Evidence of Liquid-to-Liquid Phase Transition in Deeply Cooled Confined Water Shown By Neutron and X-Ray Scattering Studies

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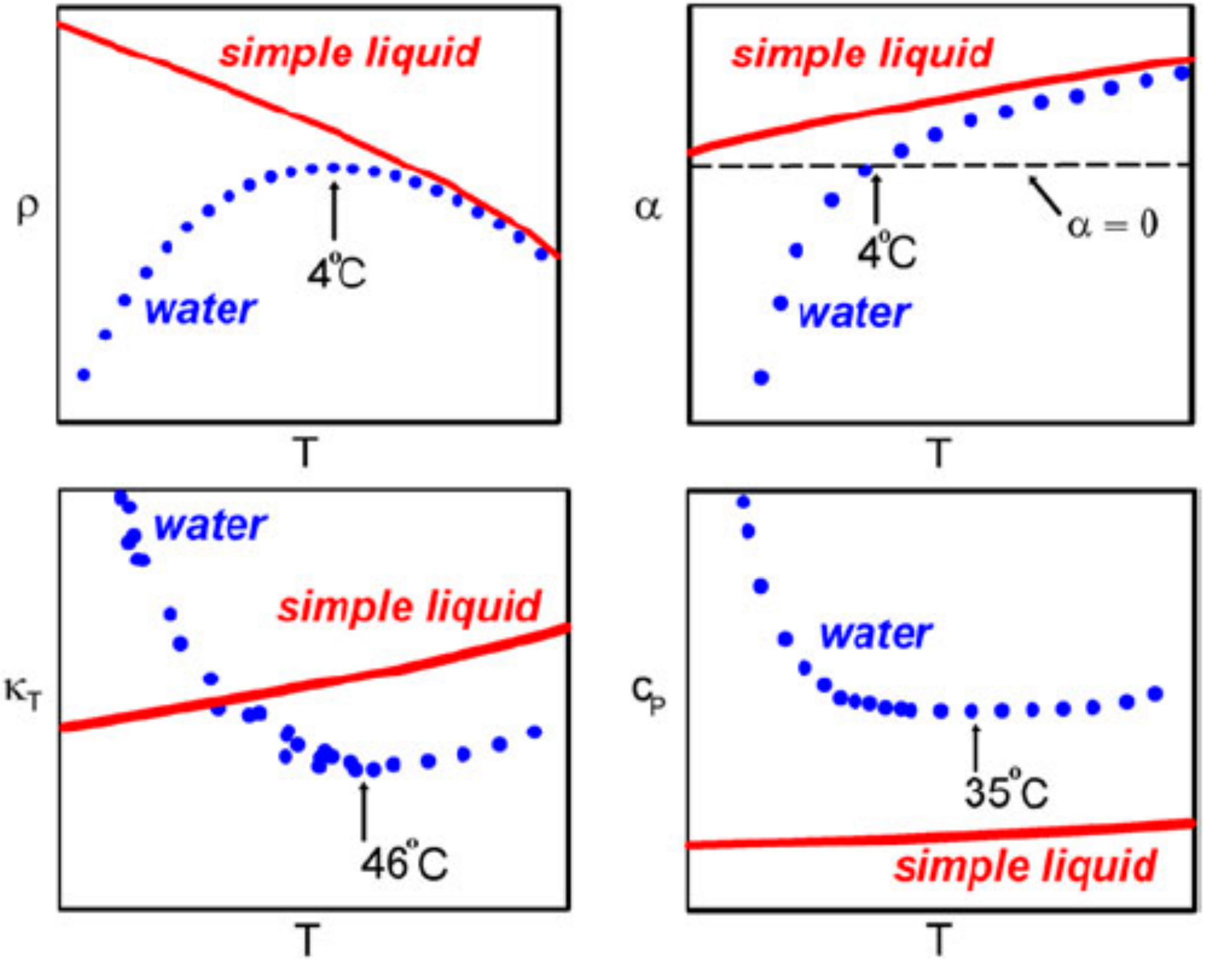
Acknowledgment

I am grateful to all my students and collaborators for their enthusiasm and hard works which made these experimental results possible

An Invited Lecture Presented at the **Course on Water and Water Systems**,
Centre Ettore Majorana in Erice, Sicily, Italy, July 22-31, 2016.

Anomalous Properties of Supercooled Water



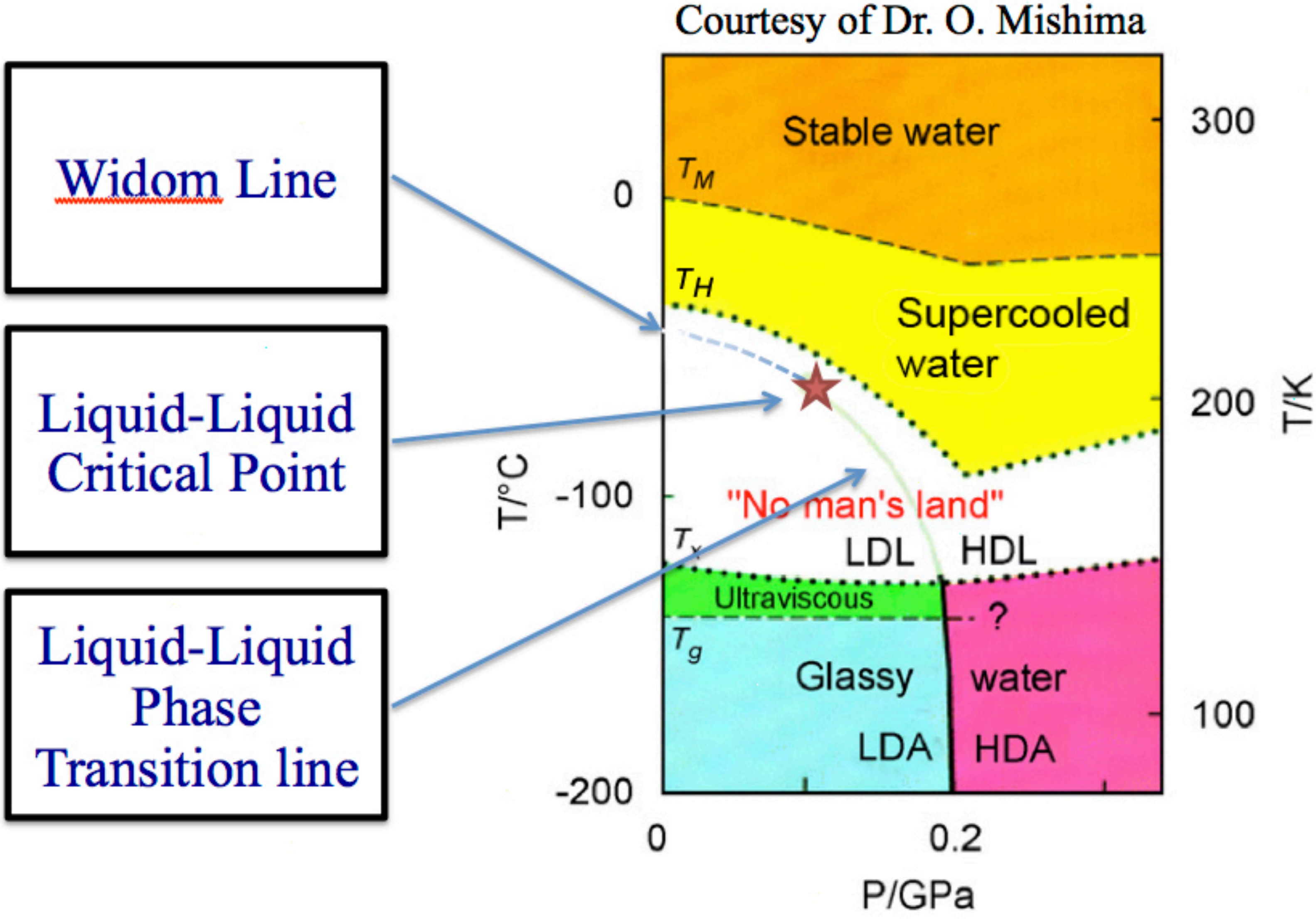
$\langle(\delta S\ \delta V)\rangle = V k_B T\alpha$

$\langle(\delta V)^2\rangle = V k_B T\kappa_T$

$\langle(\delta S)^2\rangle = N k_B c_p$

A schematic comparison of the isobaric temperature dependence of the density ρ, thermal expansion coefficient α, isothermal compressibility κ_T and isobaric heat capacity c_p for water and a simple liquid. [P. G. Debenedetti,"Supercooled and glassy water", *J. Phys.: Condens. Matter* 15, R1669 (2003)]

Liquid-Liquid Critical Point Hypothesis may provide a coherent explanation of the unusual phase behavior of water



Widom Line

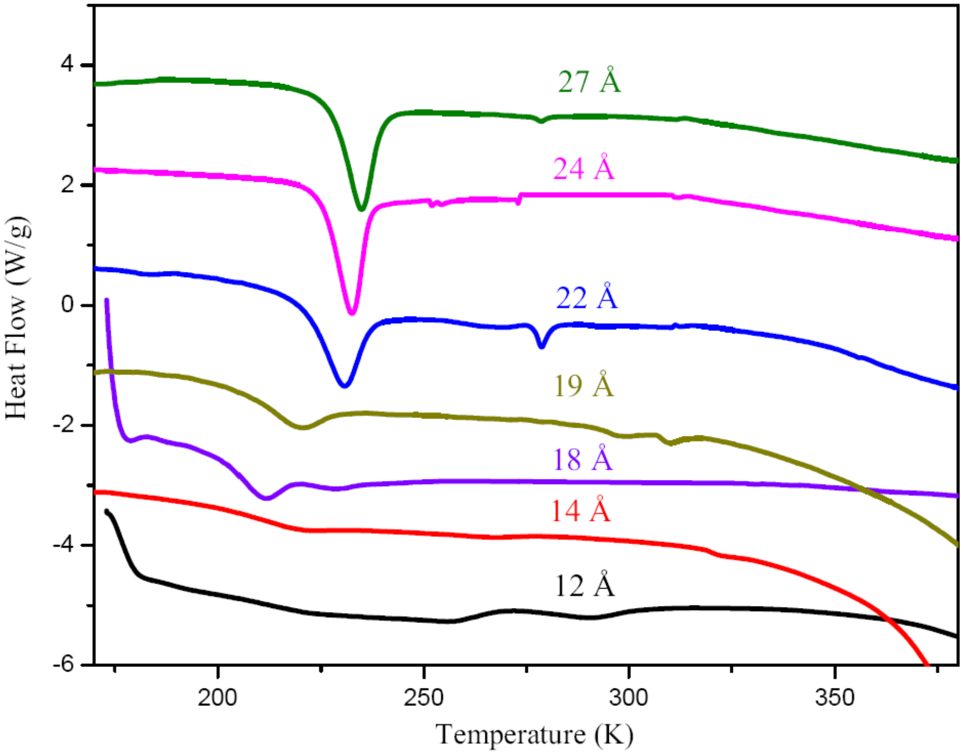
Liquid-Liquid Critical Point

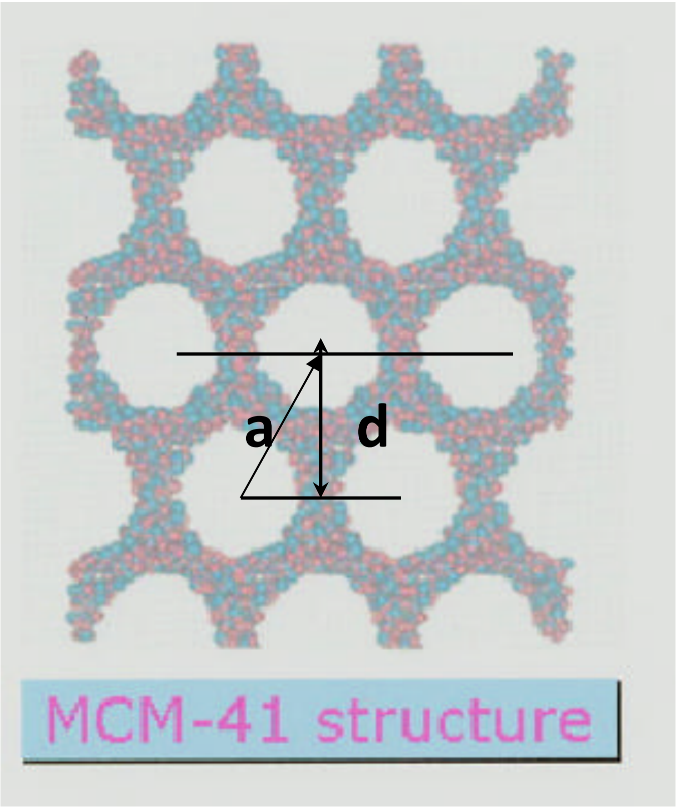
Liquid-Liquid Phase Transition line

Courtesy of Dr. O. Mishima

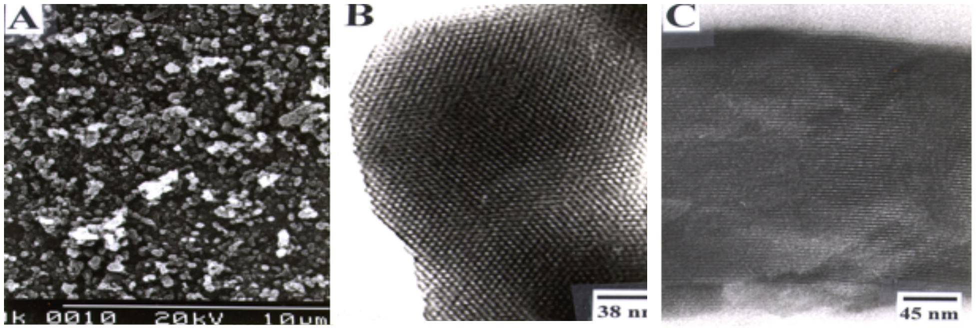
O. Mishima, H. E. Stanley, ***Nature***, *"The relationship between liquid, supercooled and glassy water"* **396**, 329 (1998).

