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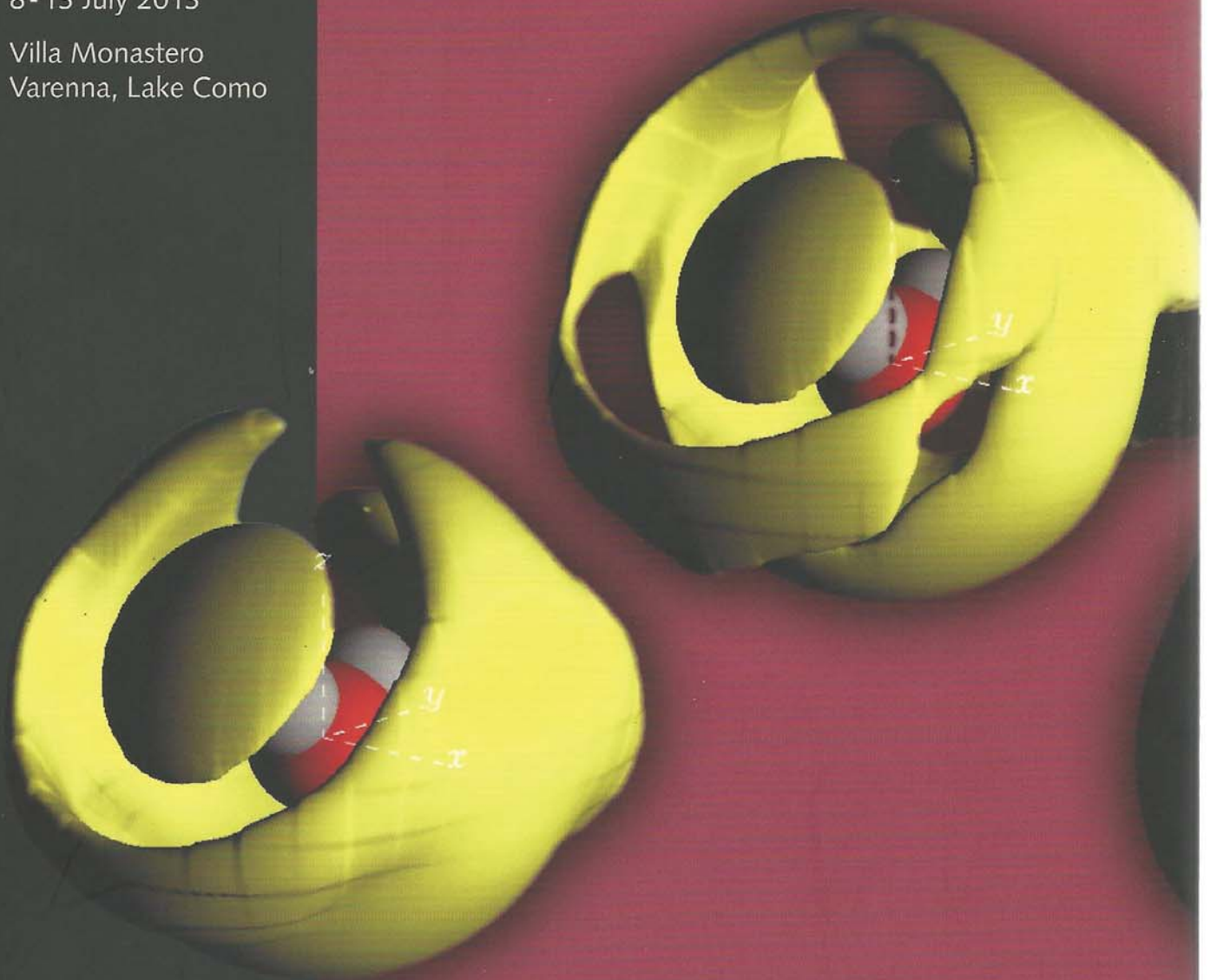
COURSE 187

**Water:  
Fundamentals as the Basis for Understanding  
the Environment and Promoting Technology**

edited by P. G. Debenedetti, M. A. Ricci and F. Bruni

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## Experimental tests of the liquid-liquid phase transition hypothesis

H. E. STANLEY

*Center for Polymer Studies and Department of Physics  
Boston University, Boston, MA 02215 USA*

F. MALLAMACE

*Dipartimento di Fisica, Università di Messina and CNR-IPCF  
I-98166, Messina, Italy*

**Summary.** — In this elementary course, we will introduce some of the 69 documented anomalies of the most complex of liquids —water— focusing on recent progress in understanding these anomalies by combining information provided by recent spectroscopy experiments and simulations on water in bulk, nanoconfined and biological environments. We will interpret evidence from recent experiments designed to test the hypothesis that liquid water has behavior consistent with the hypothesized "liquid polymorphism" in that water might exist in two different phases. We will also discuss recent work on nanoconfined water anomalies as well as the apparently related, and highly unusual, behavior of water in biological environments. Finally, we will discuss how the general concept of liquid polymorphism is proving useful in understanding anomalies in other liquids, such as silicon, silica, and carbon, as well as metallic glasses, which have in common that they are characterized by two characteristic length scales in their interactions.

Almost 40 years ago, Professor C. A. Angell and his collaborators drew attention to the experimental fact that the anomalous properties of liquid water extrapolate into the supercooled region, down to the lowest attainable temperatures, about  $-40^{\circ}\text{C}$  at atmospheric pressure [1]. Sufficient pressure permits still further supercooling down to about  $-92^{\circ}\text{C}$  [2]. Perhaps the most puzzling of these anomalies is that fluctuations in entropy and volume, and cross-fluctuations in entropy and volume, all significantly increase on lowering temperature. These results are highly nonintuitive, since one normally imagines that fluctuations should decrease on lowering temperature. Moreover, dynamic



quantities such as viscosity, coefficient of self-diffusion, thermal conductivity, and various relaxation times all display anomalies [3-9].

I learned of the Angell work 35 years ago, in April 1979, when we were both speaking at the *Faraday Symposium* "Critical Phenomena in Fluid Phases" at the University of Bristol. Ever since I have been obsessed with understanding what these data are telling us about the puzzle of liquid water—arguably the most complex of all liquids. I returned to Paris to share my excitement with Jose Teixeira, who himself had been studying anomalous properties of supercooled water. I learned from him the many other fascinating puzzles presented by water, and together we developed a qualitative picture involving the spatial correlations of low-density fluctuations (associated with that subset of water molecules with four intact hydrogen bonds) [10, 11]. The predictions were free of singularities, and so did not explain the power law divergences Angell found experimentally.

Ten years later, I was immensely fortunate that Francesco Sciortino chose to do his postdoctoral work at Boston University, and that simultaneously Peter Poole was undertaking his Ph.D. studies. Our group had just then acquired a superfast computer, and we wondered "which nut to try to crack" with this huge new "hammer". Water was the choice. Sciortino spent a summer period with the expert on simulations, Alfons Geiger, and on his return coached Poole in simulating liquid water. An initial goal was to test the Speedy-Angell hypothesis that the experimental anomalies arise from the presence of a liquid-gas spinodal emanating from the critical point into the negative pressure region, and then turning around to re-enter the region of positive pressure. We failed to find the evidence we sought [12], but instead found evidence of a strange sort of critical point, appearing at the terminus of a line of "first order" phase transitions that separated two liquids differing in their first derivatives of the Gibbs potential, the density and the entropy [13]. This made no sense ... so in all our discussions we stress that what one finds with a computer simulation depends on the assumptions which one puts into the simulation in terms of a model. We stressed that experiments are needed to make any judgments, but these are very challenging to perform. The most common reaction was humor and analogies to other water fantasies such as polywater. Accordingly, it seems sensible to devote one talk to discuss the experimental situation—ultimately it is experiments, not simulations, that will decide the possible validity of the liquid-liquid phase transition hypothesis. Of course, simulations are also relevant. Indeed, the simulation tests of the liquid-liquid phase transition (LLPT) hypothesis have dramatically increased in recent months due to a highly publicized challenge for one particular model, the ST2 model. I will not address this so-called "Limmer-Chandler challenge," in part because the Co-Director of this "Enrico Fermi" School, Professor P. G. Debenedetti, has, with his collaborators, "laid this matter to rest" [14].

