

**“Water and Water Systems”**

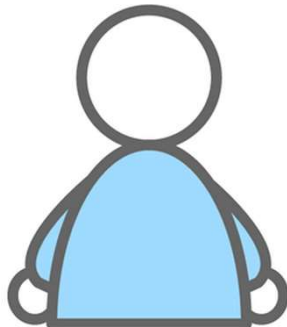
**3<sup>rd</sup> Course of the ERICE School “NEUTRON SCIENCE AND INSTRUMENTATION” 22<sup>nd</sup> July– 31<sup>st</sup> July 2016, Erice (Italy)**

# **Roles of local structural ordering in water anomalies and ice nucleation**

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*Institute of Industrial Science*  
*University of Tokyo*



**With Rui Shi and John Russo**



# Fundamental states of matter

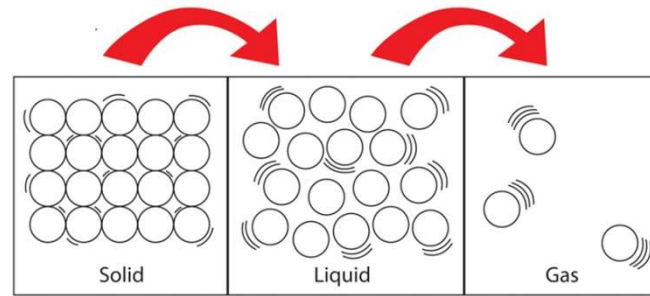
Level of physical understanding ↑

**Solid (Xtal)**

Periodicity



Disorder:  
randomness



<http://pdfcast.net/states-of-matter>

**Gas**

Mean free path  $\gg$  molecular size



**Liquid**

High density:  
Many-body correlations

**Liquid is one of the fundamental states of matter, and has unique transport properties.**

**For example, all biological phenomena take place in liquids (water).**

**Despite its importance, the physical understanding of liquids is very difficult because of its random nature and complex many-body interactions. As the result, there remain fundamental unsolved problems concerning the basic properties of liquids.**

# Unsolved problems in the physics of liquid

H. Tanaka, Eur. Phys. J. E 35, 113 (2012).

Water's anomaly

Liquid-liquid transition

**Two-order-parameter model:**

Density  $\rho$  may be not enough to describe these phenomena. We need an additional non-conserved structural order parameter  $S$ !

$$F(\rho, S)$$

We are going to show that  $S$  plays crucial roles in all these phenomena.

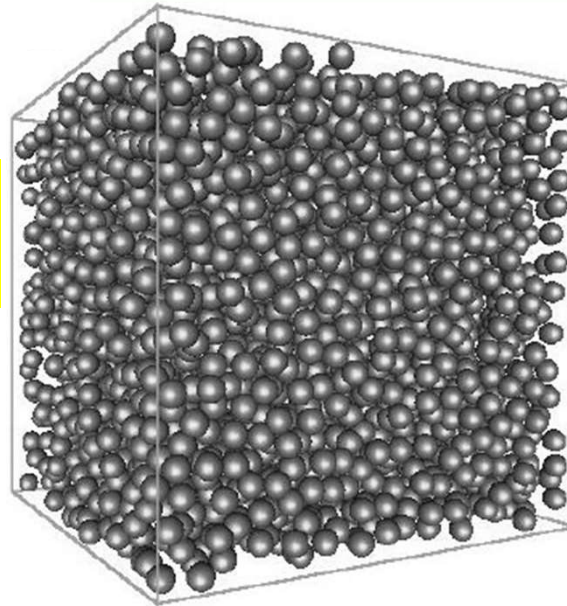
Crystallization

Glass transition

# Conventional picture of liquids

Order parameter to describe the state of a liquid

$$\rho(\mathbf{r})$$



There is no  
spatio-temporal  
hierarchy  
=  
One-level structure

Liquid-state theory and a theory of crystallization have been constructed on the assumption that liquids have homogeneous, isotropic, and random structures. Their properties can be believed to be described by two-point density correlators.

**Free energy functional**

$$F\{\rho\} = k_B T \int d\mathbf{r} \rho \left[ \ln \left( \frac{\rho}{\rho_0} \right) - 1 \right] - \frac{k_B T}{2} \iint d\mathbf{r} d\mathbf{r}' c(\mathbf{r} - \mathbf{r}') \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}'), \quad \rho_0 c_{\mathbf{k}} = 1 - S^{-1}(k)$$

**Equations of motion**

$$m \frac{\partial}{\partial t} \rho = -\nabla \cdot \mathbf{j}, \quad \frac{\partial}{\partial t} \mathbf{j} = -\rho \nabla \frac{\delta F}{\delta \rho} - \frac{\zeta_0}{m \rho_0} \mathbf{j} + \boldsymbol{\theta}$$



*Water and water-type liquids such as Si, Ge, SiO<sub>2</sub> are all extremely important liquids for human beings.*

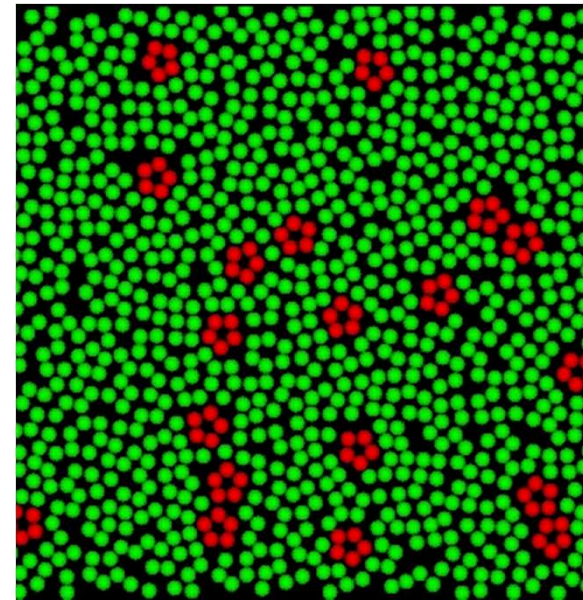
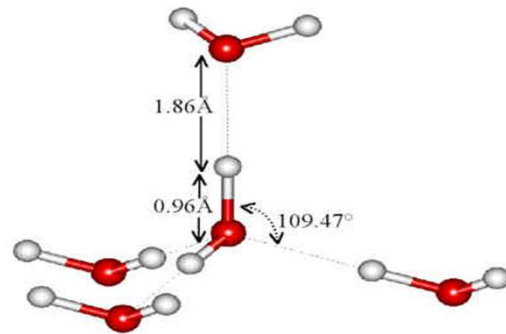
*All these liquids locally have tetrahedral symmetry due to hydrogen or covalent bonding. This feature leads to many anomalous behaviours compared to ordinary liquids, yet their physical origin have been elusive up to now.*

# Water's anomalies



All these may be explained on the basis of local structural ordering of water!

Beyond the first shell  
of tetrahedral order



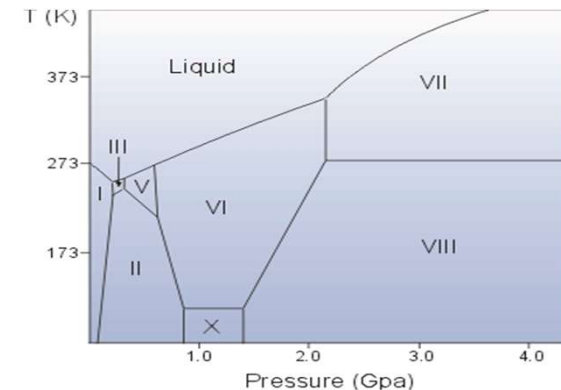
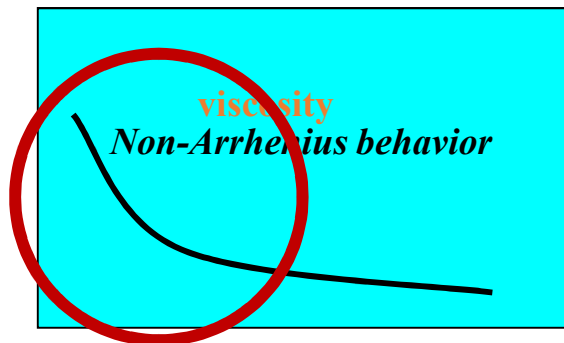
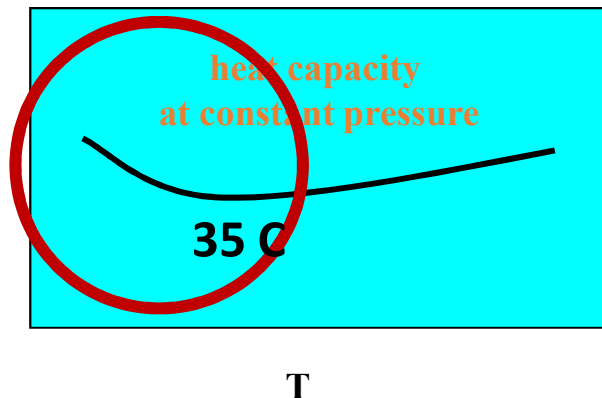
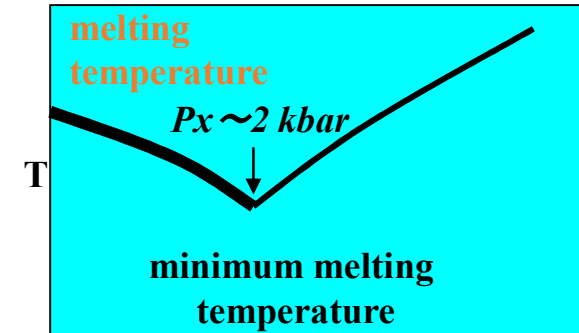
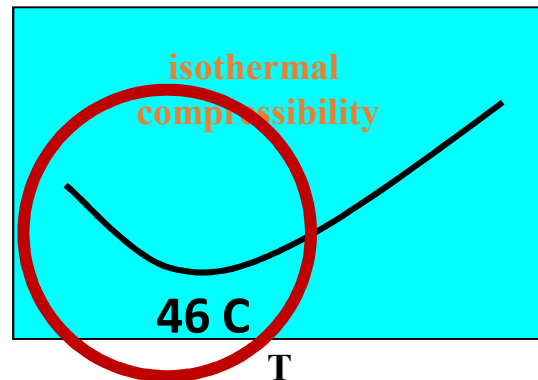
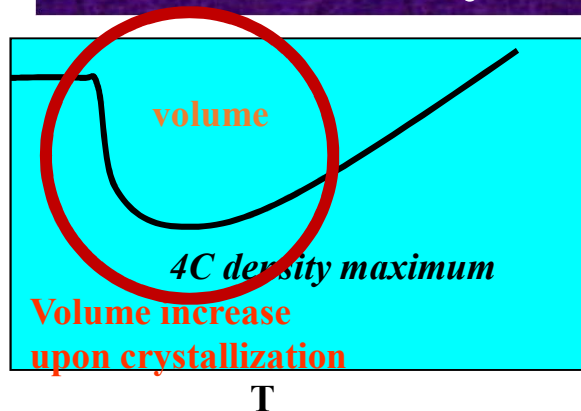
**Ice nucleation & Glass forming ability**



# Physical origin of water's anomalies



# Thermodynamic and kinetic anomalies of water



There are on-going debates on the origin of the anomaly.

*Scenarios based on singularity --- power law*

*Retracting spinodal (Speedy&Angell) or*

*Two critical-points scenario (Stanley, ....)*

*Critical-point free scenario (Angell)*

*Singularity-free scenario ---- non-power law (Debenedetti, ...)*

**These are actually related!**

K. Stokely, M. G. Mazza, H. E. Stanley, and G. Franzese, Proc. Natl. Acad. Sci. U. S. A. 107, 1301 (2010).

**Our explanation: two-state model critical-fluctuation-free scenario**

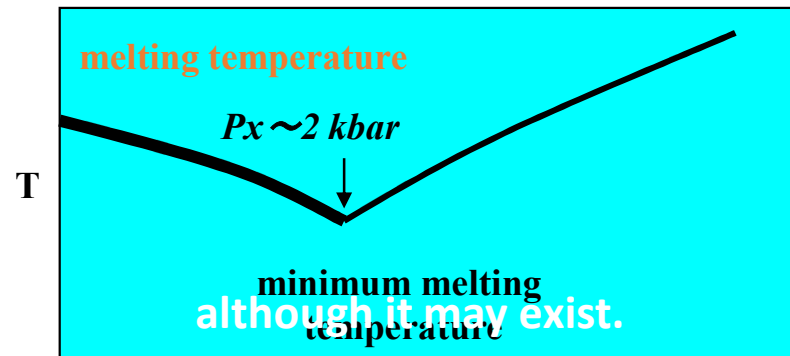
*All the anomalies may be described by a common Boltzmann factor?!*



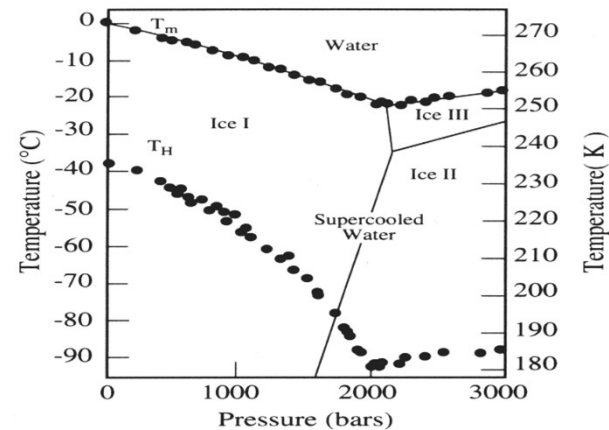
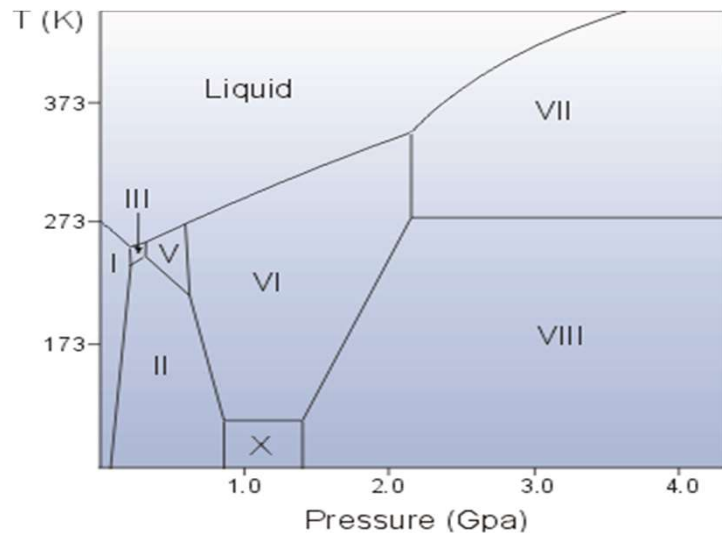
# ***P-T* phase diagram of water**

**A quite unusual feature of P-T phase diagram of water:  
Melting-point minimum!!**

**Is this feature related to the anomalies of water?**

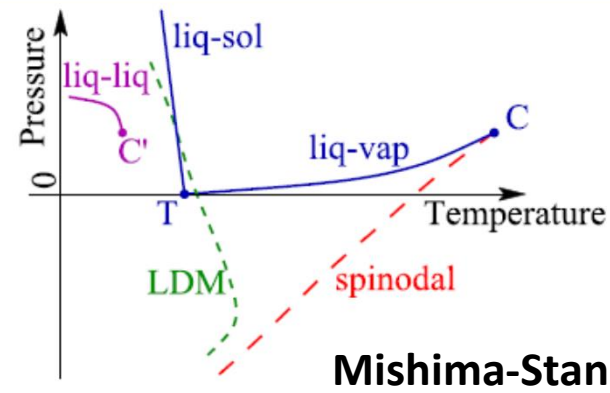
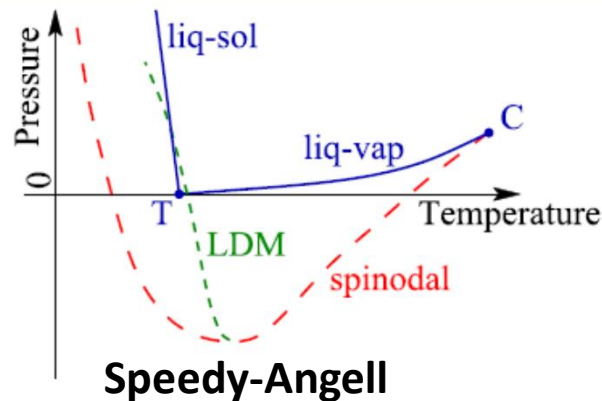


P



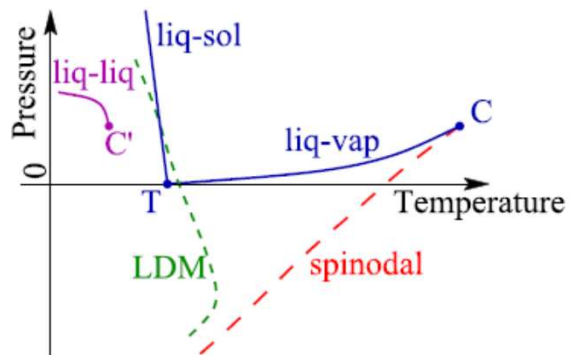
**Figure 1.5.** Crystallization temperatures of highly supercooled water droplets emulsified in hydrocarbons, as a function of pressure.  $T_H$  is the crystallization temperature;  $T_M$  is the equilibrium melting temperature. (Adapted from Kanno et al., 1975)

# Various scenarios on the singularities of water



**Figure 2.** Two scenarios proposed to explain the anomalies of supercooled water. Left: retracing spinodal [7]. Right: liquid-liquid critical point [11]. The figures show the liquid-vapour and liquid-solid equilibrium (solid blue lines), the line of density maxima (short dashed green line), the liquid-vapour spinodal (long dashed red line) and in the right panel the liquid-liquid transition (solid purple line).

