The contribution of small angle and quasi-elastic scattering to the physics of liquid water

José Teixeira

Laboratoire Léon Brillouin (CEA/CNRS) CEA Saclay F-91191 Gif-sur-Yvette Cedex France

jose.teixeira@cea.fr

Abstract. Many properties of liquid water at low temperature show anomalous behaviour. For example, density, isothermal compressibility, heat capacity pass by maxima or minima and transport properties show a super-Arrhenius behaviour. Extrapolations performed beyond the homogeneous nucleation temperature are at the origin of models that predict critical points, liquid-liquid transitions or dynamic cross-overs in the large domain of temperature and pressure not accessible to experiments because of ice nucleation.

A careful analysis of existing data can be used to test some of these models. Small angle X-ray or neutron scattering data are incompatible with models where two liquids or heterogeneities are present. Quasi-elastic neutron scattering, taking advantage and combining both coherent and incoherent scattering show that two relaxation times are present in liquid water and that one of them, related to hydrogen bond dynamics, has an Arrhenian behaviour, suggesting that the associated dynamics of the bonds, similar to the β relaxation of polymers, determines the glass transition temperature of water.

1. Introduction

The importance of water doesn't need to be emphasized. Liquid water is almost the only liquid present on the Earth surface, although it represents an extremely small fraction of the mass of the planet. It is generally accepted that life is only possible in its presence, reason why the research for life in the Universe coincides with research of water molecules in liquid state. Temperature and pressure conditions at the Earth surface allow the natural existence of the three states, liquid, ice and vapour, and associated phase transitions which feed a permanent water cycle between states through evaporation, condensation, melting and freezing processes. As well, there are circulation of big masses of liquid water in oceans with periodicities of the order of several thousand years.

Behind such behaviours there are physical processes which, contrary to the case of other liquids are complex, specific, eventually not yet well understood despite the huge amount of data available. Indeed, most of the thermodynamic properties of water show an "anomalous behaviour", an expression that means only that such properties depend on temperature and pressure much differently than for other liquids.

Knowing that a water molecule is chemically described by the simple expression H_2O, corresponding to the arrangement of one atom of oxygen and two atoms of hydrogen, the obvious question is: why is liquid water so complex? The simplest answer is that water cannot be reduced to an assembly of molecules similar to that of hard spheres or of many other simpler liquids. Between two

neighbouring water molecules both the interaction of dipolar moments and sharing of part of electronic clouds generate an attractive interaction: the intermolecular hydrogen bond, which is very directional.

Concretely, the attractive energy between two water molecules is maximum when the hydrogen atom of one molecule is almost aligned with the oxygen of a neighbouring molecule, a situation described by the notation O-H ... O. The bond length is the largest distance but the hydrogen atom can jump from one position to the symmetrical one along the bond direction.

At room temperature, at a given moment, most of hydrogen atoms are engaged in so-called "intact" bonds, meaning that, at very short times of observation, liquid water is like a gel far above its percolation threshold [1].

Due to hybridisation of molecular orbitals, the water molecule has the shape of a V with an angle HOH very close to the tetrahedral angle, that formed by the diagonals of a cube ($\cos^{-1}$ (-1/3)). Together with the directionality of the bonds, this feature generates a local structure where each molecule is surrounded by 4 neighbours, sitting at opposite vertexes of a cube. This coordination number, that characterises most of the crystalline forms of water, is very small as compared to the much more compacted structures of atomic liquids. In liquid water, because of thermal energy, the coordination number is larger than 4 but always affording a large empty volume and room for large amplitude fluctuations of intermolecular bonds which damp rapidly the extension of the oscillations of the pair correlation function. Despite the existence of a large connectivity length, the extension of the radial correlation function is small.

The energy of a hydrogen bond formed between two water molecules is relatively high: of the order of 8 kJ.mol^{-1} a value more than 3 times above the kinetic energy at room temperature. However, the lifetime of an hydrogen bond, whatever is the definition taken to evaluate it, is short - of the order of 1 ps. This is due to the large amplitude librations of the hydrogen atoms in the direction perpendicular to that of the bond which bring the light hydrogen atom out of the narrow cone where the attractive energy is high. In liquid water at room temperature, even if the number of "intact" bonds is larger than 60% of the possible bonds between neighbouring molecules, their lifetime is very short, what explains the low viscosity of water.