I believe that one learns by studying real data, so in the remainder of this short lecture I shall share with you a coherent set of data (figs. 1 to 23) that are selected because they are relevant to the question if a LLPT exists or not. We stress that it is impossible to "prove" any proposal (including the LLPT hypothesis) by experiment. Rather, all that one can do is to test whether experimental data are consistent with the proposal.

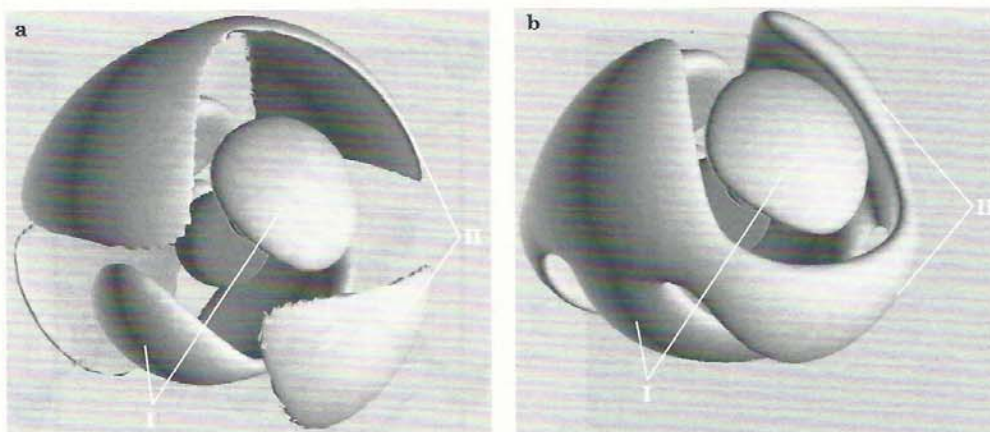


Fig. 1. – Test #1: The now-classic experiments of Soper and Ricci demonstrate the existence of structurally distinct phases, LDL and HDL. Their measurements are for  $-5^{\circ}\text{C}$ , well above the conjectured position of the LLPT line, so no abrupt transition is expected. Adapted with permission from ref. [15].

Accordingly, we present data that are consistent. We are unaware of any data that are not consistent, but we realize that at any moment new data could be created, that would contradict the LLPT hypothesis. If that happens, the hypothesis will be relegated to the “dustbin of history.”

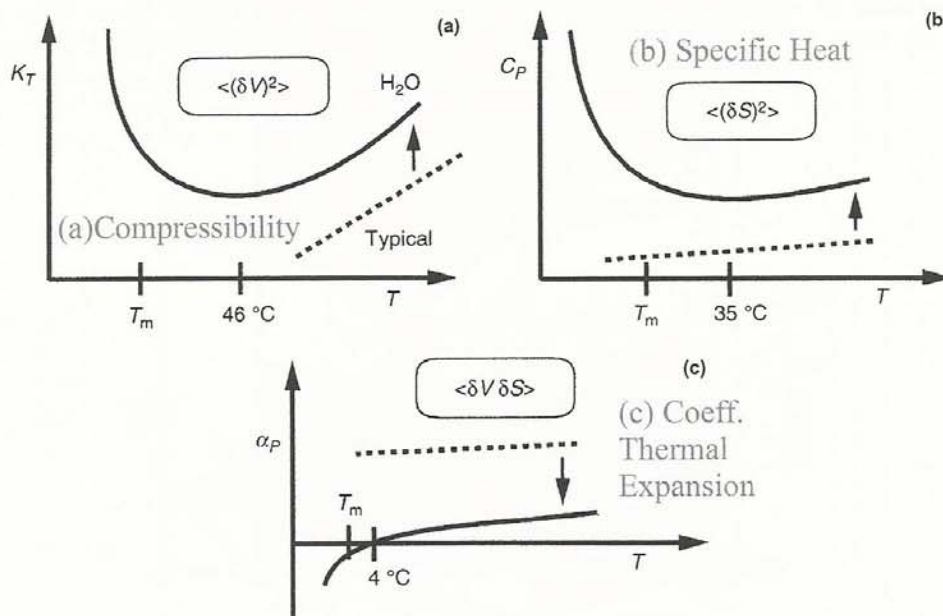
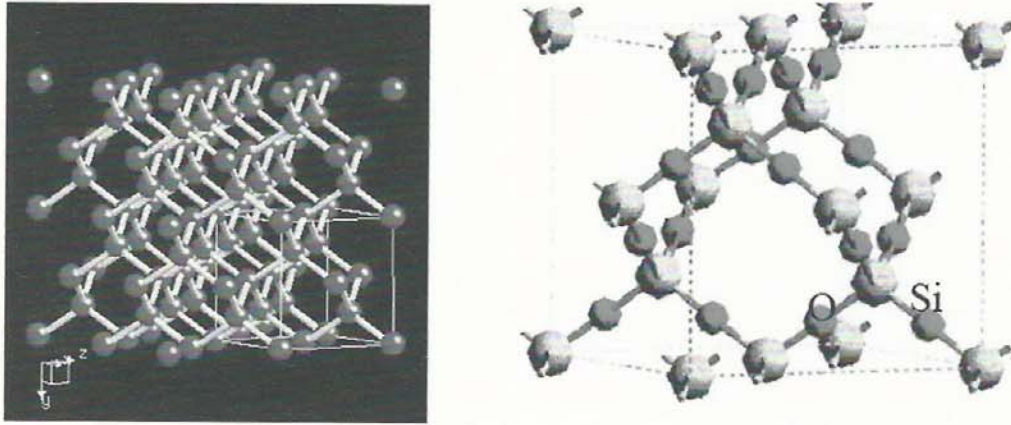


Fig. 2. – Test #2: If there were to be a liquid-liquid critical point, then it would be manifest well above the critical temperature. Indeed, experimental data on the three response functions show anomalies well above. Specifically: i) below  $46^{\circ}\text{C}$  the specific volume fluctuations (measured by the isothermal compressibility) increase on further cooling; ii) below  $35^{\circ}\text{C}$  the entropy fluctuations (measured by the constant pressure specific heat) increase; iii) below  $4^{\circ}\text{C}$ , the cross-fluctuations of specific volume and entropy become negative... a larger volume fluctuation is correlated with a smaller, not a larger, entropy.





**Silicon:** Si (Sastry,Widom,Beye) Poole/Angell: **Silica:** SiO<sub>2</sub>

Fig. 3. – Test #3: Other liquids with a local tetrahedral symmetry appear to likely possess a LLPT. These include the common materials silicon and silicon dioxide [16-19]. Tetrahedral symmetry is not required to obtain a LLPT. Indeed, any potential with two significant length scales appears to qualify [20].

