

Effects of pressure and confinement on liquid water

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 244120

(<http://iopscience.iop.org/0953-8984/20/24/244120>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 12:39

Please note that [terms and conditions apply](#).

Effects of pressure and confinement on liquid water

M-C Bellissent-Funel

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

Received 29 February 2008

Published 29 May 2008

Online at stacks.iop.org/JPhysCM/20/244120

Abstract

The effects of hydration on equilibrium protein structure and dynamics are fundamental to the relationship between structure and biological function. In particular, the configuration of water molecules near the hydrophilic–hydrophobic interfaces is of considerable relevance. The structure of water, confined in model systems developing either hydrophilic or hydrophobic interactions, is compared with that of bulk supercooled water and water under pressure, as determined by neutron scattering.

1. Introduction

Liquid water is a particularly complex molecular liquid. This is due essentially to intermolecular hydrogen bond formation. The hydrogen bonding is established between two oxygen atoms through a proton and the electronic distribution called a ‘lone pair’ which is due to the hybridization of the electronic orbitals. The H-bonds have interaction energies comparable to ionic bonds and are characterized by a high directionality which gives rise to a locally tetrahedral coordination of water molecules [1]. Another characteristic of liquid water is the short hydrogen bond lifetime (between 10^{-13} and 10^{-12} s).

In the presence of a solid substratum, water may form bonds. This is the case, for instance, of glasses where silanol groups Si–O–H are present at the interface between water and silica. It is worth noting that in the presence of biological macromolecules, such as peptides, enzymes, proteins and DNA, various behaviours can be found depending on the nature (more or less hydrophilic or hydrophobic) of each site or residue. Bonds, in particular, certainly play a major role in the structure of these macromolecules.

However, in many common situations, water is not in its bulk form but instead attached to some substrates or filling some cavities [2]. In particular, in living systems, essential water-related phenomena occur in restricted geometries in cells, and at active sites of proteins and membranes, or at their surface. We know that this interfacial or confined water plays a crucial role in the stability and the catalytic function of biological macromolecules.

This paper reports on the microscopic structural properties of confined water as compared with those of bulk water.

The structural properties of bulk water are now mostly well understood over some range of temperatures and pressures using different techniques such as x-ray diffraction [3–5], neutron scattering [6–10], molecular dynamics (M-D) [11, 12] and Monte Carlo (MC) [13] simulations. The number of models of its structure is very large and the number of experimental results enormous.

The polymorphism of water is indeed remarkable and besides these entire crystalline phases [14] one must add two amorphous solids, low-density amorphous ice (LDA) and high-density amorphous ice (HDA). Recently, a very high-density amorphous ice (VHDA) has been obtained. The microscopic structure of these forms of amorphous ice as prepared by different techniques has been studied both by x-ray [15, 16] and neutron scattering [17–19].

In this paper, we recall the structural properties of water in its bulk form as functions of temperature and pressure. We define what we call confined or interfacial water. We compare the structural properties of confined water with that of bulk water. We report also on some unusual nucleation of water confined in a porous silica glass and on structural properties of water confined in activated carbon powder.

2. Microscopic structure of bulk water

2.1. Supercooled water at normal pressure, as a function of temperature: neutron pair correlation functions $d_L(r)$

According to the temperature range of the experiment, two kinds of D₂O samples have been used: (i) pure liquid D₂O and, in order to increase the degree of supercooling of water, (ii) D₂O in emulsions with sorbitan as a surfactant. The emulsion

