Journal of Molecular Liquids 232 (2017) 304–309

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Local order in water: The fifth neighbor

Eszter Székely, András Baranyai *

Institute of Chemistry, Eötvös University, 112, PO BOX 32, 1518 Budapest, Hungary

ARTICLE INFO

Article history:
Received 7 December 2016
Accepted 21 February 2017
Available online 23 February 2017

ABSTRACT

We exploited the possibility to unfold the oxygen–oxygen pair-correlation function of liquid water modeled by the BK3 force field into distributions of the first, second, third, etc. neighbors of the central water molecule. Especially, we were interested in the 5th neighbor because its position is halfway between the first and the second coordination spheres. We found that each molecule has three tightly hydrogen bonded neighbors, a loosely bonded 4th neighbor and sometimes a non-tetrahedral 5th molecule which is a proton donor. We determined lifetimes of first shell molecules, the average reorientation or "jump" time, and the time needed to change the order of neighbors. Certain molecules can be 5th neighbors of more centers which may create multiple overlaps of first coordination shells. The density increase of water relative to hexagonal ice is caused by these overlaps and the hydrogen bond of the 5th molecule. This possibility also plays a role in fluctuations or makes possible the adaptation to high external pressure as well.

1. Introduction

In our previous paper we studied the structure of water by distinguishing the hydrogen bond (H-bond) geometries from the tetrahedral character of the oxygen-oxygen (O-O) sub-lattice [1]. We found that tetrahedrality is a much more sensitive structural marker than the ability to create H-bonds because H-bonds can be formed in the absence of tetrahedral geometry. Our study focused on the supercooled region where the variation of tetrahedrality with temperature and pressure is pronounced. We identified domain sizes, domain shapes for tetrahedral regions in water and described the structure of low-density amorphous and high-density amorphous phases as well. We unfolded the O-O pair-correlation function into distributions of the first, second, third, etc. neighbors of the central molecule which means that we created the probability distribution of distance of the individual molecules from a central molecule.

Pair-correlation function unfolding is not new. The first application of it was done 30 years ago [2]. A recent example is the paper of Moravietz et al. These authors applied decomposition of the O-O pair-correlation function into first and second coordination shells when pointing out the importance of weak van der Waals forces in the density anomalies of water [3]. In this paper we also use this tool to obtain new insight into the structure of liquid water. No surprise that in liquid state, contrary to hexagonal ice, the individual distribution of neighbors becomes less narrow indicating the increased disorder. Most remarkable is the position of the distribution of the 5th particle. This neighbor in ambient liquid water is positioned almost symmetrically between the first and the second coordination shells. The role of the 5th particle position was noticed earlier and identified as the primary cause of the enhanced density of liquid [4,5]. Other researchers also have addressed the 5th neighbor in the context of mixture models [6,7]. The emphasize of our study is on the 5th neighbor.

Such a study can only be carried out in a model system which requires caution to interpret the results as real water properties. It is essential to use a good model which minimizes the difference between the model and the real system. Our model is the polarizable BK3 force field [8]. This model proved that it performs very well in wide ranges of temperature and pressure [8,9]. At ambient condition its estimates are accurate not only qualitatively but quantitatively as well. This property is important because in the following we describe the structural features of water with respect to hexagonal ice at 273 K and 1 bar.

In this respect the accuracy of the O-O $g(r)$ is essential. The BK3 force field was fitted to half a dozen properties simultaneously but not to the partial pair-correlation functions. Most models of water produce high first peak for the O-O correlation function. The O-O $g(r)$ of BK3 was not very different from the experimental results of Soper [10]. However, considering a recent study of Skinner et al. who critically evaluated different X-ray measurements of the O-O pair-correlation function and suggested 2.57 for the height of the first peak [11], BK3 $g(r)$ is less accurate. Still, due to the exponential repulsion, BK3 shows one of the lowest first peaks of water models. The coordination number from these studies is 4.3 which is identical with our results (see below). This means that our O-O $g(r)$ shows a slightly compressed first coordination shell relative to X-ray results.

---

* Corresponding author.
E-mail address: baranyai@chem.elte.hu (A. Baranyai).

http://dx.doi.org/10.1016/j.molliq.2017.02.087
0167-7322/

Our choice is restricted only to a single state point instead of a set of state points. While in our previous paper [1] (tetrahedrality vs. H-bonds) we had to demonstrate that our results are not accidental due to some arbitrary choice of parameters, here our question is what microscopic features cause that water is denser than ice at the same temperature and pressure. In this respect, other state points are less relevant, especially because the position and the symmetry of 5th neighbor distributions are not identical which could make the comparison ambiguous. As temperature decreases, as we showed in our previous paper [1] the distribution of the 5th neighbors becomes more and more asymmetric, shifting back to the second coordination shell.

However, it is a reasonable question to ask how certain we are that our modeled water represents the melted ice and not water at other temperatures. Indeed, the thermodynamic stability separates the two phases at ~250 K for BK3 which seems a large error [8]. Error is caused by a small discrepancy of free energy, 0.2–0.4 kJ/mol, missing from the ice phase [8]. Obviously, this is a shortcoming of a classical, rigid model. Still, we believe that to use the melting temperature of 273 K is reasonable because here the predicted properties of the water phase are accurate, in fact, even the energy of melting, 6 kJ/mol, is reproduced. Nevertheless, we provide data for three additional points to remove arbitrariness: 250 K, 1 bar; 250 K, 400 bar; and 298 K, 1 bar.

In Section 2 we describe the technical details of simulation. In Section 3 we study the first coordination shell of liquid water using the unfolding technique. In Section 4 we present features of the 5th neighbor particle. In Section 5 we conclude the study.

