Pressure Dependence of Fragile-to-Strong Dynamic Cross-over Transition in Deeply Supercooled Confined Water

Studied by Quasielastic Neutron Scattering

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A talk given at SNS/HFIR User Meeting at Oak Ridge in QENS session on October 11, 2005.

Introduction

Apparent singular properties of supercooled water: existence of T_S

Mesoporous Silica Materials: MCM-41(pore sizes ≤ 18 Å)

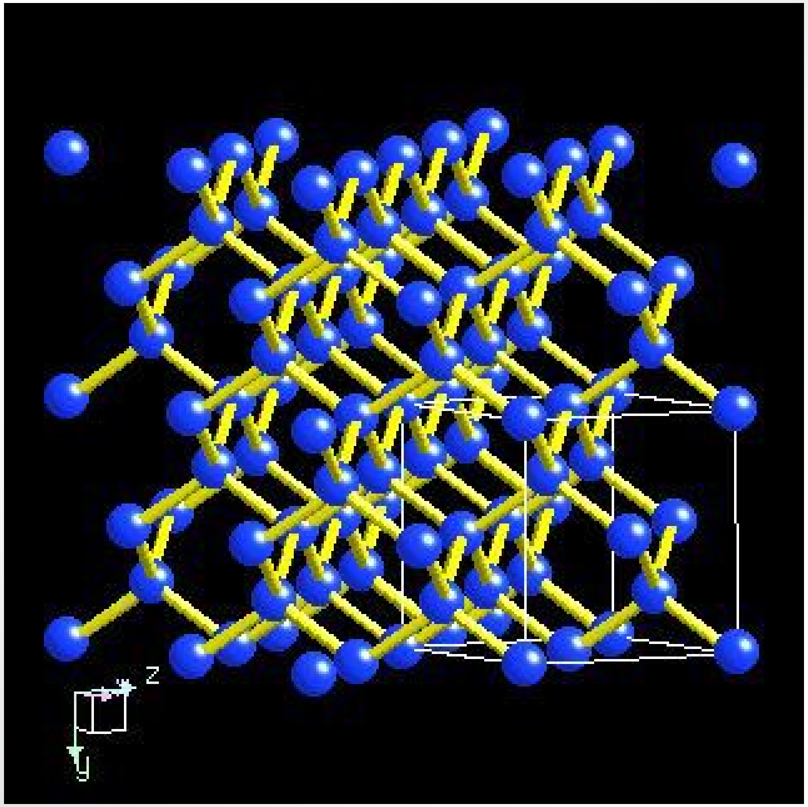
Model for dynamics of supercooled and interfacial water (RCM)

Results

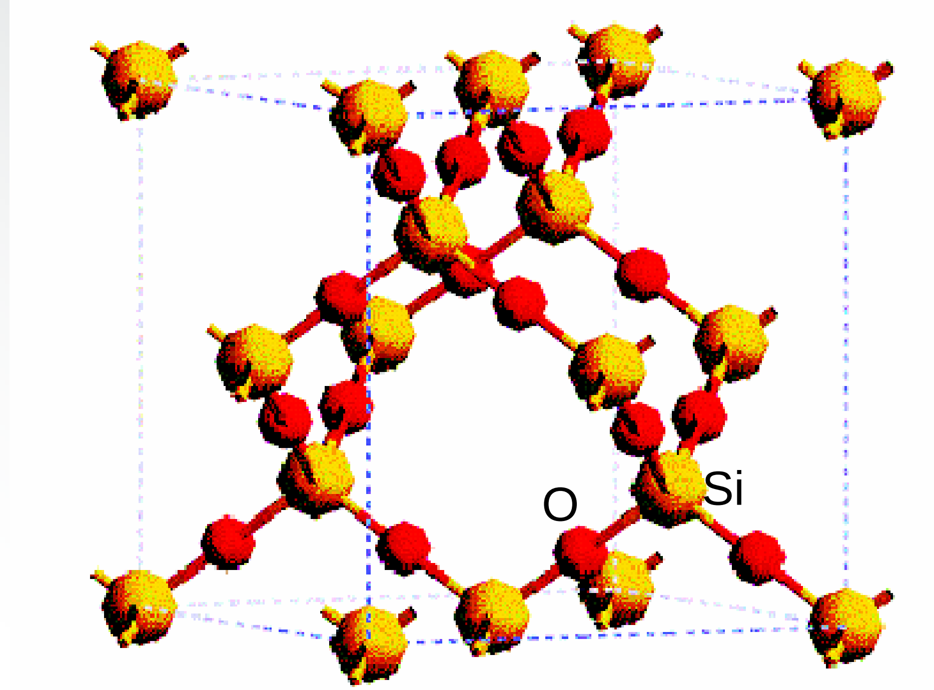
Analyses of experimental results with RCM model

Pressure dependence of fragile-to-strong cross-over transition at T_L

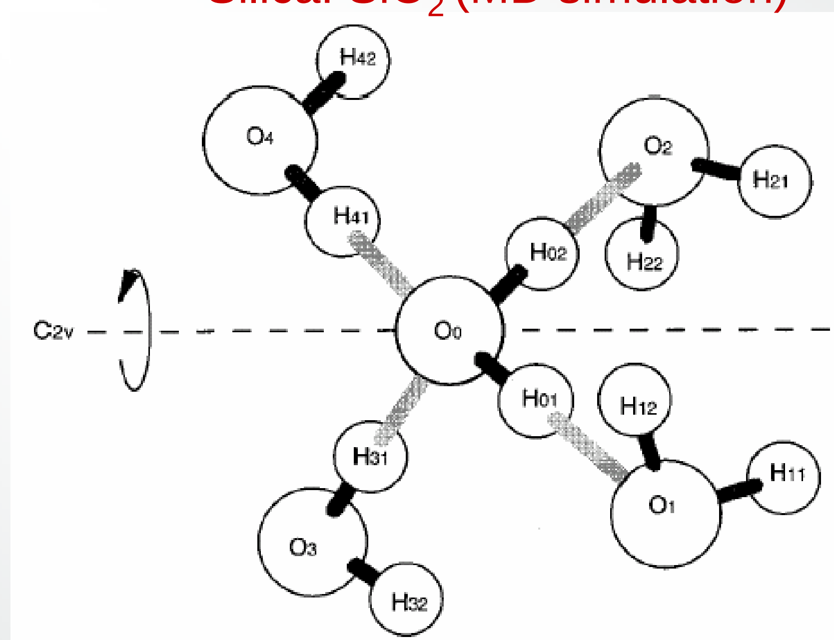
Possible location of the second Liquid–Liquid critical point



Silicon: Si (MD simulation)



Silica: SiO_2 (MD simulation)

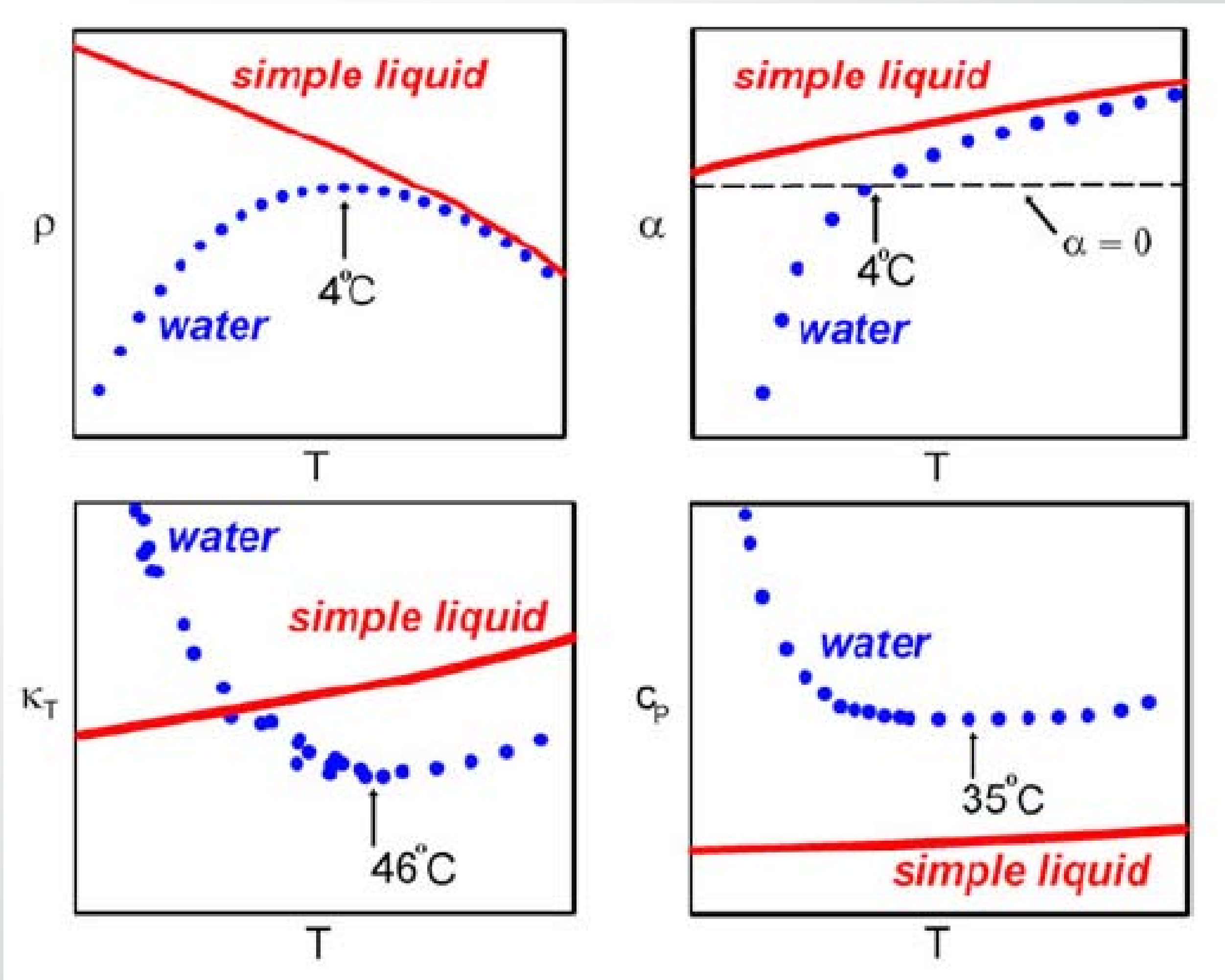


Water: H_2O (experiment)

Three important solids in our daily life the liquid state of which expands on cooling into a more open tetrahedral structure.

All show a liquid-liquid transition and a “fragile-to-strong” dynamic transition.

Anomalous Properties of 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, *J. Phys.: Condens. Matter* **15**, R1669 (2003)]

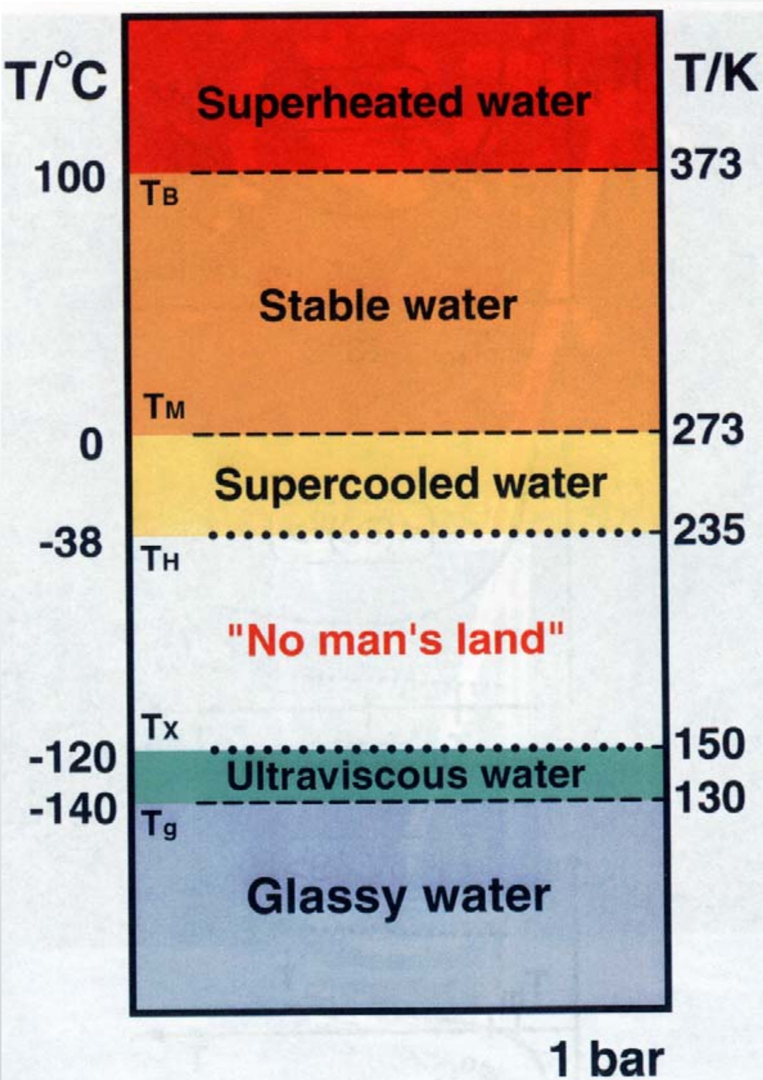


Figure 1: Schematic illustration indicating the various phases of liquid water (color-coded) that are found at atmospheric pressure. Courtesy of Dr. O. Mishima.