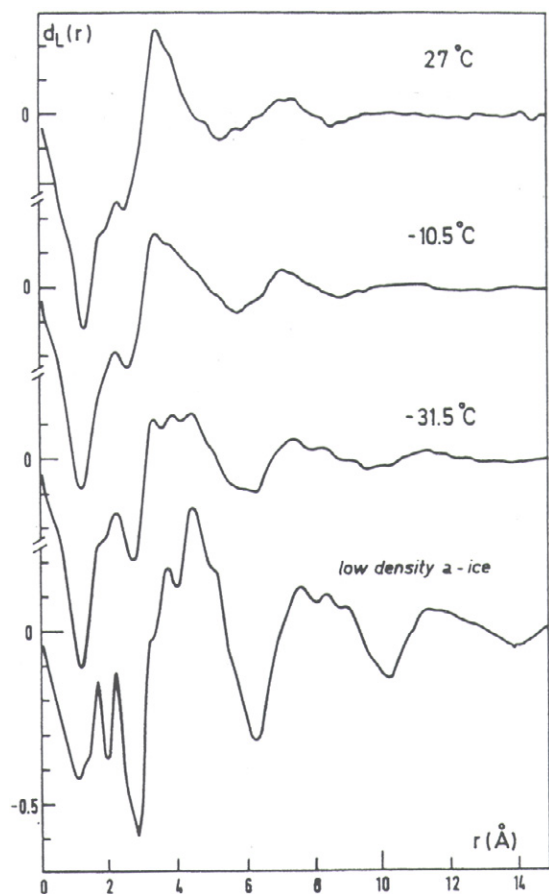


Figure 1. Neutron pair correlation functions $d_L(r)$ of supercooled D_2O , at normal pressure, as compared with that of low-density amorphous ice at 77 K [17].

was constituted either with deuterioheptane or with a mixture of deuterioheptane and CCl_4 . The average size of the water droplets in the emulsion was around some μm .

The neutron composite pair correlation functions of supercooled water [20] at -10.5 and $-31.5^\circ C$ are displayed in figure 1 and compared with that of low-density amorphous ice [17].

At $-31.5^\circ C$, in the small- r range, some features characteristic of low-density amorphous ice show up. In particular, the O-D hydrogen bond distance at 1.82 \AA and the D-D intermolecular distance at 2.31 \AA are present. In the large- r range one observes additional small oscillations that are not present at $-10.5^\circ C$ and an out-of-phase behaviour of the broad oscillations for values of r higher than 10 \AA . These features are similar to those observed in low-density amorphous ice.

At normal pressure and low temperature, the measurements confirm the increasing spatial correlations in very supercooled water as the temperature is decreased and the tendency to evolve towards the structure of low-density amorphous ice. In supercooled water, the structure present between 4.5 and 6.0 \AA is connected to the formation of tetrahedrally coordinated patches [21]. It is clear that such patches are not present in high-pressure liquid water, either because the hydrogen bonds

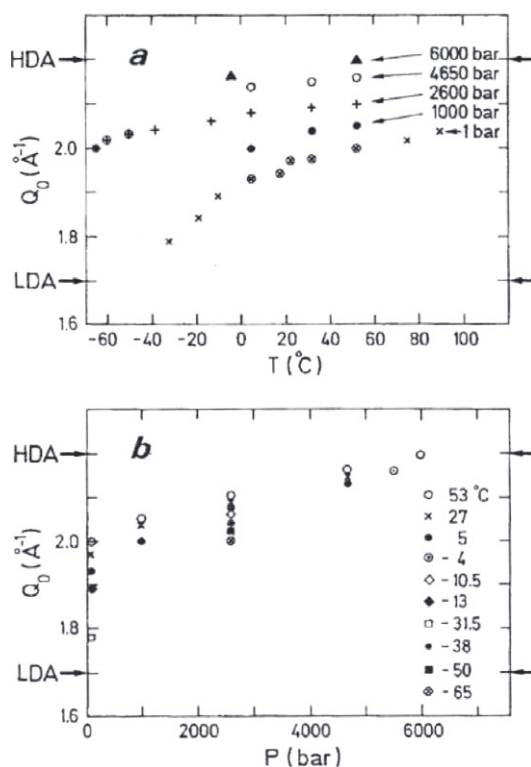


Figure 2. Evolution of the main diffraction peak position Q_0 of the structure factor: (a) at constant pressure, and as a function of temperature; (b) at constant temperature, and as a function of pressure [22].

are broken, i.e. the molecular energy is on average too low, or, more likely, because the hydrogen bond network is distorted.

2.2. Liquid water under pressure

2.2.1. Evolution of main diffraction peak Q_0 of the structure factor [22]. The microscopic structure of liquid water under pressure has been studied at pressures up to 6000 bar and for a range of temperatures from 53 down to $-65^\circ C$. The experiments have been performed by neutron diffraction with similar samples as described in section 2.1 using a Ti-Zr pressure cell made with a ‘null’ Ti-Zr alloy [22].