Frédéric Caupin *et al*, *J. Phys.: Condens. Matter* 24 284110 (2012)



**Our standpoint:**  
2<sup>nd</sup> CP may exist, but is not  
relevant to water's anomaly in an  
experimentally accessible region.

Tanaka, PRL (1998); JCP (2000)

# Scenarios based on critical phenomena of a second CP

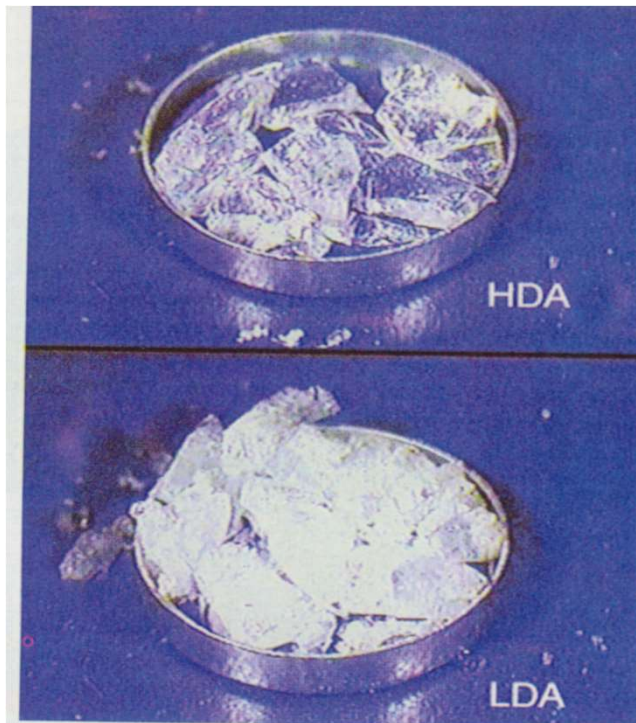
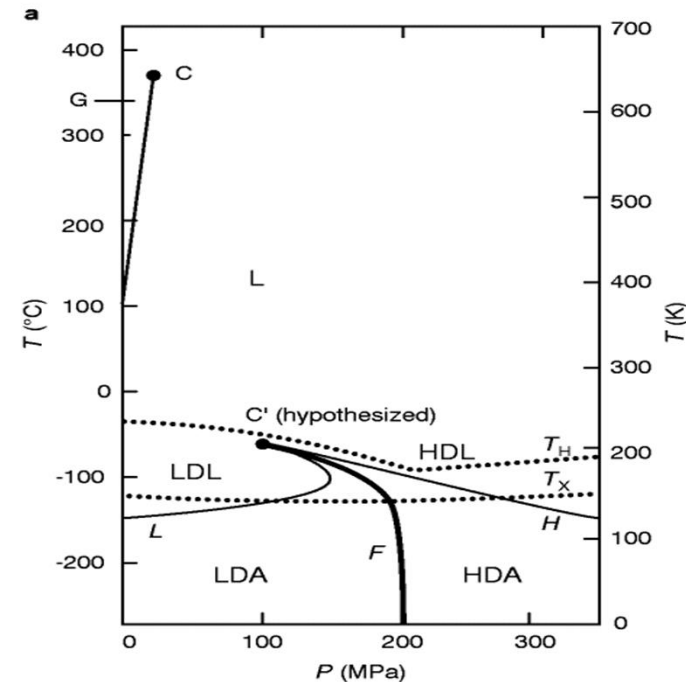
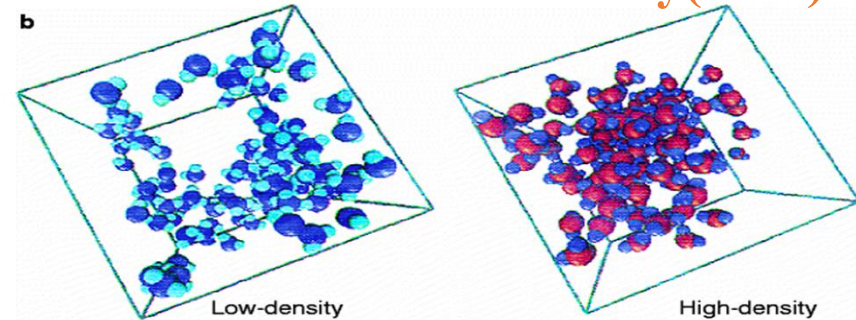


Figure 1 The two forms of glassy water. LDA is formed by rapidly cooling water at atmospheric pressure; HDA is formed by compressing either LDA or ordinary ice at low temperature. These amorphous solids might be able to coexist, as might two structurally similar liquid waters, LDL and HDL.

**Two types of amorphous ices  
(O.Mishima)**



**Mishima&Stanley(1998)**



**P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Nature 360, 324(1992).**

## Singularity scenario:

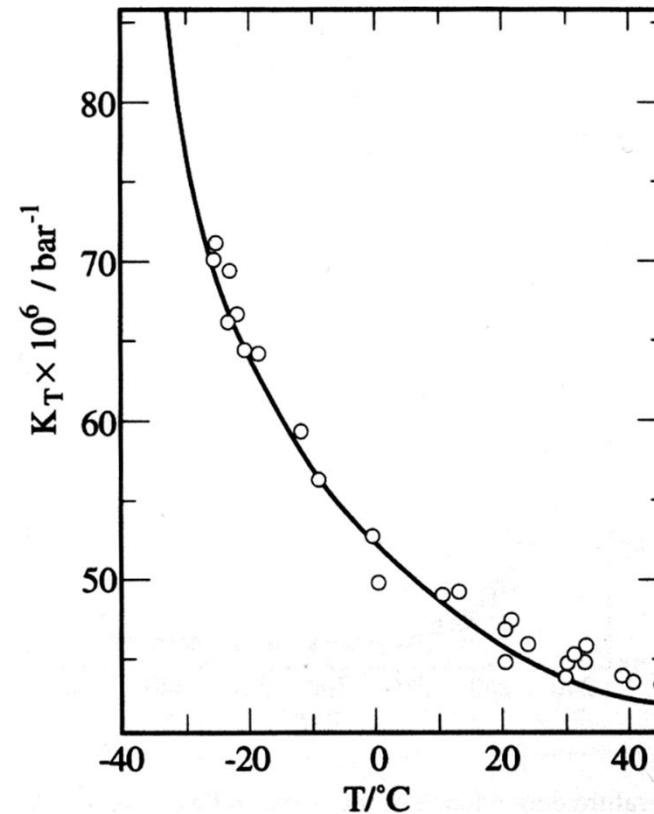
Water anomalies are a consequence of criticality associated with 2<sup>nd</sup> critical point or retracting spinodal.

Anomalies obey the power-laws diverging towards  $T_s$ .

$$(T - T_s)^{-\delta}$$
$$T_s \cong 228 \text{ K}$$

Speedy&Angell (1976)

## Isothermal compressibility



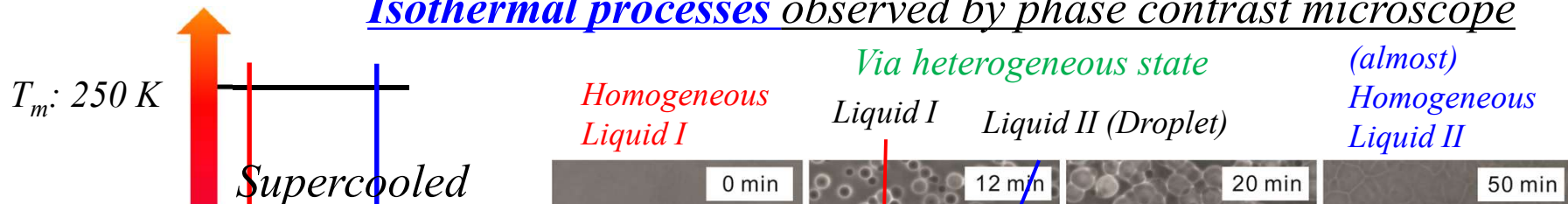
**Figure 2.12.** Temperature dependence of the isothermal compressibility ( $K_T$ ) of supercooled water at atmospheric pressure. The solid line is a fit,  $K_T = 29.65 \times 10^{-6} (\text{bar}^{-1}) (T - 228)^{-0.349}$ . (Adapted from Speedy and Angell, 1976)



# Pattern evolution of LLT in a water/glycerol mixture

K. Murata and H. Tanaka, *Nature Mater.* 11, 436 (2012)

Isothermal processes observed by phase contrast microscope



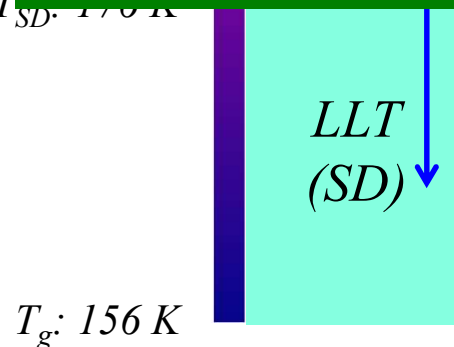
We believe that there may be LLT and a second critical point in water, although there are some debates on our results.

Nevertheless, we propose that both thermodynamic and kinetic anomalies of water may be described by a single Boltzmann factor and not by power laws.

$T_{SD}: 173\text{ K}$

Order parameter fluctuation

(NG-type at  $T=180\text{ K}$  for  $c=0.165$ , SD-type at  $T=173\text{ K}$  for  $c=0.165$ )



We observed LLT in 14 organic aqueous solutions, suggesting that LLT is mainly driven by water! *Nature Commun.* (2013)

# Long history of mixture or two-state models

In 1892, German physicist W. C. Röntgen, who became famous for his discovery of X-rays, published a paper proposing a "mixture model" according to which liquid water consists of two kinds of molecules: a tetrahedral ice-like structure, and another more loosely arranged structure.



**For example,**

**C. A. Angell: Bond-lattice model [J. Phys. Chem. 75, 3698 (1971)]**

**G. W. Robinson and coworkers:  
simple 2 state model (no asymmetric degeneracy)**

Thermodynamic properties and structural features of water at  
normal and high pressures

Solid State Ionics 145 (2001) 415–420

V.V. Sinitsyn<sup>a,\*</sup>, E.G. Ponyatovsky<sup>a</sup>, A.I. Kolesnikov<sup>a</sup>, U. Dahlborg<sup>b</sup>,  
M. Calvo-Dahlborg<sup>b</sup>

**Many others a mixture of LDL and HDL**

# Two-order-parameter model of liquid

H. Tanaka, J. Phys.: Condens. Matter (1998); Phys. Rev. Lett. 80, 5750 (1998);  
Phys. Rev. E 62, 6968 (2000)

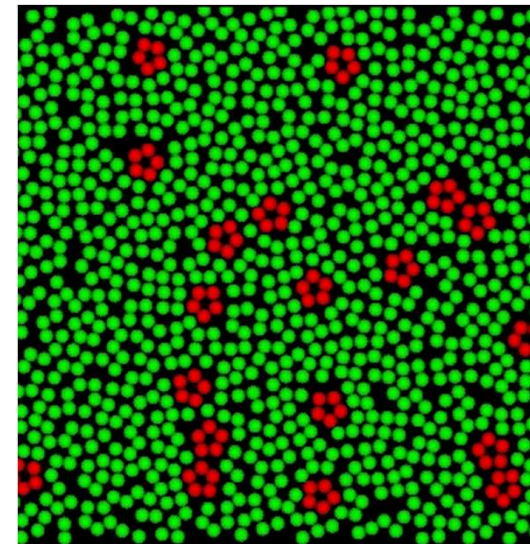
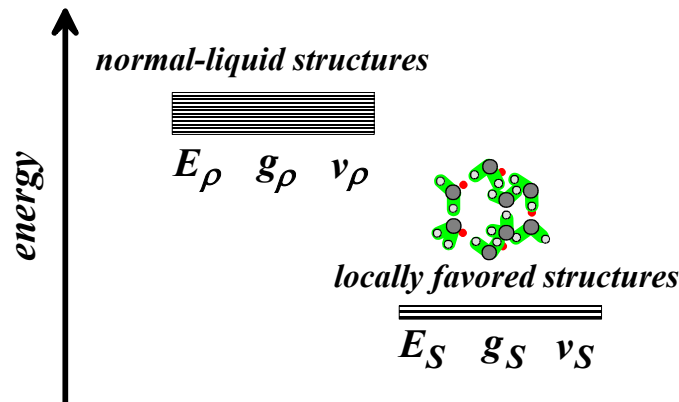
We focus on local structural ordering due to many-body correlations

Density is not enough to describe the state of liquid!

Introduction of a new **non-conserved** order parameter  $S$

$S$  = Fraction of locally favored structures

How can we specify it?



H Shintani, H Tanaka, Nature Phys. 2, 200 (2006)

- 1) LFS is more stable than NLS by  $\Delta E$ .
- 2) The volume of LFS is larger than that of NLS by  $\Delta v$  (for water).
- 3) The entropy of LFS is much smaller than that of NLS!

# Two-order-parameter model of liquid

H. Tanaka, J. Phys.: Condens. Matter (1998); Phys. Rev. Lett. 80, 5750 (1998); Phys. Rev. E 62, 6968 (2000)

## Two-state model with cooperative excitation

S. Strassler and C. Kittel, Phys. Rev. A 139, 758 (1965).

Rapoport, J. Chem. Phys. 46, 289 (1967)

$$\begin{aligned}
 f_S(S) &= U - T\sigma + [Sv_S + (1-S)v_\rho]P \\
 &= SE_S + (1-S)E_\rho - \underbrace{JS(1-S)}_{\text{cooperativity}} - k_B T \left[ S \ln \frac{S}{g_S} + (1-S) \ln \frac{1-S}{g_\rho} \right] \\
 &\quad + [Sv_S + (1-S)v_\rho]P,
 \end{aligned}$$

**J: cooperativity**  $\longrightarrow$  **Origin of LL transition**

$$\partial f / \partial \bar{S} = 0$$

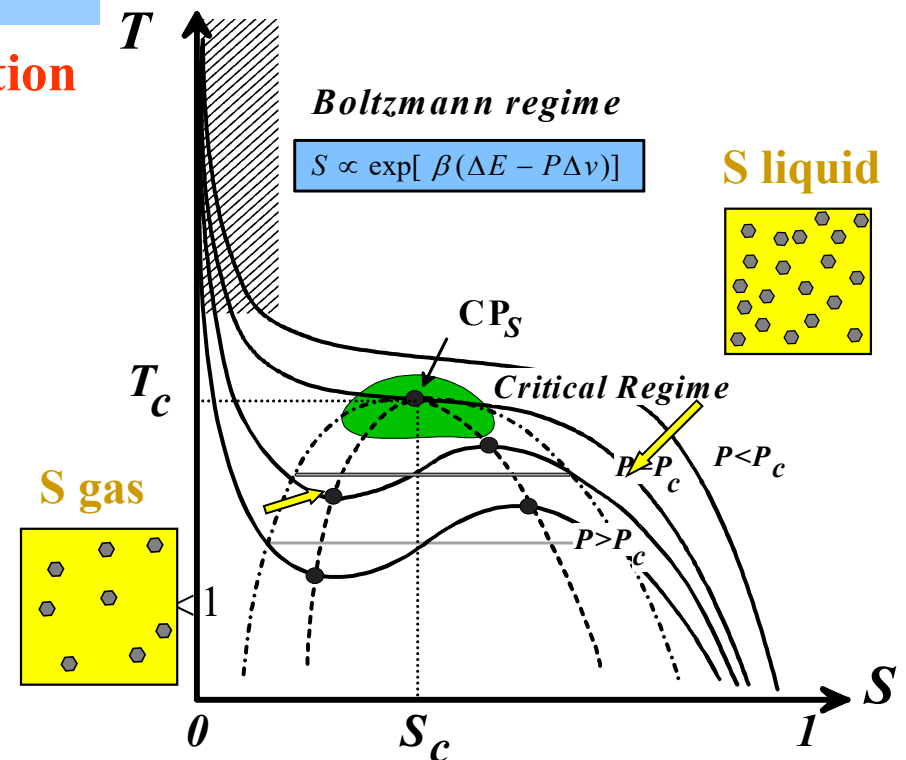
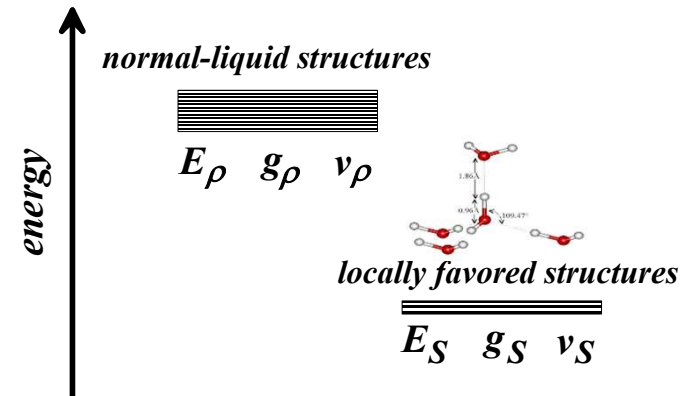
$$\frac{\bar{S}}{1-\bar{S}} = \frac{g_S}{g_\rho} \exp[\beta(E_\rho - E_S) - (v_S - v_\rho)P]$$

$$g_S \ll g_\rho$$

Large loss of entropy upon formation of LFS

**Thermodynamic equilibrium value of S for  $\bar{S} \ll 1$**

$$\bar{S} = \frac{g_S}{g_\rho} \exp[\beta(\Delta E - P\Delta v)],$$



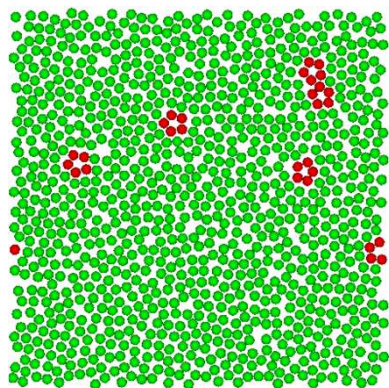


# Anomalies of Water-Type Liquids

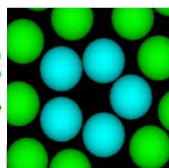
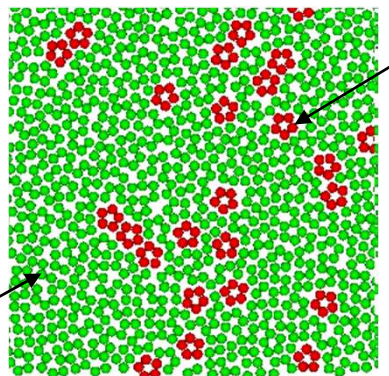
## 2D spin liquid simulation