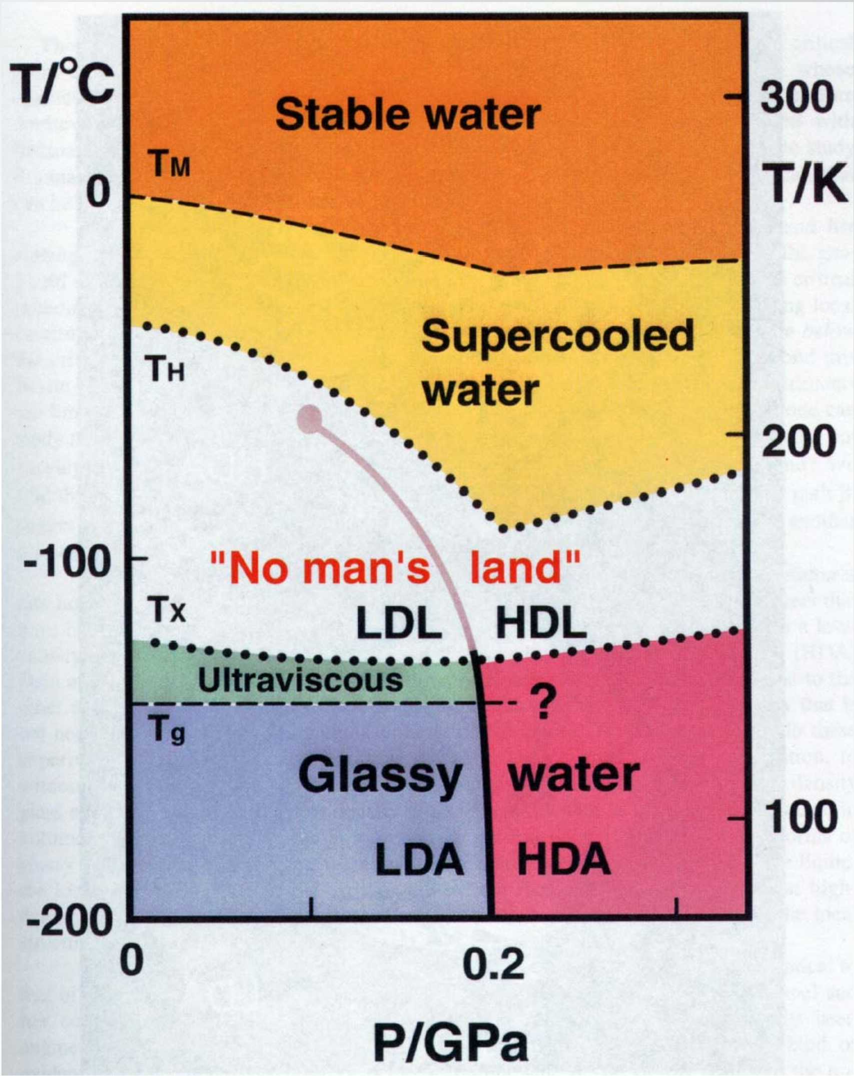
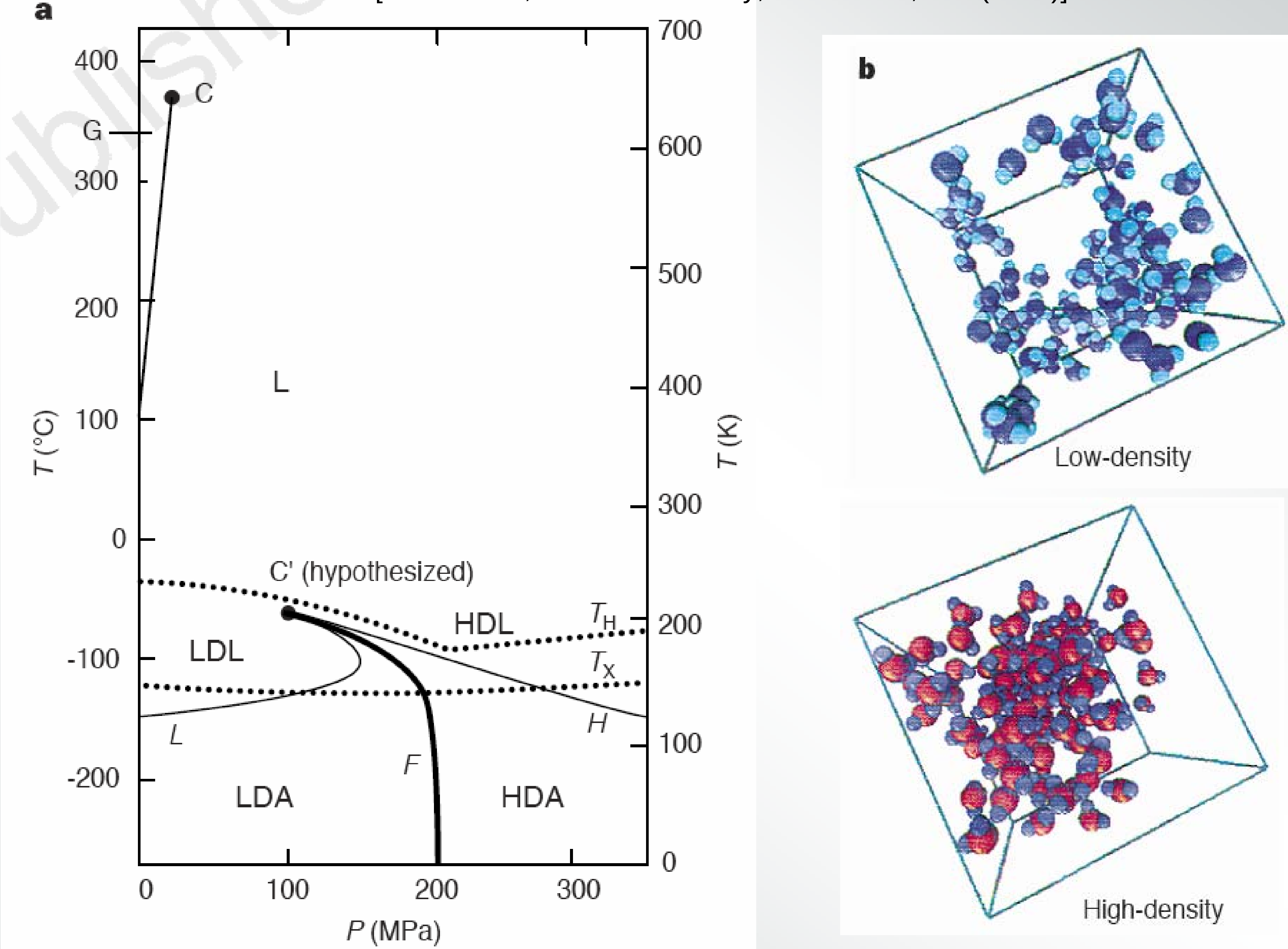


Figure 2: Generalization of Fig. 1 to incorporate a second control parameter, the pressure. The colors are the same as used in Fig. 1. Courtesy of Dr. O. Mishima.

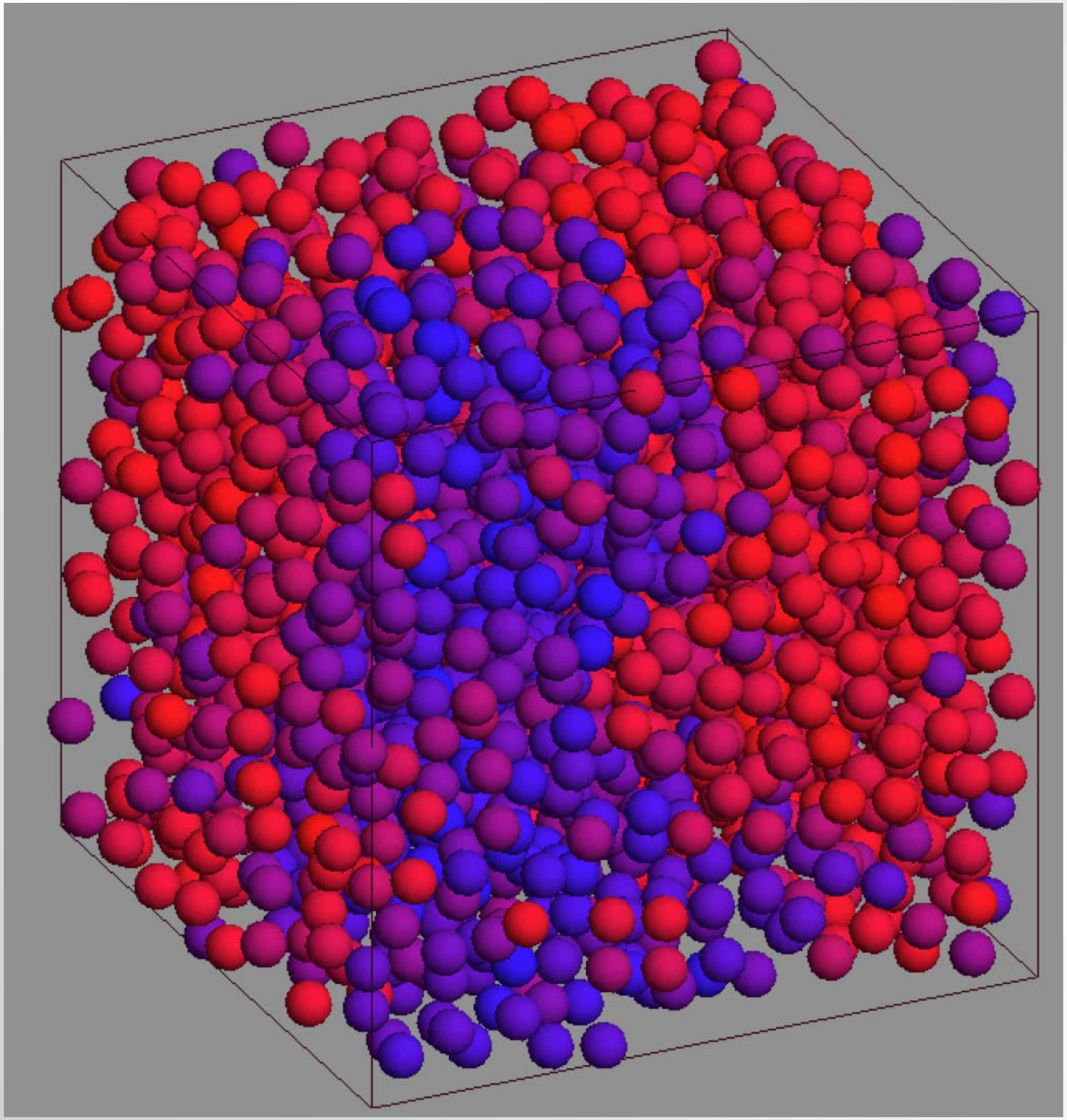
The Two Critical Points Scenario in Water

[O. Mishima, and H. E. Stanley, Nature 396, 331 (1998)]



Computer simulation image of liquid-liquid phase separation in ST2 water

by Peter Poole



Each sphere represents the oxygen atom of a water molecule; hydrogen atoms are omitted for clarity. The system consists of 1728 molecules in equilibrium at T=215 K and 1.05 g/cm^3. Under these conditions, ST2 water phase separates into a low-density liquid (LDL) and a high-density liquid (HDL) phase. The colors represent the density in the immediate vicinity of each molecule: the red end of the color map indicates higher density, the blue end, lower density. The segregation of the system into distinct LDL and HDL domains is clearly shown.

P-T Phase Diagram of Superheated Water

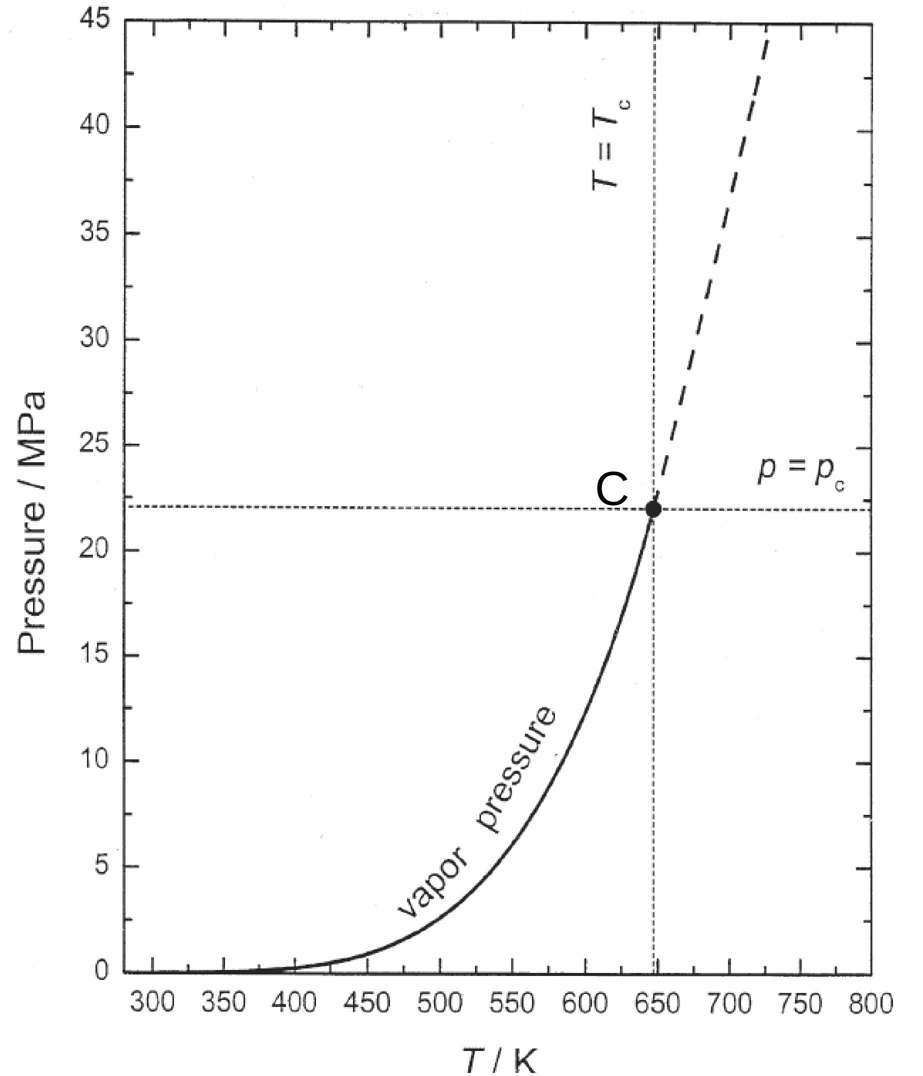


Fig. 2.1. Pressure p as a function of temperature T at $\rho = \rho_c$ for H_2O. The solid curve represents the vapor pressure corresponding to the region of vapor–liquid equilibrium. The dashed curve represents the pressure at $\rho = \rho_c$ in the one-phase region above the critical temperature.

