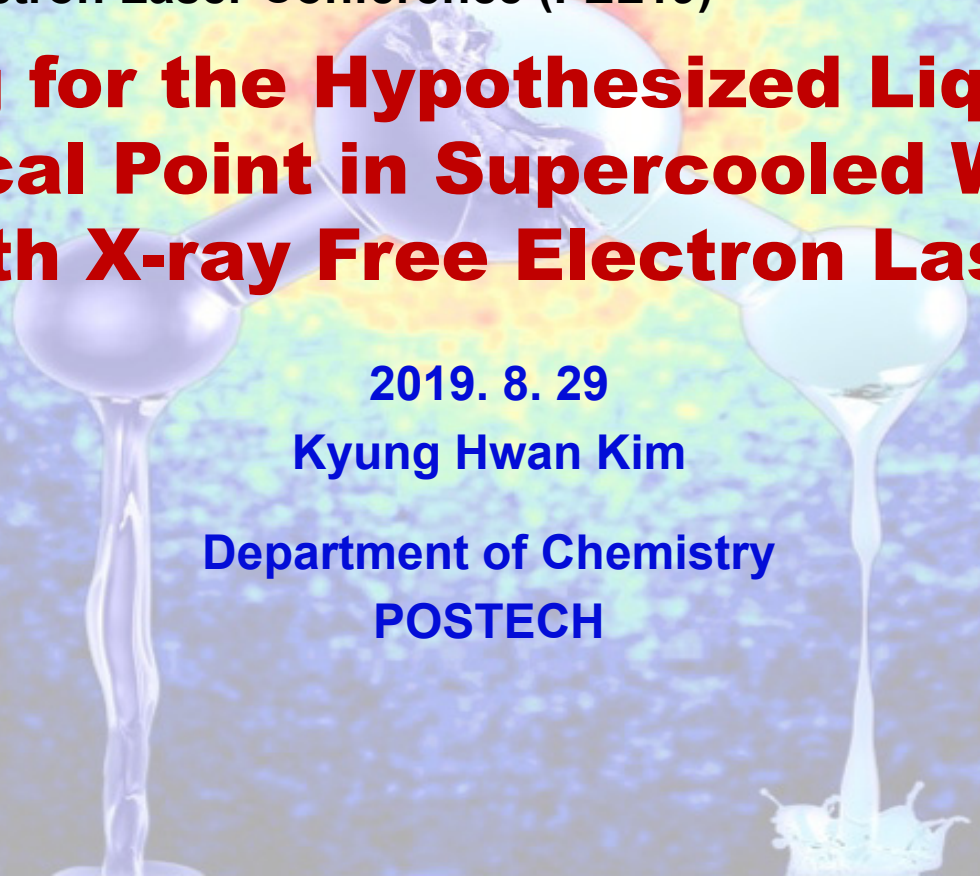
The 39th Free Electron Laser Conference (FEL19)

Searching for the Hypothesized Liquid-Liquid Critical Point in Supercooled Water with X-ray Free Electron Laser

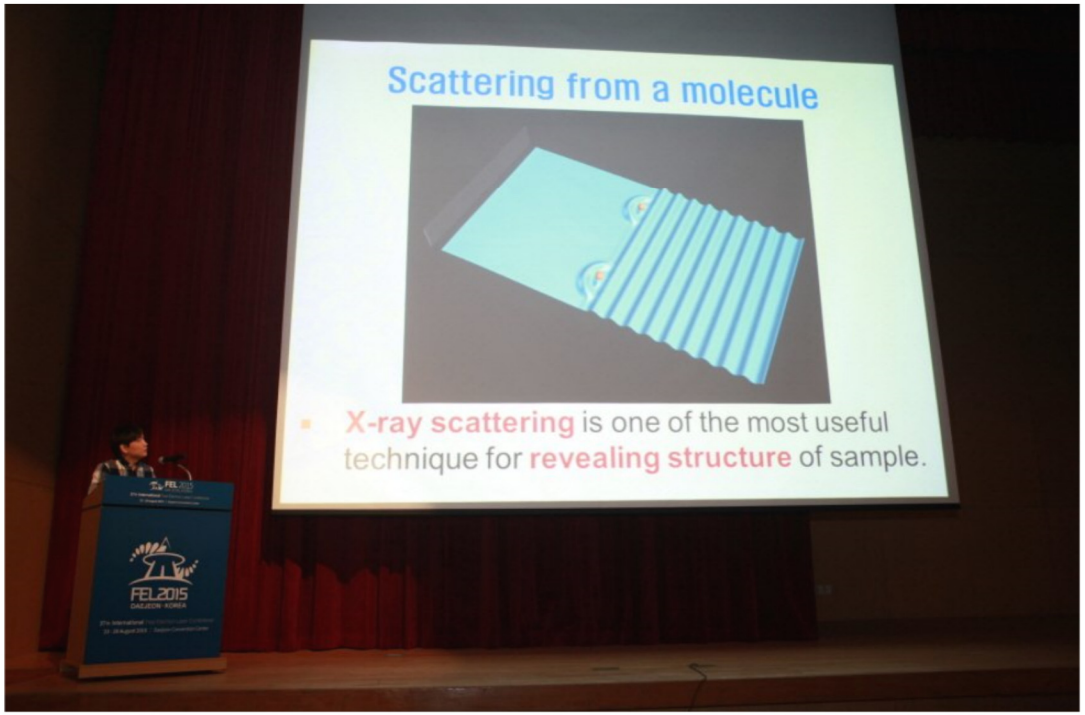
2019. 8. 29

Kyung Hwan Kim

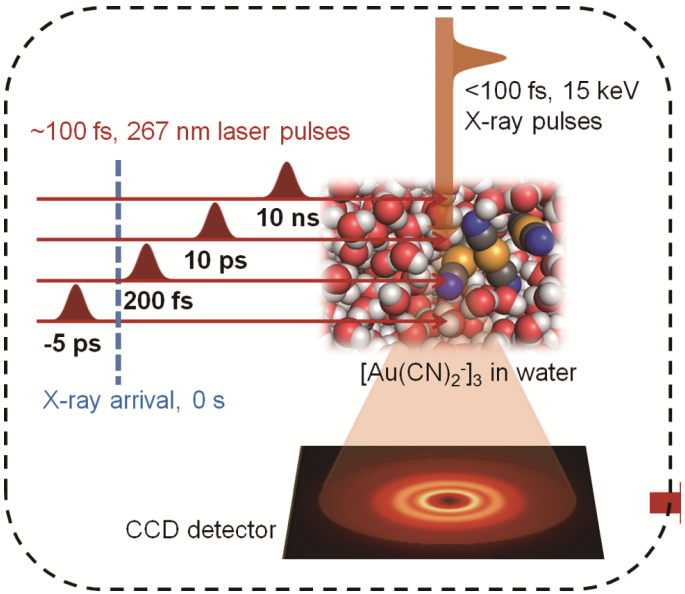
Department of Chemistry
POSTECH

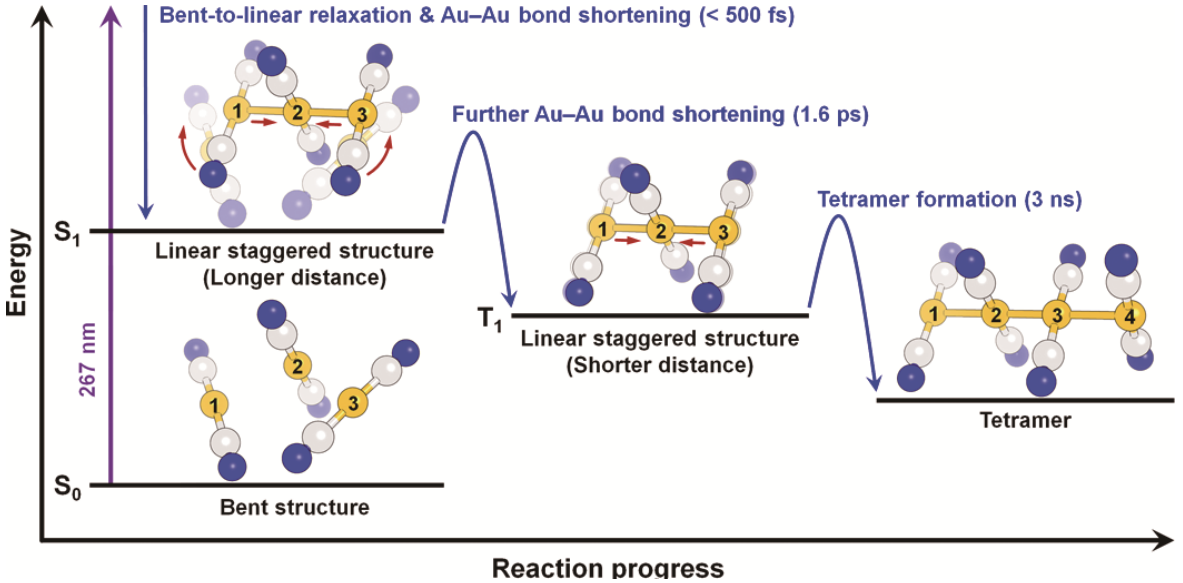



FEL2015
DAEJEON·KOREA
37th International Free Electron Laser Conference
23 - 28 August 2015 | Daejeon Convention Center


Scattering from a molecule
X-ray scattering is one of the most useful technique for revealing structure of sample.
FEL2015

Direct observation of bond formation in solution





- Laser induced Au-Au bond formation.
- The first direct observation of bond-making process in solution by utilizing ultrashort X-ray pulses.

K. H. Kim *et al.*, *Nature,* **518**, 385 (2015).
Measurements done at **SACLA**

PAL-XFEL

Beamtime at PAL-XFEL

- **The first user experiment** at PAL-XFEL (2017. 6)

- The first paper based on the user experiment.

K. H. Kim and A. Späh *et al. Science*, **358**, 1589-1593 (2017).

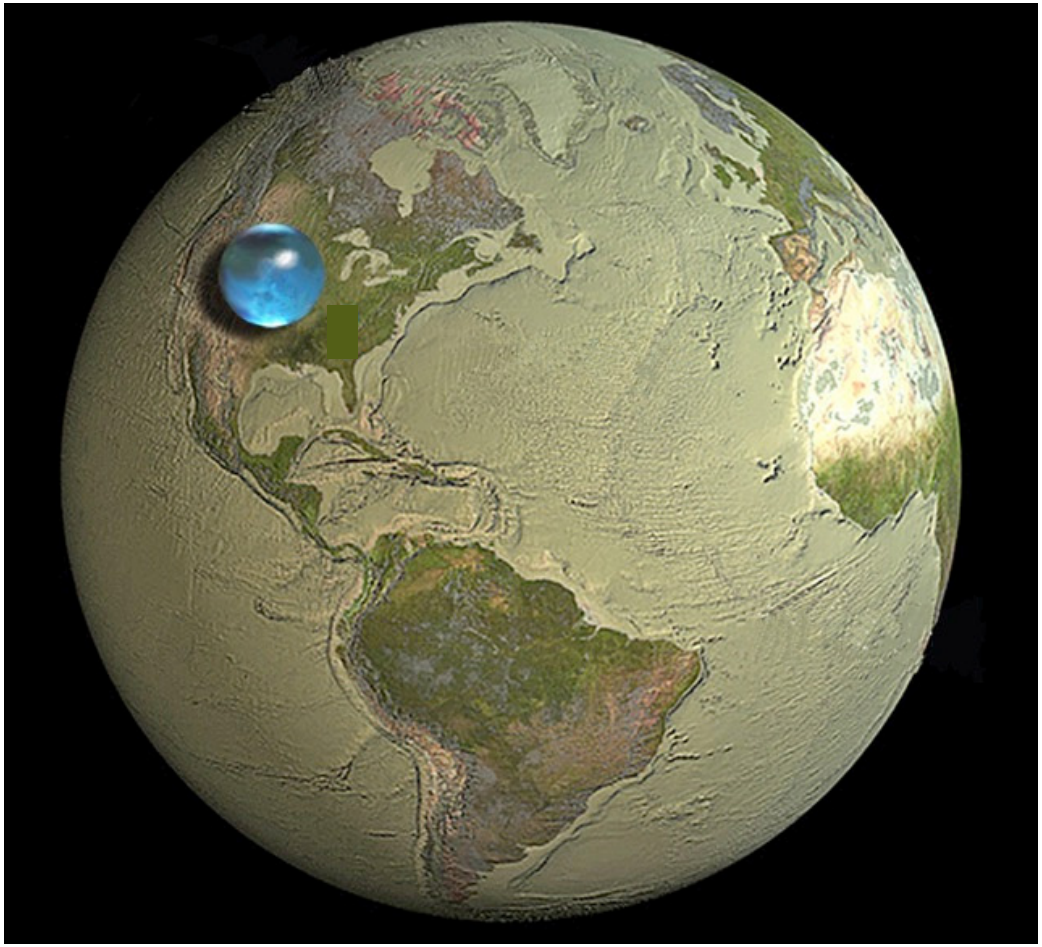
- Three more beamtime experiments afterwards.

K. H. Kim and K. Amman-Winkel *et al.* manuscript in preparation.

https://www.youtube.com/watch?v=htitSKjLwcA

Water:

One of the most important compound for life, physics, chemistry, etc…



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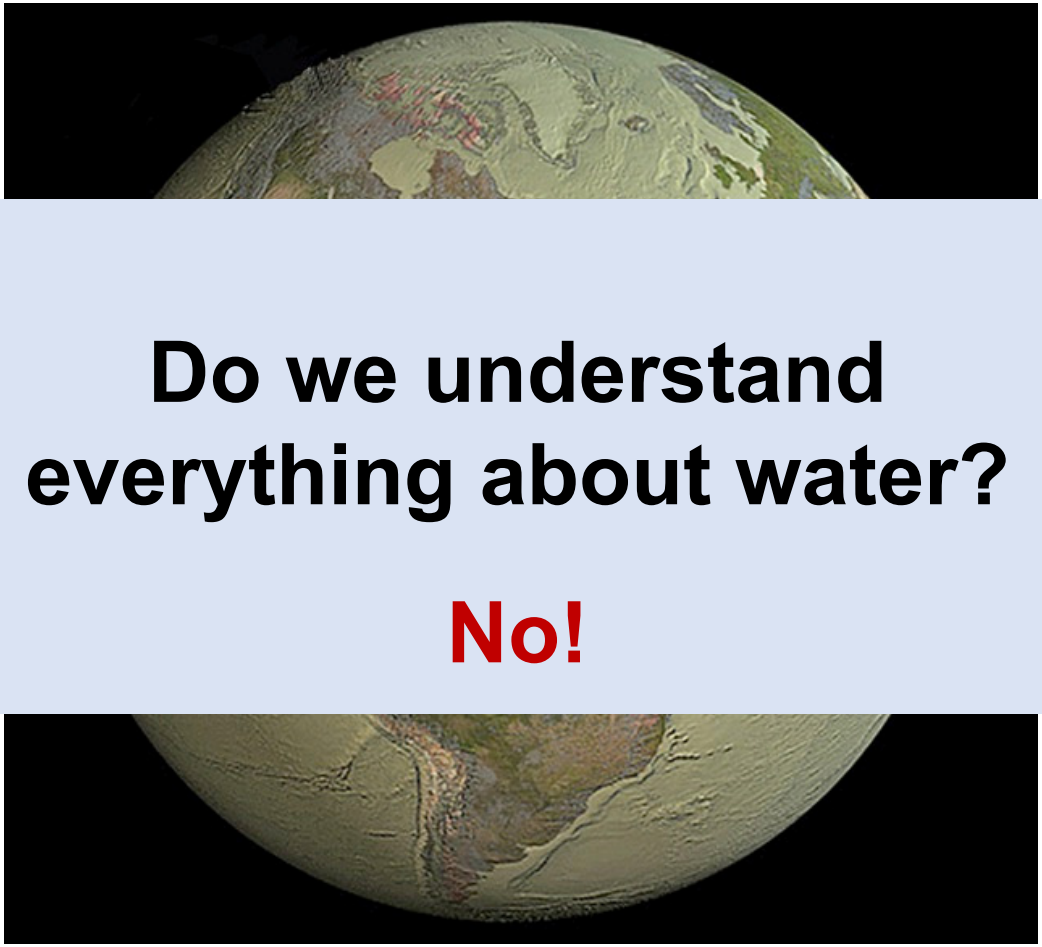


Do we understand everything about water?

No!

Anomalous Properties of Water

- The most important compound for life, physics, chemistry, etc…
- Water has numerous physical and chemical properties which are **very different from other liquids**.

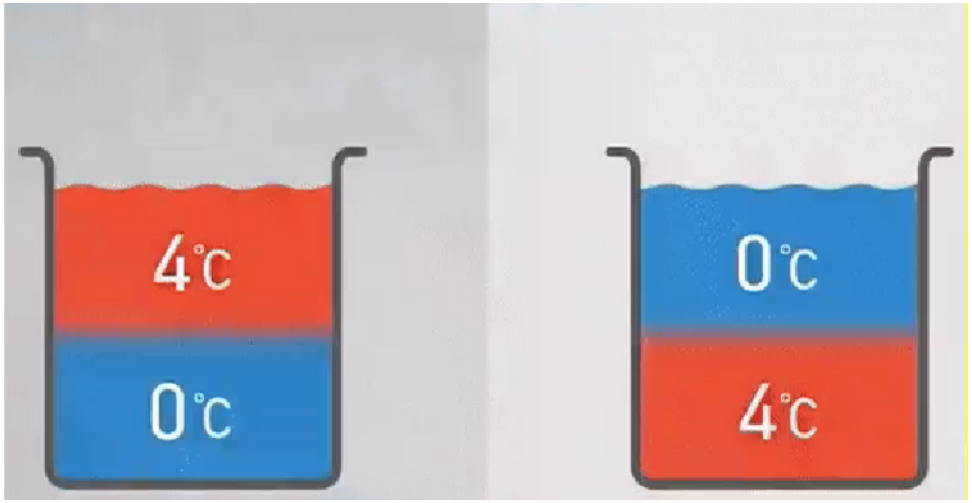
Anomalous properties of water

0 °C

4 °C

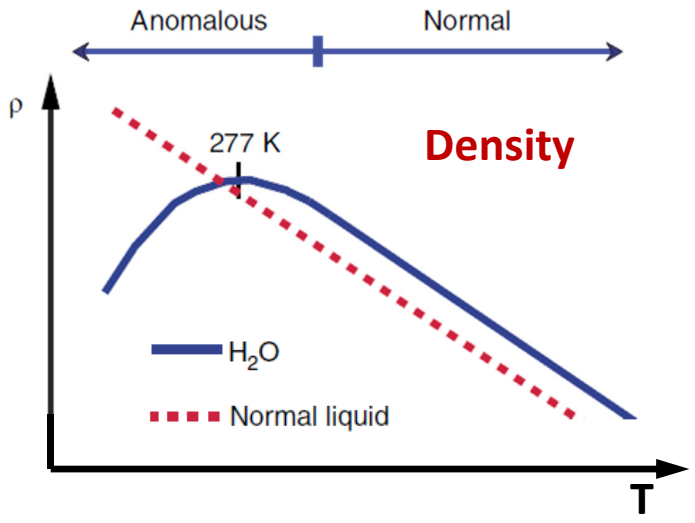
Normal liquid

Water

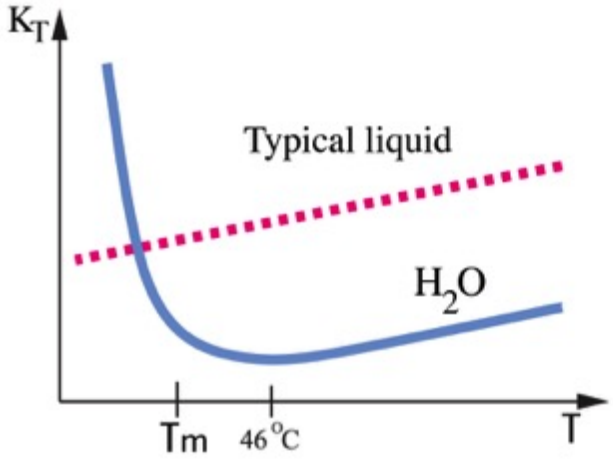


http://news.sbs.co.kr/news/endPage.do?news_id=N1004542949&plink=ORI&cooper=NAVER

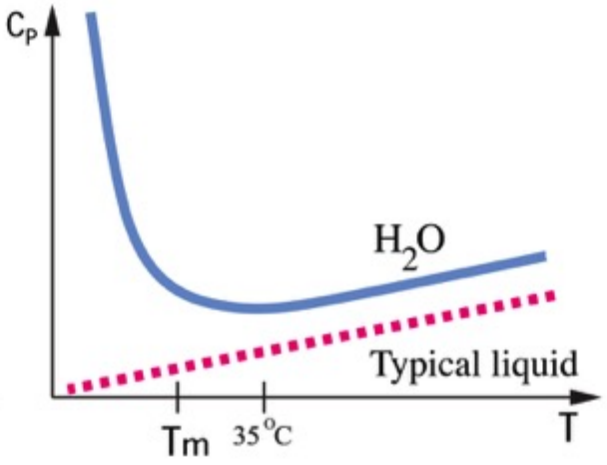
Anomalous Properties of Water



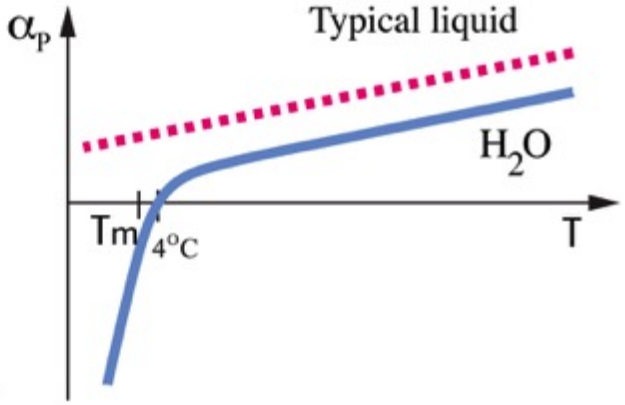
- The deviation speeds up when it become supercooled.
- Divergence towards a mysterious temperature of -45 °C.