H Shintani, H Tanaka, Nature Phys. 2, 200 (2006)

High  $T$



Low  $T$



LFS

NLS

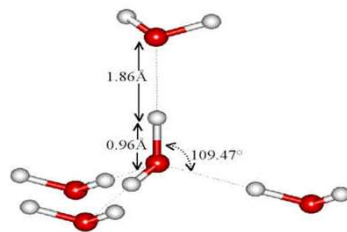
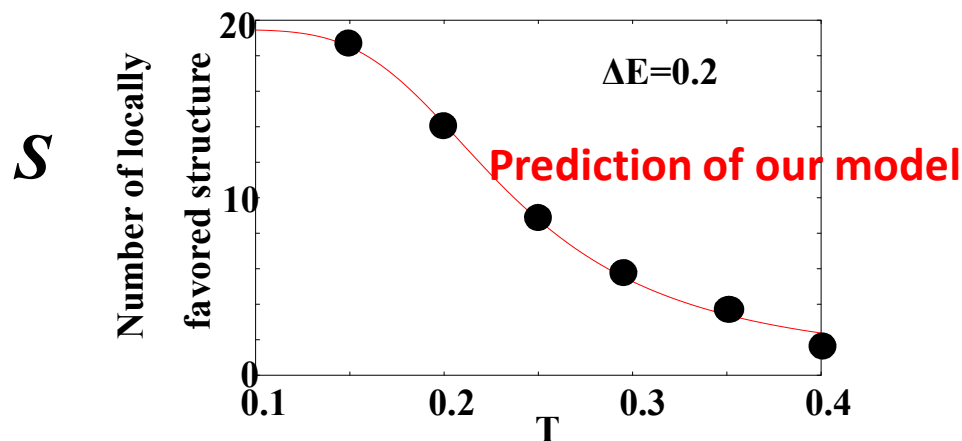
$$S(r) \cong Q_l(r) = \left[ \frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{Q}_{lm}(r)|^2 \right]^{1/2}$$

$l=6$  Steinhardt, Nelson & Ronchetti (1983)

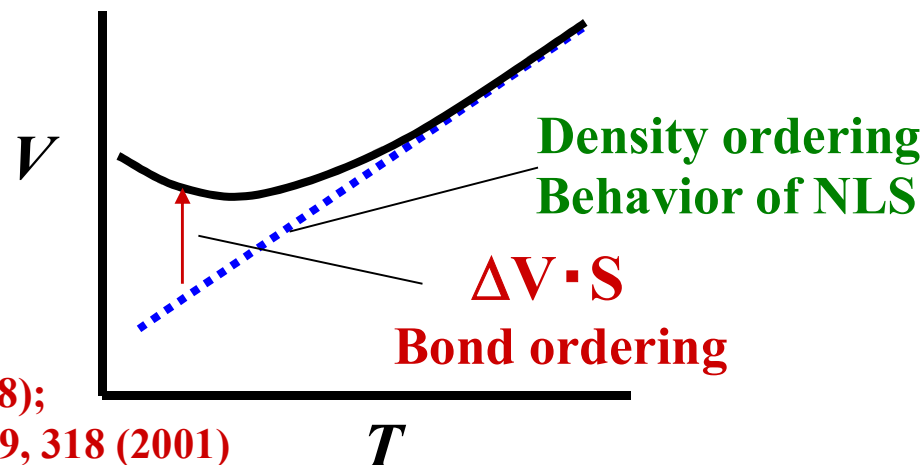
$l=3$  Wang & Stroud (1991)

For water, H. Tanaka, Phys. Rev. Lett. 80, 5750 (1998);

J. R. Errington and P.G. Debenedetti, NATURE, 409, 318 (2001)



For water-type liquids, LFS occupies more volume than NLS.



# **Difference between a mixture model and our two-order-parameter model**

**Most mixture models regard water as mixtures of two distinct species,  
e.g., as a mixture of LDL and HDL.**

**Our two-order-parameter model is constructed on the presence of microscopic locally favored structures (LFS), whose fraction  $s$  is treated as the key order parameter. The creation of LFS accompanies a large loss of entropy. LDL and HDL are also characterized by the value of  $s$  respectively.**

# Thermodynamic and kinetic anomalies of water

## Fitting of existing experimental data of water by our model

**H. Tanaka,**  
**Phys. Rev. Lett. 80, 5750 (1998);**  
**J. Chem. Phys. 112, 799(2000);**  
**Europhys. Lett. 50, 340 (2000);**  
**J. Phys.: Condens. Matter 15, L703 (2003).**

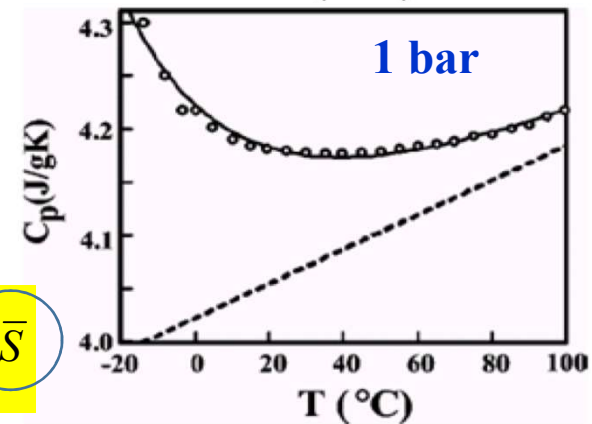
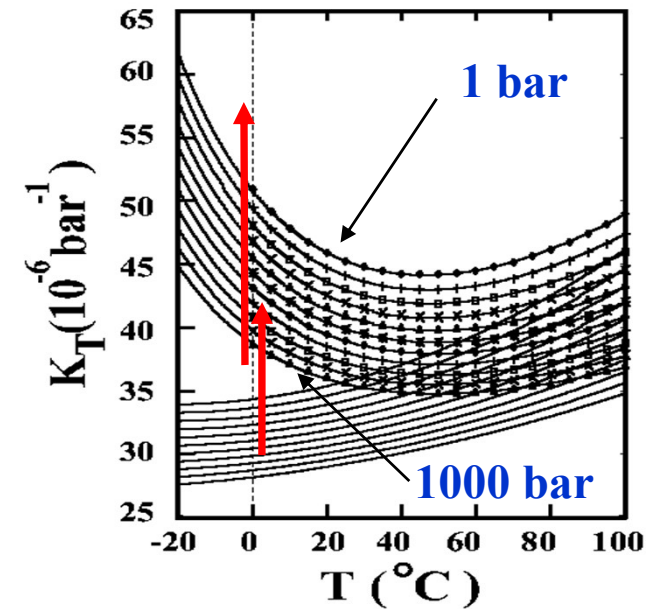
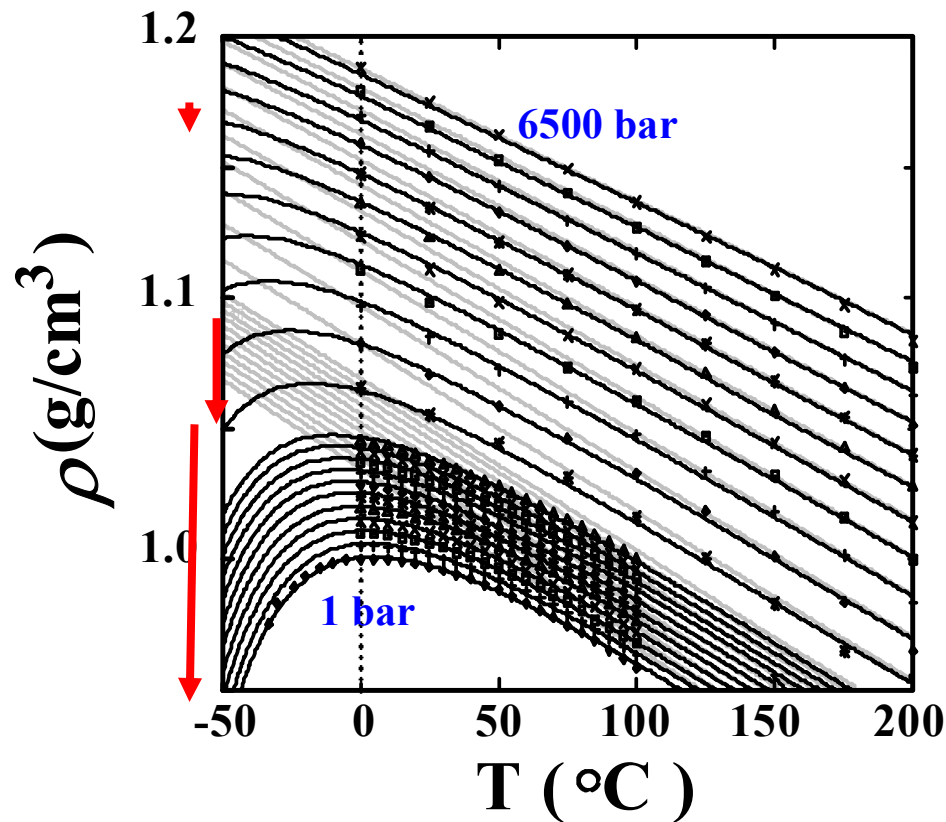
# Thermodynamic anomalies of water

$$\bar{S} = \frac{g_s}{g_\rho} \exp[\beta(\Delta E - P\Delta v)],$$

$$\Delta E \approx 3.6 \text{ kcal/mol}, \Delta v \approx 10 \text{ cm}^3/\text{mol}, g_s/g_\rho = 8.1 \times 10^{-5}$$

$$\rho(T, P) = \rho_B(T, P) - \rho_B(T, P) \frac{\Delta v_s}{v_{sp}} \bar{S}$$

$$K_T = -\frac{1}{v_{sp}} \left( \frac{\partial v_{sp}}{\partial P} \right) + \frac{1}{v_{sp}} \left[ -\left( \frac{\partial \Delta v_s}{\partial P} \right)_T + \beta \Delta v_s^2 \right] \bar{S}$$

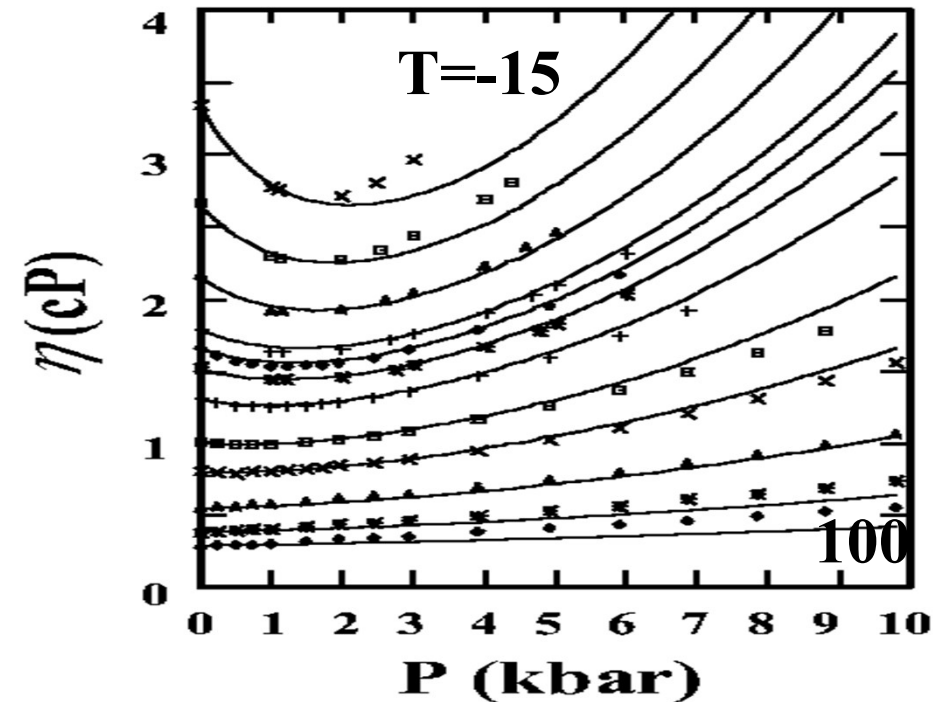
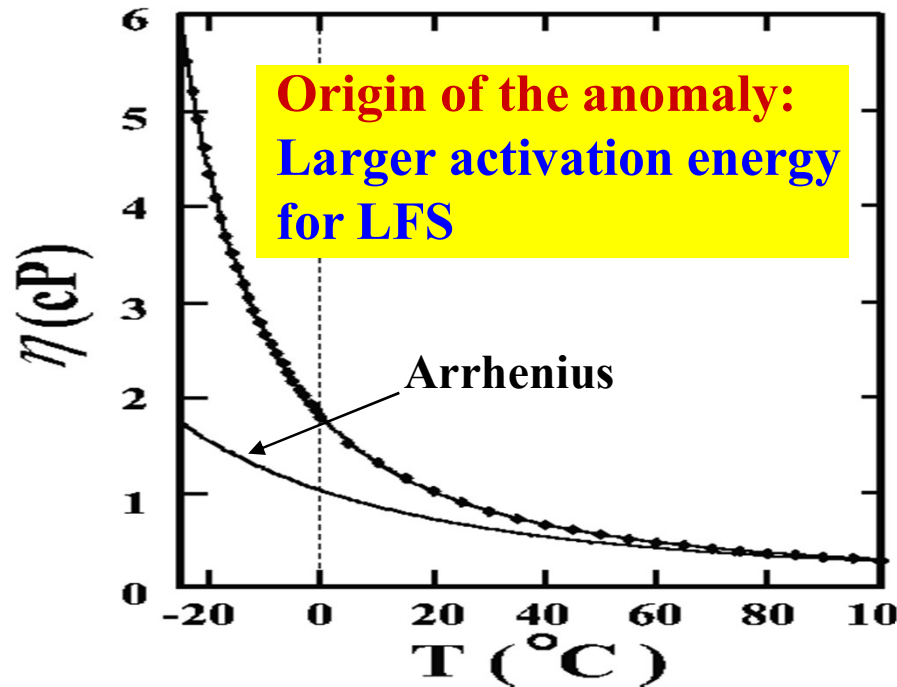


$$C_P = T \left( \frac{\partial \sigma_B}{\partial T} \right)_P + \left[ -T \left( \frac{\partial \Delta \sigma}{\partial T} \right)_P + \beta \Delta \sigma (\Delta E - \Delta v P) \right] \bar{S}$$