M. A. Anisimov, J. V. Sengers, and J. M. H. Levelt Sengers, "Near-critical behavior of aqueous systems," in *Aquesous Systems at Elevated Temperatures and Pressures: Physical Chemistry in water, Steam and Hydrothermal Solutions*, D.A. Palmer, R. Fernandez-Prini and A.H. Harvey (Eds.), 2004 Elsevier Ltd.

p - ρ Phase Diagram of Superheated Water

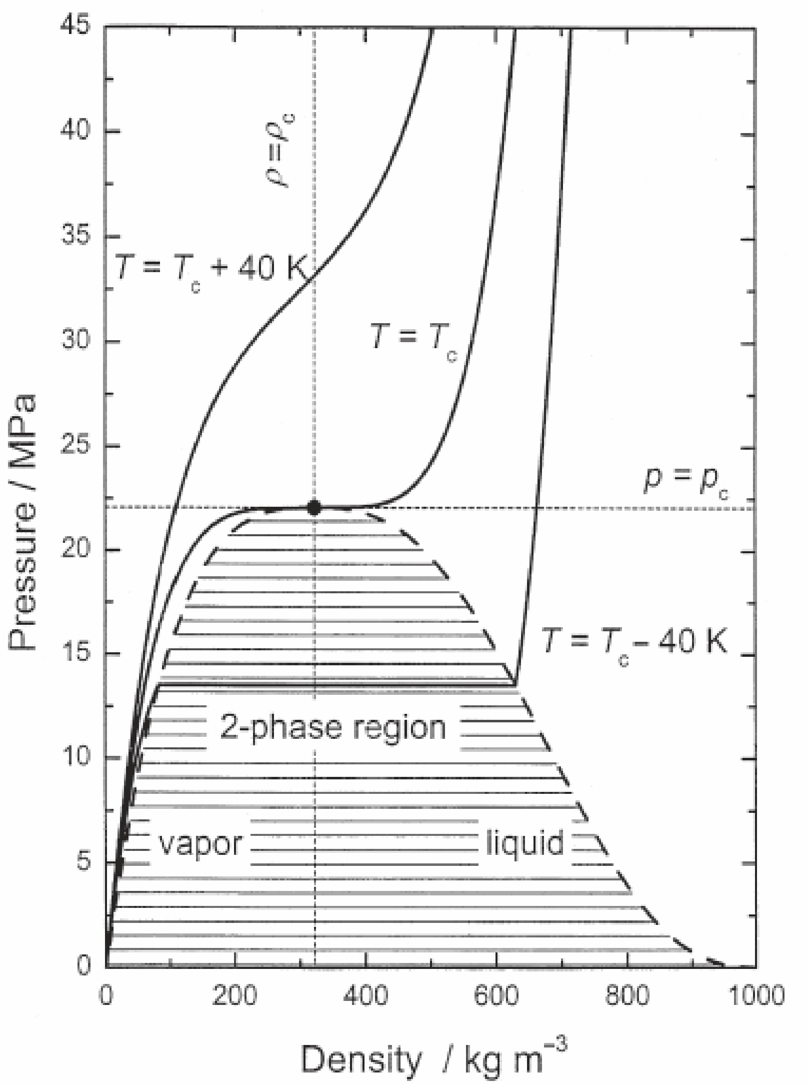
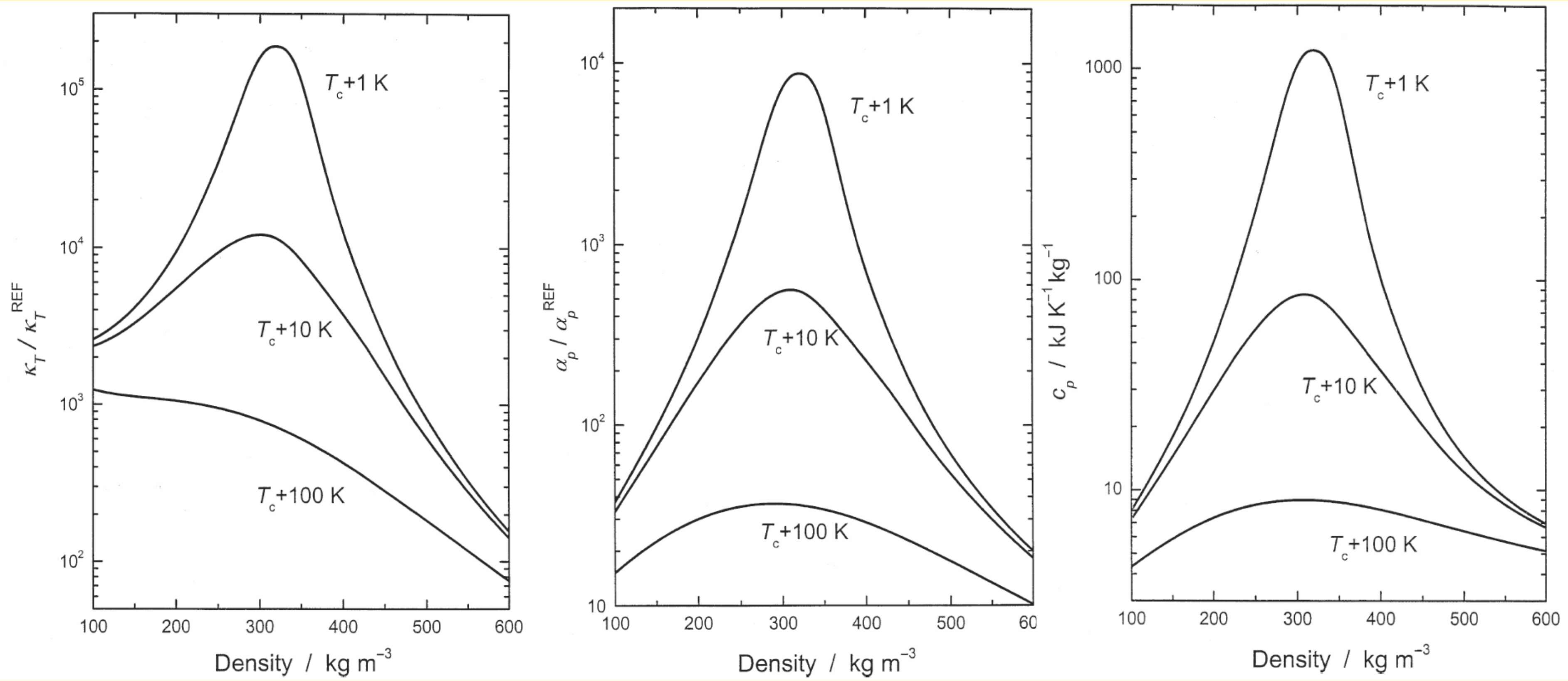


Fig. 2.2. $p-\rho$ diagram for H_2O. The solid curves represent $p-\rho$ isotherms at selected temperatures. The dashed curve represents the coexistence curve bounding the region of vapor–liquid equilibrium. The critical point is located at the top of the coexistence curve.

M. A. Anisimov, J. V. Sengers, and J. M. H. Levelt Sengers, "Near-critical behavior of aqueous systems," in *Aquesous Systems at Elevated Temperatures and Pressures: Physical Chemistry in water, Steam and Hydrothermal Solutions*, D.A. Palmer, R. Fernandez-Prini and A.H. Harvey (Eds.), 2004 Elsevier Ltd.

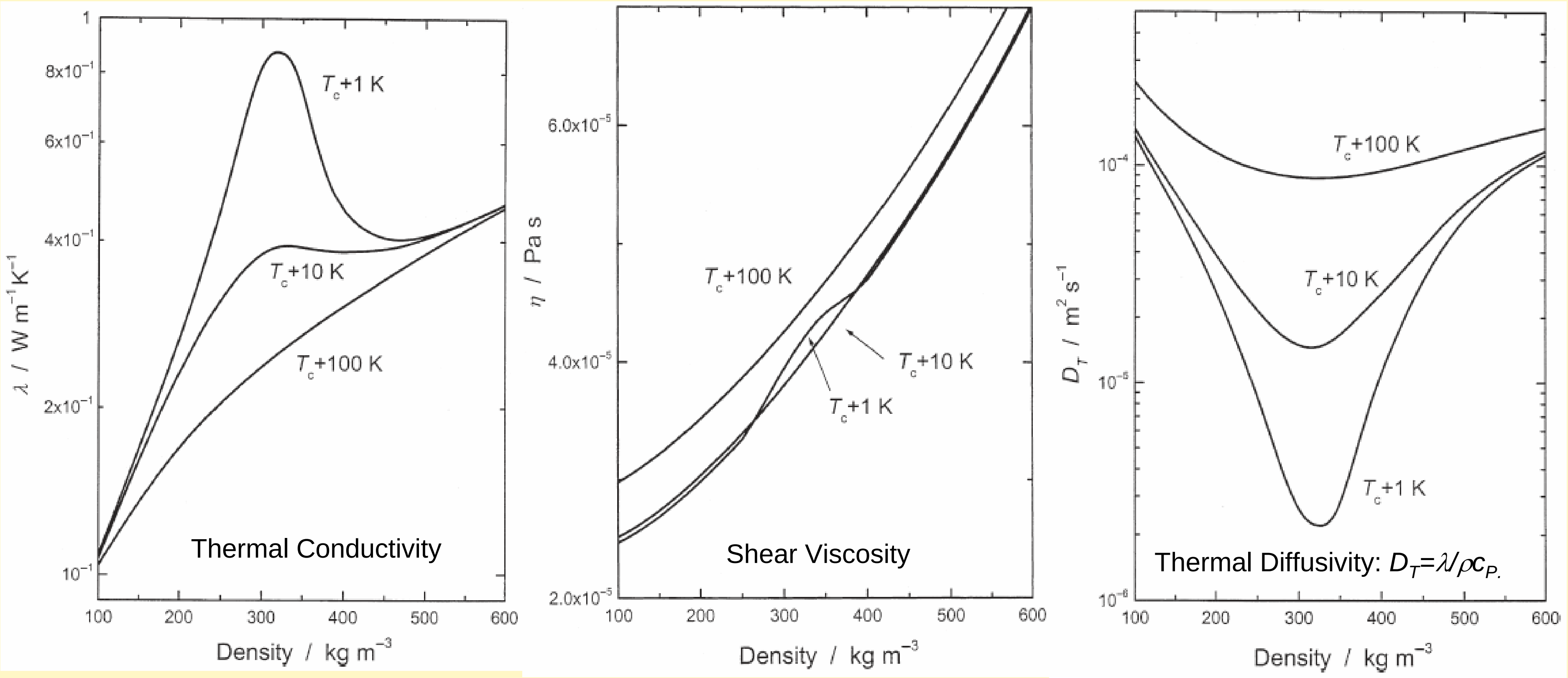
Peaking of Thermodynamic Response Function when Crossing Widom Line above T_C



The reference quantities are taken at pressures of the saturated liquid at 25 ºC.

M. A. Anisimov, J. V. Sengers, and J. M. H. Levelt Sengers, "Near-critical behavior of aqueous systems," in *Aquesous Systems at Elevated Temperatures and Pressures: Physical Chemistry in water, Steam and Hydrothermal Solutions*, D.A. Palmer, R. Fernandez-Prini and A.H. Harvey (Eds.), 2004 Elsevier Ltd.

Peaking of the Transport Coefficients when Crossing Widom Line above T_C



The reference quantities are taken at pressures of the saturated liquid at 25 ºC.

M. A. Anisimov, J. V. Sengers, and J. M. H. Levelt Sengers, “Near-critical behavior of aqueous systems,” in *Aquesous Systems at Elevated Temperatures and Pressures: Physical Chemistry in water, Steam and Hydrothermal Solutions*, D.A. Palmer, R. Fernandez-Prini and A.H. Harvey (Eds.), 2004 Elsevier Ltd.

Apparent Divergence of C_p and K_T in Supercooled Water

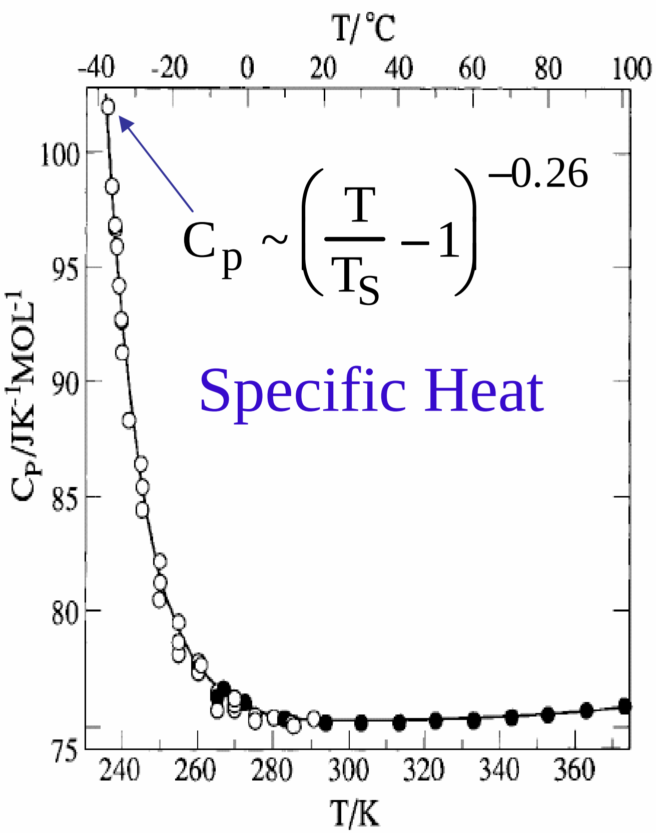


Figure 11. The temperature dependence of supercooled water's isobaric heat capacity c_p at atmospheric pressure. Literature data (●) included in the original [69], as well as measurements of Angell *et al* (○). Reprinted, with permission, from [24], Debenedetti P G, *Metastable Liquids, Concepts and Principles* copyright (1996) Princeton University Press, and adapted originally from [69].

$$T_S = 228 \text{ K}$$
$$= -45\ ^\circ\text{C}$$

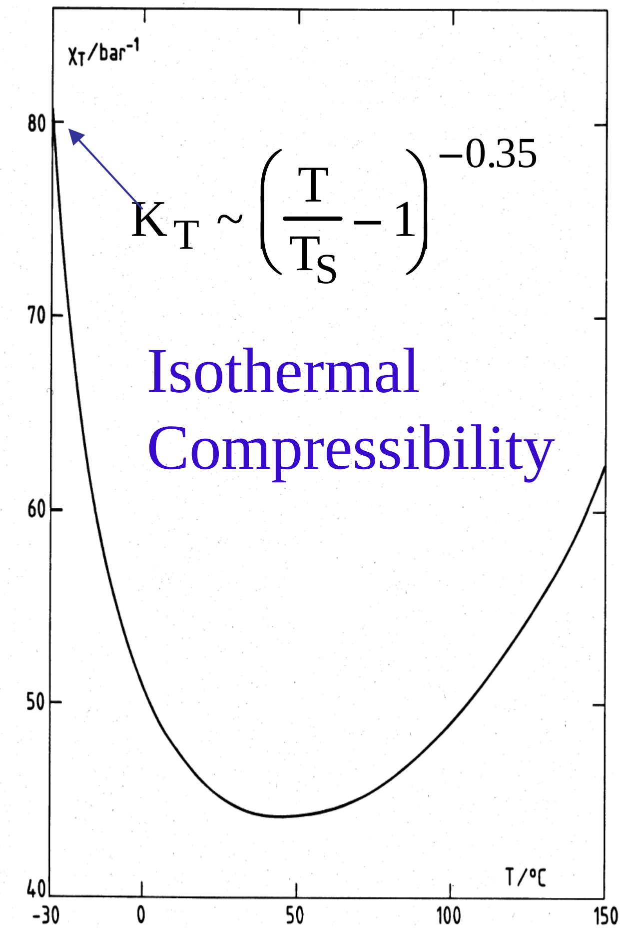


Figure 2. Isothermal compressibility of H_2O as a function of temperature. Taken from G. S. Kell, *J. Chem. Eng. Data* **20,** 97 (1975).