Isothermal Compressibility



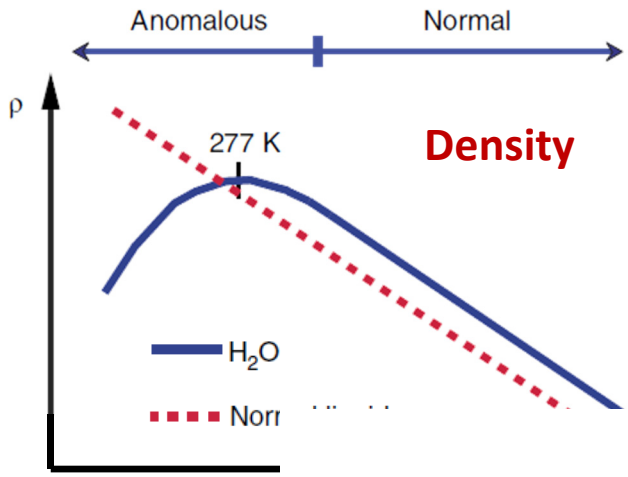
Heat Capacity



Thermal expansion

P. Kumar, S. Han, H.E. Stanley, *J. Phys.: Condens. Matter* **21**, 504108 (2009).

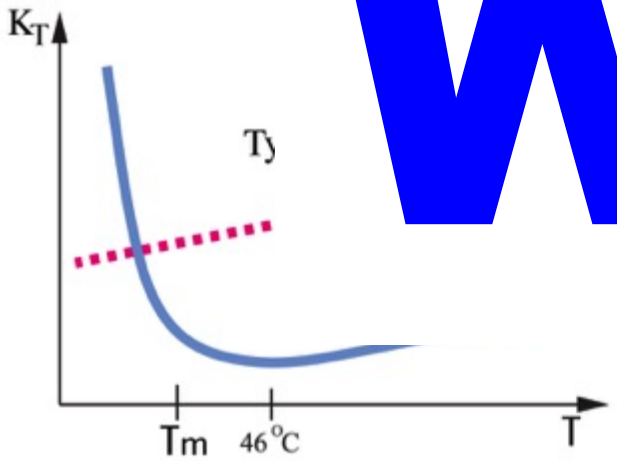
Anomalous Properties of Water



Density

- The deviation speeds up when it become supercooled.
- Divergence towards a mysterious temperature of -45 °C

Why?



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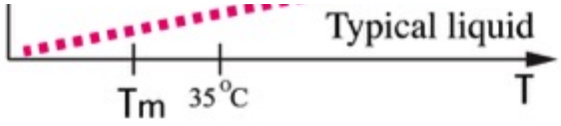

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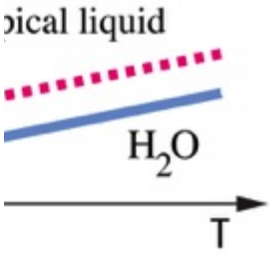

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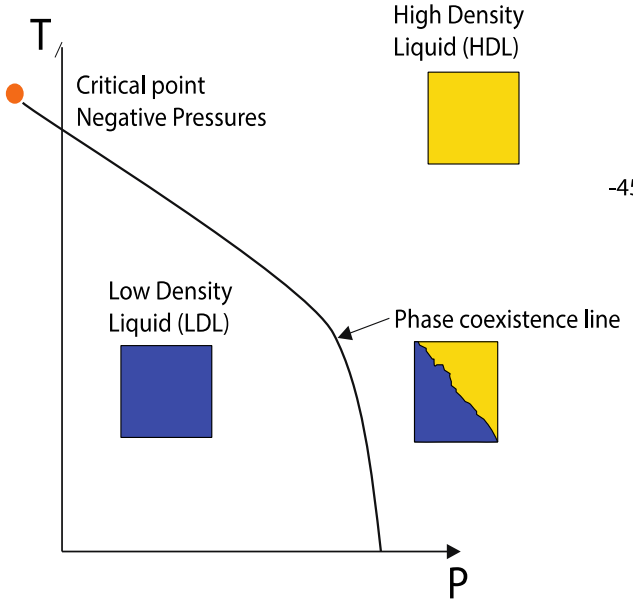
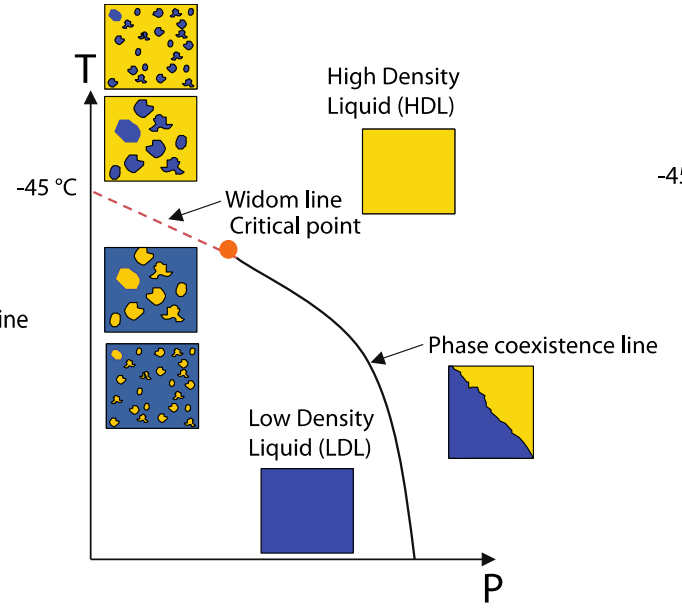
Origin of the Anomalous properties - Suggested models

Critical Point Free Model
Critical Point at negative P



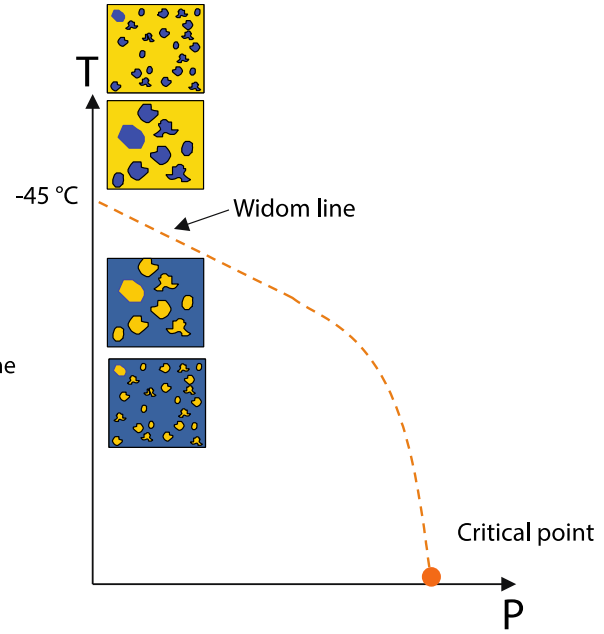
C.A. Angell, *Science* **319**, 582 (2008).

Critical Point Model
Critical Point at positive P



P.H. Poole *et al.*, *Nature* **360** (1992) 324.

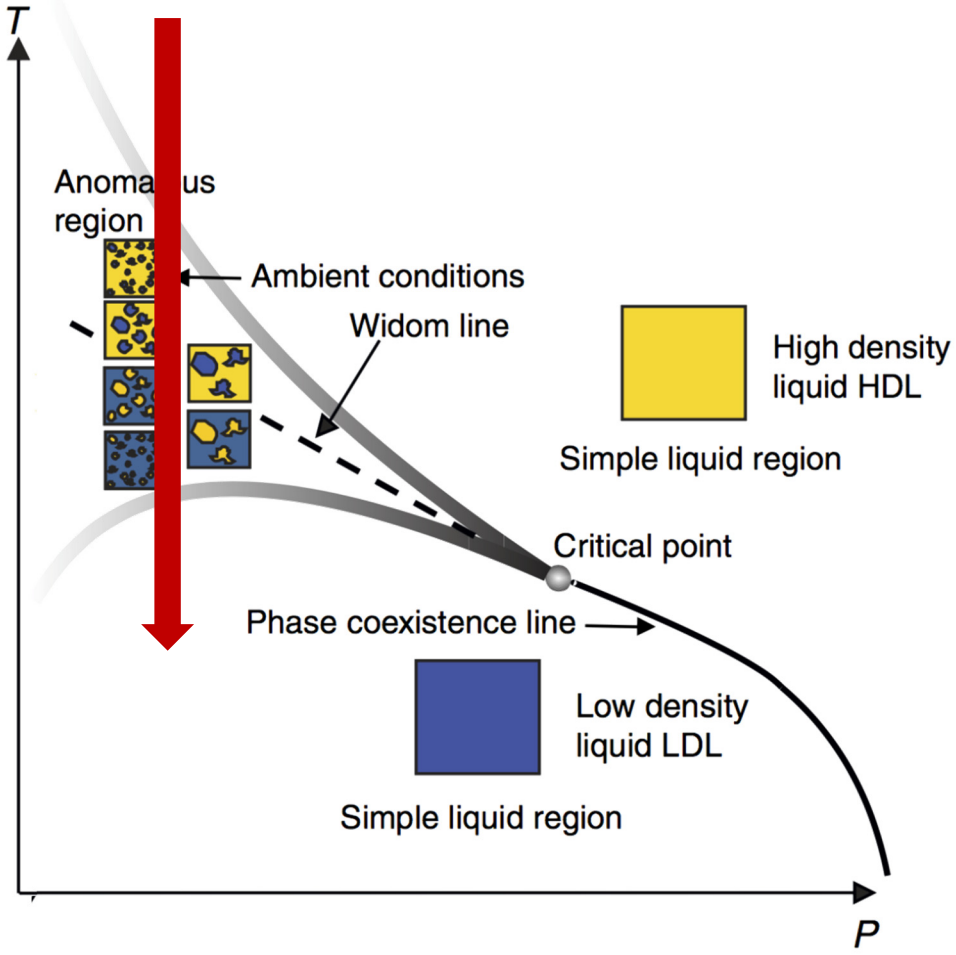
Singularity Free Model
Critical Point at 0 K



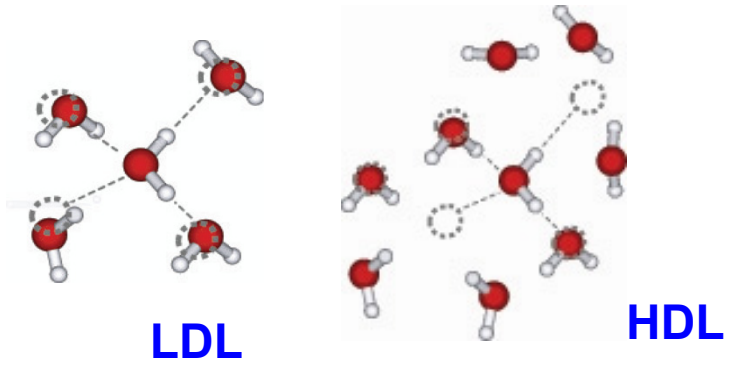
S. Sastry, *et al.*, *Phys. Rev. E* **53**, 6144 (1996)

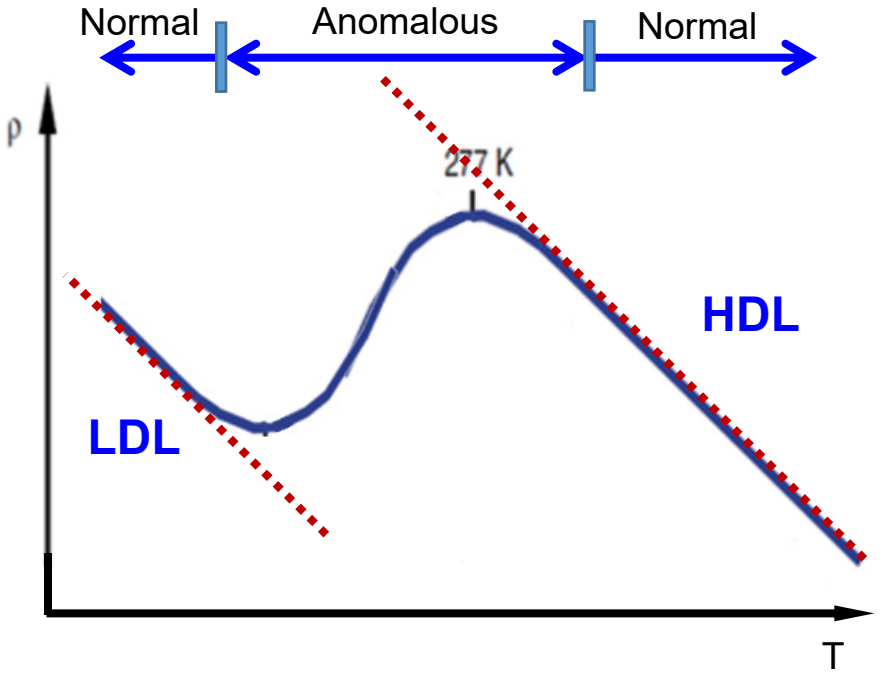
- There has been an **intense debate** for a long time.

Origin of the Anomalous properties - LLCP model



Nilsson et al. *Nat. Commun.* **6**, 8998 (2015)





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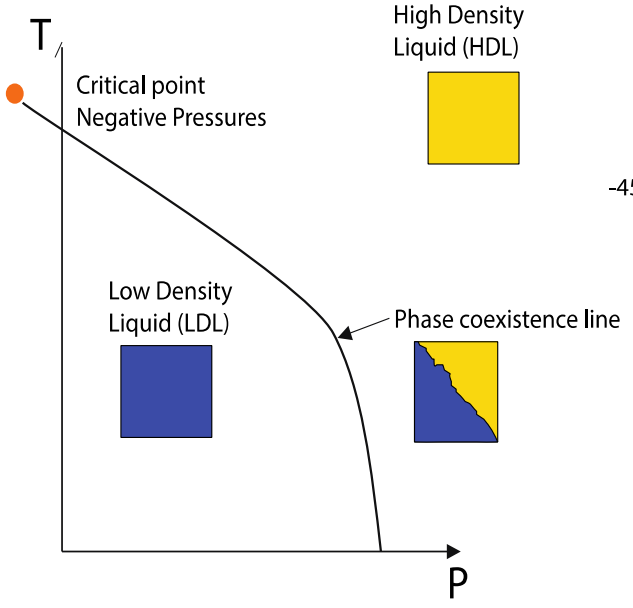

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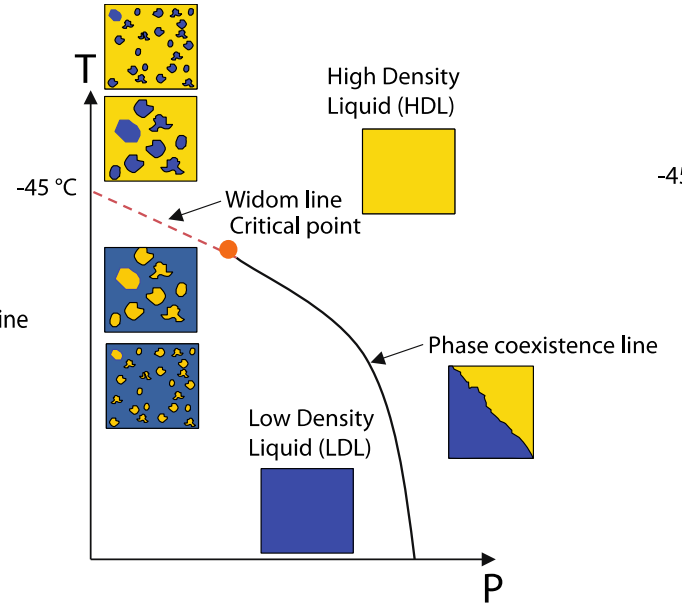

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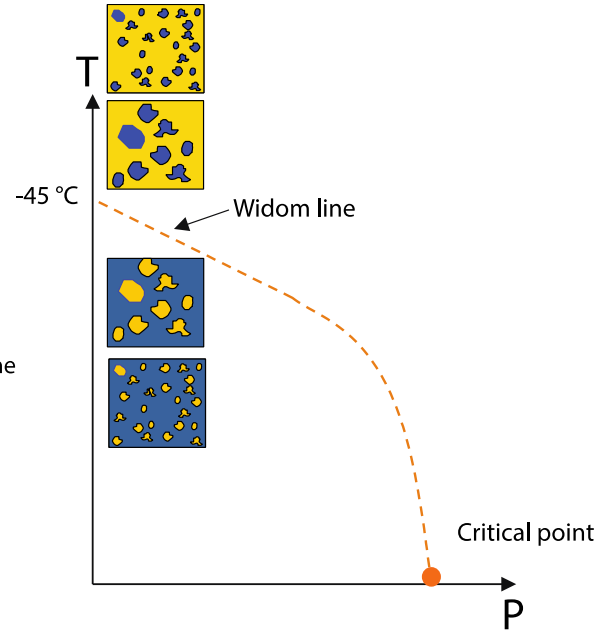

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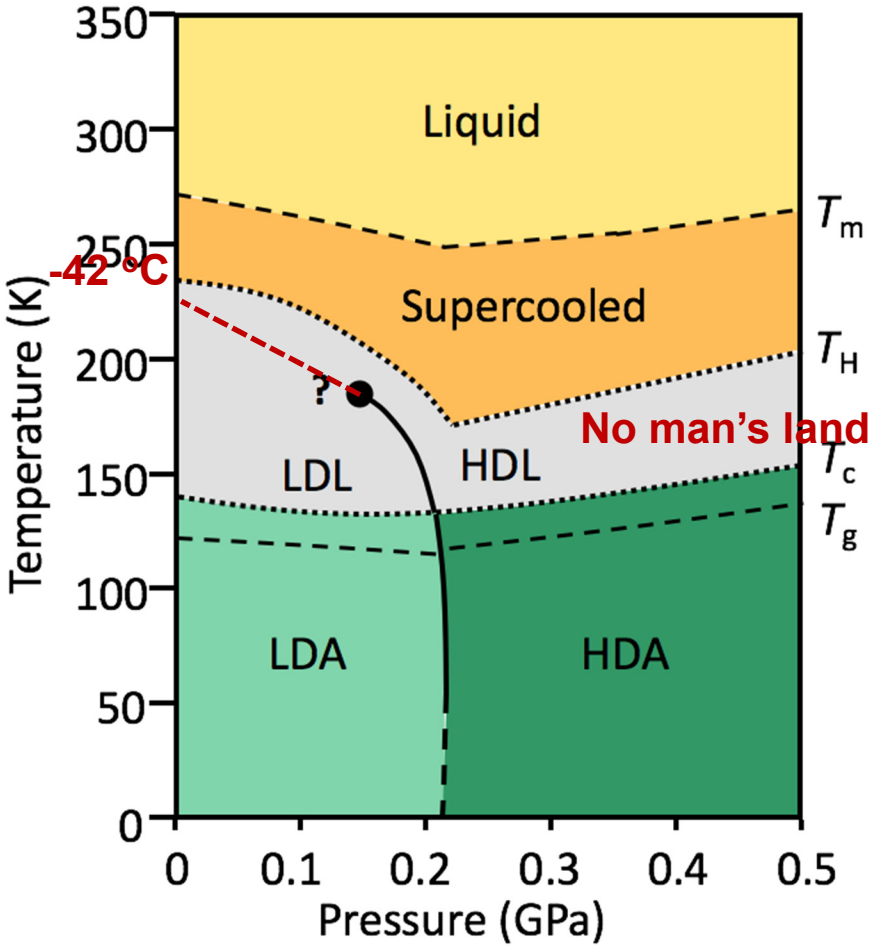
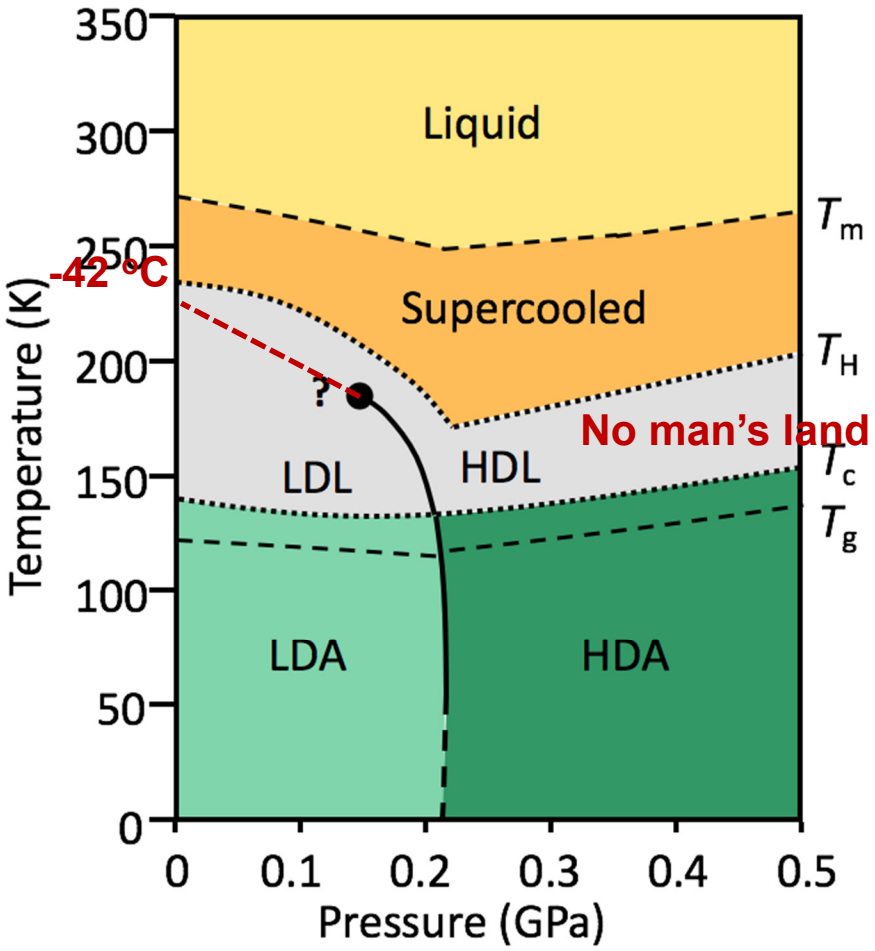
Supercooled Water



