observation of Structure Changes
An example

D20 Diffractometer / ILL

9 sets out of 1750



Production

vHDA :

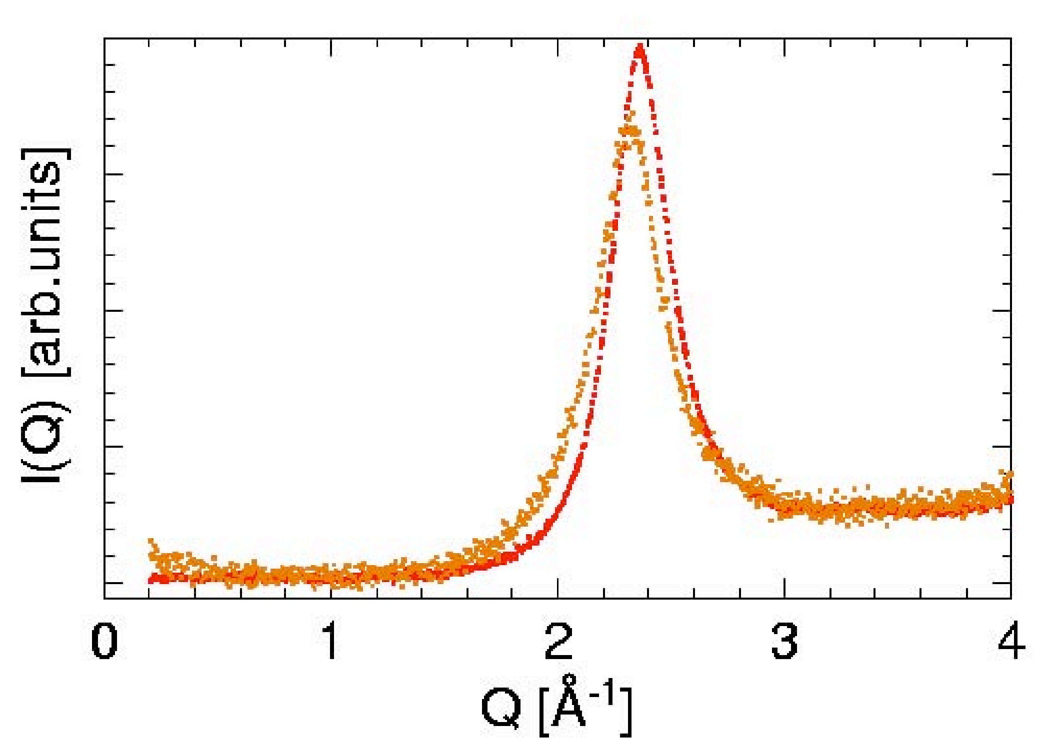
T = 155 K

p = 16 kbar

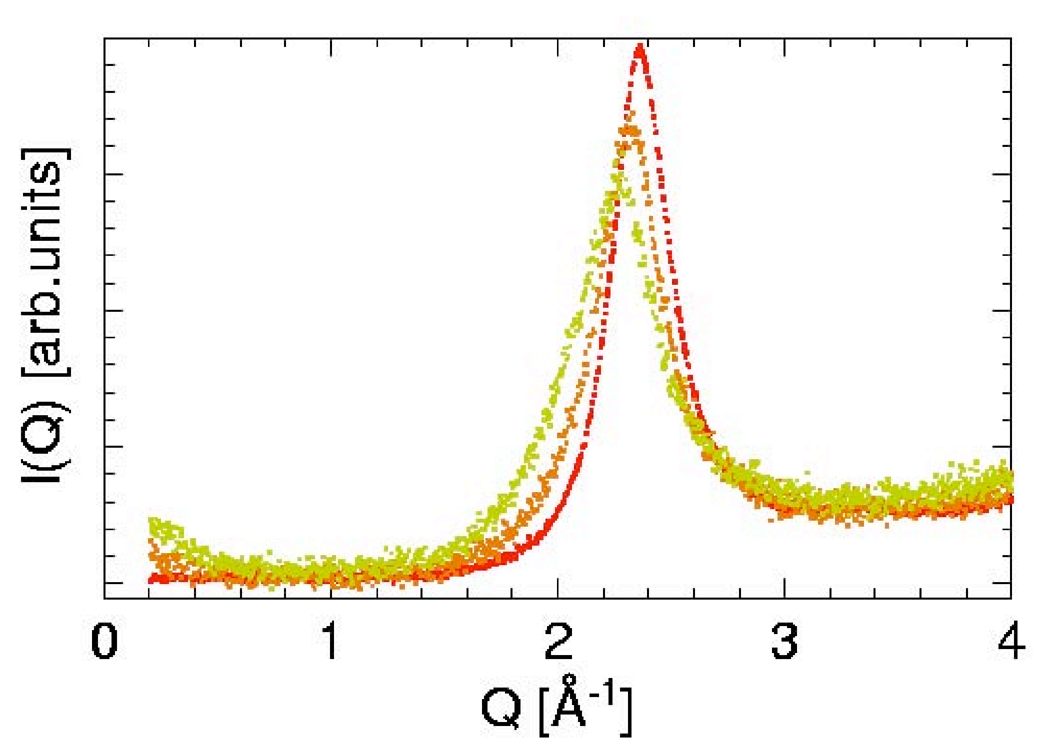
Measurement

Δt = 30 sec., M ≈ 500 mg, $T_{exp.}$ = 113 K, p_{He} = 200 mbar

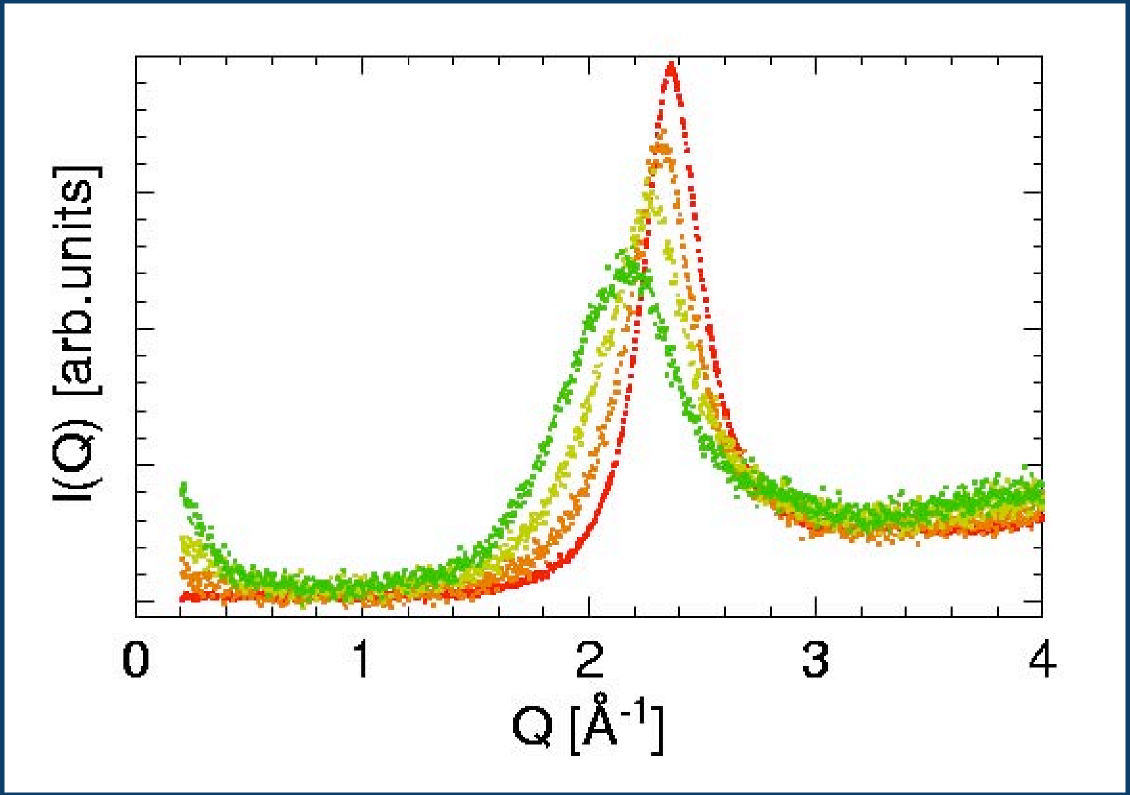
In Situ Observation of Structure Changes



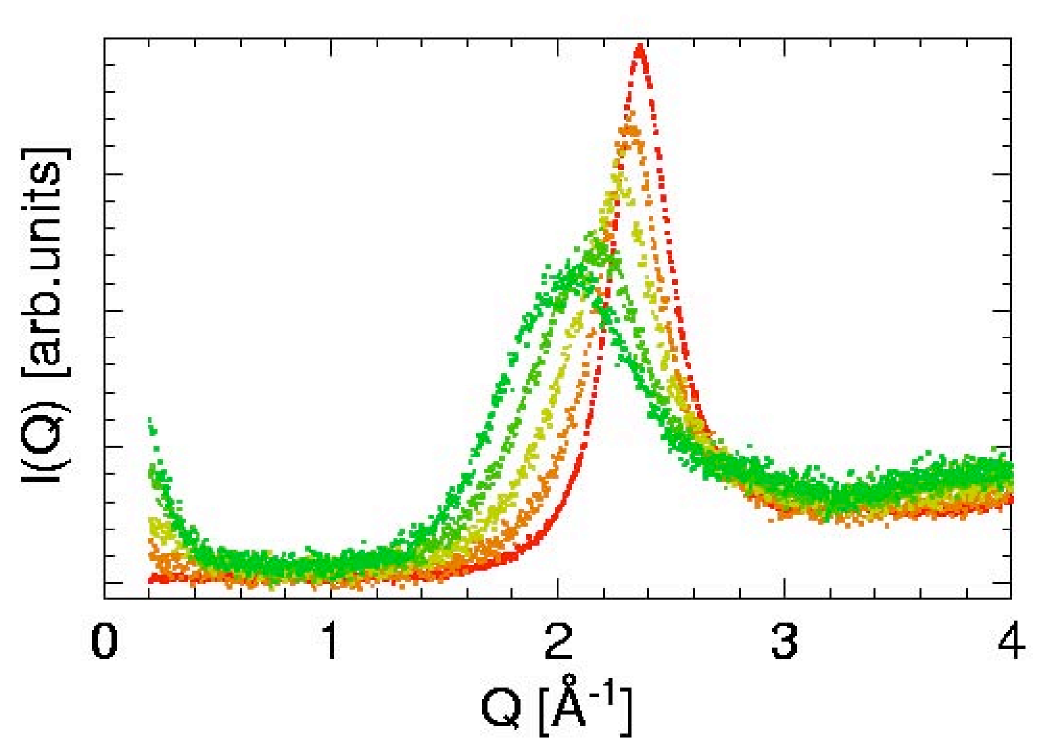
In Situ Observation of Structure Changes