C. A. Angell, et al, *JPC* **77**, 3092 (1973)

R. J. Speedy, et al, *JCP* **65**, 851 (1976)

Non-Arrhenius Transport Properties of Supercooled Water

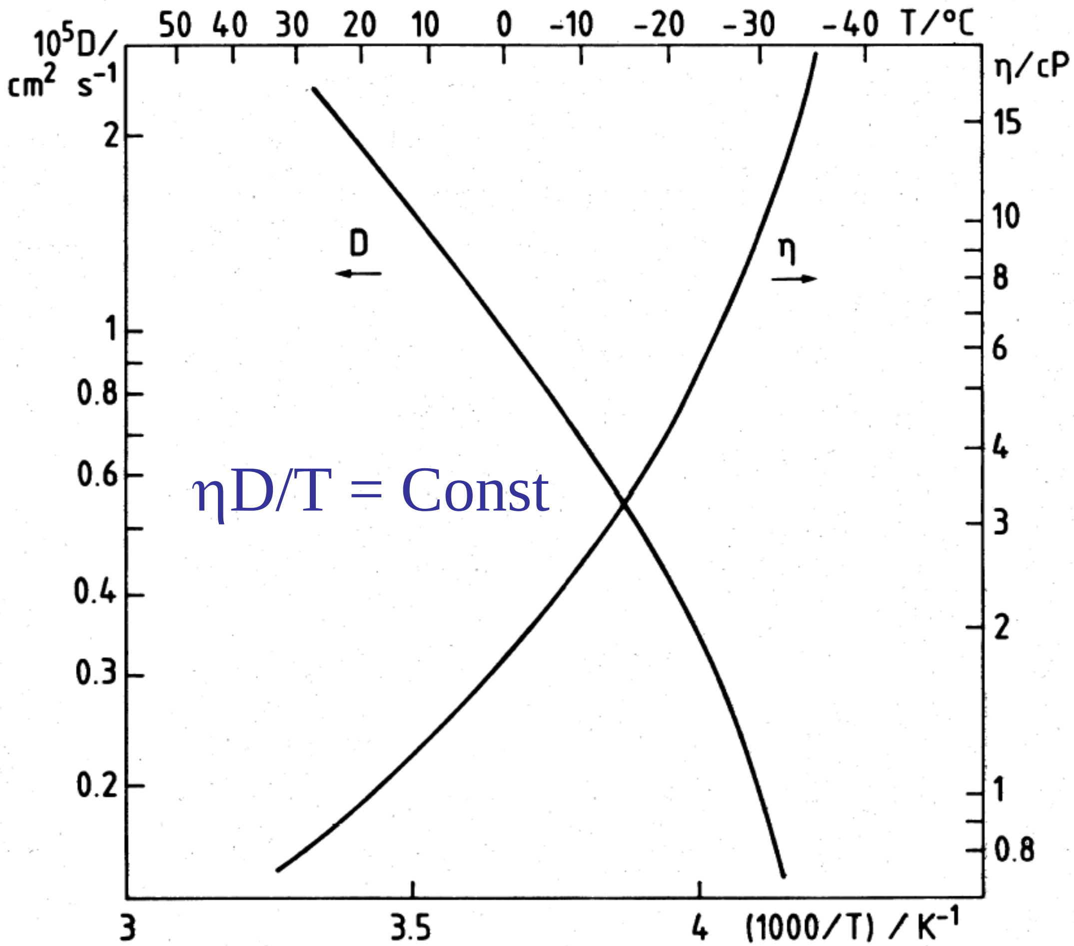


Figure 3. Self-diffusion constant and shear viscosity of H_2O at 1 atm as a function of temperature. Data taken from G. T. Gillen, D. C. Douglass, and M. R. Hoch, *J. Chem. Phys.* **57,** 5117 (1972), and Yu. A. Osipov, B. V. Zheleznyi, and N. F. Bondarenko, *Zh. Fiz. Khim.* **51,** 1264 (1977) (Engl. trans.) Note the non-Arrhenius behavior at low temperatures.

$$D(T) = D_0\left(\frac{T}{T_s} - 1\right)^{\gamma}$$

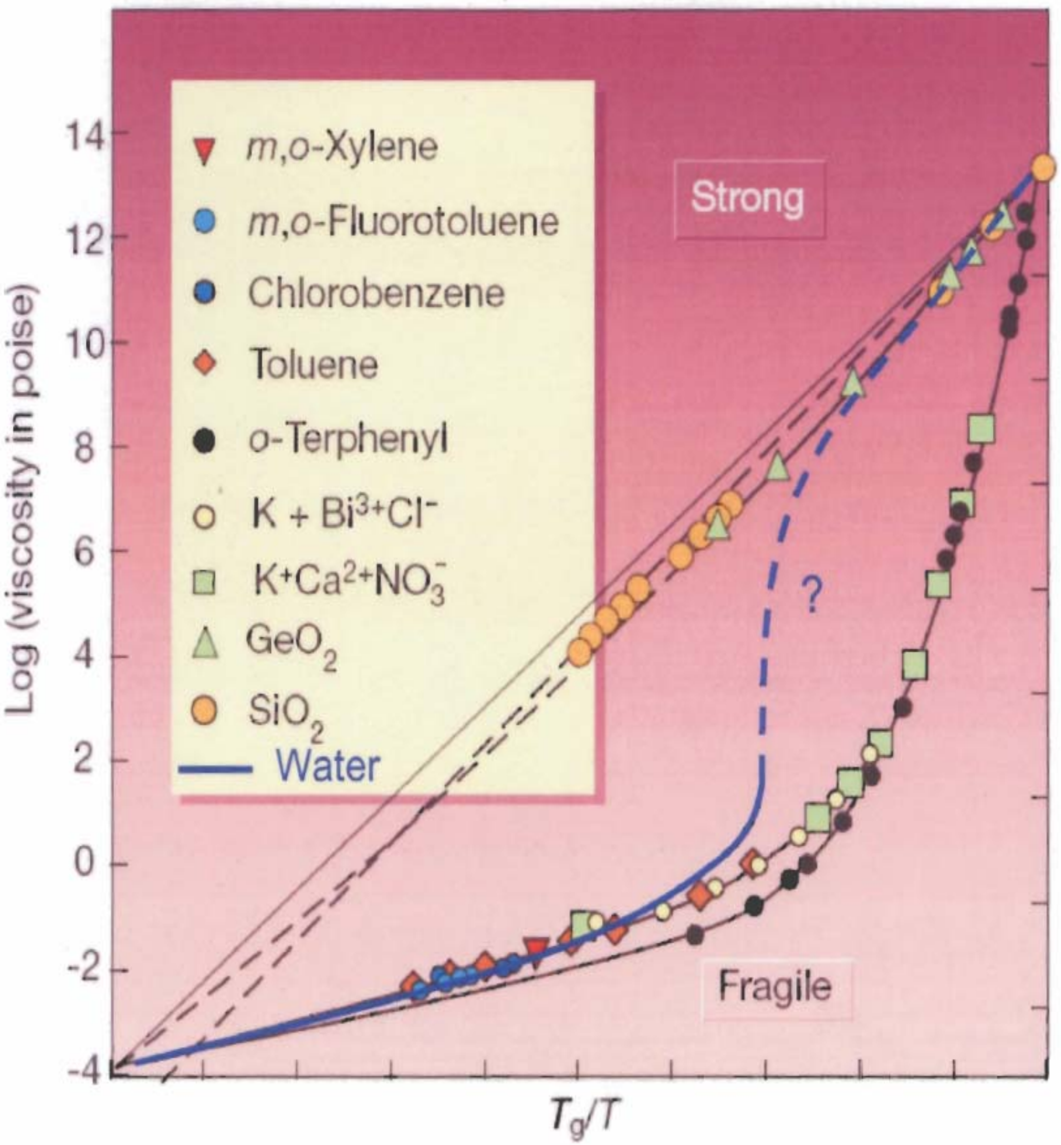
D_0=1.67 x 10^{-4} cm^2/s

T_s = 223 K

γ = 1.82

F. X. Prielmeier et al, *Ber. Bensenges, Phys. Chem.* **92,** 1111(1988)

Viscosity η or Equivalently the Structural Relaxation Time τ



P.G. Debenedetti, F.H. Stillinger, *Nature* **410**, 259 (2001)

Fragile $\tau = \tau_0 \exp\left[\frac{DT_0}{T - T_0}\right]$

Strong $\tau = \tau_0 \exp\left[\frac{E_A / k_B}{T}\right]$

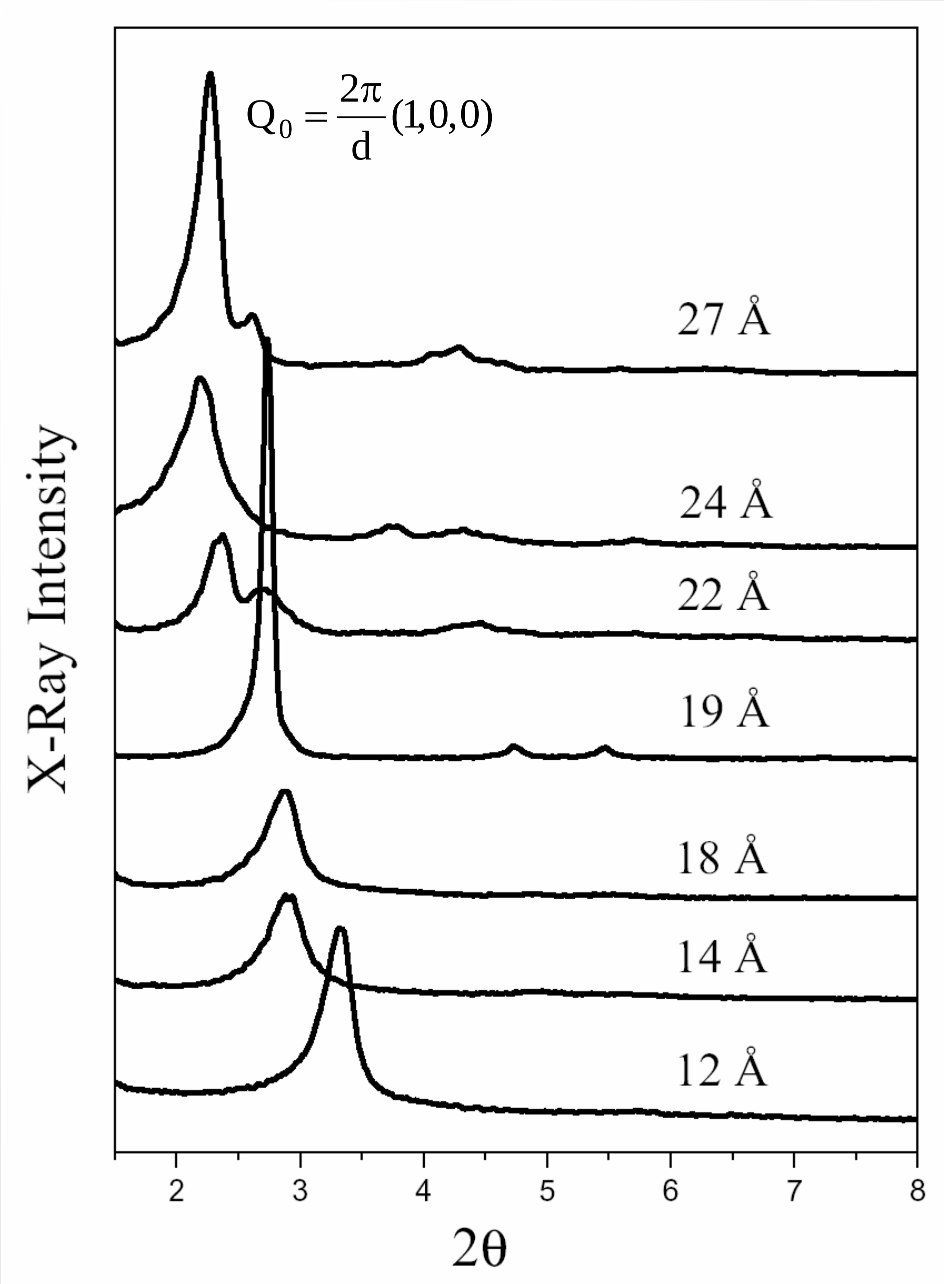
Fragile-to-Strong (F-S) transition is defined as a temperature T_L where:

$$\exp\left[\frac{DT_0}{T_L - T_0}\right] = \exp\left[\frac{E_A / k_B}{T_L}\right]$$

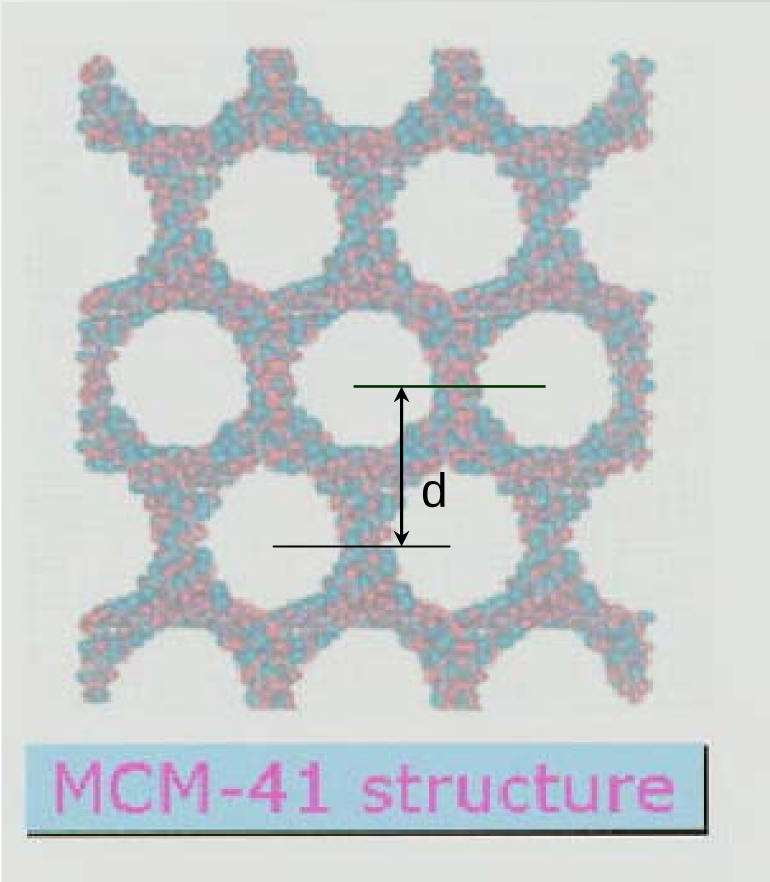
or: $\frac{1}{T_L} = \frac{1}{T_0} - \frac{Dk_B}{E_A}$

L Liu, SH Chen, *et al*,

Phys. Rev. Lett. **95**, 117802 (2005).