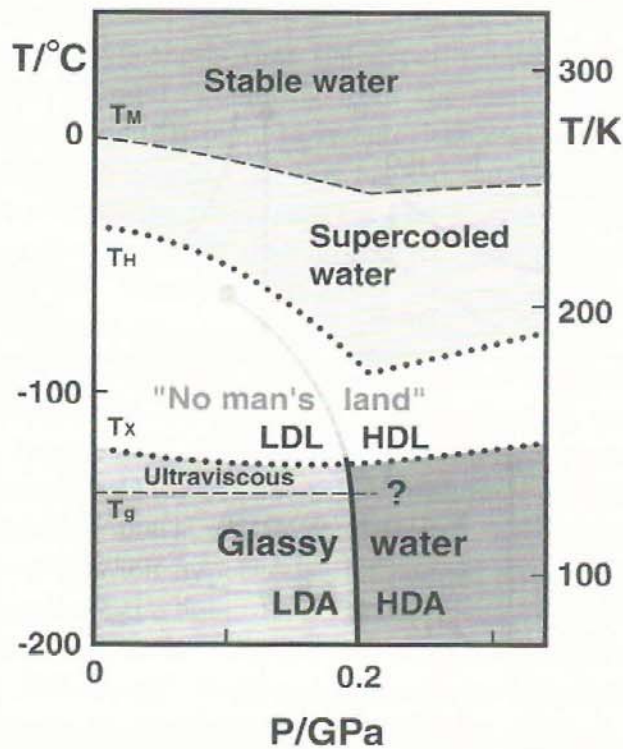


Fig. 4. – Test #4: The LLPT hypothesis implies that there exists a line of first-order transitions separating a high-density from a low-density phase, then this line should extend into the glassy region of the phase diagram [21-24]. Already 2 years after the LLPT proposal, Mishima succeeded to identify exactly such a transition separating high-density amorphous ice (HDA) and low-density amorphous ice (LDA). Adapted with permission from ref. [21].

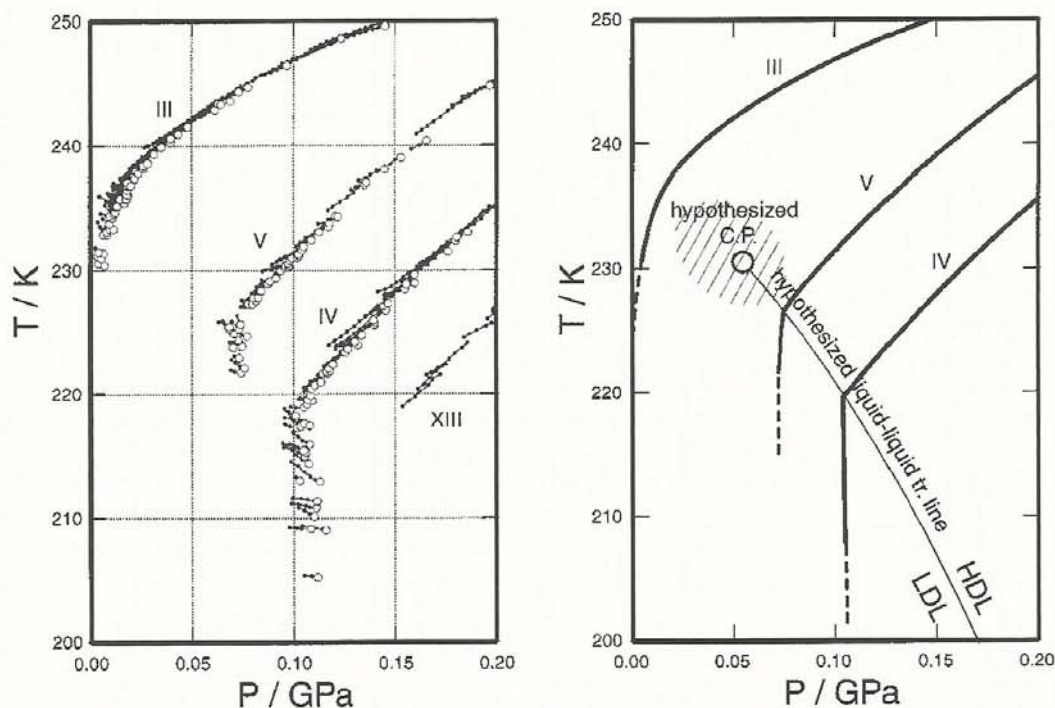


Fig. 5. - Test #5: Mishima and Stanley demonstrated experimentally that the extensions of the ice polymorphs Ice IV and Ice V display "kinks" (discontinuous changes in slope) on crossing the hypothesized LLPT line. The extension of the ice polymorph Ice III does not cross, and indeed no kink is found [22, 25]. Adapted with permission from ref. [25].

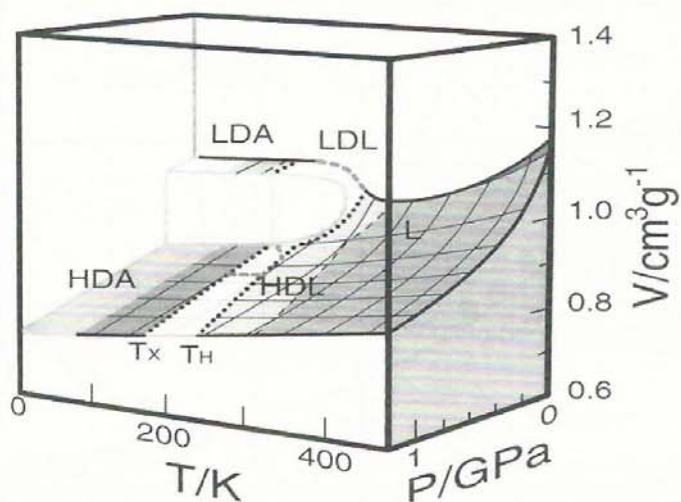


Fig. 6. - Test #6: The Gibbs potential of the ice polymorphs is known. Hence the Gibbs potential of the liquid along the LLPT lines can be obtained, and by interpolation the Gibbs potential as a function of pressure and temperature can be approximately determined. Since volume is the pressure derivative of the Gibbs potential, the entire volume-pressure-temperature phase diagram of water can be obtained deep into the "no man's land" [23, 26].