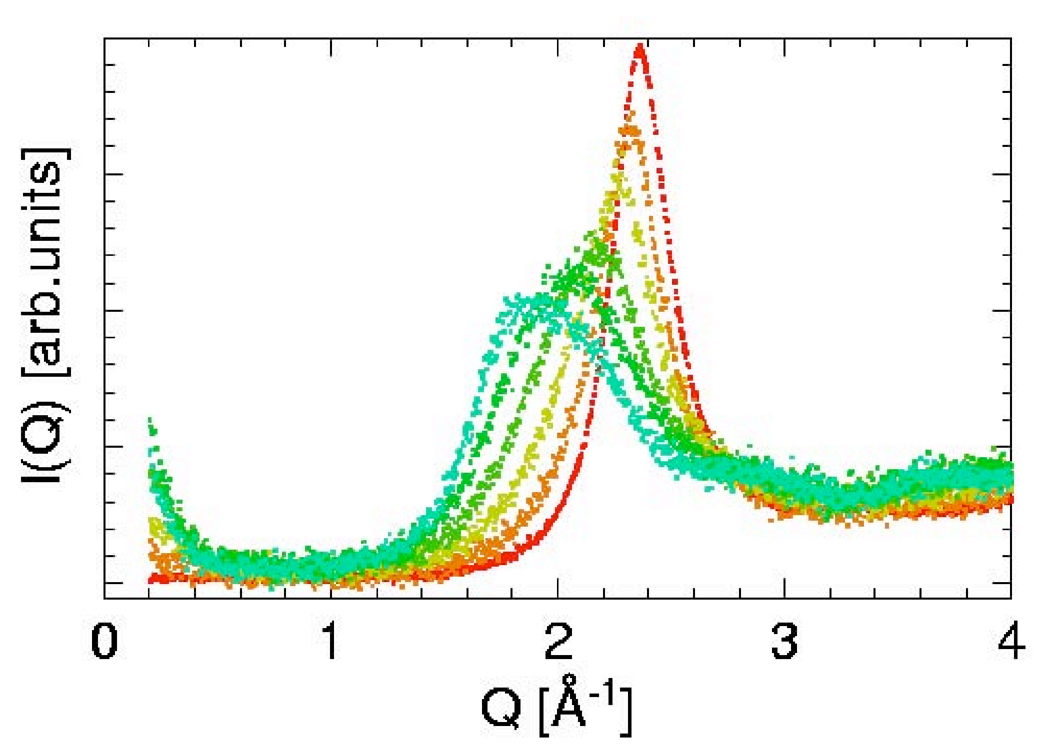
In Situ Observation of Structure Changes



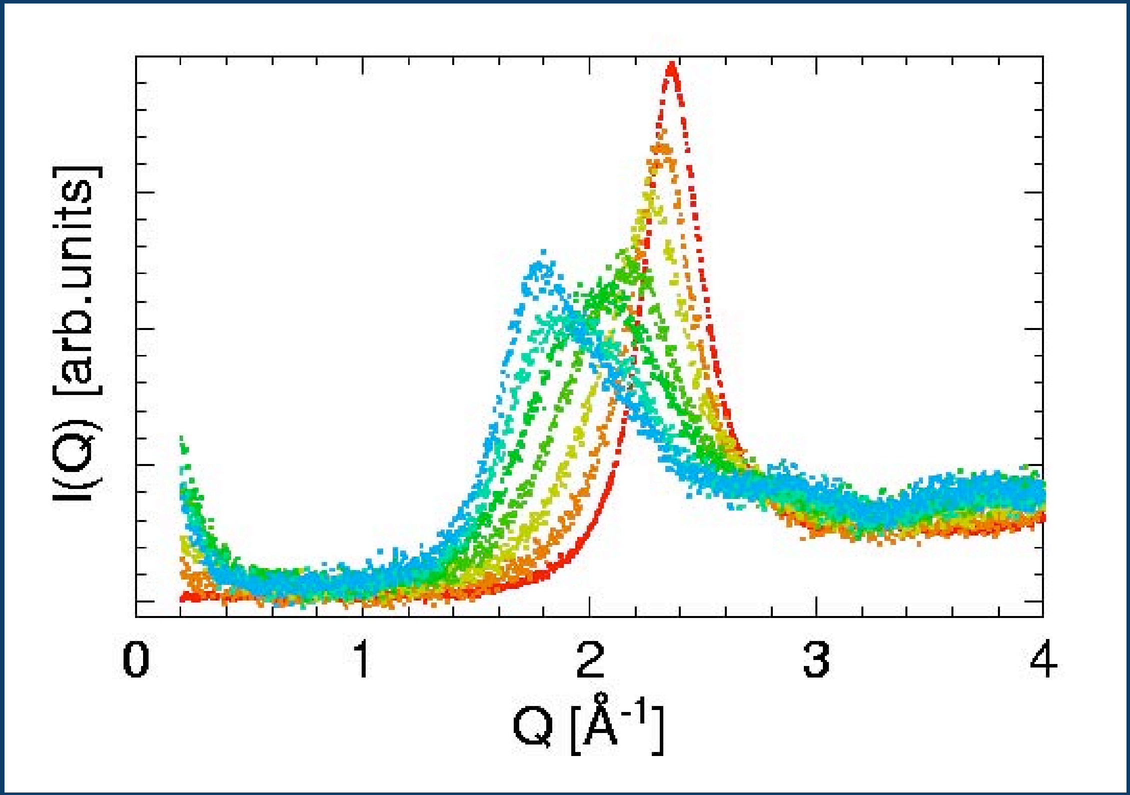
In Situ Observation of Structure Changes



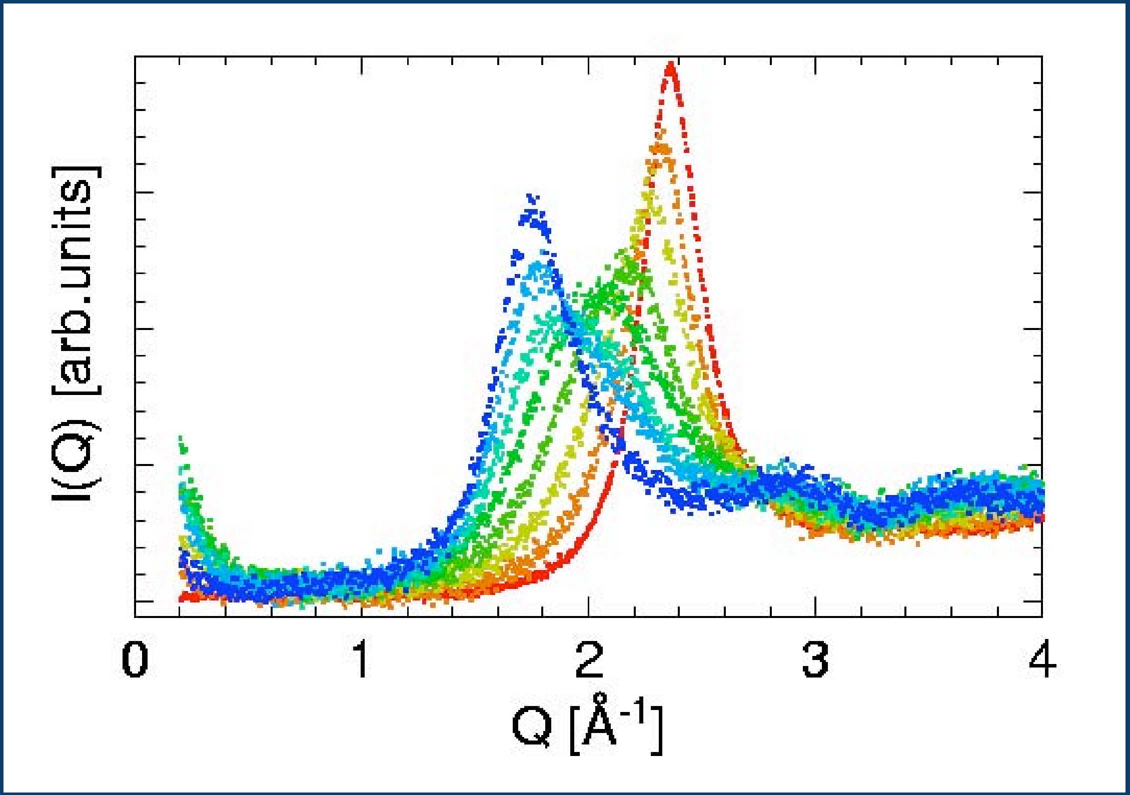
In Situ Observation of Structure Changes



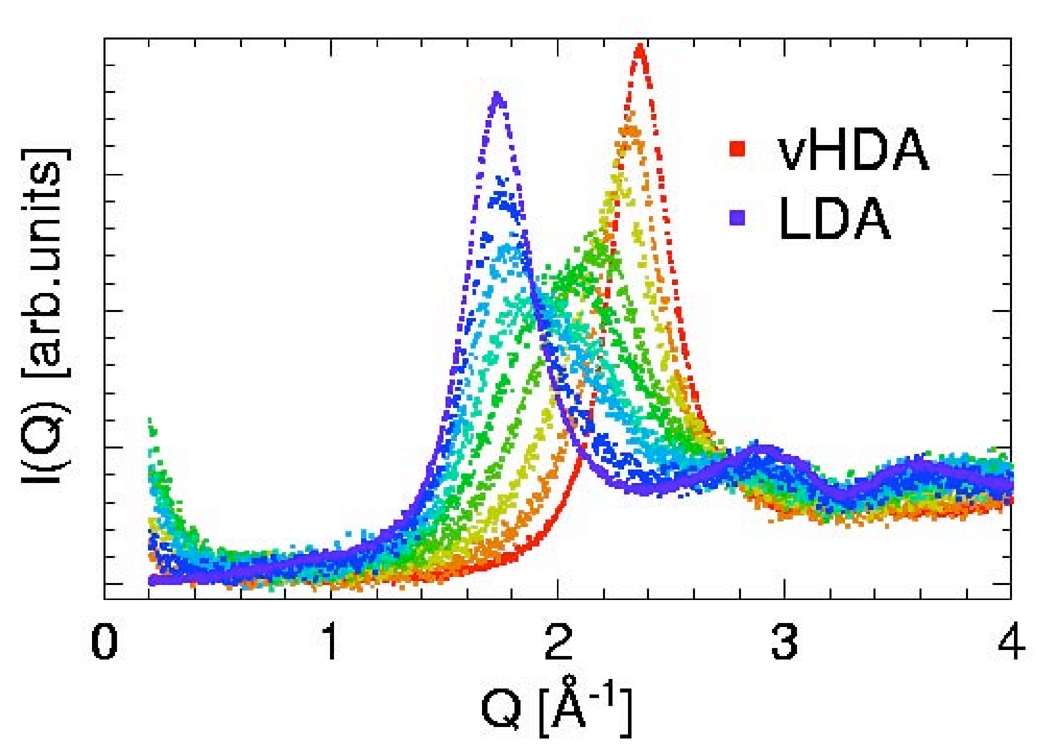
In Situ Observation of Structure Changes



In Situ Observation of Structure Changes



In Situ Observation of Structure Changes



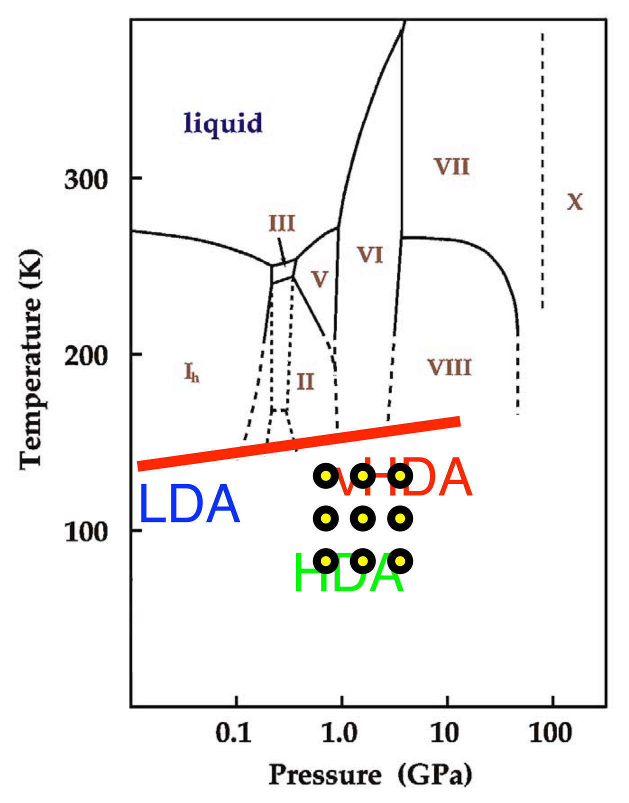
Continuous changes of structure and dynamics in amorphous ice,