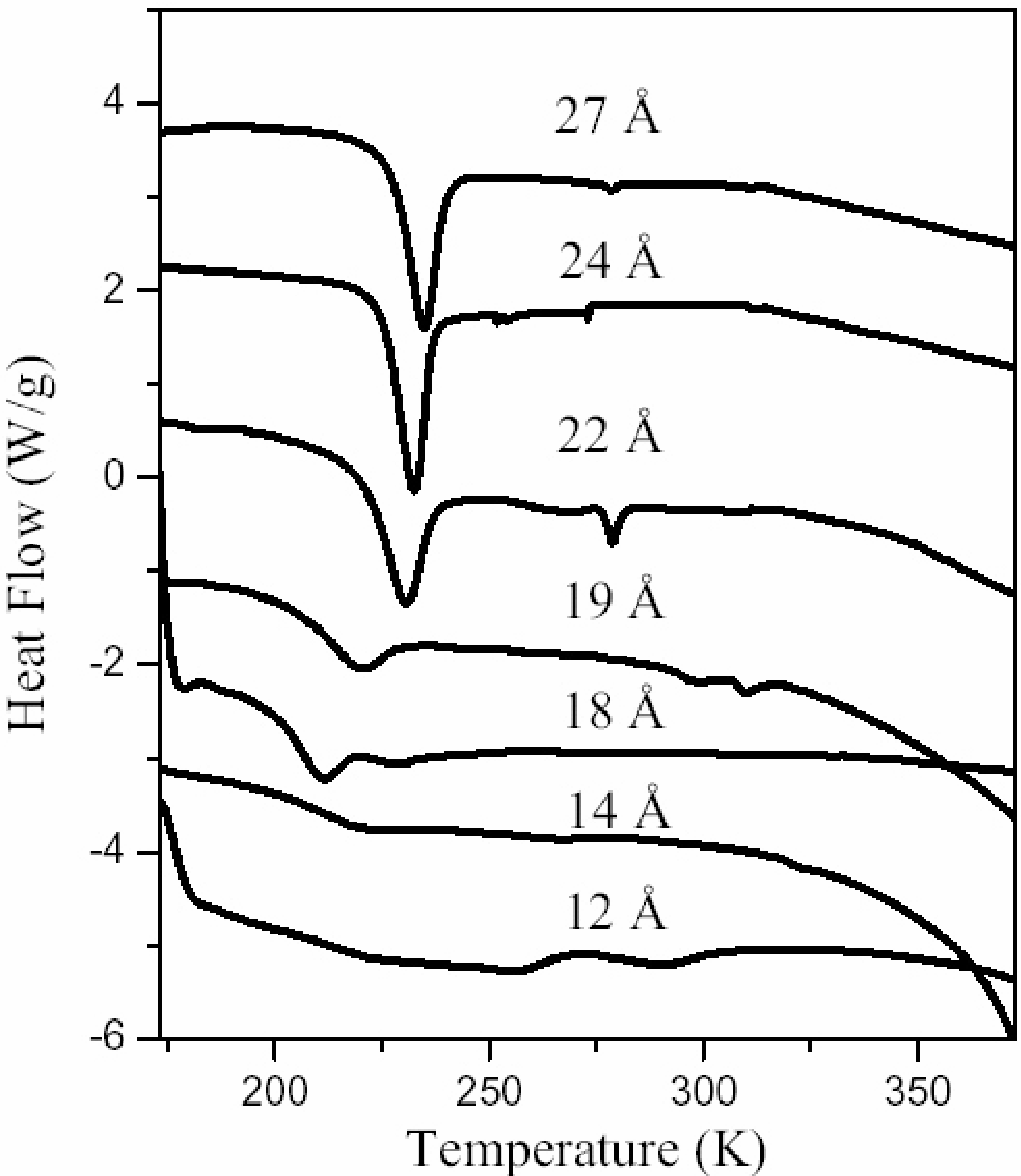


$Q_0 = \frac{2\pi}{d}(1,0,0)$
27 Å
24 Å
22 Å
19 Å
18 Å
14 Å
12 Å
X-Ray Intensity
2 3 4 5 6 7 8
2θ



d
MCM-41 structure

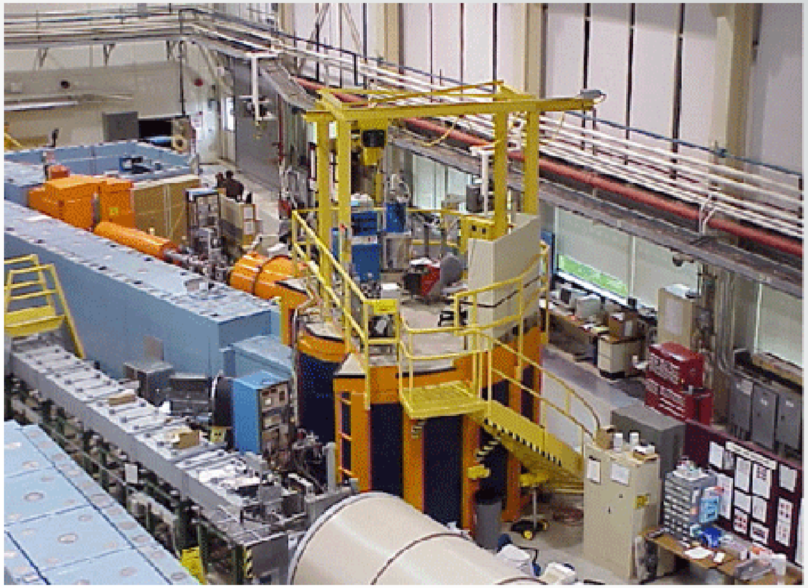
DSC Figure (Mou & Yen)



Pressure experiments at NCNR

With the newly built high pressure system, up to 4.1 kbar, at NCNR, we have done a series of experiments at DCS and HFBS spectrometers. Until now, the total experiments took about 16 weeks of the two spectrometer beam time. Altogether, 1100 spectra were collected and analyzed, spanning 10 pressures: ambient, 100, 200, 400, 800, 1200, 1400, 1600, 2000, and 2400 bars. Pressure dependence of the cross-over transitions for confined supercooled water has been detected, for the first time.

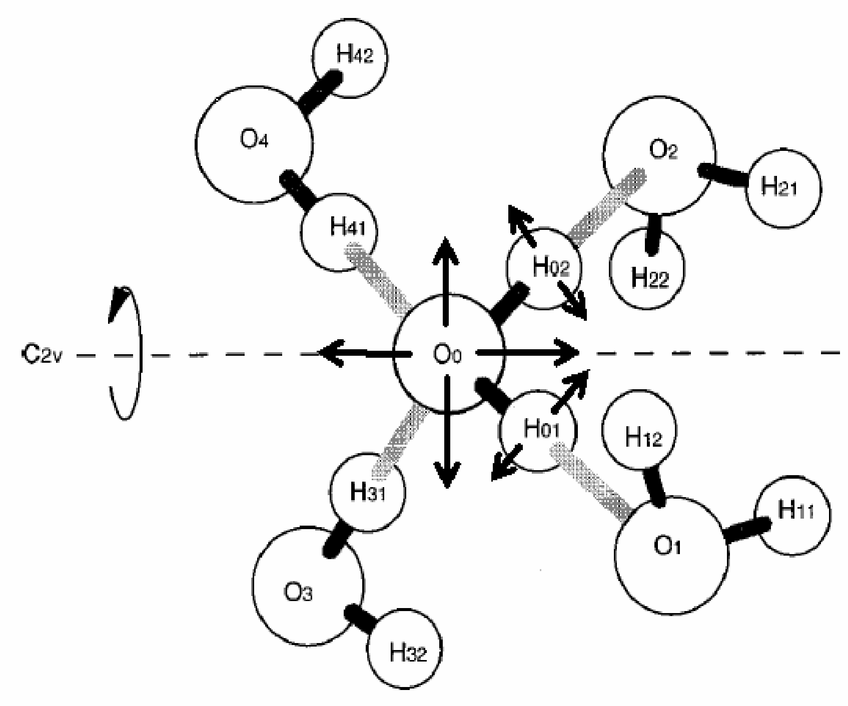
Spectrometers in NIST



Disk Chopper (DCS) and Backscattering (HFBS) spectrometers with resolutions 20 μeV and 0.8 μeV respectively, have Q ranges: 0.2 $Å^{-1}$ - 2.0 $Å^{-1}$, which is broad enough to simultaneously measure both translational and rotational dynamics of the water molecules.

Relaxing-Cage Model

On lowering the temperature below the freezing point, there is a tendency to form around a given water molecule a hydrogen-bonded, tetrahedrally coordinated first neighbor shell (cage). At short times, less than 0.05 ps, the water molecule performs harmonic vibrations and librations inside the cage. At long times, longer than 1.0 ps, the cage eventually relaxes and the trapped particle can migrate through the rearrangement of a large number of particles surrounding it. Thus, there is a strong coupling between the single particle motion and the density fluctuations of the fluid.



Experiment Measures Double Differential Cross Section ⇒ Dynamic Structure Factor

$$\frac{d^2\sigma_H}{d\Omega d\omega} = 2N \frac{\sigma_H}{4\pi} \frac{k_f}{k_i} S_H(Q,\omega)$$

Dynamics Structure Factor $S_H(Q, \omega)$ = FT [Intermediate Scattering Function $F_H(Q, t)$]

$$S(Q,\omega) = pR(Q_0,\omega) + (1-p)FT\left\{F_H(Q,t)R(Q_0,t)\right\}$$

For Q < 1.1 Å^{-1}, $F_H(Q,t) \approx F_T(Q,t)$.

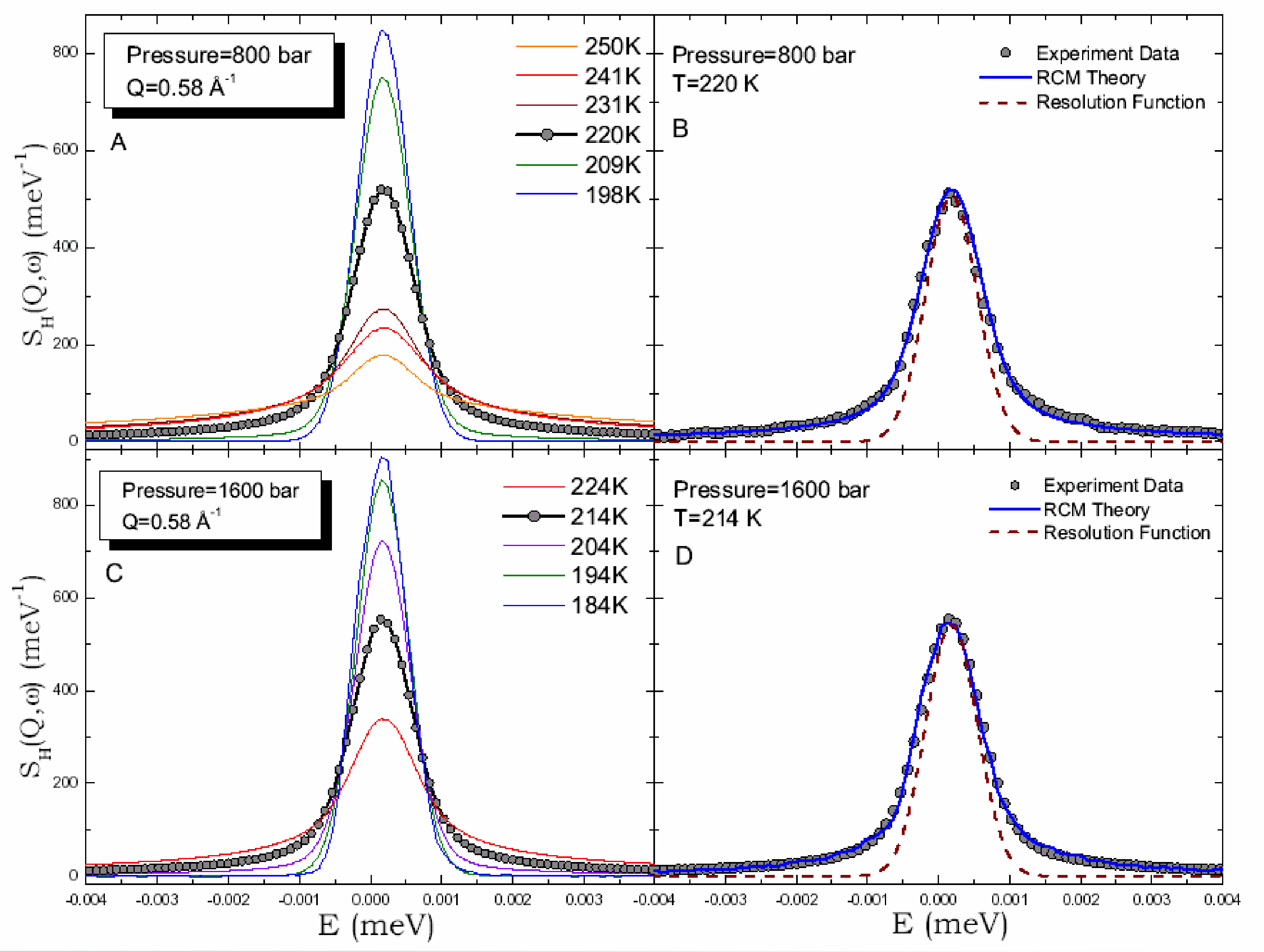
$$F_T(Q,t) = F_T^s(Q,t)\exp\left[-\left(t/\tau_T\right)^\beta\right], \qquad \tau_T = \tau_0 (aQ)^{-\gamma};$$

$F_T^s(Q,t)$ is calculated from known proton density of states.