Differential scanning calorimetry (DSC) data show no freezing peaks for water confined in MCM-41 of pore diameters below 19 Å





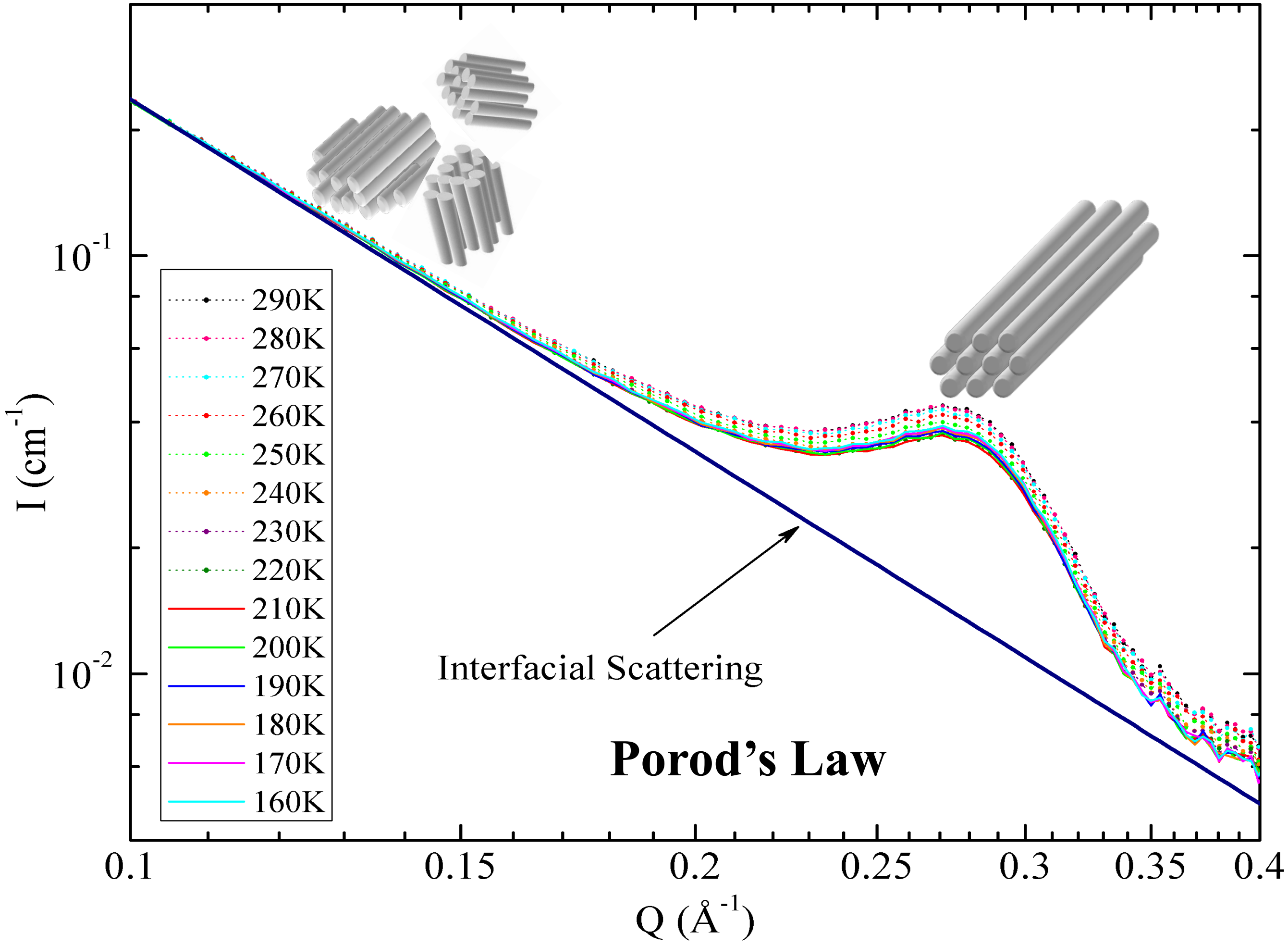
1-D cylindrical tubes arranged in a 2-D hexagonal structure. d = sqrt(3)/2*a



SEM and microtome TEM micrographs of micron size grains of MCM-41 powder sample. Within each grain is a perfect 2-d hexagonal lattice without defects.

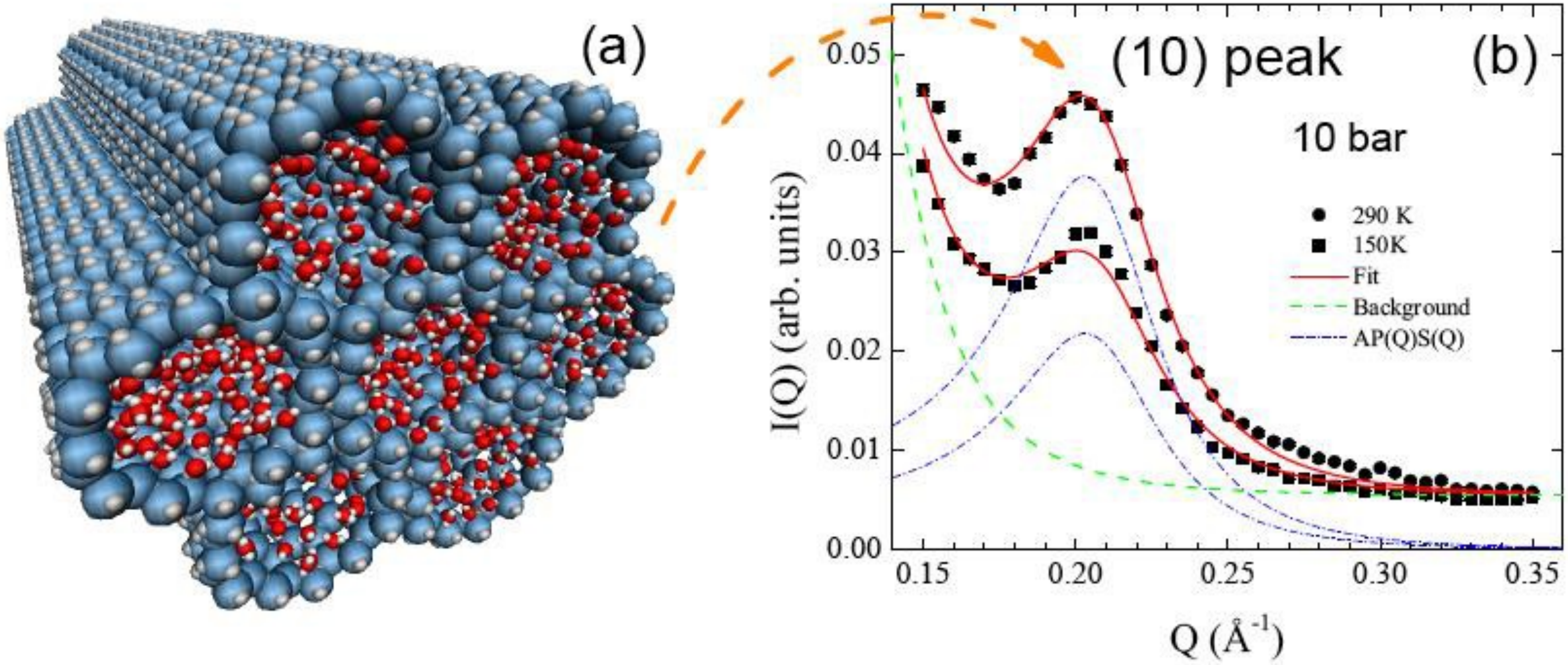
K.-H. Liu and C.-Y. Mou et al., JCP 139, 064502 (2013).

MCM-41 Powder and SANS Intensity Distribution



Powder-like MCM-41 sample

Detection of the Liquid-Liquid Transition by Density Measurement Method: Small Angle Neutron Scattering [1, 2]



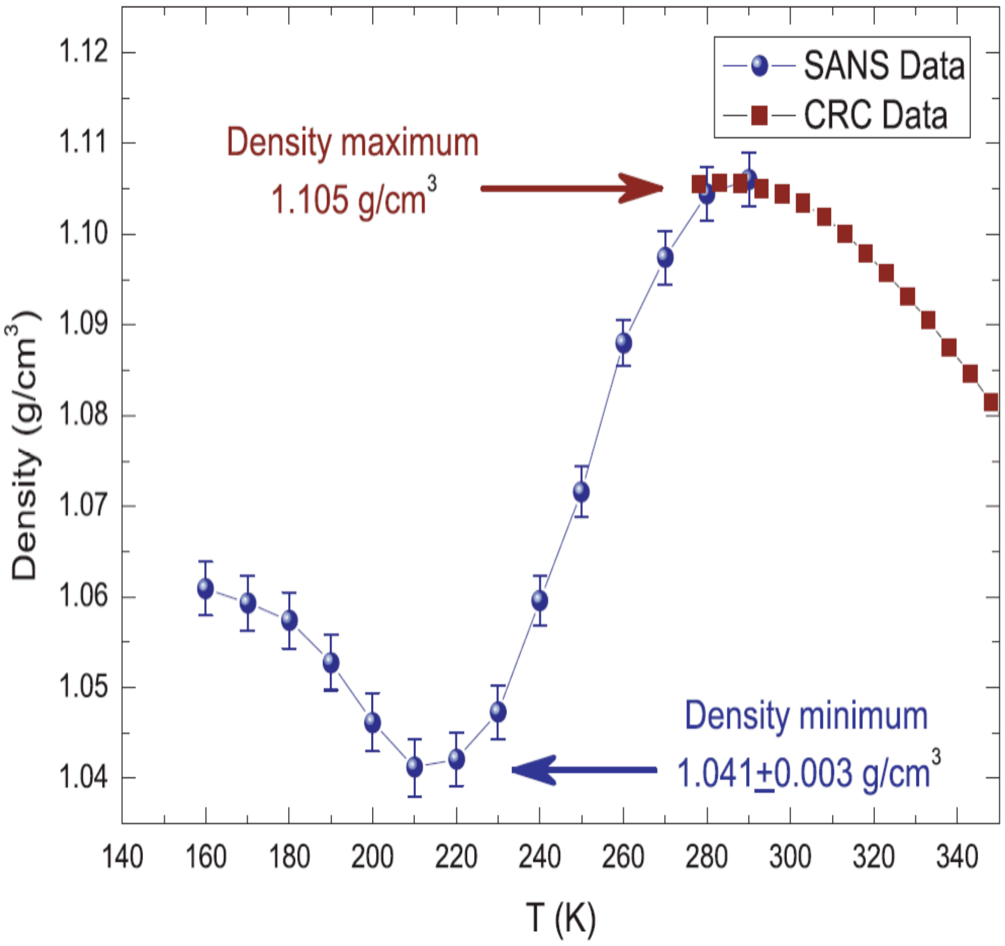
Two dimensional hexagonal order → Bragg Peak at $Q=0.21$ Å^{-1} in its neutron diffraction pattern.

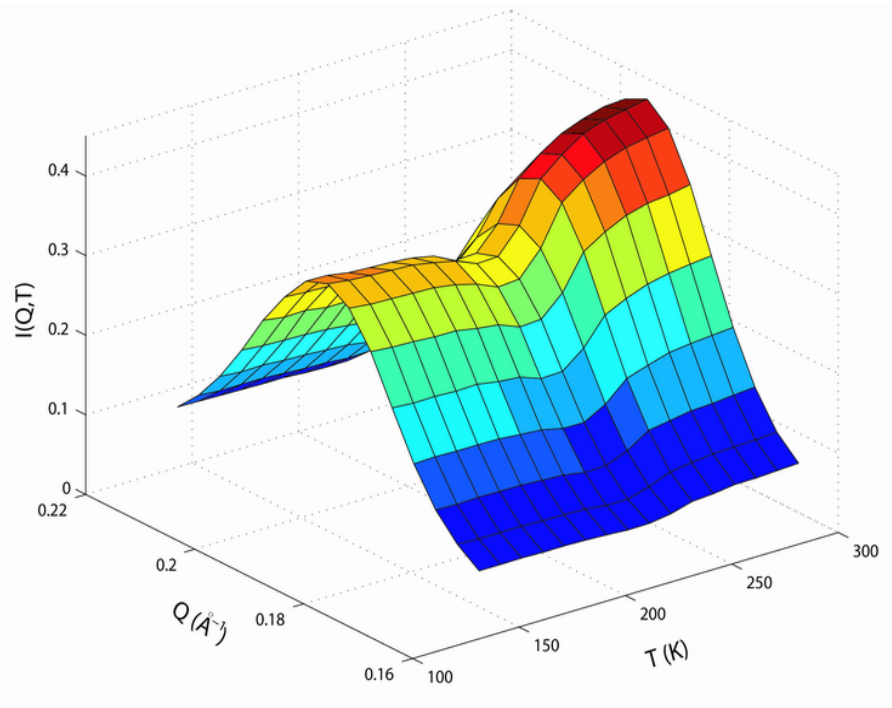
The intensity of this Bragg peak is a function of the density of the confined water:
Higher density → Higher Bragg peak;
Lower density → Lower Bragg peak.

[1] D. Liu, et al.,"Observation of the Density Minimum in Deeply Supercooled Confined Water" Proc. Natl. Acad. Sci. USA, **104,** 9570, 2007.
[2] Y. Zhang, et al.,"Density Hysteresis of Heavy Water Confined in a Nanoporous Silica Matrix" Proc. Natl. Acad. Sci. USA, **108**, 12206, 2011.

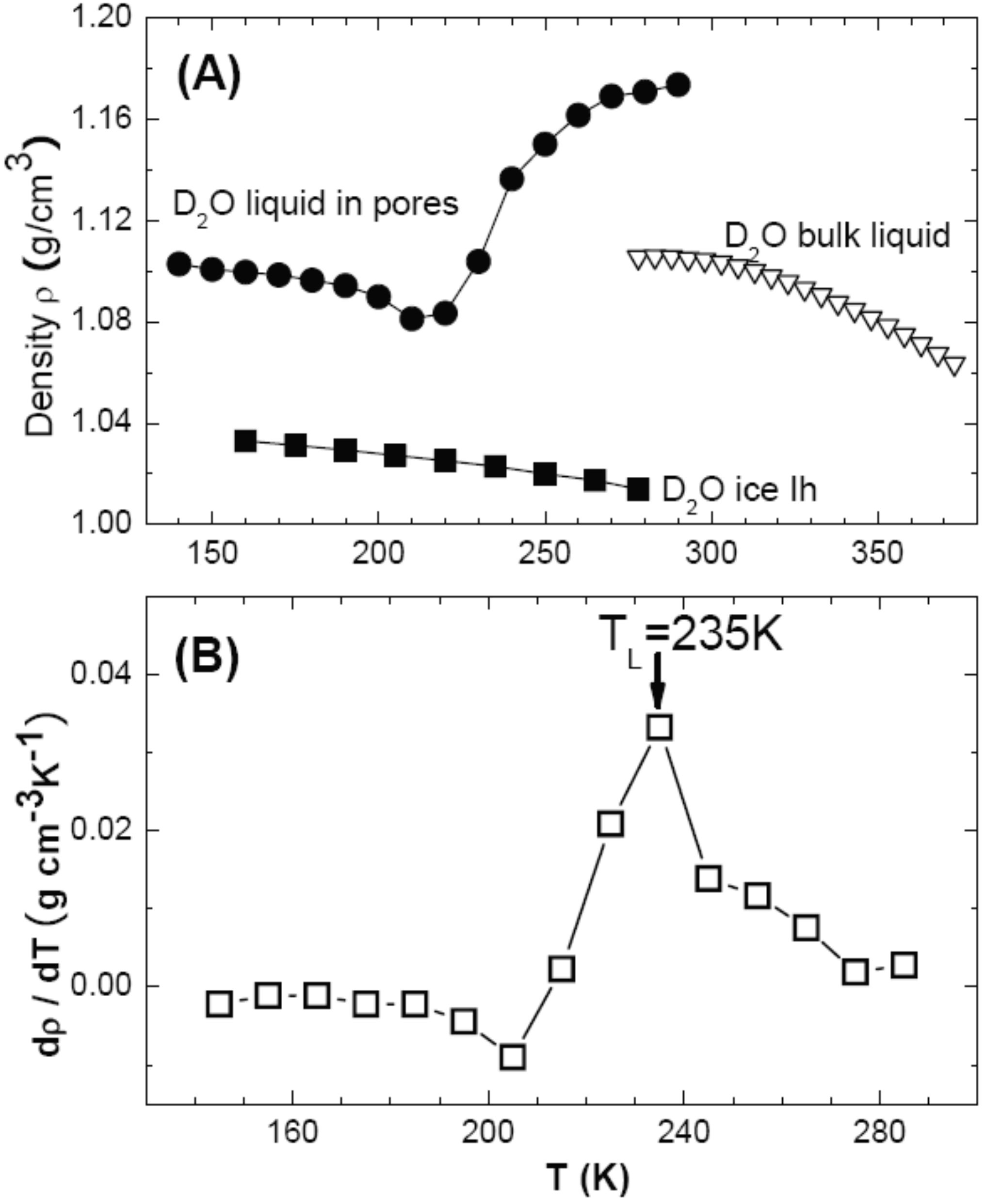
Observation of the density minimum in deeply supercooled confined water

D. Liu, Y Zhang, C.-C. Chen, C.-Y. Mou, P. Poole, and S.-H. Chen, *PNAS* **104** 9570 (2007) [cited 157]





The picture shows the direct experimental observation of the density minimum in supercooled confined water by measurements of a series of Small Angle Neutron Scattering intensity distributions as functions of temperature and wave-vector transfer. The saddle point in the middle of the surface indicates the density minimum point occurring at ~210K (D_2O).