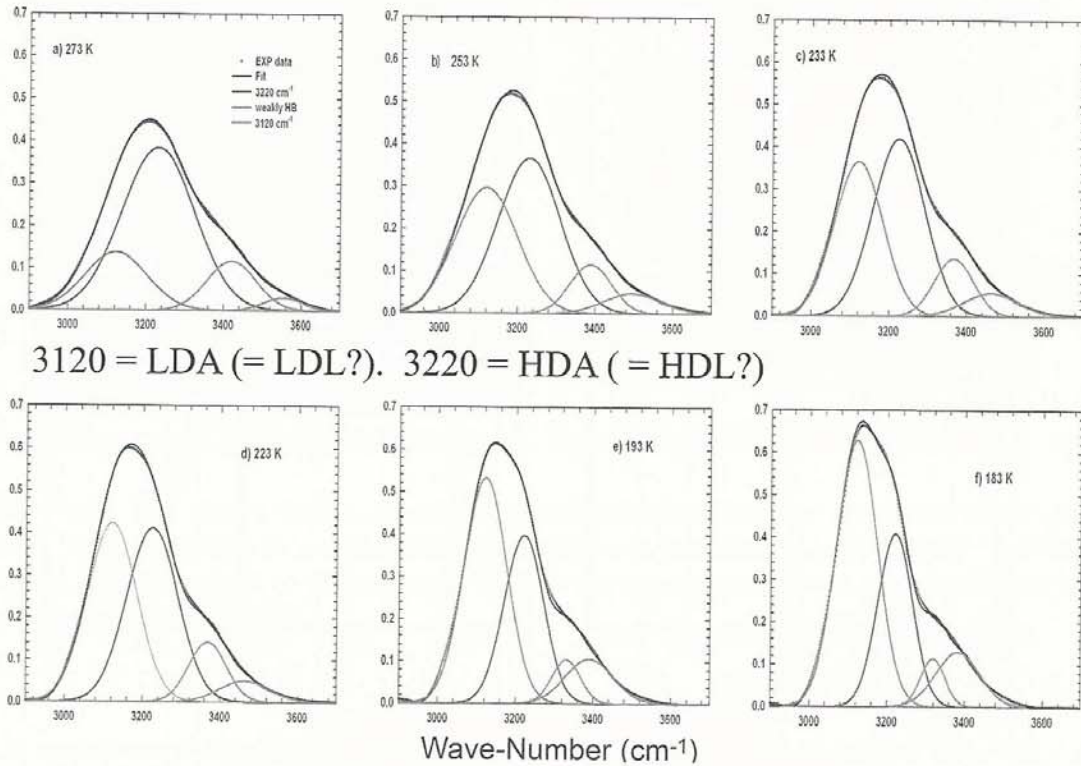


Fig. 7. – Test #7: The FTIR spectrum of confined water has been measured on decreasing temperature at atmospheric pressure. The component due to LDL monotonically increases, while that due to HDL monotonically decreases. The two components become approximately equal at the temperature corresponding to the crossing of the Widom line at a fixed pressure of one atmosphere. Adapted with permission from refs. [27, 28].

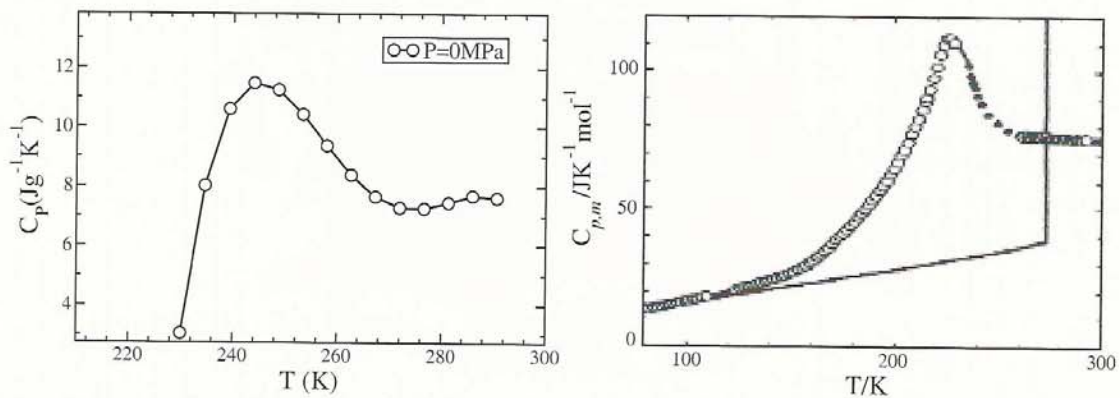


Fig. 8. – Test #8: As temperature is lowered, the constant pressure specific heat of confined water has a pronounced maximum on crossing the Widom line, both in experiments of the Oguni group (right) and in simulations of Xu, Kumar, and their collaborators (left). Adapted with permission from refs. [29, 30].



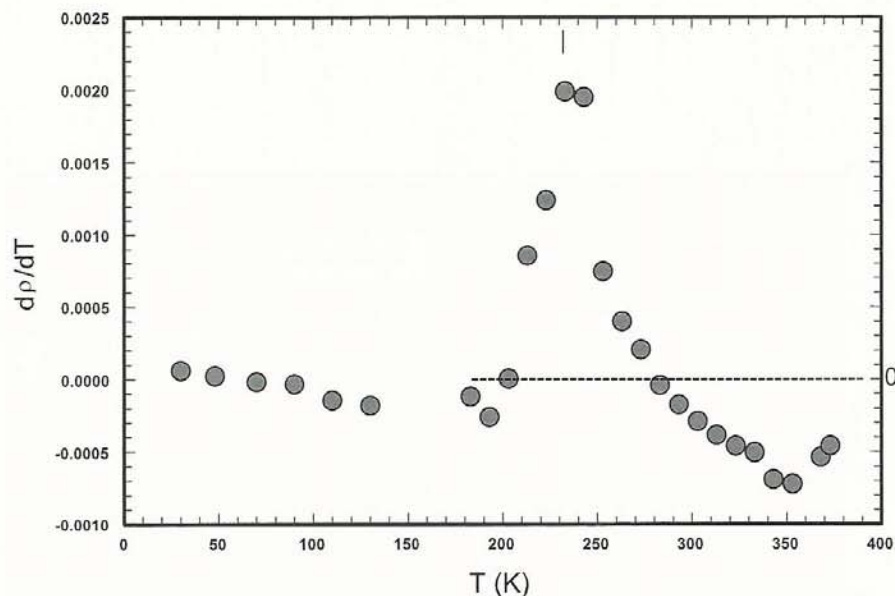


Fig. 9. – Test #9: The cross-correlations of volume and entropy, positive for typical liquids, is negative for water below 277 K. The negative of this cross-correlation function is proportional to  $d\rho/dT$ , which therefore becomes positive below 277 K, and continues to increase, reaching a sharp maximum on crossing the Widom line. Note that the counterintuitive change of slope occurs at approximately 350 K, far above 277 K. Adapted with permission from ref. [31].

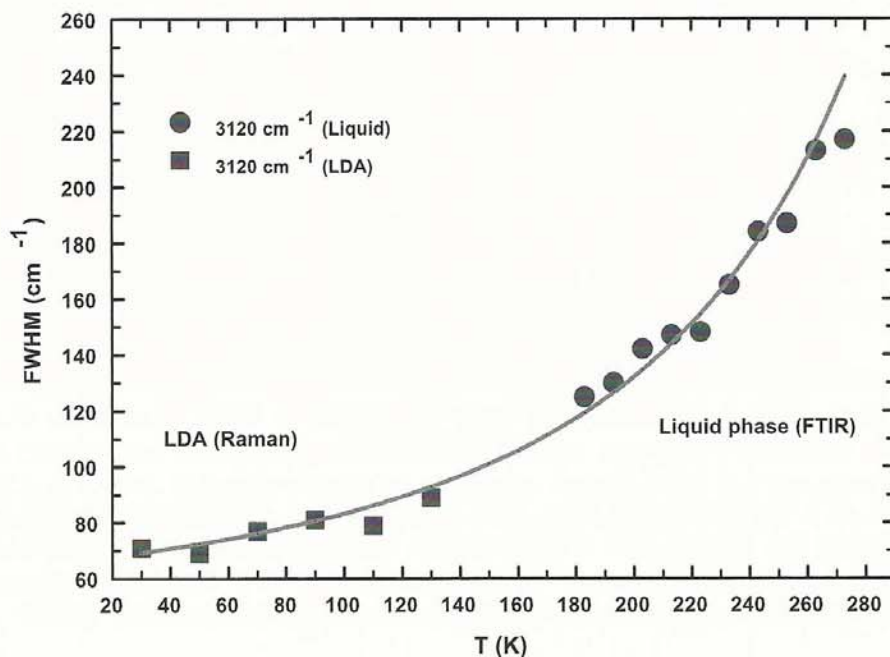


Fig. 10. – Test #10: The width of the measured FTIR peak in confined water at 3120 wave numbers decreases on lowering the temperature, and extrapolates exactly to the value measured for LDA, the low-density form of the amorphous solid. Adapted with permission from ref. [26].