# Viscosity anomaly of water

H. Tanaka, JCP 112, 799 (2000).

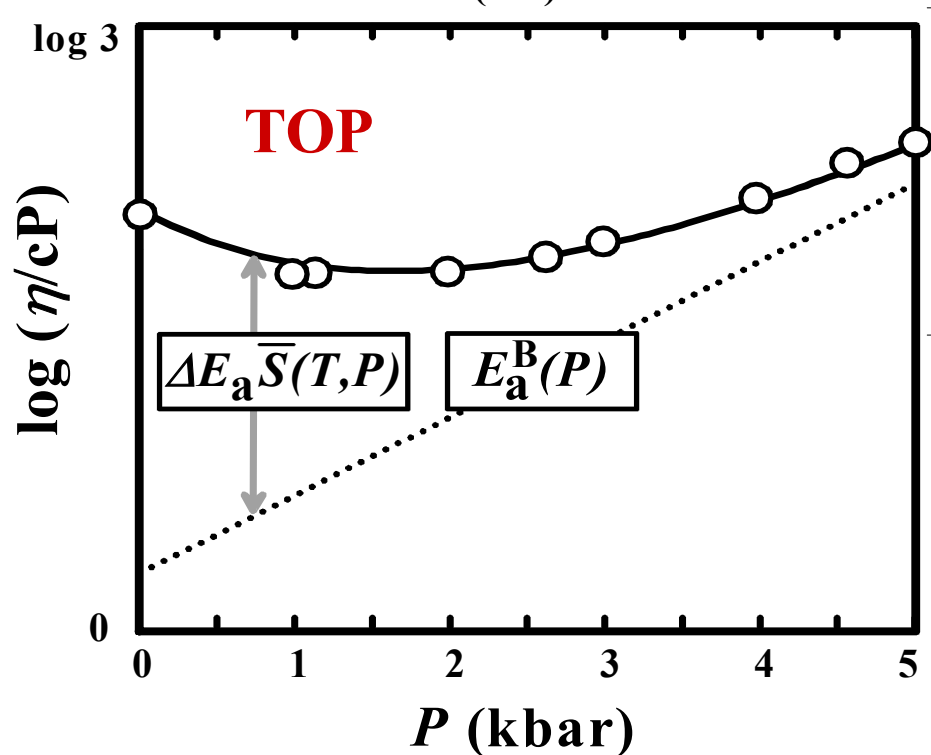
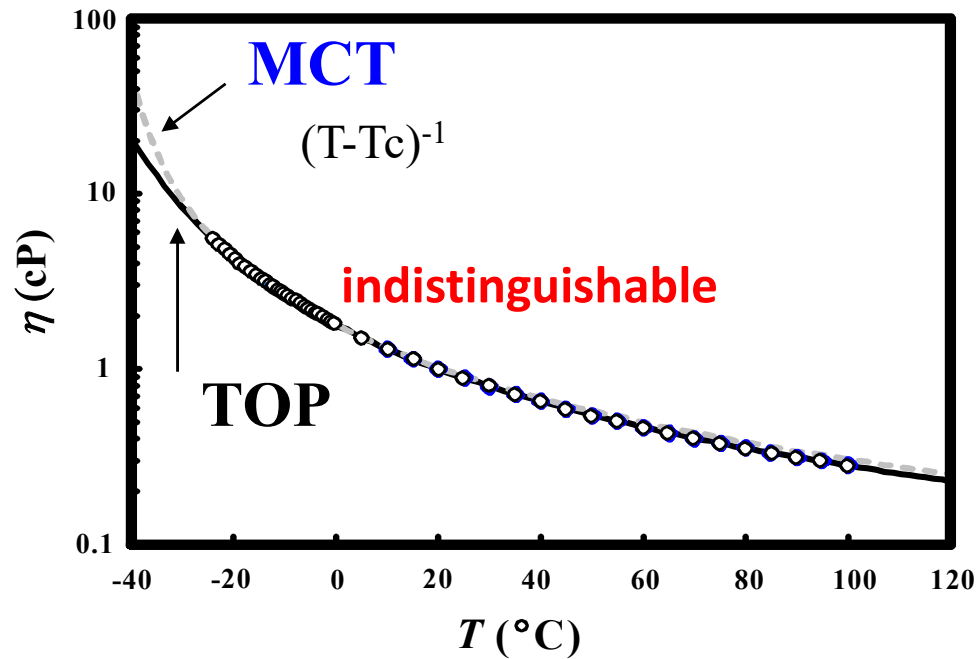


The activation energy for flow should be averaged over all molecules participating NLS and LFS.  
Assumption: Compared to the key timescale of transport, the lifetime of LFS is much shorter.

$$\eta(T, P) = \eta_0 T^{\frac{3}{2}} \exp[\beta(E_a^B(P) + \Delta E_a \bar{S}(T, P))]$$

$$E_a^B(P) = E_a^B(0) + cP$$

$$\Delta E \approx 3.6 \text{ kcal/mol}, \Delta v \approx 10 \text{ cm}^3/\text{mol}, g_s / g_\rho = 8.1 \times 10^{-5}$$



**A popular scenario:**

**Two critical points+MCT**

$$T_c \cong 228 \text{ K}$$

**But MCT alone cannot explain the thermodynamic anomalies?!**

**Critical anomaly of  $\eta$ : logarithmic**  
 **$T_c/T_g \sim 1.2$  in ordinary liquids**

**$T_g$  of water  $\sim 136 \text{ K}$**

**Viscosity is still low around 230 K**

**Power Law  
or  
Boltzmann factor**

**TOP model:**

**It can explain the  $P$ -dependence of viscosity quite naturally with the same Boltzmann factor  $S$ !**

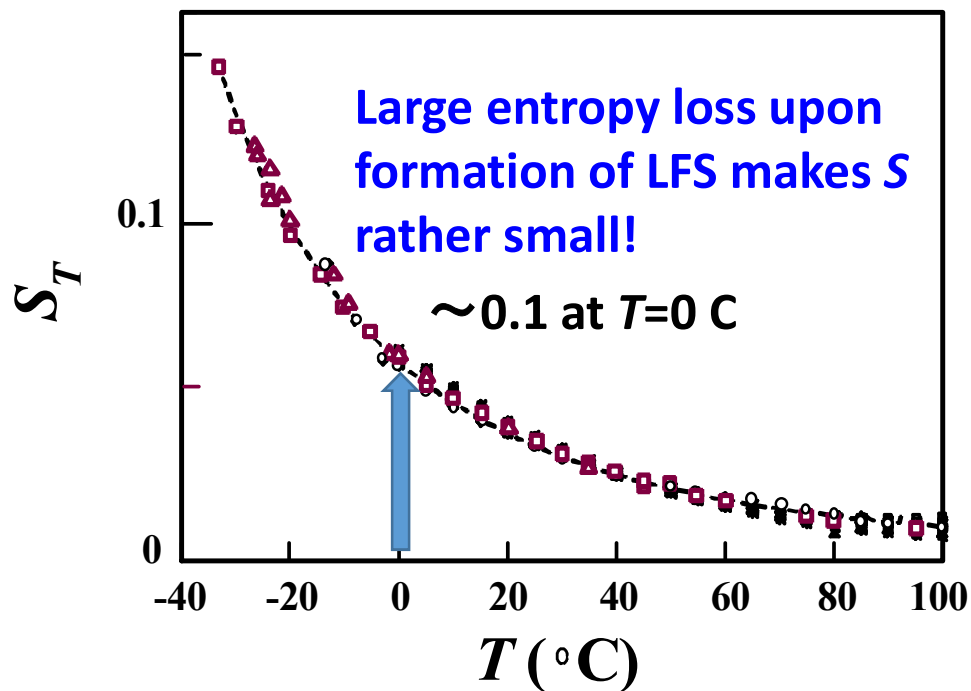
**H. Tanaka, J. Phys.: Condens. Matter 15, L703 (2003).**

# $T$ - $P$ dependence of $S$

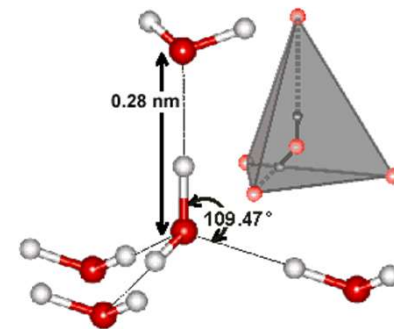
Thermodynamic equilibrium  
value of  $S$  for  $\bar{S} \ll 1$

$$\bar{S} = \frac{g_s}{g_\rho} \exp[\beta(\Delta E - P\Delta v)],$$

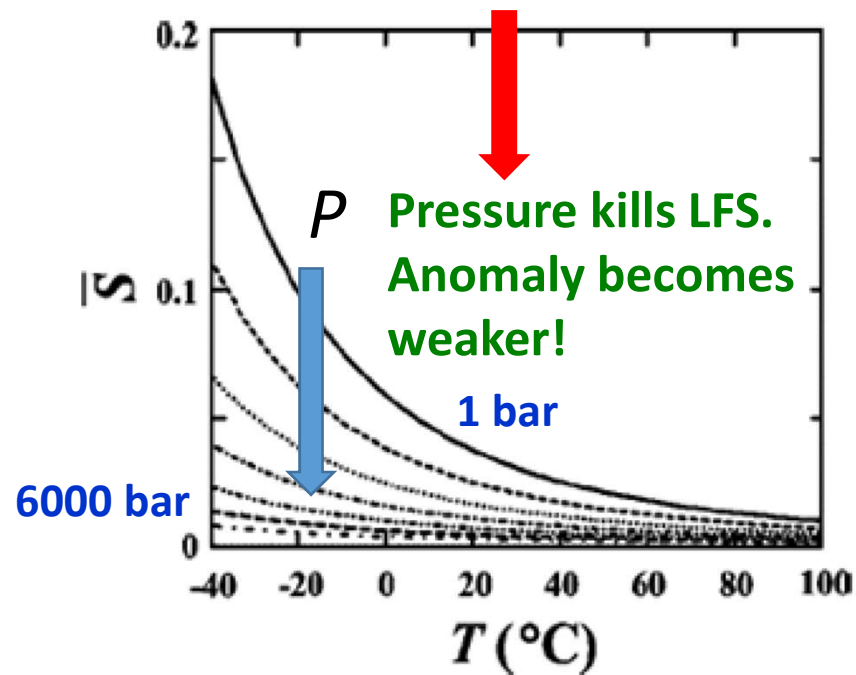
$\rho, K_T, C_P, \eta$



$S$ : Fraction of water molecules participating in locally favored structures



Larger specific volume



$$\Delta E \approx 3.6 \text{ kcal/mol}, \Delta v \approx 10 \text{ cm}^3/\text{mol}, g_s/g_\rho = 8.1 \times 10^{-5}$$

## Other mixture models (there are too many to be mentioned!!)

C. A. Angell: Bond-lattice model [J. Phys. Chem. 75, 3698 (1971)]

### Fraction of broken hydrogen bonds

Substitution of the above parameters into eq 4 yields the percentage of the possible hydrogen bonds which are

Most of previous mixture models estimate the fraction of ice-like structures to be 50-70% around 0 C. Note that these models regard water as a mixture of two distinct (fixed) structures (e.g., HDA and LDA).

In these models, fluctuations effects (or, a large entropy of normal liquid structures) are ignored.

+4	0.4585	0.4703
+20	0.4014	0.4104
+40	0.3422	0.3475
+60	0.2925	0.2945
+80	0.2501	0.2404

J. Phys. Chem. 1994, 98, 2222-2230

2222

#### FEATURE ARTICLE

#### Properties of Liquid Water: Origin of the Density Anomalies

Mary Vadamuthu, Surjit Singh, and G. Wilse Robinson\*

Subpicosecond and Quantum Radiation Laboratory, Departments of Physics and Chemistry, Box 41061, Texas Tech University, Lubbock, Texas 79409-1061

Received: September 30, 1993; In Final Form: December 10, 1993\*

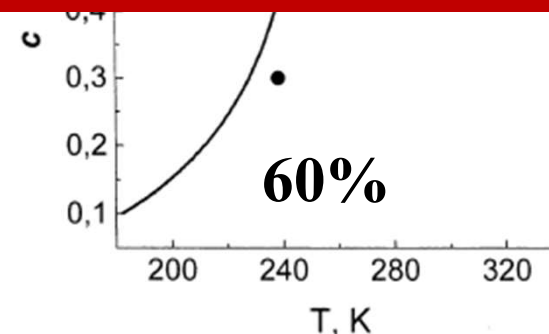
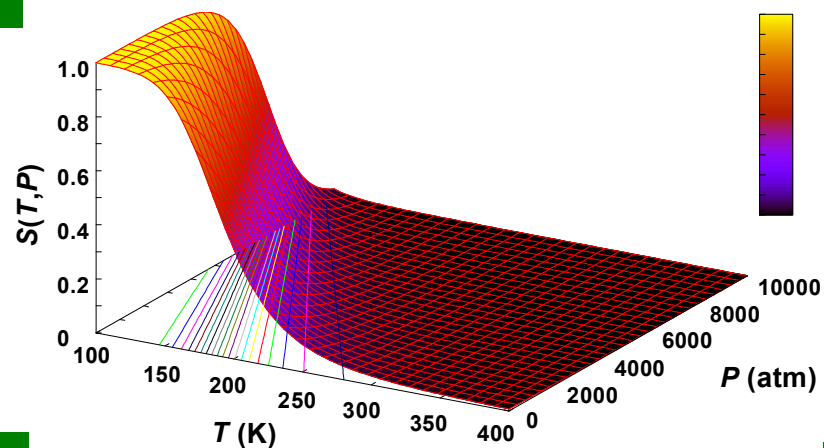


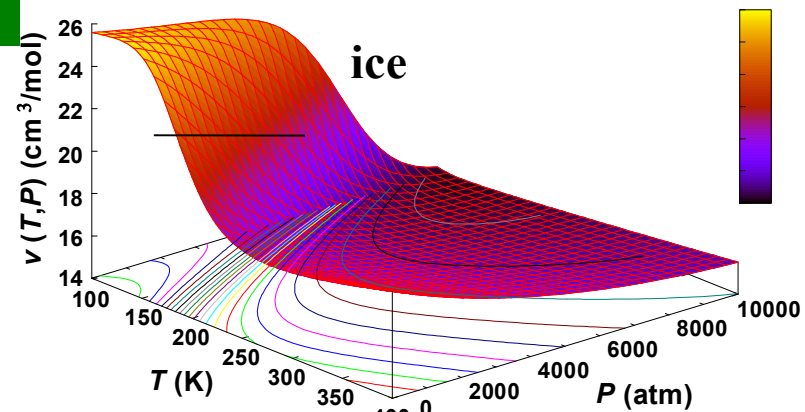
Fig. 2. Temperature dependence of  $c$  parameter at atmospheric pressure. The line is the calculation within two-level model, solid points—from the structural data using Eq. (2) [11].

# Prediction of thermodynamic anomalies using the parameters we determined

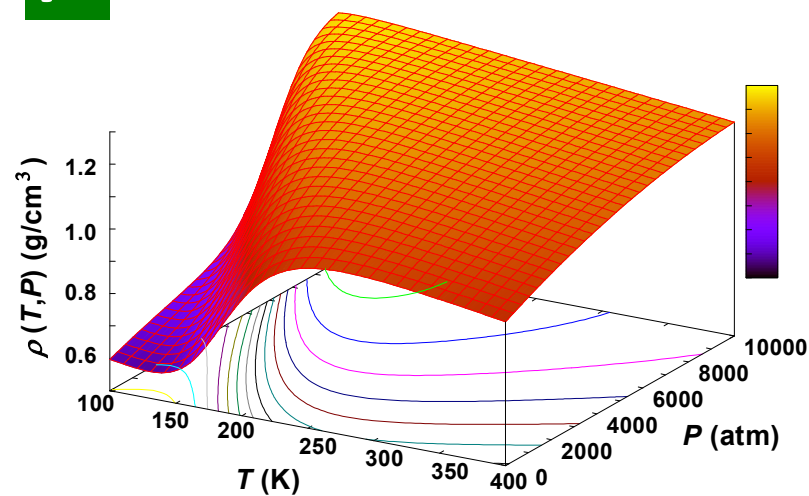
**S**



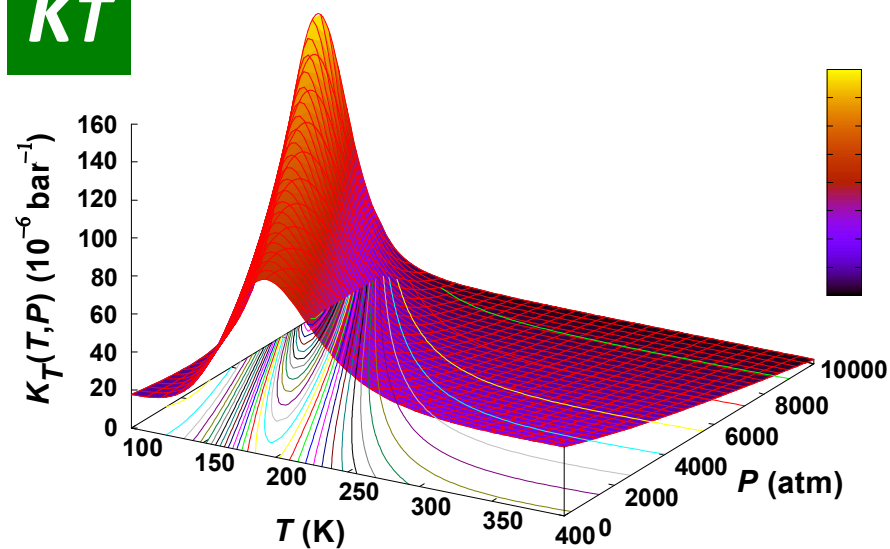
**V**



**$\rho$**



**KT**





# Recent successful two-state model description of the ST2 model for supercooled water

V. Holten, J. C. Palmer, P. H. Poole, P. G. Debenedetti, and Mikhail A. Anisimov

JCP 140, 104502 (2014)