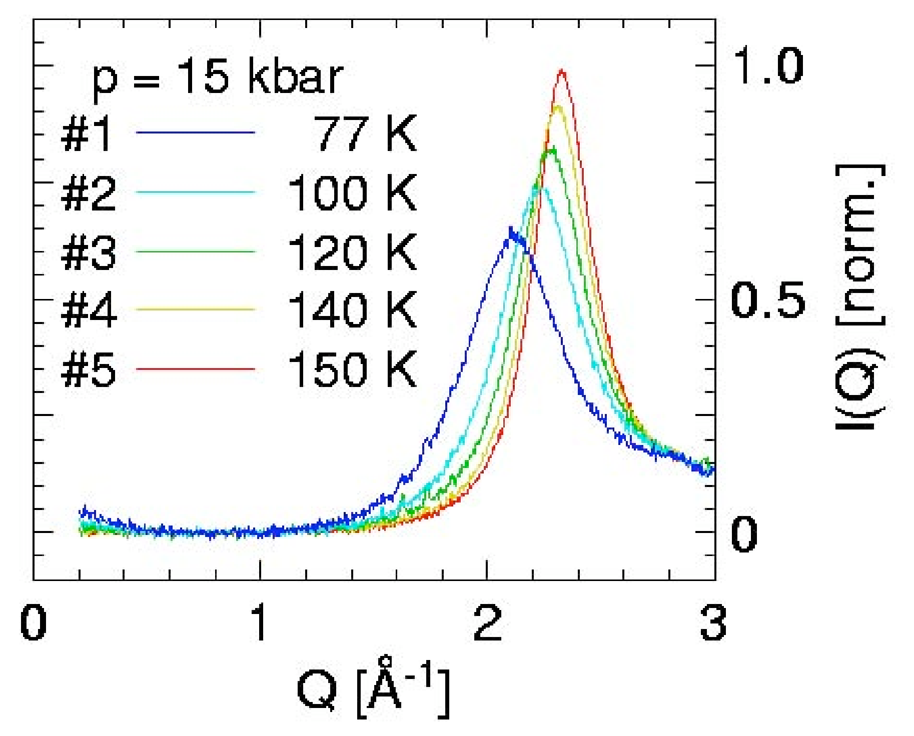
however, transient heterogeneous character of samples !

(v)HDA dependence on preparation temperature

D22 and D20 / ILL

M.M. Koza et al. J. Non-Cryst. Solids 2006





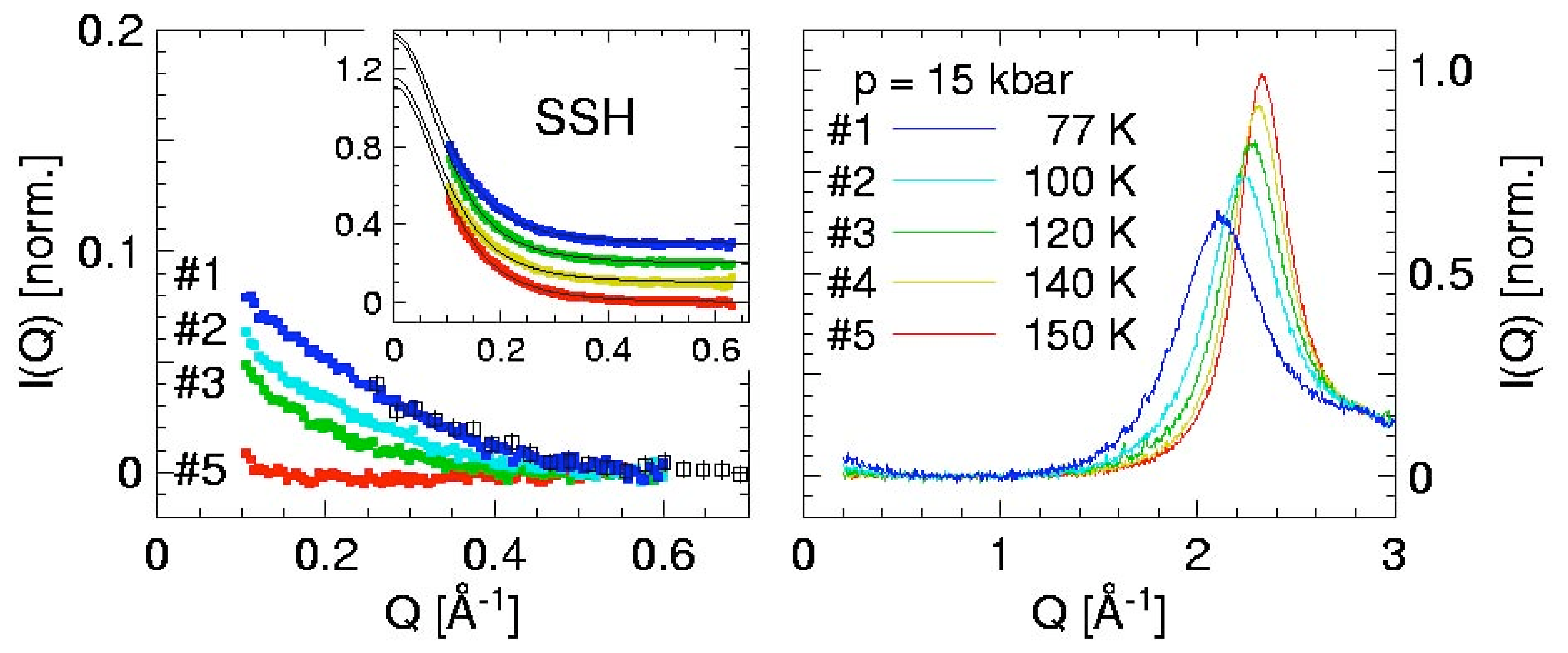
The more extreme the preparation conditions are the 'denser' is the sample !

M.M.Koza et al. *Phys.Rev.Lett.* 94, 125506, (2005)

(v)HDA dependence on preparation temperature

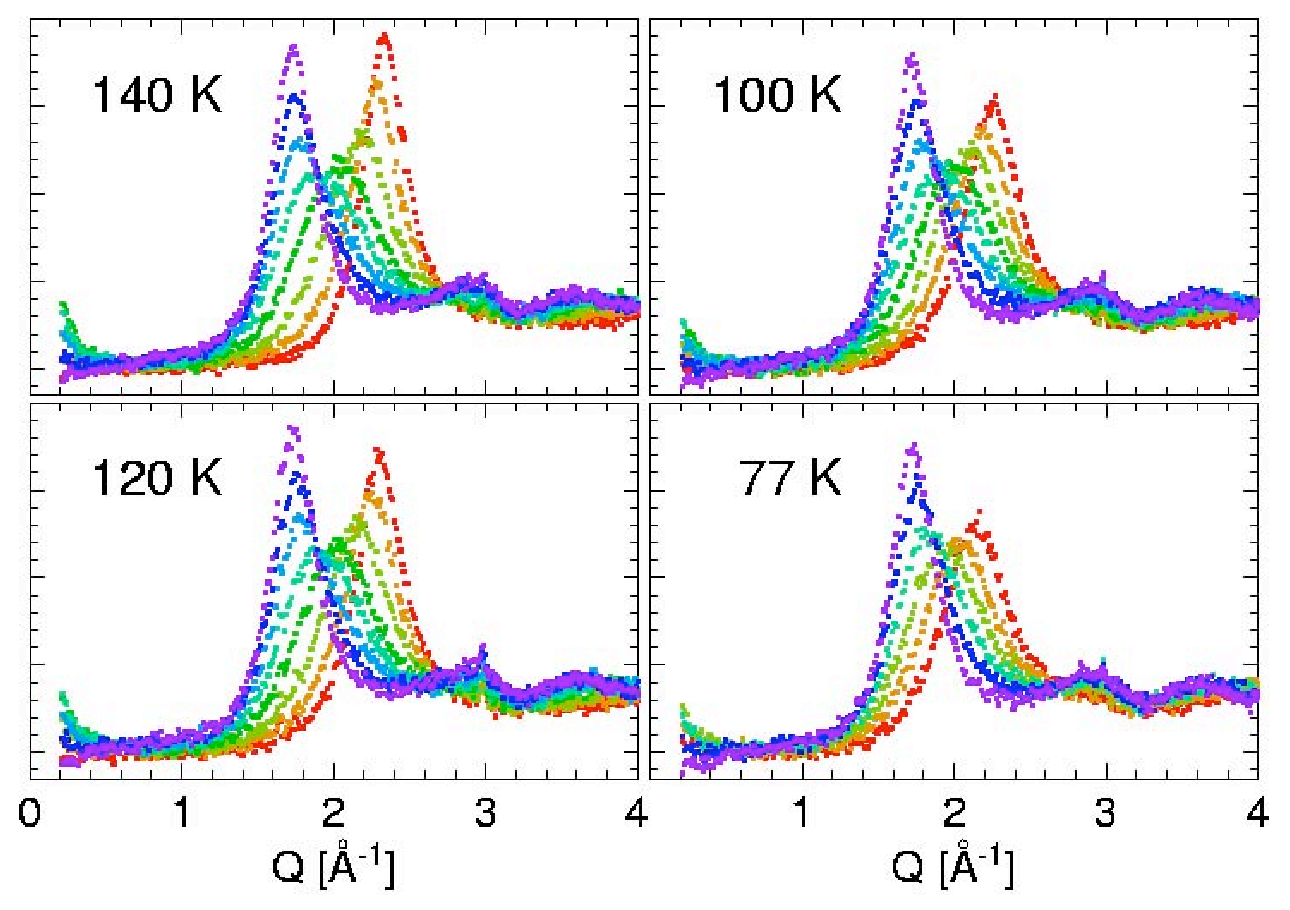
D22 and D20 / ILL

M.M. Koza et al. J. Non-Cryst. Solids 2006



The more extreme the preparation conditions are and the less heterogeneous is the structure !