https://www.youtube.com/watch?v=Fot3m7kyLn4

Expedition to the LLCP



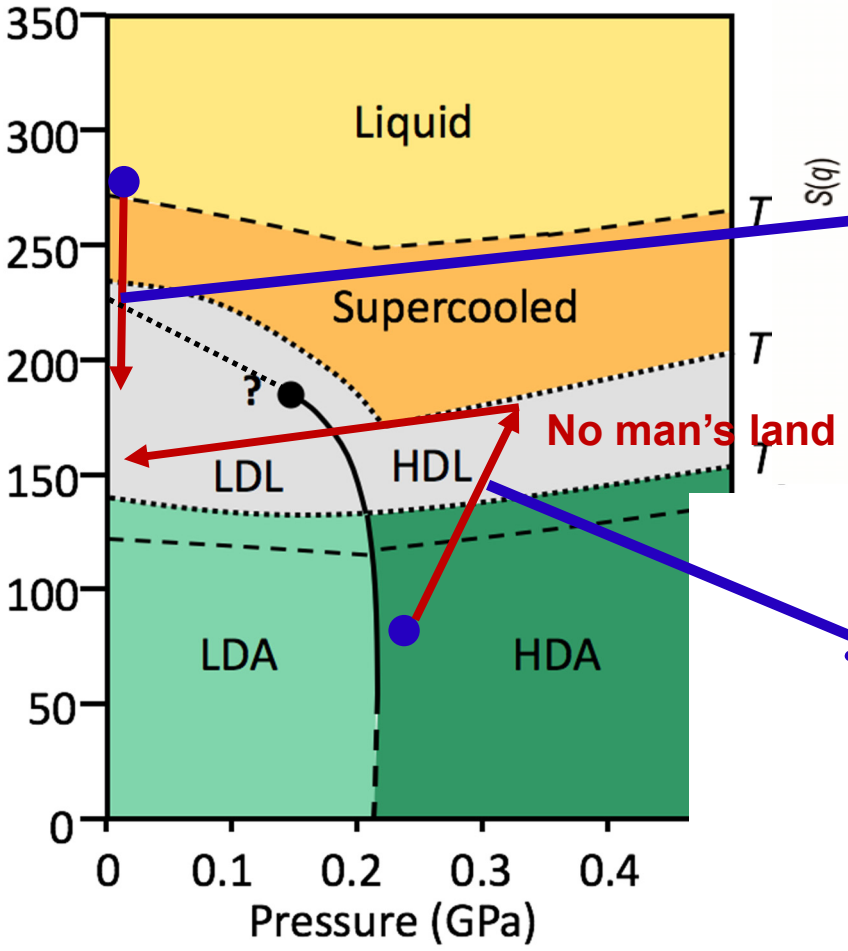
- Crystallization has prevented measurements below the homogeneous nucleation temperature (T_H) leading to a "no-man's land".
- Phase transition between HDL and LDL, second critical point, and Widom line are **hidden in No man's land** and were experimentally inaccessible.

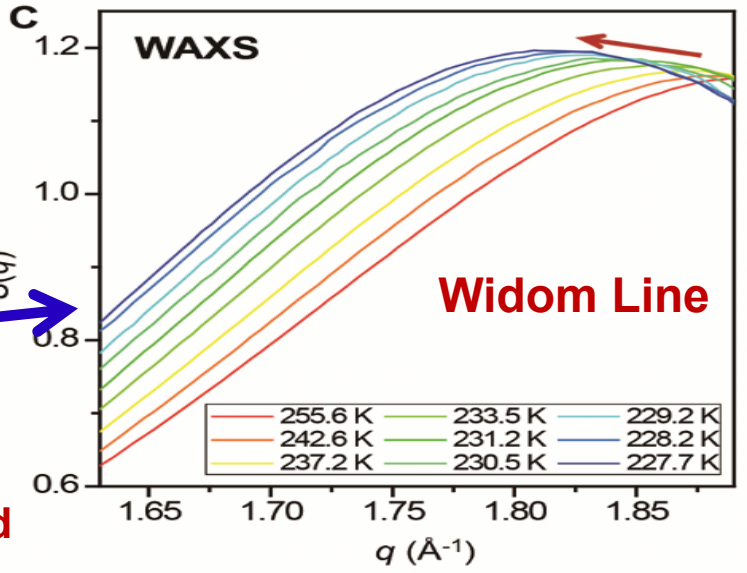
Make deeply supercooled bulk liquid water for a very short time

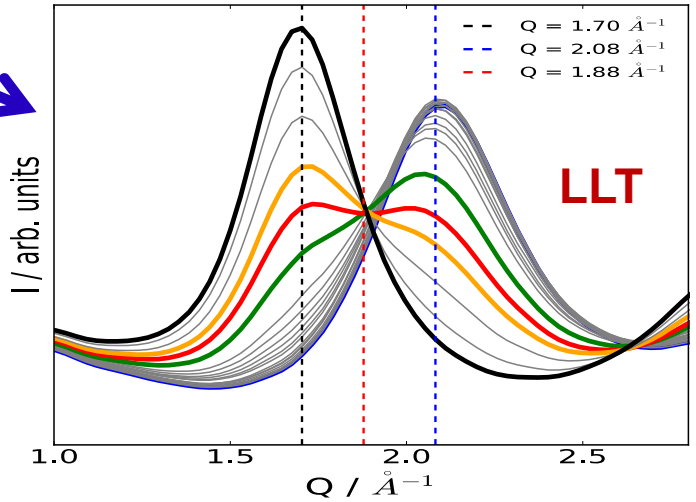
+

Advent of 4th generation X-ray source (X-ray free electron laser)

Expected Results: WAXS

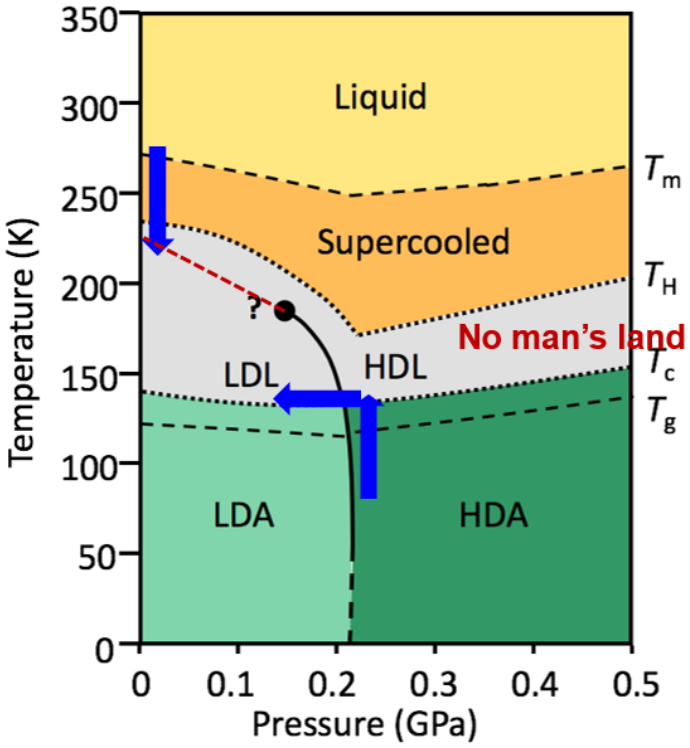






The Mystery of Water Revealed from X-ray Experiments at PAL-XFEL

Experimental verification of the hypothesized LLCP model.



LLCP model shown in the phase diagram

The structural origin of water's anomalous properties are reveled by verifying **LLCP** model **(Widom line & LLT)** experimentally.

- **From above:**
  - Evaporative fast cooling of micron-sized droplets.
  - Cooling rate > Crystallization
  - Searching for the Widom line

K. H. Kim and A. Späh *et al. Science,* **358**, 1589 (2017)

- **From below:**
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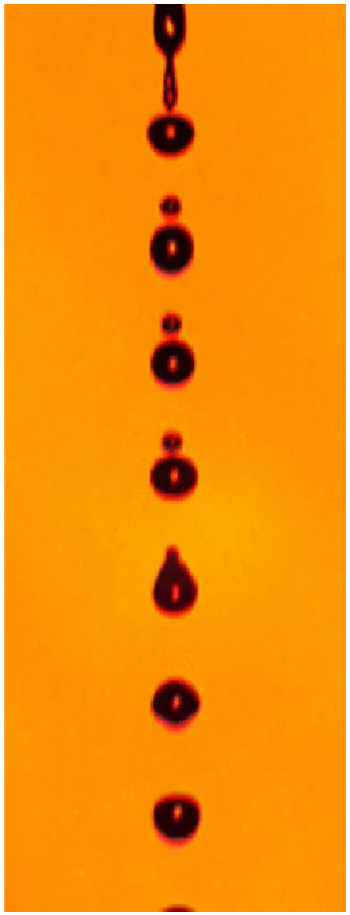
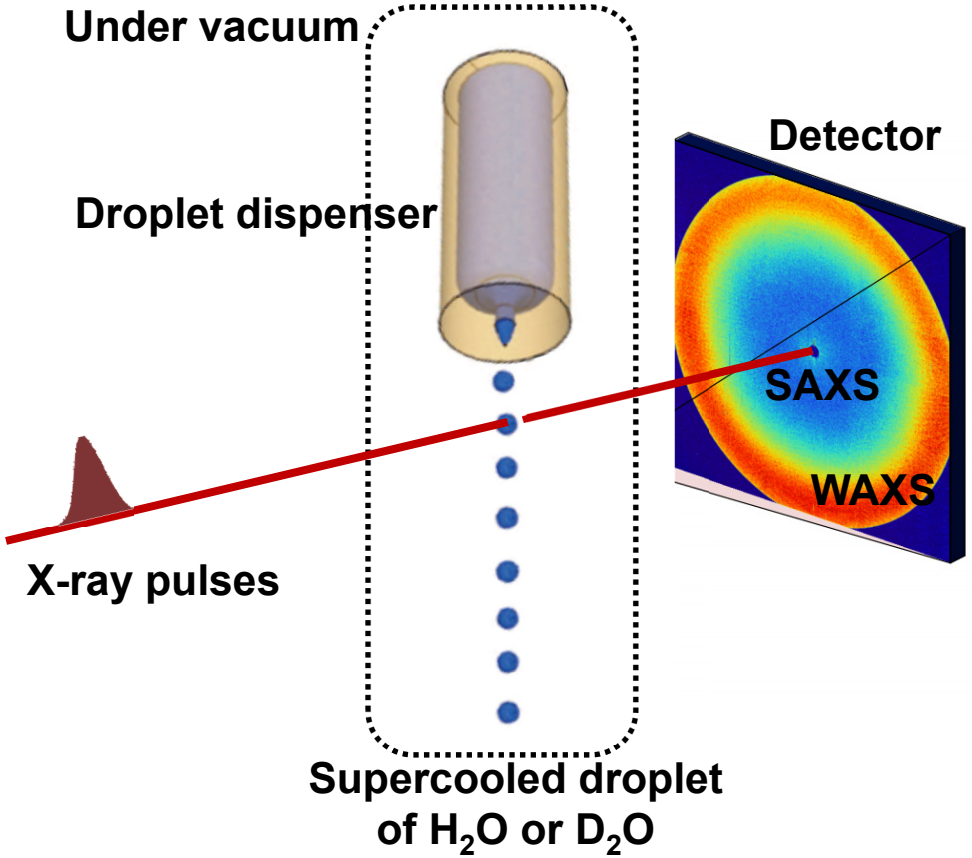
K. H. Kim and K. Amman-Winkel *et al.* manuscript in preparation.

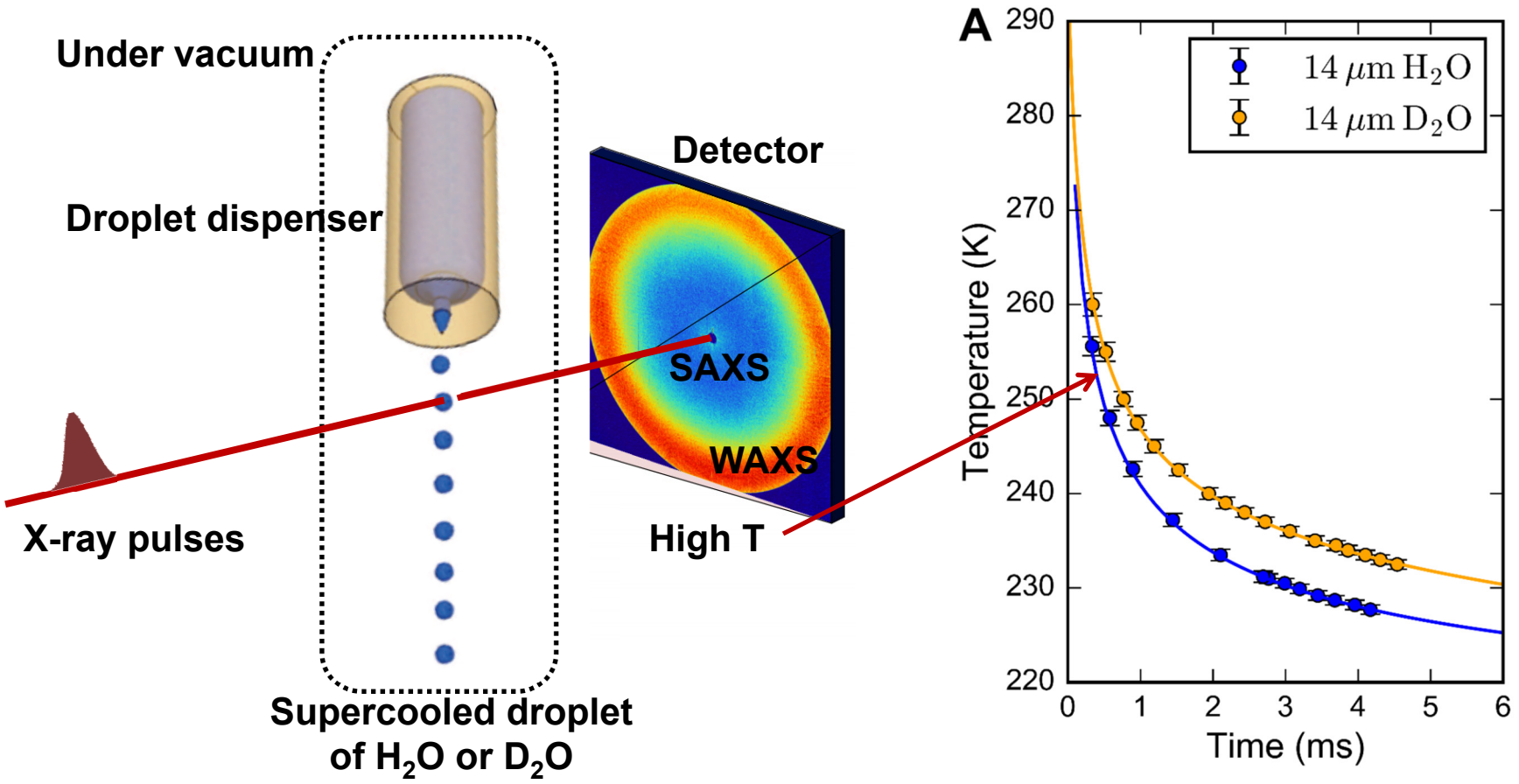
Evaporative cooling





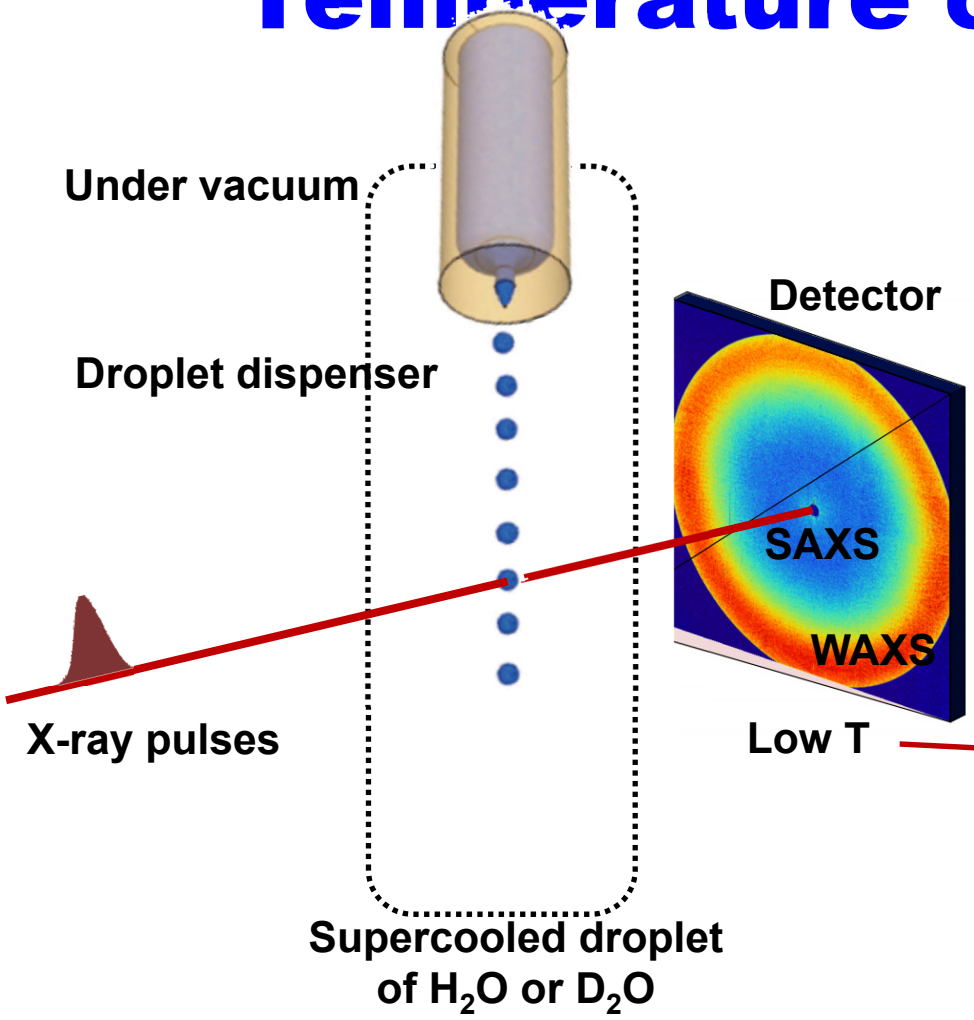
- Cooling rate is faster than homogeneous nucleation rate down to ~227 K.