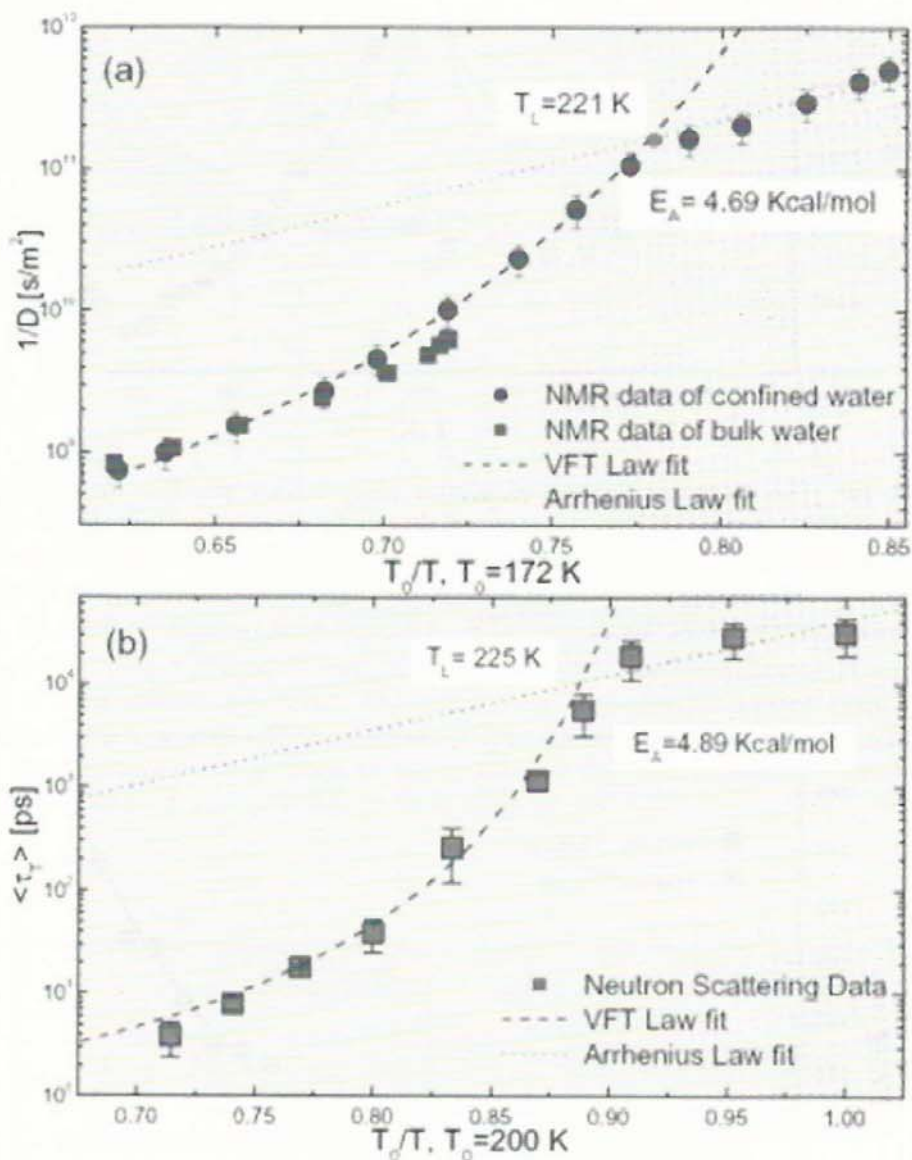


Fig. 11. – Test #11: Dynamic properties also display sudden behavior changes on lowering the temperature across the Widom line. Two examples: (a) the self-diffusion constant measured by NMR changes from fragile behavior to strong behavior [32]. (b) The same dynamic crossover occurs, at the same temperature, in the alpha relaxation time measured by QENS [33,34].

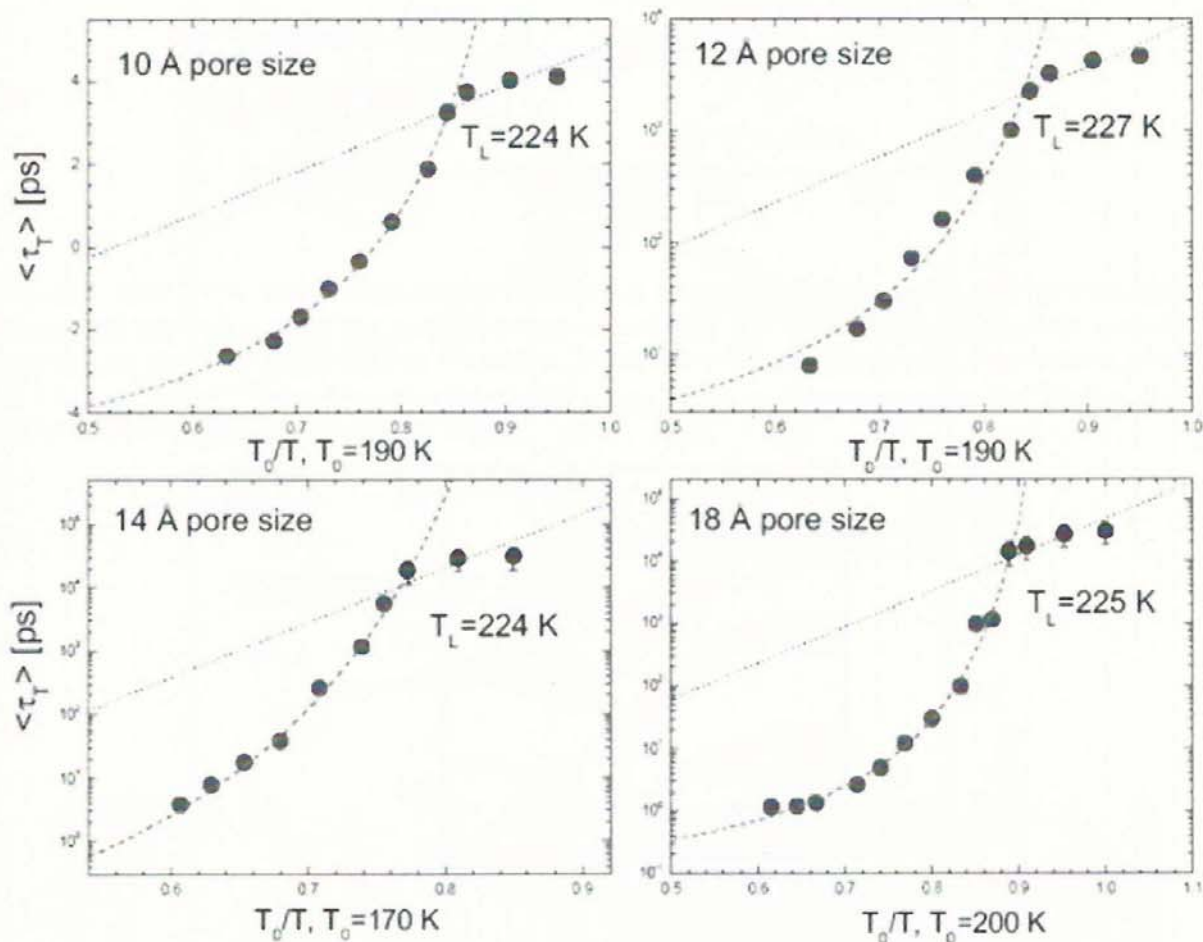


Fig. 12. – Test #12: The same fragile-to-strong crossover occurs, at the same temperature (about 225 K) for four different confined water systems, with tube diameters 0.10 nm, 0.12 nm, 0.14 nm, and 0.18 nm. These data are consistent with the possibility that the Widom-line phenomena are a property of bulk water, not an artifact of confinement, for otherwise the crossover temperatures would depend on the diameter. Adapted with permission from ref. [35]