Absolute values of density of heavy water in 19 Å pores of MCM-41 measured by SANS

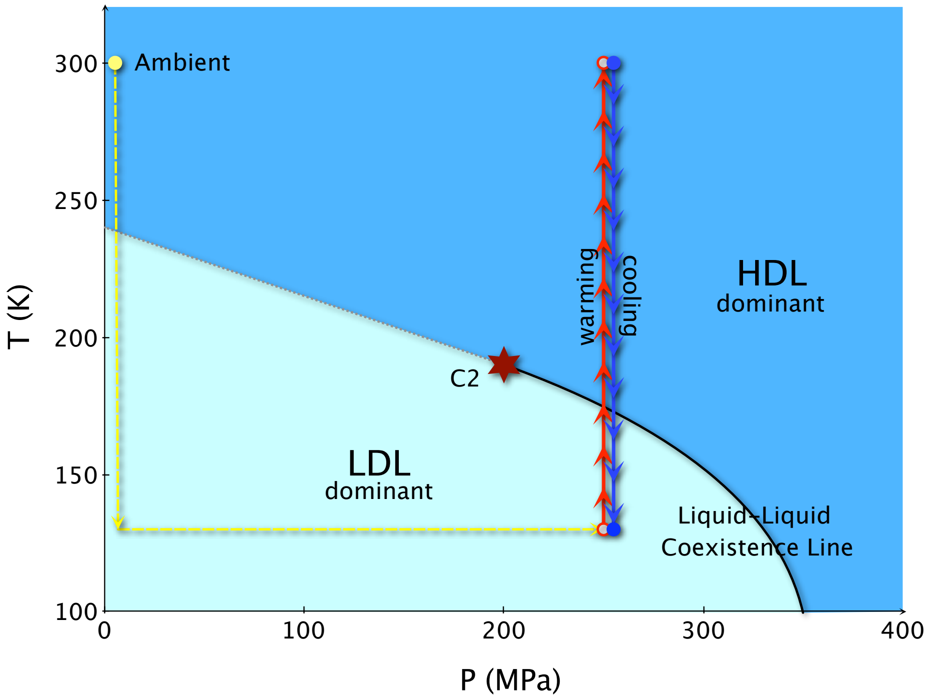
(A) Average D_2O density inside the 19 Å pore measured by SANS method as a function of *T*. It shows that the density of confined D_2O is 8% higher than bulk D_2O at room temperature.

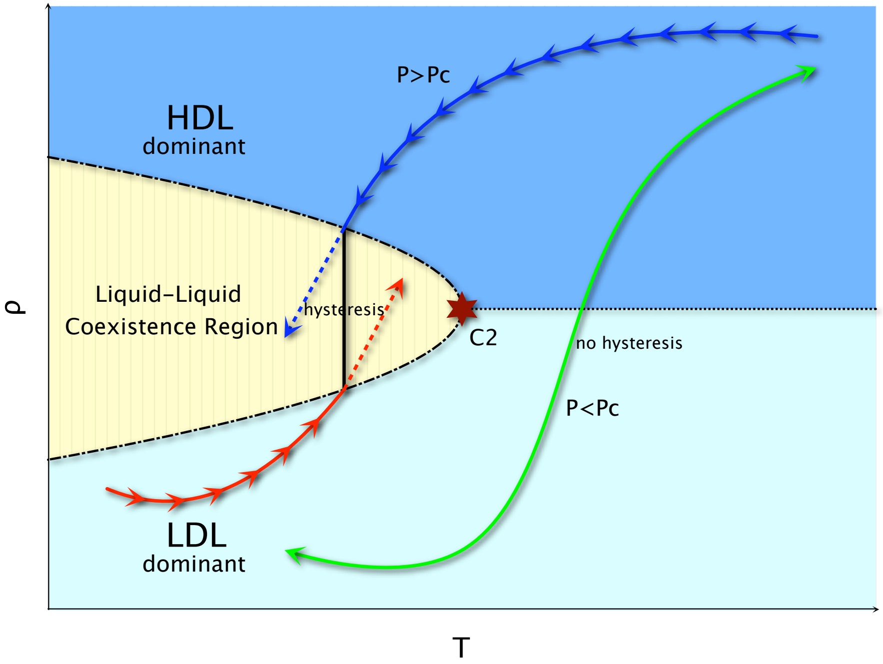
(B) The temperature derivative of density *vs.* *T* shows a peak at T_L = 235K for D_2O. This gives a direct evidence of crossing of the Widom line.

Density Measurement of 1-D Confined Water by Small Angle Neutron Scattering Method - Pore Size and Hydration Level Dependences

D. Liu, Y. Zhang, Y. Liu, J.-L. Wu, C.-C. Chen, C.-Y. Mou, S. -H. Chen, *J. Phys. Chem. B* **112,** 4309 (2008)

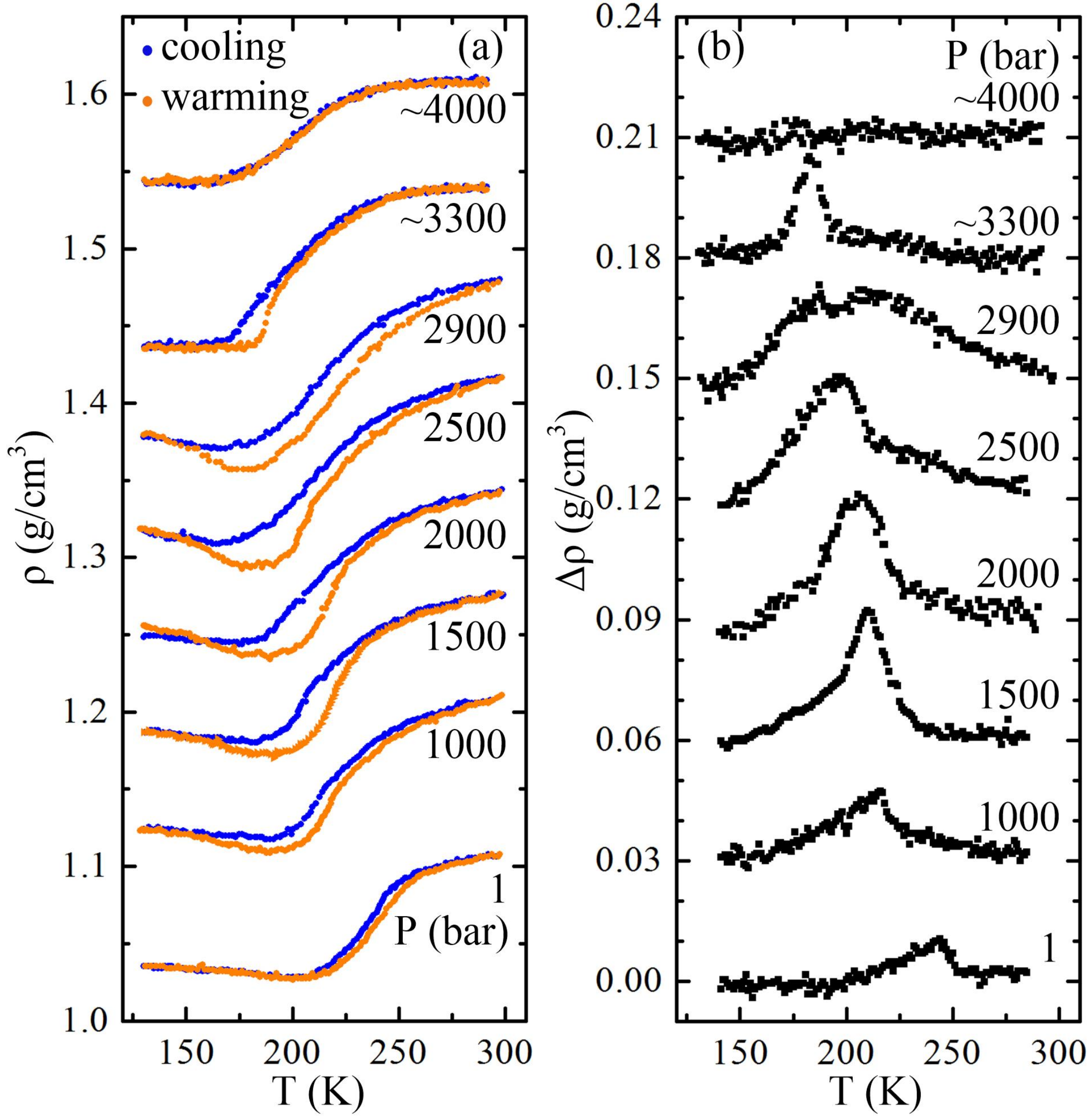
Method for Detection of the Liquid-Liquid Phase Transition





Y. Zhang, A. Faraone, W. Kamitakahara, K-H Liu, C-Y Mou, J. Leao & S.H. Chen*,
Density hysteresis of heavy water confined in nanoporous silica matrix, PNAS **108**, 12206-12211 (2011).

Evidence of the 1st-order Liquid-Liquid Phase Transition:Density Hysteresis [1, 2]



For each pressure, we measured the density by performing continuous temperature scans with warming and cooling routes. The speed of changing temperature is 0.2 K/min. The results are as follows:

1. Density hysteresis phenomenon appears at all pressures below 3500 bar;

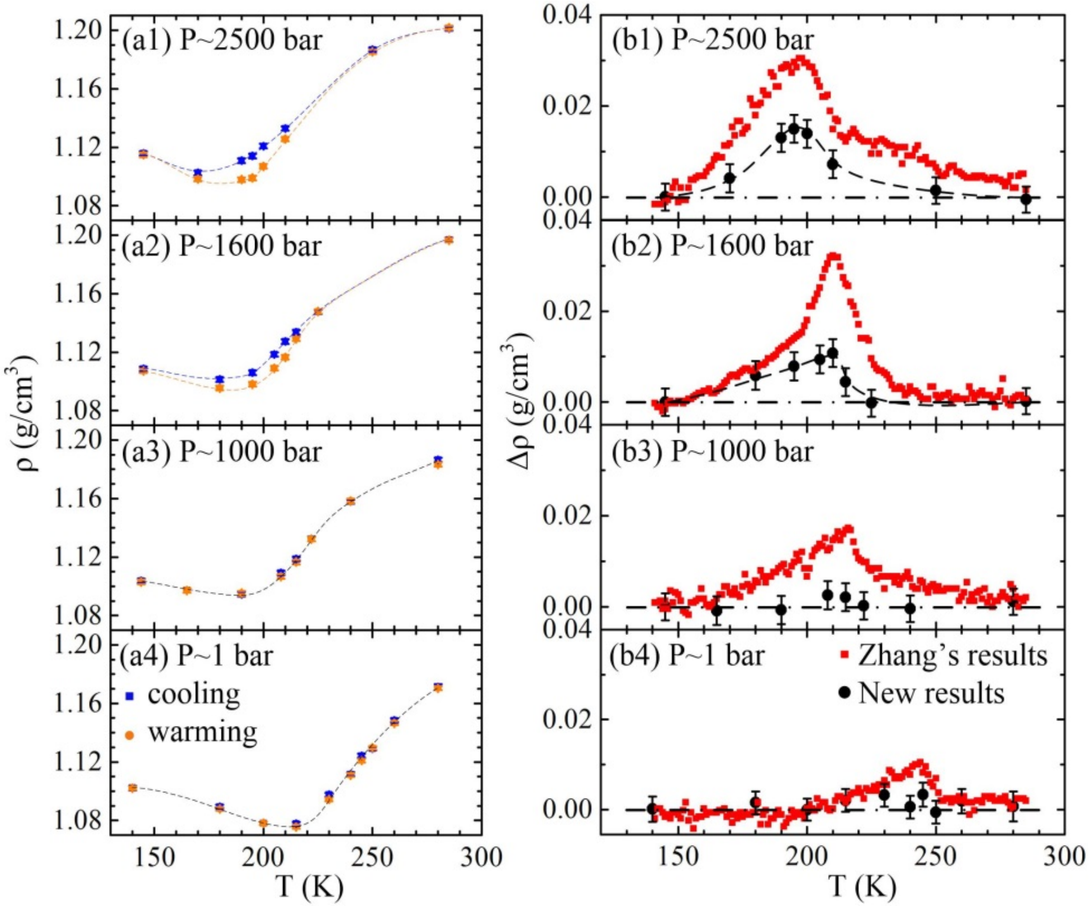
2. Below 1.5 kbar, the hysteresis enhances as P increases.

3. Above 1.5 kbar, the amplitude of the hysteresis stabilizes at 0.03 g/cm^3.

4. The temperature of the hysteresis shifts to lower T as P increases.

[1] Y. Zhang, et al., *Proc. Natl. Acad. Sci. USA*, **108**, 12206, 2011.
[2] Z. Wang, et al., *J. Chem. Phys*., **141**, 014501, 2014.

Evidence of the 1st-order Liquid-Liquid Phase Transition--Density Hysteresis



In the previous experiment [1], the author changes the temperature with a constant speed of 0.2 K/min by the temperature controller.

In this method, the sample temperature keeps on changing. It is quite possible that it cannot reach equivalence to the temperature of the sample holder. Thus, this method can introduce TEMPERATURE LAG between heating scan and cooling scan, and then produce a “false” hysteresis.

In order to remove this uncertainty, we performed the temperature scan with a new protocol: after the temperature reaches the desired temperature, we wait for additional 30 min to let the heat transfer completely finish. The result is shown in the above figure [2].

[1] Yang Zhang, et al., *Proc. Natl. Acad. Sci. USA*, **108**, 12206 (2011).

[2] Zhe Wang, K. Ito, Juscelino B. Leao, L. Harriger, Y. Liu and S.H. Chen*, *The Liquid-Liquid Phase Transition and its Phase Diagram in Deeply-Cooled Heavy Water Confined in a Nanoporous Silica Matrix, J. Phys. Chem. Lett.*, **6**, 2009-2014 (2015).

