Pressure Dependence of Fragile-to-Strong Transition and a Possible Second Critical Point in Supercooled Confined Water

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The anomalous behaviors of thermal dynamic response functions and transport properties of supercooled water imply the existence of a Liquid-to-Liquid (L-L) transition line and the associated second low-temperature critical point. However, both the L-L transition line and second critical point are predicted to lie inside the inaccessible "No man's land." (See Fig. 1)

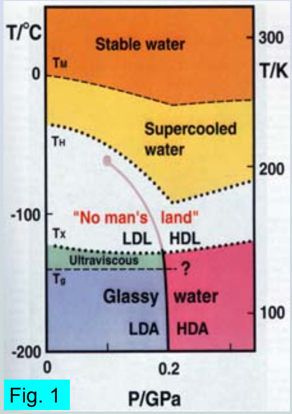


Fig. 1

Fig. 1: Schematic illustration indicating the various phases of liquid water (color-coded). Courtesy of Dr. O. Mishima. The figure is taken from H. E. Stanley, "Mysteries of Water" Les Houches Lecture, May 1998.

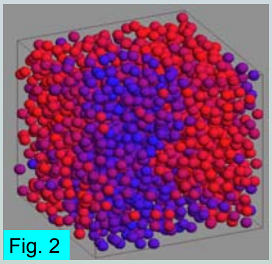


Fig. 2

Computer simulation image of the liquid-liquid phase separation in ST2 water , generated by P. Poole. (See Fig. 2)

The calculated Q-independent average relaxation time ($\langle\tau_T\rangle$) shows a fragile-to-strong (F-S) dynamic cross-over transition for pressures less than 1500 bar. Above this pressure, it is no longer possible to discern the characteristic feature of the F-S transition. (See Fig. 5~8)

