

A POSSIBLE BOOLCHAND INTERMEDIATE PHASE IN WATER

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The structure of water as a function of temperature was modelled. A faint peak before the first main peak in the diffraction pattern of the water in the region of the anomaly was evidenced. The peak was interpreted as the signature of a regular packing of quasi-planar clusters. The special structure with clusters with low coordination water molecules demonstrated by modeling, points out to the formation of a kind of Boolchand intermediate phase. The intermediate phase window is reflected in the anomaly of the specific heat and compressibility.

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1. Introduction

Around 1980 J. C. Phillips [1] developed a new theory where the network glasses were viewed as space-filling network subjected to bond stretching and bond bending constraints. P. Boolchand [2] extended his own data on the stiffness transition in chalcogenide glasses and discovered the so-called intermediate phase defined by two abrupt stiffness transitions [3]. The Boolchand phase is characterized by a nearly vanishing non-reversible enthalpy of the glass transition and a nearly zero internal network stress. The new intermediate phase has been identified and its limits were accurately established in several chalcogenides, oxides, in silver based electrolytes and even in alcohols, sugars and proteins [4, 5]. The disordered networks of covalent, ionic and H-bonded solids acquire unusual functionalities in intermediate phases, which are formed in a narrow but well-defined range of connectivity. No intermediate phase has been reported in liquid materials up to now, after our knowledge.

Water is an ubiquitous liquid. In spite of many efforts of the scientists the structure of water as a function of temperature is not well known. The anomaly at 4 °C is the most popular one, but few scientists discussed another anomaly situated around 50 °C. No definite structural explanations have been reported in the literature for both anomalies. We are pursuing a program of structural modeling of the water structure in the frame of the valence force field theory applied to water molecules.

A general structural feature of water viewed as a system of clusters is discussed. The special structure of water around 50 °C is considered. The structure factor fits well the XRD pattern of water. The water structure has been interpreted as an evidence of a phase similar to the Boolchand intermediate phase in solid disordered networks.

2. Experimental and modelling

The experimental data of X-ray diffraction, carefully measured by Narten et al. [6] for various temperatures, are illustrated in Fig. 1.

In Fig. 1b is shown at large scale the structure factor of water around the 50 °C, below the first diffraction peak. It is remarkable the presence of a small large peak at $Q \sim 0.7 \text{ \AA}^{-1}$. This peak

was observed also in amorphous materials with layer – like structure and has been called first sharp diffraction peak (FSDP). Its appearance is probably related to a special structure of the molecular clusters in the material.

After careful examination of the XRD patterns in the region of the water anomaly, we observed on the XRD curve recorded at 50 °C a small but convincing diffraction peak in the low angles region, before the main split peak. In order to demonstrate the significance of this peak and to extract its parameters (position on the 2θ scale and width), we calculated the derivative of that part of XRD pattern. Surprisingly, a significant modulation peak appeared. From this modulation we calculated the exact position and width of the XRD pre-peak. These are: $Q=0.88 \text{ \AA}^{-1}$ ($d = 7.14 \text{ \AA}$) and $\Delta Q = 0.15 \text{ \AA}^{-1}$. The peak parameters are in agreement with the packing of quasi-planar cage configurations at a distance of $1.23 d$ (8.78 \AA). The thickness of the ordered packing is $\sim 30 \text{ \AA}$, that corresponds to 3-4 packed layers.

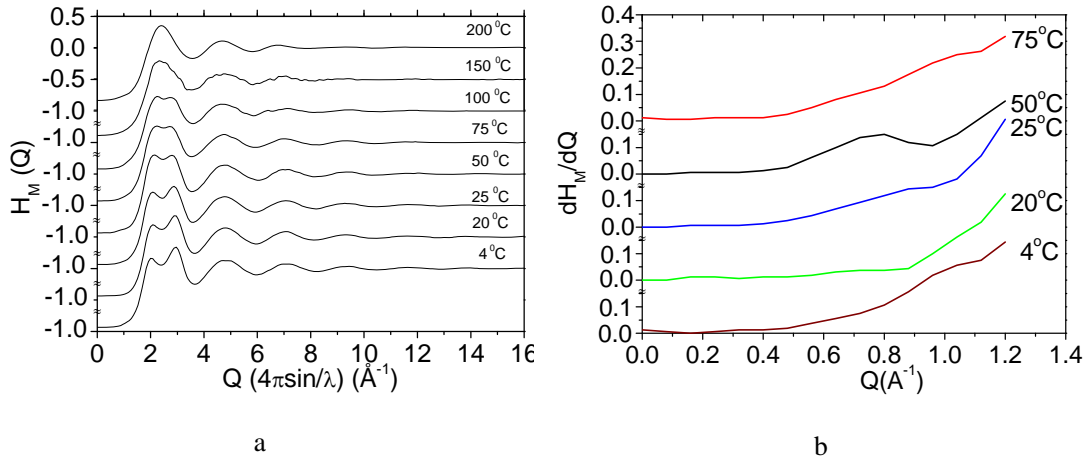


Fig. 1 a X-ray diffraction pattern of the liquid water at different temperatures b The region at low angles (FSDP region) in the X-ray diffraction pattern of the water measured at 50 °C. Derivative of the XRD curve is shown in order to point out the FSDP.