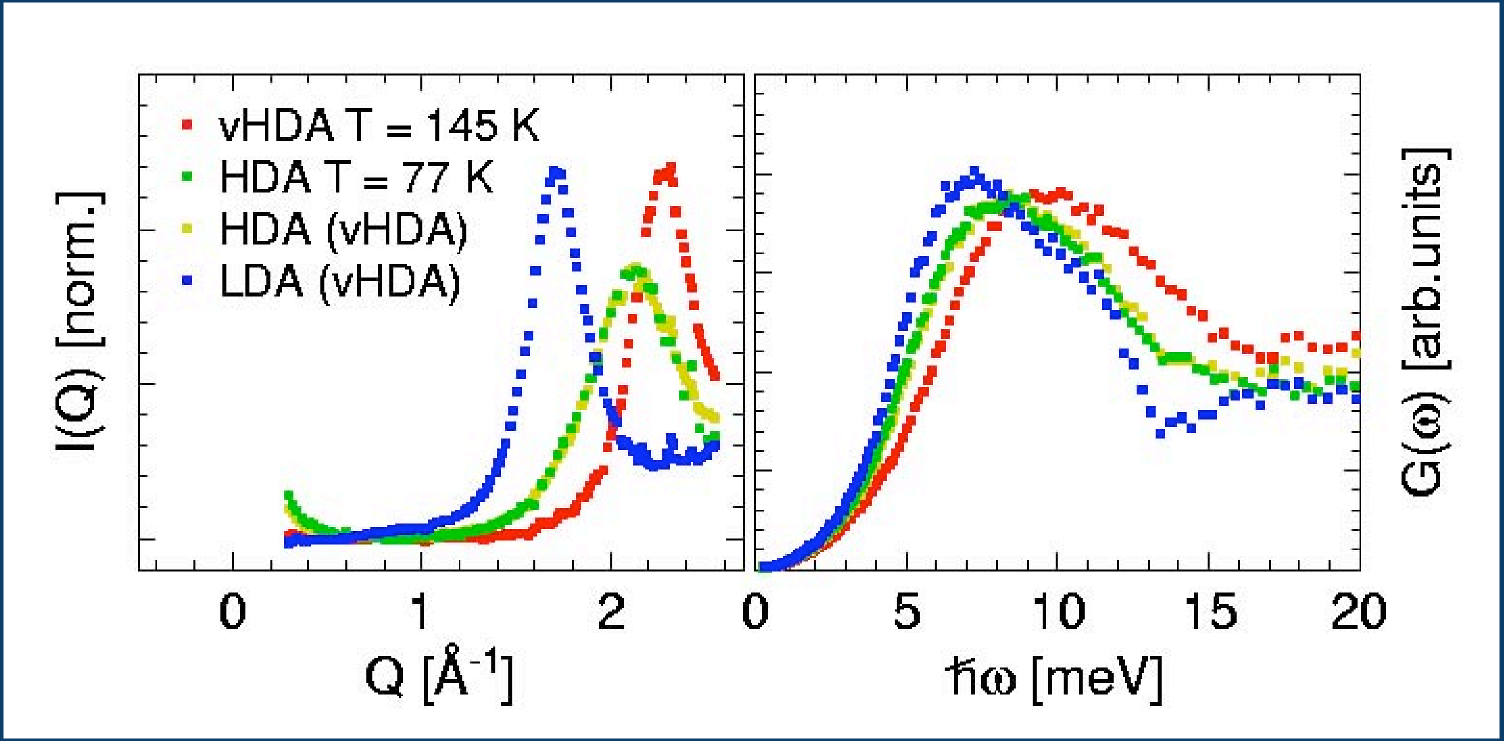
How “universal” are the intermediate states



Can we reproduce intermediate transformation stages no matter what the initial sample state is ?

How “universal” are the intermediate states

IN6 time-of-flight spectrometer / ILL

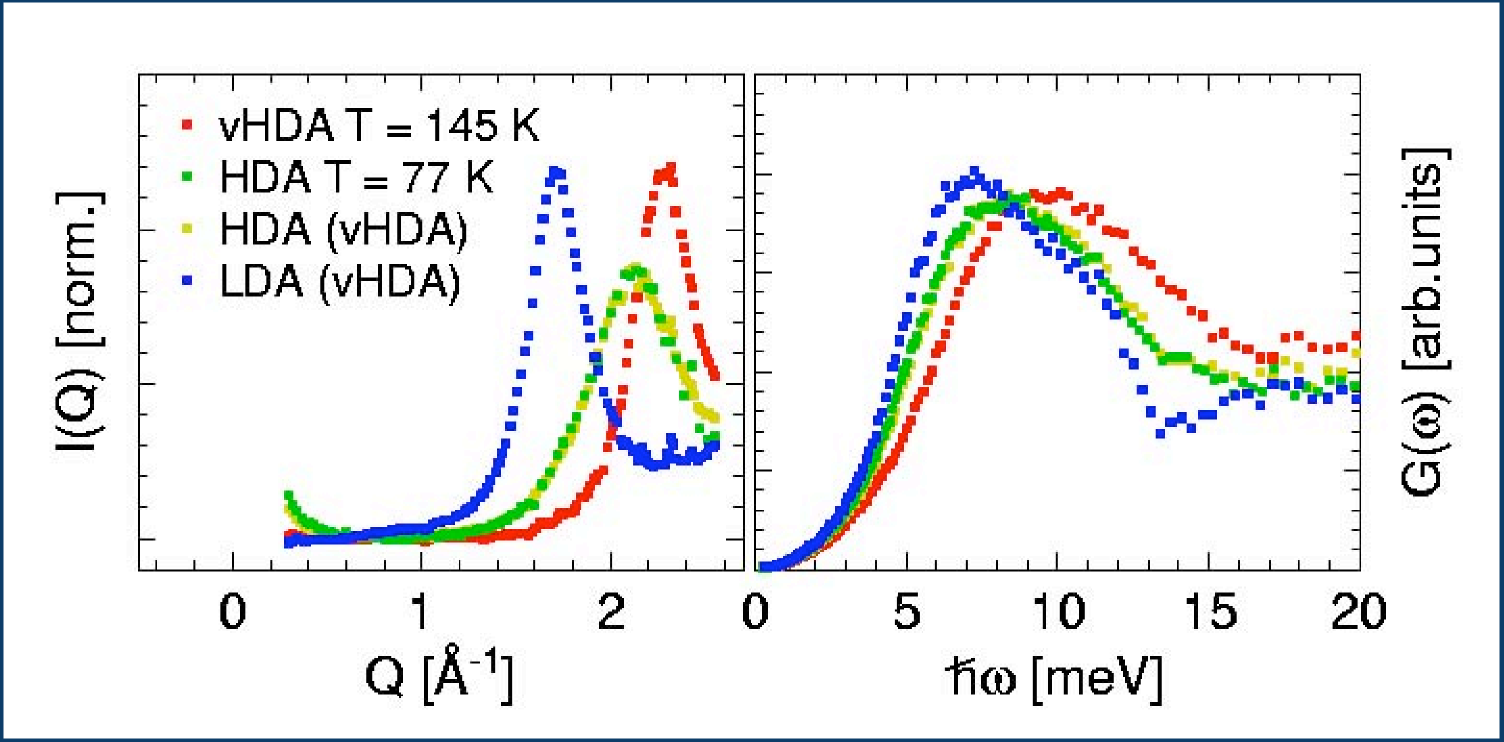


Phys.Rev.Lett. 94, 125506, (2005)

The answer is yes from a structural and vibrational point of view

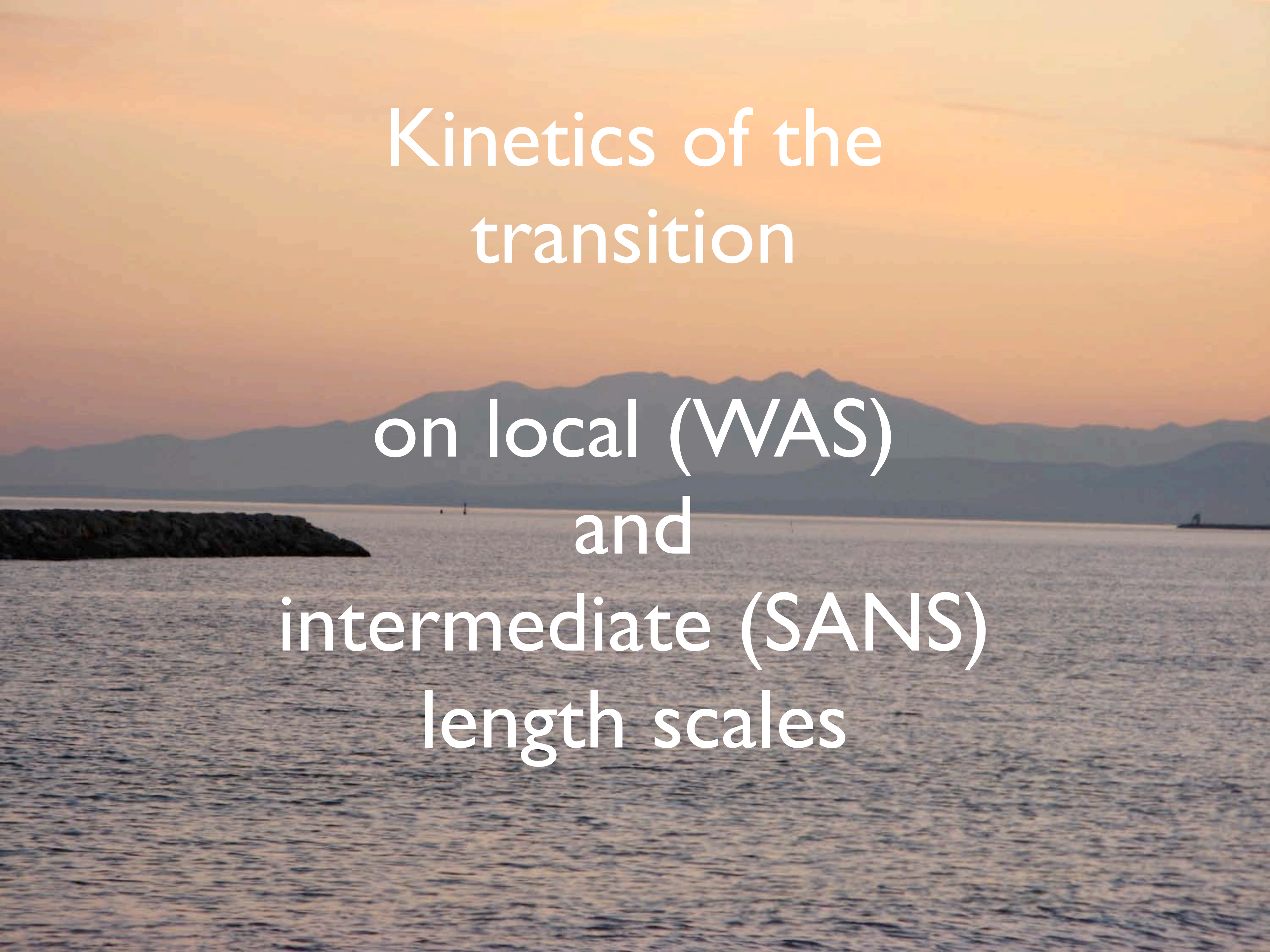
Reproducibility of intermediate Structures

IN6 time-of-flight spectrometer / ILL



Phys.Rev.Lett. 94, 125506, (2005)

Are the matching intermediate stages equal in terms of 'thermodynamics' ?
Thermodynamics - in the sense of energy landscape !



Kinetics of the transition

on local (WAS)
and
intermediate (SANS)
length scales

Kinetics of the (v)HDA to LDA Transition

1. Start measurements before heating samples to nominal T.
2. Keep nominal temperature until transformation is finished.
3. Heat to 130 K for ½ hour.
4. Cool to 78 K and measure LDA.