The temperature and pressure dependences of most of water properties are very different from those of other liquids, particularly at low temperature when the number of intact bonds is higher. Qualitatively, some properties can be understood. For example, larger the average number of bonds per molecule and smaller the coordination number. Indeed, this number decreases from 4.6 at room temperature to 4.3 at 0° C [2]. In crystalline ice I_h it is equal to 4. This temperature dependence of the coordination number explains the existence of a temperature of maximum density of the liquid and the lower density of ice, the effects due to the formation of bonds compensating the normal thermal expansion.

Shortly, the anomalous properties of liquid water are due to three features:
- large number of intermolecular directional hydrogen bonds
- local tetrahedral arrangement
- short lifetime of hydrogen bonds

Among the unusual thermal and transport properties of water, isothermal compressibility and thermal capacity pass through minima at 46 and 30 °C, respectively. They represent enhanced density and entropy fluctuations.

Numerical extrapolations of such temperature dependences diverge around -45° C, which is close to the temperature of homogeneous nucleation of ice as first noticed by G. S. Kell [3]. As well, R. Speedy and C.A. Angell [4] have shown that several thermodynamic and transport properties of supercooled water (metastable state) could be well represented by power laws similar to those describing critical phenomena, through a reduced temperature parameter $(T-T_s)/T_s$, with T_s = -42° C. Because nucleation prevents experiments at temperatures below -30° C, in some cases -35° C, data are scarce in the interesting temperature domain where the anomalies are larger and show apparent divergences.

Instead a rapid quenching of liquid water yields formation of a glassy state with a structure similar to that of amorphous ice obtained by vapour deposition on a cold surface, what confirms the continuity between room temperature and glassy water. Consequently, the properties of water between the lowest temperatures accessible to experiment (around -35 °C) and the temperature of the glass transition (135 K) are unknown and have been object of many speculations since almost 50 years!

The discovery of a high density form of amorphous ice [5] contributed substantially to the discussion of the properties of liquid water in the large temperature range extending over 100°, from 240 K down to 135 K, in some cases the resurgence mixture models left out since 40 years.

Very schematically, the approaches based either in "critical" phenomena or in mixture models are the following:

1) Existence of a spinodal line on the low temperature side of the phase diagram of water, along which a real divergence of water properties does exist. This line is an extension of the normal spinodal that starts from the critical point on the high temperature side [4].

2) Assuming that there is a first order transition between the two forms of amorphous ice (high and low density), the coexistence line can be extrapolated till a "low temperature critical point" (LTCP). The position of this point is extremely diverse depending on extrapolations and on effective potentials used in molecular dynamic simulations but it would be placed at pressures above atmospheric pressure. From this point, another extrapolation of the coexistence line beyond the LTCP is the loci of extrema of the values of water properties. For example, compressibility or heat capacity, don't diverge but show "bumps" when crossing this extrapolated line (sometimes called "Widom line") [6] .

3) Similar ideas about existence of a line, loci of extrema but due to a dynamic crossover: the temperature dependence of the transport properties of supercooled water are non-Arrhenian or Arrhenian, at temperatures above or below this line, respectively. Crossing the line by decreasing temperature corresponds to what is called a "fragile to strong liquid transition" where the words fragile and strong correspond to non-Arrhenian and Arrhenian behaviour, respectively [7].

4) A pure mixture model that supposes that, with decreasing temperature, water goes from a high density homogeneous liquid at high temperature to a low density form at very low temperature. In between, i.e. room temperature and supercooled water are mixtures of the two hypothetic liquids, with clusters of the low density phase immersed in the high density phase at higher temperatures and the opposite at lower temperatures [8].

There is a large and controversial literature about these models, and others, which are mostly based on several computer simulations of molecular dynamics of water, a few of them being compatible with the existence of a LTCP. In other cases, extrapolations are done from data obtained either in aqueous solutions or under confinement. Indeed, in such conditions, water doesn't freeze or freezes at very low temperatures. However, because one or more of the three features at the origin of the specific behaviour of water, which are mentioned above, most of these results are irrelevant for the case of bulk water. Actually, under confinement or in aqueous solutions, the anomalies vanish.

