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## The puzzling problem of water properties at low temperature. An experimentalist view

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**Abstract.** Water is at once the most familiar substance, the one for which we have the most data, and a liquid with anomalous properties that make it unique. Many theoretical models provide explanations for the abnormal behaviour of water. The most recent ones are based on numerical simulations of molecular dynamics made from effective potentials that reproduce the tetrahedral geometry of hydrogen bonds. From the experimental side, homogeneous nucleation of hexagonal ice limits the range of temperature accessible to experiments. There is therefore no experimental data at atmospheric pressure in a wide temperature range extending from the homogeneous nucleation temperature (230 K) to the glass transition (135 K). However, water anomalies are the most important in the supercooled domain. Therefore, a large number of theoretical models, often based on extrapolations of data or analogies, have been developed without being able to be compared to non-existent experimental data. In all cases, the temperature domain where homogeneous nucleation takes place plays a crucial role in the anomalies observed at low temperature. Here, we present shortly structural models that predict the existence of a low-temperature critical point and a liquid-liquid transition between two phases of different structures by comparing them with experimental data. Other models are based on dynamic transitions or the existence of two types of relaxation, at the molecular and hydrogen bonding levels, which may correspond to two glass transitions.

**Keywords.** Supercooled water, critical point, water anomalies, neutron scattering.

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### INTRODUCTION

Water is virtually the only natural liquid on the surface of the planet Earth. The solid and vapour phases are present as well in large quantities, which is unique on Earth and rare on other planets. The importance in the biosphere, the climate and many physical and chemical processes make water the best-known substance for which the most accurate data are available. However, at the level of the fundamental physics, water is an “anomalous liquid”, i.e. whose properties are very different from those of an “ideal” liquid described by the Statistical Physics.

Among the “anomalies” of the properties of liquid water are the well-known lower density of the ice or the maximum density of the liquid at

about 4 °C even if, in reality, their banality is not currently associated with abnormal behaviour. Indeed, it is at the molecular scale that it is difficult to explain why the ordered molecules in ice occupy a larger volume than in the disordered liquid state.

Essentially all the thermodynamic and transport properties of liquid water (compressibility, specific heat, viscosity...) depend anomalously on temperature and pressure, especially at low temperature.

To find plausible models and explanations, it is therefore essential to study the properties of water at the lowest possible temperatures. Measurements of the thermodynamic properties of water can be made below  $T_m = 0$  °C, the melting point of ice, since water, like other liquids, can remain liquid below the melting point as long as there are no nuclei that initiate the heterogeneous nucleation of ice. There is however a limit to this “supercooled” state, that of the homogeneous nucleation which, at atmospheric pressure, takes place at  $T_N = 230$  K = -43 °C. Therefore, for many properties, we have measurements that extend to -25, sometimes -30 °C. In all cases, it is found that the anomalous behaviour accelerates as the temperature decreases. Thus, the density decreases by 1.6 % between 4 °C and -30 °C while the decay is only 0.7 % in the same temperature interval between 4 °C and 38 °C.

Isothermal compressibility, specific heat and other properties have similar behaviour. Figure 1 depicts the temperature dependence of isothermal compressibility at ambient pressure. There a minimum at 46 °C and an anomalous sharp increase on the low temperature side. Numerical extrapolations are consistent with a divergence although the numerical values remain far from those measured near a critical point.

To describe the properties of a liquid, semi-empirical equations of state based on numerical fits of the data are established. In the case of water, these equations of state lead to apparent divergences of several properties at temperatures a little below  $T_N$ , which raises the problem of the existence or not of a true divergence, similar to that which one would observe near a critical point or a spinodal line. Thus, for example, the remarkable equations of G.S. Kell,<sup>1</sup> which reproduces the density and the isothermal compressibility of water with an accuracy of  $10^{-5}$  between -30 and 150 °C, but extrapolates to infinite for  $T = -56$  °C and -51 °C, respectively. Equations of state describe more accurately properties of liquid water in domains of temperature and pressure covered by experiment but their extrapolations cannot be reliable, i.e. several extrapolations are numerically compatible with existing data.<sup>2</sup>

In this context, one of the first conjectures<sup>3</sup> were based on fits of thermodynamic properties by power laws

diverging at -42 °C, which postulated the existence of a re-entrant spinodal line that, passing through negative pressures would impose a stability limit in the liquid state at low temperature.<sup>4</sup> Despite the fact that formation of a glassy state by quenching does not exclude the existence of a re-entrant spinodal,<sup>5</sup> the experiments of J. Dubochet et al.<sup>6</sup> showing that the amorphous state of water can be reached by rapid quenching of the liquid, that is to say crossing the region of the postulated spinodal line, had a great impact in discussions on extrapolations.