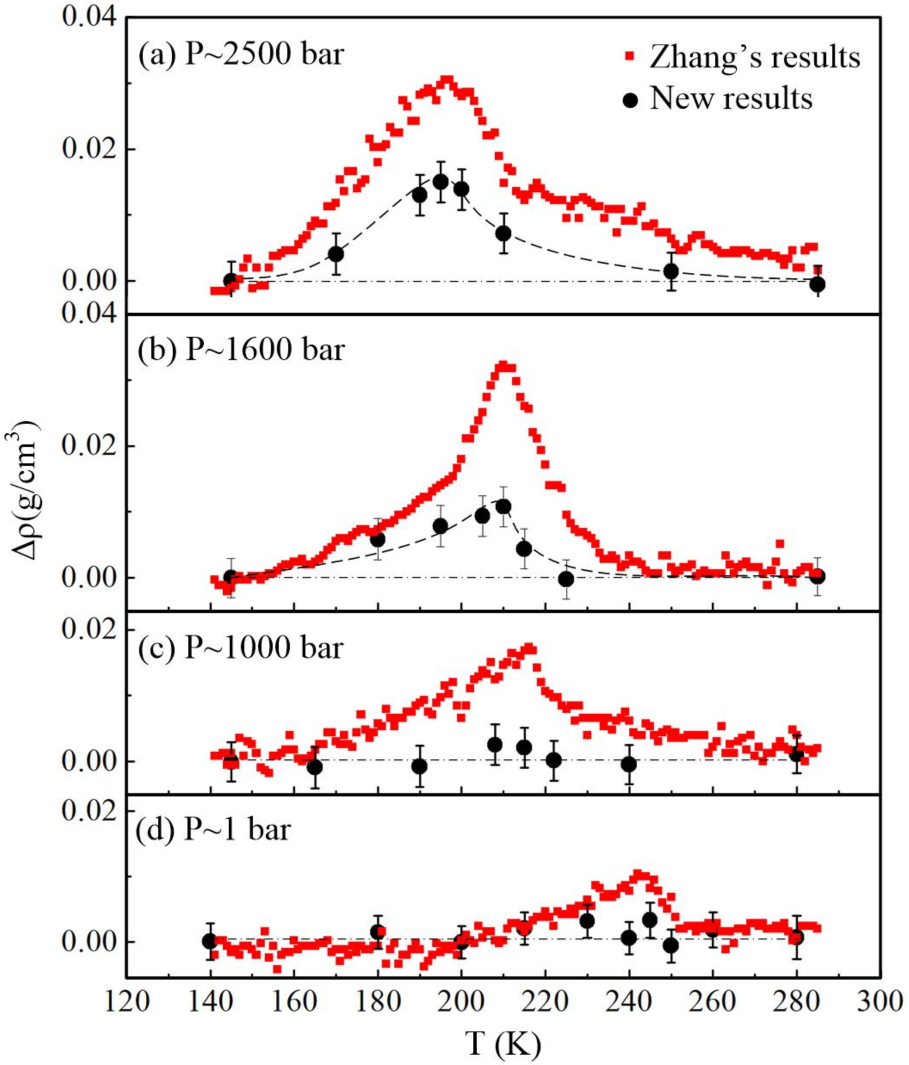
Evidence of the 1st-order Liquid-Liquid Phase Transition--Density Hysteresis [1]

The new result shows that:

1. **Effective hysteresis only appears when P>1.5 kbar;**
2. **The amplitude of the hysteresis increases as the pressure increases.**

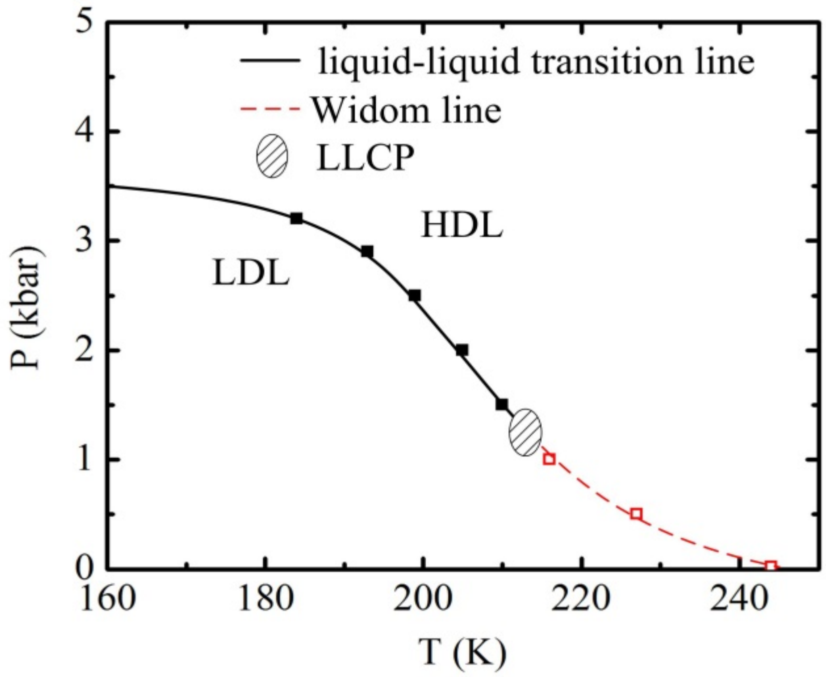
It suggests that:

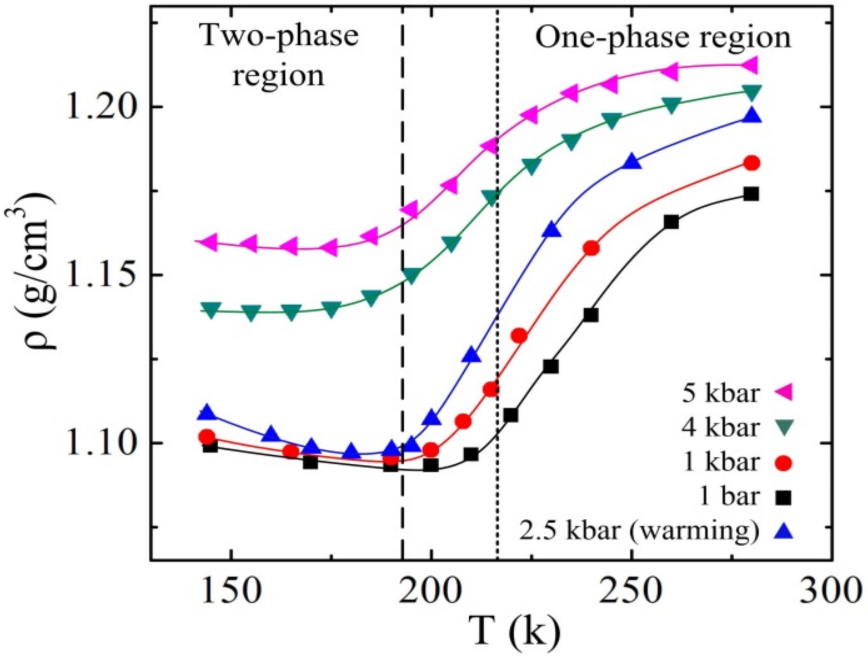
1. The end point of the liquid-liquid transition line (the critical point) locates at P_c =1.5±0.3 kbar, T_c=213±3 K.
2. The liquid-solid transition, proposed by Limmer and Chandler, is not consistent with this experimental result.
3. The low-pressure "false" hysteresis detected in the previous study is because of the temperature lag, rather than a phase transition.



[1] Zhe Wang, K. Ito, Juscelino B. Leao, L. Harriger, Y. Liu and S.H. Chen*, *The Liquid-Liquid Phase Transition and its Phase Diagram in Deeply-Cooled Heavy Water Confined in a Nanoporous Silica Matrix, J. Phys. Chem. Lett.*, **6**, 2009-2014 (2015).

Evidence of the 1st-order Liquid-Liquid Phase Transition-- the Equation of State [1]





We measure the density of the confined water as a function of T at different P (the equation of state) to test the obtained phase diagram (Shown in the right figure).

There is a clear gap between curves representing 1bar, 1kbar and 2.5 kbar (LDL), and the curves representing 4 kbar and 5 kbar (HDL). It suggests a phase separation between LDL and HDL at a pressure happen within this gap.

The isothermal compressibility (χ_T) of HDL is much larger than that of LDL. This is a reflection of the difference between the local structures of HDL and LDL.

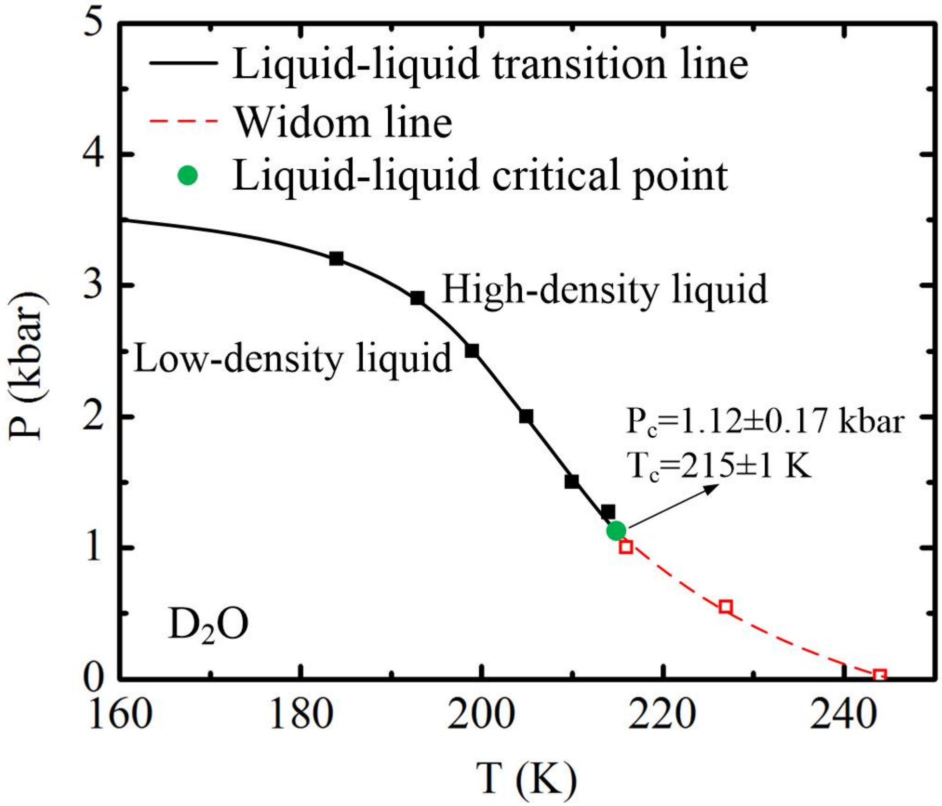
The sharp distinction on χ_T fades out as entering the one-phase region, which suggests that the LDL and HDL phases mix in this region.

[1] Zhe Wang, K. Ito, Juscelino B. Leao, L. Harriger, Y. Liu and S.H. Chen*, *The Liquid-Liquid Phase Transition and its Phase Diagram in Deeply-Cooled Heavy Water Confined in a Nanoporous Silica Matrix,* J. Phys. Chem. Lett., 6, 2009-2014, (2015).

Evidence of the 1st-order Liquid-Liquid Phase Transition--the Phase Diagram

Based on the latest experimental results, following phase diagram of the confined heavy water is obtained.

Zhe Wang, Kanae Ito and Sow-Hsin Chen, "Detection of the liquid-liquid transition in the deeply cooled water confined in MCM-41 with elastic neutron scattering technique", *Nuovo Cimento C* (2016) [1].



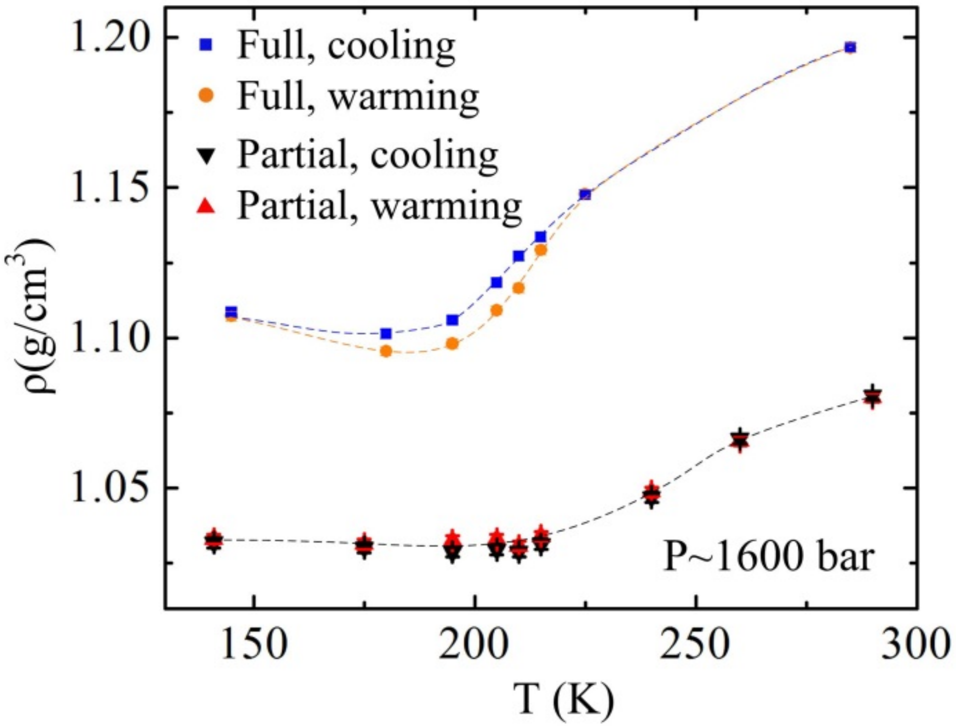
■ "Genuine" hysteresis, indicates crossing of the liquid-liquid transition line.

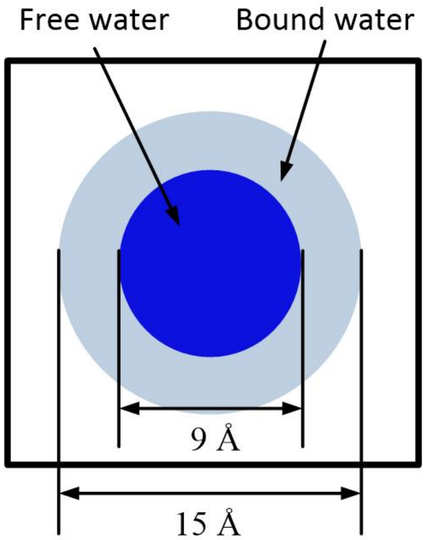
□ "Apparent or No" hysteresis, indicates crossing of the Widom line.

The black solid squares and the red open squares denote the positions of the maximum density differences obtained by the continuous temperature scans at pressures higher than the critical pressure and lower than the critical pressure, respectively. The former represents the LLPT line (denoted by a black solid line), while the latter represents the Widom line (denoted by a red dashed line). These two lines intersect at the LLCP, whose position is denoted by a solid green circle [1].

Zhe Wang, K. Ito, Juscelino B. Leao, L. Harriger, Y. Liu and S.H. Chen*, *The Liquid-Liquid Phase Transition and its Phase Diagram in Deeply-Cooled Heavy Water Confined in a Nanoporous Silica Matrix,* J. Phys. Chem. Lett., **6**, 2009-2014 (2015).

Absence of the 1st-order Liquid-Liquid Phase Transition in Partially-Hydrated Sample [1]





Cross section of the water confined in a pore of MCM-41 (fully-hydrated sample) [2]

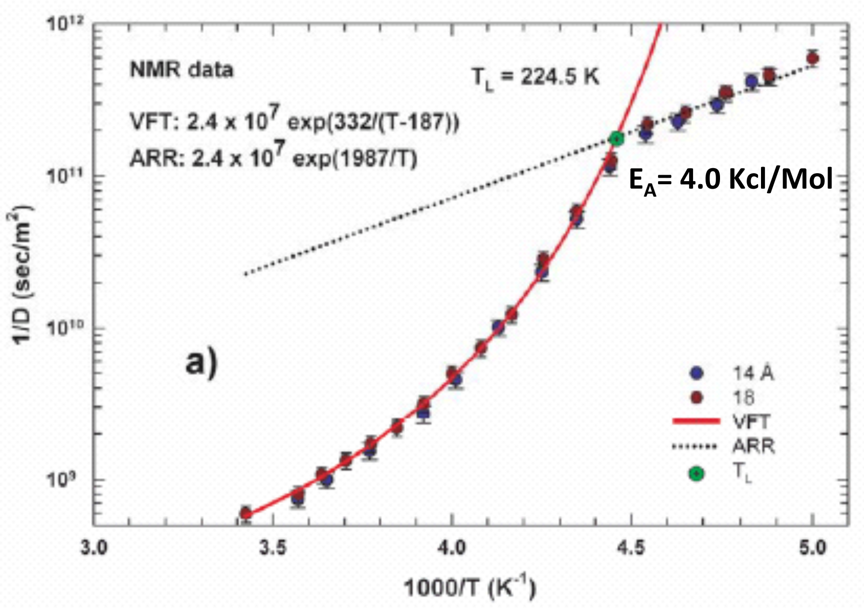
We measured a 80% partially-hydrated sample at ~1.6 kbar. In this sample, the amount of free water decreases by more than 50% compared to its fully-hydrated counterpart.

