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A molecular level explanation of the density maximum of liquid water from computer simulations with a polarizable potential model

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Abstract

Differences in the structure of water are investigated on the basis of a recent set of Monte Carlo simulations with a polarizable water model at temperatures corresponding to the same density below and above the density maximum. The simulations reproduced well the experimental differential pair correlation function of the molecular centers and its running coordination number. It is shown that with increasing temperature an increasing number of molecules leaves the tetrahedral hydrogen-bonded network. These interstitial molecules are located in the cavities of the tetrahedral network of the other molecules, forming closely packed structural units with their neighbours. The effect of the increasing number of these closely packed patches on the density of the system can compensate the increasing thermal motion of the molecules up to a certain point. These two opposite effects are shown to be responsible for the appearance of the density maximum of liquid water at 277 K. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

The structural and thermodynamic properties of liquid water have been studied extensively in the past decades by experimental as well as computer simulation methods. In particular, a lot of effort has been made to understand the origin of the anomalous properties of water, particularly the presence of a density maximum at 277 K. Despite statements to the contrary [1,2], there are now an increasing number of indications that the density maximum as well as the other anomalous thermodynamic properties of liquid water can be explained by the appearance of molecules located in the cavities of the tetrahedral network. The presence of such interstitial molecules has been known for a long time from diffraction experiments which revealed that the coordination number of the O–O partial pair correlation function up to its first minimum is significantly greater than 4 [3–7]. Furthermore, interstitial molecules have also been identified in several simulation studies. Svishchev and Kusalik found that, in addition to the tetrahedrally aligned peaks of the hydrogen-bonded neighbours, the orientational pair correlation function $g(r, \Omega)$ of the SPC/E [8] water model shows also

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a peak in a non-tetrahedral position at a distance of ∼3.5 Å in the entire temperature range of 263–373 K [9]. This peak has been assigned to the interstitial molecules, and can be related to the 'five-or-more bonded' water molecules of Sciortino et al. [10]. The position of this peak indicates that preferentially the interstitial neighbours form closely packed patches with the central molecule and its H-acceptor neighbours. Indeed, the distribution of the O–O–O angle formed by two neighbouring O atoms around the central one has been found to have two distinct maxima, a broad one around the tetrahedral angle and a sharp one at ∼60° [11]. This latter maximum is a sign of the closely packed structural units around the interstitial molecules. Interstitial water molecules have recently been identified in simulated configurations of TIP4P [12] water at 298 K by Yeh and Mou with the use of Voronoi polyhedra analysis [13]. Moreover, in recent ab initio calculations of water clusters built up by 6–8 molecules, various low-lying minima of the potential energy surface have been found in which some of the molecules are in positions similar to that of the interstitial molecules in the liquid phase [14,15]. It should be noted that the above idea of liquid water being a mixture of tetrahedral network-forming and interstitial molecules is markedly different from the popular 'iceberg' model of the 1960s [16], in which liquid water was described as a mixture of ordered and disordered *domains* of several tens of molecules.

In understanding the origin of the density maximum of water the isochoric temperature difference (ITD) X-ray diffraction study of Bosio et al. [17] is of great importance. They measured the difference of the X-ray structure factor of water at temperature pairs corresponding to the same density on the two sides of the density maximum. These differential structure factors were determined with considerably larger accuracies than the structure factors themselves, since in the data reduction process the complicated ρ-dependent correction terms cancelled out. They have observed only slight changes in the structure of the first coordination shell of the molecules. However, they found that in the higher-temperature states the number of neighbours at a distance of 3–4 Å is significantly larger than in the lower-temperature states. This is compensated by the decrease of the number of neighbours in the distance range of 4–5 Å. In light of the subsequent studies [9–11,13] these neighbours can be identified as the interstitial neighbours and the second neighbours of the tetrahedral network, respectively. Hence, the anomalous increase of the density of water with increasing temperature from the supercooled region up to 277 K can be attributed to the fact that some of the second hydrogen-bonded neighbours leave the tetrahedral network, become interstitial and thus can be located closer to the central molecule.