The amorphous state obtained by quenching, glassy water, has a structure identical to that of the amorphous form obtained by deposition on a support at very low temperature. The glass transition temperature is of the order of 135 K, i.e. more than 100 °C below the supercooled domain accessible to the experiments. The temperature dependence in this vast temperature range, sometimes called “no man’s land”,<sup>7</sup> is unknown. Yet it is not trivial since the numerical divergences are only apparent. The “no man’s land” is therefore a territory of speculation! Several models have been proposed to describe the temperature dependence of the properties of water, without ever reaching discriminant tests.

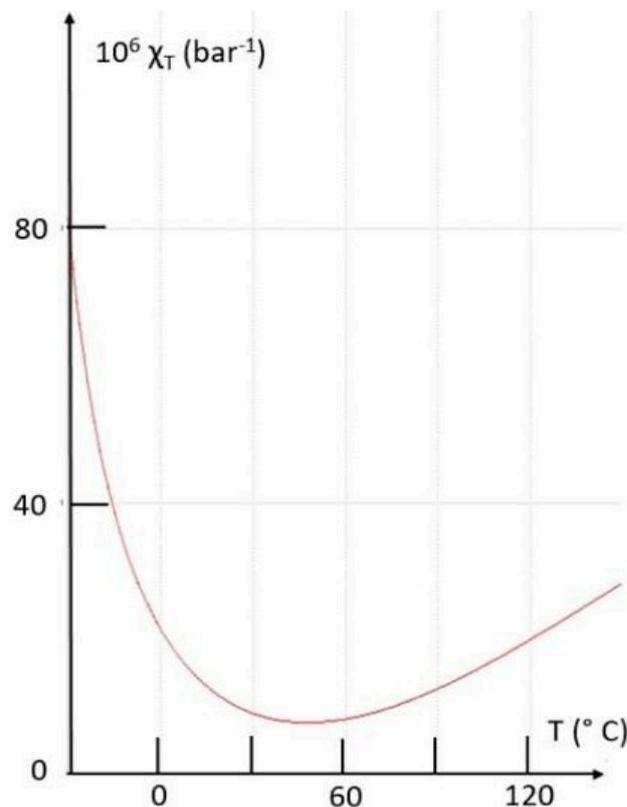


Figure 1. Isothermal compressibility of liquid water at atmospheric pressure. There is a minimum at 46 °C.

An experimental fact occupies an important place in the arguments developed on this temperature domain inaccessible to the experiment. This is the discovery in 1984 of a form of high-density amorphous (HDA) ice,<sup>8</sup> obtained by compression at very low temperature of the crystalline ice. Its density ( $1.17 \text{ g.cm}^{-3}$  at 77 K) is much higher than that of amorphous ice, which is obtained by quenching ( $0.94 \text{ g.cm}^{-3}$  at 77 K, so close to that of ice). The structural study<sup>9</sup> shows that interstitial sites between the first and second neighbours are occupied, which corresponds to strong distortions of the hydrogen bond network, probably due to the collapse of a network of very directional links as well as the weak coordination of the water molecules, barely higher than 4 in the liquid phase.

Following the discovery of HDA ice, some models of supercooled water postulate the existence of a high density liquid that would correspond to the melting of HDA ice, therefore to the existence of two forms of liquid water, having very different densities and structures, though similar to those of high and low density amorphous ice respectively.<sup>10</sup>

If, despite their metastability, the amorphous states are represented in a pseudo-phase diagram, the transition line separating the two forms of amorphous ices of different densities would be prolonged by a line separating the two liquids and a liquid-liquid transition would be the pendant of the transition between the two forms of amorphous ices. This idea consists to consider HDA as a glass, just like the amorphous form of low density, LDA is the glassy form of liquid water. The line of separation of the two liquid phases would end at a critical point where a certain number of thermodynamic properties would have a singular behaviour.