The purpose of this paper is to show the contribution of a few neutron scattering experiments within the context of the proposed models. A precise analysis of data, even at room temperature, show that some models are hardly incompatible. In section 2, Small angle Scattering data are discussed. In section 3, arguments will be presented about different interpretations of quasi-elastic neutron scattering. Section 4, mostly based on the previous discussion, presents a possible framework for the explanation of water anomalies, free of critical behaviour.

2. **Small Angle Scattering**
Small angle X-ray and neutron scattering probes spatial correlations at scales of the order of 1 nm. One of the more frequent applications of these techniques is the evaluation of sizes of nano-particles, aggregates or inclusions, in situations where two phases can be identified and contribute to the scattered intensity through a "contrast", which is a difference between the density scattering length of each phase. In the case such entities have small interactions, the scattered intensity is described by a "form factor", square of the amplitude of the Fourier transform of the individual particles. The other contribution to

the scattered intensity is due to the number fluctuations which is determined by the isothermal compressibility of the sample.

At small values of the momentum exchange Q, the general expression of the scattered intensity $S(Q)$ is:

$$S(Q) = k_1(\Delta\rho)^2 + k_2(\Delta c)^2 + k_3(\Delta\rho\Delta c) \tag{1}$$

where $\Delta\rho$ and Δc represent number and concentration fluctuations, respectively, k_i are constants and the last term takes into account an eventually cross term.

In the case of a homogeneous liquid, only the first term exists and the previous equation reduces to:

$$S(Q) = k_1 (\Delta\rho)^2 = Nk_BT\chi_T f(Q) \qquad\qquad with\, f(Q=0) = 1 \tag{2}$$

In this expression, N is the number of molecules, k_B is the Boltzmann constant, T the temperature and χ_T the isothermal compressibility.

Far from the liquid-vapour critical point, the magnitude of $S(Q)$ is small what implies careful measurements of the absolute intensity. For example, in the case of deuterated water (D_2O) at room temperature, measured by neutron small angle scattering, $S(Q=0) = 0.0071$ cm^{-1}, to be compared with $S(Q=\infty) = 0.0407$ cm^{-1}. This value is very small even compared with other liquids because the compressibility of water is also very small.

Showing that the experimental value of $S(0)$ coincides with the contribution of number fluctuations, in 1974, R.W. Hendricks et al [9] demonstrated the homogeneity of liquid water, excluding contributions due to another phase of different density, which would imply a contrast and a non-zero value of k_2 in equation (1).

The temperature domain of observation has been extended in the supercooled region, down to -20° C [10] confirming the absence of heterogeneities in liquid water, thus of a mixture of two liquids with different densities (figure 1).
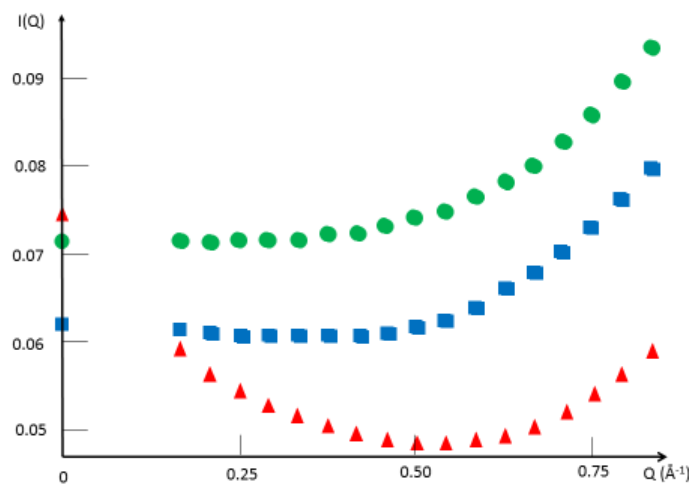

Figure 1
X-ray scattering of liquid water [10]. Green circles: 65° C; blue squares: 25° C; red triangles: -20° C. Points at $Q=0$ are obtained from eq. (2).