In XRD curves of water it is observed a split main peak. The second component of the peak changes with the temperature. Its intensity decreases and at high temperatures practically disappears.

The modeling of the complex feature of the structure factor of water for different temperatures is an useful approach for revealing the structure of water and its evolution with temperature.

By melting, a phase transition occurs in ice. The ordered diamond-like arrangement of the water molecules is destroyed. The diamond cages stepwise collapse. The density of the water increases till the maximum value at 4 °C. We interpret this feature as a consequence of gradual softening of the bond bending force constants in the H_2O molecular network, equivalent to the loss of sp^3 hybridization and tendency to sp^2 one. The water clusters that form and destroy at a high rate are randomly oriented. By softening the force constants of the H-mediated valence bonds the water molecules build more or less extended and more or less distorted clusters. (Fig. 2). The distorted clusters may pack as rafts and this packing gives rise probably to a special low-angle peak called first sharp diffraction peak (FSDP).

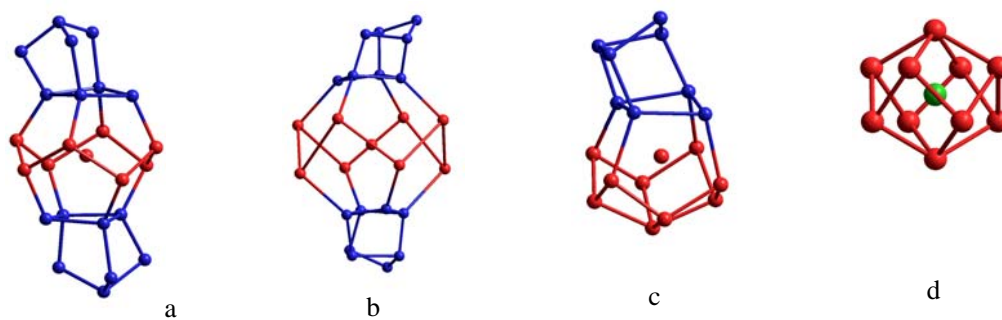


Fig. 2. Structural model of the basical cluster for water at a) 4 °C b) 50 °C c) 150 °C d) 200 °C
a. 24+1 water molec. b. 24+1 water molec. c. 17+1 water molec. d. 10+1 water molec.

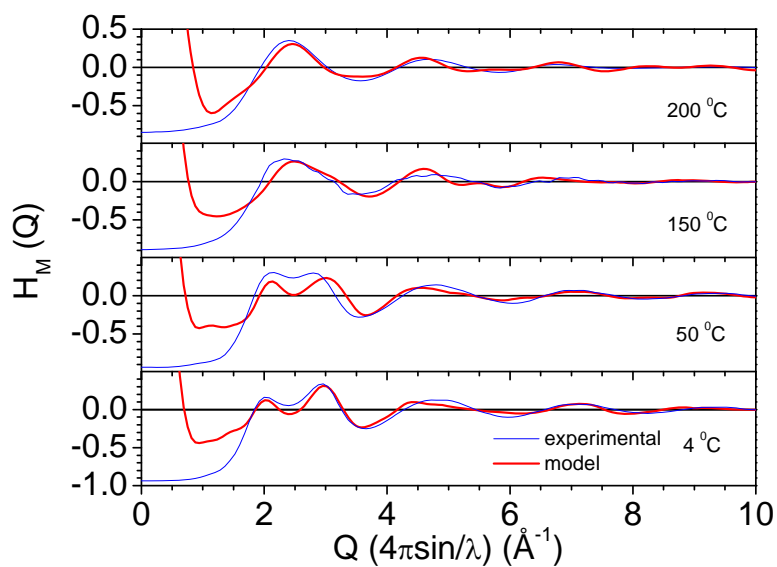


Fig. 3. XRD pattern for experimental and calculated from the relaxed models at
a) 4 °C b) 50 °C c) 150 °C d) 200 °C

The model for 50 °C water reproduces enough good the FSDP (Fig 3). The discrepancy in intensity and width is due to the statistical character of the cluster model. From the model we calculated the position of FSDP at $Q \sim 1.136 \text{ \AA}^{-1}$ $d = 5.53 \text{ \AA}$ in satisfactory agreement with the experimental Q .