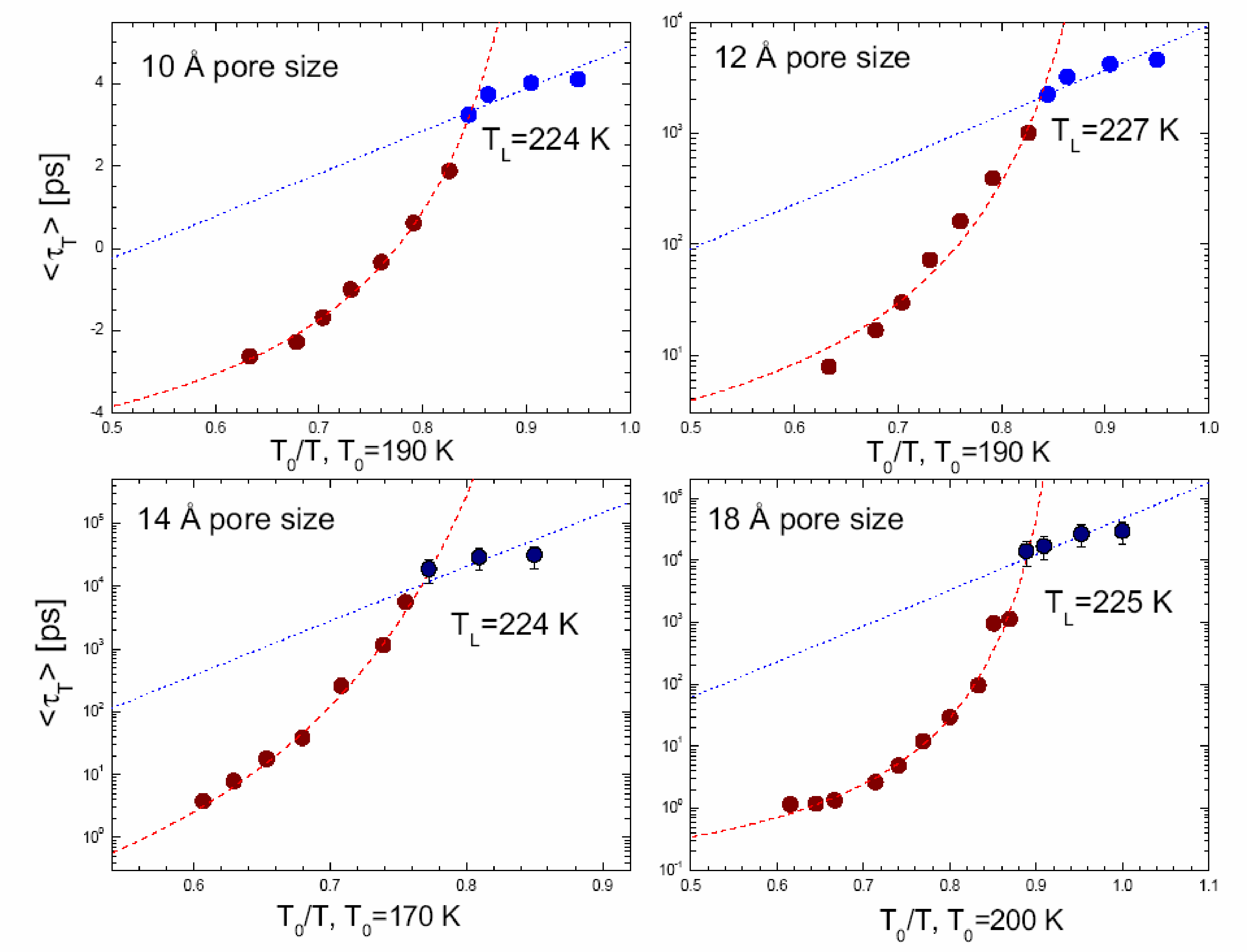
Fitting parameters: p, β, γ, τ_0, from which we calculate the average translational relaxation time:

$$\langle \tau_T \rangle = \frac{\tau_0}{\beta} \Gamma\left(\frac{1}{\beta}\right)$$

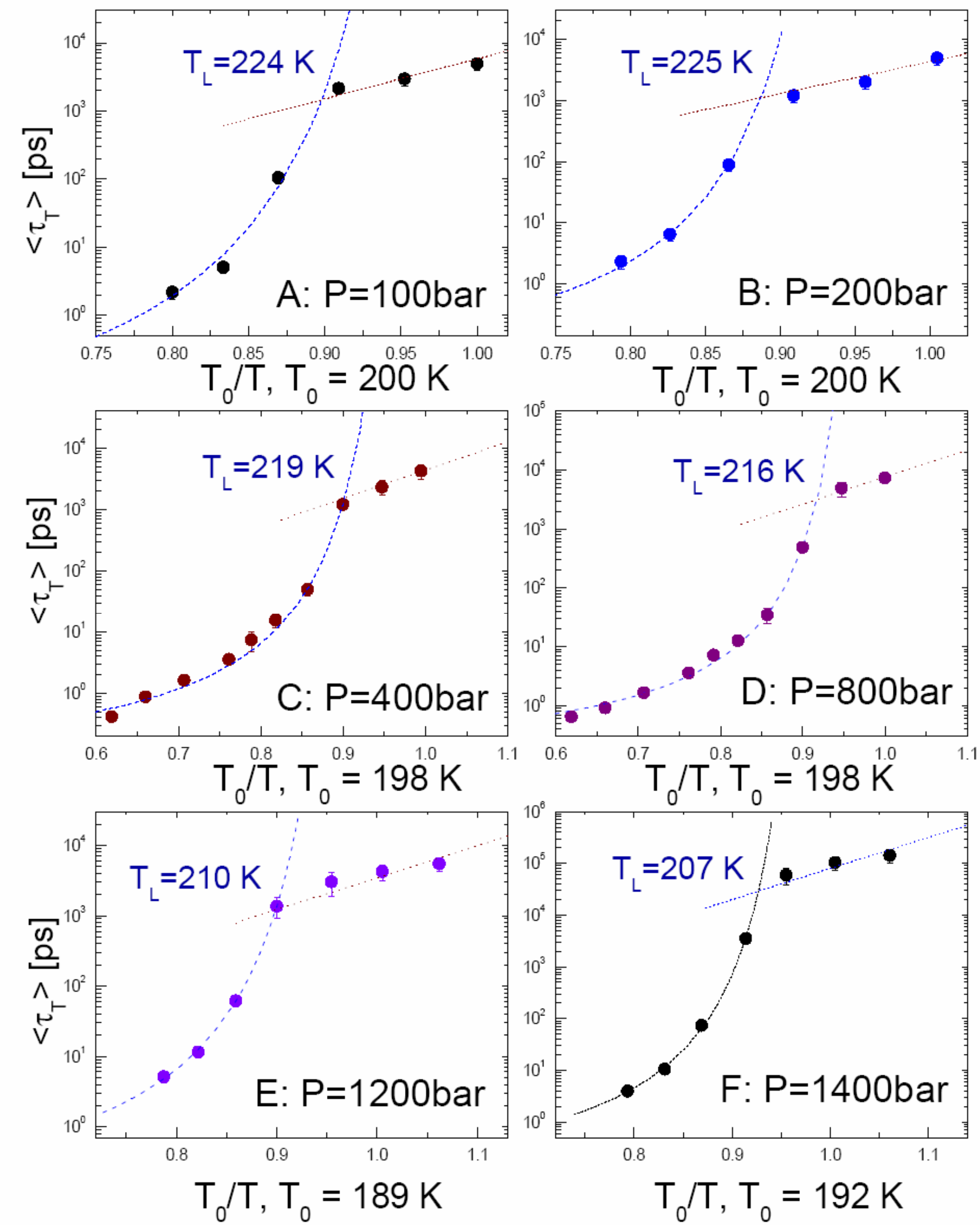
QENS Spectra of the Supercooled Confined Water Under Pressure

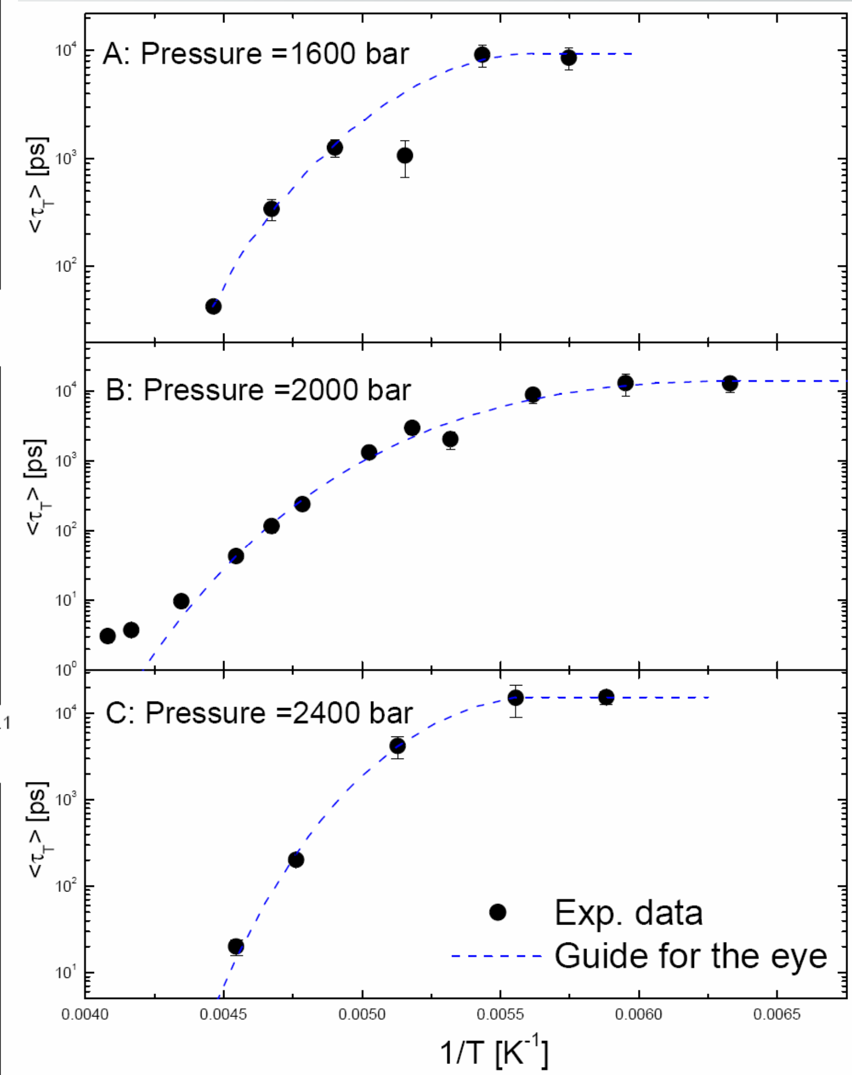


Temp. Dependence of Ave. Trans. Relax. Times (P = 1 bar)



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 Commu.* **121**, 10843-10846 (2004)