Independently, the evaluation of the density, compressibility or thermal capacity of the eventual coexisting phases necessary to fit the observed extrema results suppose implicitly aberrant temperature

dependences of the properties of each constituent [11]. Instead, it is worth noticing that, at low temperature, the function *f(Q)* in equation (2) has a small *Q* dependence denoting a small correlation length of the order of 5 to 8 Å, depending on the assumptions of the performed analysis [10]. It is important to emphasize that, even for large values of the correlation length as observed in liquids with high compressibility at the vicinity of critical points, a correlation length of number fluctuations corresponds to a decay of density fluctuations seen around the origin of the pair correlation function. In any case can it be associated to heterogeneities visible in real space.

In the case of water, an increase of the correlation length of number fluctuations associated to a parallel increase of isothermal compressibility and to some form of critical behaviour with decreasing temperature cannot be excluded. However, nucleation of the crystalline phase prevents large density fluctuations.

3. Quasi-elastic neutron scattering

Quasi-elastic neutron scattering (QENS) is one of the rare techniques that probes individual dynamics of atoms and molecules. Due to the extremely large incoherent cross section of protons, the scattered intensity of liquids containing hydrogen atoms probes the ensemble average of the time-dependent correlation function *<r(0).r(t)>* where *r(t)* is the position of each hydrogen atom at time *t*. Analysis of QENS of bulk water can be done assuming a decoupling between motions of the whole molecules and motions of hydrogen atoms relative to the molecular centres of mass [12], but other strategies are possible, namely in conjunction with molecular dynamics simulations [13].

In the first case, coupling between global and internal motions of hydrogen atoms does exist but its contribution is often neglected. Relaxations are described in energy space by Lorentzian functions which are the Fourier transforms of single exponentials *exp (-t/τ)*.
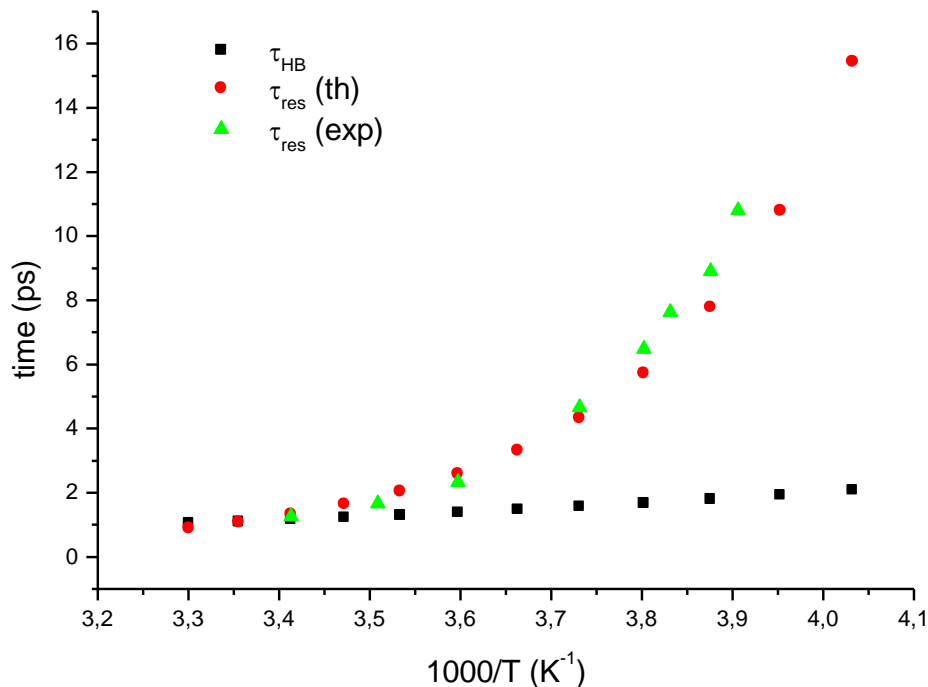

Figure 2

Black squares and green triangles: respectively, hydrogen bond lifetime and residence time of liquid water evaluated by QENS [12], plotted in function of the reciprocal temperature. Red dots: The same residence time calculated from the hydrogen bond time and the number of intact hydrogen bonds [15].