Although this explanation seems reasonable, it has, to our knowledge, not yet been tested directly by computer simulations. The main reason for this is the fact that the commonly used simple nonpolarizable water models generally fail to reproduce the density maximum. For instance, the SPC [18] and TIP3P [12] models do not have any density maximum in the temperature range of 223–373 K [19]. The TIP4P model has a density maximum at 248 K, almost 30 K below the experimental value [19]. Similar results were obtained for the SPC/E model, for which the temperature of the density maximum has been found to be 235 K [20] and 245 K [21] from two different studies. However, recently developed polarizable water models, such as the PPC model of Kusalik et al. [22] and the Brodholt–Sampoli–Vallauri (BSV) model [23] proved to be able to reproduce the temperature of the maximum density accurately [24,25]. By performing simulations from 268 up to 328 K at every 5 K we have shown in a previous study that the maximum density of the BSV model occurs at 278 K [25]. This result and the fact that BSV model reproduces the partial pair correlation functions of ambient water reasonably well [23,26–28] allow us to make a meaningful investigation on the origin of the density maximum of water by analyzing the differences in the configurations obtained at different temperatures around 278 K.

The aim of this Letter is to confirm the fundamental role of the interplay between tetrahedral and interstitial water molecules, whose existence has been detected earlier both by theoretical and experimental means. The analysis of configurations produced by using a realistic polarizable potential model provides a sound basis for the interpretation of the anomalous properties of water at a molecular level. We compare several structural properties at temperatures below and above the density maximum, in order to characterize the change of the fraction of the interstitial and network-forming molecules with the temperature, and show that indeed these changes are responsible for the anomalous behaviour of the density of water.

2. Monte Carlo simulations

The details of the Monte Carlo simulations have been described in the previous paper [25], therefore only a brief summary is given here. The simulations were performed on the (N, p, T) ensemble at 10^5 Pa with 256 water molecules. Cubic simulation box and standard periodic boundary conditions were used. The interaction of the molecules were described by the polarizable BSV model [23]. This model has a TIP4P-like geometry, the O–H bond length and H–O–H bond angle being 0.9572 Å and 104.52°, respectively. Two positive charges of 0.499 e are placed on the H atoms, the compensating negative charge is at a site along the bisector of the H–O–H angle at 0.20 Å from the O atom. In addition, a polarizable point dipole is located at the center-of-mass of the molecule. The non-electrostatic part of the interaction is described by Lennard-Jones interactions between the O atoms with the parameters $\sigma =$ 3.2 Å and $\varepsilon / k_B = 108.25$ K. At 9 Å all interactions were truncated to zero, the long-range part of the electrostatic interactions was taken into account by the reaction field correction method [29–31] whereas that of the Lennard-Jones interactions by the approximation assuming that $g_{OO}(r) \equiv 1$ beyond 9 Å [32]. The exact formulae used for calculating the energy of the system are given in our previous papers [25,27].

3. Results and discussion

In order to visualize better the small but significant differences between structures at different temperatures we have used the ITD approach of Bosio et al. [17]. Therefore, we have calculated the $X(T_2) - X(T_1) = \Delta X(T_2 - T_1) = \Delta X(\Delta T)$ difference of various structural properties X between temperatures T_1 and T_2 which correspond to the same density below and above the density maximum. We have explored two temperature pairs: $T_1 = 273$ K, $T_2 = 283$ K and $T_1 = 268$ K, $T_2 = 288$ K. The simulated densities corresponding to these temperature pairs agree very well with each other, their difference is below 0.25% for both temperature pairs. The $\Delta g(r)$ differential center-of-mass–center-of-mass pair correlation functions obtained are shown in Fig. 1. For comparison, the experimental $\Delta g(r)$ of Bosio et al. [17] are also given for $\Delta T = 8.4$ K and $\Delta T = 23.3$ K. The simulated $g(r)$ at the temperature of the maximum density, 278 K, is also shown. As is seen, the simulated functions reproduce well the oscillation of the experimental curves at short and intermediate distances (i.e., below 6 Å), especially for $\Delta T = 20$ K. Although the first minimum is considerably sharper as resulted from the simulations in both cases, this is of little importance since it only describes changes within the hydrogen-bonded neighbours belonging to