Strikingly, the density hysteresis totally disappears in the partial-hydrated sample.

It shows that: (1) the free water, not the bound water, undergoes a liquid-liquid transition, and (2) a well-developed hydrogen-bond network in free water is the necessary condition for water confined in MCM-41 to exhibit liquid-liquid transition.

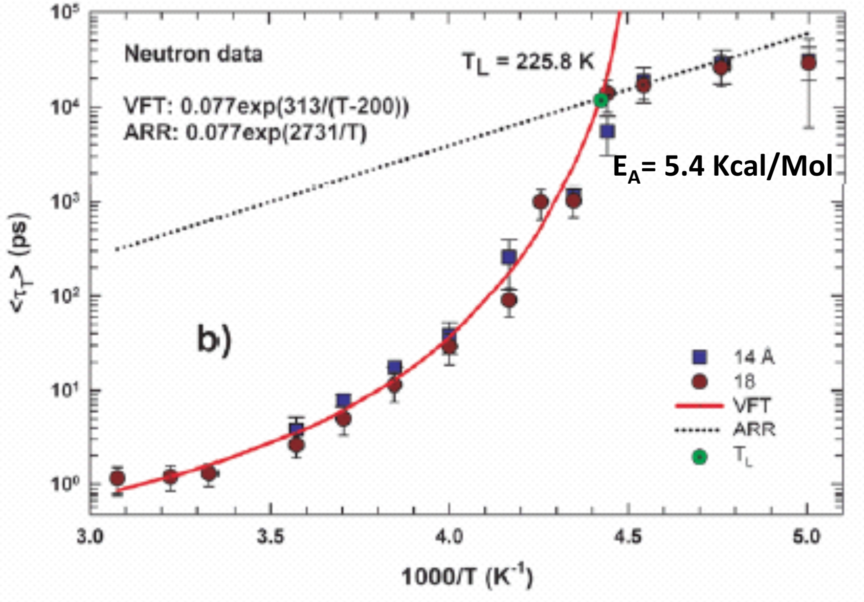
[1] Zhe Wang, K. Ito, Juscelino B. Leao, L. Harriger, Y. Liu and S.H. Chen*, *The Liquid-Liquid Phase Transition and its Phase Diagram in Deeply-Cooled Heavy Water Confined in a Nanoporous Silica Matrix,* J. Phys. Chem. Lett., **6**, 2009-2014, (2015).
[2] P. Gallo, M. Rovere., S.H. Chen *J. Phys. Chem. Lett.*, **1**, 729, (2010).

Fragile-to-Strong Dynamic Crossover Observed in Confined Water



FSC shown by 1/D of confined water in MCM-41-S-14 and MCM-41-S-18 measured by NMR

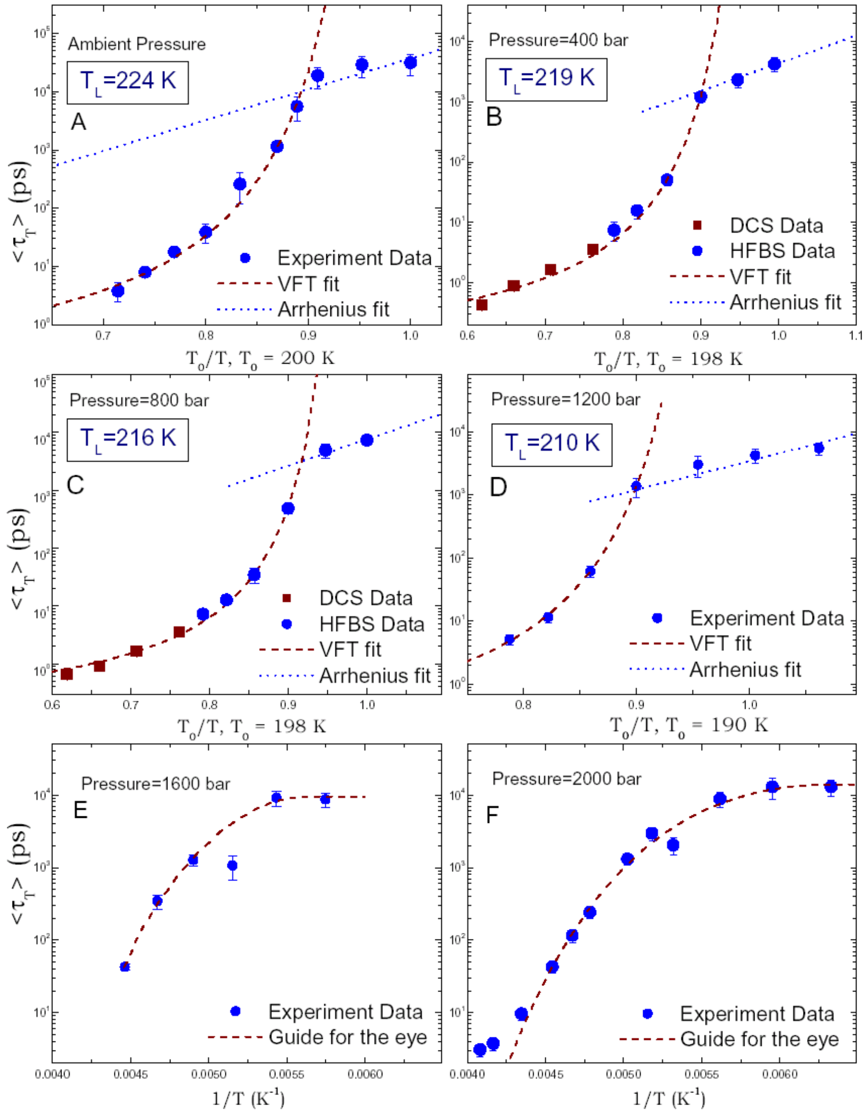
F. Mallamace, M. Broccio, C. Corsaro, A. Faraone, U. Wanderlingh, L. Liu, C.-Y. Mou, and S.-H. Chen, “The fragile-to-strong dynamic crossover transition in confined water: NMR results,” *J. Chem. Phys.* 124, 161102-161105 (2006).



FSC shown by $\langle\tau_T\rangle$ of confined water in MCM-41-S-14 and MCM-41-S-18 measured by QENS

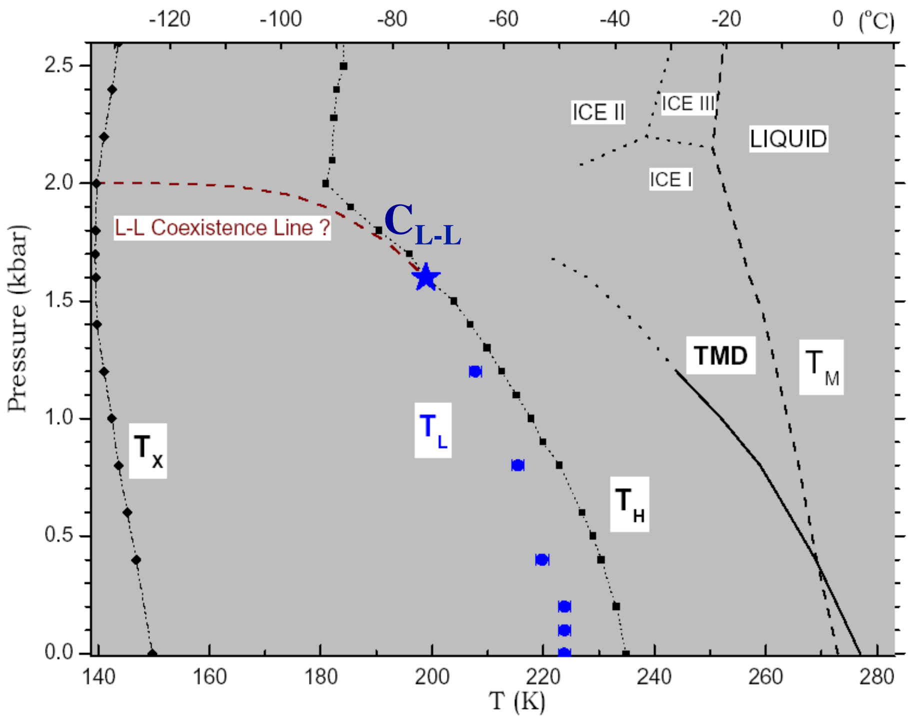
A. Faraone, L. Liu, C.-Y. Mou, C.-W. Yen, and S.-H. Chen, “Fragile-to-strong Liquid Transition in Deeply Supercooled Confined Water,” *J. Chem. Phys. Rapid Communication* 121, 10843-10846 (2004).

Fragile-to-Strong Dynamic Crossover under Pressure



"Relation between the Widom Line and the Strong-Fragile Dynamic Crossover in Systems with a Liquid-liquid Phase Transition", Limei Xu, P. Kumar, S.V. Buldyrev, S.H. Chen, P.H. Poole, F. Sciortino, H.E. Stanley, *PNAS* ***210**, 16558* (2005).

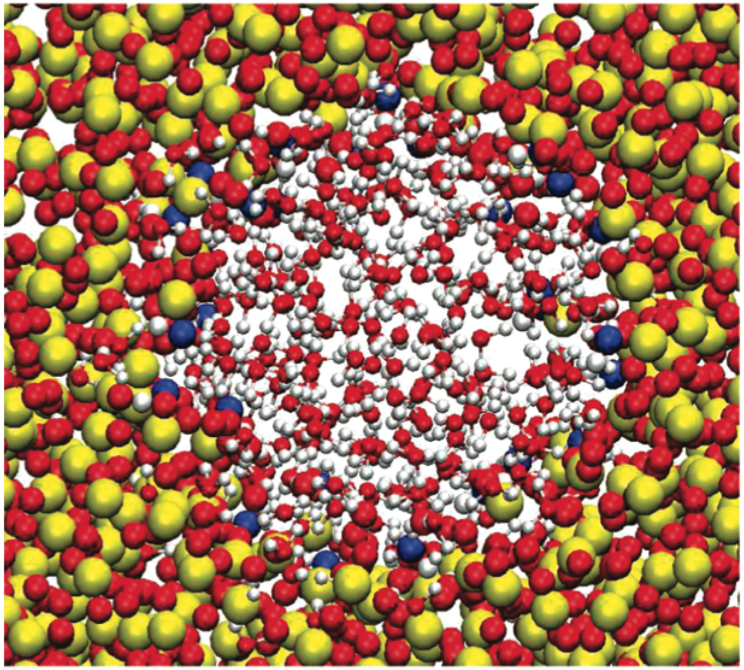
Pressure vs. Temperature Phase Diagram of H_2O

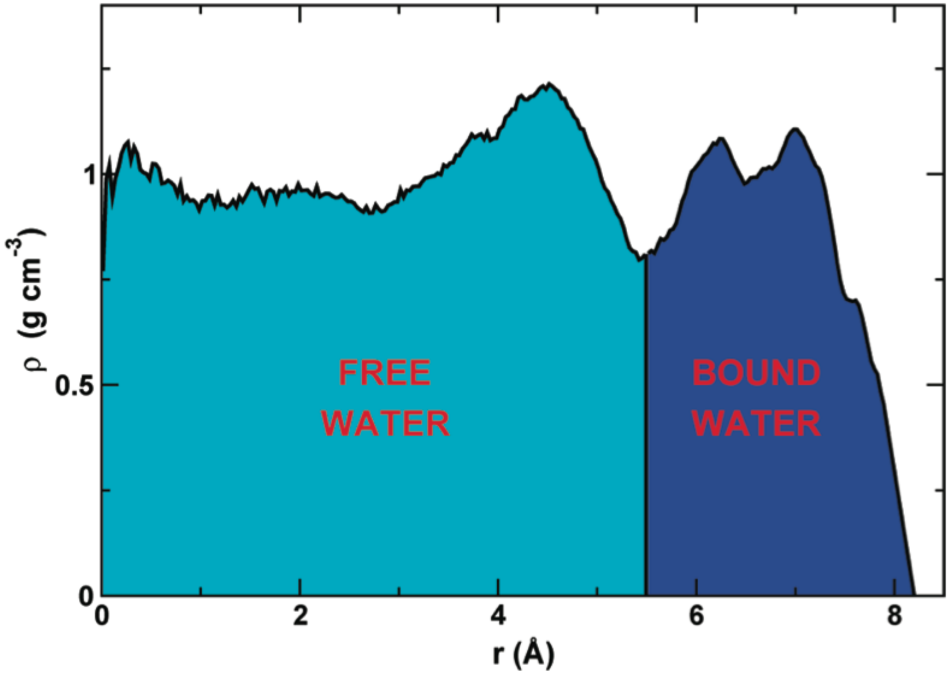


An extensive quasi-elastic neutron scattering experiment as a function of temperature at high pressures, by Chen's Group at MIT, indicates the approximate location of the second (liquid-liquid) critical point of water, C_{L-L}, for the first time.

Li. Liu, S.H. Chen, A. Faraone, C.W. Yan and C.Y. Mou, *Phys. Rev. Lett.* ***95**,* 117802 (2005).

Simulation Cell and Water Density Profile



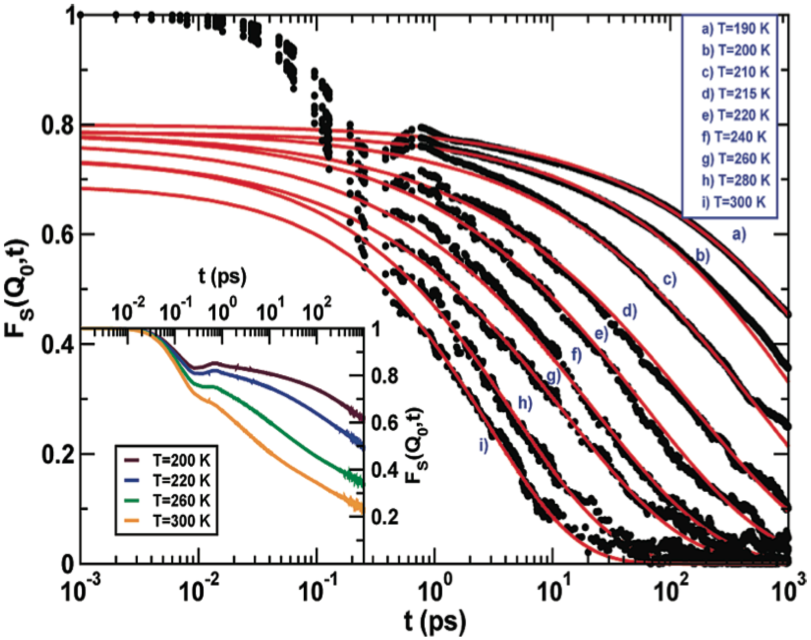


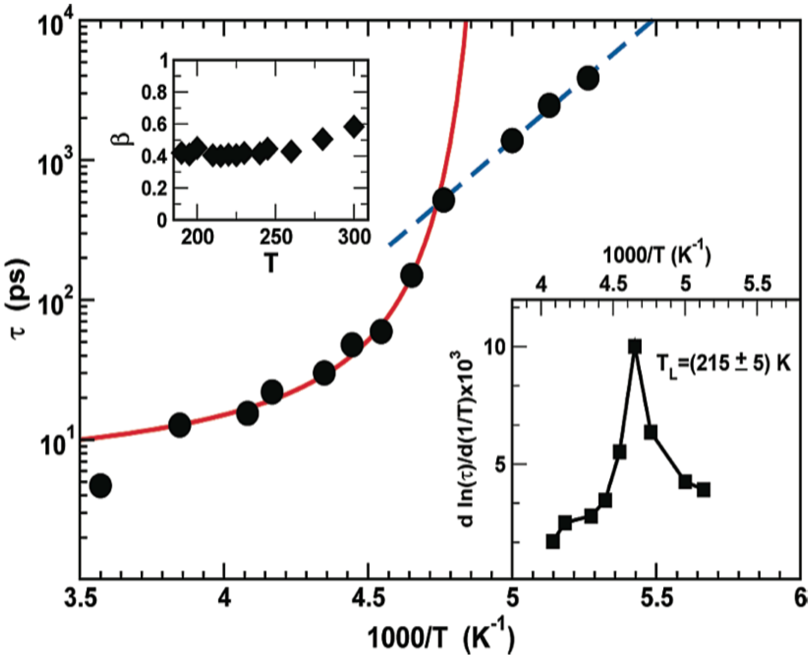
Left: projection in the x-y plane of the snapshot of the N = 380 water molecules configuration inside of the silica cavity at T = 220 K. A portion of the silica surface is shown. The larger spheres are silicon atoms, and the darker are acidic hydrogens.