Temperature calibration

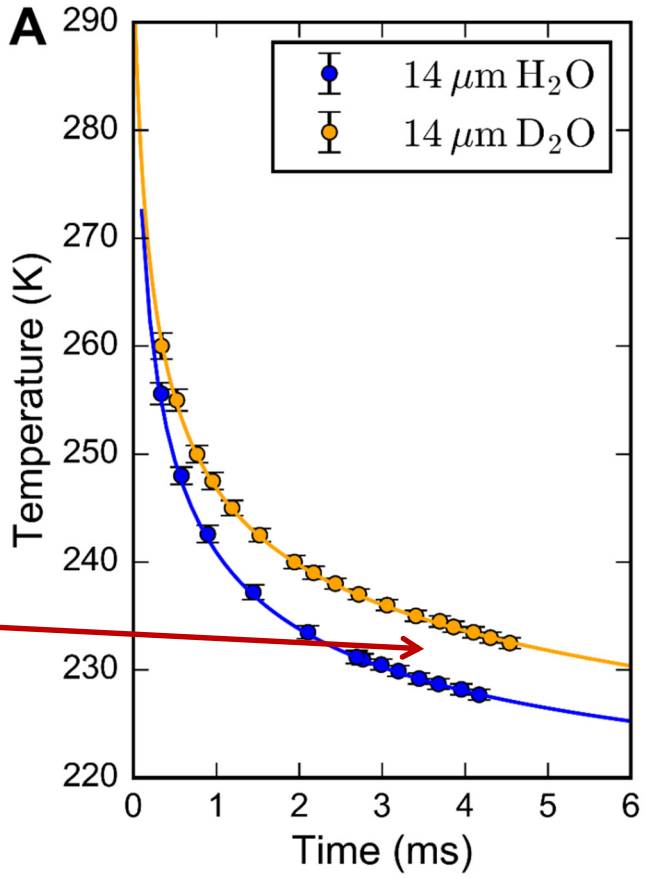


- Knudsen theory of evaporative cooling
- Based on the size and speed of the droplets

Temperature calibration



Low T



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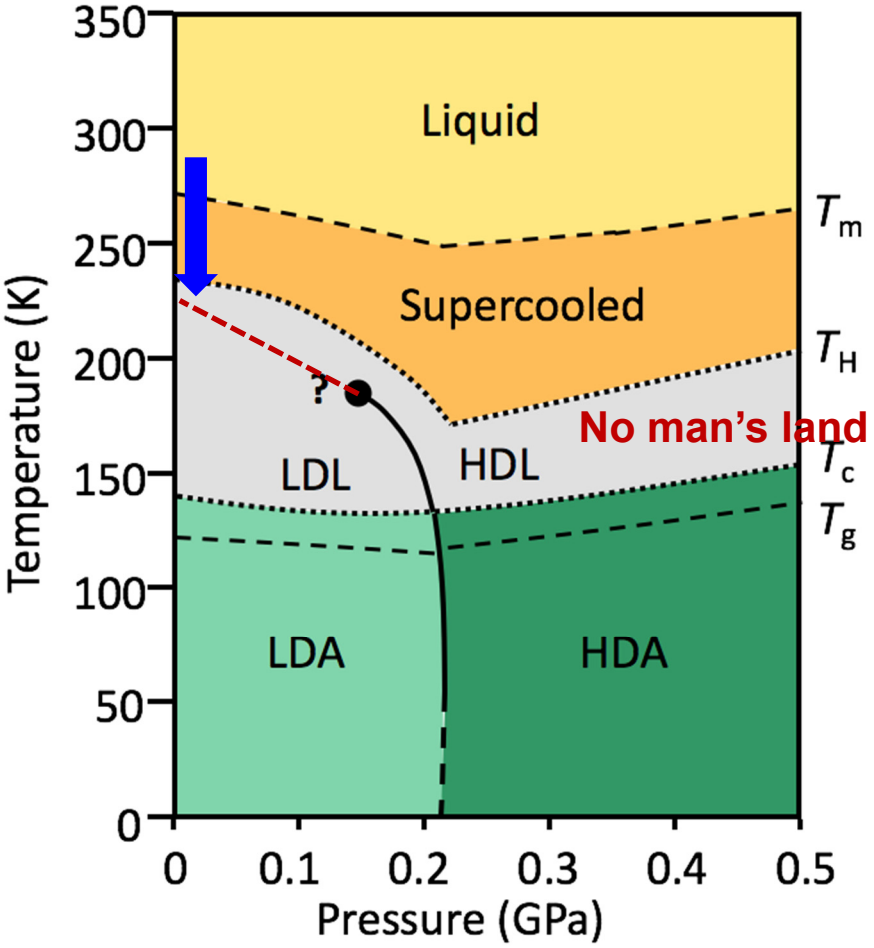
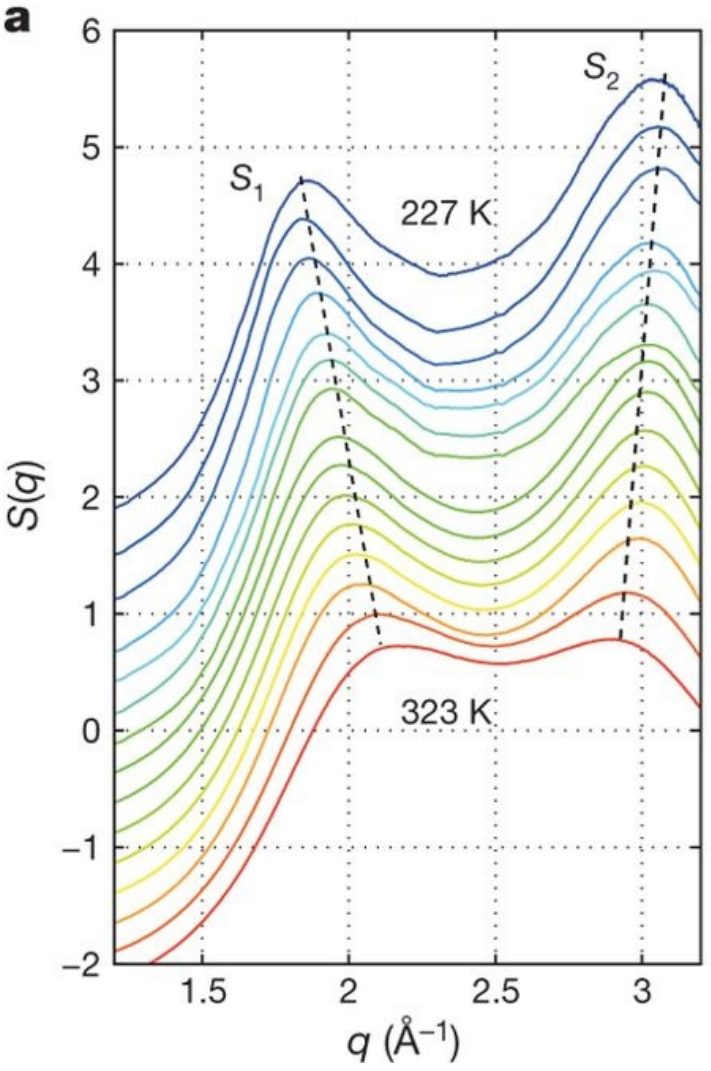
Entering into no man's land at LCLS



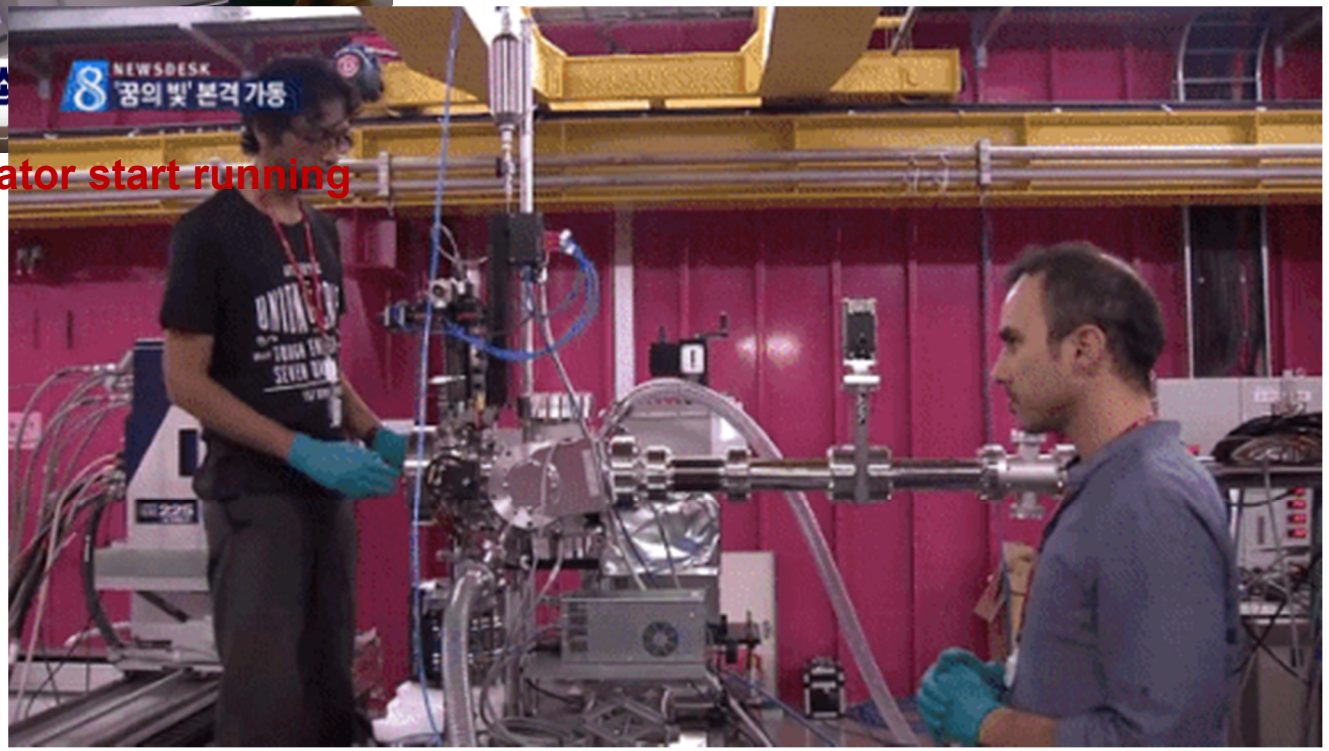


J. A. Sellberg *et al.*, *Nature* **510**, 381-384 (2014)

Beamtime at PAL-XFEL

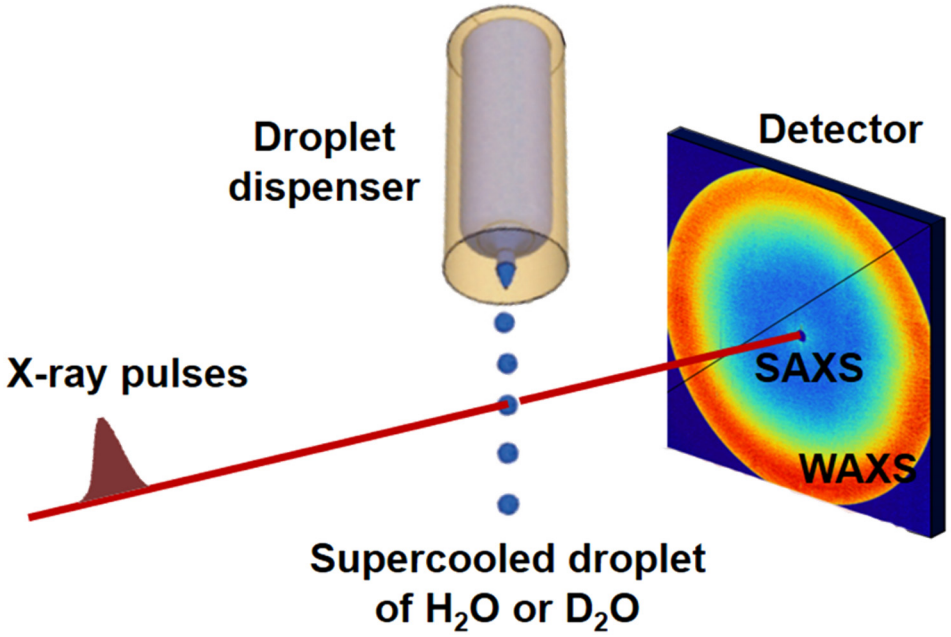
4th generation accelerator start running

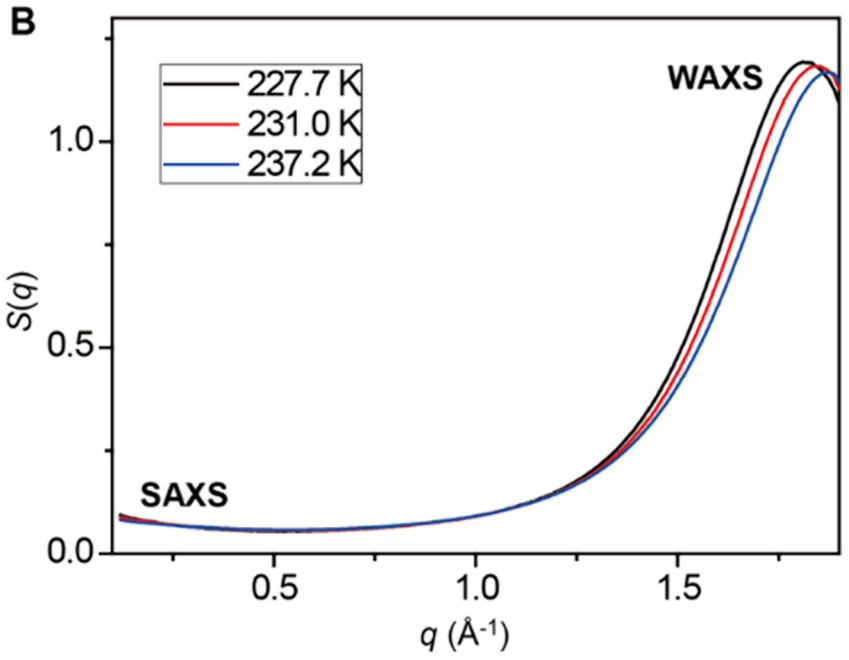
- **The first user experiment** at PAL-XFEL (2017. 6)



https://www.youtube.com/watch?v=htitSKjLwcA

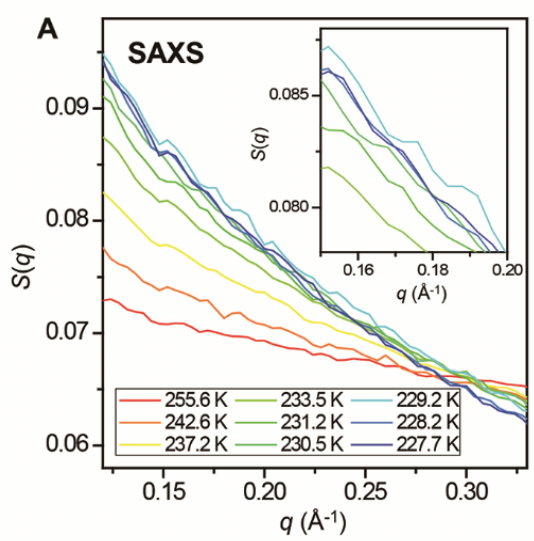
X-ray scattering (SAXS/WAXS)

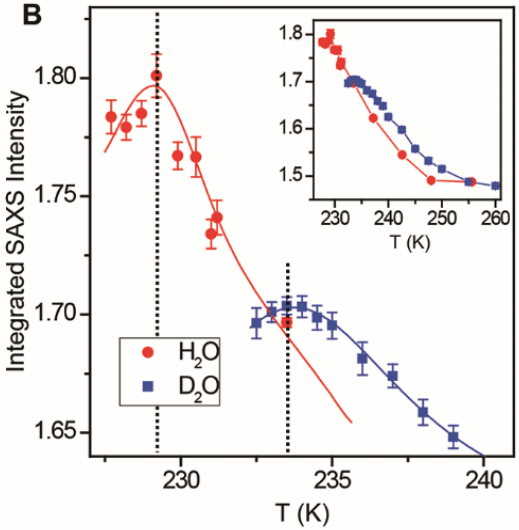


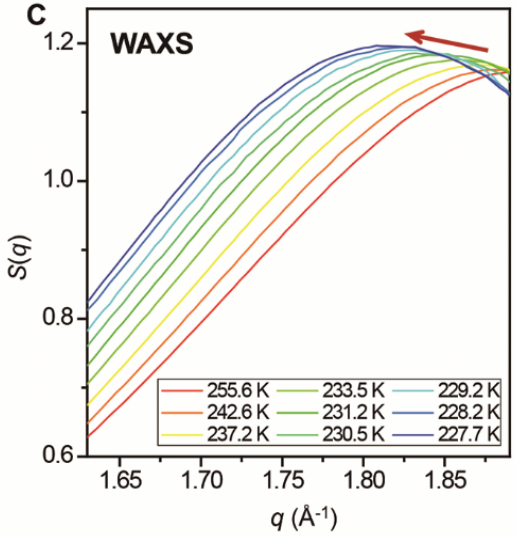


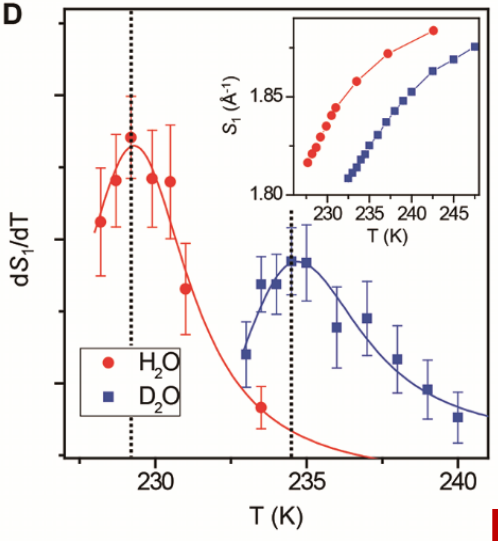
- Measure SAXS and WAXS at the same time with large area detector (Rayonix MX 225)

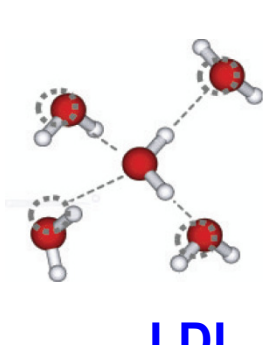
Beyond the Widom line

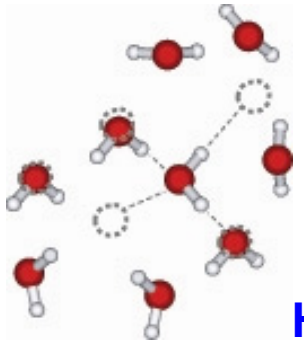




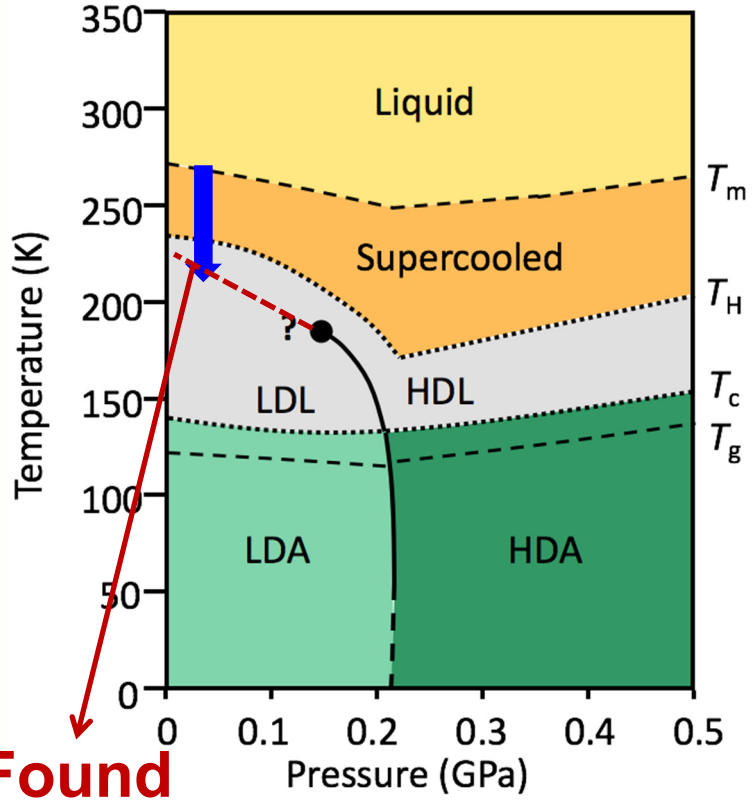








LDL HDL



K. H. Kim *et al. Science,* **358**, 1589 (2017)

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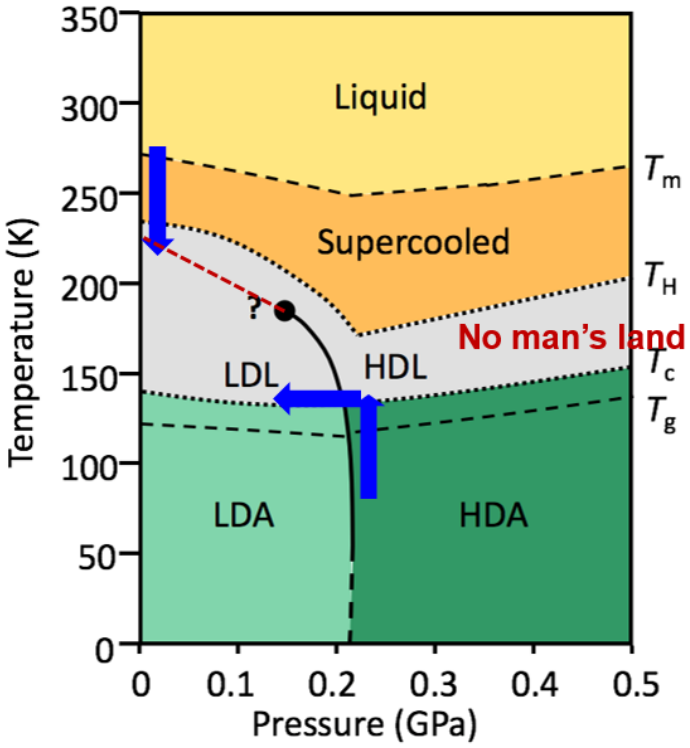

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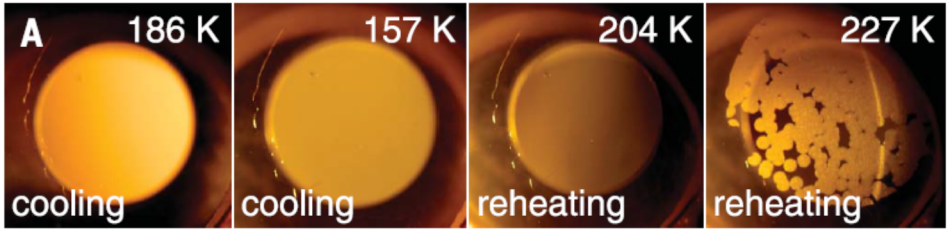
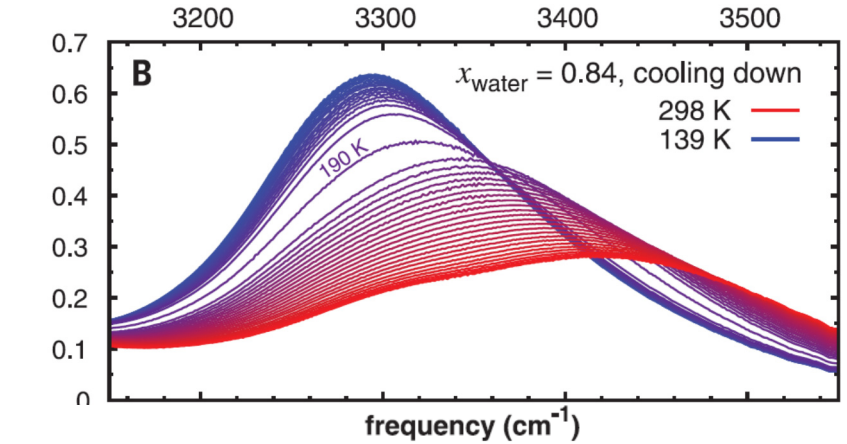
LLT in aqueous solution

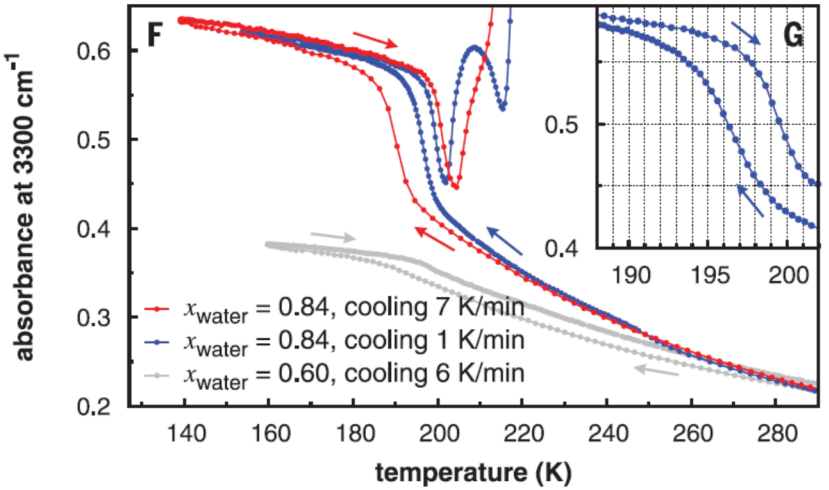
WATER STRUCTURE

A liquid-liquid transition in supercooled aqueous solution related to the HDA-LDA transition

Sander Woutersen,[1]* Bernd Ensing,[1,2] Michiel Hilbers,[1]
Zuofeng Zhao,[3] C. Austen Angell[3]*







- Found LLT from ionic liquid hydrazinium trifluoroacetate (N_2H_5TFA) solution (0.84 mole fraction of water)

Woutersen et al., *Science* **359**, 1127–1131 (2018)

Absence of LLT?