Analysis of the QENS spectra of supercooled water separates a narrow component describing the molecular self-diffusion at different length scales and a wider one that corresponds to motions of hydrogen atoms around the oxygen atom, similar to large amplitude librations. Because of the high directionality of intermolecular motions, this component is associated to the dynamics of the bonds, what means that, in some way, it measures hydrogen bond lifetimes. The remarkable result of this analysis is that, while the self-diffusion component follows the strongly non Arrhenius behaviour of transport properties of water, the temperature dependence of the hydrogen bond lifetime is Arrhenius at all measured temperatures, i.e. -20° C, with an activation energy that corresponds to the energy of the bonds. This result is also found in recent computer simulations [14].

Moreover, it was shown that the anomalous temperature dependence of the molecular residence time can be evaluated from the hydrogen bond lifetime taking into account the temperature dependence of the number of intact bonds. [15]

Figure 2 depicts the temperature dependence of the residence time and of the hydrogen bond lifetime as well as the evaluation of the residence time based on the temperature dependence of the number of intact bonds.

When water is confined either in tiny pores or sitting on hydrophilic surfaces, a variety of relaxation times coexist depending on local environment and structure. Discrimination between several populations is not or not always possible, what may justify a heuristic method that describes all the relaxations by a global stretched exponential, *exp $(-t/\tau)^\beta$* , with $0<\beta<1$. From this analysis, an average value $<\tau>$ of the ensemble of relaxation times can be extracted and interpreted.

Obviously, the same analysis can be applied to bulk water and the quality of the fits does not allow to discriminate between the consideration of two components and the heuristic approach.

The analysis of the dynamics of coherent scattering of water gives the solution of the conundrum. For this purpose, a sample of deuterated water has been measured by a triple-axis instrument and by a spin-echo spectrometer. In the first case, one measures the function $S(Q,\omega)$ while the second technique measures the intermediate function $I(Q,t)$, Fourier transform in time domain of $S(Q,\omega)$.

Both functions are linear combinations of the three partial pair correlation functions $S_{ij}(Q,\omega)$ where the indexes i and j refer to oxygen and deuterium atoms. Two Q values where selected. To one of them (Q_1=1.95 Å^{-1}) corresponds approximately the maxima of the three partials, thus the well-known maximum of the total $S(Q,\omega)$ around 2 Å^{-1}. To the larger value Q_2=3.54 Å^{-1} corresponds a local maximum of the partial DD, and negligible contributions of the other partials. With this choice, the measurement of $S(Q,\omega)$ at Q_1 gives information about the molecular dynamics while the measurement at Q_2 is dominated by the dynamics of deuterium atoms.

In both cases, i.e. measurements of $S(Q,\omega)$ and of $I(Q,t)$, it was clearly established that the temperature dependence of the linewidths (or relaxation times) was very important at Q_1 and hardly seen at Q_2, justifying experimentally the decomposition of the incoherent scattered intensity into two components discriminating non-Arrhenius residence times from Arrhenius hydrogen bond lifetimes.

4. **Discussion and conclusion**

Experimental data presented in the preceding sections allow a critical analysis of the different models that have been proposed to describe water properties in the temperature range that, at atmospheric pressure, extends from -30° C to the glass transition temperature. Necessarily based either on a few effective potentials extended to low temperatures or on simpler numerical extrapolations, they are not always compatible with experimental data.

This is the case of all mixture models which suppose that liquid water is a mixture of two liquids of different densities in relative concentrations that change with temperature.

The two liquids, would correspond to two of the different forms of amorphous ice: low and high density amorphous ice (LDA and HDA, respectively) with densities that differ by about 20%.

Such large difference of density generates a X-ray or neutron contrast that would be detected as a "concentration fluctuation" contribution to the scattered intensity similarly to what happens in any liquid mixtures, for example water-ethanol [10, 16].

Moreover, as pointed out above, assuming that the density of two liquids have a monotonous temperature dependence, the maximum of water density at 4° C cannot be explained without accepting very unusual temperature dependences of the densities of the two liquids [11].

Similarly, the results obtained by QENS exclude any complexity of the water dynamics that could generate distributions of residence times and relaxations described by stretched exponentials. Indeed, the separation into two components is the right way to take into account the dynamics of the hydrogen bonds and that of the whole molecule.