Right: density profile of oxygen atoms of water along the pore at T = 300 K. With the chosen number of particles, the effective density inside of the pore is around 0.98 g/cm^3, while the density in the inner part of the pore ($0 < r < 5.5$ Å) is around 1.0 g/cm^3.

P. Gallo, M. Rovere and S.H. Chen, *Dynamic Crossover in Supercooled Confined Water*, JPCL (2010) **1**, 729-733

The α-relaxation Time Extracted From Analyses of the Free Water and Its Arrhenius plot





Left-frame: self-intermediate scattering function (SISF) of the oxygen atoms of the free water for $Q_0 = 2.25$ Å^{-1} from T = 300 K (bottom) to 190 K (top). The continuous lines are the fit to the Kohlrausch-William-Watts (KWW) formula $Fs(Q,t) = f_Q \exp[-(t/\tau)^{\beta}]$, where f_Q is the height of the plateau, τ is the alpha-relaxation time, and β is the Kohlrausch exponent. Inset: SISF of the oxygen atoms of all of the water molecules for $Q_0 = 2.25$ Å^{-1} for a selected set of temperatures.

Right frame: Arrhenius plot of the relaxation time τ as a function of 1000/T. At high temperature, below 300 K, the points are fitted with VFT formula (bold line) $\tau = \tau_0 \exp[BT_0/(T - T_0)]$, where B is the fragility parameter and T_0 is an ideal glass transition temperature. The parameters extracted from the fit are B = 0.25 and T_0 = 200 K. At low temperature, the fit is done with the Arrhenius function (long dashed line) $\tau = \tau^A_0 \exp[E_A/k_B T]$, where E_A is the activation energy. We find from our data an activation energy of E_A = 34 kJ/mol. Lower inset: inverse temperature derivative of the logarithm of τ. Upper inset: β values.

P. Gallo, M. Rovere and S.H. Chen, *Dynamic Crossover in Supercooled Confined Water*, JPCL (2010) 1, 729-733.

Detection of the Liquid-Liquid Transition by Boson Peak

- **In the confined water, boson peak begins to appear between 230 K -240 K at ambient pressure.**
- **This onset temperature is close to the dynamic crossover temperature T_L and hysteresis temperature.**

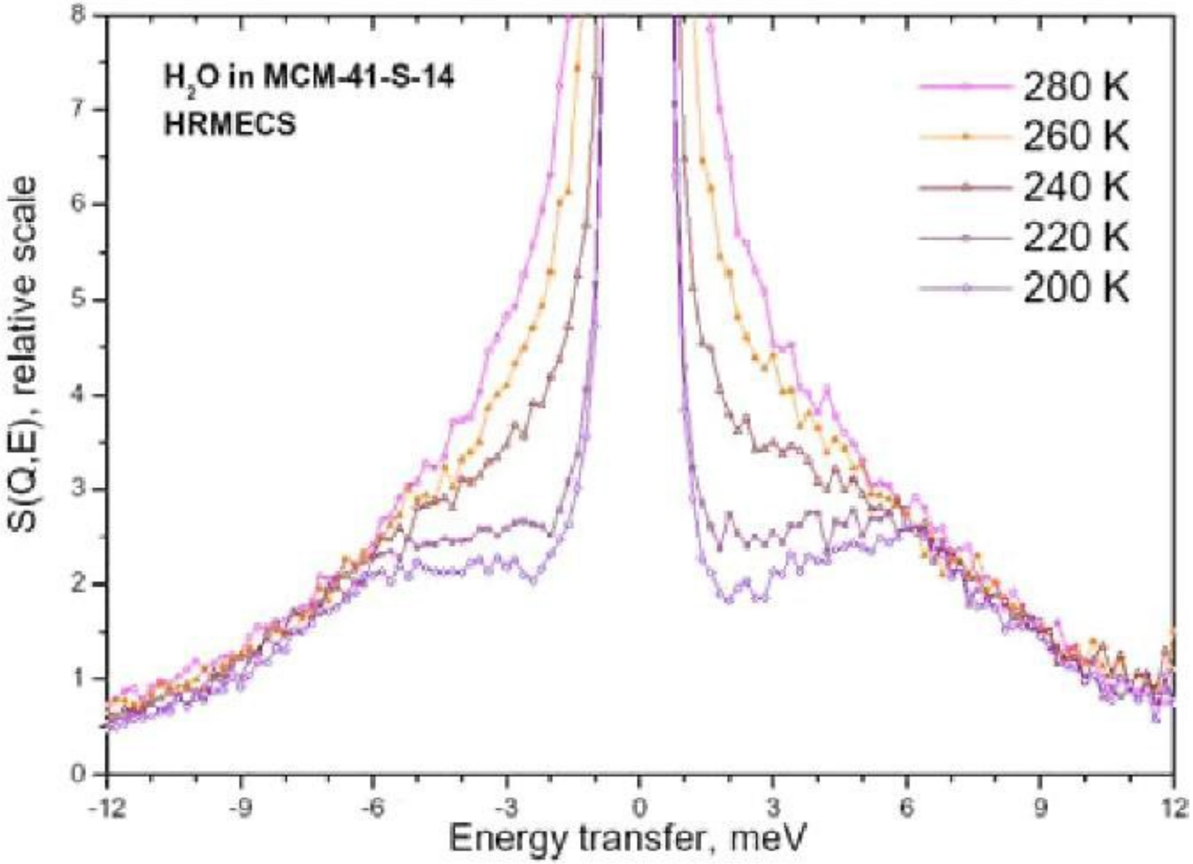
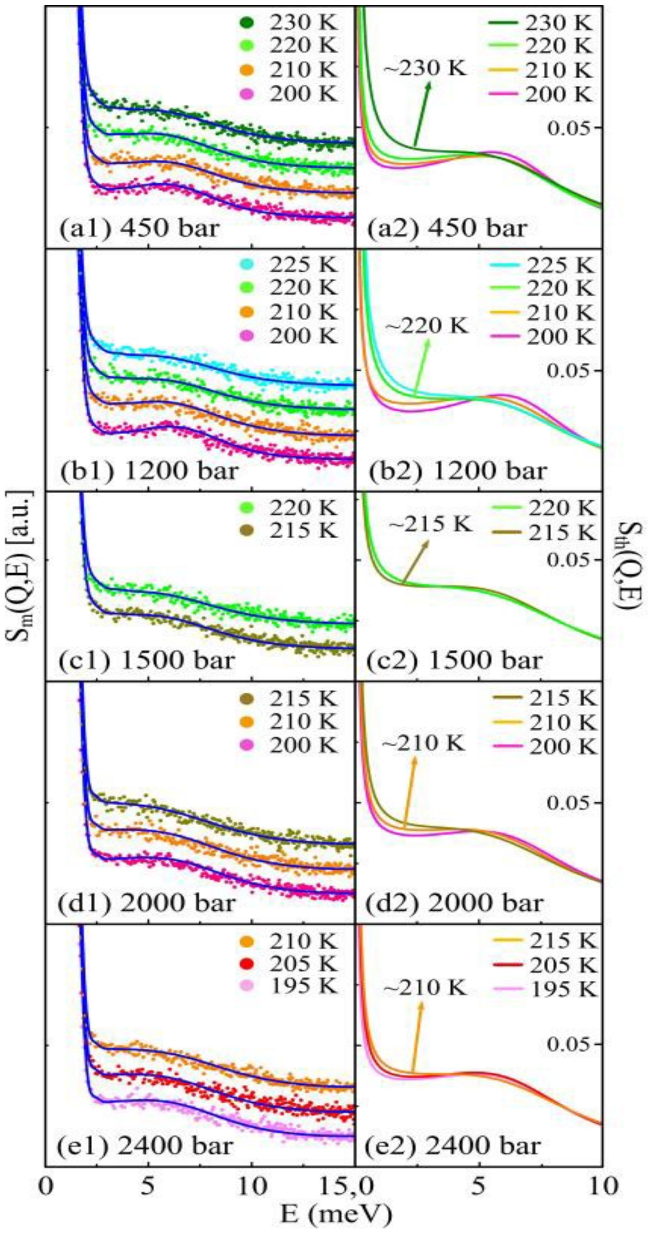


Fig.1. The Boson peaks of water confined in MCM-41 [1].

[1] S.-H. Chen et al., AIP Conf. Proc. 982, 39, 2008.

Detection of the Liquid-Liquid Transition by Dynamic Measurement

Boson Peak in One-Phase Region



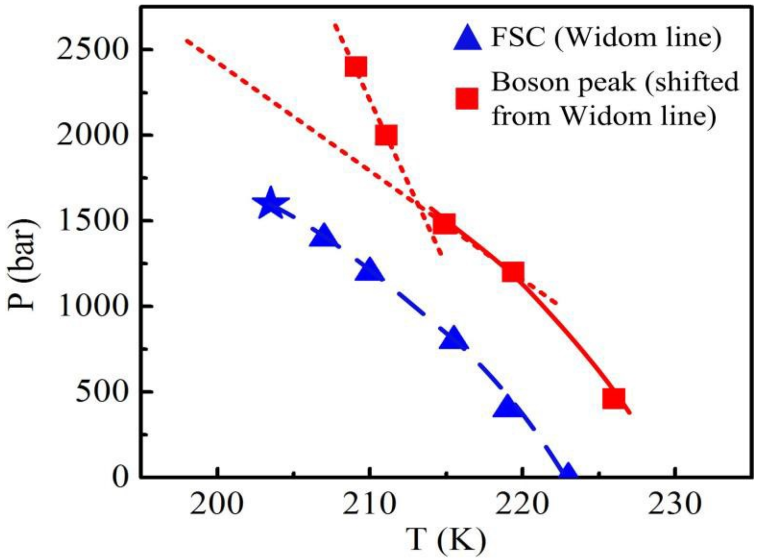


Figure. The red squares represent the point that the boson peak emerges. The blue triangles demarcate the Fragile-to-Strong Crossover (FSC). The blue dashed line denotes the Widom line. The blue star denotes the estimated location of the liquid liquid critical point, obtained from the FSC measurements [Liu et al., PRL, 2005]. The red line is shifted about 7 K higher than the Widom Line.

- **Below critical pressure, the locus of the emergence of the boson peak is parallel to the Widom line. This result is consistent with the computer simulation study***[2] P. Kumar, et al., Sci. Rep. 3, 1980, 2013.*
- **Above critical pressure, the locus of the emergence of the boson peak in the (P,T) plane has a different slope as compared with its behavior below critical pressure.**
- **These results suggest that the inelastic neutron spectrum may respond to the existence of the HDL and LDL** *[1] Z. Wang, et al., Phys. Rev. Lett., 112, 237802, 2014,"Boson Peak in Deeply Cooled Confined Water: A Possible Way to Explore the Existence of the Liquid-to-Liquid Transition in Water".*

Detection of the Liquid-Liquid Transition by Dynamic Measurement

Boson Peak in Two-Phase Region

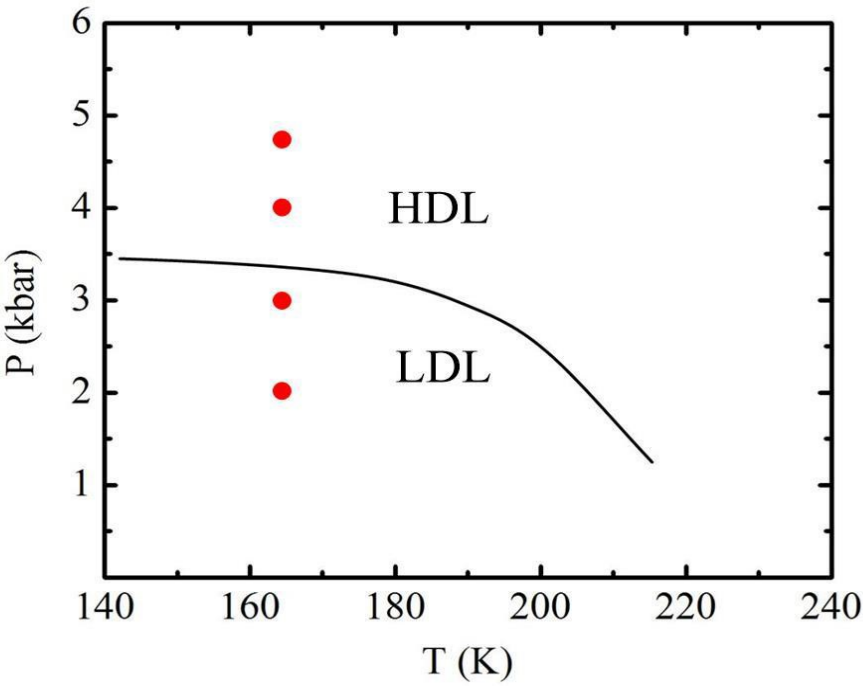


Fig. 1. The phase separation line of the deeply-cooled heavy water confined in MCM-41 [1]. The red circles denote the measurement points of the boson peak.

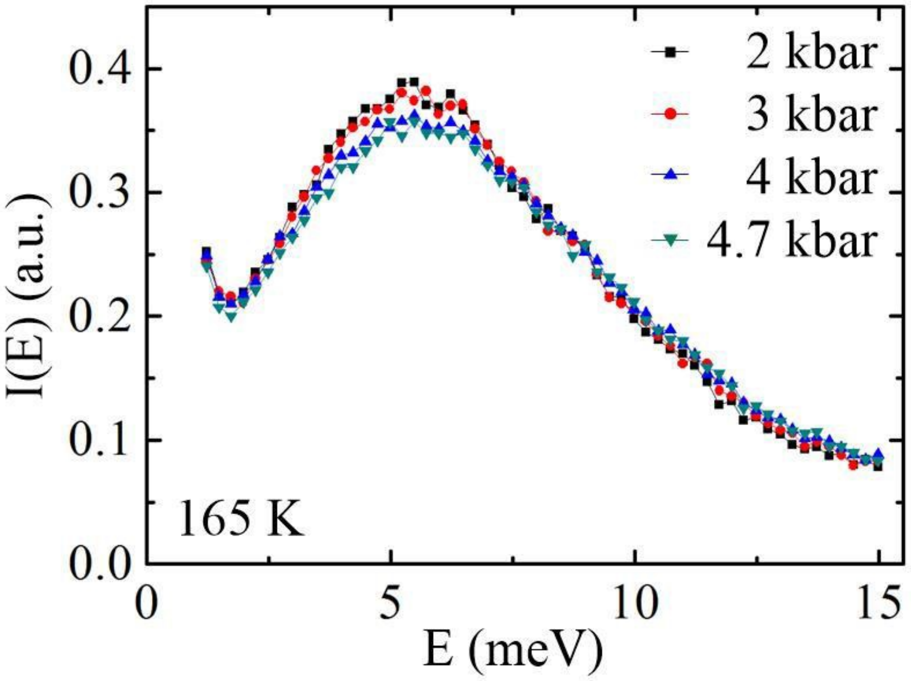


Fig. 2. The measured spectra (boson peak) of the confined H_2O at T=165 K and under 4 pressures: 2, 3, 4, and 4.7 kbar [2].