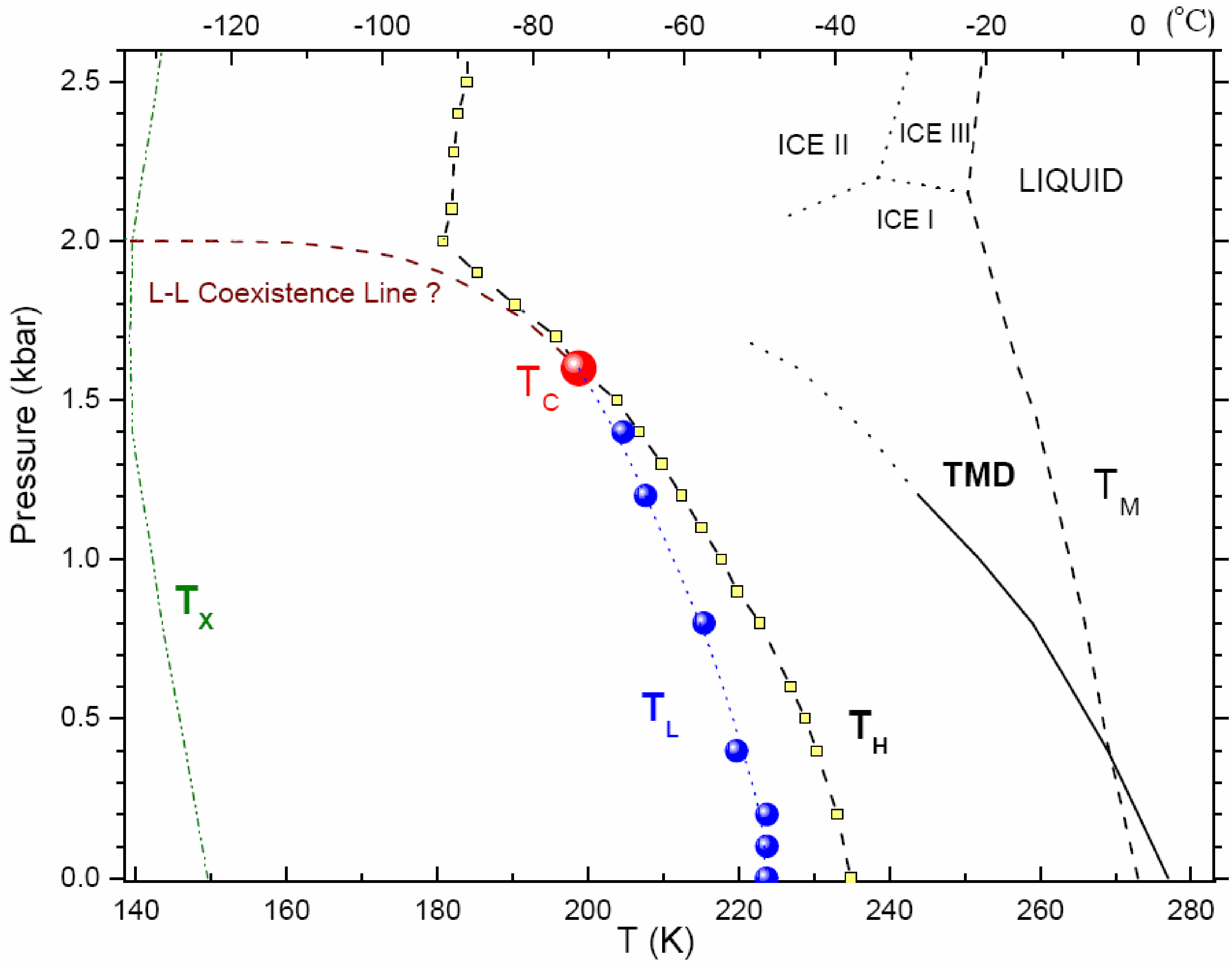


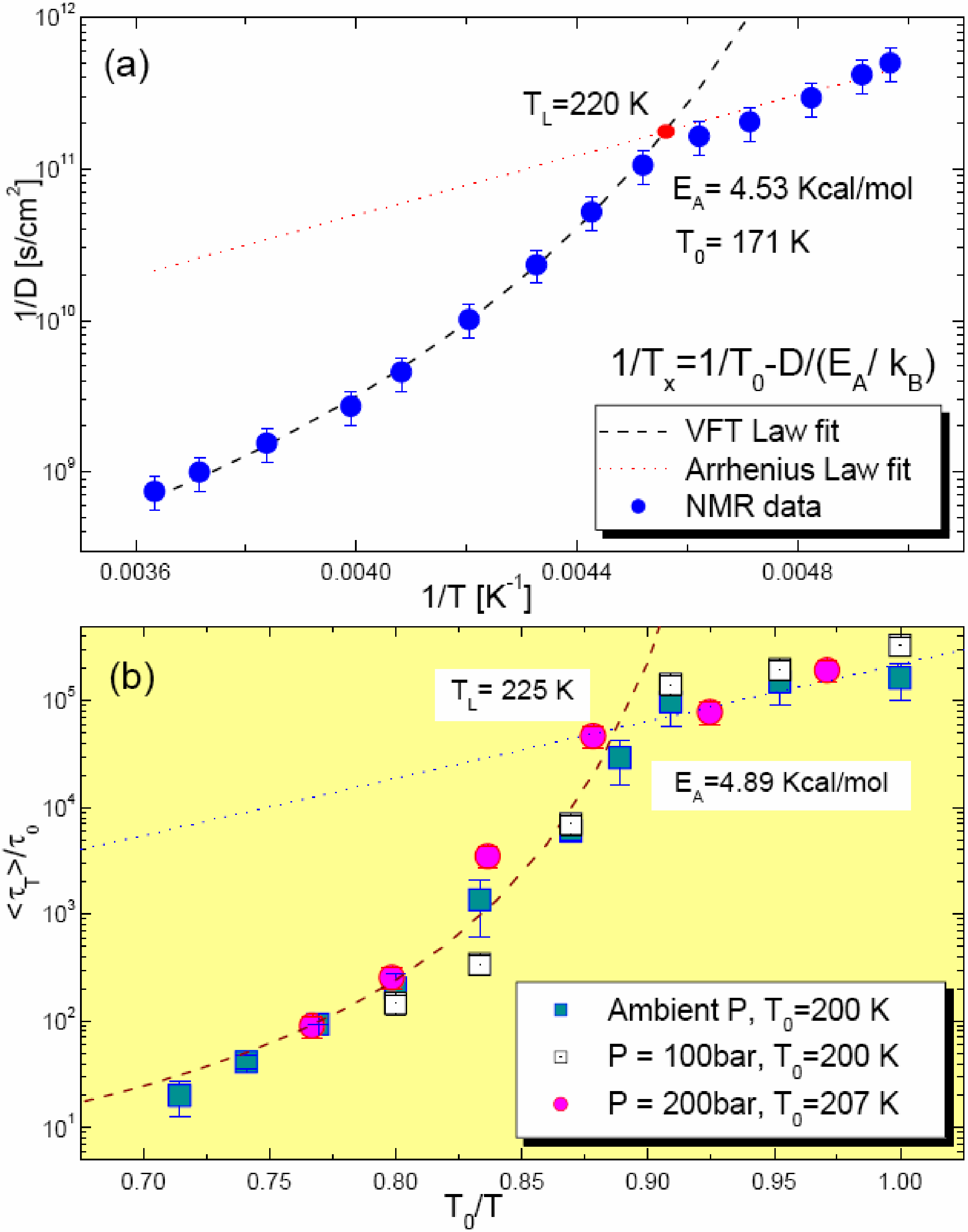


Temperature dependence of the average translational relaxation time of water, $<\tau_T>$, plotted in $log(<\tau_T>)$ vs T_0/T or $1/T$, where T_0 is the ideal glass transition temperature. Data from 100, 200, 400, 800, 1200, 1400, 1600, 2000, and 2400 bars are shown in the above two figures.

Pressure vs. Temperature Phase Diagram of H_2O

[Part of the results are shown in L Liu, SH Chen, *et al*, *Phys. Rev. Lett.* ***95***, 117802 (2005)]





Self-Diffusion Coefficient by NMR

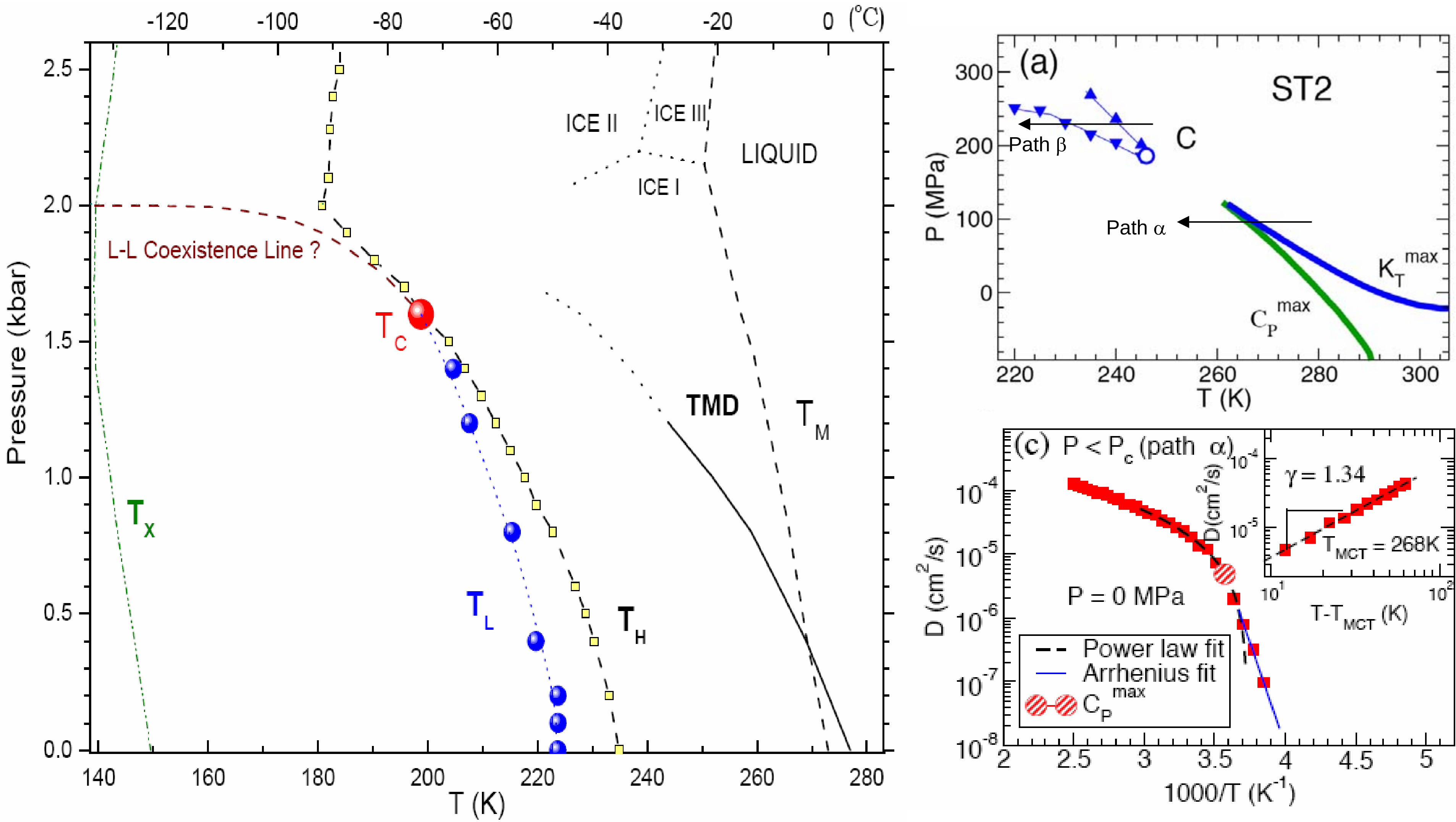
Mallamace *et al*. (to be published)

Average Structural Relaxation Time by Neutron Scattering

Faraone et al,

J. Chem. Phys. **121**, 10843 (2004).

Comparison between our QENS results and MD simulation of ST2 model water



The figures in right hand side show that, according to ST2 model of water, the locus of F-S transition coincides with the locus of C_p^{max}.

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

Conclusion

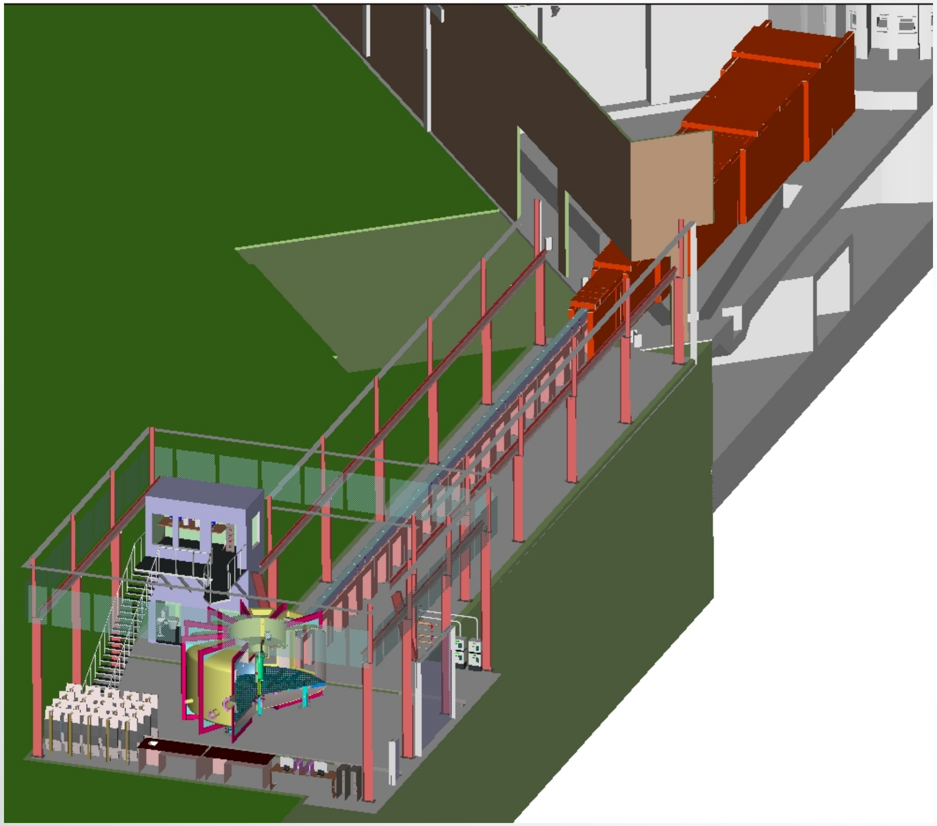
1. **Is the fragile-to-strong transition a liquid-to-liquid transition?**
2. **If so, what is the nature of the high-temperature (fragile) and the low-temperature (strong) phases?**
3. **The relation of the F-S transition line to the liquid-liquid coexistence line.**
4. **The lower end point of the liquid-liquid coexistence line, or the upper end point of the Widom line, is the second low-temperature critical point.**

Technical support from staff members of NCNR:

E. Mamontov, J. Leão, Y. Qiu, C. Brown, J. R. D. Copley, D.A. Neumann

This project is funded by DE-FG02-90ER45429 and 2113-MIT-DOE-591.

High Resolution Backscattering Spectrometer at SNS

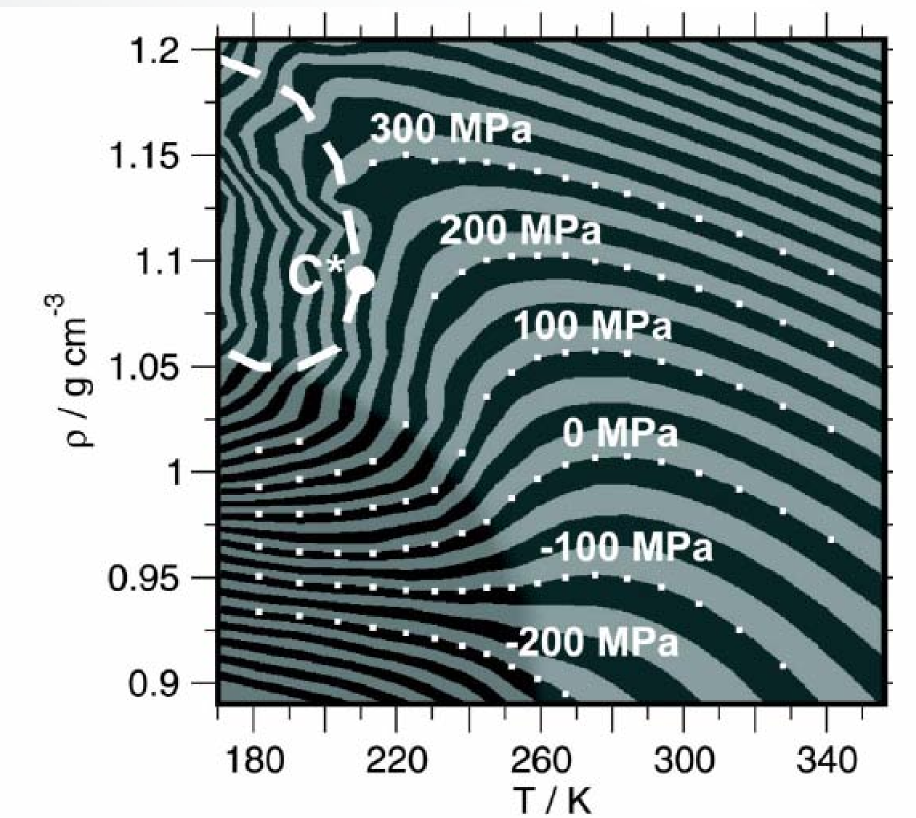


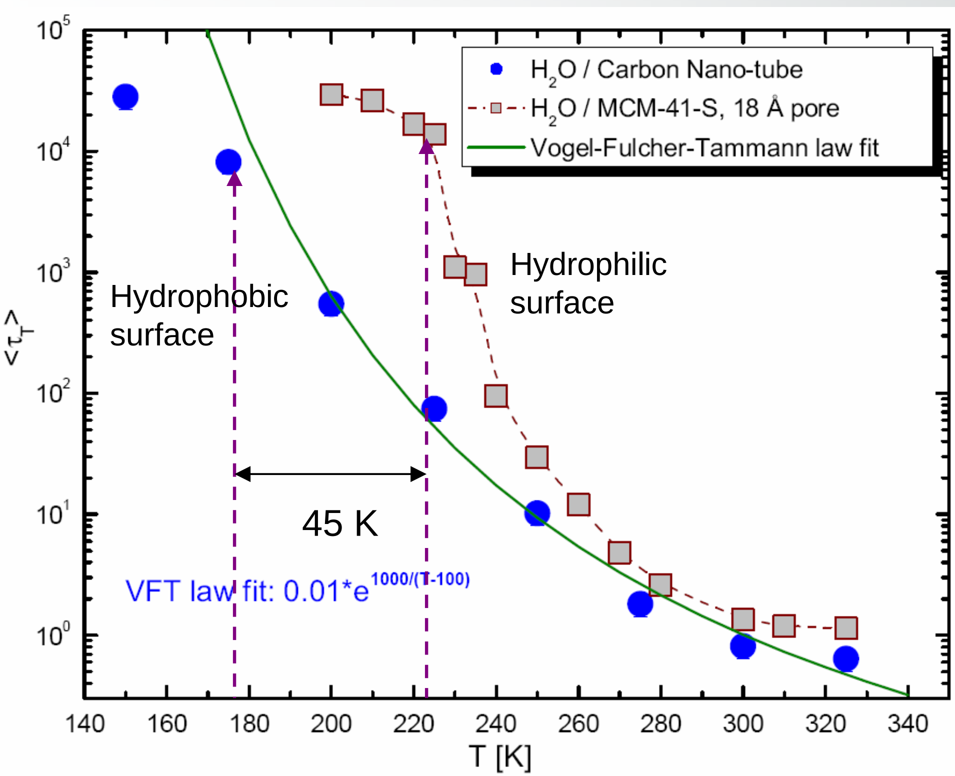
- Crystal analyzer (Si) with 84 m incident flight path
- 2.7 μeV resolution at the elastic position with 250 μeV bandwidth
- Can operate up to 18 meV energy transfer with 10 μeV resolution
- Unprecedented intensity

- Performance gains over comparable reactor backscattering instruments >60 (depending on bandwidth needed)
- High-Q option (with Si 311) 500x IN13 and 18x IRIS (with 3 times Q range and better resolution!)