Diffraction :

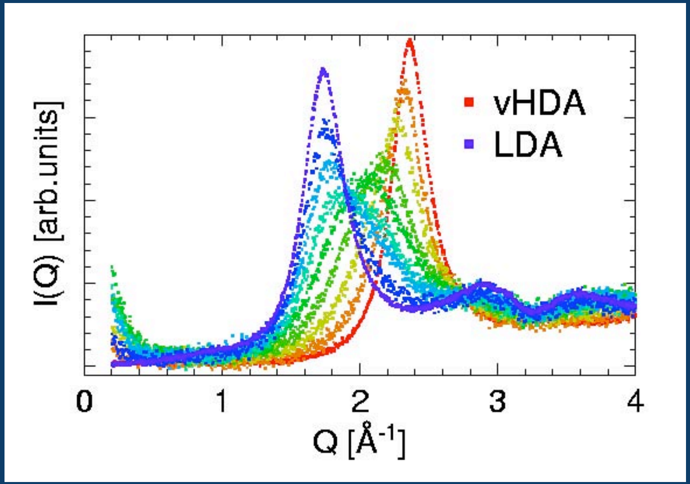
Initial state (vHDA) = 1

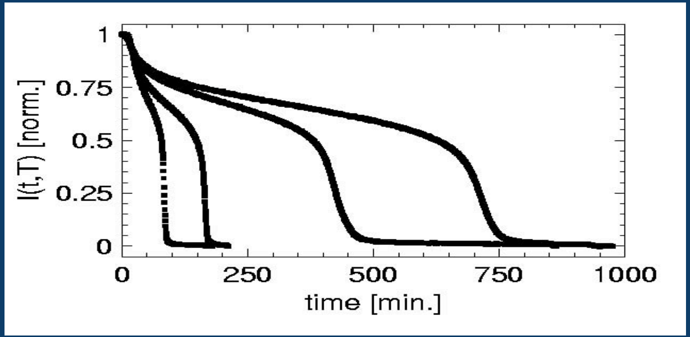
Final state (LDA) = 0

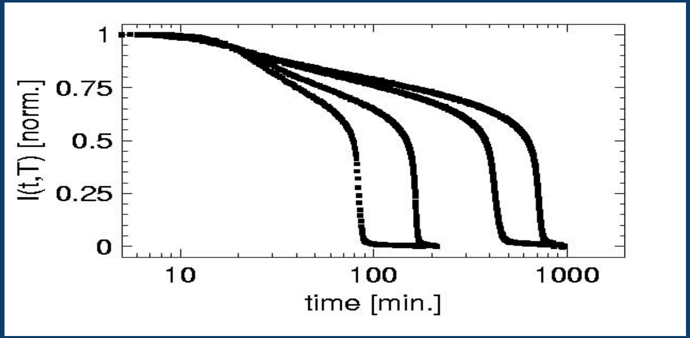
SAS regime :

Final state (LDA) = 0

SSH = 1

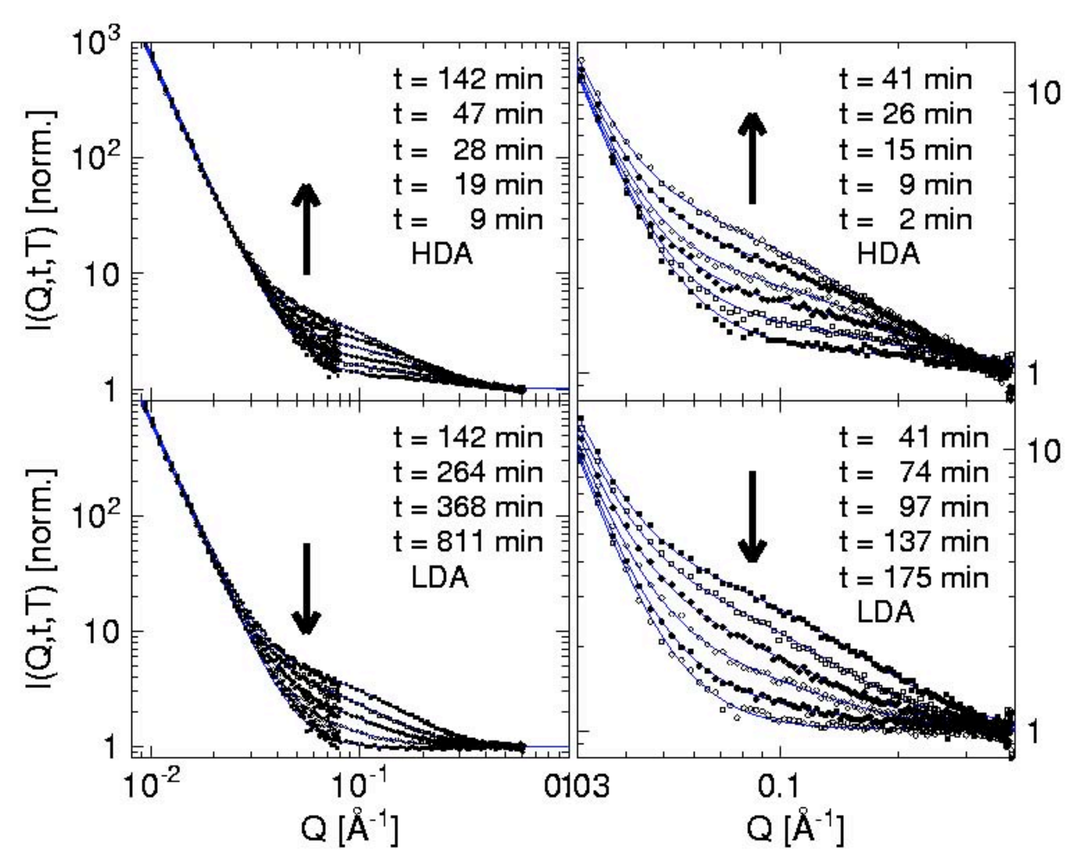






Evolution of the SANS Signal

103 K 105 K



$N = 35 \text{ molec./nm}^3 * (5 * 2\pi/6*10^{-1} \text{ nm})^3 = 5 * 10^6 \text{ molecules}$

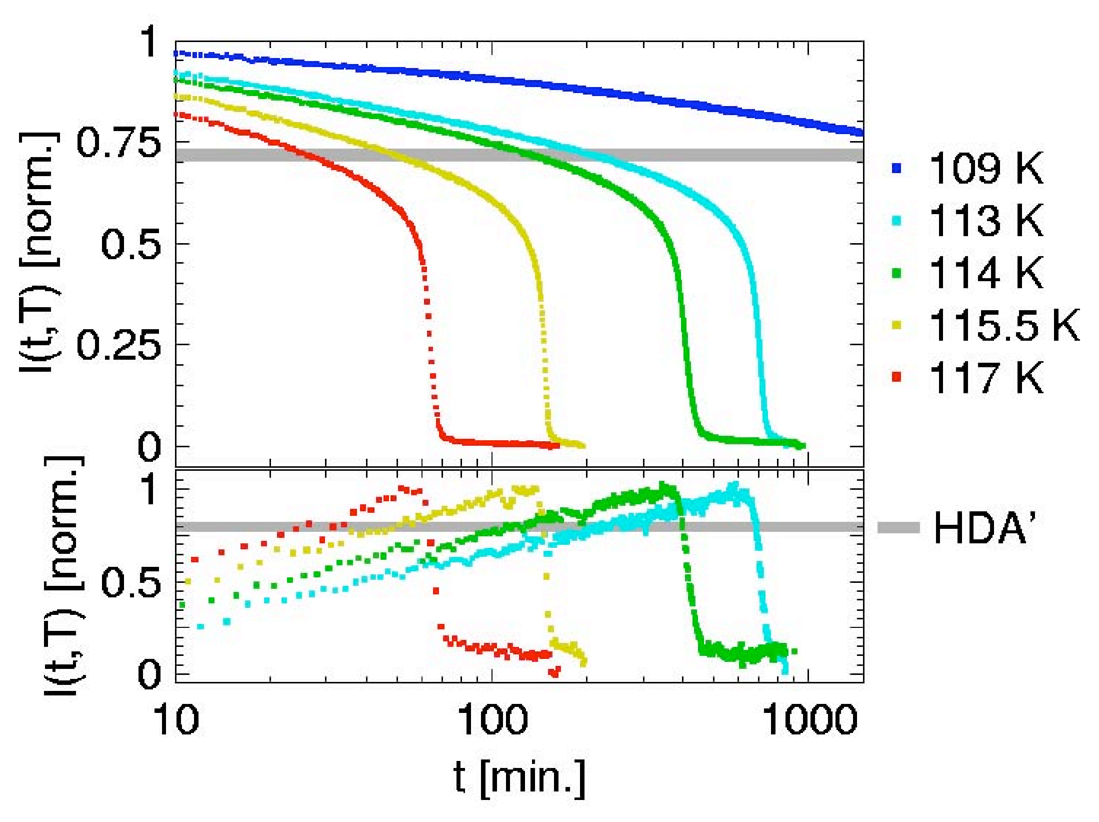
The entire SANS formfactor can be reproduced !

Kinetics of the (v)HDA to LDA Transition

Single sample prepared at p = 16 kbar and T = 155 K

WAS

SANS



Phys.Rev.Lett. 94, 125506, (2005)

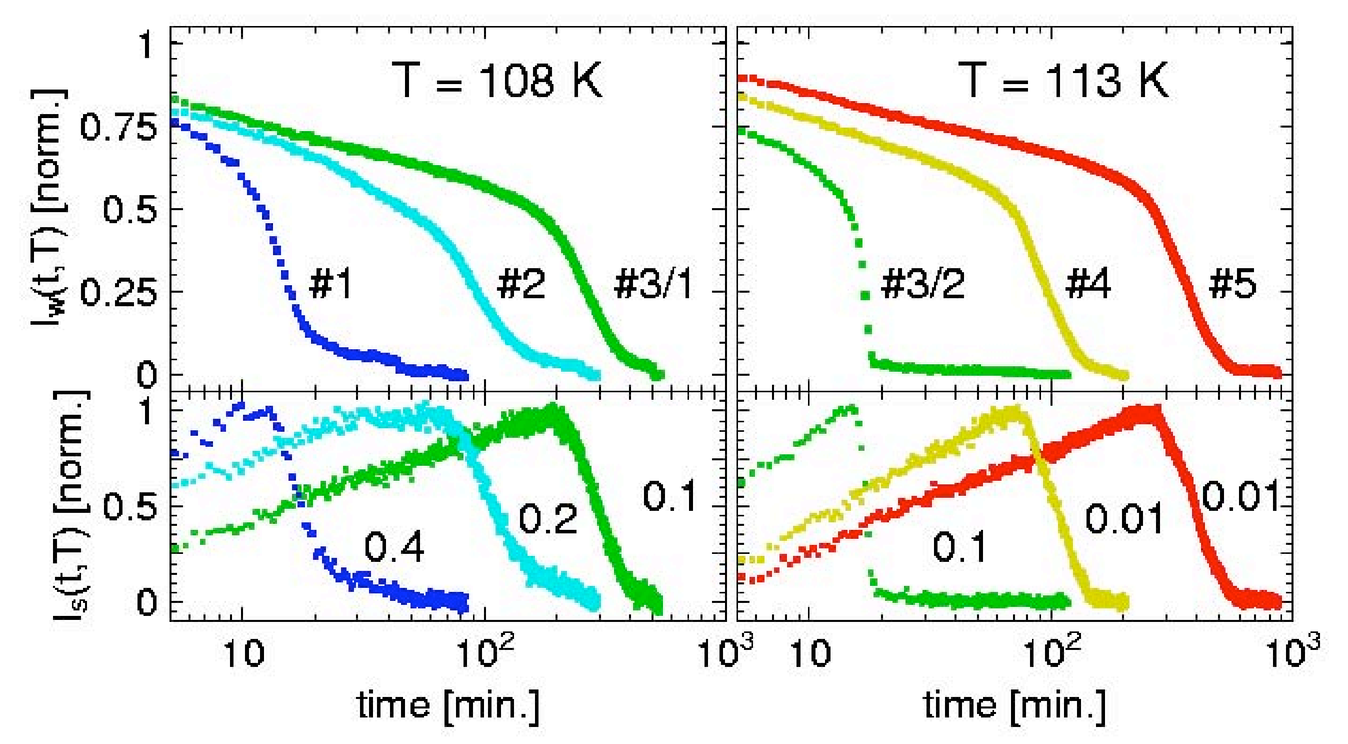
The transformation does not obey a simple nucleation and growth process !