This model is supported by the fact that some numerical simulations of the molecular dynamics of water do indeed predict the existence of one critical point at low temperature and high pressure. However, such numerical simulations are based on effective potentials that try to reproduce at best the thermodynamic properties and the molecular structure in a pressure and temperature range not too far from the ambient conditions.<sup>11</sup>

Of the many potentials,<sup>12</sup> ST2 and TIP4P potentials actually predict a singular behaviour of isothermal compressibility near a critical point around 200 K and 0.1 GPa, so deep inside the no man's land.<sup>13</sup>

This critical point would be the extreme point of the transition line separating high and low density liquids, itself an extension of the line separating the two forms of amorphous ice, HDA and LDA, as mentioned above. It can therefore be seen either as a demixion point of

two liquids, or as a critical point identical to that, liquid-vapour, on the high temperature side of the phase diagram of water. Both interpretations exist in the literature. They correspond to different interpretations of certain structural measurements.

In the context of the existence of a critical point at high pressure and low temperature, anomalies observed experimentally at atmospheric pressure and at low temperature are explained by another analytical extension of the same line of separation of liquid phases beyond the critical point, line often called "Widom line".<sup>14</sup> As a result, the thermodynamic properties would only present "bumps" when crossing the Widom line. A problem remains open: how to explain that the anomalies are reduced under pressure? Concretely, starting from the ambient pressure side, a high pressure point of the phase diagram is closer to the critical point than another point at the same temperature and lower pressure. Therefore, anomalies should be larger for the second point conditions, what is not the case.

On the other hand, it is important to note that the Widom line deduced from the numerical models almost coincides with the homogenous nucleation line of ice.

Other models neglect the structural aspects and postulate rather a dynamic transition taking place also in the same field of pressure and temperature, or near the homogeneous nucleation line.

In this article, we discuss, in a non-exhaustive way, the consequences of the most popular models by comparing them with the experimental results available for supercooled water.

## MIXTURE MODELS

The idea that liquid water can be a mixture of two liquids is not new. This is even one of the first conjectures formulated to explain the maximum density at 4 °C. W. Röntgen in 1892 conjectured the existence of different types of water molecules.<sup>15</sup> Other mixing models have been proposed, including the elaborated one by G. Némethy and H.A. Scheraga,<sup>16</sup> never confirmed by experience. Mixing models envisage either different types of molecules,<sup>17</sup> or molecular arrangements such as two types of dimers or pentamers<sup>18</sup> or the coexistence of two liquids of very different structures and densities coexisting in the form of clusters, one of the two phases immersed in the second.<sup>19</sup>

All these models are hardly compatible with measurements of the structure of liquid water. Indeed, the pair correlation function,  $g(r)$ , shows the existence of a single very narrow peak at  $2.8 \text{ \AA}$ , representative of the

distance between close neighbours, perfectly defined by the intermolecular links.<sup>20</sup> The existence of aggregates of different densities is equally incompatible with X-ray scattering measurements,<sup>21-22</sup> which show that small-angle scattering is due solely to the number fluctuations at the origin of isothermal compressibility. Moreover, the isothermal compressibility, so the small angle scattering of water, are very weak compared to those of other liquids. As well, if one limits oneself to the known thermodynamic data, it is impossible to explain the maximum of density or the minimum of compressibility by the mixture of two liquids whose density would differ by about 10%.<sup>23</sup>

About these models, one can note the ambiguity of the definition of the critical point at low temperature. If it is a demixing point, nucleation of one of the two phases should be detected but there would be no anomaly in the isothermal compressibility. In contrast, density fluctuations with increasing coherence length explain the increase in compressibility observed at low temperatures.

In a recent experiment, X-ray and neutron scattering at very low temperature and high pressure<sup>24</sup> measured the water-lithium chloride eutectic mixture. No anomalies were observed what excludes enhanced density fluctuations or nucleation of a distinct phase. Therefore, solid poly-amorphism does not imply liquid poly-amorphism.

Nevertheless, it is important to note that measurements made on aqueous solutions can only provide additional information on the behaviour of bulk water. Indeed, the addition of small amounts of any solute decreases or eliminates abnormalities of pure water, as for example in the case of ethanol<sup>25</sup> even in the presence of hydrogen bonds. In fact, the breaking of the tetrahedral structure is sufficient to make the behaviour of water similar to that of other associated liquids. The same applies to samples of water confined in small pores. There is a very significant reduction in the melting temperature, or even its suppression,<sup>26</sup> but the thermodynamic anomalies are also suppressed.