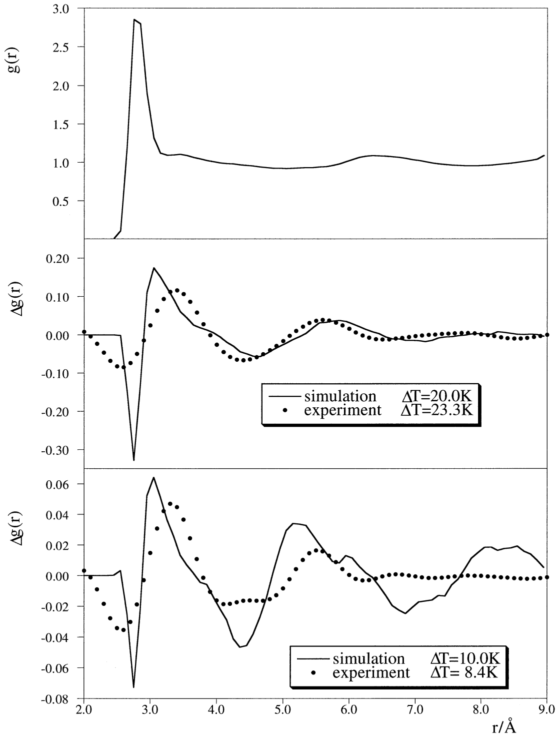

Fig. 1. Bottom: differential center-of-mass–center-of-mass pair correlation function of water. Solid line: simulation results with the BSV model with $\Delta T = 10$ K, dots: experimental results of Bosio et al. [17] with $\Delta T = 8.4$ K. Middle: same as in the bottom, but with $\Delta T = 20$ K for the simulation and $\Delta T = 23.3$ K for the experimental results. Top: center-of-mass–center-of-mass pair correlation function of BSV water at 278 K, the temperature of its density maximum.

the first coordination shell. This is also demonstrated by Fig. 2, which shows the differential running coordination number $\Delta c(r)$ as obtained from the simulations with $\Delta T = 20$ K and from the experiment with $\Delta T = 23.3$ K. $c(r)$ is calculated as

$$c(r) = 4\pi\rho\int_0^r R^2 g(R)\,\mathrm{d}R. \tag{1}$$

As is evident, at the position of the first minimum of $g(r)$ at 3.3 Å $\Delta c(r)$ is found to be zero both from the experiment and from the simulations. This means that although the distance between the hydrogen-bonded neighbours slightly decreases with decreasing temperature, the structure of the first coordination shell remains practically unchanged. However, the number of neighbours around 3.5 Å increases significantly at the expense of the number of neighbours between 4 and 5 Å as the temperature increases.

Since the experimental $\Delta g(r)$ is considerably better reproduced with $\Delta T = 20$ K than with $\Delta T = 10$ K, and considering also that the small structural differences become more evident with larger ΔT (as they can less be washed out by the uncertainties of the simulations) we only present results for $\Delta T = 20$ K in the following. Besides the accurate reproduction of the temperature of the density maximum itself, the good reproduction of the experimental differential pair correlation function and running coordination number of Bosio et al. [17] gives confidence in the following results.

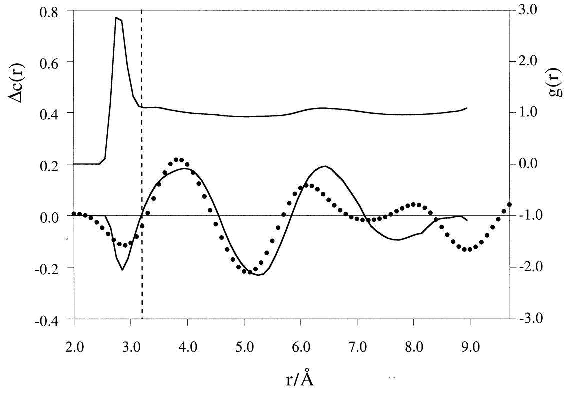

Fig. 2. Differential running coordination number of water as obtained from simulations with the BSV model with $\Delta T = 20$ K (solid line) and from the ITD X-ray diffraction experiment of Bosio et al. [17] with $\Delta T = 23.3$ K (dots). The simulated pair correlation function of the center-of-mass of the water molecules at 278 K, the temperature of the density maximum, is also shown. The dashed vertical line indicates that $\Delta c = 0$ at the position of the first minimum of $g(r)$.