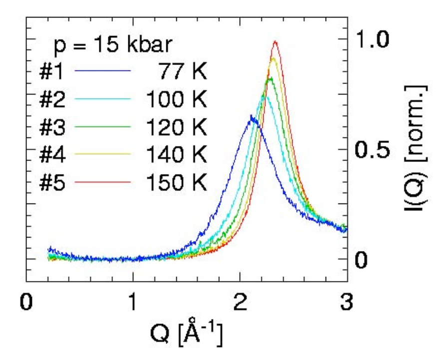
The second transition step is temperature driven !

Maximum heterogeneity at the 'center' of the transformation !

Kinetics of the (v)HDA to LDA Transition

Samples prepared at different conditions





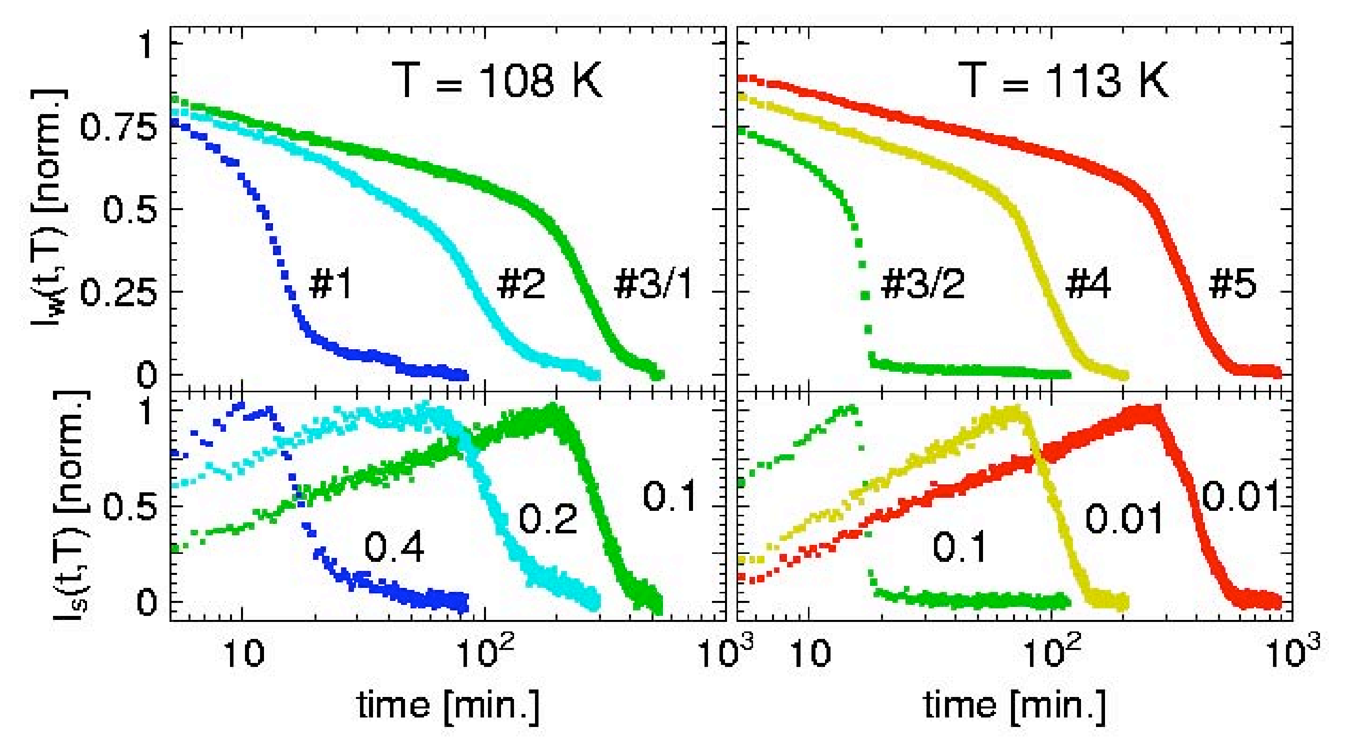
The higher the annealing temperature is the slower is the kinetics !

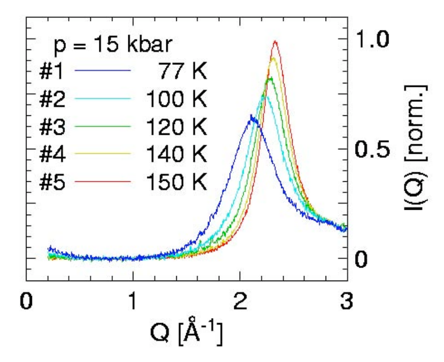
Different “HDA” structures transform on different time scales !

Different “HDA” are different in terms of “energetics” !

Kinetics of the (v)HDA to LDA Transition

Samples prepared at different conditions





Arrhenius activation energies :

HDA to LDA : $\Delta E \approx 40$ kJ/mol

(v)HDA to LDA : $\Delta E \approx 65$ kJ/mol

So far ...

- There exist only two homogeneous structures (v)HDA and LDA .
- Intermediate transition stages are heterogeneous structures .

  The broader the strong S(Q) maximum is the more heterogeneous is the amorphous structure ! This applies as well to all initial stages !
- This applies also to all “HDA” structures .
- Different “HDA” structures show different kinetic behaviour .

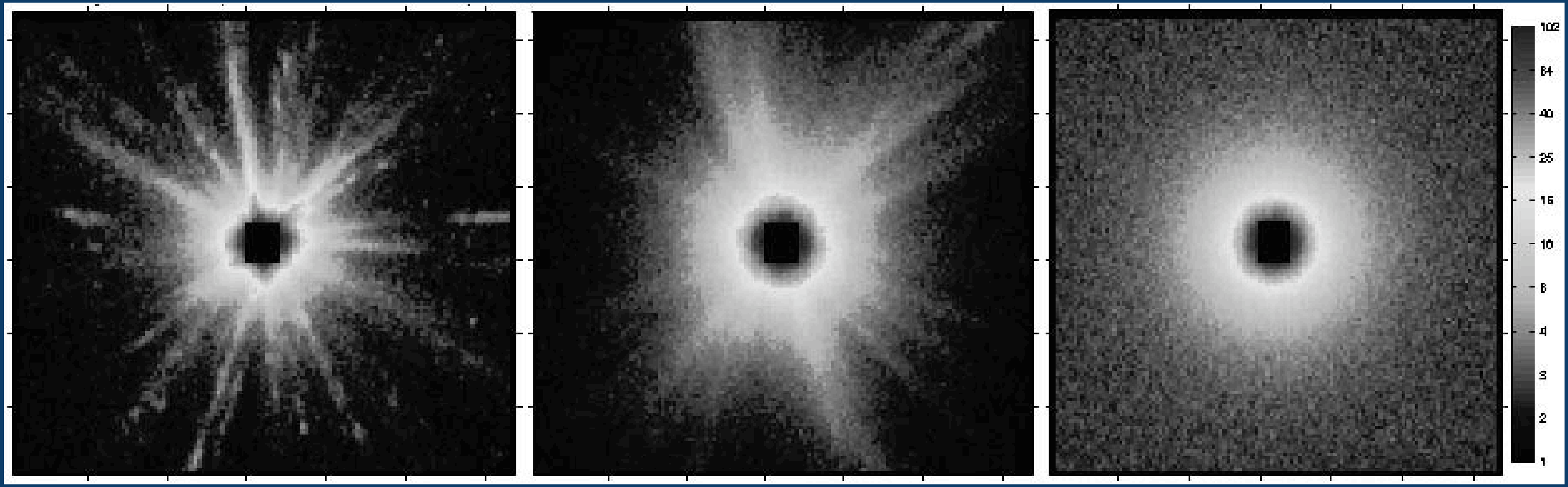
  You don't know the “energetics” of the system !
- The initial structure and its kinetics depend on T, p, annealing time, (compression rate ?).
- The better annealed the initial structure is the slower is the transformation the higher is the onset temperature.
- The transformation shows a complex kinetics wherein two stages can be identified.

Precompressed Ice Samples

0 kbar

9 kbar

18 kbar

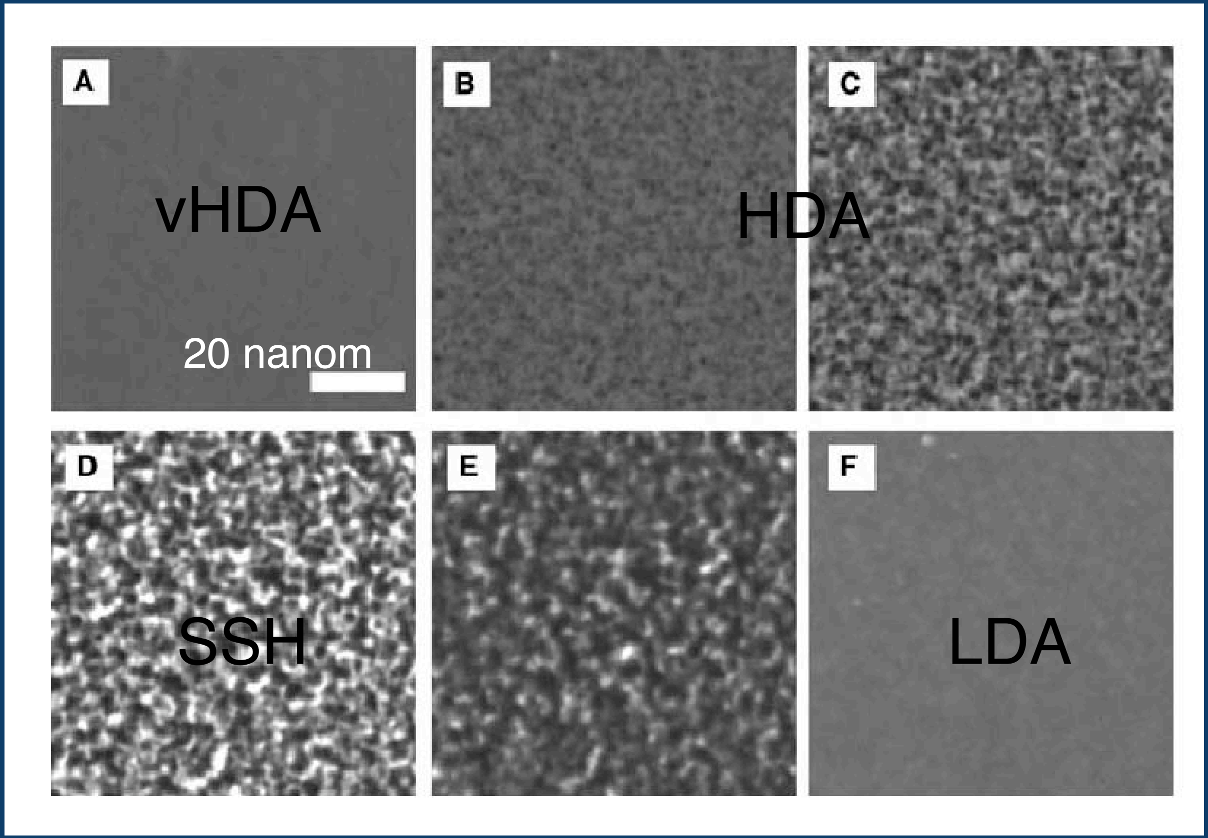


Dislocations, stacking faults, impurities, ...