From normal pressure to 6000 bar, the effect of temperature becomes smaller, which confirms that the effect of pressure is to reduce the anomalies of liquid water that evolves to a normal associated liquid [23]. Figure 2(a) gives the evolution of the main diffraction peak position Q_0 of the structure factor, at constant pressure, and as a function of temperature. Figure 2(b) gives the evolution of Q_0 at constant temperature, and as a function of pressure [22].

2.2.2. Neutron pair correlation functions $d_L(r)$ [22]. Figure 3 gives the composite pair correlation functions of water under 6000 bar and, at respectively -4 and $53^\circ C$, as compared with that of high-density amorphous ice. Upon increasing the temperature up to $53^\circ C$ it appears that there is a slight evolution of the $d_L(r)$ functions that present the characteristics of that of high-density amorphous ice [17]. All the peaks are

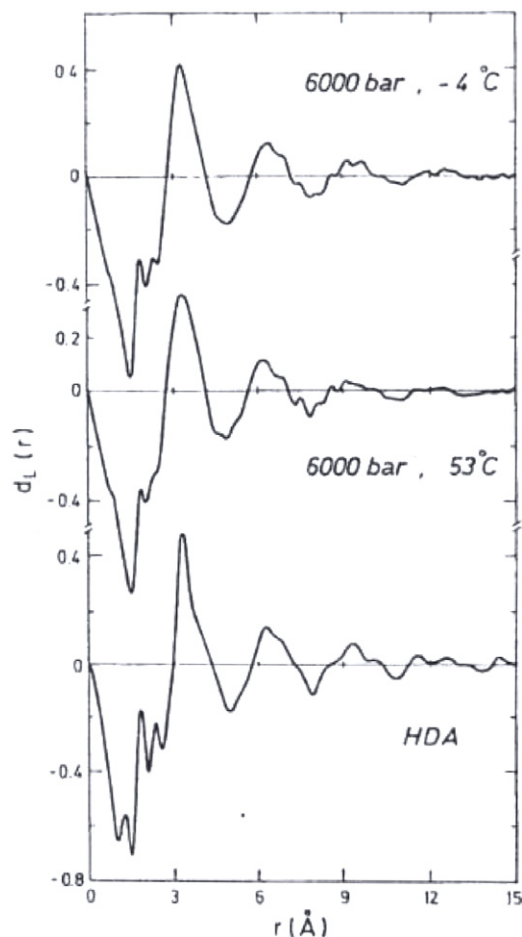


Figure 3. Neutron pair correlation functions $d_L(r)$ of liquid D_2O , under 6000 bar, as compared with that of high-density amorphous ice (HDA) at 77 K [17].

broader, showing that interatomic correlations become weaker as the pressure is increased at high temperature. A very broad peak is present at 3.34 Å and a minimum exists at 5.0 Å, i.e. in the region where there is a maximum for the low-density form. The O–D hydrogen bond distance and the D–D intermolecular distance are shifted respectively to 1.84 Å and 2.36 Å. Moreover, the peaks observed by x-ray [16] at 2.8 Å and around 4.6 Å appear as small bumps.

On the one hand, at normal pressure and low temperature, the measurements confirm the increasing spatial correlations in very supercooled water as the temperature is decreased and the tendency to evolve towards the structure of low-density amorphous ice. On the other hand, the structural study of liquid water, at 6000 bar and respectively -4°C and 53°C [22], confirms the tendency that high-density amorphous ice appears as the limit of liquid water at high temperature and high pressure.

Under a pressure of 6000 bar, the highest pressure to be reached with our pressure experimental set-up, the $d_L(r)$ function of liquid water at 53°C exhibits features which are characteristic of high-density amorphous ice. If, for the supercooled water the structure present between 4.5 and 6.0 Å is connected to the formation of tetrahedrally coordinated patches, it is clear that such patches are not present in high-pressure liquid water, either because the hydrogen bonds are

broken, i.e. the molecular energy is on average too low, or, more likely, because the hydrogen bond network is distorted.