LETTER

542 | NATURE | VOL 569 | 23 MAY 2019

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Absence of amorphous forms when ice is compressed at low temperature

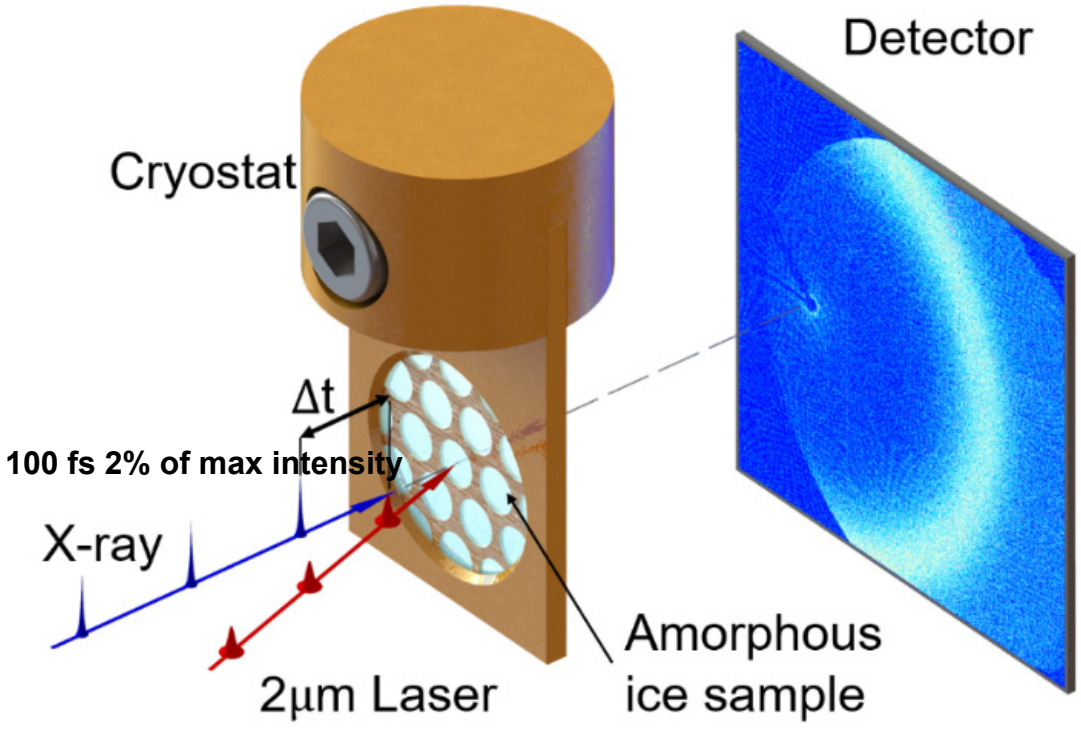
Chris A. Tulk[1]*, Jamie J. Molaison[1], Adam R. Makhluf[2], Craig E. Manning[2] & Dennis D. Klug[3]

By contrast, fast compression yields HDA but no ice IX, and direct transformation of ice I to ice XV′ is structurally inhibited. These observations suggest that HDA formation is a consequence of a kinetically arrested transformation between low-density ice I and high-density ice XV′ and challenge theories that connect amorphous ice to supercooled liquid water.

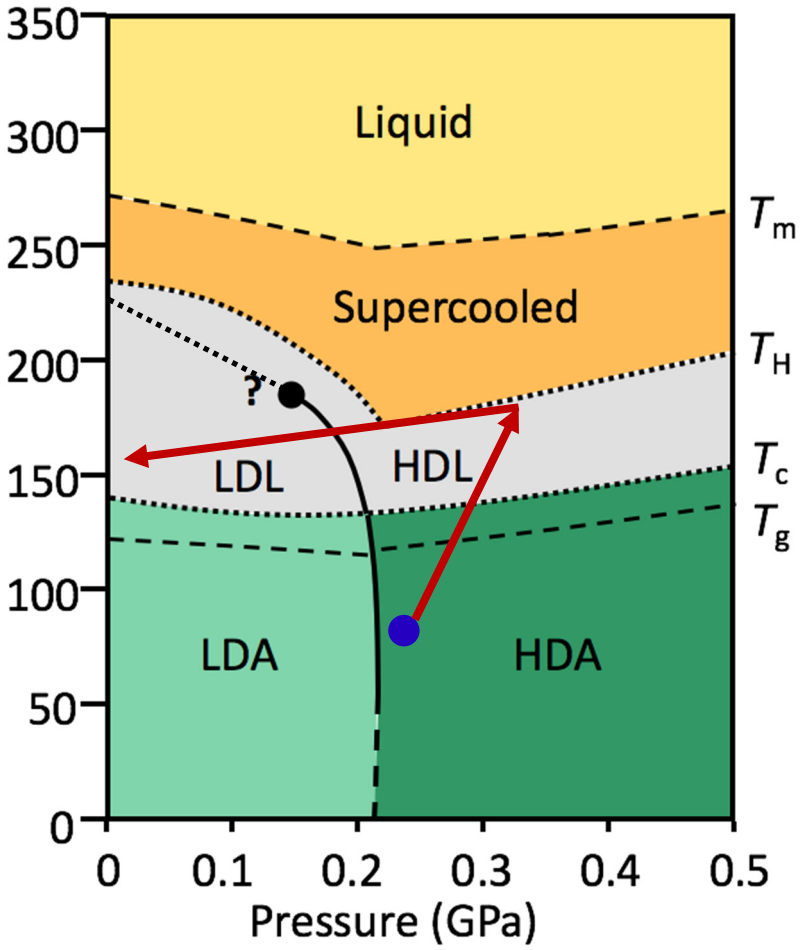
C. Tulk et al., *Nature* **569**, 542–546 (2019)

Direct & Clear evidence of the Liquid-Liquid Transition from pure bulk water?

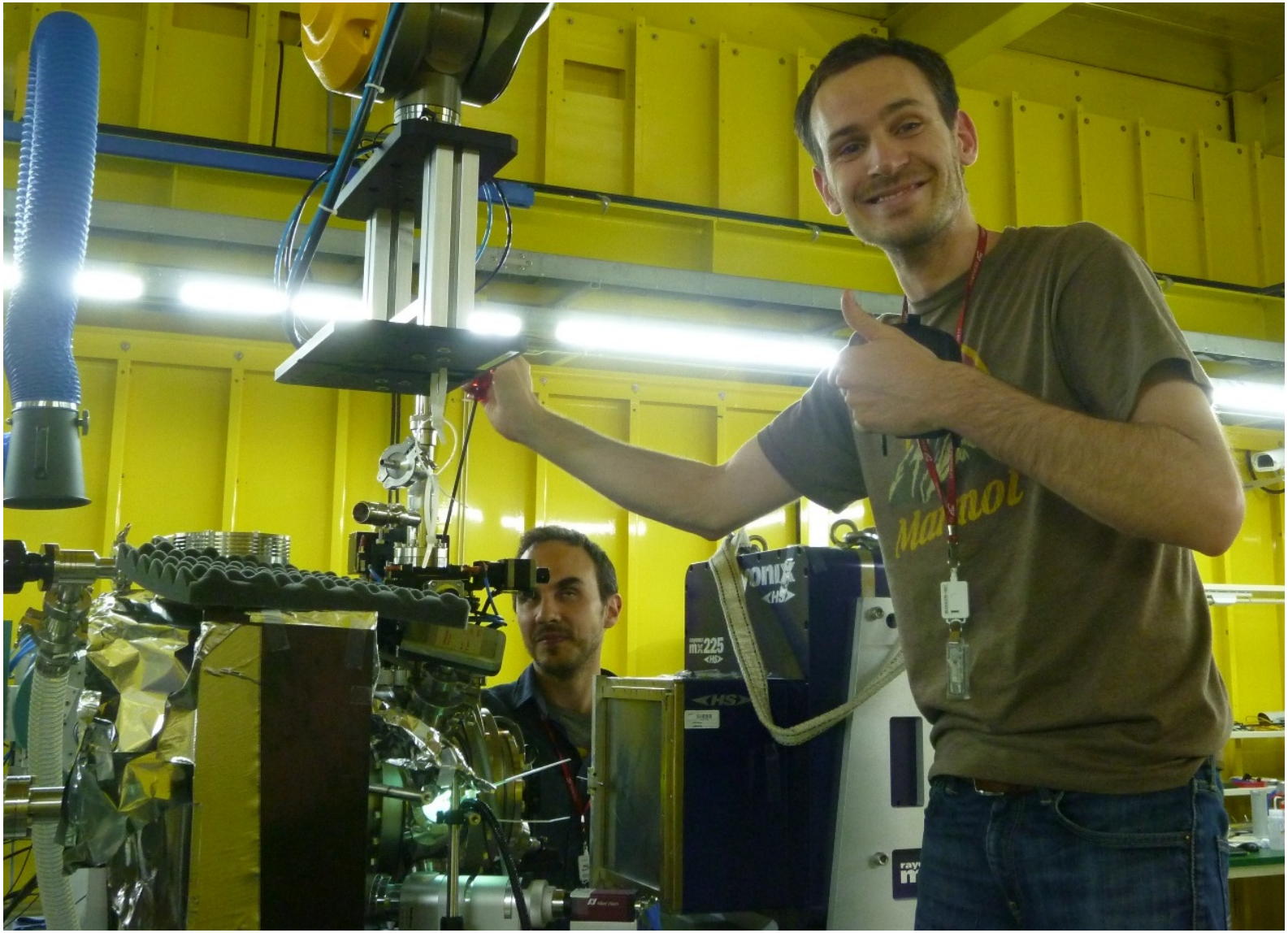
Introduce the Pump-Probe Scheme to Heat HDA to HDL



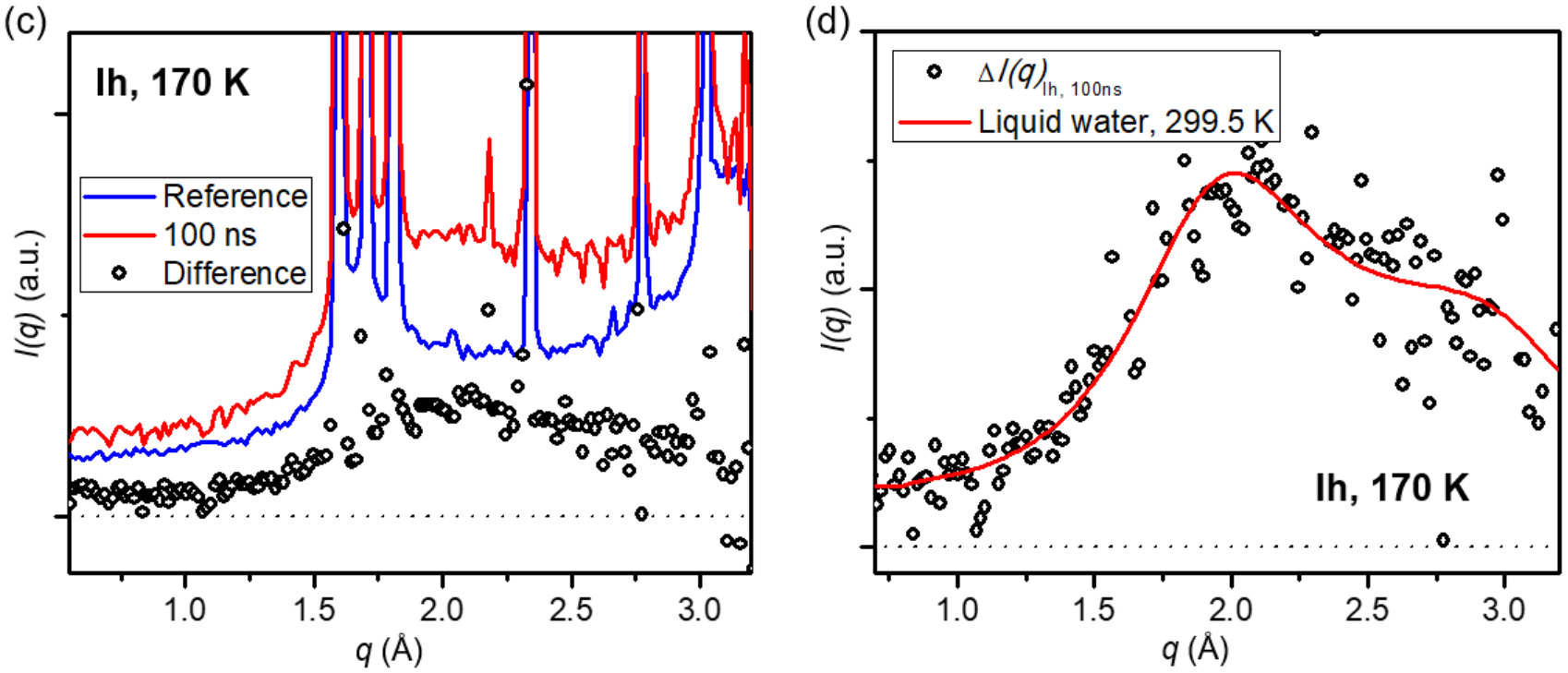
50 fs 2mm IR pulse 250 mJ
Excites OH stretch and bend



Experimental Setup



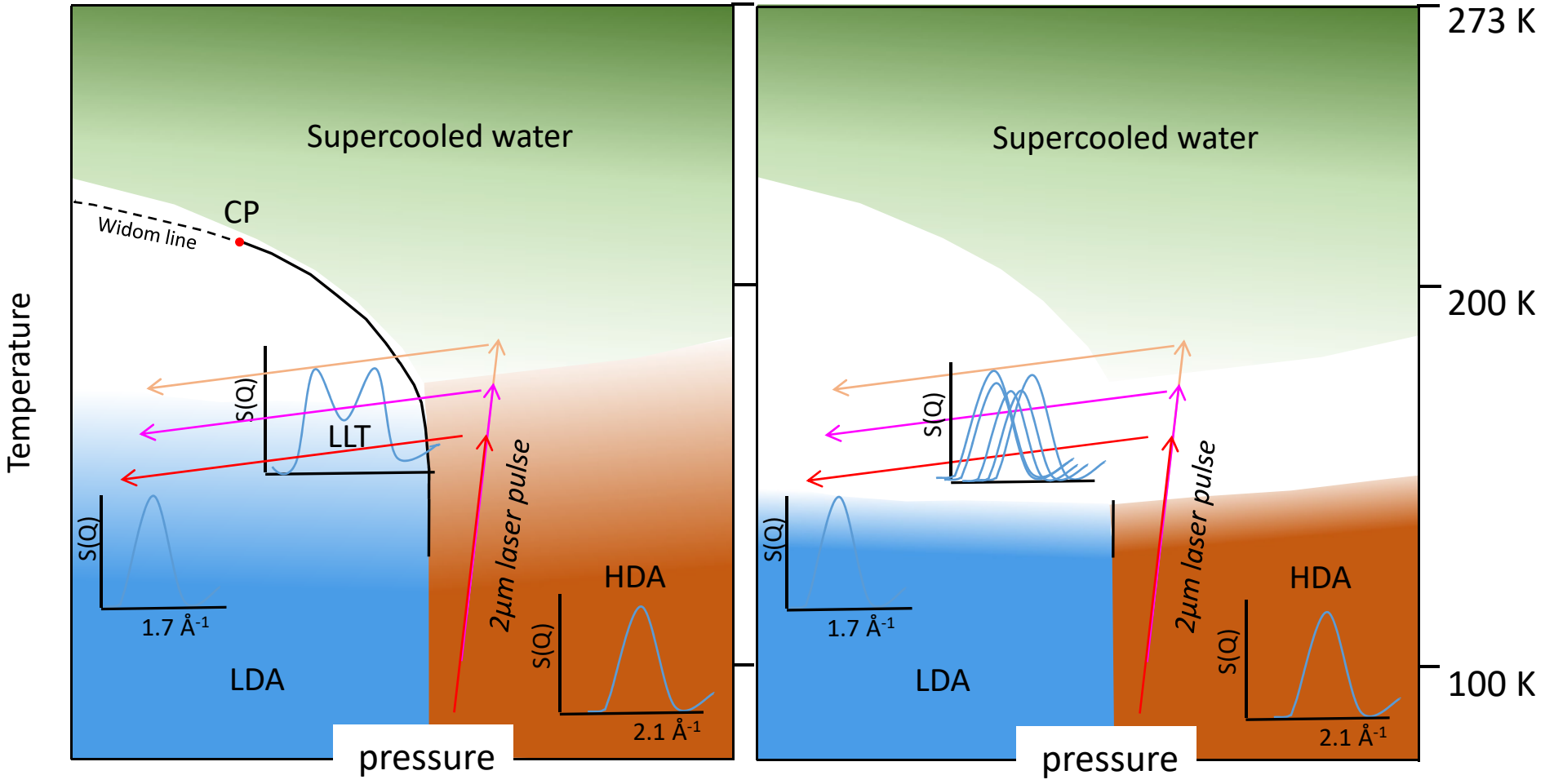
Melting of hexagonal ice



- We see liquid water at early delays
- Recrystallize after ~ 3us.
- T jump of ~100 K