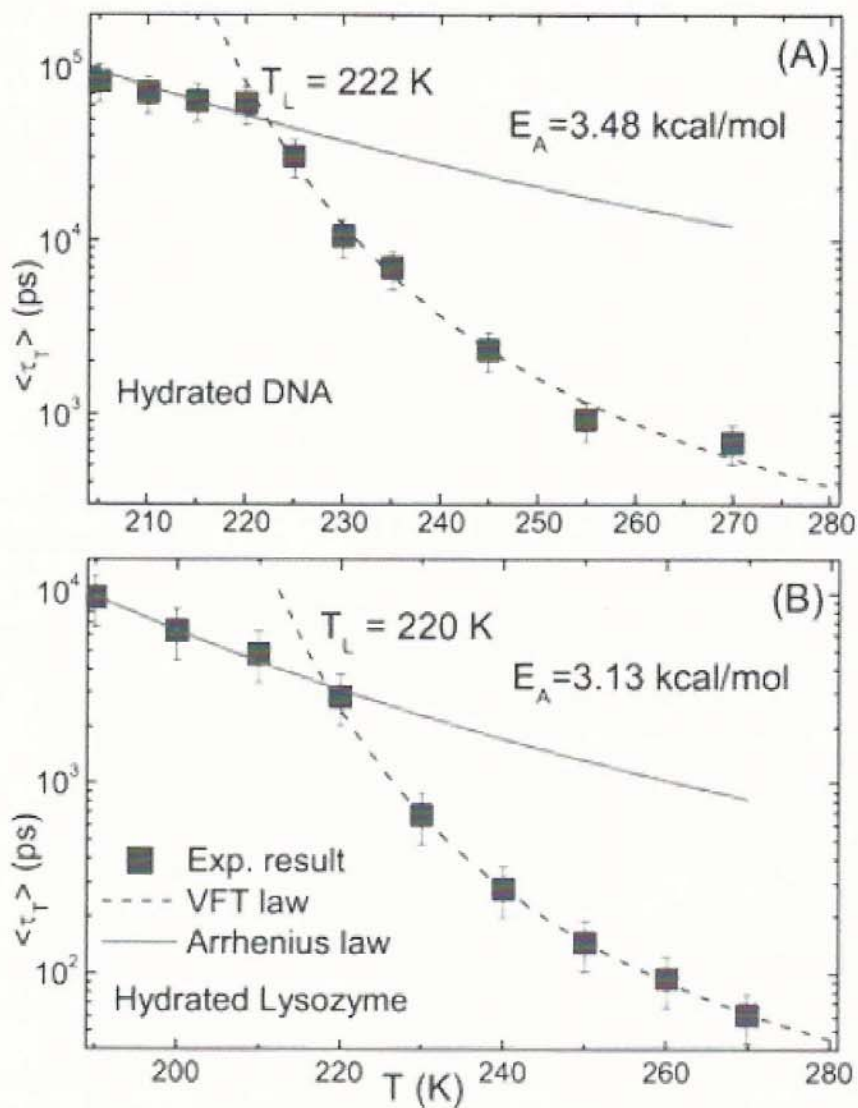


Fig. 13. - Test #13: The anomalies in confined water seem not to depend on the fact that the water is confined to nanometer tubes of 2 nm diameter. Evidence supporting this statement arises from experiments on protein hydration water (water near a macromolecule such as DNA or lysozyme). Very recently the same phenomena were discovered for water confined in cement [36]. Adapted with permission from refs. [37-39].

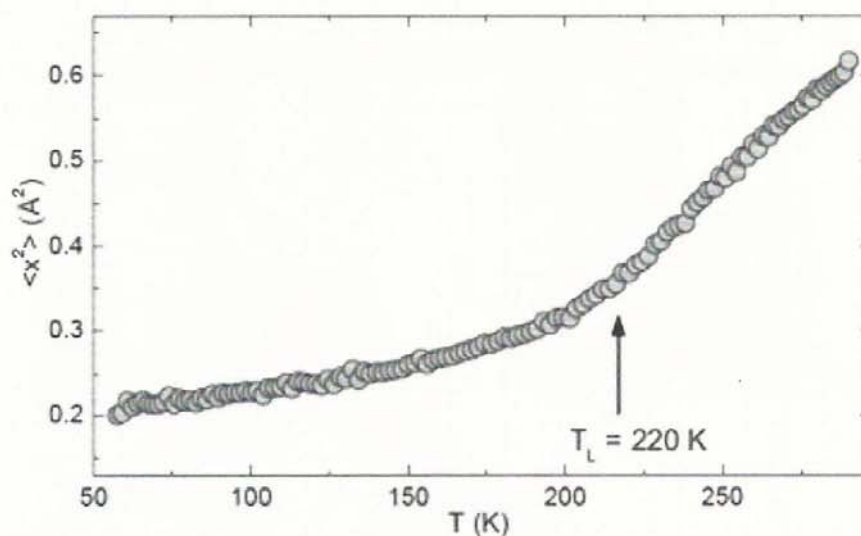


Fig. 14. – Test #14: The abrupt change in diffusion constant associated with the “protein glass transition” also occurs for the same systems on crossing the Widom line, consistent with the speculation that the protein glass transition is not associated with protein, nor with a glass, and in fact is not a transition at all but a crossover that occurs on crossing the Widom line. Adapted with permission from ref. [38].

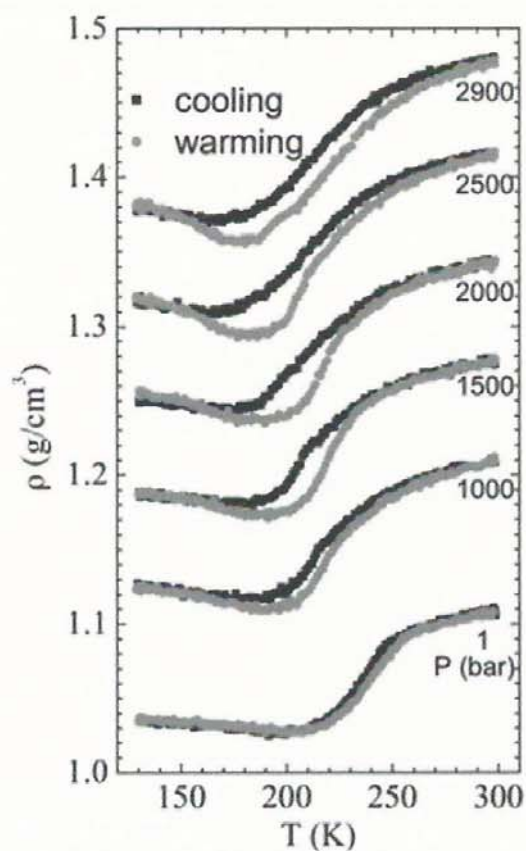


Fig. 15. – Test #15: The same hysteresis loops that Mishima obtained in his classic 1994 experiments in tuning the pressure to cross the LDA to HDA transition was recently shown to also occur on crossing the LLPT phase transition line. Adapted with permission from ref. [40].