#### DYNAMIC MODELS

In other approaches, the abnormal behaviour of water was attributed to purely dynamic transitions. Thus, measurements of the molecular dynamics of hydration water on lysozyme protein,<sup>27</sup> can be interpreted by a discontinuity of the temperature dependence of the relaxation time associated with diffusion. At high temperature this time varies very strongly with temperature (sometimes called “fragile” liquid behaviour) while at low temperature, the temperature dependence is of the

Arrhenius type (“strong” liquid). The fit of the experimental neutron quasi-elastic neutron scattering<sup>27</sup> data sets the transition to 220 K at atmospheric pressure, so very close to the homogeneous nucleation temperature  $T_N$  and the postulated Widom line. This may actually correspond to a dynamic transition.

In addition, the measurements made on samples of bulk water demonstrate the coexistence of two times characterizing the molecular dynamics,<sup>28,29</sup> which depends on time in a very different way. The residence time, a measure of the time during which a molecule is inside the cage formed by neighbouring molecules, follows the anomalous temperature dependence of other transport properties, such as viscosity. A much shorter time, of the order of the ps, is related to the lifetime of the intermolecular bonds and its dependence of the temperature is of the Arrhenius type even at the lowest temperatures accessible to this type of experiments, that is to say -20 °C. Spin echo relaxation time measurements, with momentum transfers selected in order to be able to discriminate these two times,<sup>30</sup> as well as measurements of the imaginary part of the susceptibility by X spectroscopy,<sup>31</sup> also show the existence of two relaxation times. Finally, it is remarkable that in the analysis of the quasi-elastic spectrum of neutrons on the melting line of the ice VII, one always finds this short time, which characterizes the dynamics of the hydrogen bonds.<sup>32</sup>

The strong directionality of the intermolecular potential due to the hydrogen bonds is at the origin of a very short life time if one takes into account the energy, which is of the order of 8 kJ / mol, thus greater than 1000 K. We speak here of the time during which a hydrogen atom remains inside the cone where the bond can be established, whose opening is of the order of 30°. This is the time of allegiance defined by F. Stillinger.<sup>33,34</sup> Otherwise, a bond can break and reform between the same neighbouring molecules. This often happens at low temperatures when the number of “intact” hydrogen bonds is very large, which generates a gel-like structure with residence times that increase very rapidly with temperature. Figure 2 shows the residence times and lifetime of the hydrogen bonds as a function of temperature in a Arrhenius plot. The apparent divergence of the first should correspond to the formation of a macroscopic gel. Yet, as we have seen, the homogenous nucleation of ice takes place around -43 °C, when the liquid is still very fluid.

In addition, the structure of the supercooled liquid changes rapidly as the temperature decreases. It is remarkable that, also towards -25 °C, the position of the first peak of the structure function,  $S(k)$ , decreases approaching that of the amorphous ice.<sup>35</sup> This means

that, between this limit temperature of possible measurements and  $T_g$ , thus in all the extension of the no man's land, there is practically no structural changes. Only hydrogen bonds maintain a fast dynamic over this wide temperature range because of the smooth Arrhenius temperature dependence of its characteristic time.

This amounts to admitting the existence of two glass transitions. The first, occurring near  $-43^\circ\text{C}$ , corresponds to the arrest of the molecular diffusion. Indeed, the structure measured at the lowest accessible temperatures ( $-30^\circ\text{C}$ ) is practically identical to that of the low-density amorphous ice, LDA, however  $100^\circ$  above  $T_g$ .<sup>35</sup> Near the homogeneous nucleation temperature, it is the hydrogen bonds, which keep a sufficiently fast dynamic to prevent the formation of the amorphous phase. Between  $T_N$  and  $T_g$ , small displacements of the hydrogen atoms are sufficient to form the crystalline phase. It is only at 135 K that the hydrogen bonds are frozen and that the LDA phase is formed with a small change of enthalpy.

This type of behaviour is the analogue of the alpha and beta dynamics that characterize the dynamics of many polymers. However, in the case of water, it is the beta dynamics, that of the hydrogen bonds, that determines the thermodynamic properties and the existence of a vast no man's land.

