Vol 14 No 4, April 2005
1009-1963/2005/14(04)/0785-06

Chinese Physics

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A molecular level study of liquid water with a flexible water model*

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(Received 11 March 2004; revised manuscript received 16 December 2004)

The structural properties of water at different temperatures and pressures have been investigated by using a flexible water model and the inherent structure mechanism. The presence of 60° peak in the O–O–O angle distribution function and the behaviours of the hydrogen bonds in the first shell indicate that some water molecules in the second shell move toward the central molecules through the bending (not breaking) of hydrogen bonds and even become first-shell molecules of the central molecule on the basis of the O–O cutoff distance but not first-shell molecules by means of the hydrogen-bond criterion. The inherent-structure analysis of the O–O radial distribution functions at different pressures shows that the first peak is almost independent of the pressure; the position of second peak moves from 0.45 to 0.32nm as the pressure increases from 1×10^5Pa to 1×10^9Pa. This particularly evident pressure effect, i.e. the constant nearest-neighbours and the transformation of outer-neighbours on the basis of O–O distance, together with the results at different temperatures, gives a positive evidence for the two-state outer-neighbour mixture model: liquid water is a mixture of Ice-Ih-type-bonding and Ice-II-type bonding structures.

Keywords: liquid water, molecular-dynamics simulation
PACC: 6120, 8670E

1. Introduction

Due to its clear importance in life, water is one of the most widely studied substances. Much is already known experimentally about the odd behaviour of this substance compared with other liquids. For example, the volume of water increases by about 9% when water freezes at 0°C at atmospheric pressure. The melting point is lowered with increasing pressure. An enormous amount of theoretical effort[1,2] has gone into developing models of water so far. Nevertheless, many important questions still remain in dispute, especially those concerning on the structure of liquid water. It is a common opinion that the structure of liquid water is not easy to understand even though water seems to be a very simple molecule consisting of just two hydrogen atoms attached to an oxygen atom.

The currently popular two-state outer-neighbour mixture model[3−8] is successful in creating a molecular-level picture for understanding the anomalies of water. In this model, a low-density structure resembling the local structure in normal Ice Ih is mixed with a high density structure similar to Ice II, which is based on the presence of open second-neighbour O–O structure at 0.45nm and a dense second-neighbour structure at near 0.34nm obtained from the bending of hydrogen bonds without changing of the O–O nearest-neighbour distance (0.28nm). Although this mixture model gives a reasonable explanation of some abnormal properties, there are not many direct tests from the computer simulations.

The structural properties of liquid water have been studied extensively in the past decades by molecular dynamics (MD) simulations. Among them, the rigid model has dominated the developmental efforts and applications in liquid water calculations: as in transferable intermolecular potential (TIP) serials,[9−12] simple point charge (SPC),[13] and ST2[14] etc. It is becoming increasingly apparent, however, that flexible water potential may in fact be better suited to simulating liquid water due to the strong coupling between inter- and intramolecular interactions.[15] Along this line, existing

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rigid-model potentials have been adjusted into a flexible model: for example, flexible TIPS[16] from TIP serials, SPC/F[16,17] from SPC, MST-FP[18] from ST2. These results indicate that when adding flexibility to the rigid model potential we can reliably reproduce the experimental density, energy, and O–O radial distribution function of water at 298K and 1×10^5Pa.[17] In addition, Soper[19] has shown that the empirical potential (including intra- and inter-molecular interactions) refinement procedure leads to improved reliability in the extracted radial distribution functions. With the limited number of parameterizations performed, many developed models show some deficiency in the structural, vibrational or thermodynamic properties of water.[16] A flexible water model potential[17] developed by Ferguson is based upon the popular SPC rigid model, and the flexibility was achieved by using cubic and harmonic bond stretching terms and a harmonic angle bending term. The calculated values compare well with experimental results for a wide range of thermodynamic and structure properties,[17,20] including the density energy, O–O radial distribution function (RDF), vibrational frequencies of gas and liquid, dielectric constant, the Kirkwood g factor, and the free energies. Using this potential, we have recently carried out MD simulations of the local inherent structure and the temperature dependence of H-bonds of liquid water.[21] Our results have shown good agreement with others in ordinary O–O–O angle distribution functions (ADFs) and also some interesting behaviours on inherent O–O–O ADFs. More applications in explicit calculations and theoretical analysis by using this promising flexible water model are expected. How this flexible water model reproduces the outer-neighbour mixture model is of great interest.

A comprehensive approach to study the local structure of liquid state of matter is through the classification of atomic configurations,[22–25] according to multi-dimensional potential-energy minima that can be reached by a minimization algorithm in a computer simulation of these systems. The inherent structure formalism is a way to partition the configuration space for the vibrations of an n-body system into various regions. Within each region there is one local minimum of the potential-energy surface that can be reached by a minimization algorithm. This process is the basis for the partitioning of configuration space and the structure at a local minimum is the inherent structure of corresponding region. The idea of resolving observable order in liquid into the vibration and the inherent structural parts offers a way to classify their microstructure and to discover the kind of the short-range order in many materials.[21,22,26,27] In particular, it has been shown that the inherent structure mechanism is of great value in identifying and classifying the local structure and H-bond status in water under various conditions.[2,28–30]

In this work, we have employed the flexible water model potential to study the microstructural properties of liquid water by MD simulations and the inherent structure mechanism, in the hope of confirming the two-state outer-neighbour mixture model. The rest of this paper is organized as follows. In the next section we show the computational methods. In Section 3 we present and discuss the results. Finally we give a brief summary in Section 4.