This behavior is not specific to Water

Triphenyl Phosphite

Apparent liquid – liquid phase transition in Triphenyl Phosphite



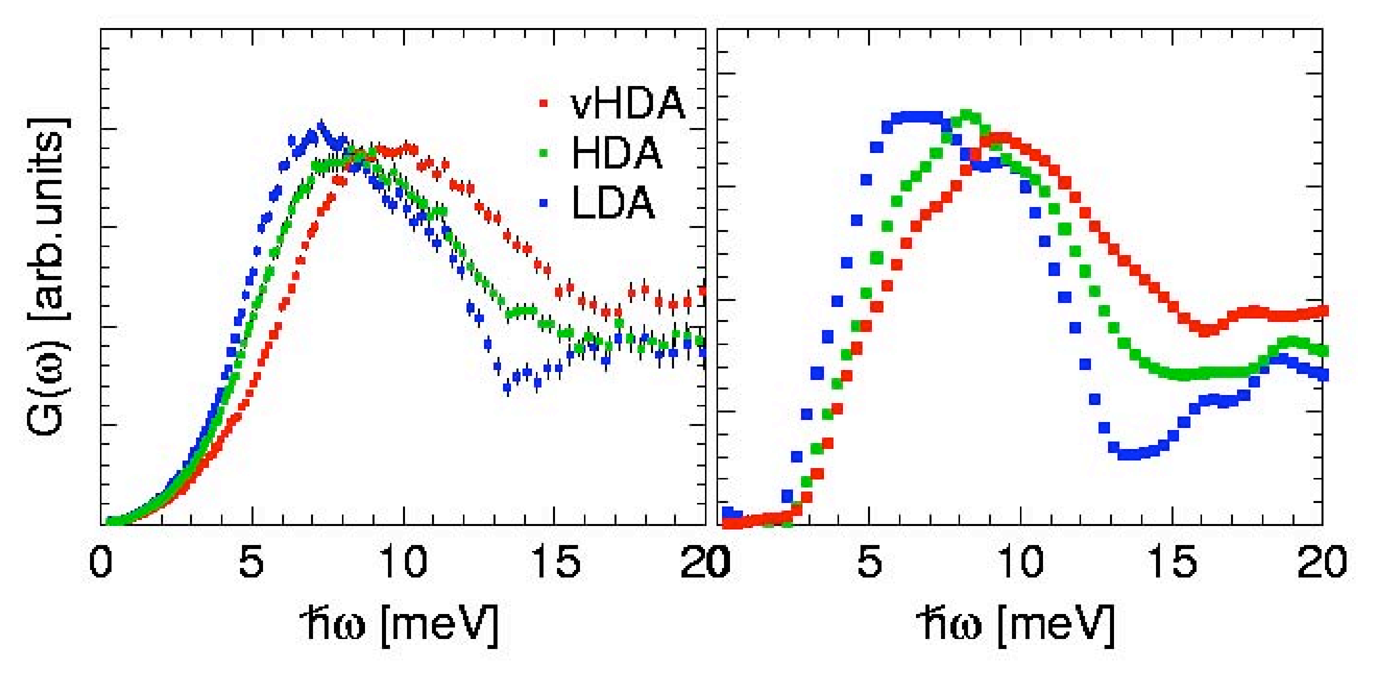
R.Kurita and H.Tanaka, *Science* 306, 845, (2004)
SANS: C. Alba-Simionesco *EPL* 52, 297, (2000)

So what about the transition scenario?

Let us have a look at the dynamics

Recent Simulation Results

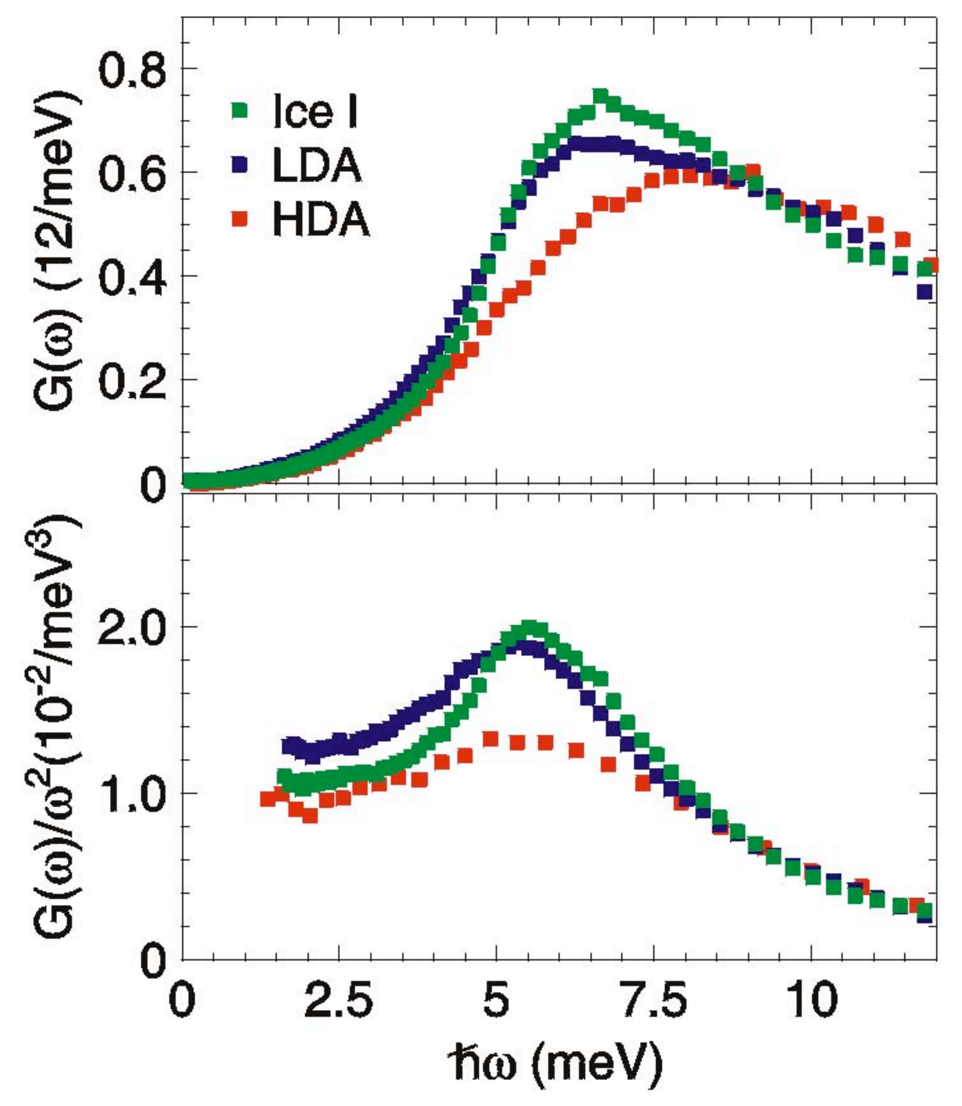
By courtesy of Roman Martonak



M.M. Koza et al., *PRL* 94, 125506, (2005)

R. Martonak et al., *PRL* 92, 225702, (2004)

'Crystal-like' Phonons in Amorphous Ice !

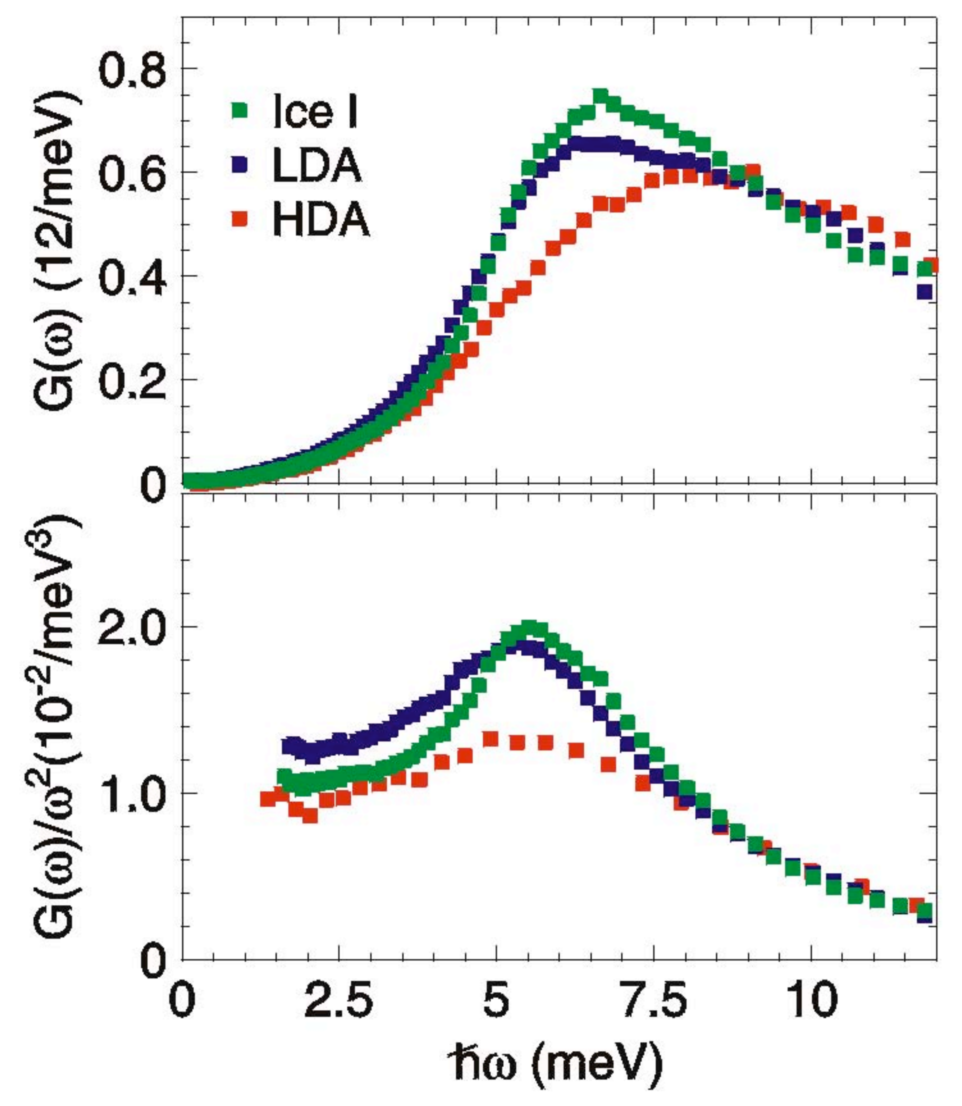


M.M.Koza et al., PCCP 7, *1423*, (2005)

IN6 / ILL

$\Delta E = 0.15$ meV

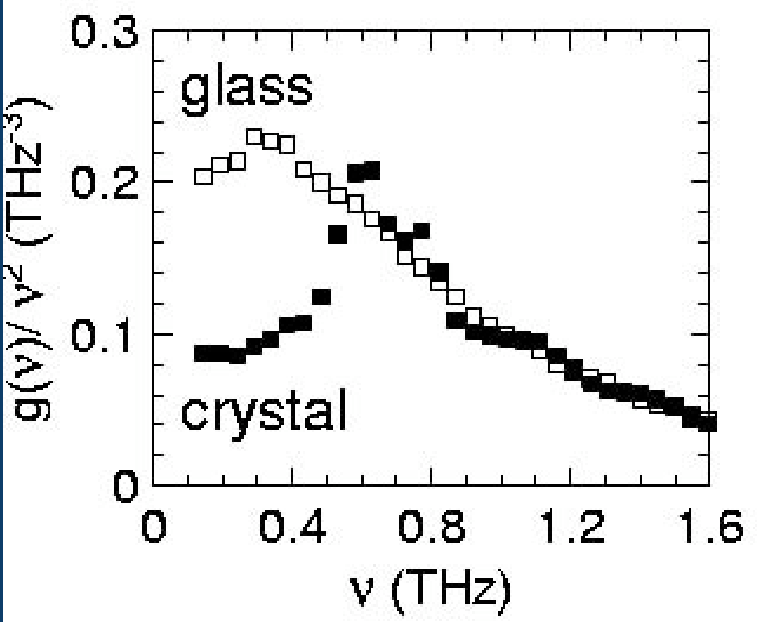
'Crystal-like' Phonons in Amorphous Ice !