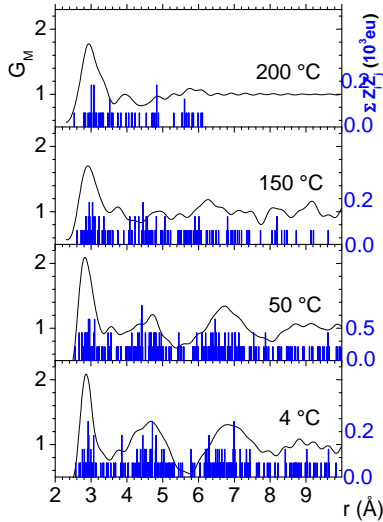


Fig. 4. Experimental RDF of water at different temperatures compared with the histograms of the models

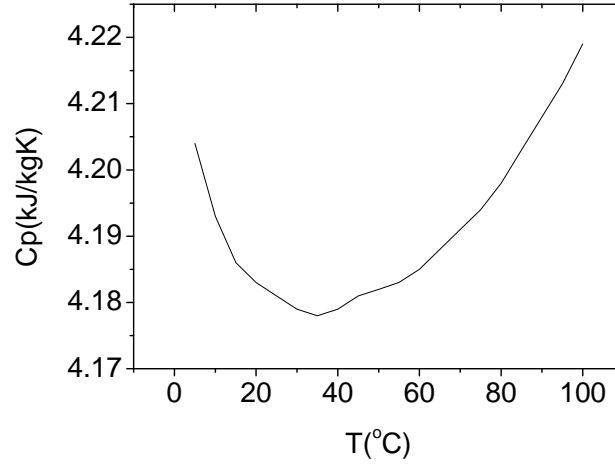


Fig. 5. The C_p as a function of temperature for liquid water (experimental)

Let's look now to the case of solid and liquid chalcogenides (e. g. GeSe_2 or As_2Se_3). As well known, the structure of these materials are layer-like. This structure gives rise to a prominent first sharp diffraction peak both in the amorphous solid state and in liquid state [7]. During liquid heating the FSDP continues to increase and becomes narrower this demonstrating a better ordering of the disordered layers in the structure. Elliott [8, 9] explained the FSDP in network glasses and liquids as a chemically-ordered pre-peak due to interstitial voids ordered around cation-centered clusters.

We admit that a similar process takes place in water. Due to the weakening of the bonding constraints, the spatial configuration of the molecules forming the water clusters becomes more ordered and the ordered planes define a diffraction peak at low angles (large inter-cluster distances). Due to the existence of two distances, short and long, characteristic to the softening of the bond bending force constant and of the approaching to octahedral configurations, the two sub-peaks of the main peak are intense. The two peaks approaches one to another and finally unite in a single larger peak at 150 °C. This feature can be explained by the formation of new clusters and of a more complex system of molecules.

The FSDP at ~50 °C is explained by a special configuration of water molecules (see Fig. 3 b). Models with packing of various type of clusters have been built and relaxed by computer with the equilibrium bond angle and bonding distance force constants specific to valence force field theory [10, 11].

3. Discussion

The pre-peak in the diffraction pattern at 50 °C seems to be related to the water anomaly. In the table 1 and Fig. 4 below we show the behaviour of the caloric parameters around this temperature:

Table 1. The water anomaly around 50 °C

Temperature	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
Specific heat $C_p(\text{J.mol}^{-1}.\text{K}^{-1})$	75.38	75.30	75.29	75.33	75.39	75.49	75.61	75.76
Isothermal compressibility $K_T(\text{GPa}^{-1})$	0.4589	0.4477	0.4424	0.4417	0.4450	0.4516	0.4614	0.4743

Finally, we remark that the water anomaly, which is related especially to the caloric and mechanical parameters is similar with the observations of a similar anomaly in many glasses in a narrow window of compositions, judging after the non-reversible enthalpy curves determined by various authors and well-documented [1-5].

Recent developments suggest that classification of glasses based on their elastic response in terms of the three regimes: flexible, intermediate and stressed-rigid is not limited to covalent networks but may well be a generic feature of the disordered state of matter. A common thread linking various systems is the interplay between short-range forces that serve as constraints, and long range ones that stabilize different macroscopic structures (as e.g. protein, organic polymers and DNA [12]). The basic interactions operating at different length scales are important in self-organization of the matter at any scale.

If a similar phase appears in water then a window related to the interval stress-rigid – stress-free state of water must be defined. For lower temperatures the water molecules form clusters that show the tendency to form links characterized by tetrahedral bridges between molecules.