Perspective Future Research

- TIP5P model of water predicts existence of the second low-temperature critical point, C*.
- Comparison of F-S transition in water confined in hydrophilic and hydrophobic cylindrical pores.

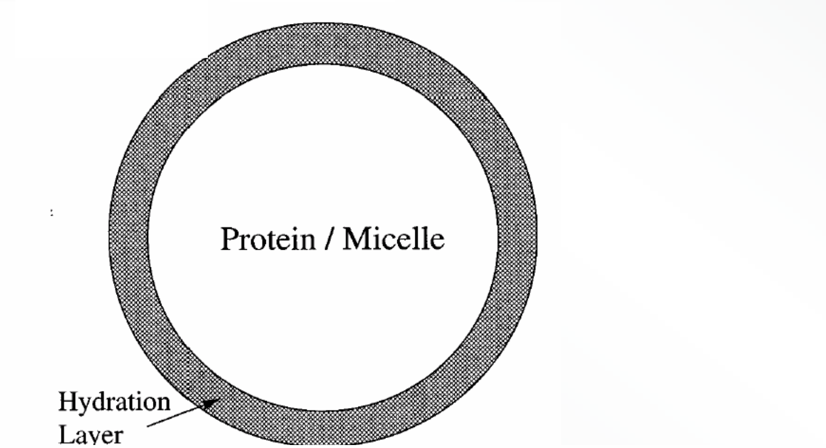


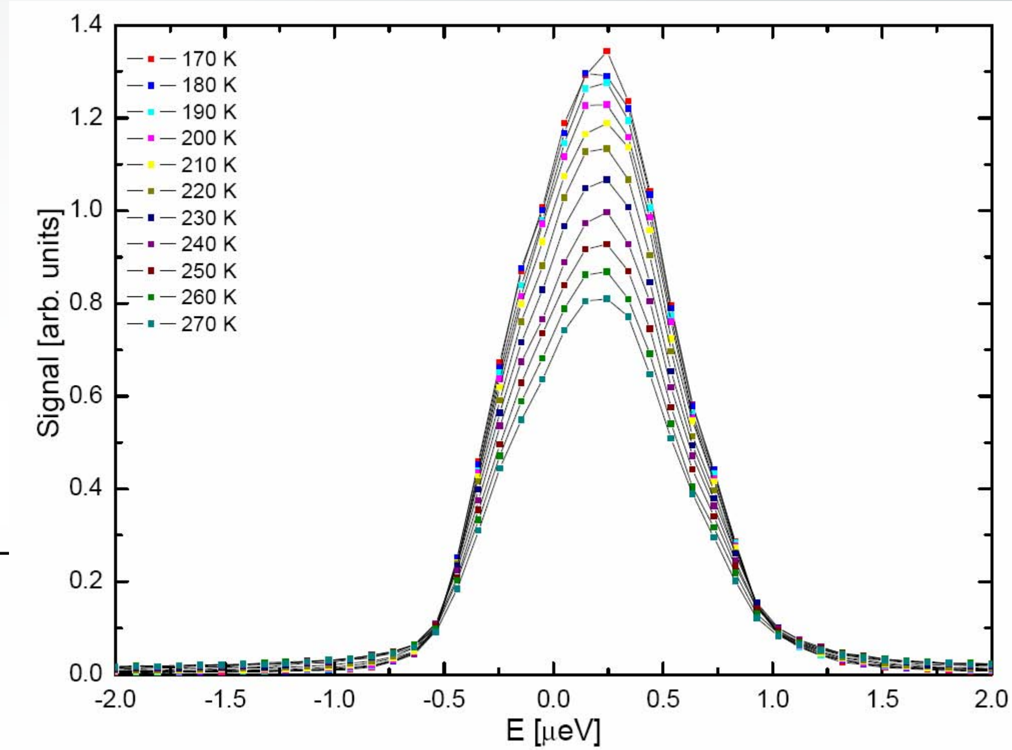


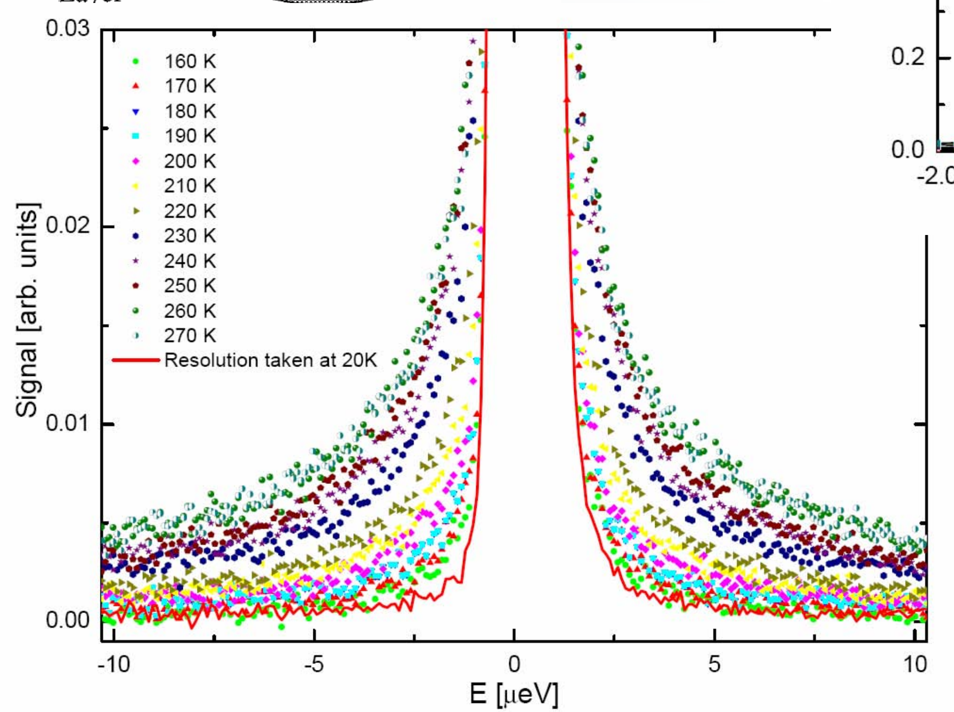
D. Paschek, *Phys. Rev. Lett.* **94**, 217802 (2005).

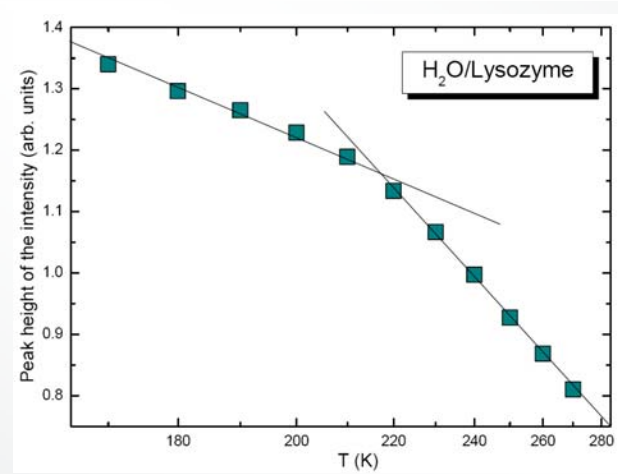
Future Prospect: Dynamics of Protein Hydration Water

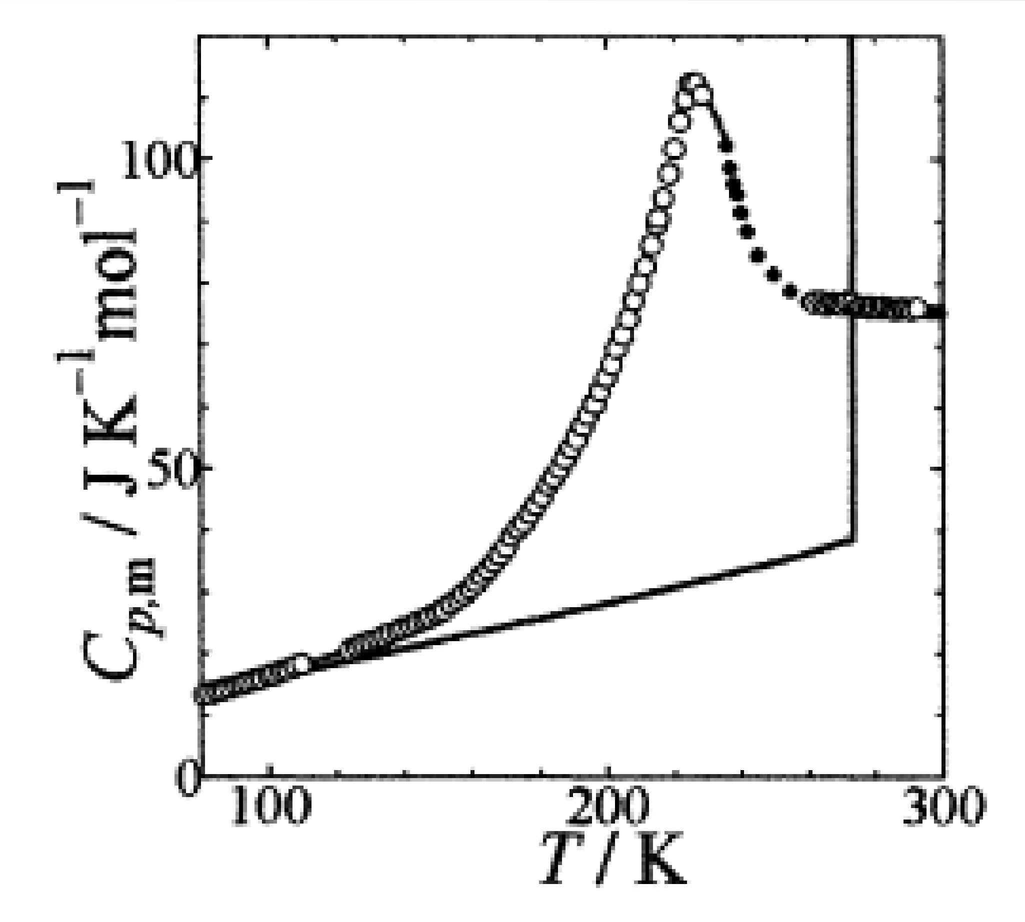
Experiments done on September 23, 2005











Heat capacity of internal water contained in nano-pores of silica gel with 30 Å pore size. This figure is the Fig. 2 of reference (S. Maruyama, K. Wakabayashi, M. Oguni, “Thermal Properties of Supercooled Water Confined within Silica Gel Pores,” *AIP conference prodeedings* 708, 675 (2004)).

Excitation of O-H stretch vibration of a bound water dimmer with a simultaneous breaking of an H-bond

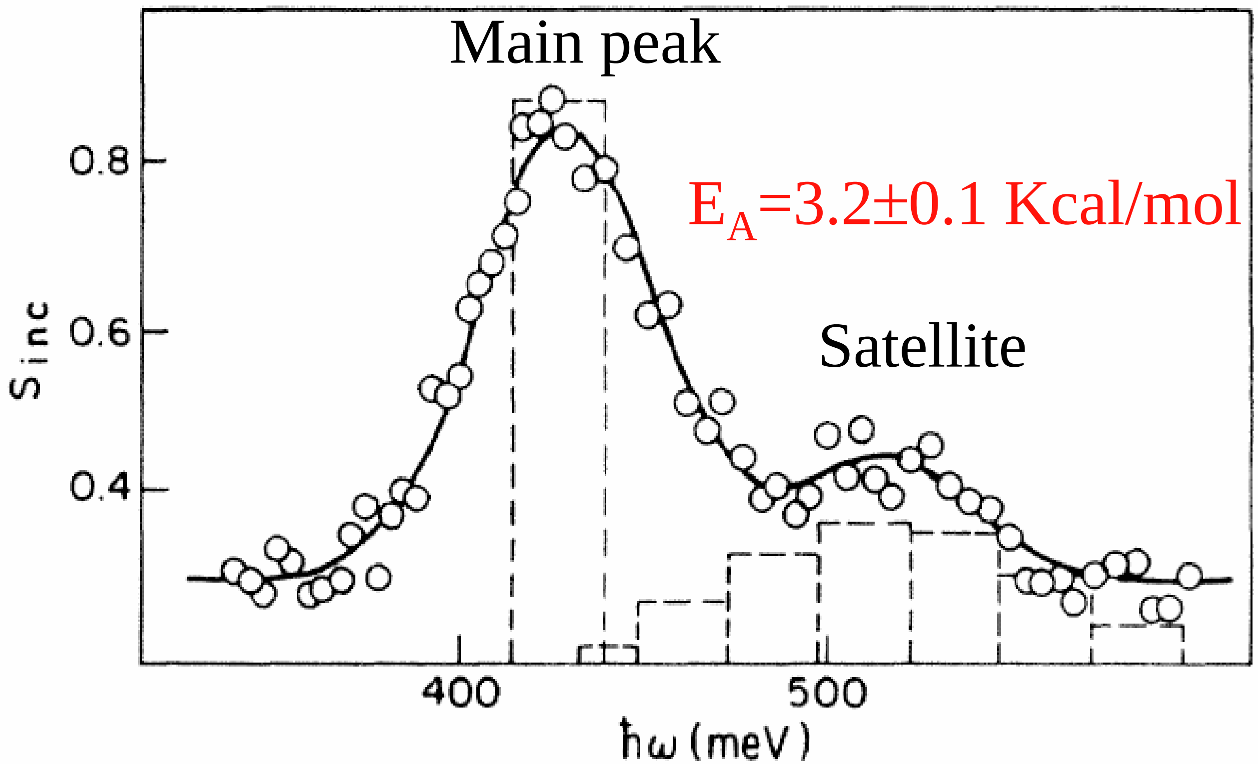


FIG. 5. Experimental data for $S_{inc}(Q,\omega)$ at $T=-15\,^{\circ}\mathrm{C}$ and $Q=11$ Å^{-1} in the high- energy region, compared with our calculations (histogram).

M. A. Ricci, S. H. Chen, "Chemical-bond spectroscopy with neutrons", *Phys. Rev. A* **34**, 1714 (1986)

Evidence of a Liquid-Liquid Structural Transition at 225 K from Librational Band of Water