Two Scenarios

First scenario: Spindodal of LLT Second scenario: Continuous



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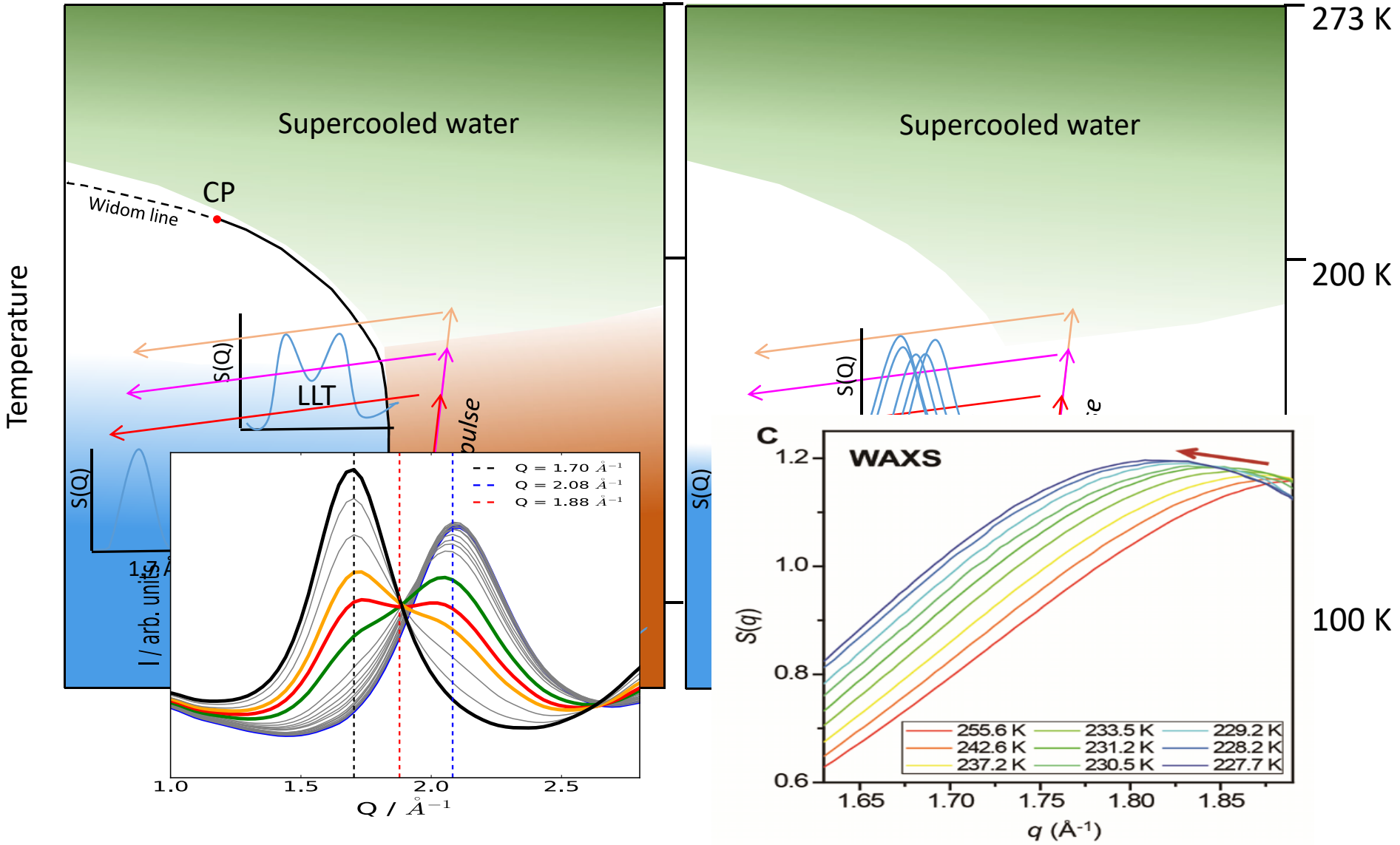
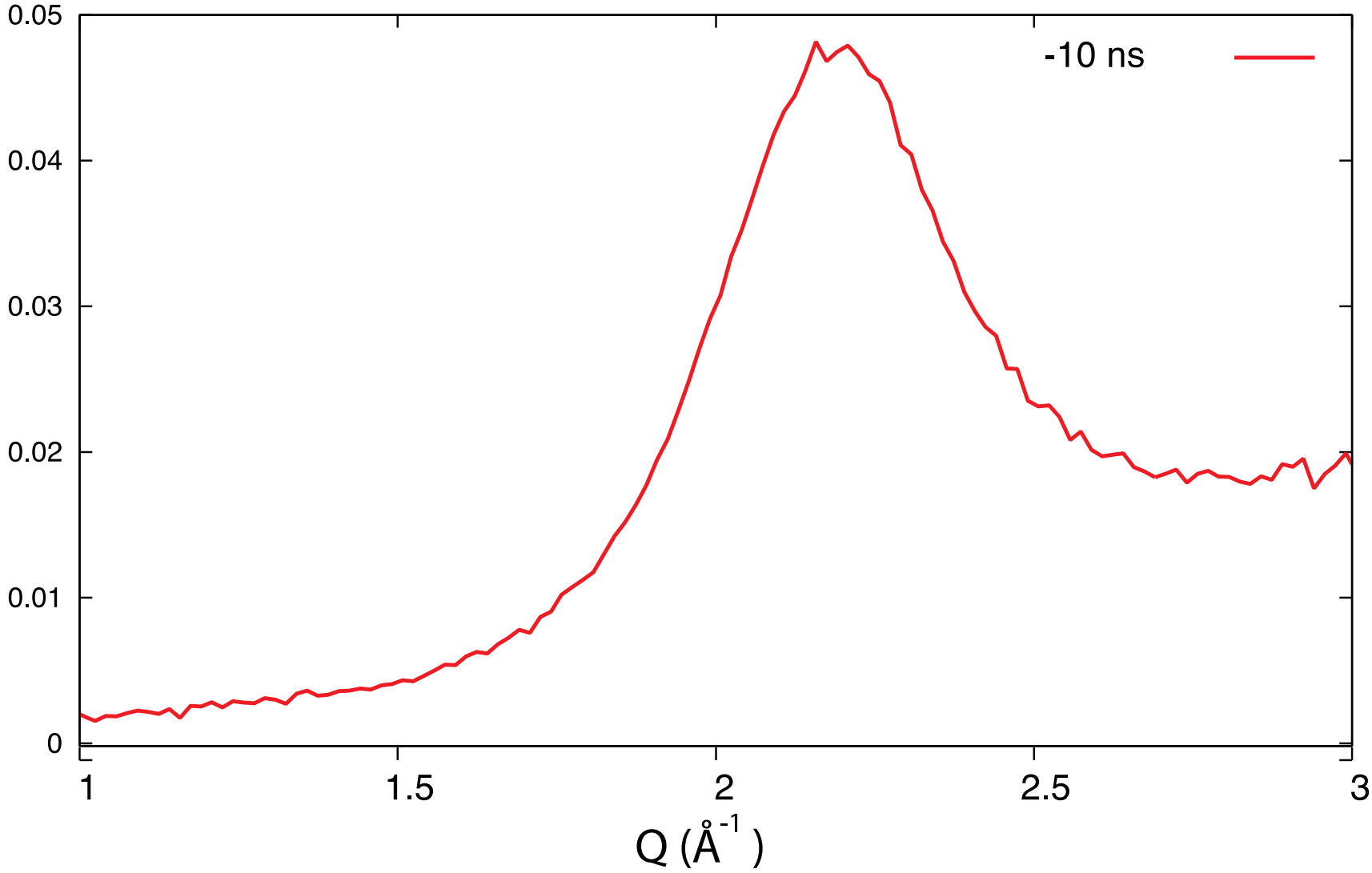
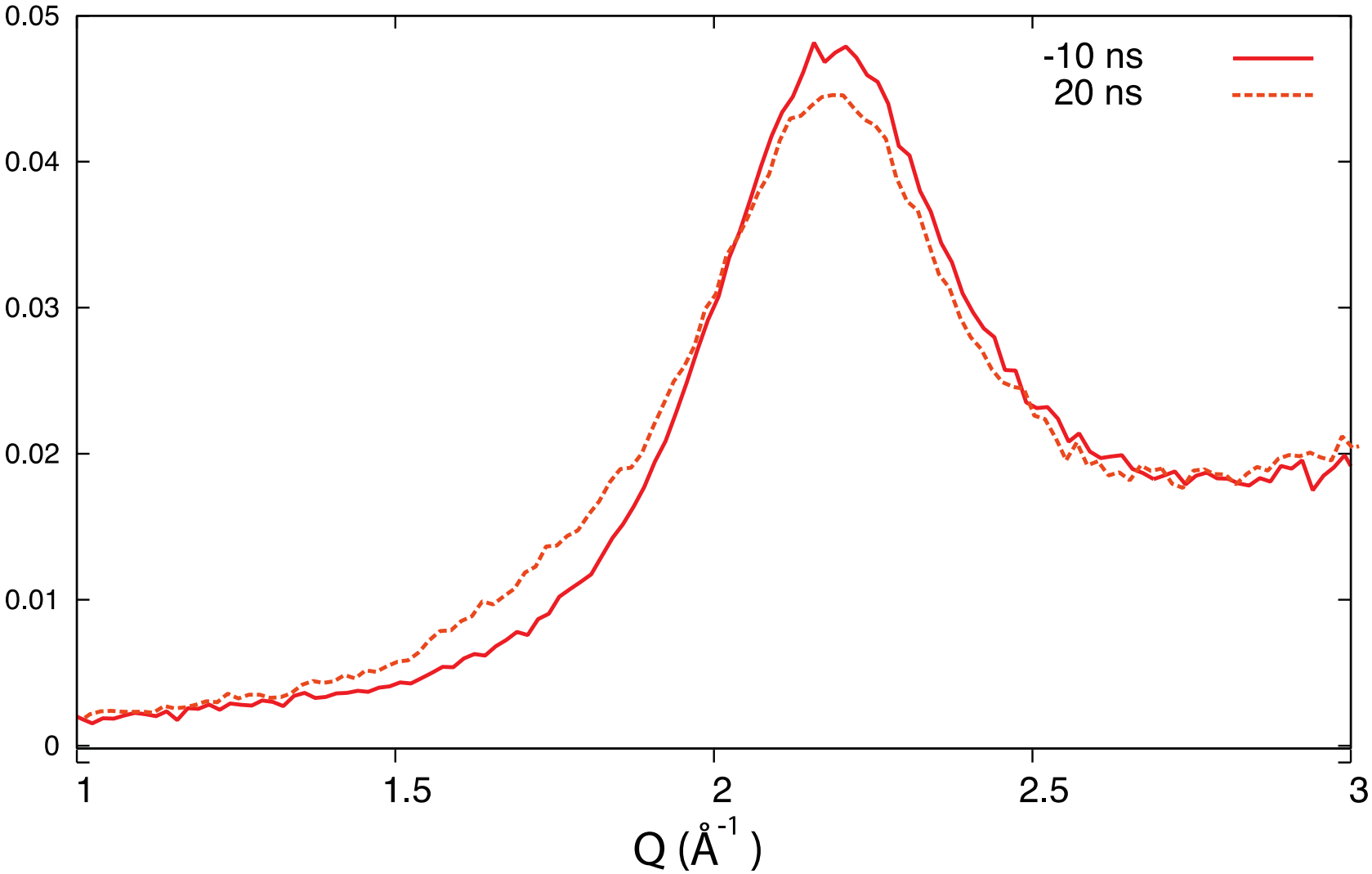


Pump-Probe X-ray Scattering 10ns-3μs



K. H. Kim, K. Amann-Winkel et al. Unpublished

Pump-Probe X-ray Scattering 10ns-3μs



K. H. Kim, K. Amann-Winkel et al. Unpublished

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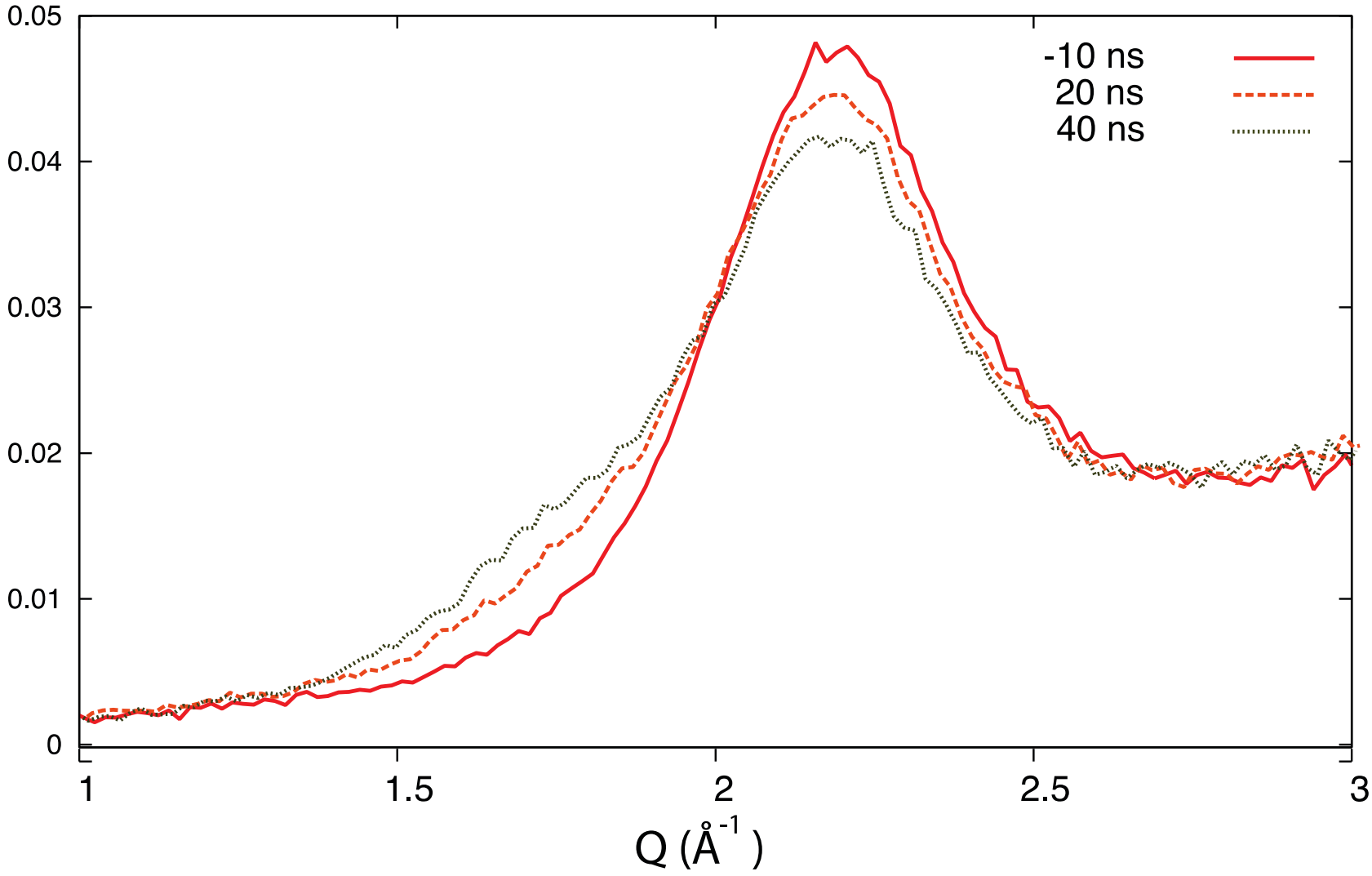

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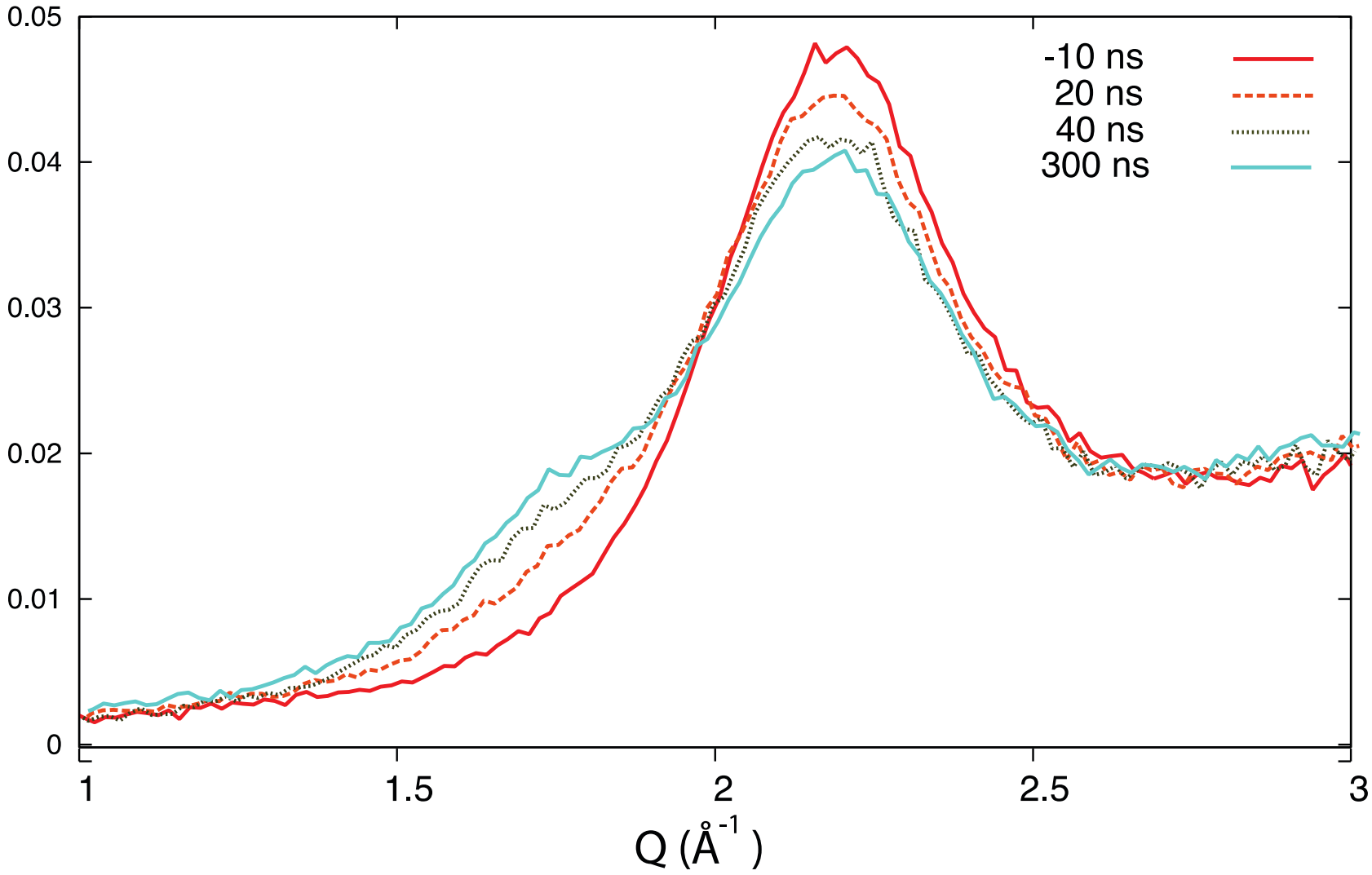

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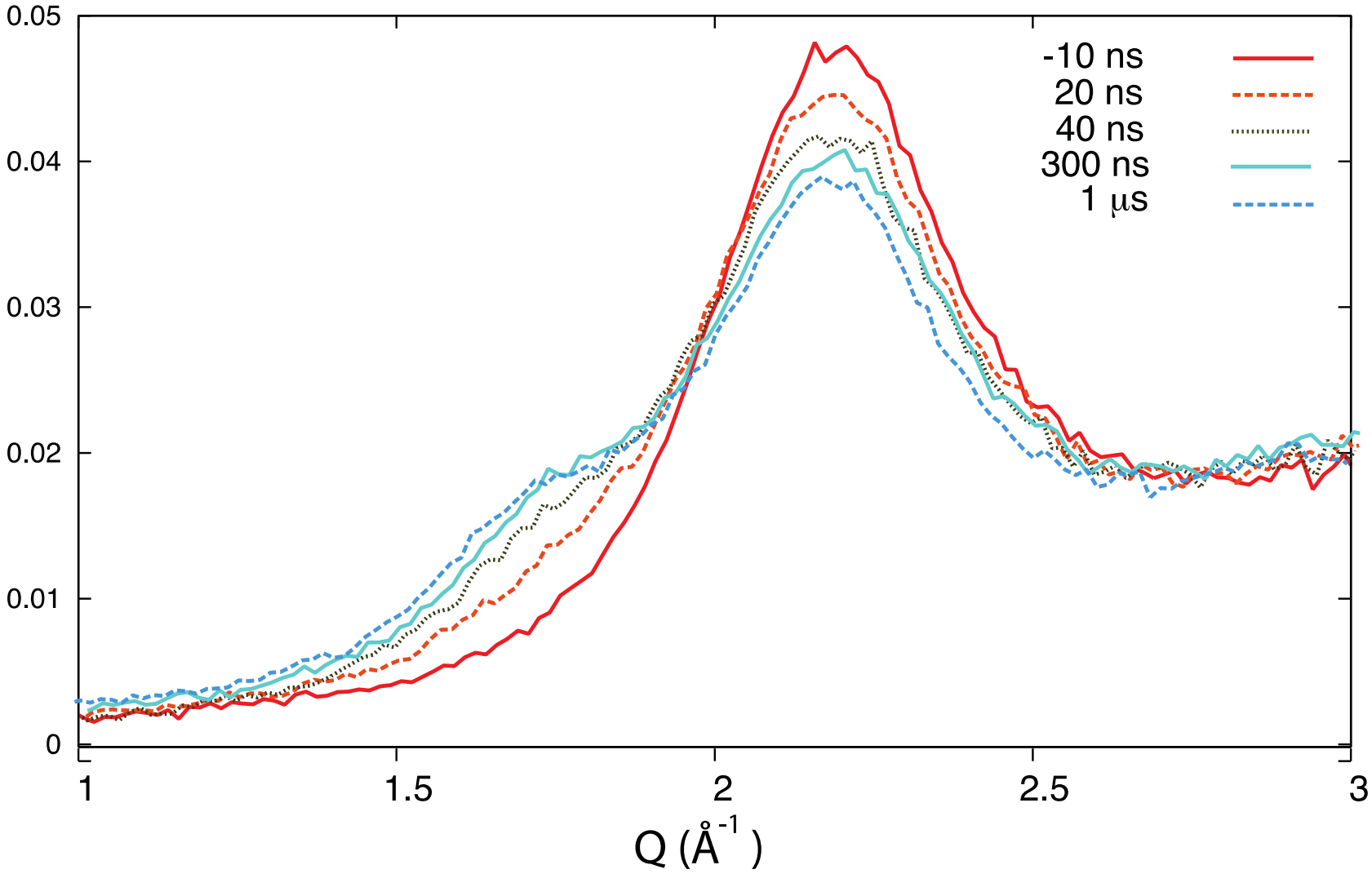
Pump-Probe X-ray Scattering 10ns-3μs