Therefore, the bottom limit under 40 °C should corresponds to coordination 4, while the upper limit (above 50 °C) corresponds to lower coordination (according to the model) and even much lower if free molecules are considered in the model.

A glass upon heating softens at characteristic temperature known as the glass transition temperature, T_g , when molar volumes (V) and enthalpy (H) undergo a qualitative change. The temperature derivatives of these quantities i.e. thermal expansion and specific heat also change measurably and are used to detect the glass transition. Structural relaxation is reflected in viscosity.

To understand the elastic phase transition, a structural approach to the elastic thresholds has resulted in a floppy – intermediate – stressed rigid classification of network glass [13].

The intermediate phases consist of optimally constrained backbones that open in between floppy (under constrained) and stressed – rigid (over constrained ones).

The phase separation as a function of constraint proved to have high impact in apparently unrelated: from glass science to protein folding. Proteins fold in transition states that separate the denatured from the folded state, and there are growing indications that the transition states actually form part of an intermediate phase as suggested by Thorpe [14].

The constraint counting algorithms show that the similarity between biological and glassy networks could be very advanced.

The idea of the paper is to accept the existence of intermediate phase in water.

The structure of water as a function of temperature, carefully analyzed by various authors shows an evolution with temperature from a complex cluster of tetrahedrally bonded water molecules up to a complex structure of bunches of cage-like clusters of molecules and finally clusters of quasi-separated molecules.

We have shown that the region around 40-50 °C, characterized by anomalous behavior of specific heat and other constants, fits the concept of intermediate structure.

In this structure special clusters are packed and thus, the structure factor exhibits a small and broad peak visible at low angles before the main peak.

A modeling approach using clusters shows that the structure is physically realistically.

It is useful to compare the water system with e.g. a chalcogenide glass system. In the chalcogenide glass the mean coordination number is $r=2.28$ for quasi – tetrahedral unit and $r=2.40$ (e.g As-Se) for the pyramidal unit. These are the limits of the intermediate phase in As-Se.

Taking into account the specific structure of water we are led to admit that the anomaly in the range 40-50 °C is the signature of the intermediate phase in water.

In the calculations of Wernet et al. [15] it is admitted that the most water molecules have a broken acceptor H-bond. Therefore, each molecule has an average 2.2 ± 0.5 at 25 °C and 2.1 ± 0.5 H-bond at 90 °C. The coordination corresponds to the model presented and fits well the Boolchand intermediate phase.

Taking into account the X-ray diffraction patterns and modeling results the following conclusions can be drawn.

After melting the ice, the structure of water in the range 0-4 °C is that of a network with more or less flattened tetrahedra, as a function of the gradual softening of the bond bending force constant in the network. By raising the temperature a tendency to loss the correlations between water tetrahedra could be guessed. Thus, the clusters formed in water start to move freely and, step by step, disaggregate at higher temperatures.

The cluster becomes more and more limited in size and for more than 150 °C, practically, associations are very rare and only for short times.

We discovered at the temperature of 40-50 °C a pre-peak in the diffraction pattern that correlates well with the packing of anisotropic clusters used in modeling the structure at that temperature. We explain the anomaly of water at high temperature as due to the formation of a new configurational state similar to the Boolchand phase observed in disordered materials (glasses and organic substances).

Due to their specific anisotropic structure of the clusters around 40-50 °C, it is suggested they play an important role in the delimitation of spaces to be occupied by biomolecules in the life structures.

The water molecules form clusters with two types of water molecules: W_4 (molecules with tetrahedral surrounding) and W_2 (molecules with two linking bonds usually situated at the margin of the clusters).

Owing to tetra-coordinated molecules, there appear different domains of composition W_4+W_2 where the under-lying networks are optimally constrained (this is the intermediate phase or reversibility window) [16] or under-constrained or floppy and over-constrained structures by variation of the temperature.

With the increase in W_2 content for increasing temperature the water system will keep optimally constrained inter-cluster bridges by incorporation of W_2 - W_2 dimers or W_2 rings. Thus the network of cluster and dimmers will be self-adaptive in the arrangement of W_4/W_2 compositions (this would approach to the reversibility window $\frac{W_2}{W_4} = \frac{0.2}{0.8} \rightarrow \frac{0.27}{0.73}$) from 0.25 to 0.37 known in chalcogenides glasses..

4. Conclusions

We have demonstrated by modeling that water at different temperatures is characterized by specific structure of clusters of water molecules where cages of molecules and free molecules are included. A special structure at around 50 °C succeed to explain the XRD pattern with a small FSDP at low diffraction angles.

The anomaly at ~50 °C was ascribed to a particular structure of water clusters [3]. The structure is suggested to be similar to the intermediate phase discovered by Boolchand et al. in many solids, amorphous and biological materials.

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