3. Microscopic structure of confined water

In many technologically important situations, water is not in its bulk form but is instead attached to some substrates, or filling small cavities. Common examples are: water in porous media, such as rock or sandstones, and water in biological material such as in the interior of cells or attached to surfaces of biological macromolecules and membranes. This is what we define here as the ‘confined’ or ‘interfacial water’.

Water in confined space has attracted a considerable amount of interest in recent years. It is commonly believed that the structure and dynamics of water are modified by the presence of solid surfaces, both by a change of hydrogen bonding and by modification of the molecular motion that depends on the distance of water molecules from the surface [2].

3.1. Hydrophilic interactions

Among the hydrophilic model systems, let us mention clay minerals [24, 25] and various types of porous silica [26, 27]. In the last case, the authors have interpreted their results in terms of a thin layer of surface water with more extensive H-bonding, lower density and mobility and lower nucleation temperature as compared to bulk water.

The structure of water confined in a Vycor glass¹ has been studied by neutron diffraction. Vycor glass is a porous silica glass, characterized by quite a sharp distribution of cylindrical interconnected pores, and hydrophilic surfaces. We present here some of our results which have been obtained as functions of the level of hydration from full hydration (0.25 g water/g dry Vycor) down to 25% and temperature [28]. Based on the information that the dry density of Vycor is 1.45 g ml^{-1} , the porosity 28% and the internal cylindrical pores of cross-sectional diameter 50 Å, the 50% hydrated sample has three layers of water molecules on its internal surface and a 25% hydrated sample corresponds roughly to a monolayer coverage.

3.1.1. Fully and partially hydrated Vycor. Results for two levels of hydration of Vycor demonstrate that the fully hydrated case is almost identical to bulk water and the partially hydrated case is little different. However, the three site–site radial correlation functions are indeed required for a sensible study of the orientational correlations between neighbouring molecules [29]. An interesting feature is that we observe, as in the differential analysis measurements, supercooling of water to a much lower temperature of -27°C in a partially hydrated sample compared to a fully hydrated sample (-18°C) [28].

It seems that the confinement of the water favours the nucleation of cubic ice that appears superimposed on the spectrum of liquid water and whose proportion can be deduced from the intensity of the (111) Bragg peak. The proportion of cubic ice increases with decreasing temperature. In fact, at -100°C , the spectrum of confined water looks similar to

¹ Vycor brand porous no. 7930 is a product of Corning Glass Works.

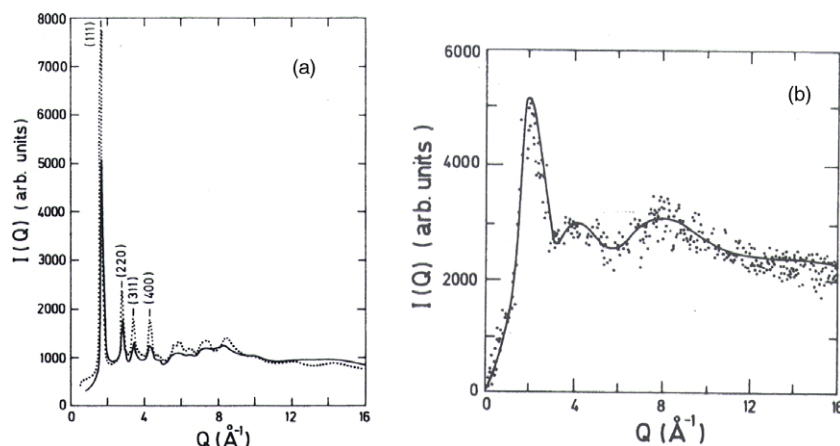


Figure 4. (a) Spectrum of cubic ice (-198°C) (dotted line) compared with that of confined D_2O at -100°C from fully hydrated Vycor (full line) [28]. (b) Spectrum of confined D_2O at -18°C from fully hydrated Vycor after subtraction of Bragg peaks. There is 23% liquid water [28].

that of cubic ice (figure 4(a)). This is in sharp contrast to bulk water that always nucleates into hexagonal ice. In figure 4(b), we show a spectrum which gives clear evidence of water which is present below the Bragg peaks at -18°C obtained by subtraction of the weighted spectrum of the same sample cooled down to -100°C . The main diffraction peak position is close to 2 \AA^{-1} . It looks like confined water from fully hydrated Vycor behaves like water under pressure [22]. From high-energy x-ray experiments Reichart and coworkers [30] have observed at the ice– SiO_2 interface the formation of a quasiliquid layer displaying a large density close to 1.2 g cm^{-3} , and to that of confined water from fully hydrated Vycor.