K. H. Kim, K. Amann-Winkel et al. Unpublished

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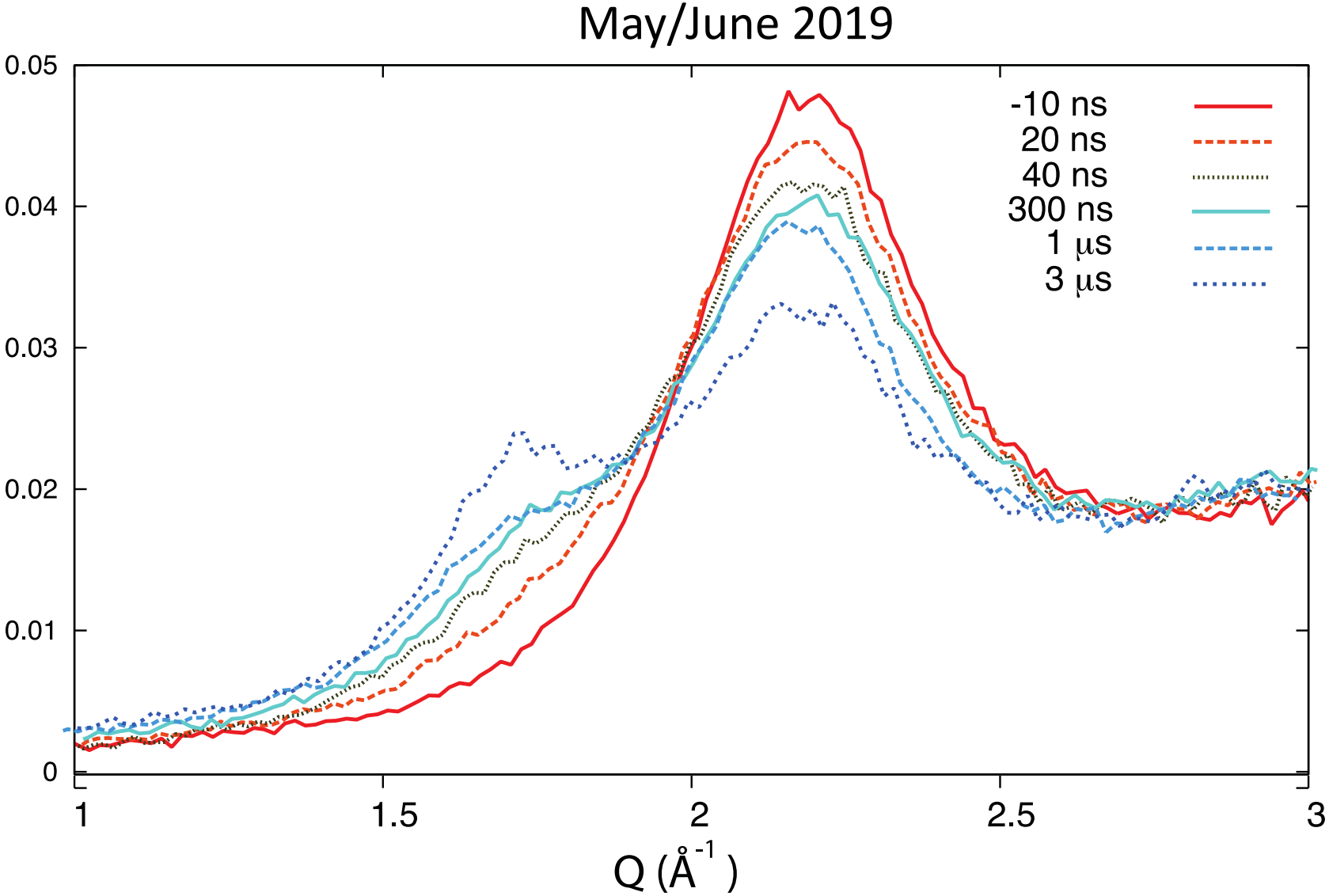

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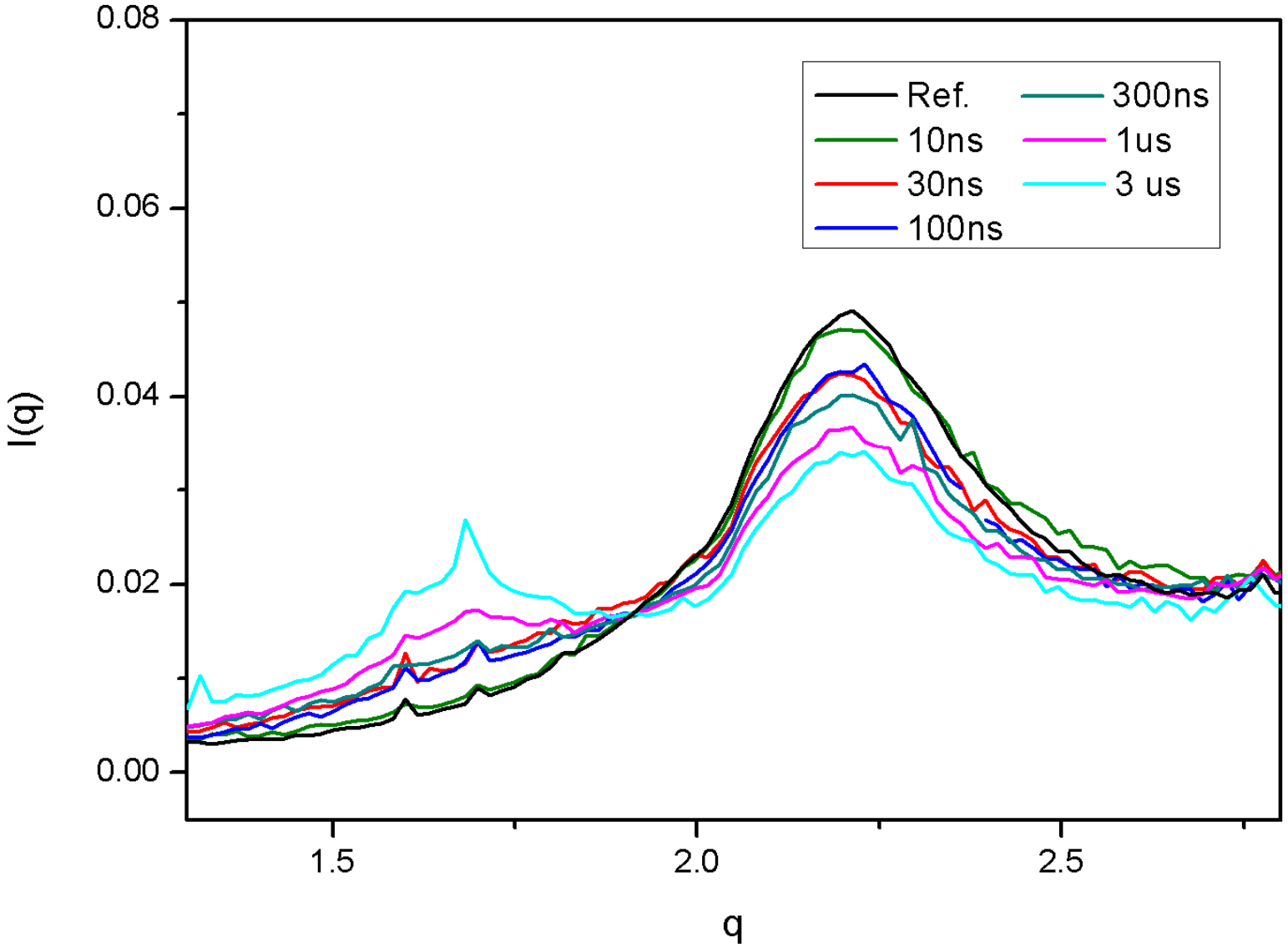
Pump-Probe X-ray Scattering 10ns-3μs

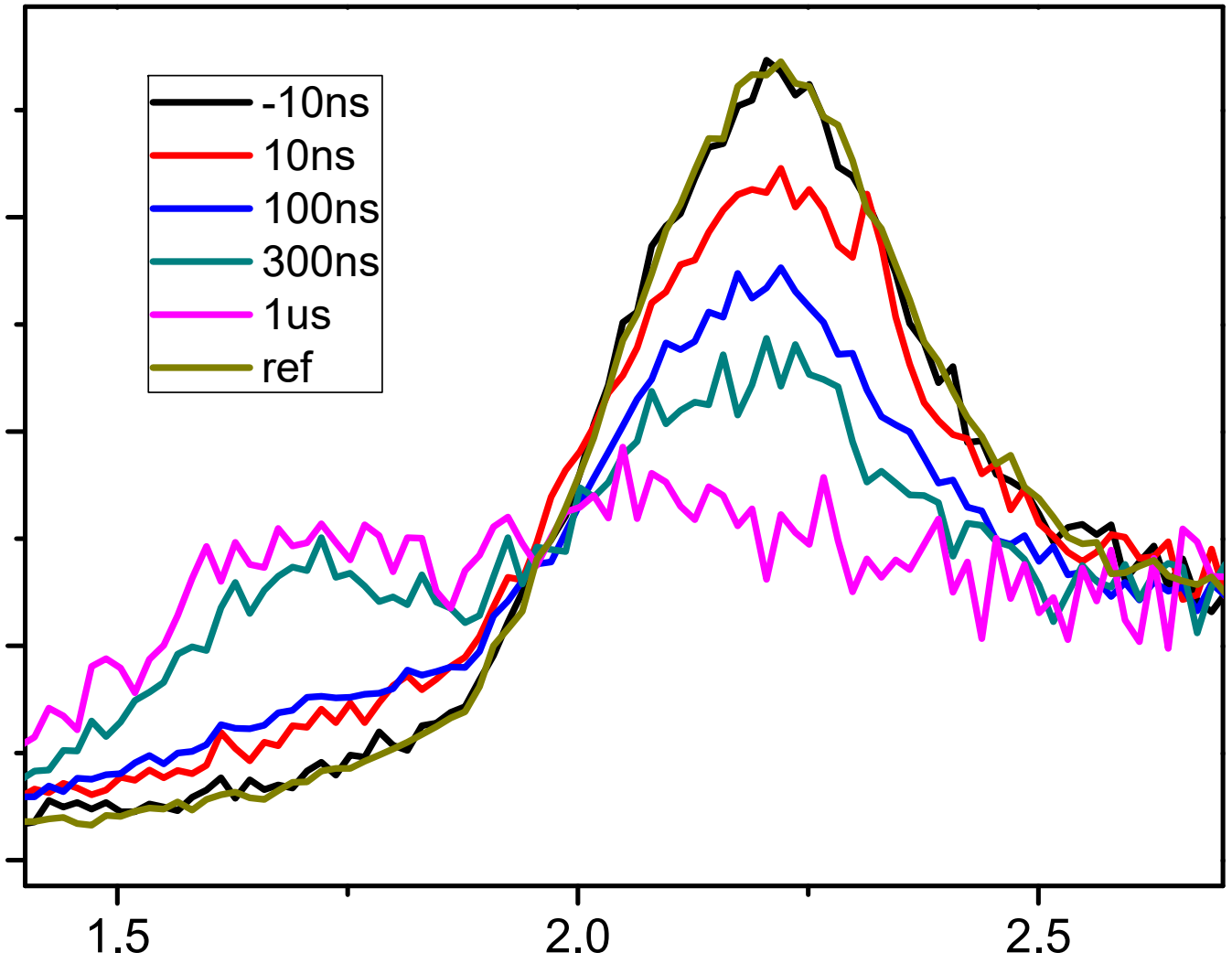
Nov/Dec 2018



K. H. Kim, K. Amann-Winkel et al. Unpublished

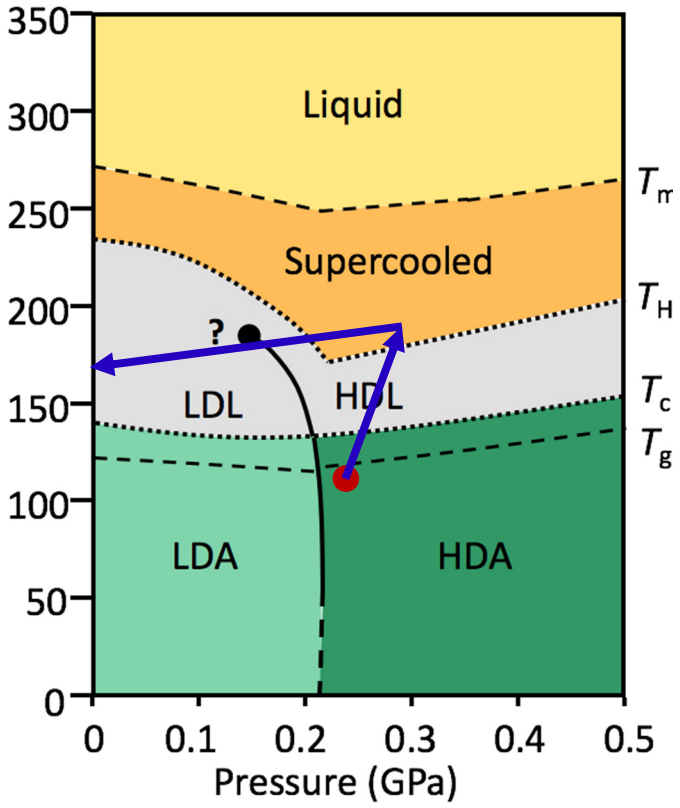
Pump-Probe X-ray Scattering 10ns-3μs

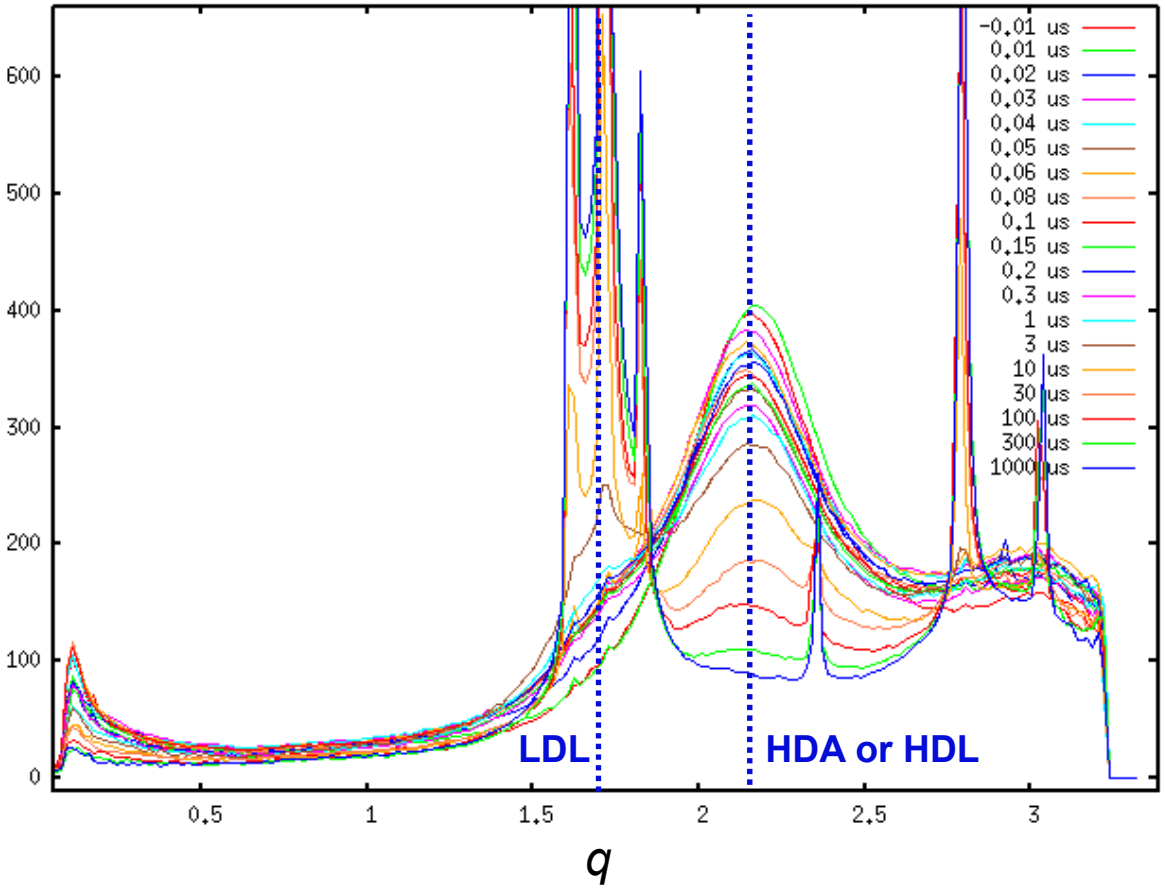
May/Jun 2018



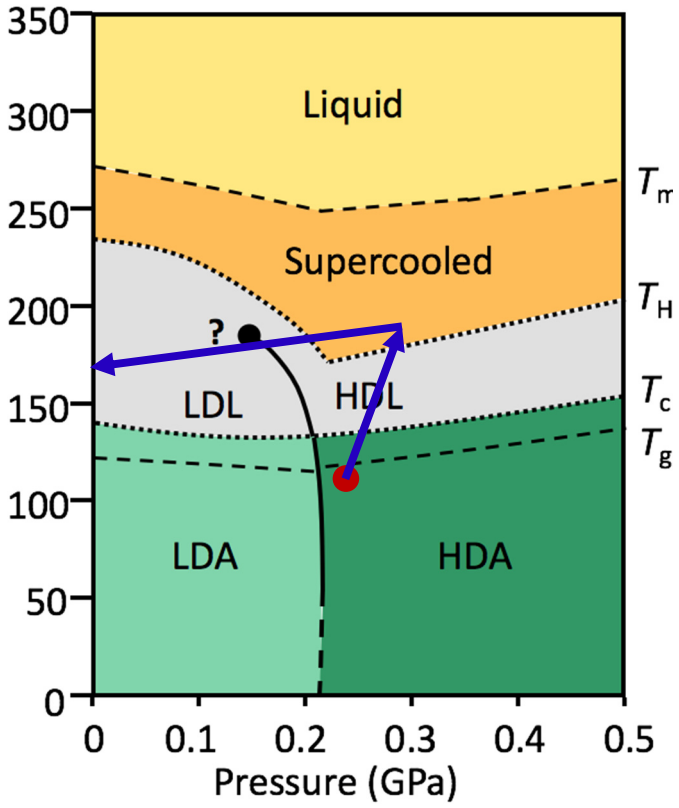
K. H. Kim, K. Amann-Winkel et al. Unpublished

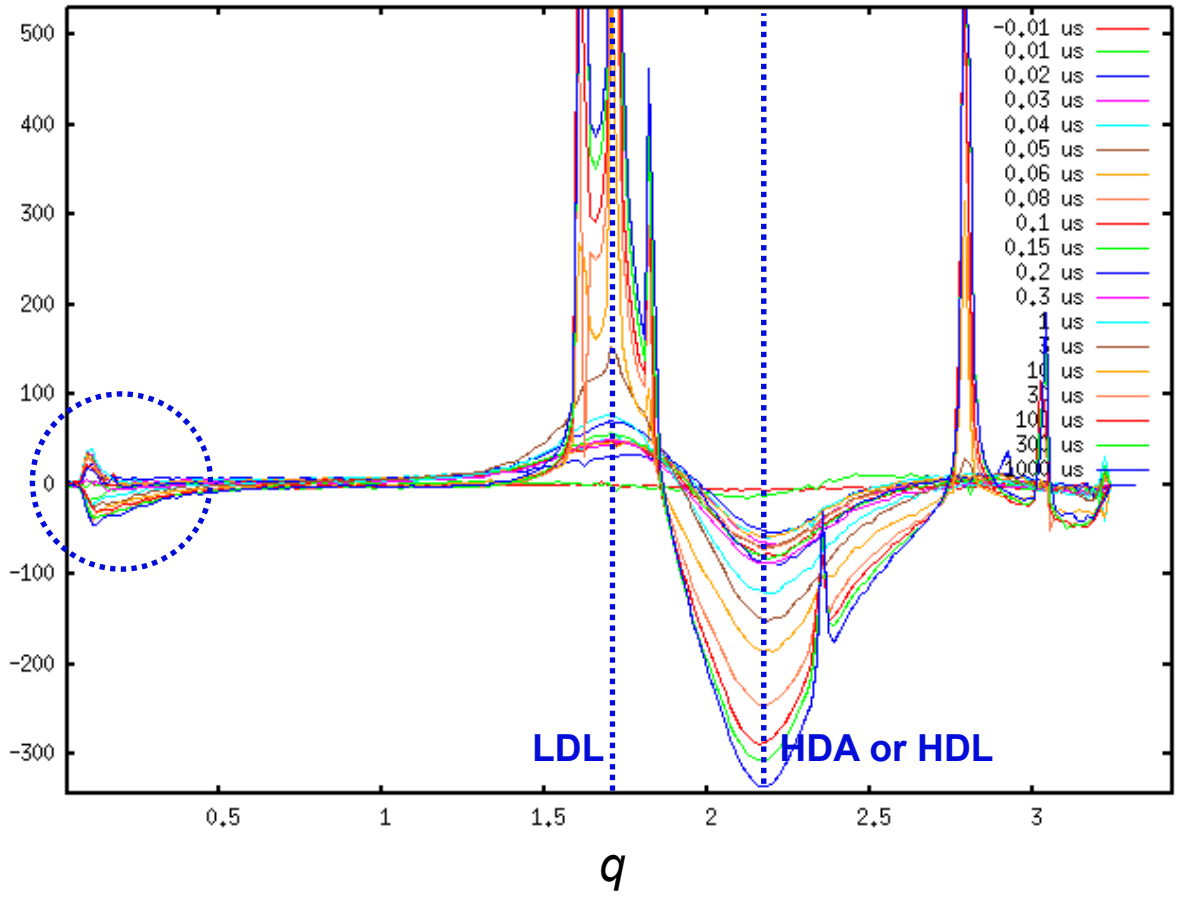
LLT from HDA


Liquid
Supercooled
?
LDL
HDL
LDA
HDA
T_m
T_H
T_c
T_g
350
300
250
200
150
100
50
0
0
0.1
0.2
0.3
0.4
0.5
Pressure (GPa)