2. Details of simulation

The molecular dynamics simulations were done with our home made code. The number of the molecules was 500. The temperature and pressure was controlled by Nosé-Hoover thermostat [12] and Andersen barostat [13], respectively The equations of motions were integrated by the explicit, reversible integrator of Martina *et al.* with the time-step of 2 fs [14]. The rotational degrees of freedoms were handled by quaternions with the algorithm of Rozmanov and Kusalik [15]. The Coulomb interactions were calculated by Ewald sum [16,17]. The real-space cutoff was half of the boxlength, and the standard non-electrostatic long-range corrections for the energy and pressure were also used. The positions of the charge-on-spring particles were determined with self-consistent iteration in 3–5 steps using a second order predictor [18]. Length of a run was 5 ns.

3. The unfolded oxygen-oxygen pair-correlation function: the first coordination shell

We may not say that the findings presented below are properties of real water because the results were obtained by a model. Since at present this is one of the most powerful classical model in the literature, these behaviors are worth checking. Experimental methods, ab initio molecular dynamics, or suitable QM/MM calculations can confirm or confute these results.

In Fig. 1 an enhanced part of the O-O pair-correlation function is shown for water and ice at 273 K and 1 bar. The blue curve refers to hexagonal ice, the red one to water and the green curves are distributions of the first, second, etc. neighbors in the water phase. In water the distributions of the 4th and 6th neighbors are wider than in ice. The 4th neighbor goes beyond the water $g(r)$ minimum, while the 5th and the 6th neighbors move closer to the central oxygen atom contrary to ice where they belong exclusively to the second coordination shell. The convention to determine the coordination number in water is to integrate $\rho 4\pi r^2 dr g(r)$ till its first minimum, where ρ is the number density. In the case of BK3 water the minimum of $g(r)$ is at 3.32 Å, where the value of the integral is 4.31. Unfolding of water $g(r)$ makes it possible to determine the distribution of coordination numbers. There are two ways to do it. Either we integrate the individual neighbor distribution functions till the first minimum of water O-O $g(r)$ (method I), or we use O-O distribution of ice as far as its first minimum, and consider that part of molecules in the first coordination shell which is below the blue curve (see Fig. 1).

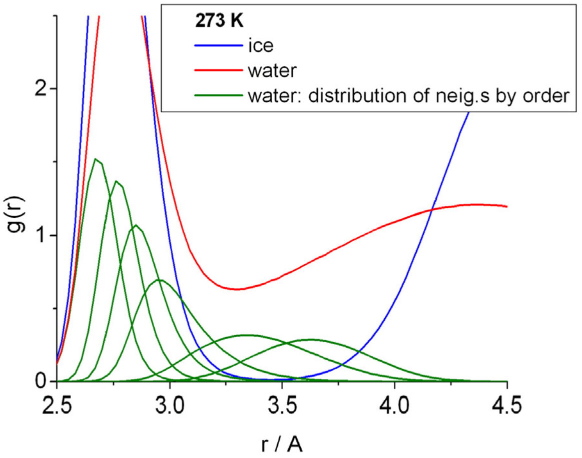

Fig. 1. Enhanced oxygen - oxygen pair-correlation functions are shown for hexagonal ice (blue) and water (red) using the BK3 model at 273 K and 1 bar. The green curves show distributions of the 6 neighbors closest to the central molecule's oxygen atom in water. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Since the integral of each neighbor curve is unity, the case when the central oxygen has only three neighbors can be obtained if one integrates that part of the 4th neighbor distribution, g^4_{OO}, which is above the blue curve minus the area below the blue curve from their crossing point, r_{4x}, as far as g^{ice}_{OO} minimum, R = 3.32 Å: $n_3 = 4\pi\rho\int_{r_{4x}}^{R} dr(g^4_{oo} - g^{ice}_{OO})\, r^2$. This provides the fraction of 4th neighbors which does not belong to the first coordination shell, i.e. for these cases the coordination is only three. To obtain the coordination of 6 we calculate the $n_6 = 1 - 4\pi\rho\int_{r_{6x}}^{R} dr(g^6_{oo} - g^{ice}_{OO}) r^2$. For coordination of 5: $n_5 = 1 - n_6 - 4\pi\rho\int_{r_{5x}}^{R} dr(g^5_{oo} - g^{ice}_{OO})\, r^2$. Since we neglect the very rare cases when the coordination is 2 or 7, the remaining fraction of coordination gives n_4. This is method II, when we defined the coordination relative to the first peak of the ice O-O $g(r)$. (Table 1) For comparison we also determined the coordination numbers for the inherent structure of water (method III) using the same procedure as for method I.

Not a surprise that the three columns of Table 1 are different but justifiable. Even a visual observation of Fig. 1 shows that the minimum number of coordination is 3 (the contributions of the 2nd or 7th neighbors by method I are not zero but negligible). For method I the average number of neighbors is 4.31, and coordination with 4 and 5 neighbors is dominant. Interestingly, in method III, for the inherent structure, we obtained the same number for average neighbors, 4.31, but with different distributions. In coordination the 4th neighbor is even more dominant with a small amount of 5th neighbors. In method II coordination with 3 neighbors is much larger leading to the coordination number of 3.92.

Table 1
Fractions of coordination with N neighbors. Estimated error is ±0.002 (see text for further details).

N	Method I	Method II	Method III
3	0.0939	0.2941	0.02630
4	0.5713	0.5414	0.6876
5	0.2663	0.1189	0.2310
6	0.0685	0.0456	0.0551