3.1.2. Monolayer water coverage at Vycor surface. Results relative to a 25% hydrated Vycor sample indicate that, at room temperature, interfacial water has a structure similar to that of bulk supercooled water at a temperature of about 0°C which correspond to a shift of about 25 K [31]. Therefore the structure of interfacial water is characterized by an increase of the long-range correlations that corresponds to the building of the H-bond network as it appears in low-density amorphous ice [17]. There is no evidence of ice formation when the sample is cooled from room temperature down to -196°C (liquid nitrogen temperature) [31]. Moreover, we have demonstrated the existence of a liquid–liquid transition in the interfacial water [31].

3.2. Hydrophobic interactions

Among model systems developing hydrophobic interactions, one experimental investigation of particular interest concerns the structure of water contained in activated carbon powder [32]. The structure of water has been determined both by x-ray and neutron diffraction, as functions of hydration, from room temperature down to 77 K. In agreement with previous work [26, 28], this study gave support to the existence of a region near the interface where the properties of water are markedly different from those of the bulk liquid. From x-ray measurements, which yield information about the oxygen–

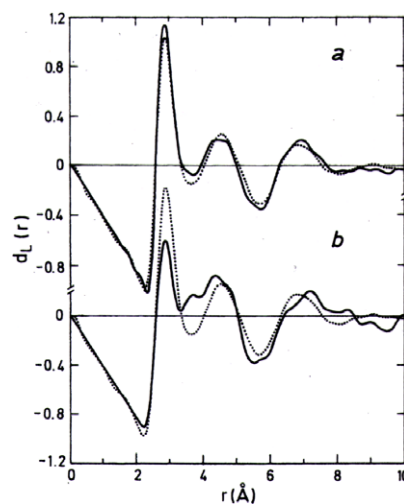


Figure 5. The x-ray pair correlation functions, $d_L(r)$, of water contained in activated carbon, at room temperature shown by solid lines for 188% (curve a) and 42% (curve b). For comparison the $d_L(r)$ of bulk water at the same temperature is also drawn (dotted line) [32].

oxygen distribution function, it appears that, at the lowest investigated water content (42% hydration level), a distortion of the tetrahedral ordering is clearly observed (figure 5(b)). Neutron scattering experiments can be analysed to describe the intermolecular correlations (figure 6): at a low degree of hydration the hydrogen bonding is modified and water molecules are more ordered. It is not possible to determine the thickness of the affected layer. However, a crude determination from the specific area indicates that, for a hydration level equal to 50%, the thickness does not exceed 5 \AA . This value must be compared with the computer simulations data [33] which indicates that structural modifications do not extend beyond 10 \AA from the solid surface. When partially hydrated samples are cooled down to 77 K, no crystallization peak is detected by differential thermal analysis. X-rays and neutrons show that an amorphous form is obtained and its structure is different from those of the low- and high-density amorphous ices already

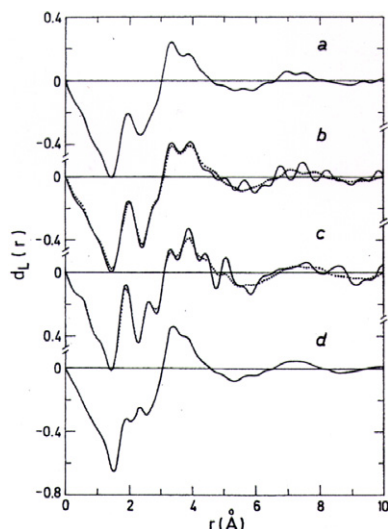


Figure 6. The neutron pair correlation functions, $d_L(r)$, of water contained in activated carbon at room temperature shown by solid lines for 200% (curve a), 50% (curve b) and 25% hydration (curve c), and bulk water at the same temperature (curve d) [32].