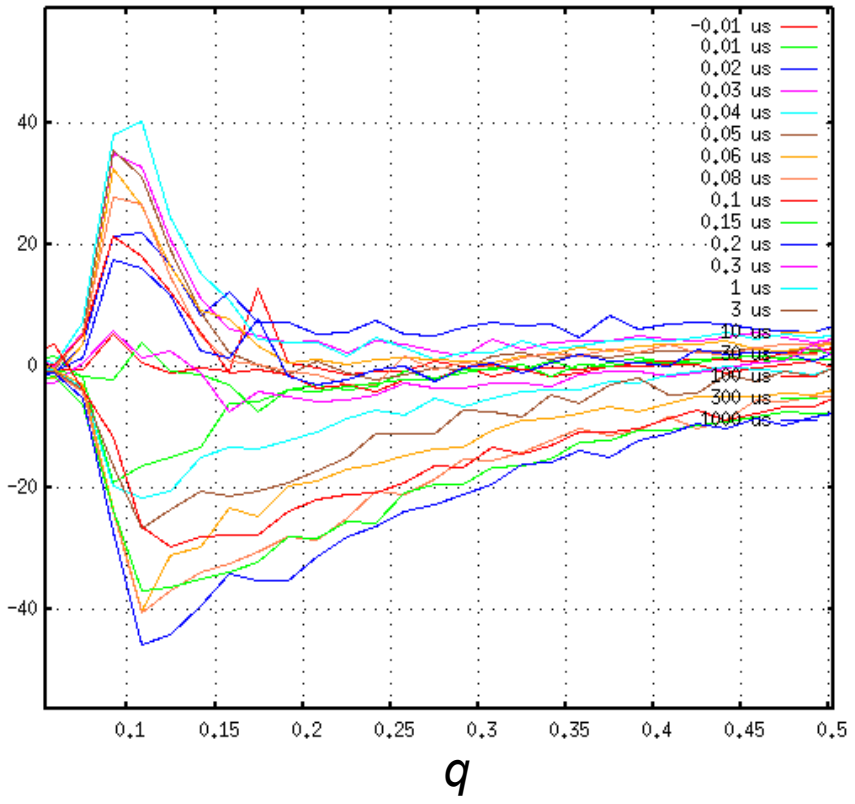

-0.01 us
0.01 us
0.02 us
0.03 us
0.04 us
0.05 us
0.06 us
0.08 us
0.1 us
0.15 us
0.2 us
0.3 us
1 us
3 us
10 us
30 us
100 us
300 us
1000 us
LDL
HDA or HDL
600
500
400
300
200
100
0
0.5
1
1.5
2
2.5
3
q

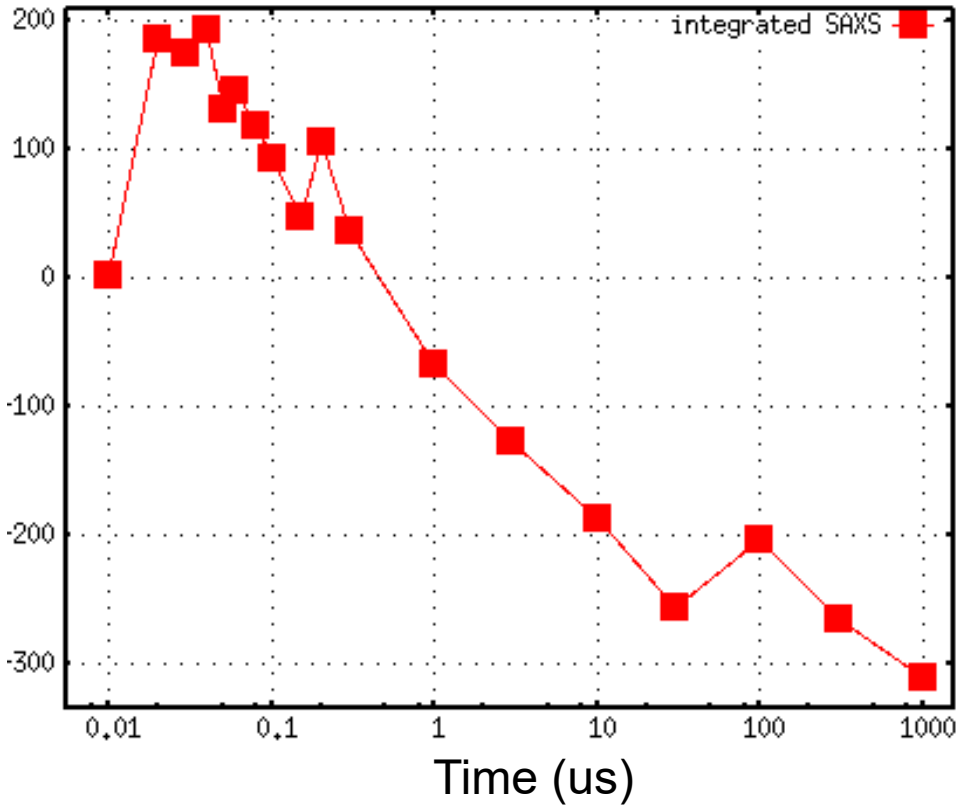
LLT from HDA


Liquid
Supercooled
LDL
HDL
LDA
HDA
?
T_m
T_H
T_c
T_g
350
300
250
200
150
100
50
0
0
0.1
0.2
0.3
0.4
0.5
Pressure (GPa)


LDL
HDA or HDL
q
-0.01 us
0.01 us
0.02 us
0.03 us
0.04 us
0.05 us
0.06 us
0.08 us
0.1 us
0.15 us
0.2 us
0.3 us
1 us
3 us
10 us
30 us
100 us
300 us
1000 us

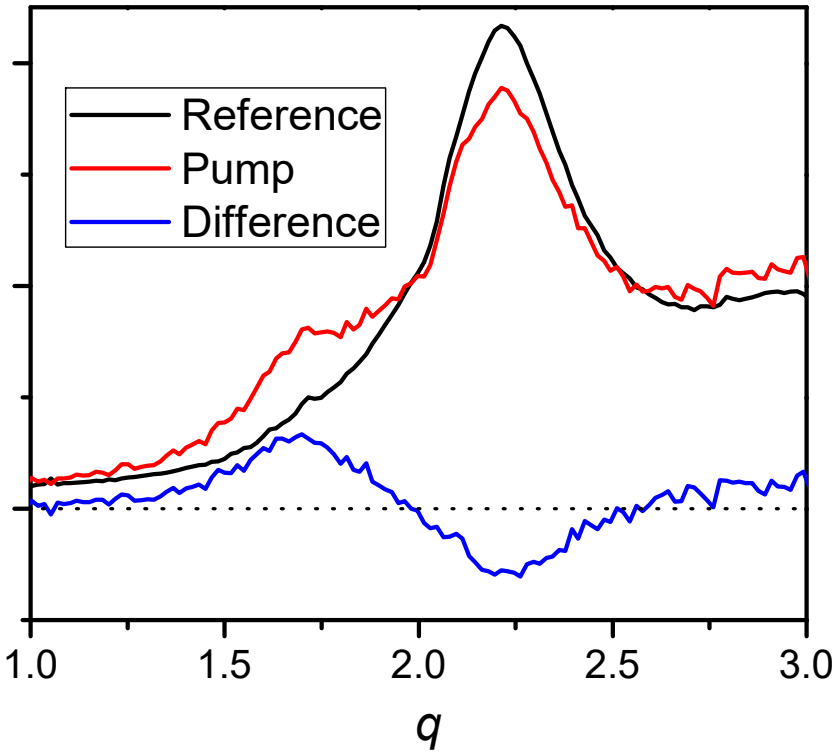
SAXS enhancement

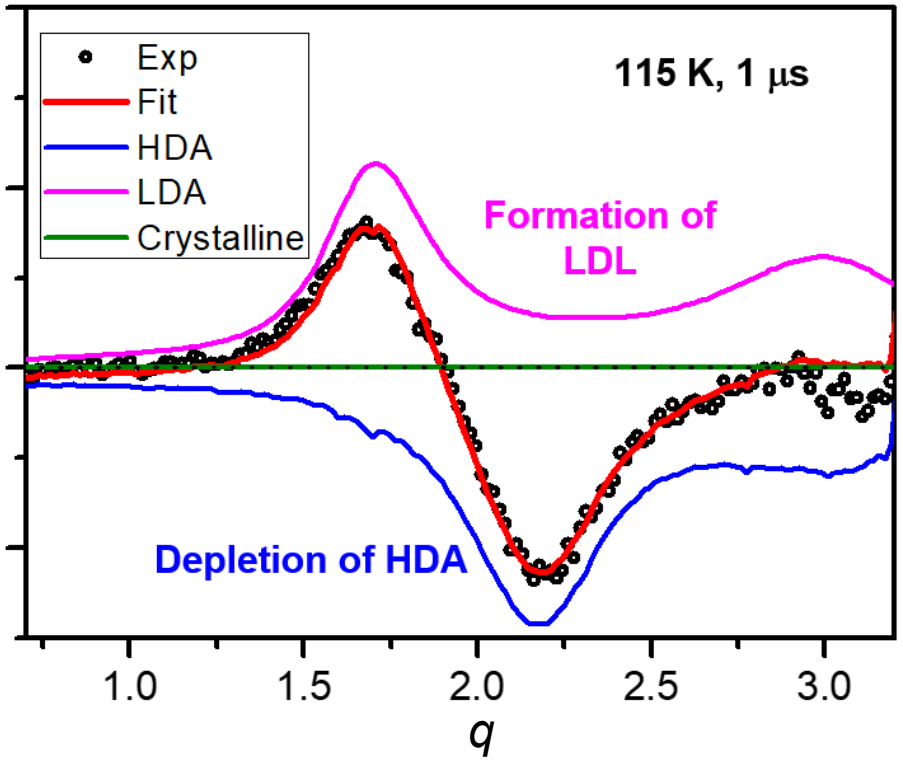




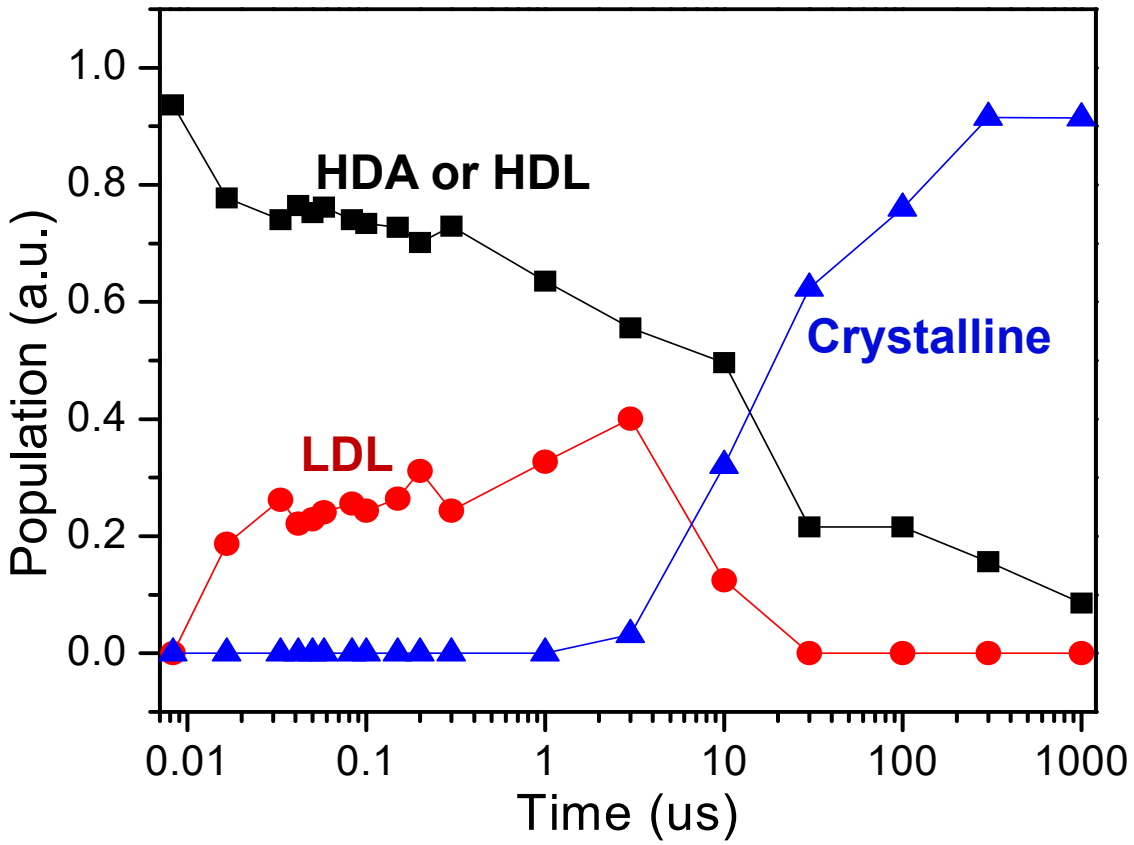
- Integrated intensity shows an enhancement at early delays

Difference & Fit





LLT from HDA

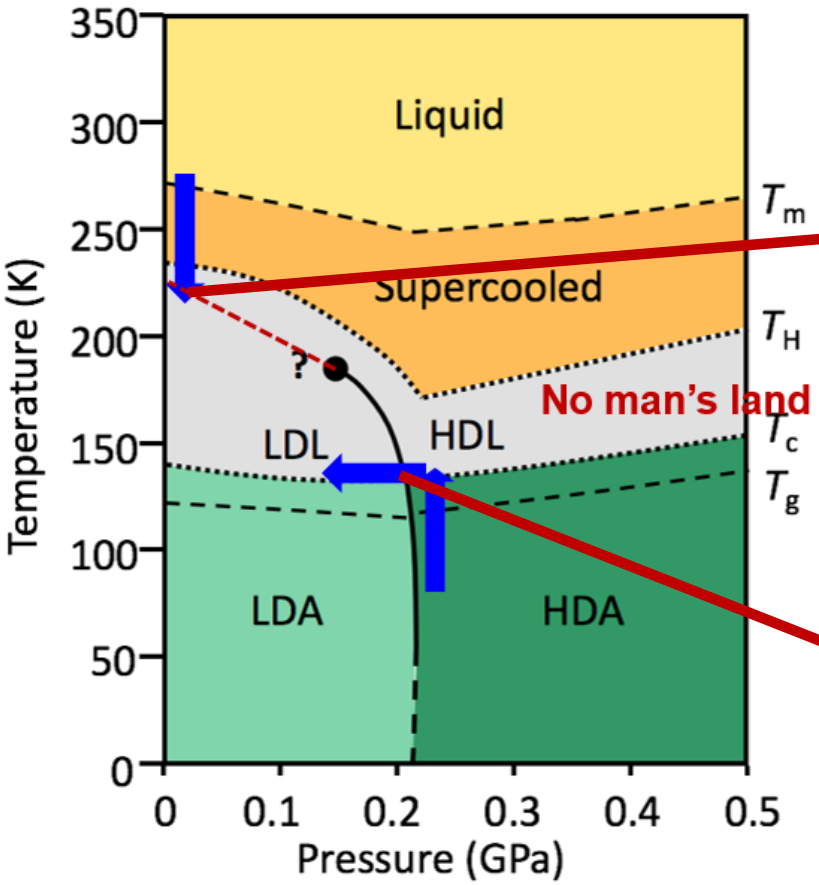


- Liquid-liquid transition at early delays.
- Crystallization at later delays.
- **Direct evidence of the LLT**

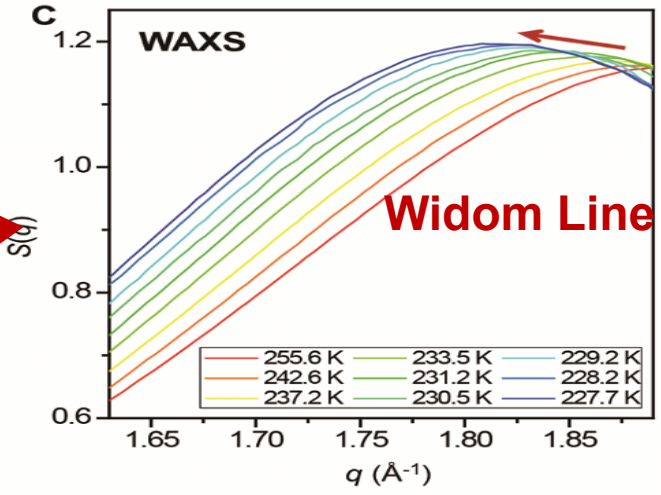
K. H. Kim and K. Amman-Winkel *et al.* manuscript in preparation

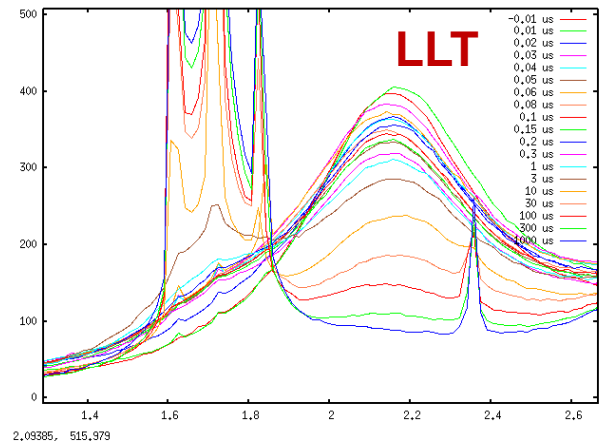
Summary

Fully Consistent with the LLCP Model



LLCP model shown in the phase diagram



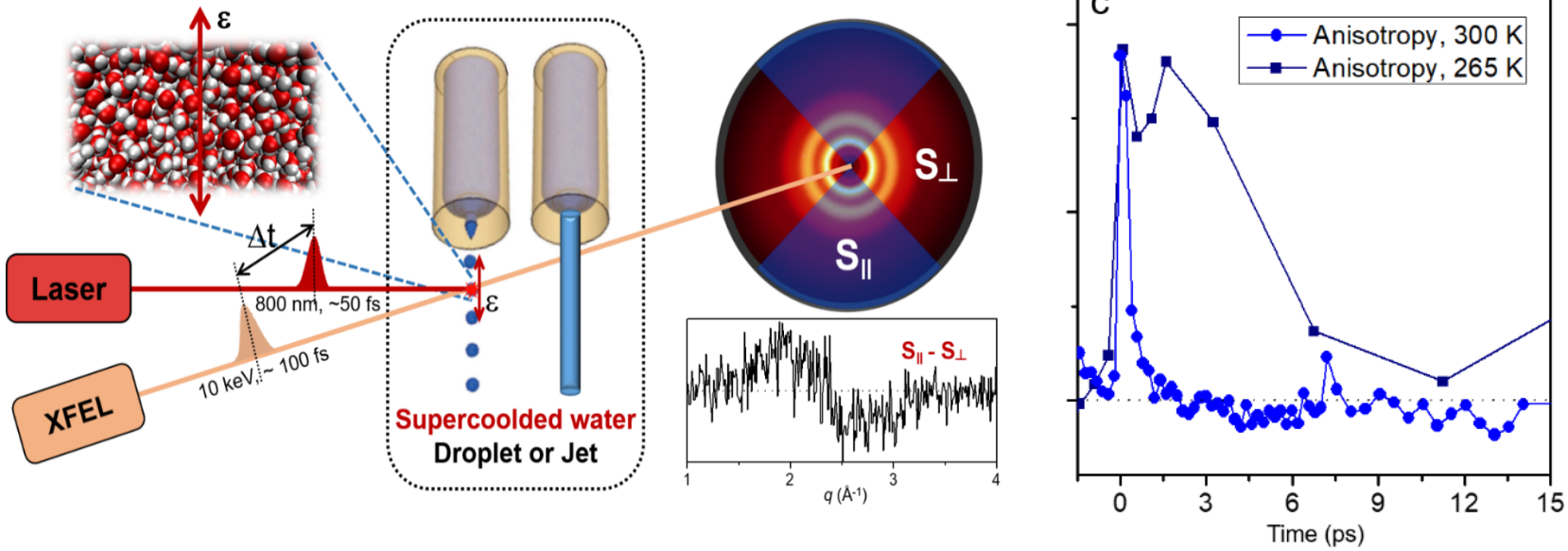


K. H. Kim and A. Späh *et al. Science,* **358**, 1589 (2017)

K. H. Kim and K. Amman-Winkel *et al.* manuscript in preparation.

European XFEL

- Planned experiment on 2019. 9 (FXE).
- **Fragile to strong transition** of water at deeply supercooled regime



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Thank you!