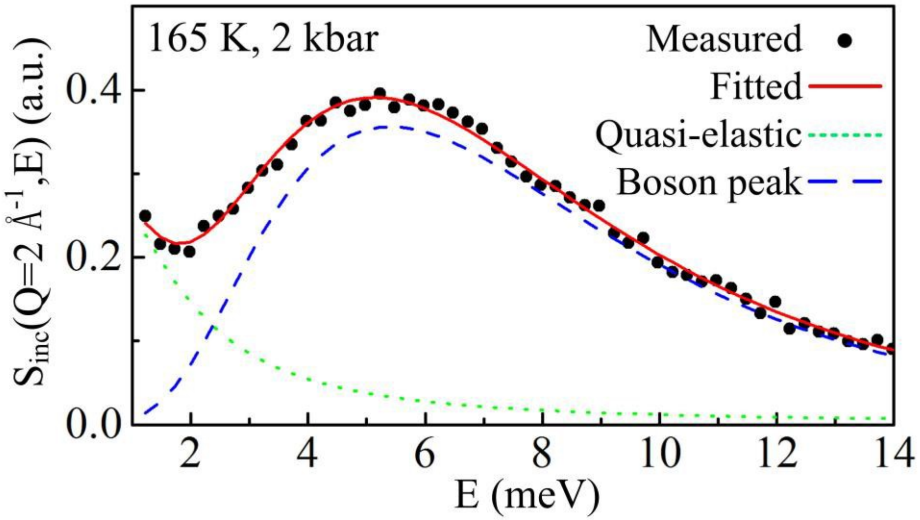
1. **The amplitude of boson peak decreases as the pressure (or density) increases within 2 to 8 meV.**
2. **The change in spectra between the 3000 bar (in LDL) case and 4000 bar (in HDL) case is most significant.**

[1] Zhe Wang, K.Ito, J.B.Leao, L. Harriger, Y. Liu, S.-H. Chen, *Liquid-Liquid Phase Transition and Its Phase Diagram in Deeply Cooled D_2O Confined in Nanoporous Silica Matrix, J Phys Chemistry Letters,* ***6,*** *2009, (2016).*

[2] Zhe Wang, Alexander I. Kolesnikov, Kanae Ito, Andrey Podlesnyak, and Sow-Hsin Chen, *Pressure Effect on Boson Peak in Deeply Cooled Confined Water: Evidence of a Liquid-Liquid Transition*, *PRL,**115**, 235701(2015).*

Detection of the Liquid-Liquid Transition by Dynamic Measurement

Boson Peak in Two-Phase Region



The measured spectrum can be fitted well by Lorentzian + Lognormal distribution

$$S_{inc}(Q,E) = \frac{1}{\pi}\frac{A_1\gamma}{E^2+\gamma^2} + \frac{A_2}{\sqrt{2\pi}\sigma E}\, exp\left[\frac{-(E_{BP}-lnE)^2}{2\sigma^2}\right]$$

Fitting parameteres: A_1, γ, A_2, σ, E_{BP} .

We define the following three quantities:

1. **M: the mean frequency of the boson peak.**
2. **H: the height of the boson peak.**
3. **V: the variance of the boson peak.**

[1] **Zhe Wang, Alexander I. Kolesnikov, Kanae Ito, Andrey Podlesnyak, and Sow-Hsin Chen,** *Pressure Effect on Boson Peak in Deeply Cooled Conned Water: Evidence of a Liquid-Liquid Transition*, PRL, **115**, 235701(2015).

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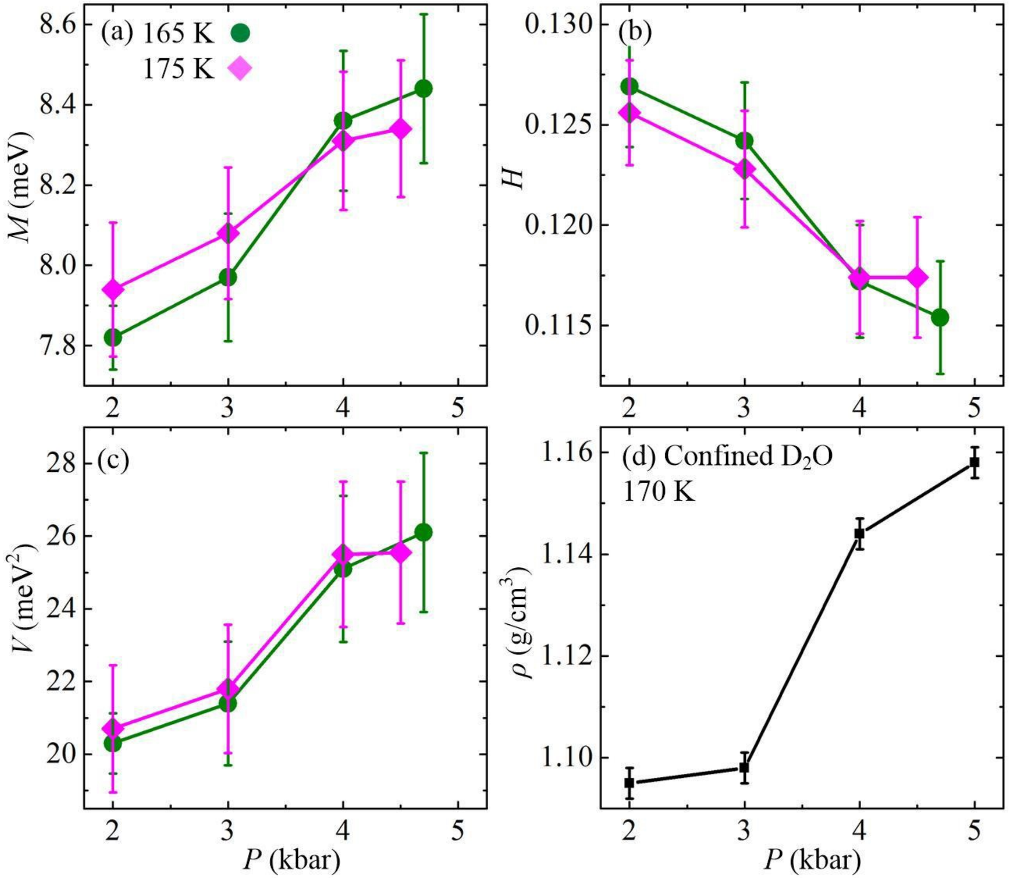
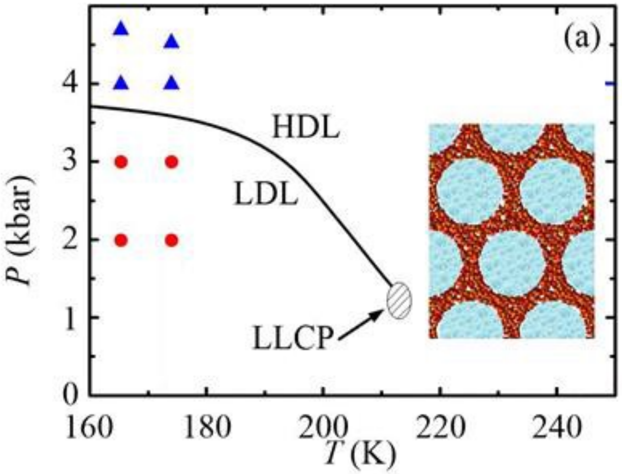




As the confined water system transforms from LDL and HDL:

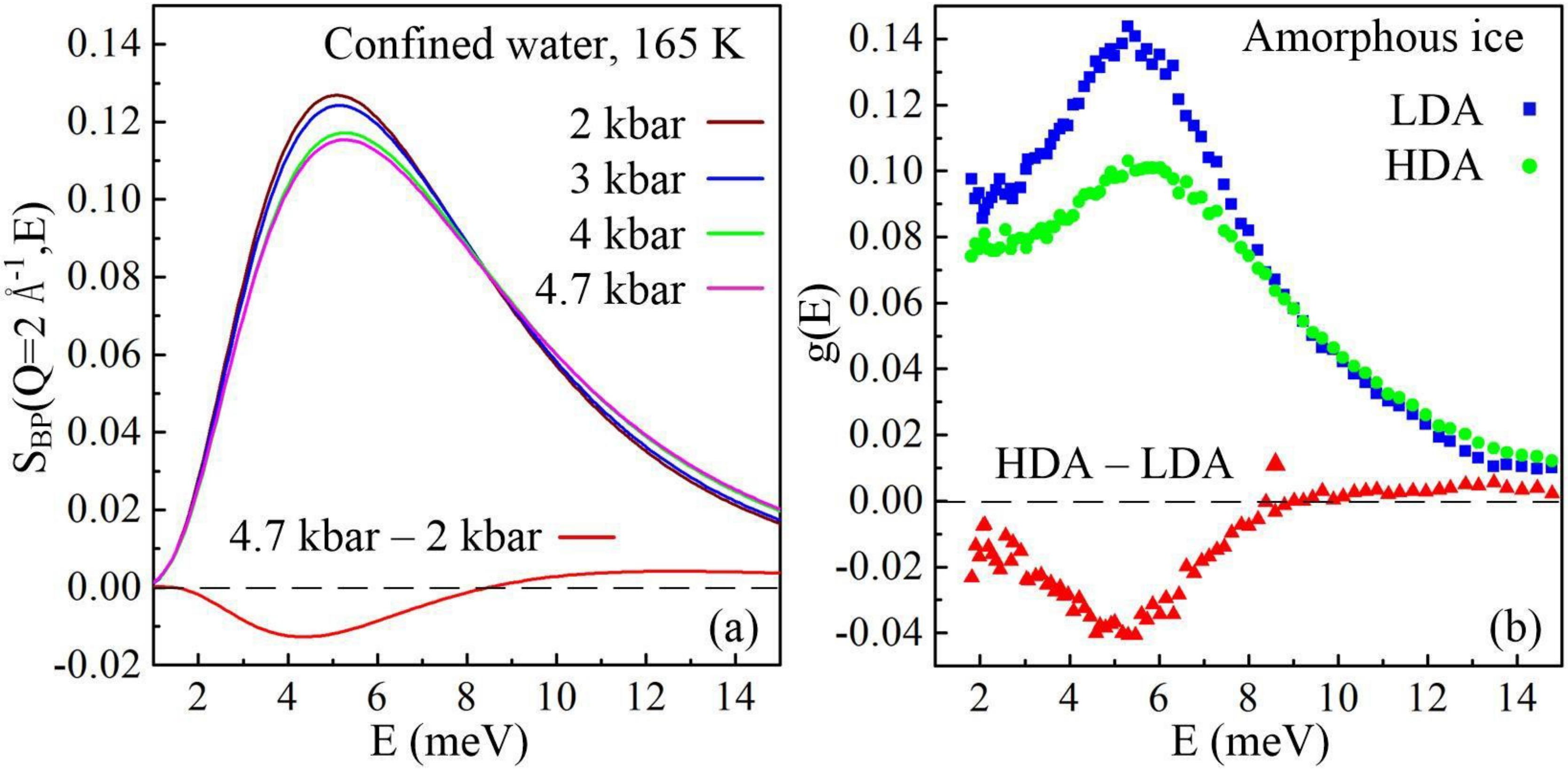
1. **both M and V undergo an abrupt change to higher values.**
2. **the height H decreases.**

These changes indicate a change of the density of the system.

Zhe Wang, Alexander I. Kolesnikov, Kanae Ito, Andrey Podlesnyak, and Sow-Hsin Chen, *Pressure Effect on Boson Peak in Deeply Cooled Confined Water: Evidence of a Liquid-Liquid Transition*, PRL,**115**, 235701 (2015)**.**

Detection of the Liquid-Liquid Transition by Dynamic Measurement

Boson Peak in Two-Phase Region



The spectral difference of HDL-LDL [1] is similar to that of HDA-LDA [2]. It indicates that

1. The local structure change from LDL to HDL is similar to that from LDA to HDA.

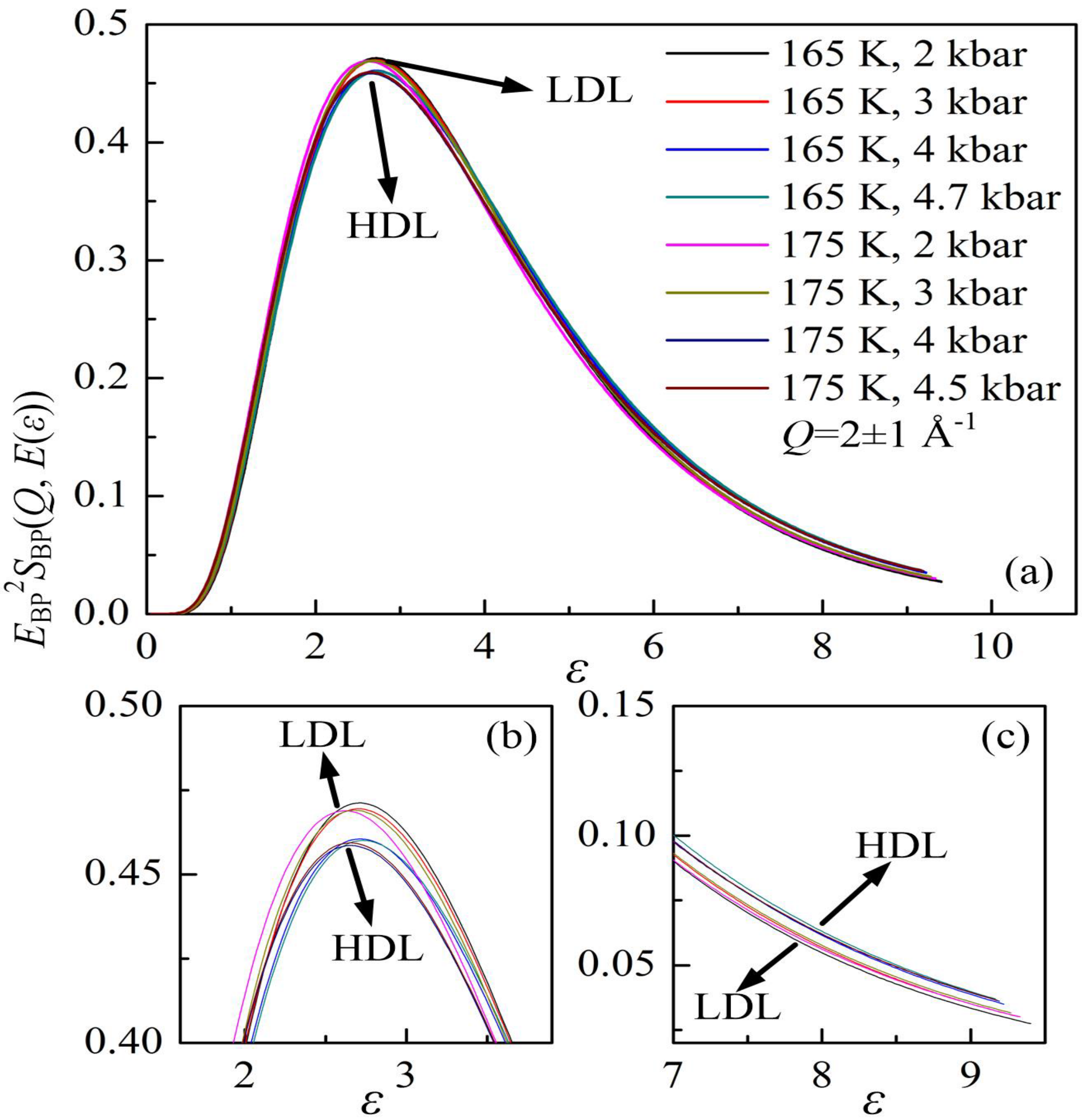
2. LDL and HDL are thermodynamic extensions of LDA and HDA into the liquid state.