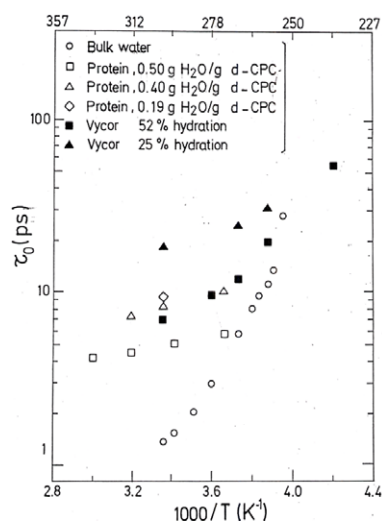


Figure 7. Arrhenius plot of the residence time τ_0 for bulk water, for two levels of hydration of Vycor and for three levels of hydration of a C-phycoyanin protein.

known [17]. This phenomenon looks similar in model systems developing either hydrophilic or hydrophobic interactions. However, in order to characterize more precisely the nature of the amorphous phase, the site-site partial correlation functions need to be experimentally obtained and compared with those deduced from molecular dynamics simulations. Samples with lower levels of hydration corresponding to one monolayer coverage of water molecules are under investigation.

4. Conclusion

To conclude let us focus on the microscopic dynamics of water confined in Vycor, as studied by inelastic neutron scattering. The short time diffusion (a few picoseconds) of water molecules close to the Vycor surface has been described

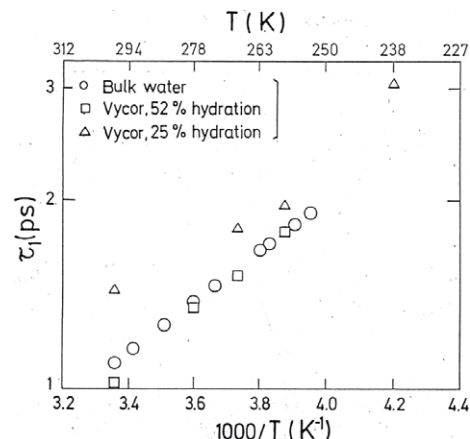


Figure 8. Arrhenius plot of the H-bond lifetime τ_1 for bulk water and for two levels of hydration of Vycor.

in terms of a simple model for all the studied samples [34]. At short times, the water molecules, close to some hydrophilic surface, perform very local rotational jumps characterized by D_t and τ_1 , as in bulk water, but with a longer residence time τ_0 on a given site.

Figures 7 and 8 represent respectively the residence time τ_0 and the H-bond lifetime τ_1 of water molecules for bulk and confined water.

An alternative model, the relaxing cage model, has been successful in accounting for data from nanosecond time molecular dynamics simulations of supercooled water [35]. The relaxing cage model uses an idea borrowed from mode-coupling theory (MCT) of supercooled liquids. Mode-coupling theory focuses its attention on the ‘cage effect’ in the liquid state, that can be pictured as a transient trapping of molecules by their neighbours as a result of the lowering of the temperature [36]. In this model, diffusion is strongly coupled to the local structural rearrangements or the structural relaxation. This sophisticated model leads to the same conclusion as the simple model, let us say, a retardation of water molecules at the surface of hydrophilic model systems.

References

- [1] Walrafen G 1981 *Water: A Comprehensive Treatise* vol 1, ed F Franks (New York: Plenum) chapter 5
- [2] Bellissent-Funel M-C and Teixeira J 2004 Structural and dynamic properties of bulk and confined water *Freeze-Drying/Lyophilization of Pharmaceutical and Biological Products* ed L Rey and J C May (New York: Dekker) pp 53–77
- [3] Narten A H and Levy H A 1972 *Water: A Comprehensive Treatise* vol 1, ed F Franks (New York: Plenum) p 311
- [4] Egelstaff P A 1983 *Adv. Chem. Phys.* **53** 1
- [5] Okhulkov A V, Demaniets Yu N and Gorbaty Yu E 1994 *J. Chem. Phys.* **100** 1578
- [6] Chen S H and Teixeira J 1985 *Adv. Chem. Phys.* **64** 1
- [7] Dore J C 1985 *Water Science Reviews* vol 1, ed F Franks (Cambridge: Cambridge University Press) p 3
- [8] Bellissent-Funel M-C 1991 *Hydrogen Bonded Liquids (NATO ASI Series C* vol 329) ed J C Dore and J Teixeira (Dordrecht/Boston/London: Kluwer Academic) p 117