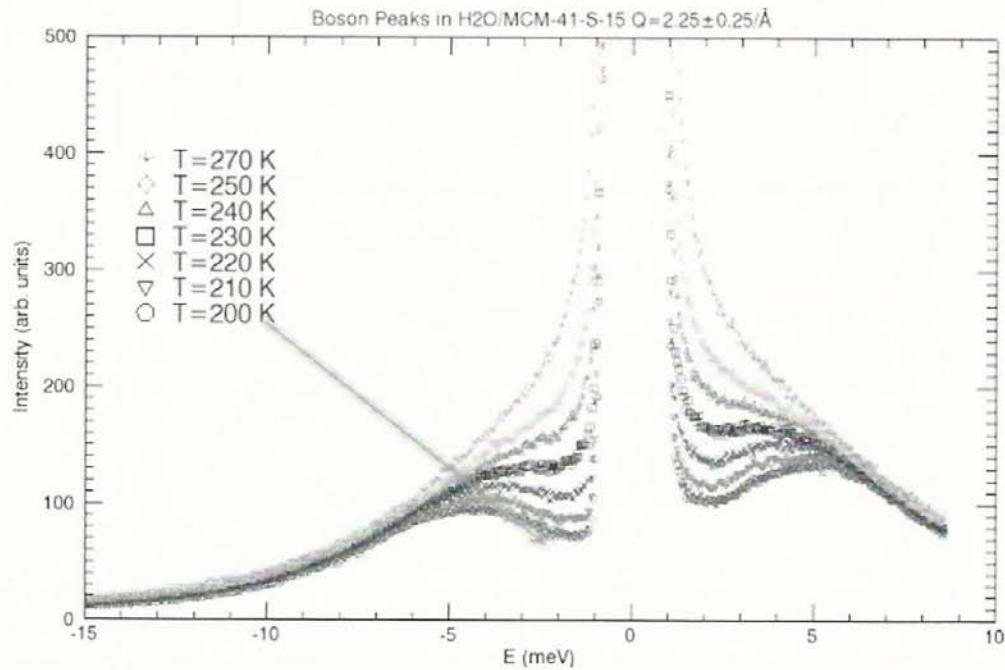


Fig. 16. – Test #16: An additional peak (called the Boson peak) appears in simulations, and in very recent experiments, when water is cooled below the Widom temperature as if the extra “rigidity” of molecules with a LDL local structure supports a new vibration. Adapted with permission from refs. [41,42].

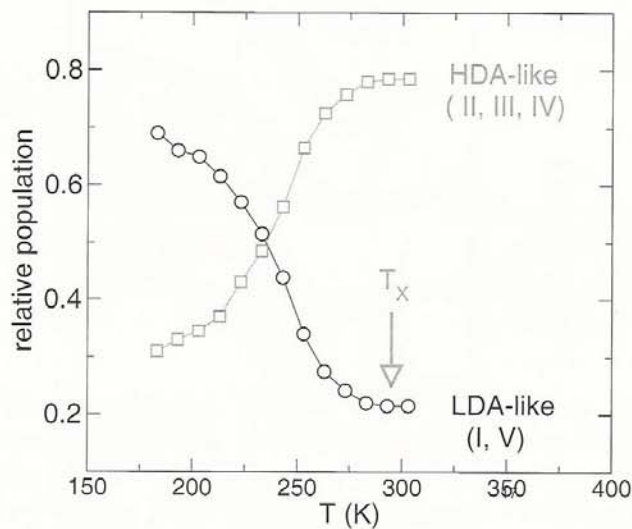


Fig. 17. – Test #17: The Stokes-Einstein relation between viscosity and relaxation time breaks down on lowering the temperature below a breakdown value that is within experimental error of the Widom temperature. This experimental fact is consistent with the idea that local LDL fluctuations begin to dominate below the Widom temperature. Adapted with permission from refs. [43,44].

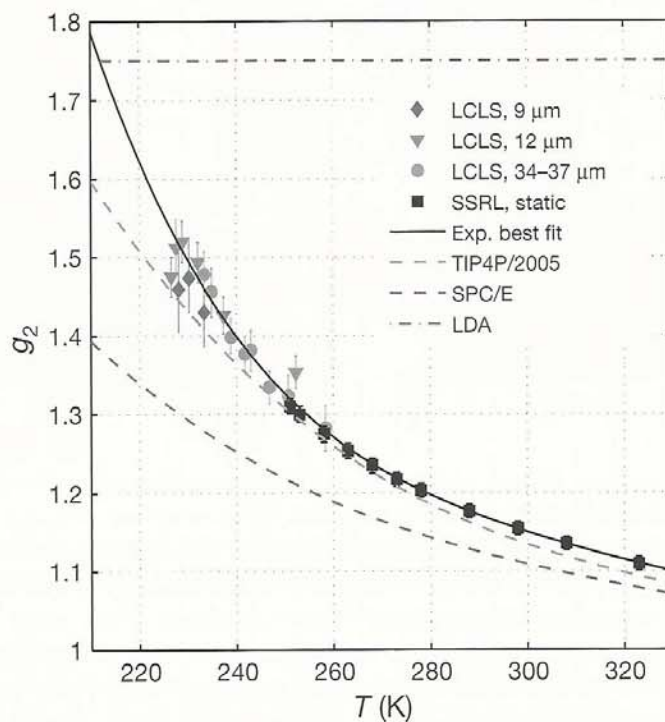


Fig. 18. – Test #18: Experiments in the “no man’s land” below the homogeneous nucleation temperature  $T_H$  are challenging. In addition to the 1998 Mishima experiments mentioned above, a very recent work from Nilsson and collaborators makes it clear that one can probe the “no man’s land” below  $T_H$ , and that the resultant data are smooth extensions of results above  $T_H$ . Adapted with permission from ref. [45].

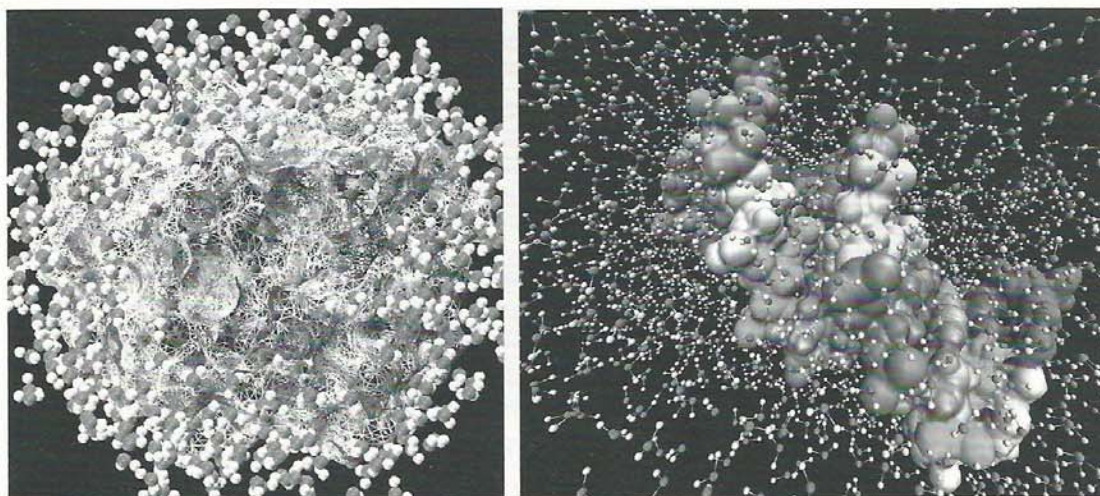


Fig. 19. – Test #19: Artist’s view of water molecules associated with (a) lysozyme and (b) RNA. Courtesy of S.-H. Chen.