It remains to explain the existence of several amorphous phases, including that of high density (HDA) that can be obtained by compression of hexagonal ice or compression of low-density amorphous ice (LDA). On the one hand, there is not exactly one line of coexist-

ence of these two forms of amorphous ice. In fact, one goes from LDA to HDA only by compression, while the transition HDA towards LDA results from the heating of HDA above 120 K. Thus, HDA is stable at atmospheric pressure if the temperature is sufficiently low. More important is the question of whether there is a liquid with the HDA ice structure, i.e. if HDA is a symmetrical glass of glass having the LDA structure. Recent results of C.A. Tulk et al.<sup>36</sup> show that HDA is rather a kinetically arrested transformation between low-density ice I and high-density ice XV.

As a result, the water anomalies must actually go through bumps near the temperature  $T_N$  of nucleation of ice. For example, the compressibility must reach a maximum value towards  $T_N$  and remain practically constant between  $T_N$  and  $T_g$ . Therefore, the line that defines the homogeneous nucleation in the plane (P, T) plays a capital role, formally analogous to that of line Widom but in the absence of a critical point and liquid-liquid transition. As far as compressibility is concerned, one can try to evaluate a coherence length of density fluctuations. There is no exact method to do this because it is a very small effect but we can say that it is a very small value, certainly less than  $1\text{ nm}$ <sup>21,37</sup> which can be explained by the formation of the gel phase.

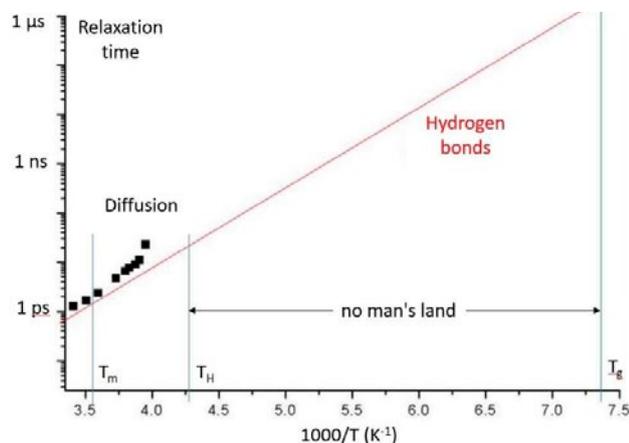
This does not exclude the fact that, in certain situations of confinement, water can have a high apparent density. This is the case of hydration water at hydrophilic sites of proteins.<sup>38</sup>

## CONCLUSION

From the large amount of data available, it can be said that liquid water is a homogeneous liquid at all temperatures and pressures. The various theories that have been proposed agree on the existence of anomalies of the temperature dependence of most thermodynamic and transport properties near the line that defines the nucleation of hexagonal ice, i.e. around  $-43^\circ\text{C}$  at atmospheric pressure.

Computer simulations of molecular dynamics predict divergences in response properties, including isothermal compressibility and specific heat. Two actual potentials even foresee the existence of a critical point situated towards 200 K and a few kbar of pressure, in spite of the fact that the anomalies of the water at ambient temperature decrease quickly under pressure.

Given the intrinsic difficulty of entering the "no man's land", it is possible that extrapolations, analogies and speculations continue to be made on the behaviour of deeply supercooled liquid water. Nevertheless, recent



**Figure 2.** Schematic representation of the two times that characterize dynamics of liquid water. Squares represent experimental evaluations of the molecular residence time showing the anomalous super-Arrhenius temperature dependence. The red line is an extrapolation of the hydrogen bond lifetime evaluated at temperatures above  $-20^\circ\text{C}$ .<sup>28</sup>  $T_m$ ,  $T_H$  and  $T_g$  are the melting, homogeneous nucleation and glass transition temperatures, respectively.

results show that high-density amorphous ice is not a glass, what eliminates the possibility of a high density liquid. Also, the consideration of two characteristic times (that of the molecular dynamics and the one of the hydrogen bonding) makes it possible to reach relatively classical explanations of the unusual behaviour of the water.

Probably, future studies should look more in detail at the nature of the hydrogen bond, which implies approaches beyond the thermodynamic scale. In fine, a complete knowledge of hydrogen bonds in water could lead to the determination of the true molecular potential.