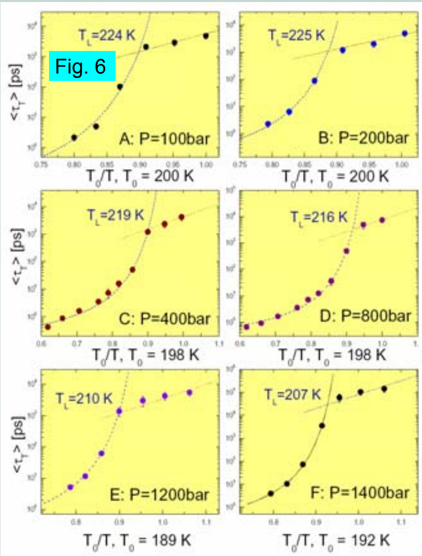


Fig. 6

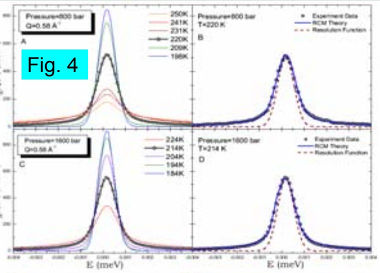


Fig. 4

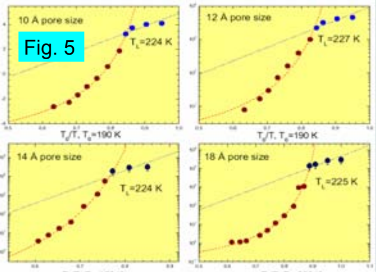


Fig. 5

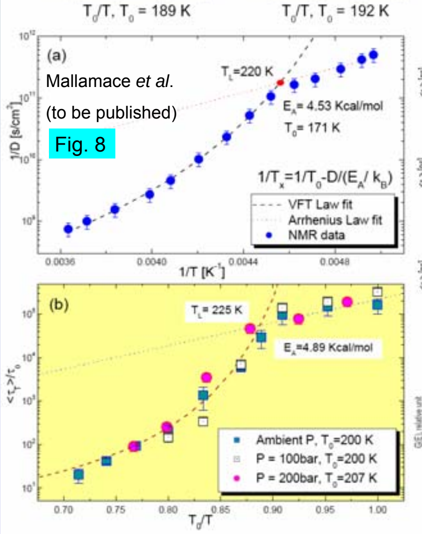


Fig. 8

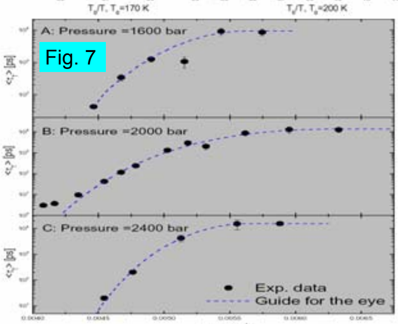


Fig. 7

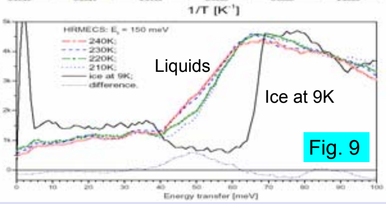
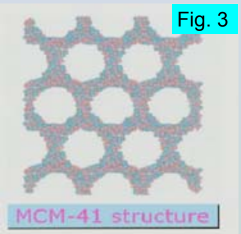


Fig. 9

We investigated, using quasi-elastic and inelastic neutron scattering, the slow single-particle dynamics of water confined in lab synthesized nanoporous silica matrices, MCM-41-S, with pore diameters ranging from 10 Å to 18 Å (see Fig. 3). Inside the pores of these matrices, the freezing process of water is strongly inhibited.

Fig. 3



We analyzed QENS spectra with a relaxing-cage model (RCM) and determined the temperature and pressure dependences of the Q-dependent translational relaxation time. (See Fig. 4)

Relaxing-Cage Model (RCM)

Experiment Measures Double Differential Cross Section ⇒ $\frac{d^2\sigma_H}{d\Omega d\omega} = 2N\frac{\sigma_H}{4\pi}\frac{k_f}{k_i}S_H(Q,\omega)$

Dynamic Structure Factor

Dynamics Structure Factor $S_H(Q,\omega)$ $S(Q,\omega) = pR(Q_0,\omega) + (1-p)FT\{F_H(Q,t)R(Q_0,t)\}$

= FT [Intermediate Scattering Function $F_H(Q,t)$]

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

$F_T(Q,t) = F_T^S(Q,t)\exp[-(t/\tau_T)^\beta]$, $\tau_T = \tau_0(aQ)^{-\gamma}$; $\langle\tau_T\rangle = \frac{\tau_0}{\beta}\Gamma\left(\frac{1}{\beta}\right)$

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

Fragile e.g. VFT law $\tau = \tau_0\exp\left[\frac{DT_0}{T-T_0}\right]$

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

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

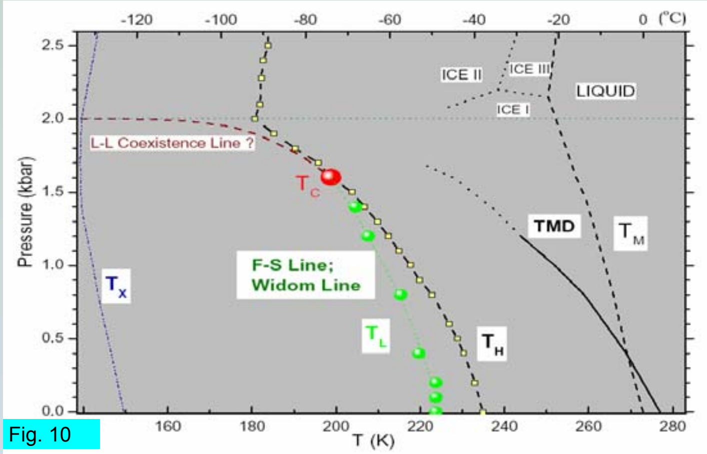


Fig. 10

New Phase Diagram (L Liu, SH Chen, *et al*, *PRL* **95**, 117802 (2005)).

Discussions and Conclusion

- **We detected a new kind of dynamic cross-over phenomena called fragile-to-strong (F-S) transition in deeply supercooled water experimentally, for the first time.**
- **The high-temperature (fragile) liquid corresponds to a higher density liquid (HDL), and the low-temperature (strong) liquid corresponds to a lower density liquid (LDL) (see Fig. 9).**
- **The F-S transition line is the so-called Widom line which is the extension of the L-L coexistence line above the critical point.**
- **We propose that the lower end point of the L-L coexistence line, or the upper end point of the Widom line, is the second low-temperature critical point ($P_C = 1500 \pm 100$ bar, and $T_C = 200 \pm 8$ K).**

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