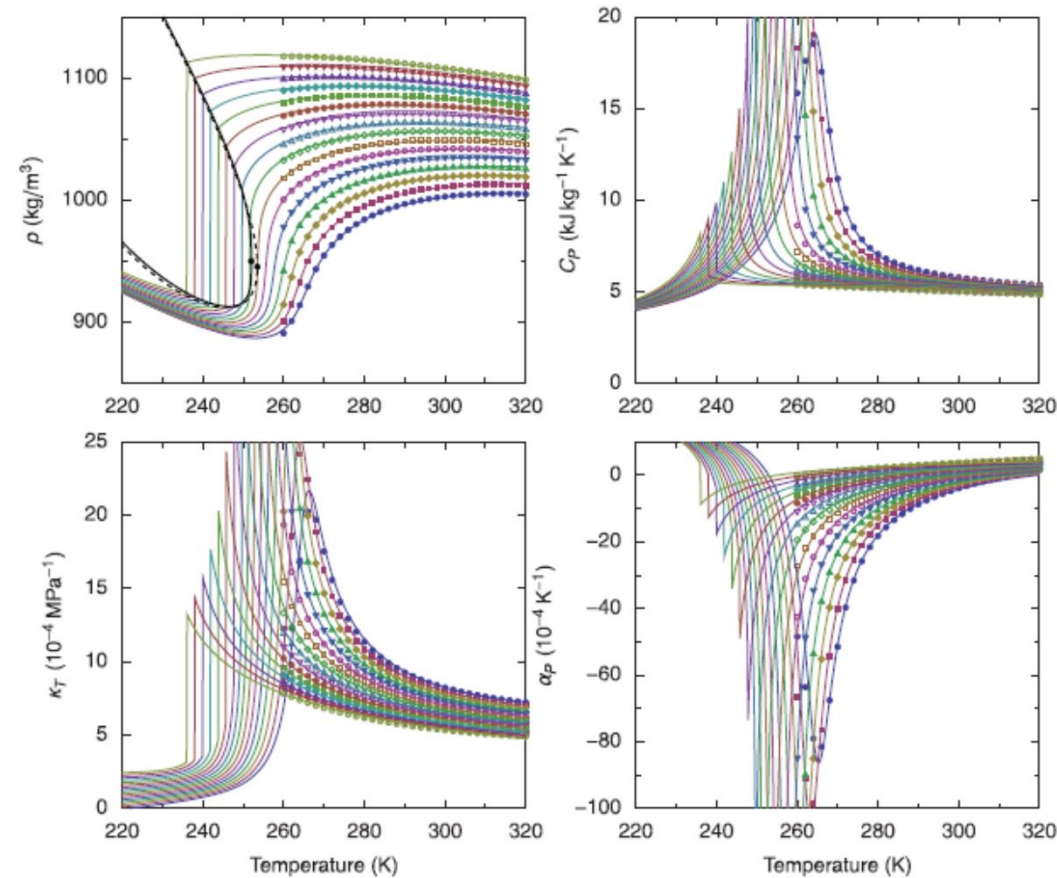
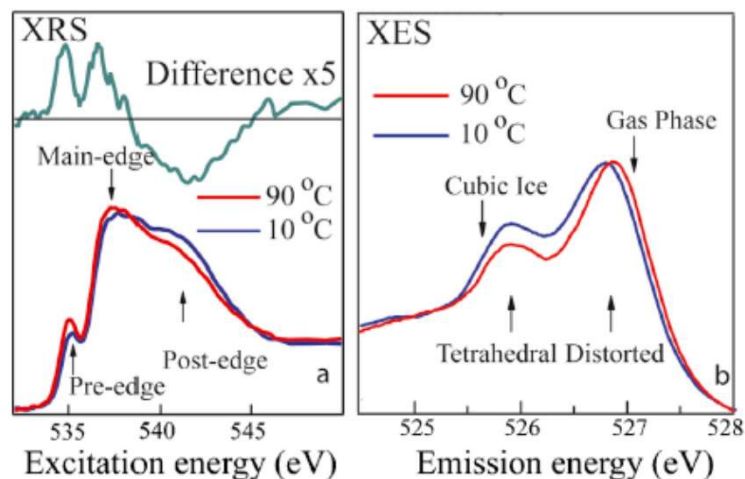
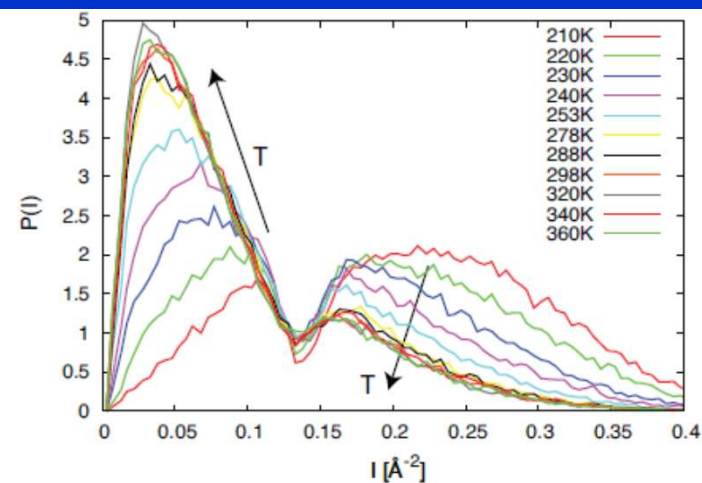
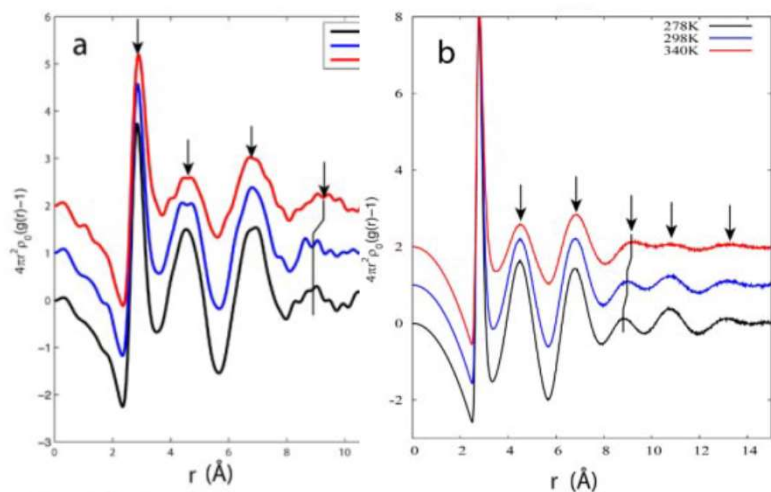


FIG. 5. Density  $\rho$ , isobaric heat capacity  $C_p$ , isothermal compressibility  $\kappa_T$ , and expansivity  $\alpha_p$  along isobars, predicted by the crossover equation of state. The data points are obtained from polynomial fits to raw data for the volume and energy for the ST2(I) model. In the density graph, the black curves indicate the phase coexistence densities (dashed: mean-field equation; solid: crossover equation), and the black dots represent the mean-field and crossover locations for the critical point. Isobar pressures are 100 MPa to 250 MPa in steps of 10 MPa.

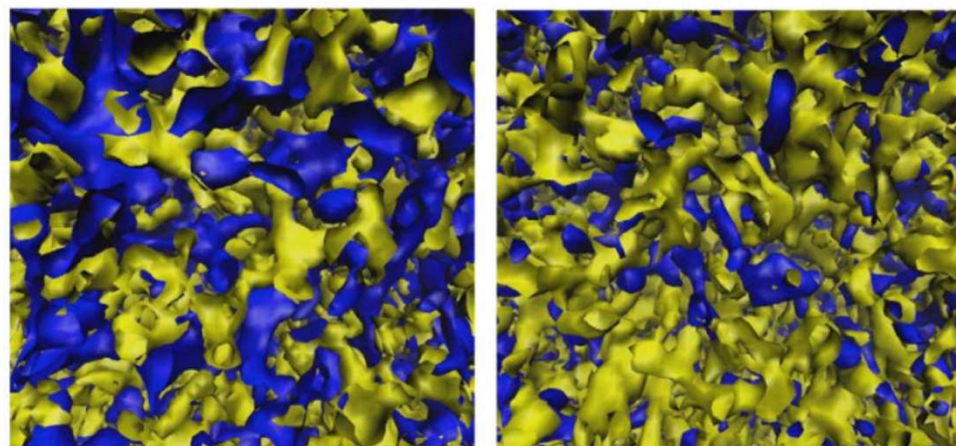
# Strong experimental and simulation supports (Nilsson & Pettersson) (See Nature Communications review paper)



**Fig. 2.** (a) X-ray Raman scattering spectra of liquid H<sub>2</sub>O at 10 and 90 °C normalized to have the same area and the difference between the two spectra magnified by a factor of 5 [10]. (b) The lone-pair 1b<sub>1</sub> region of the O 1s soft X-ray emission spectra of liquid D<sub>2</sub>O at 10 and 90 °C using a non-resonant excitation energy of 550 eV. The positions of the corresponding 1b<sub>1</sub> state of crystalline ice and gas phase water are indicated with arrows [11]. The spectra were normalized to give the same peak height of the distorted component.



**Fig. 18.** Distributions of the local structure index parameter  $I(l)$  obtained from energy-minimized "inherent structures" in simulations at ambient and elevated pressures, shown as function of temperature. A temperature and pressure invariant isosbestic point is seen around  $l = 0.13\text{--}0.14 \text{ \AA}^{-2}$ . Figure adapted from Ref. [108].



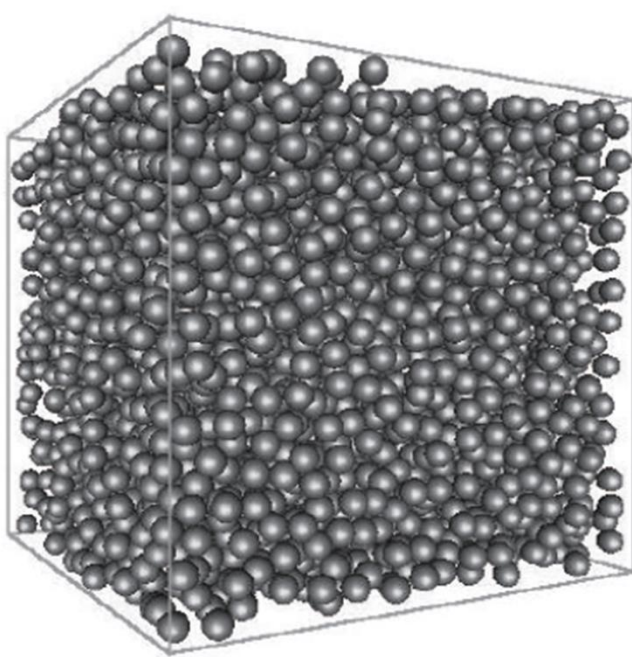
**Fig. 28.** – Isosurfaces at 253 K (left) and 340 K (right) of high-density fields (yellow) and high tetrahedrality (blue) from TIP4P/2005 simulations [11]. The length of the box is  $\sim 106 \text{ \AA}$ . Reproduced from ref. [17].



But good fittings of the model to the data seem not to be enough to convince people of the relevance of the two-order-parameter (or two-state) model to water.

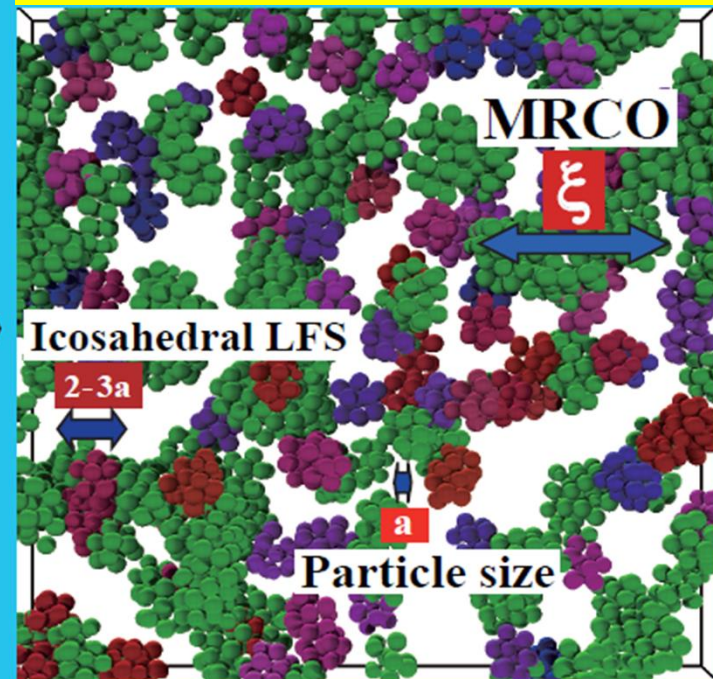
**Significant thermal fluctuations make everything obscure.**

Continuum model (random nature)  
Continuous distribution



VS

Two-order-parameter model  
Bimodal distribution



So we need

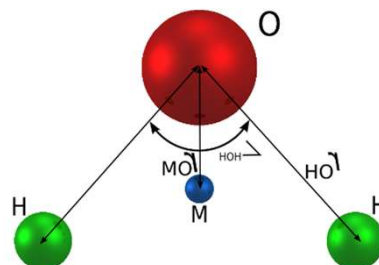
**Microscopic support for our  
two-order-parameter model  
from simulations**

John Russo and Hajime Tanaka  
Nature Commun. 5, 3556 (2014).

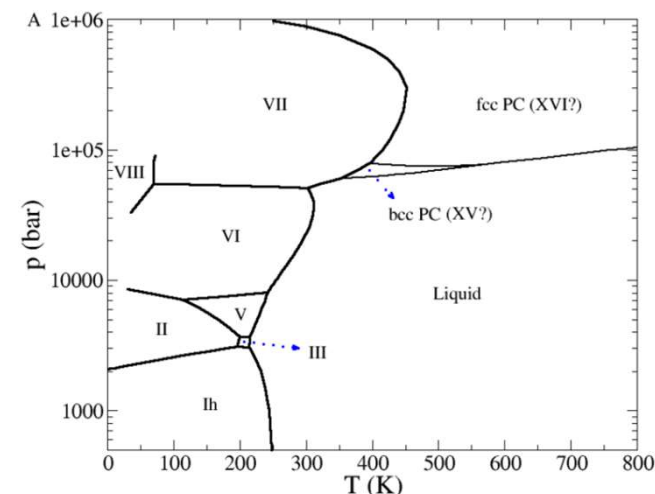
# Water models we employed

**TIP4P/2005** Abascal&Vega, JCP 123, 234505 (2005)

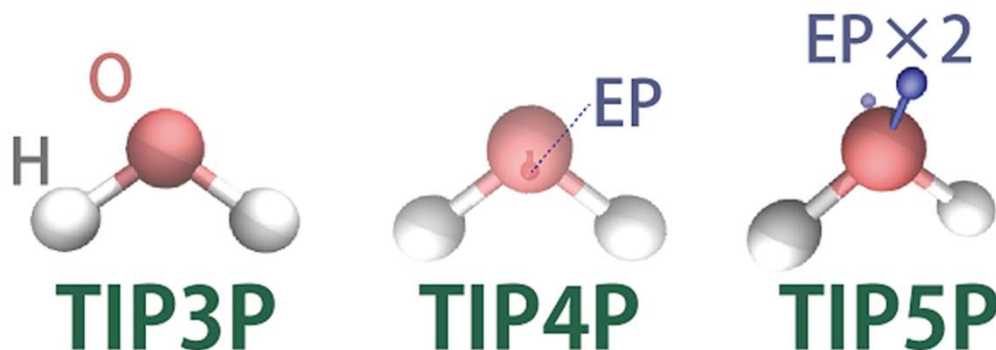
a rigid four site model which consists of three fixed point charges and one Lennard-Jones center



**Atomistic model, which gives the most accurate representation of water at supercooled conditions and thermodynamic predictions across the whole phase diagram!!**