#### REFERENCES

1. D.S. Kell, Density, Thermal Expansivity, and Compressibility of Liquid Water from 0° to 150°C: Correlations and Tables for Atmospheric Pressure and Saturation reviewed and expressed on 1968 Temperature Scale, *Journal of Chemical and Engineering Data* 20, 97-105 (1975).
2. F. Caupin, V. Holten, C. Qiu, E. Guillerm, M. Wilke, M. Frenz, J. Teixeira and A.K. Soper, Comment on “Maxima in the thermodynamic response and correlation functions of deeply supercooled water”, *Science* 360 (6390), eaat1634 (2018).
3. R.J. Speedy and C.A. Angell, Isothermal compressibility of supercooled water and evidence for a thermodynamic singularity at -45 °C, *J. Chem. Phys.* 65, 851-858 (1976).
4. M.E.M. Azouzi, C. Ramboz, J.F. Lenain and F. Caupin, A coherent picture of water at extreme negative pressure, *Nature Physics* 9, 38-41 (2013).
5. G. Pallaresa, M. El Mekki Azouzi, M.A. González, J.L. Aragonés, J.L.F. Abascal, C. Valeriani and F. Caupin, Anomalies in bulk supercooled water at negative pressure, *Proc. Natl. Acad. Sci. U.S.A.* 111, 7936-7941 (2014).
6. J. Dubochet, R. Lepault, A. Freeman, J.A. Berri-man and J.-C. Homo, Electron microscopy of frozen water and aqueous solutions, *J. of Microscopy*, 128, 219-237 (1982).
7. H.E. Stanley, S.V. Buldyrev, M. Canpolat, O. Mishima, M. R. Sadr-Lahijany, A. Scala and F. W. Starr, The puzzling behavior of water at very low temperature, *Phys. Chem. Chem. Phys.* 2, 1551-1558 (2000).
8. O. Mishima, L.D. Calvert and E. Whalley, ‘Melting ice’ I at 77 K and 10 kbar: a new method of making amorphous solids, *Nature* 310, 393-395 (1984).
9. L. Bosio, G. P. Johari and J. Teixeira, X-Ray study of high-density amorphous water, *Phys. Rev. Lett.* 56, 460-463 (1986).
10. C. Huang, K.T. Wikfeldt, T. Tokushima, D. Nordlund, Y. Harada, U. Bergmann, M. Niebuhr, T.M. Weiss, Y. Horikawa, M. Leetmaa, M.P. Ljungberg, O. Takahashi, A. Lenz, L. Ojamäe, A.P. Lyubartsev, S. Shin, L.G.M. Pettersson and A. Nilsson, The inhomogeneous structure of water at ambient conditions, *Proc. Natl. Acad. Sci. U.S.A.* 106, 15214-15218 (2009).
11. C. Vega and J. L. F. Abascal, Relation between the melting temperature and the temperature of maximum density for the most common models of water, *J. Chem. Phys.* 123, 144504 (2005).
12. B. Guillot, A reappraisal of what we have learnt during three decades of computer simulations on water, *J. Mol. Liquids* 101, 219-260 (2002).
13. J.C. Palmer, F. Martelli, Y. Liu, R. Car, A.Z. Panagiotopoulos and P.G. Debenedetti, Metastable liquid-liquid transition in a molecular model of water, *Nature* 510, 385-388 (2014); K.T. Wikfeldt, C. Huang, A. Nilsson and L.G.M. Pettersson, Enhanced small-angle scattering connected to the Widom line in simulations of supercooled water, *J. Chem. Phys.* 134, 214506 (2011).
14. L. Xu, S.V. Buldyrev, C. A. Angell and H. E. Stanley, Thermodynamics and dynamics of the two- scale spherically symmetric Jagla ramp model of anomalous liquids, *Phys. Rev. E* 74, 031108 (2006).
15. W.C. Röntgen, Ueber die Constitution des flüssigen Wassers, *Annalen der Physik und Chemie* XLV, 91-97 (1892).
16. G. Némethy and H.A. Scheraga, Structure of Water and Hydrophobic Bonding in Proteins. I. A Model for the Thermodynamic Properties of Liquid Water, *J. Chem. Phys.* 36, 3382-3400 (1962).
17. C.A. Cerdeiriña, J. Troncoso, D. González-Salgado, P.D. Debenedetti and H.E. Stanley, Water’s two-critical-point scenario in the Ising paradigm, *J. Chem. Phys.* 150, 244509 (2019).
18. O. Mishima and H.E. Stanley, The relationship between liquid, supercooled and glassy water, *Nature* 396, 329-335 (1998).
19. L.G.M. Pettersson and A. Nilsson, The structure of water; from ambient to deeply supercooled, *J. Non-Crystalline Solids* 407, 399-417 (2015).
20. A.K. Soper and M.G. Phillips, A New determination of the structure of water at 25 °C, *Chem. Phys.* 107, 47-60 (1986).
21. L. Bosio, J. Teixeira and H.E. Stanley, Enhanced density fluctuations in supercooled H<sub>2</sub>O, D<sub>2</sub>O, and Ethanol-Water solutions: Evidence from Small-Angle X-Ray Scattering, *Phys. Rev. Lett.* 46, 597-600 (1981).