[1]] **Zhe Wang, Alexander I. Kolesnikov, Kanae Ito, Andrey Podlesnyak, and Sow-Hsin Chen,** *Pressure Effect on Boson Peak in Deeply Cooled Confined Water: Evidence of a Liquid-Liquid Transition*, PRL,**115,** 235107 (2015).

[2] M. M. Koza, Phys. Rev. B, 78, 064303, 2008.

Boson Peaks in Two-Phase Region

These figures show that boson peaks can be rescaled with respect to E_{BP}: E —> $\varepsilon=E/E_{BP}$ [1].



All the curves can be grouped into two master curves [2].

One represents LDL, the other represents HDL.

Their difference is due to the structural change leading to density change of these two phases of water[3].

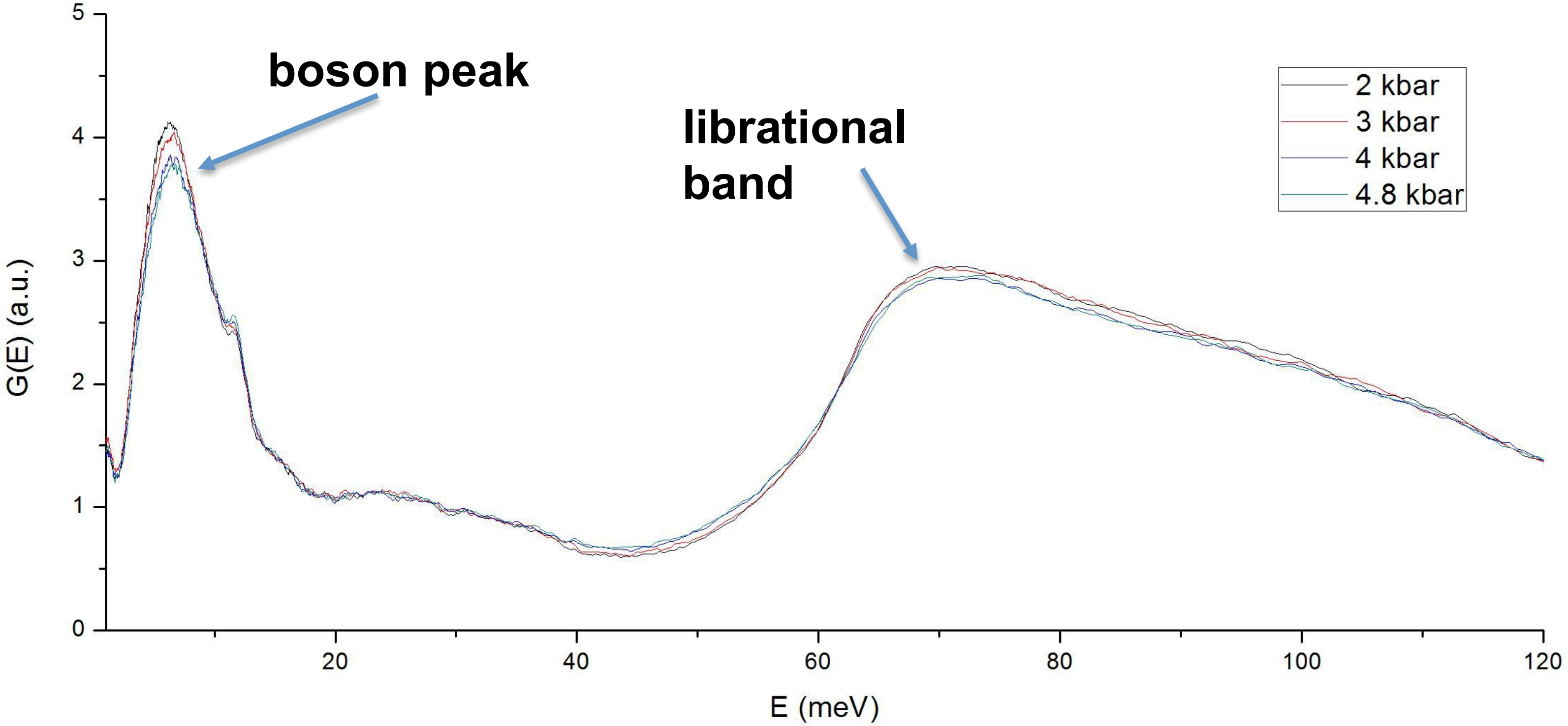
[1] T. S. Grigera, V. Martin-Mayor, G. Parisi, and P. Verrocchio, *Nature* 422, 289, 2003.

[2] Zhe Wang, Alexander I. Kolesnikov, Kanae Ito, Andrey Podlesnyak, and Sow-Hsin Chen, *Pressure Effect on Boson Peak in Deeply Cooled Confined Water: Evidence of a Liquid-Liquid Transition*, PRL,**115,** 235701(2015).

[3] A. Monaco, A. I. Chumakov, G. Monaco, et al., Phys. Rev. Lett. 97, 135501, 2006.

Detection of the Liquid-Liquid Transition by Dynamic Measurement

Librational Motion

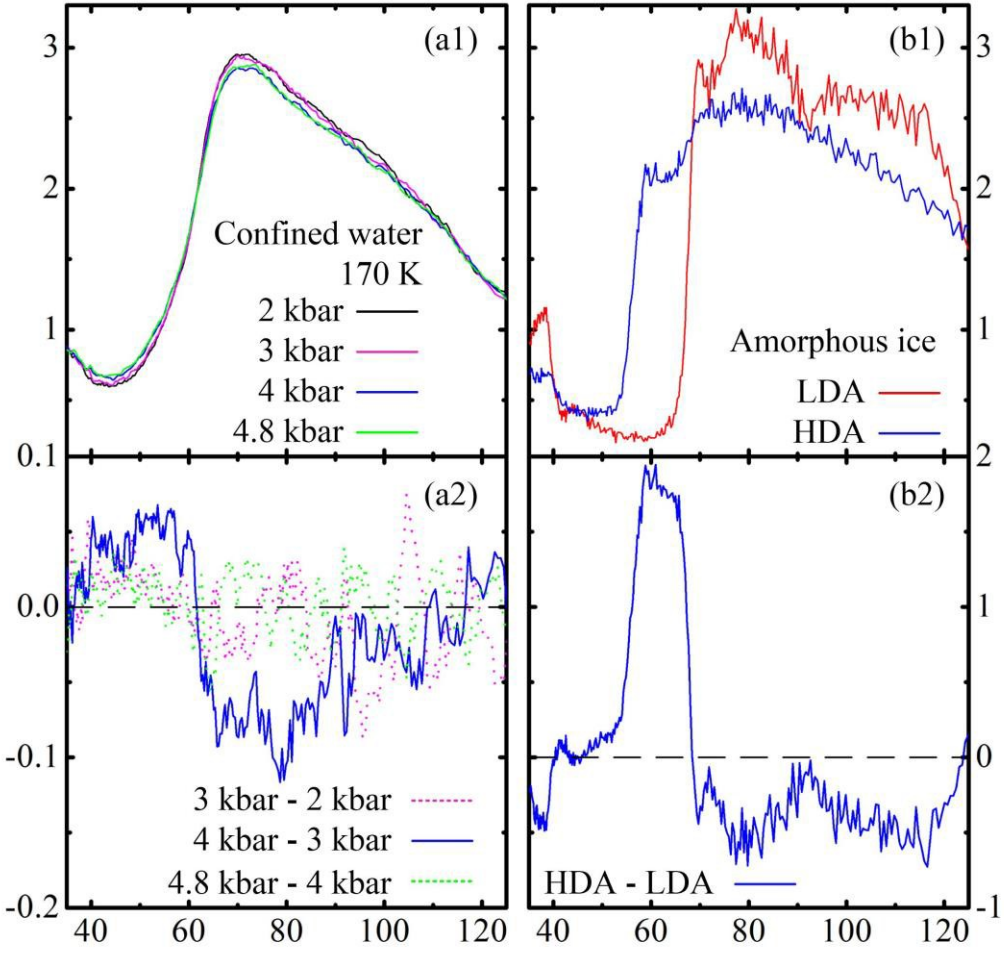


We perform a measurement on the vibrational Density of States (vDoS) of the confined water at 170 K and at 2 ,3, 4, and 4.8 kbar. The low-frequency part is consistent with the CNCS result on boson peak.

[1] **Zhe Wang, Alexander I. Kolesnikov, Kanae Ito, Andrey Podlesnyak, and Sow-Hsin Chen,** *Pressure Effect on Boson Peak in Deeply Cooled Conned Water: Evidence of a Liquid-Liquid Transition*, PRL, **115,** 235701(2015).

Detection of the Liquid-Liquid Transition by Dynamic Measurement

Librational Motion



[1] Zhe Wang, Alexander I. Kolesnikov, Kanae Ito, Andrey Podlesnyak, and Sow-Hsin Chen**,** *Pressure Effect on Boson Peak in Deeply Cooled Confined Water: Evidence of a Liquid-Liquid Transition,* PRL,**115,** 235701, 2015 (a1 and a2).

[2] A. I. Kolesnikov, et al., Phys. Rev. B 59, 3569, 1999 (b1 and b2).

[3] J. Li, et al., J. Mol. Liq. 010, 1, 2002.

1. **The energy of the low-energy side of the librational band measured at 4 kbar (HDL) is lower than that measured at 3 kbar (LDL) by a few meV. It indicates that the hydrogen bond between the central water molecule and first shell becomes weaker from LDL to HDL [1].**
2. **This change is similar to the change from LDA to HDA [2,3] (but with much smaller amplitude).**

Summary

(1) Elastic Neutron Diffraction measurements of D_2O give the density profile (density as a function of T) of supercooled water. It shows a pronounced hysteresis phenomenon above 1500 bar. This is the strongest evidence so far for the presence of a 1st order liquid-liquid phase transition line above this pressure. More recently, by directly measuring the densities in the pure LDL and HDL phases, we are able to determine the LLPT line and the associated Widom line of D_2O. From this the critical temperature is estimated to be at T_c= 215±1 K. The critical pressure is also estimated to be P_c=1.12±0.17 Kbar.

(2) The discovery of the Dynamic Crossover phenomenon in H_2O by Quasi-Elastic Neutron Scattering measurements identifies the existence of the Widom line for pressures below 1600 bar. This indicates the presence of one-phase region below this pressure.

(3) Parallel to the density measurement for D_2O, we also test the phase diagram by measuring dynamic properties of the system, including the Boson Peak and the Librational Band in H_2O.

(4) These Inelastic Neutron Scattering experiments give a strong evidence for the emergence of the LDL phase on the lower pressure side of the 1st order liquid-liquid phase transition line mentioned in point (1), as the result of thermodynamic continuation of the LDA amorphous ice into the liquid state. Likewise, the HDL phase above the 1st order liquid-liquid phase transition line is the continuation of the HDA amorphous ice into the liquid state as well.

Thus We Give Clear Evidence for Existence of the Liquid-Liquid Phase Transition (LLPT) in the Confined Water.

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Young-Laplace Effect

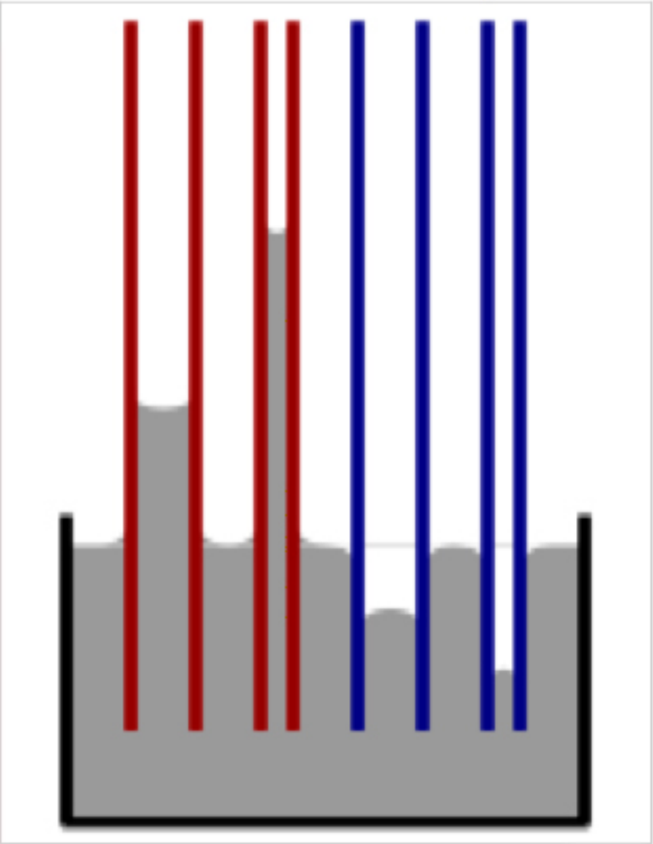
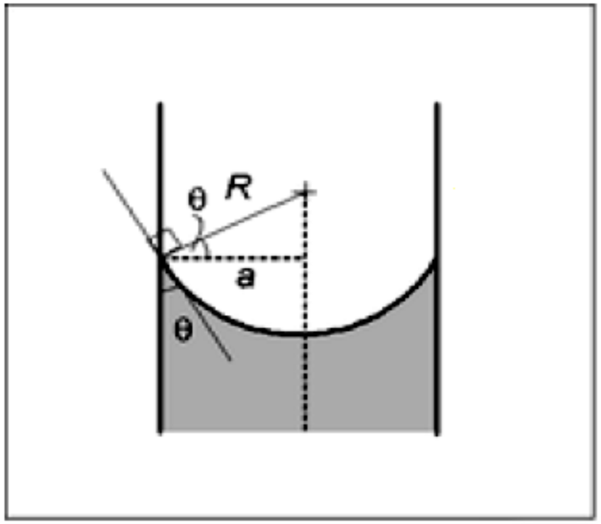


Illustration of capillary rise.
Red=contact angle less than 90°;
blue=contact angle greater than 90°

http://en.wikipedia.org/wiki/Young%E2%80%93Laplace_equation



Spherical meniscus with
wetting angle less than 90°

This is the case for MCM-41S

the pressure difference may be written as:

$$\Delta p = \frac{2\gamma \cos\theta}{a}.$$

$$\Delta p = p_{\text{outside}} - p_{\text{inside}}$$

For silica capillary tube of radius a =10 Å, Θ = 20° and the surface tension of water γ= 86 dyne/cm^2 at T = 200 K, then Δ*p* = 1620 bar. So, the Mishima's value 2000 bar in his phase diagram would appear in our phase diagram as: 2000 bar + 1620 bar = 3620 bar, which is approximately correct.

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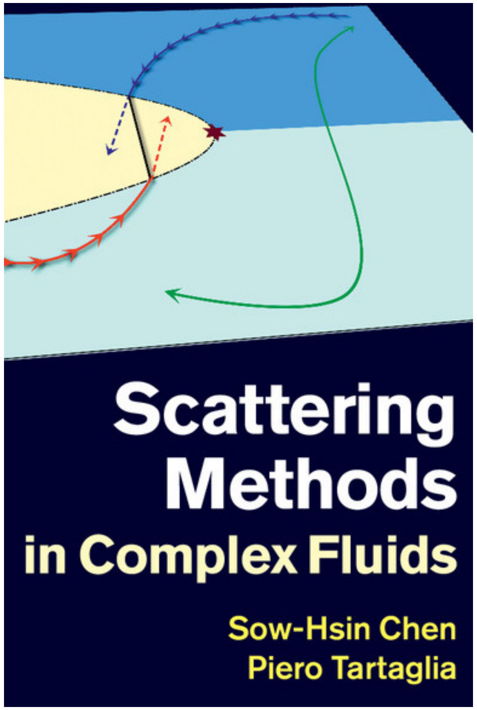
Thank you for your attention



Scattering Methods in Complex Fluids

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