M.M.Koza et al., PCCP *7, 1423*, (2005)

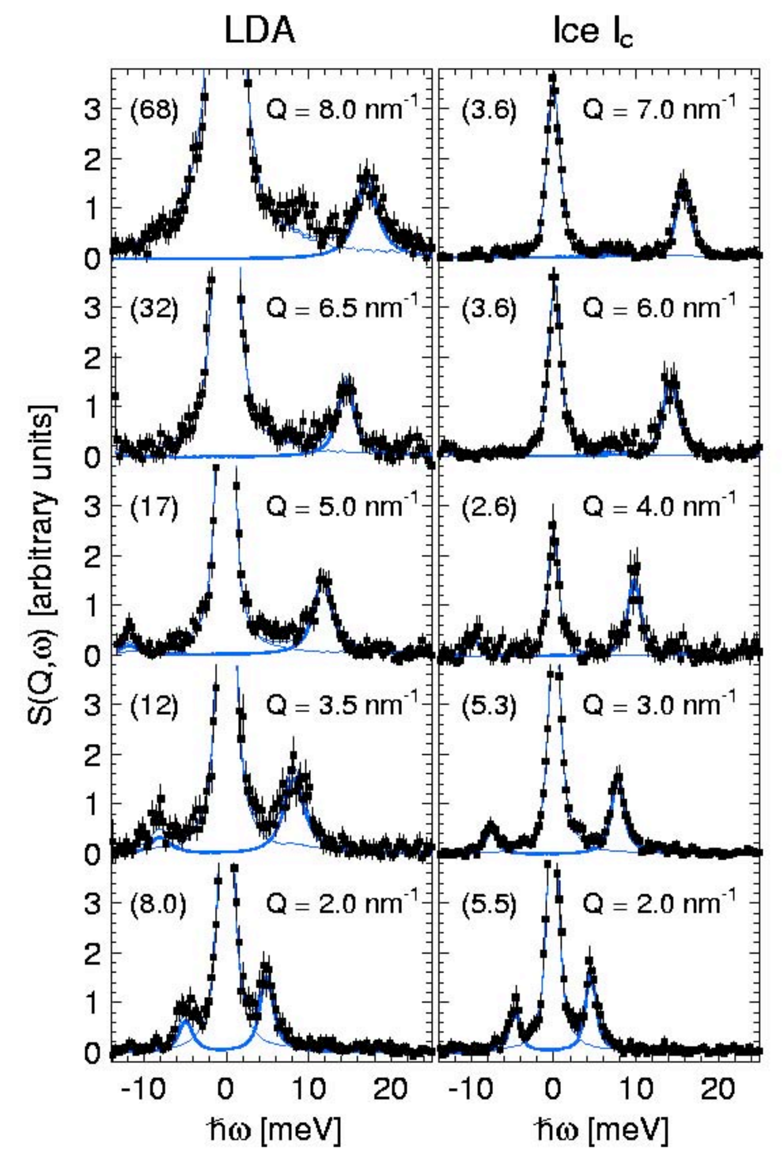
ortho-Terphenyl

A.Toelle et al., Eur.Phys.J. B 5, (2000)



1 THz = 4.14 meV

'Crystal-like' Phonons in Amorphous Ice !



High-resolution X-ray scattering
ID16 / ESRF

$\Delta E = 1.5$ meV

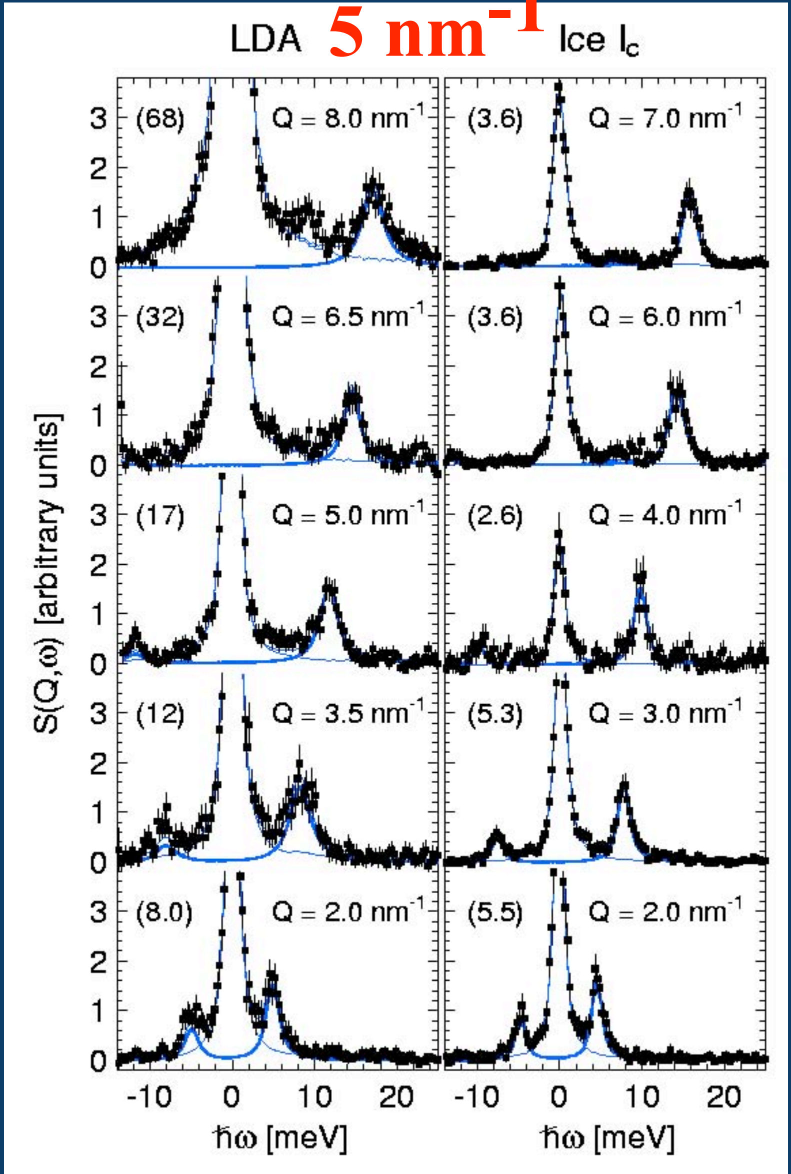
LDA: $v_l = 3550 \pm 50$ m/s

Ice I: $v_l = 3750 \pm 50$ m/s

H.Schober, M.M.Koza, A.Toelle, F.Sette, C.Maschivecchio, F.Fujara, PRL 85, (2000)

M.M.Koza, H.Schober, B.Geil, M.Lorenzen, H.Requardt, PRB 69, (2004)

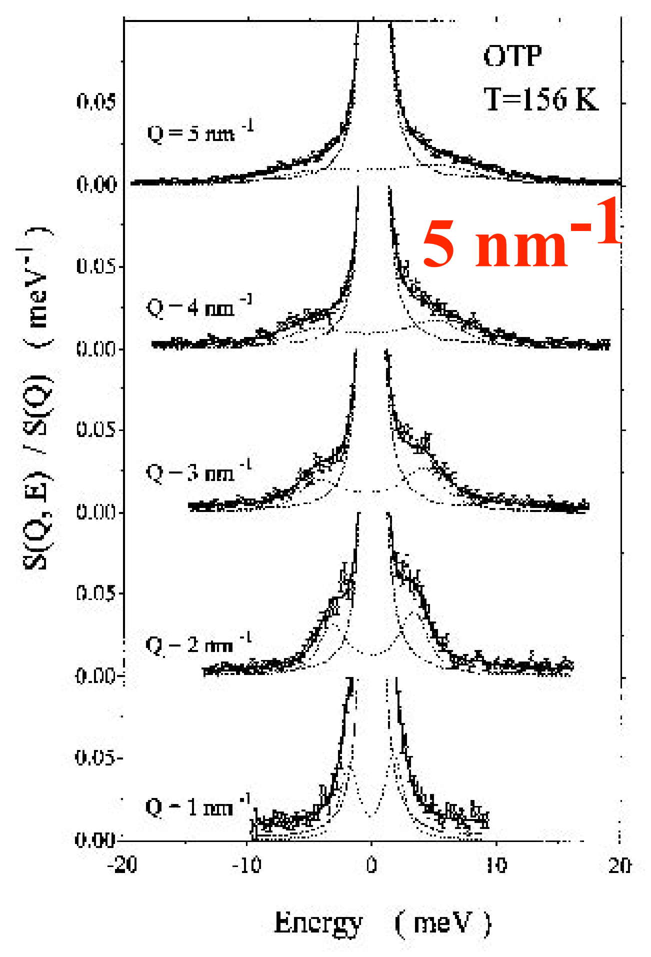
'Crystal-like' Phonons in Amorphous Ice !



5 nm^{-1}

ortho-Terphenyl

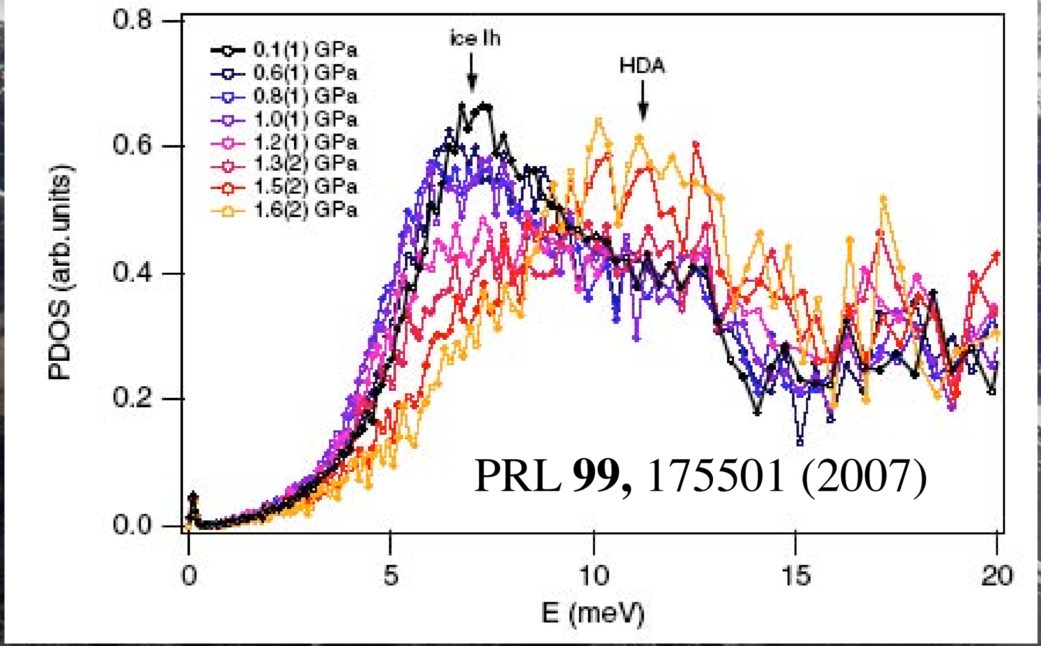
G. Monaco et al., *PRL* 80, 2161, (1998)



5 nm^{-1}

No signs of a glass

Mechanical instability?



PRL **99,** 175501 (2007)