22. A. K. Soper, J. Teixeira, and T. Head-Gordon, Is ambient water inhomogeneous on the nanometer-length scale?, *Proc. Natl. Acad. Sci. U.S.A.* **107**, E44 (2010).
23. G. Johari and J. Teixeira, Thermodynamic analysis of the two-liquid model for anomalies of water, HDL-LDL fluctuations and liquid-liquid transition, *J. Phys. Chem. B* **119**, 14210-14220 (2015).
24. L.E. Bove, F. Pietrucci, A.M. Saitta, S. Klotz and J. Teixeira, On the link between polyamorphism and liquid liquid transition: the case of salty water, *J. Chem. Phys.* **151**, (2019).
25. O. Conde, J. Teixeira and P. Papon, Analysis of sound velocity in supercooled H<sub>2</sub>O, D<sub>2</sub>O and Water- Ethanol mixtures, *J. Chem. Phys.* **76**, 3747-3753 (1982).
26. J. C. Dore, B. Webber, M. Hartl, P. Behrens, T. Hansen, Neutron diffraction studies of structural phase transformations for water-ice in confined geometry, *Phys. A: Stat. Mech. Appl.* **314**, 501-507 (2002).
27. S.-H. Chen, L. Liu, E. Fratini, P. Baglioni, A. Faraone, and E. Mamontov, Observation of fragile-to-strong dynamic crossover in protein hydration water, *Proc. Natl. Acad. Sci. U.S.A.* **103**, 9012-9016 (2006).
28. J. Teixeira, M.-C. Bellissent-Funel, S.-H. Chen and A. J. Dianoux, Experimental determination of the nature of diffusive motions of water molecules at low temperatures, *Phys. Rev. A* **31**, 1913-1917 (1985).
29. J. Qvist, H. Schober and B. Halle, Structural dynamics of supercooled water from quasielastic neutron scattering and molecular simulations, *J. Chem. Phys.* **134**, 144508 (2011).
30. J. Teixeira, A. Luzar and S. Longeville, Dynamics of Hydrogen Bonds: How to Probe their Role in the Unusual Properties of Liquid Water, *J. Phys.: Cond. Matter* **18**, S2353-S2362 (2006).
31. A. Arbe, P. Malo de Molina, F. Alvarez, B. Frick, and J. Colmenero, Dielectric Susceptibility of Liquid Water: Microscopic Insights from Coherent and Incoherent Neutron Scattering, *Phys. Rev. Lett.* **117**, 185501 (2016).
32. L. E. Bove, S. Klotz, Th. Strässle, M. Koza, J. Teixeira and A.M. Saitta, Translational and rotational diffusion in water in the gigapascal range, *Phys. Rev. Lett.* **111**, 185901 (2013).
33. F.H. Stillinger, Water revisited, *Science* **209**, 451-457 (1980).
34. A. Luzar and D. Chandler, Hydrogen-bond kinetics in liquid water, *Nature* **379**, 55-57 (1996).
35. M.-C. Bellissent-Funel, L. Bosio, J. Dore, J. Teixeira and P. Chieux, Spatial correlations in deeply supercooled water, *Europhys. Lett.* **2**, 241-245 (1986).
36. C.A. Tulk, J.J. Molaison, A.R. Makhluף, C.E. Manning and D.D. Klug, Absence of amorphous forms when ice is compressed at low temperature, *Nature* **569**, 542-545 (2019).
37. G.N.I. Clark, G.L. Hura, J. Teixeira, A.K. Soper and T. Head-Gordon, Small-Angle Scattering and the Structure of Ambient Liquid Water, *Proc. Nat. Acad. Sci. (USA)* **107**, 14003-14007 (2010).
38. D. Russo and J. Teixeira, Mapping water dynamics in defined local environment: From hindered rotation to vibrational modes, *Journal of Non-Crystalline Solids* **407**, 459-464 (2015).