This result doesn't necessary contradict QENS of water under confinement [7]. In such cases, indeed, several relaxation times are present. For example, the formation of bonds and their lifetime depend on the interface [17] and molecular diffusion is not the same for molecules more or less close to the interfaces. The main merit of analysis of such situations using stretched exponentials to account for the variety of relaxation times is to define an average time $<\tau>$ that can be followed in function of external parameters, namely the temperature, although its numerical value is not necessarily very significant.

It was established [7] that the temperature dependence $<\tau>$ is super-Arrhenius above 220 K and Arrhenius at lower temperatures, what was interpreted as dynamic cross-over of water under confinement, in this case hydration water of lysozyme. Trying to relate this observation to the dynamics of supercooled water, it is possible that, at temperatures below 220 K, all translational motions are frozen and that the only contribution to the incoherent scattering is due to the hydrogen bond dynamics, with an Arrhenian dependence on temperature. In other words, dynamics of bulk and confined water are similar below 220 K.
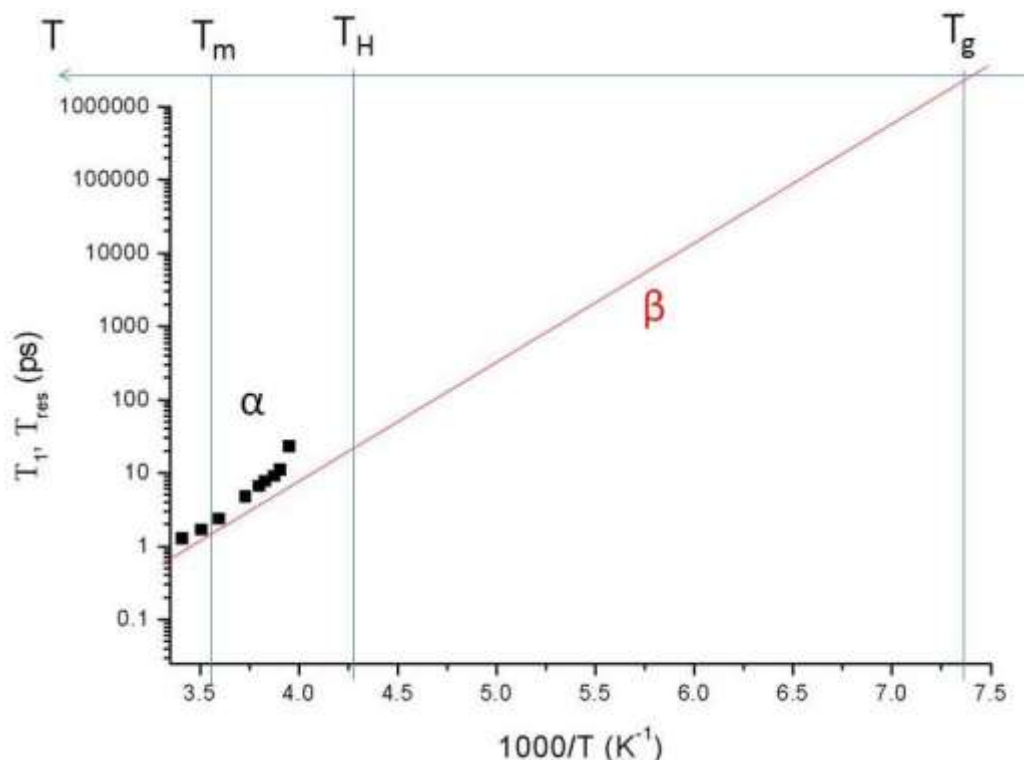

Figure 3

Schematic representation of α and β relaxation in liquid water. Black squares are measured values of the residence time. In the same temperature range, the straight line represents the Arrhenius temperature dependence of hydrogen bond life-time which extrapolates to the glass transition at T_g. T_M is the melting temperature and T_H is the temperature of homogeneous nucleation of crystalline ice.