**TIP5P** Jorgensen and Mahoney (2000)





# Key question: How to pick up the relevant structural order

## Comparison between hard spheres and water

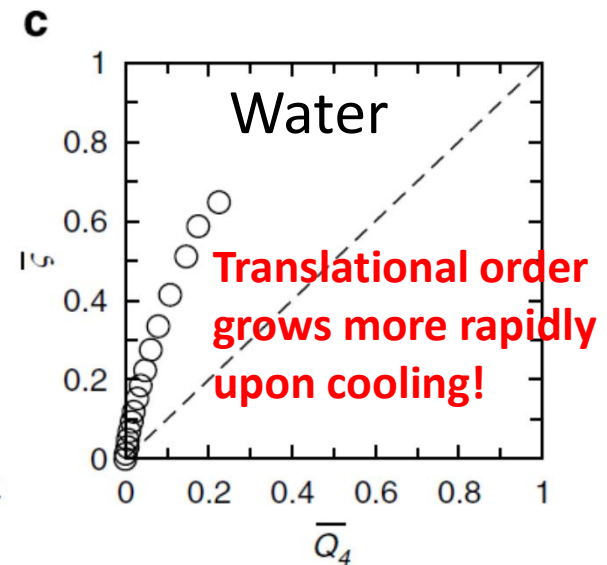
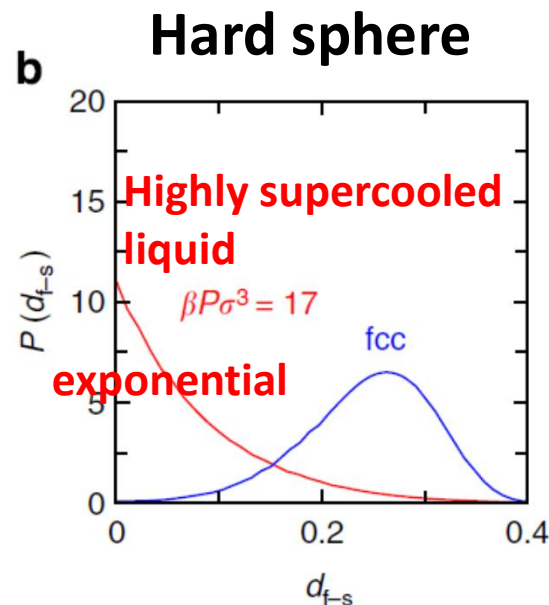
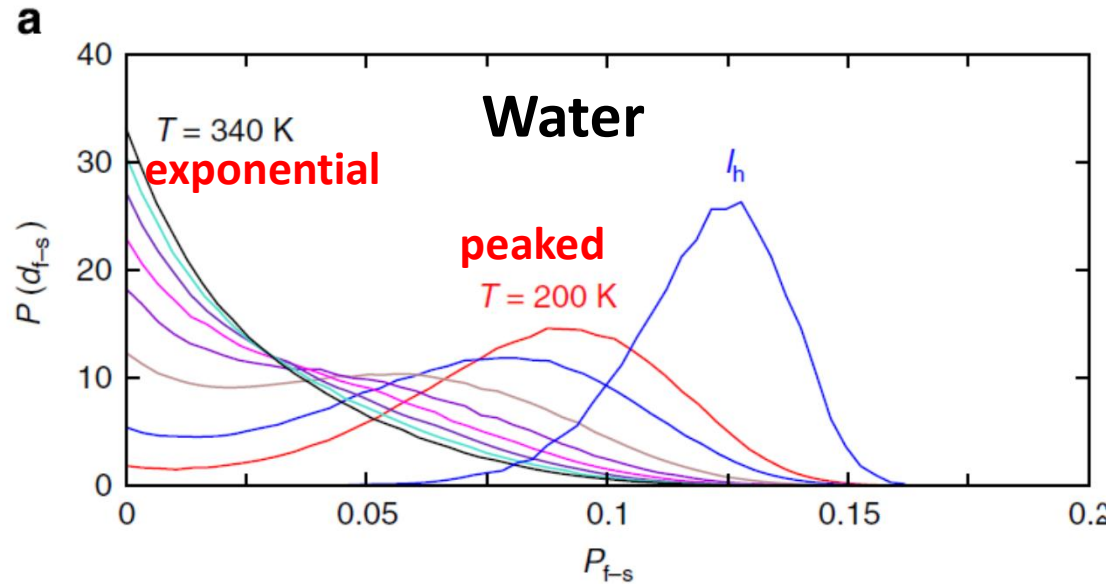
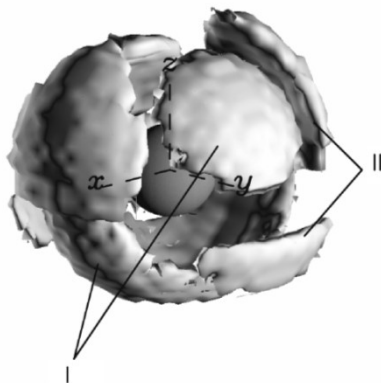
Probability distribution function of the distance between the first and second shell

The importance of the 2<sup>nd</sup> shell formation  
Soper & Ricci, PRL (2000)

(a) Low density water



(b) High density water

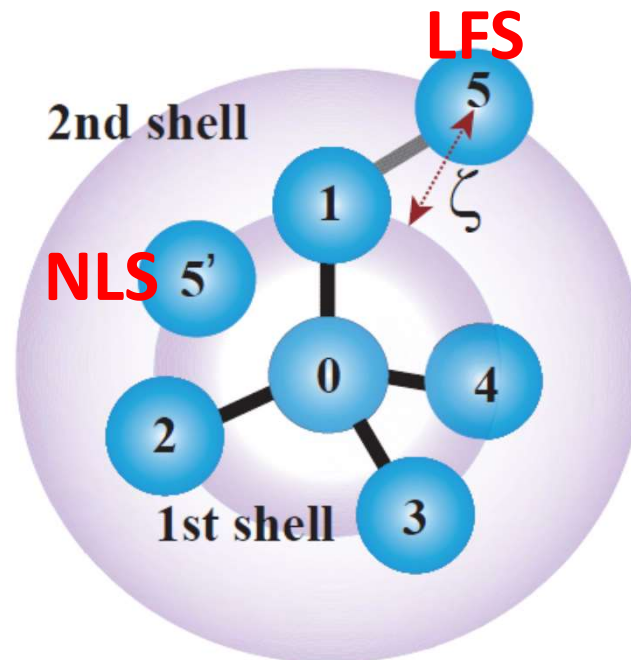


# Seeking locally favored structures in water by numerical simulation of TIP4P/2005

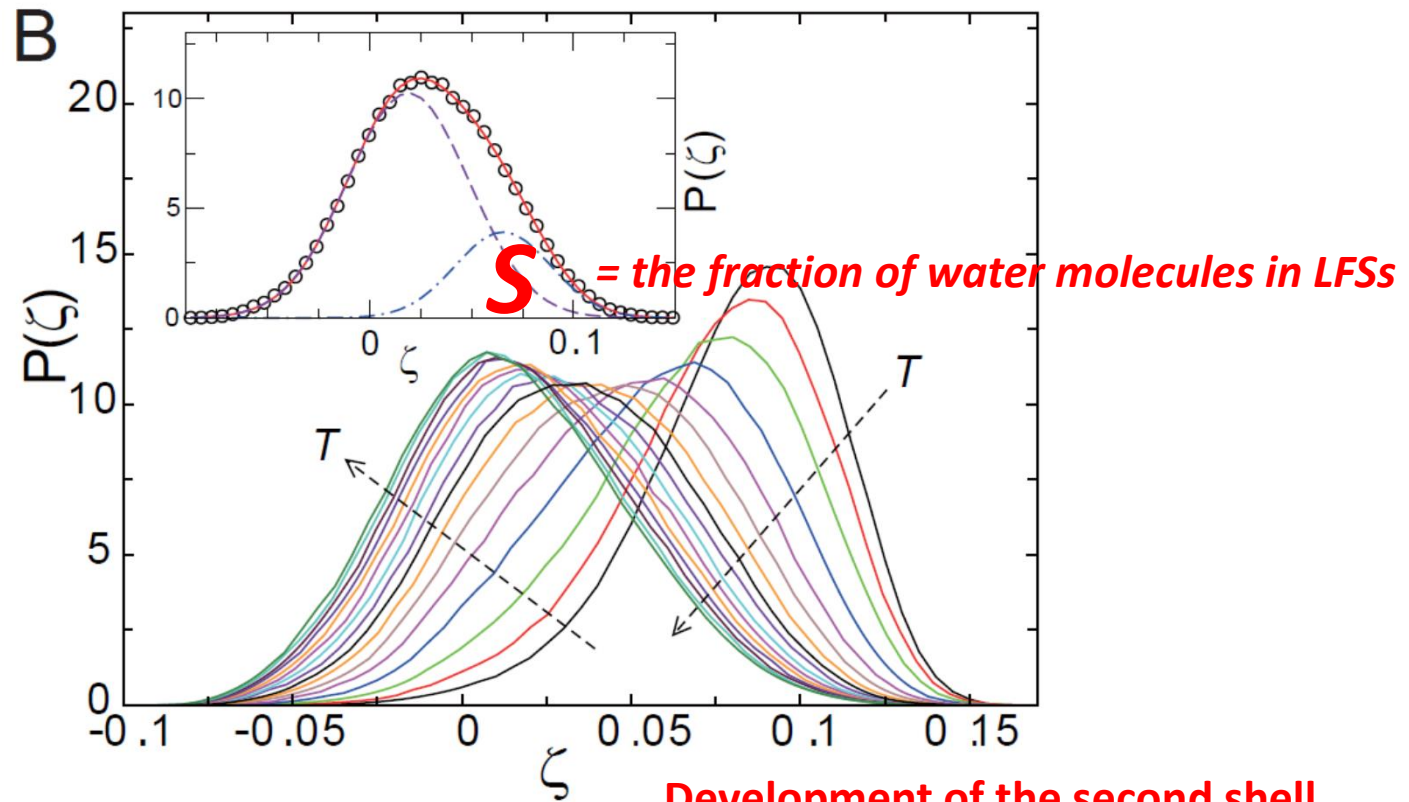
## A new structural order parameter relevant for the description of water's anomalies

= the difference between the distance of the first neighbor **not hydrogen bonded** to 0 (with label 5), and the distance of the last neighbor **hydrogen bonded** to 0 (labeled 4).

=translational order of the second shell



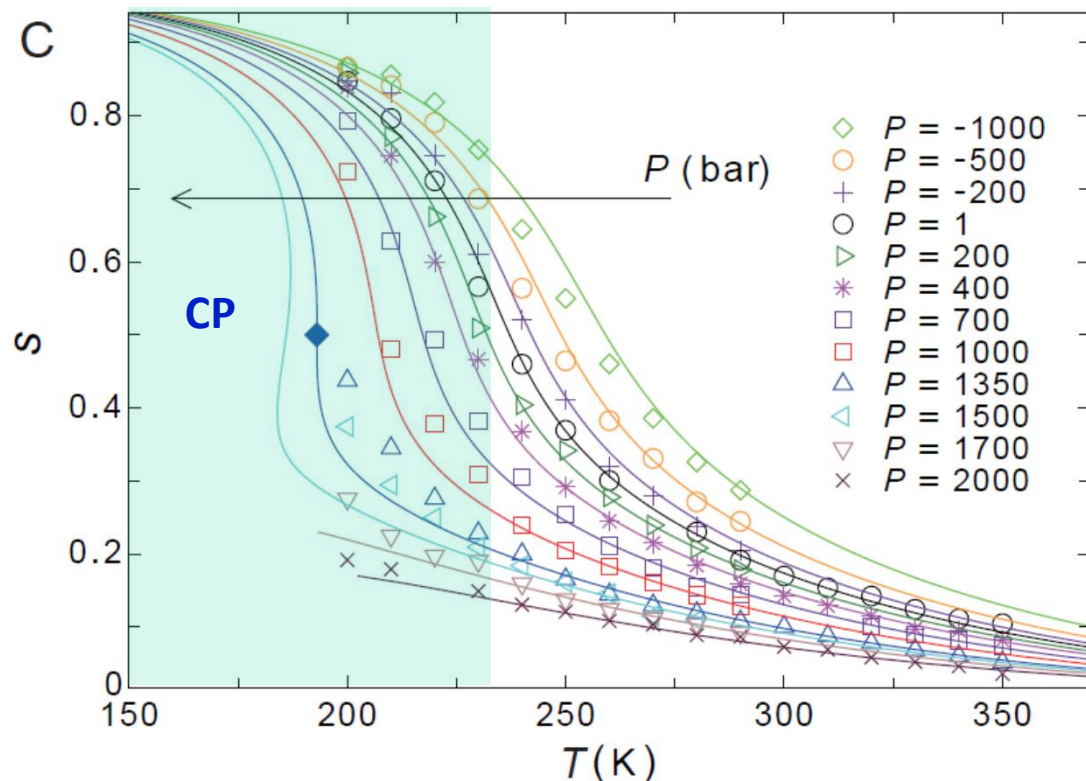
# Bimodal distribution of $\zeta$ of water



Sum of two Gaussians

$$P(\zeta) = \frac{P(0)}{\exp(-\frac{m_\rho^2}{2\sigma_\rho^2})} \exp\left(-\frac{(\zeta-m_\rho)^2}{2\sigma_\rho^2}\right) + \left(1 - \frac{\sigma_\rho\sqrt{2\pi}P(0)}{\exp(-\frac{m_\rho^2}{2\sigma_\rho^2})}\right) \frac{\exp\left(-\frac{(\zeta-m_S)^2}{2\sigma_S^2}\right)}{\sigma_S\sqrt{2\pi}}$$

# $T, P$ dependence of the fraction of locally favored structures $S$ and comparison with our two-state model



## Critical Point of TIP4P/2005

Abascal, Vega, J. Chem. Phys. 133, 234502 (2000).

$$T_c = 193 \text{ K and } P_c = 1350$$

Overduin & Patey, J Chem Phys 138, 184502 (2013)

**Either lower temperature  
or absence**

Limmer & Chandler, J. Chem. Phys. 138, 214504 (2013)

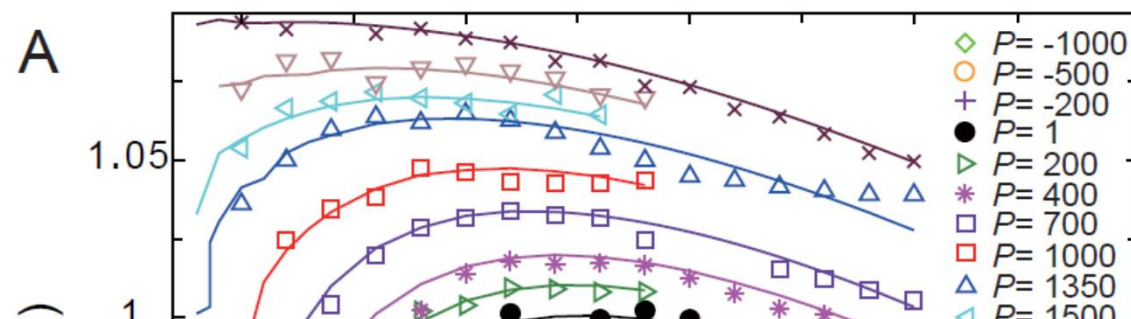
**The absence of 2<sup>nd</sup> CP**

$$G = G_\rho + s\Delta G + k_B T [s \log s + (1 - s) \log(1 - s)] + Js(1 - s)$$

$$\Delta G + k_B T \log \left( \frac{s}{1 - s} \right) + J(1 - 2s) = 0$$

$$-\Delta G = a_1 \hat{T} + a_2 \hat{P} + a_{11} \hat{T}^2 + a_{12} \hat{T} \hat{P} + a_{22} \hat{P}^2$$

# Density anomaly & compressibility anomaly

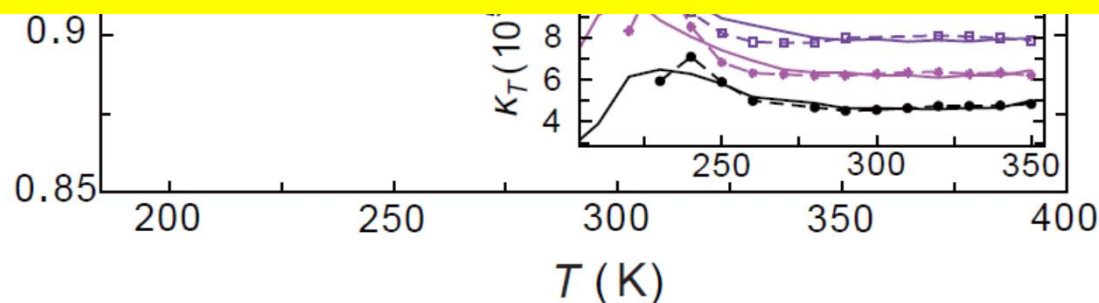


$$A = A_\rho + s\Delta A$$

$$V_\rho = b_0(P) + b_1\bar{T} + b_2\bar{T}^2$$

$$\Delta V = \frac{\partial \Delta G}{\partial P} = \frac{-a_2 + a_{12}\hat{T} - 2a_{22}\hat{P}}{P_c}$$

**We emphasize that we determine the structural order parameter on the basis of the structural data alone and then reproduce the thermodynamic anomaly!**



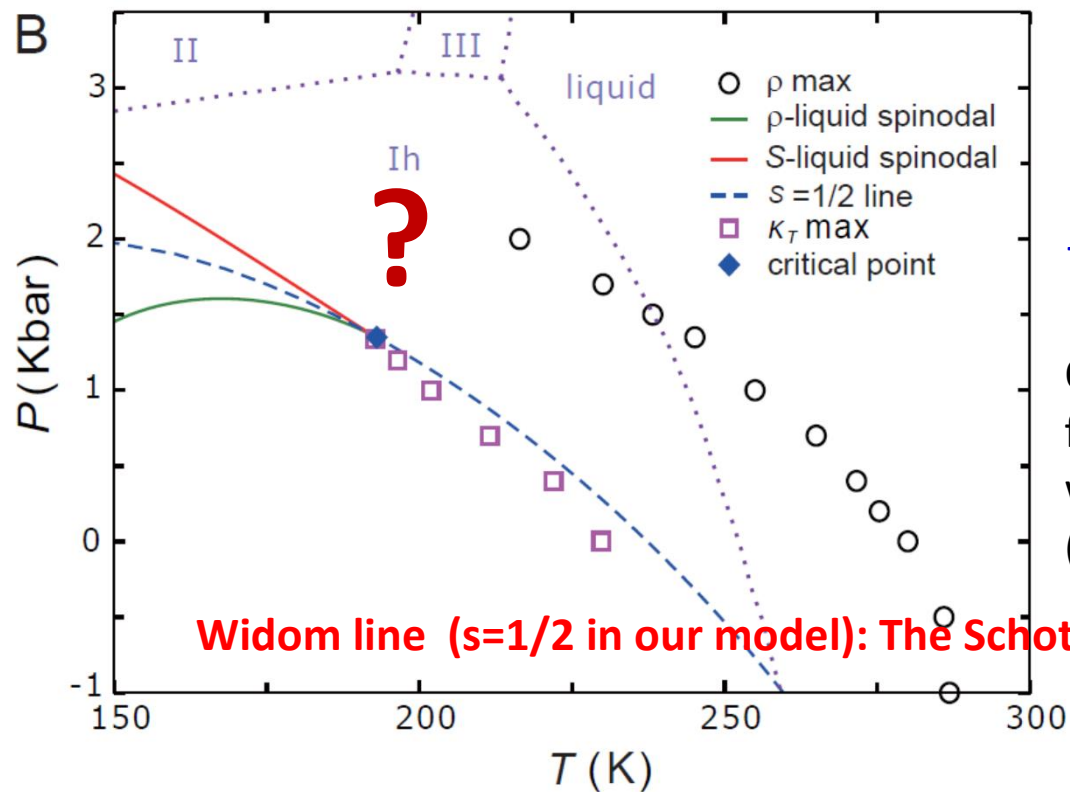
**These results strongly support our explanation of water's anomalies based on the two-order-parameter model.**



# **$T$ - $P$ phase diagram of TIP4P/2005 water**

Critical point of TIP4P/2005  $T_c = 193$  K and  $P_c = 1350$

Abascal & Vega, Widom line and the liquid-liquid critical point for the TIP4P/2005 water model. J. Chem. Phys. 133, 234502 (2010).