- [9] Bellissent-Funel M-C and Bosio L 1995 *J. Chem. Phys.* **102** 3727
- [10] Bellissent-Funel M-C 1995 *Physical Chemistry of Aqueous Systems* ed H J White Jr, J V Sengers, D B Neumann and J C Bellows (New York: Begell House) p 332
- [11] Poole P H, Sciortino F, Essmann U and Stanley H E 1992 *Nature* **360** 324
- [12] Harrington S T, Zhang R, Poole P H, Sciortino F and Stanley H E 1997 *Phys. Rev. Lett.* **78** 2409
- [13] Madura J D, Petit B M and Calef D F 1988 *Mol. Phys.* **64** 325
- [14] Hobbs P V 1974 *Ice Physics* (Oxford: Clarendon)
- [15] Mishima O, Calvert L D and Whalley E 1985 *Nature* **314** 76
- [16] Bizid A, Bosio L, Defrain A and Oumezzine M 1987 *J. Chem. Phys.* **87** 2225
- [17] Bellissent-Funel M-C, Teixeira J and Bosio L 1987 *J. Chem. Phys.* **87** 2231
- [18] Bellissent-Funel M-C, Bosio L, Hallbrucker A, Mayer E and Sridi Dorbez R 1992 *J. Chem. Phys.* **97** 1282
- [19] Loerting T, Salzmann C, Kohl I, Mayer E and Hallbrucker A 2001 *Phys. Chem. Chem. Phys.* **3** 5355
- [20] Bellissent-Funel M-C, Teixeira J, Bosio L and Dore J C 1989 *J. Phys.: Condens. Matter* **1** 7123
- [21] Boutron P and Alben R 1975 *J. Chem. Phys.* **62** 4898
- [22] Bellissent-Funel M-C and Bosio L 1995 *J. Chem. Phys.* **102** 3727
- [23] Stanley H E and Teixeira J 1980 *J. Chem. Phys.* **73** 3404
- [24] Hawkins R K and Egelstaff P A 1980 *Clays Clay Minerals* **28** 19
- [25] Soper A K 1991 *Hydrogen-Bonded Liquids* vol 329, ed J C Dore and J Teixeira (Dordrecht/Boston/London: Kluwer Academic) p 147
- [26] Dore J C, Coveney F and Bellissent-Funel M-C 1992 *Recent Developments in the Physics of Fluids* ed W S Howells and K Soper (Bristol: Hilger) p 299
- [27] Christenson H K 2001 *J. Phys.: Condens. Matter* **13** R95
- [28] Bellissent-Funel M-C, Bosio L and Lal J 1993 *J. Chem. Phys.* **98** 4246
- [29] Bruni F, Ricci M A and Soper A K 1998 *J. Chem. Phys.* **109** 1478
- [30] Engemann S, Reichert H, Dosch H, Bilgram J, Honkimäki V and Snigirev A 2004 *Phys. Rev. Lett.* **92** 205701
- [31] Zanotti J-M, Bellissent-Funel M-C and Chen S-H 2005 *Europhys. Lett.* **79** 91
- [32] Bellissent-Funel M-C, Sridi-Dorbez R and Bosio L 1996 *J. Chem. Phys.* **104** 10023
- [33] Lee S H and Rossky P J 1994 *J. Chem. Phys.* **100** 3334
- [34] Bellissent-Funel M-C 2003 *Eur. Phys. J. E* **12** 83
- [35] Chen S H 1999 *Hydration Processes in Biology: Theoretical and Experimental Approaches* vol 305, ed M-C Bellissent-Funel (Amsterdam/Berlin/Oxford/Tokyo/Washington, DC: IOS Press)
- [36] Gotze W and Sjogren L 1992 *Rep. Prog. Phys.* **55** 241