Taking into account these results, mixture models or postulating the existence of heterogeneities are not compatible with the available experimental data. Likely, more attention should be paid to the fact that both the extrapolated values of criticality and dynamic crossover coincide with the experimental value of homogeneous nucleation temperature, T_H, within a few degrees. Actually, it has been established since a long time [18] that the local structure of liquid water converges to that of LDA at T_H, far above the glass transition temperature, T_g , what means that at T_H, the remaining disorder is due only to hydrogen bonds and rotations of hydrogen atoms around the centres of mass of water molecules. Similarly to polymer dynamics, it is possible to call α relaxation, that related to translational motions of molecules and β relaxation that of hydrogen bonds, the first being strongly non-Arrhenius while the second is Arrhenius [19] (figure 3).

However, contrary to the case of polymers, at the macroscopic level it is the β relaxation that imposes the glass transition. Between T_H and T_g, small amplitude rotations of hydrogen atoms allow crystallisation of the stable crystalline form of ice, what is consistent with the relatively small enthalpy change observed at the glass transition.

This relatively simple picture, free of heterogeneities or critical behaviour is compatible with available experimental data and also with the majority of effective potentials used in computer simulations.

Because of the large extension of the domain of stability of liquid water it is unlikely that a general consensus about its properties can be reached. At the best, experiments performed in the accessible regions of temperature and pressure can reduce the number of postulated models. The present work based in two neutron scattering techniques is presented in this context. Other experiments and comparisons will be necessary to solve, whenever possible, what is called the "water conundrum". [20].

References
[1]   Geiger A, Stillinger FH and Rahman A 1979 *J. Chem. Phys.* **70** 4185
[2]   Némethy GN and Scheraga HA 1962 *J. Chem. Phys.* **36** 3382
[3]   Kell GS 1975 *J. Chem. and Engineering Data* **20** 97
[4]   Speedy RJ and Angell CA 1976 *J. Chem. Phys.* **65** 851
[5]   Mishima O, Calvert LD and Whalley E 1984 *Nature* **310** 393 and 1985 *Nature* **314** 76
[6]   Mishima O and Stanley HE 1998 *Nature* **396** 329
[7]   Chen S-H, Liu L, Fratini E, Baglioni P, Faraone A and Mamontov E 2006 *PNAS* **103** 9012.
[8]   Pettersson LGM and Nilsson A 2015 *J. Non-Crystalline Solids* **407** 399
[9]   Hendricks RW, Mardon PG and Shaffer LB 1974 *J. Chem. Phys.* **61** 319
[10]   Bosio L, Teixeira J and Stanley HE 1981 *Phys. Rev. Lett.* **46** 597; Bosio L, Teixeira J and
            Bellissent-Funel M-C 1989 *Phys. Rev.* **A39** 6612 (1989); Clark GNI, Hura GL,
            Teixeira J,Soper AK and Head-Gordon T 2010 *PNAS* **107** 14003
[11]   Johari G and Teixeira J 2015 *J. Phys. Chem. B* **119** 14210
[12]   Teixeira J, Bellissent-Funel M-C, Chen S-H and Dianoux AJ 1985 *Phys. Rev.* **A31** 1913
[13]   Qvist J, Schober H and Halle B 2011 *J. Chem. Phys.* **134** 144508
[14]   Martiniano HFMC and Galamba N 2013 *J. Phys. Chem. B* **117** 16188
[15]   Stanley HE and Teixeira J 1980 *J. Chem. Phys.* **73** 3404; Teixeira J 2008 *Pramana -J. of Physics*
            71 761
[16]   d'Arrigo G and Teixeira J 1990 *J. Chem. Soc. Faraday Trans.* **86** 1503
[17]   Russo D, Ollivier J and Teixeira J 2008 *Phys. Chem. Chem. Phys.* **10** 4968
[18]   Bosio L, Teixeira J, Dore JC, Steytler D and Chieux P 1983 *Mol. Phys.* **50** 733; Bellissent-Funel
            M-C, Bosio L, Dore JC, Teixeira J and Chieux P 1986 *Europhys. Lett.* **2** 241
[19]   Swenson J and Teixeira J 2010 *J. Chem. Phys.* **132** 014508; Teixeira J, *Water* 2010 **2** 702
[20]   Luzar A 2000 *J. Chem. Phys.* **113** 10663