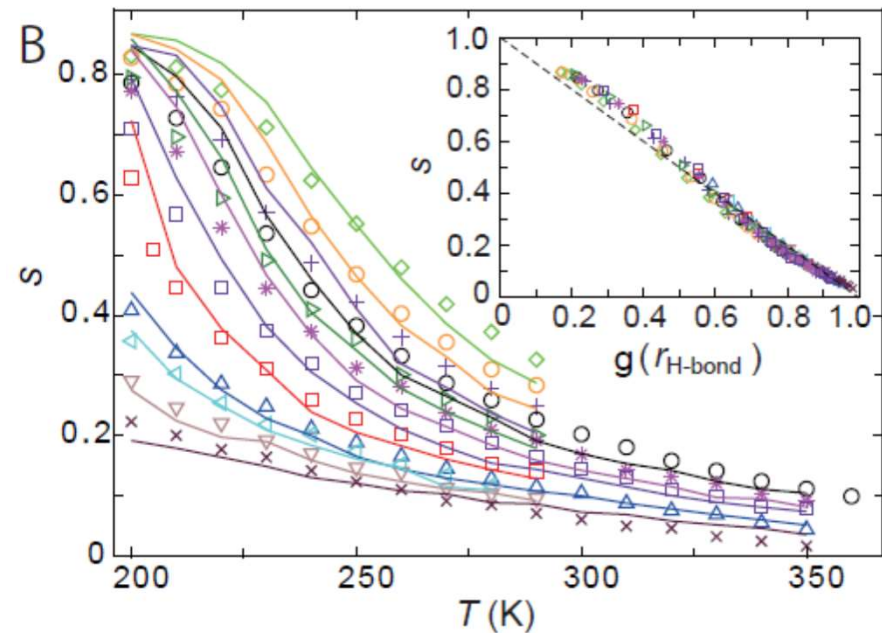
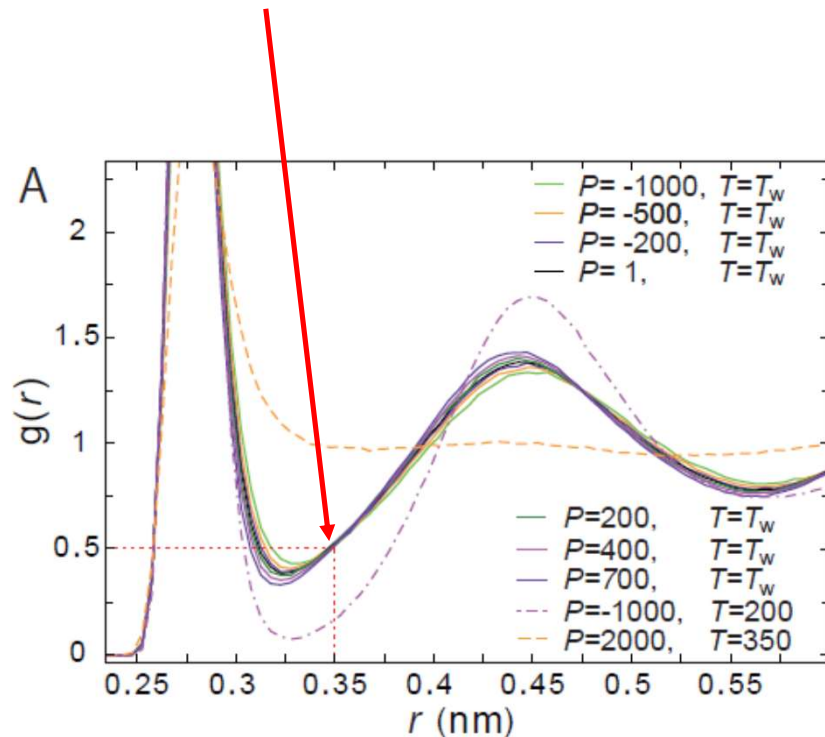
The critical point may be lower or absent.

Overduin & Patey, An analysis of fluctuations in supercooled TIP4P/2005 water. J. Chem. Phys. 138, 184502 (2013).

# Experimental access to the order parameter $S$

## Radial distribution function of oxygen atoms $g(r)$

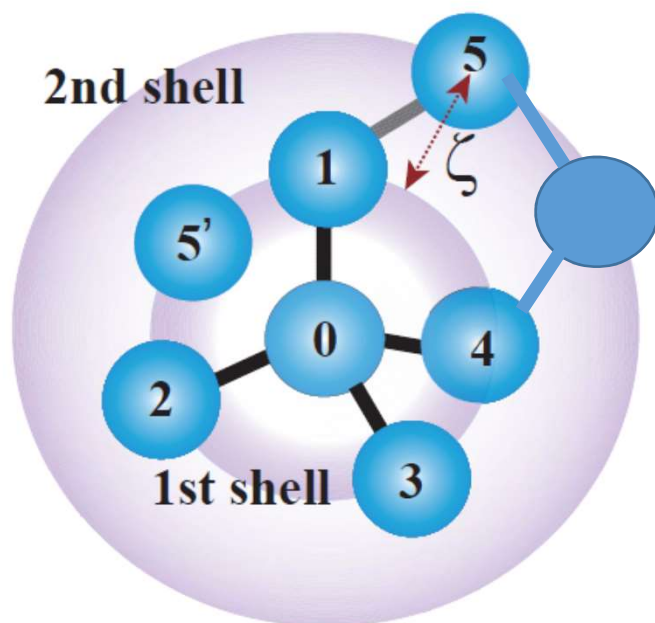
The presence of the isosbestic point at  $r_{\text{H-bond}}=0.35$  nm on the Widom line where  $s=0.5$ .



$$s \cong 1 - g(r_{\text{H-bond}})$$

# Structural characterization of or locally favored structures in water

Tendency to form a closed pentagonal ring!



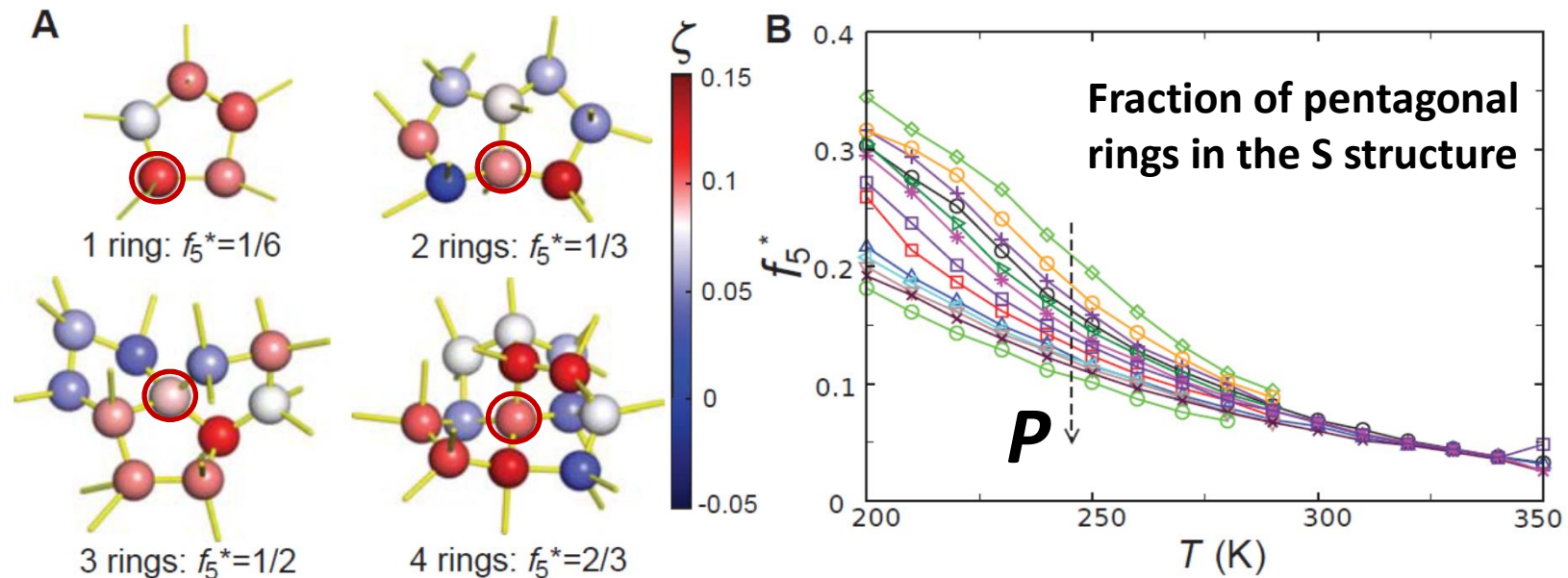
## Why pentagonal rings?

Although the formation of a pentagonal ring accompanies the distortion of tetrahedral symmetry, the entropy loss is much smaller compared to the formation of a hexagonal ring!

4-member ring: too much distortion

6-member ring: too much entropy loss

# Importance of pentagonal rings in water structures: Frustration against crystallization



Locally favored structures include more pentagonal rings upon cooling, which leads to frustration against crystallization into ice I, which is made of only hexagonal rings.

# Water's dynamic anomaly

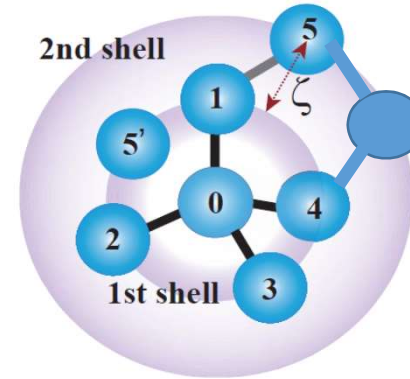
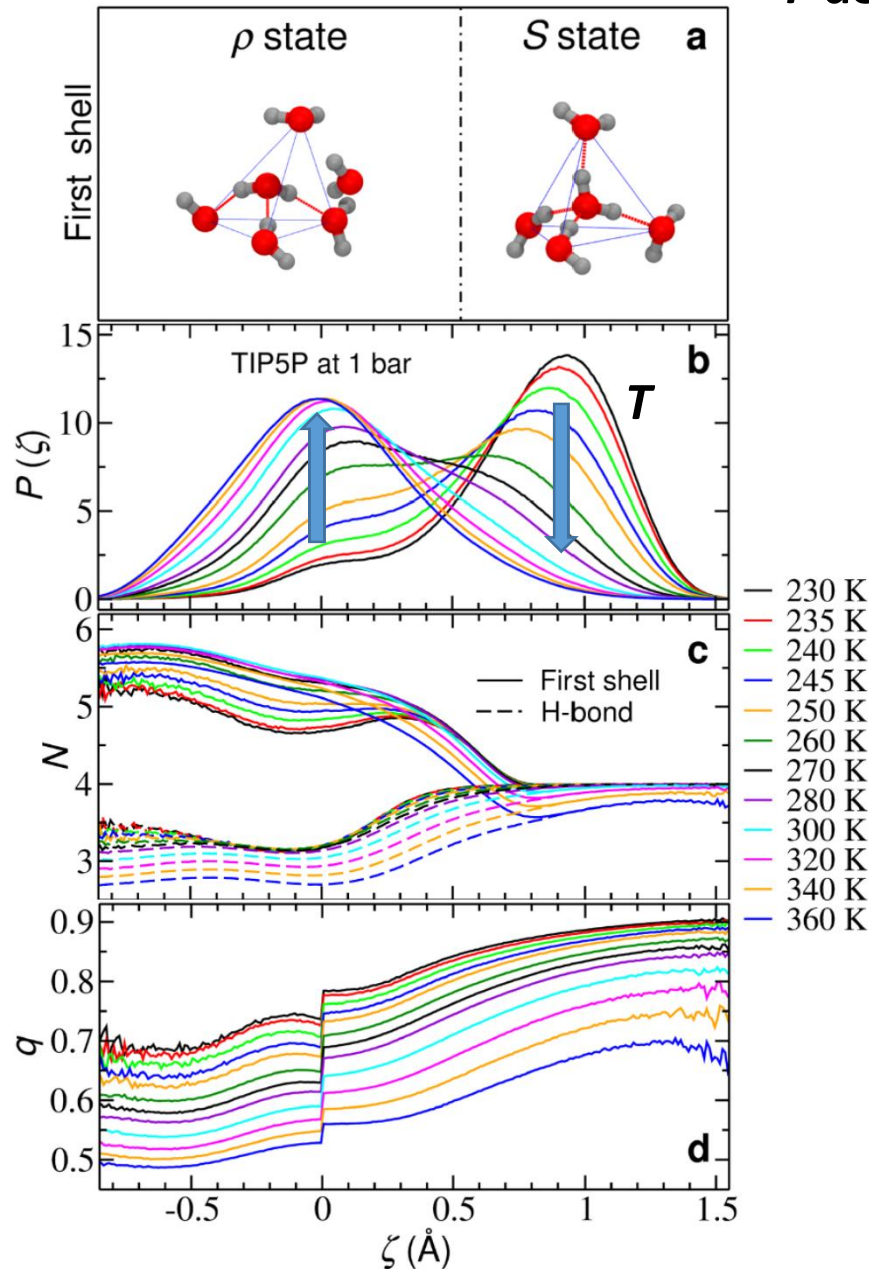
**Rui Shi**, John Russo, and Hajime Tanaka



# Microscopic signatures of the two-state feature

TIP5P water

$T$ -dependence



**S state:** the number of the nearest neighbor molecules are 4 and all hydrogen-bonded. It also has the high tetrahedral local symmetry.

**$\rho$  state:** many water molecules penetrate into the first shell and the number of hydrogen bonds is smaller than 4. The local symmetry is distorted from the tetrahedral one due to the penetration.

## ***P*-dependence**

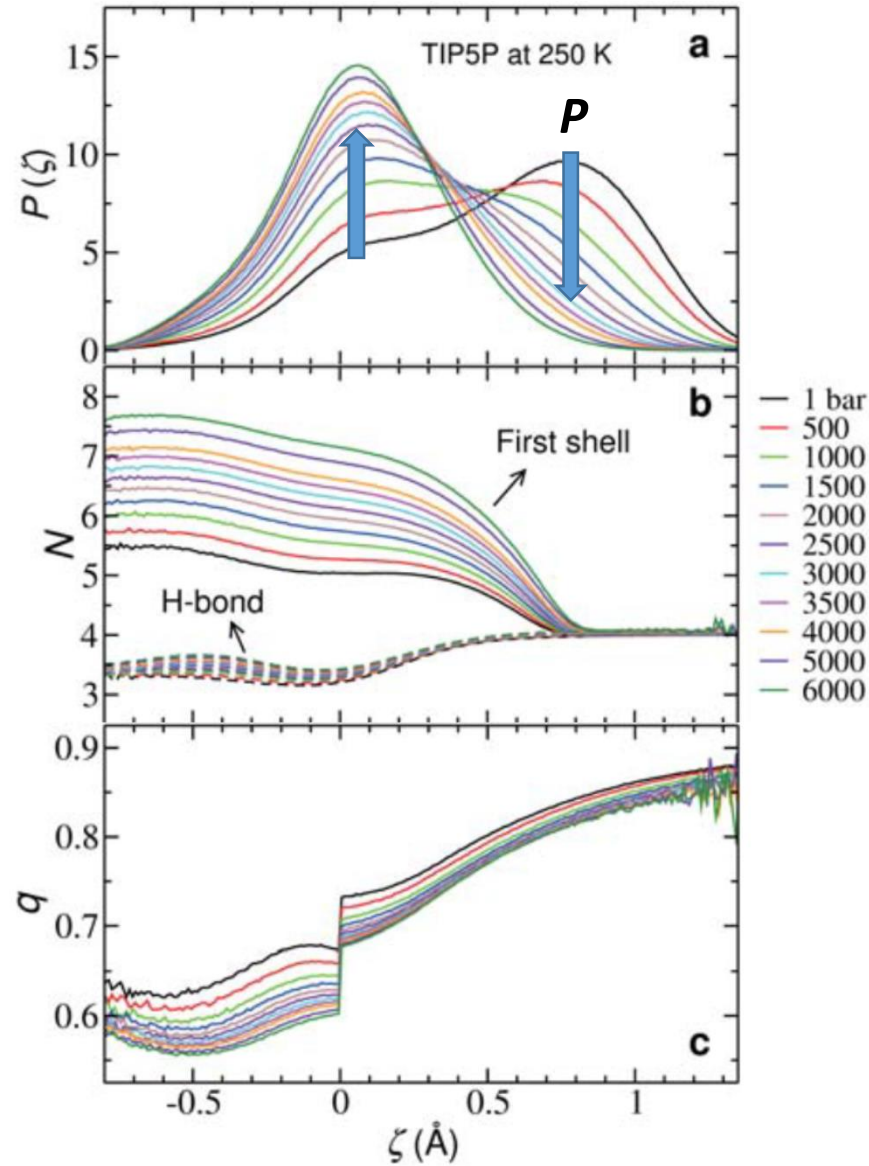


Figure S1. **Water's local structure at 250 K for different pressures.** **a**, Distribution of order parameter  $\zeta$ . **b**, Numbers of first-shell ( $r < 0.35$  nm) and H-bonded water as a function of  $\zeta$ . **c**, Tetrahedral order parameter  $q$  as a function of  $\zeta$ .