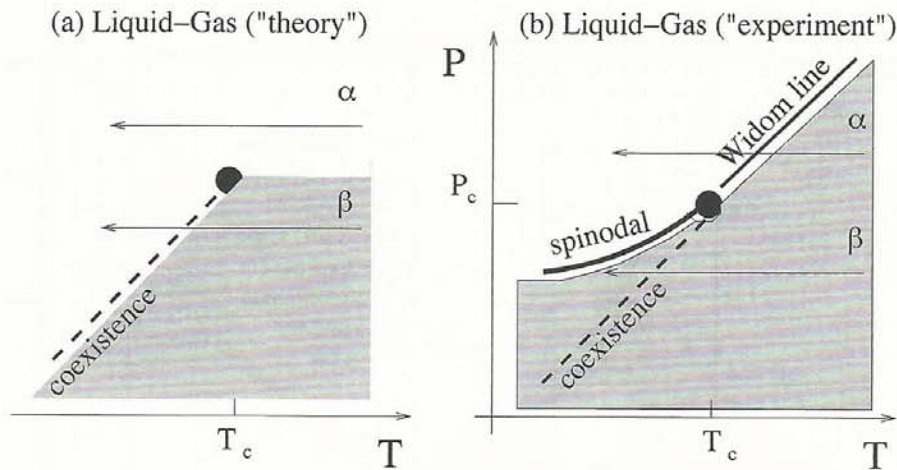


Fig. 20. – Test #20: Pressure-Temperature phase diagram in the general region of the liquid-gas critical point, contrasting (a) the classroom explanation, emphasizing that along a constant-pressure path  $\alpha$  nothing of interest happens, with (b) the experimental facts, that along a constant-pressure path  $\alpha$  there is a sharp maximum on decreasing the temperature and crossing the Widom line, with apparent exponents the same as those if the path were at the critical pressure. If the constant pressure path is for a pressure below the critical pressure  $P_c$ , then the classroom explanation leads students to believe that an abrupt first-order transition occurs with a discontinuous jump in properties such as the volume and entropy that are first derivatives of the Gibbs potential, and (b) where the fluid becomes metastable until the system reaches the spinodal (the limit of metastability). Adapted with permission from ref. [30].

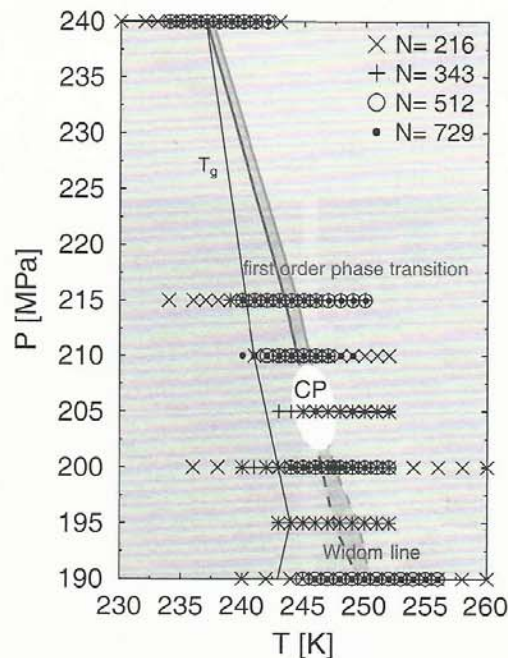


Fig. 21. – Test #21: A “numerical experiment” showing simulations of the ST2 water model near the hypothesized liquid-liquid critical point for four different system sizes,  $N = 216, 343, 512,$  and  $729$ . There are greatly enhanced fluctuations in density and entropy, which are almost identical when the first-order transition line is crossed and when the Widom line is crossed, corresponding to the experimental fact that the isothermal compressibility and the constant-pressure specific heat have extremely sharp maxima just above and just below the critical point. Adapted with permission from refs. [46, 47].

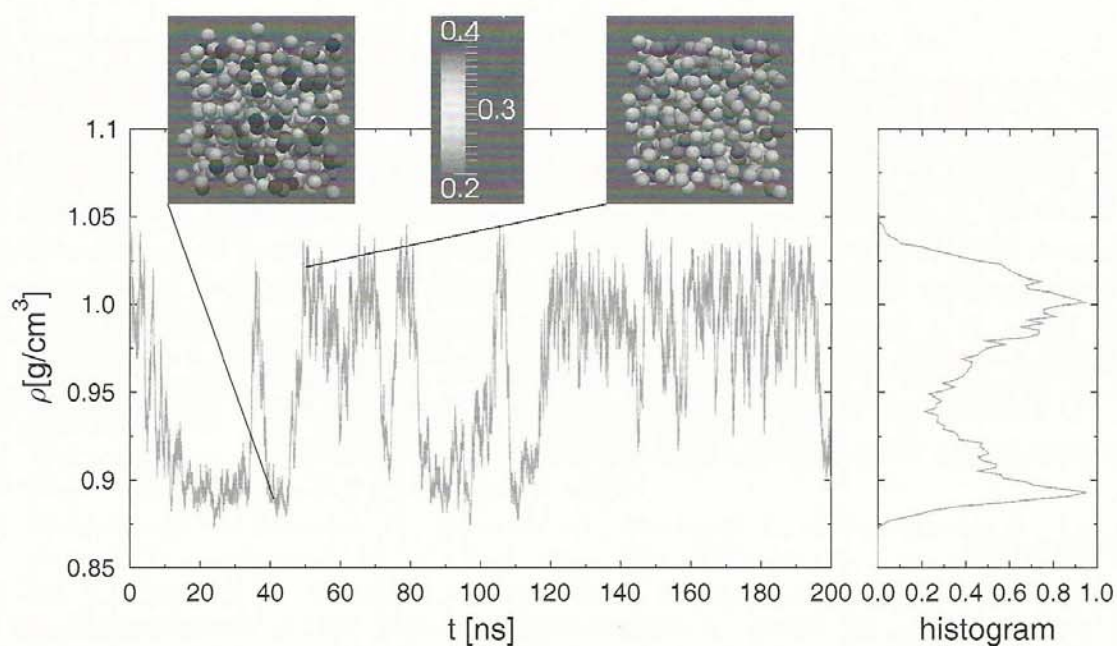


Fig. 22. – Test #22: Time dependence of the density for 20 percent of the total run of 1000 ns for a state point just below the critical point. It is clear that the system “flips its phase” from the low-density liquid to the high-density liquid, and back again. This phase flipping occurs on all different time scales. Adapted with permission from refs. [46, 47].

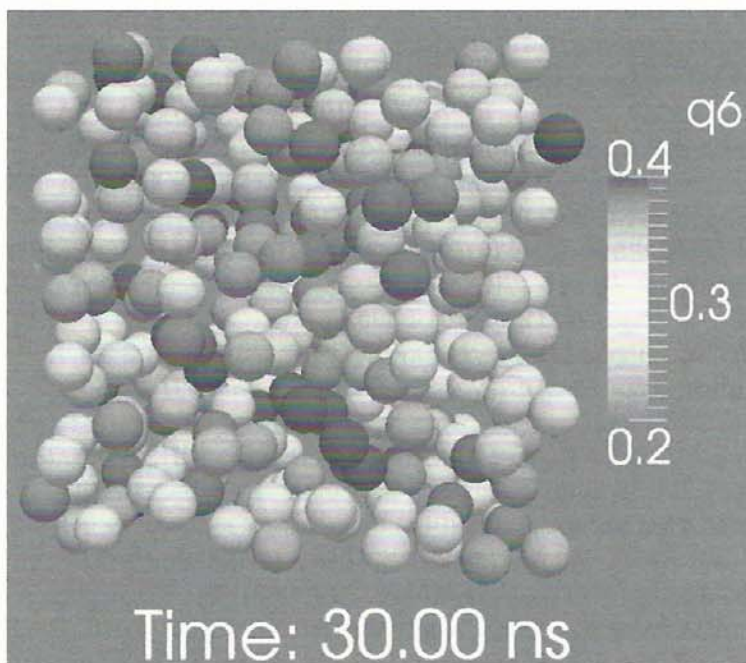


Fig. 23. – Test #23: One frame of a movie showing the time development of the local density associated with each of the ST2 water molecules. The color code corresponds to the local density, with dark blue being the lighter density and red being the heavier local density. We notice that the density fluctuations are *correlated in space*, corresponding to the fact that a quantitative measure of the density fluctuations, the isothermal compressibility, is much larger than it would be if there were no spatial correlations. Courtesy of T. A. Kesselring.



\* \* \*

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