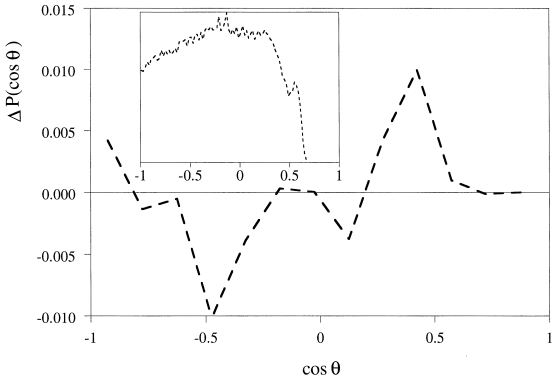

Fig. 3. Differential cosine distribution of the θ angle formed by the O atom of two neighbouring molecules within the O–O distance of 3.3 Å around the O atom of the central molecule (O–O–O angle) as resulted from the simulations with the BSV model with $\Delta T = 20$ K. The inset shows the $P(\cos\theta)$ distribution at 278 K, the temperature of the density maximum.

Fig. 3 shows the differential cosine distribution of the O–O–O angle θ, formed by the O atoms of two neighbour molecules within 3.3 Å from the O atom of the central molecule around this central O atom (the $P(\cos\theta)$ distribution at 278 K is also reported in the inset). As is evident, the increase of the temperature increases the distribution between 0.2 and 0.5, i.e., in the angular range of 60°–80°, whereas it lowers the distribution between -0.6 and -0.2, i.e., between 100° and 125°. This fact clearly demonstrates that with increasing temperature the fraction of interstitial molecules, that form closely packed structural units with the network-forming molecules, increases, whereas the fraction of molecules belonging to the tetrahedral network decreases.

Similar conclusions can be drawn from the differential distribution of the tetrahedral angular and distance order parameters (S_g and S_k, respectively) of Chau and Hardwick [33], which are shown in Fig. 4 together with their distribution at 278 K. These order parameters are defined as

$$S_\mathrm{g} = \frac{3}{32}\sum_{i=1}^{3}\sum_{j=i+1}^{4}\left(\cos\theta_{ij} + \frac{1}{3}\right)^2, \tag{2a}$$

$$S_\mathrm{k} = \frac{1}{3}\sum_{i=1}^{4}\frac{(r_i - \bar{r})^2}{4\bar{r}^2}, \tag{2b}$$

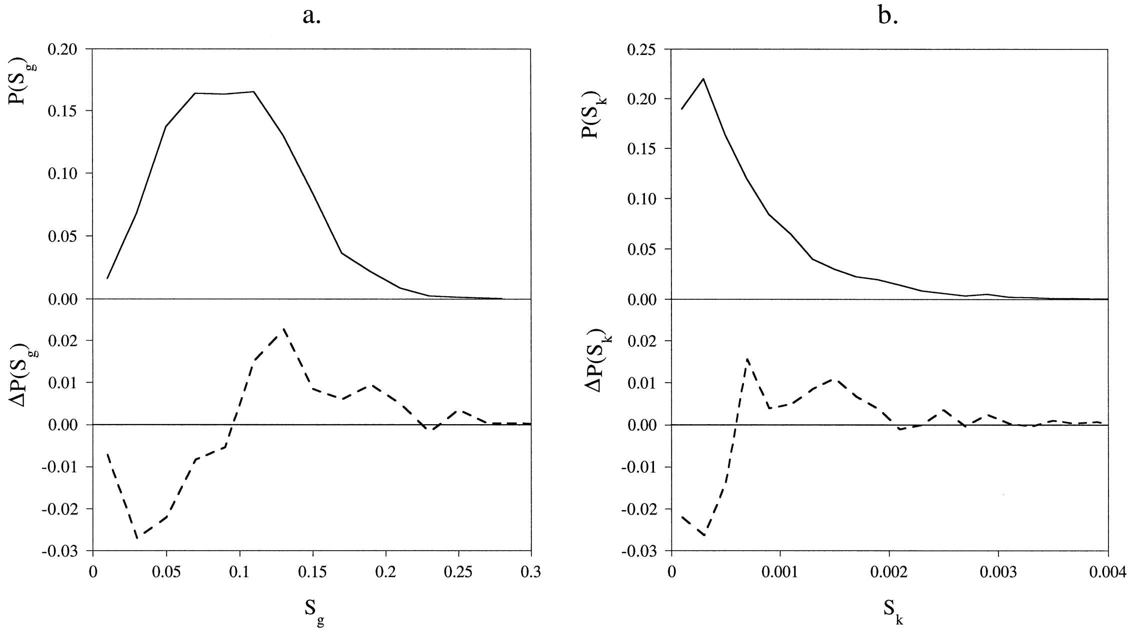

Fig. 4. Top: distribution of the tetrahedral angular (a) and distance (b) order parameter as resulted from the simulations with the BSV model at 278 K, the temperature of the density maximum. Bottom: differential distributions with $\Delta T = 20$ K. For the definition of the order parameters, see the text.