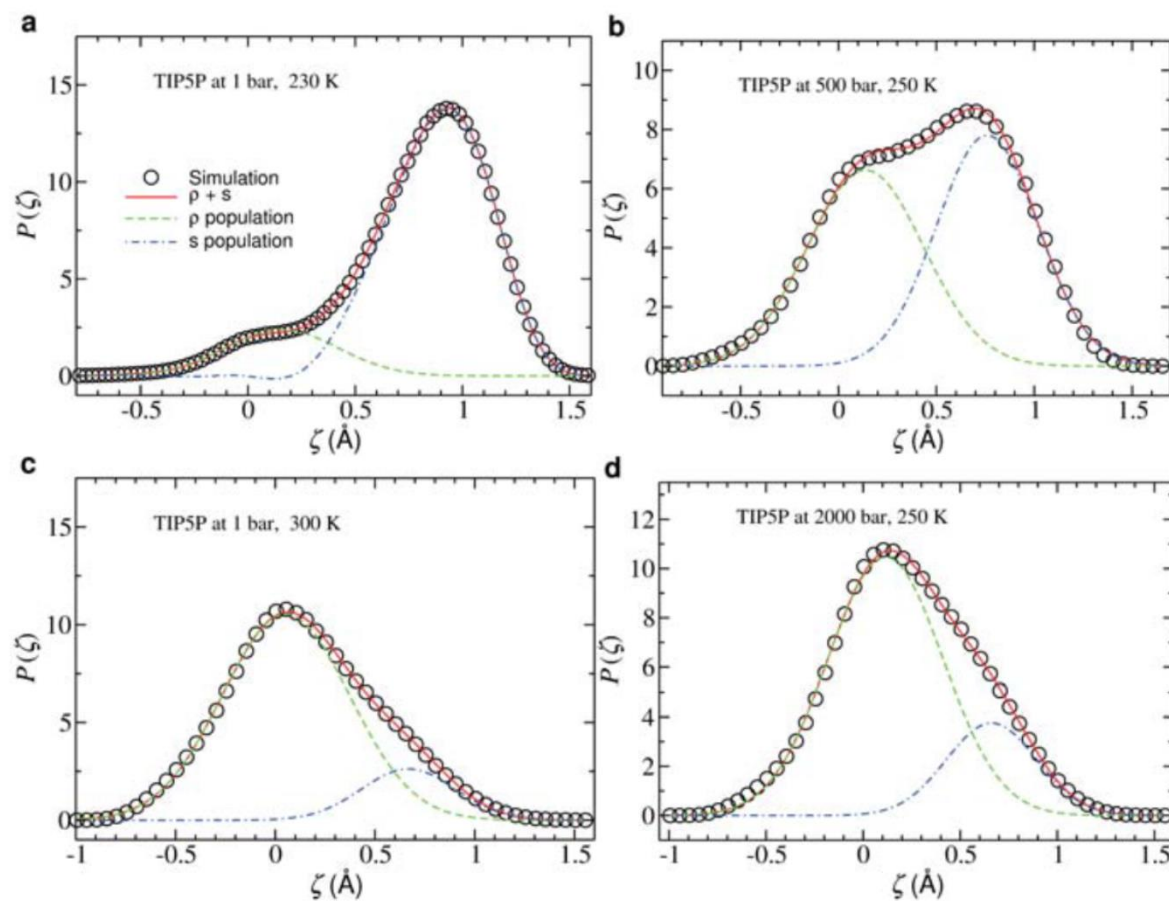
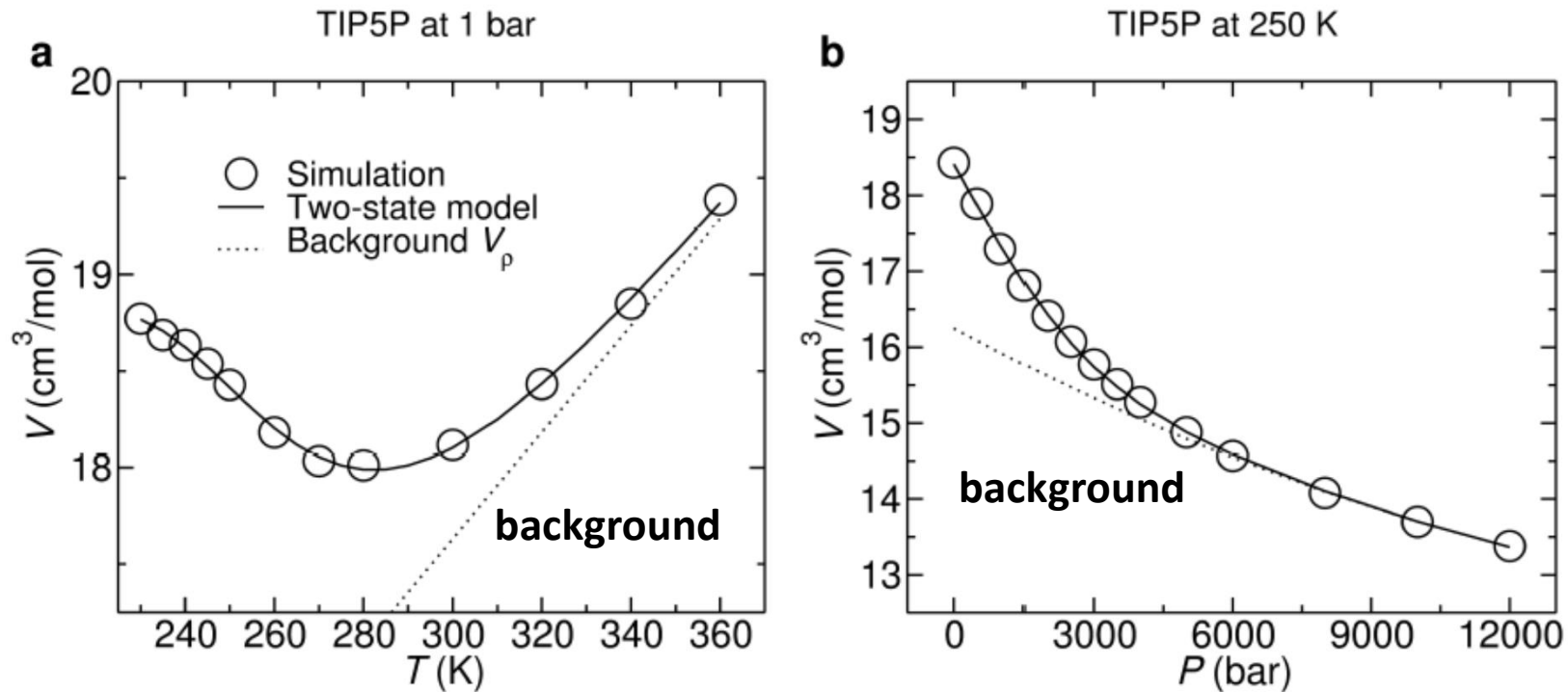


Figure S4. **Decomposition of the distribution of order parameter  $\zeta$  into two states.** **a**, 230 K and 1 bar. **b**, 250 K and 500 bar. **c**, 300 K and 1 bar. **d**, 250 K and 2000 bar. Circles denote simulation data. Red solid lines are the fitting results. Green broken lines and blue dot-dashed lines represent  $\rho$  and  $S$  state distributions, respectively.

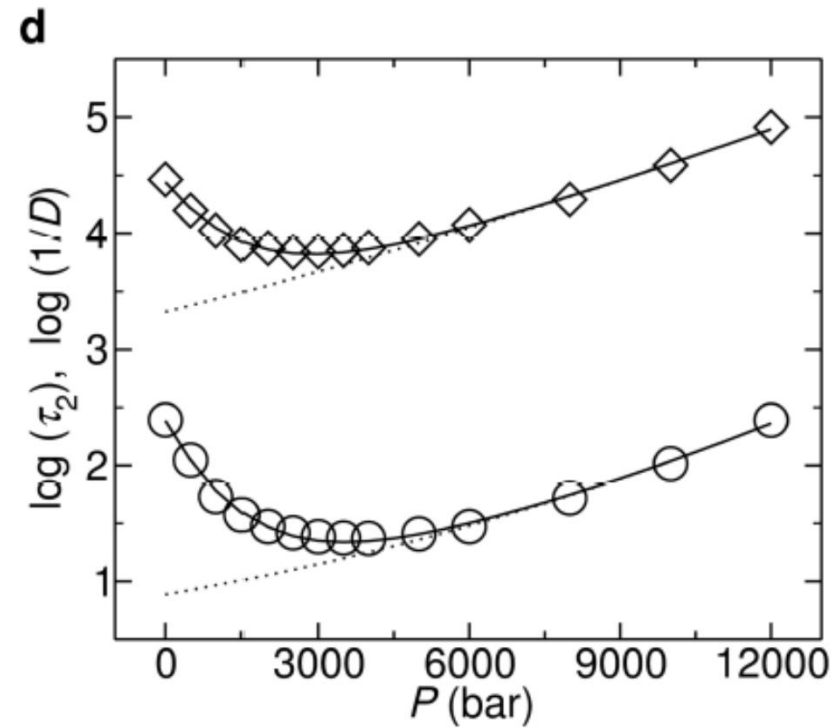
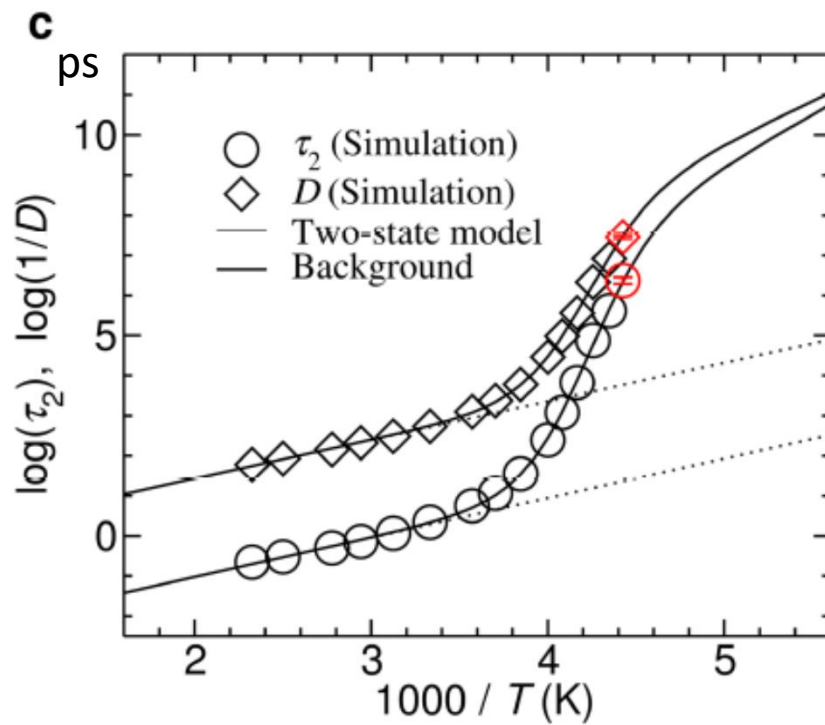
# Volume anomaly as a function of T and P



$$v = v_\rho + s\Delta v, \text{ where } \Delta v = v_s - v_\rho$$

$$s = \frac{1}{1 + \exp\left(\frac{\Delta E - T\Delta\sigma + P\Delta V}{k_B T}\right)}$$

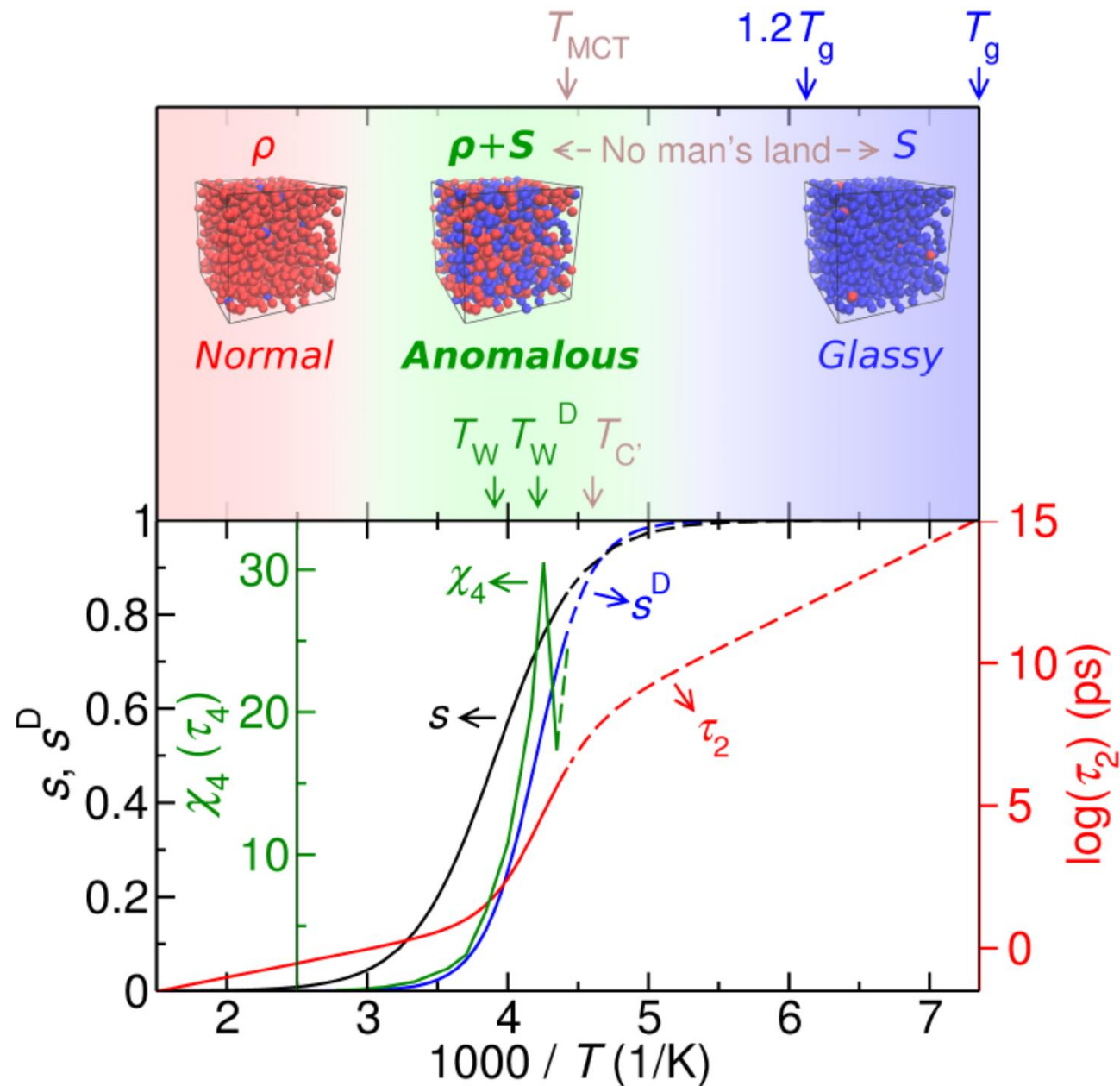
# Kinetic anomalies as a function of $T$ and $P$



$$X = X_0 \exp \left[ \frac{E_a^\rho + \Delta E_a \cdot s^D}{k_B T} \right]$$



# Summary of water's static and dynamic anomalies



# Summary

## Thermodynamic anomalies

- Water's anomalies are the consequence of formation of locally favored structures with high translational order in the second shell and can be described by a common Boltzmann factor.
- A second critical point may exist, but it does not affect the thermodynamic & kinetic behaviors seriously in the experimentally accessible region.
- Water's anomalies can be interpreted as the Schottky-type anomaly characteristic of the two-state model.  
The static Widom line is the line of the order parameter  $s=1/2$ .

## **Dynamic anomalies**

**Water's dynamical anomalies, including dynamic slowing down upon cooling, diffusion maximum under compression, "fragile-to-strong" transition, dynamic heterogeneity and breakdown of the Stokes-Einstein-Debye relation, are all quantitatively captured by a simple two-state model of the locally favoured structures, that also describes all thermodynamic anomalies consistently.**

## **Unified description of water's anomalies**

**The only difference between thermodynamic and dynamic anomalies is that the former is directly controlled by the fraction of S state, i.e. locally favoured structures, whereas the latter by coarse-grained S state. This is a direct consequence of the following general fact: a thermodynamic quantity linked to static structures is given by the average over all individual states as long as there is little cooperativity, whereas the motion of a molecule cannot be determined locally because of its intrinsic coupling to the motion of neighbouring molecules. Thus, we conclude that water's thermodynamic and dynamic anomalies can be explained primarily by the microscopic two-state model in a unified matter**

*Thank you !*

Thank you !