where indices i and j run through the four nearest neighbours of the central molecule, θ_{ij} is the O–O–O angle formed by the ith and jth neighbours, r_i is the distance of the ith neighbour from the central molecule, and $\bar{r} = \frac{1}{4}\sum_{i=1}^{4} r_i$ is the average distance of the first four neighbours. S_g and S_k measure the tetrahedricity of the arrangement of the first four neighbours around the central molecule. For a perfect tetrahedral arrangement both order parameters are 0, and their values increase with decreasing tetrahedricity [33]. As is evident from Fig. 4, the differential distribution of both order parameters are zero around the most probable order parameter values (i.e., around the maximum position of the $P(S_g)$ and $P(S_k)$ distributions), and they are positive at order parameter values larger and negative for values smaller than these most probable values. Since the increase of S_g and S_k means that the arrangement of the neighbours is less tetrahedral, these findings indicate significantly higher tetrahedricity at the lower-temperature state.

Finally, in Fig. 5 the difference of the fraction $f(i)$ of the molecules having exactly i hydrogen-bonded neighbours is shown. Two molecules are considered here as being hydrogen bonded if their

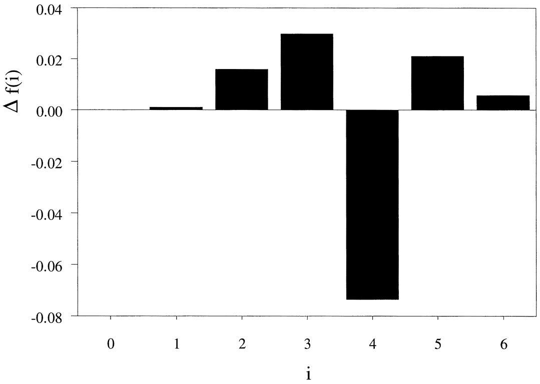

Fig. 5. Differential distribution of the $f(i)$ fraction of molecules having exactly i hydrogen-bonded neighbours, as resulted from the simulations with the BSV model with $\Delta T = 20$ K.

O–O and shortest O–H distance are smaller than 3.25 and 2.45 Å (i.e., the first minimum position of the $g_{OO}(r)$ and $g_{OH}(r)$ functions), respectively. As is clear from Fig. 5, the increase of the temperature depletes strongly the fraction of the four-bonded molecules and increases the number of molecules with hydrogen-bonded neighbours other than 4. This finding again clearly demonstrates that with increasing temperature an increasing number of molecules departs from the tetrahedral hydrogen-bonded network (in which, ideally, every molecule should have exactly four hydrogen-bonded neighbours), leaving molecules with less than four hydrogen-bonded neighbours behind. The increase of the fractions $f(5)$ and $f(6)$ is also consistent with the increase of the number of interstitial molecules, since these molecules can also form distorted hydrogen bonds with their neighbours [10]. Thus, several molecules can have more than four hydrogen-bonded neighbours (i.e., four regular and one or two interstitial ones).

Summarizing, the present work shows that the increase of the temperature gives rise to an increase of the number of interstitial water molecules, which leave the tetrahedral hydrogen-bonded network and are located in its cavities. Contrary to the loosely packed tetrahedral network, in which every molecule has only four nearest neighbours, these interstitial molecules are forming closely packed structural units with the surrounding network-forming molecules. This is reflected in the increase of $g(r)$ around 3.5 Å at the expense of its decrease between 4 and 5 Å as well as in the increase of the $P(\cos\theta)$ distribution of the O–O–O angles in the angular range of 60°–80° at the expense of its decrease between 100° and 125° with increasing temperature. This increase of the number of closely packed structural units around the interstitial molecules increases the density of the system, thus compensating the opposite effect of thermal expansion. The balance between these two effects gives rise to the appearance of the density maximum at 277 K.

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