2. Computational methods

The MD calculations were performed in the isothermal-isobaric ensemble at a pressure of $\sim 1\times10^5$Pa at temperatures ranging from 278 to 368K, and at a temperature of 298K and different pressures from 1×10^5Pa to 1×10^9Pa. Here pressure and temperature coupling were performed with scaling[31] and stochastic collisions.[32] In previous work by Ferguson,[17] two sets of parameters were presented with and without switch function.[33] In the present work, the parameters with no switch functions were adopted due to the fairly small differences between the outcomes with and without them. The system consisted of 216 water molecules under periodic boundary conditions with 0.85nm spherical cutoffs based on O–O separation, which gave a box of ~1.86nm for an experimental density of 0.997 g/mL at 298K and $\sim 1\times10^5$Pa. The equations of motion were integrated using the velocity Verlet algorithm with 1fs time-step. The starting coordinates for each calculation came from a box equilibrated at either 298K and $\sim 1\times10^5$Pa or under the conditions close to these. The structural properties of liquid water were analysed by two different methods. (1) By directly using the configurations obtained, we calculated the structure properties at different temperatures and pressures in order to compare our results with experimental data and to analyse the configuration at different temperatures and pressures. (2) Following Stillinger and Weber,[22–25] we relaxed the system to its local minimum by a conjugate gradient energy minimization and then analysed the inherent structure under different thermodynamic conditions. Our results were obtained by averaging 40 configura-

tions.

3. Results and discussion

The description of the structure of a liquid is basically provided by the radial distribution functions (RDFs). The O–O, O–H, and H–H RDFs at 298K along with the experimental data have been presented in Ref.[21]. The first peak of the O–O RDF is slightly shifted toward a denser packing of the neighbours compared to the earlier diffraction data,[34] but is in pretty good agreement with the recent x-Ray scattering experiments,[35,36] neutron diffraction data[19] and theoretical results from Car–Parrinello MD simulations,[37] and so is the first peak of the O–H RDF. The first peak of H–H RDF is slightly higher than the experimental one. We have also calculated the inherent RDFs from the corresponding configurations at the potential minima resulting from the conjugate gradient energy minimization. By comparing all the inherent and ordinary RDFs separately, it is immediately obvious that the mapping onto nearby potential-energy minima enhances structural features that are otherwise largely obscured by thermal motions. The inherent RDFs are nearly independent of the temperature.

As is well known, there are two characteristic features in the water structure: the hydrogen bond and the tetrahedral ordering. Each water-molecule may join four nearest molecules by hydrogen bonds and these molecules form more or less perfect tetrahedral configurations akin to those in Ice Ih. A distance of 0.28nm separates the pairs of the central molecule and those in the tetrahedral vertices, and the distance between the tetrahedral vertices is about 0.45nm. So there exist the first peak at 0.28nm (representing the first shell or the inner shell) and the second peak at 0.45nm (representing the second shell or the outer shell) in the O–O RDFs. A water molecule can either promote or inhibit the hydrogen bond in its neighbouring molecules depending on its geometry.[38] Thus the bending or even the breaking of hydrogen bonds may exert a negative influence on the tetrahedral ordering, and the weakening of tetrahedral ordering may inhibit hydrogen bonds.

The triplet correlations of nearest oxygen atoms are very important for analysing short-range order, if considering the tetrahedral nature of water. This is conveniently measured by the distribution function of the O–O–O angle of a trimer, $g_3(\theta)$. Here θ is the angle between two vectors that join a central oxygen atom with two nearest oxygen neighbours. Figure 1(a) shows $g_3(\theta)$ at different temperatures. In this figure, there are two peaks around 50–60° and 100° for all temperatures, which are denoted P_1 and P_2, respectively. This is in good agreement with the result of Ref.[35]. With increasing temperature, the height of P_1 is enhanced while the height of P_2 is lowered. Figure 1(b) presents the corresponding $g_3(\theta)$ obtained from the inherent structure configurations with the cutoff distance (0.31nm) of the first minimum of the inherent O–O RDF. Comparing these two figures, it is clear that P_1 of the inherent structure becomes far smaller than that obtained from the corresponding ordinary structure. The presence of P_1 results from the mismatching water molecules in the first shell, and P_2 represents the tetrahedral ordering of water.[21,38] Further study of the change of P_1 in the ordinary structure with the nearest-neighbour number shows that: P_1 nearly disappears for the four and fewer nearest neighbours; the height of P_1 is increased with the nearest-neighbour number. This indicates that the introduction of another water molecule into the first shell of the water molecule, which has four nearest-neighbours, increases the mismatching type of water molecules. On the other hand, the lowering of P_1 in the corresponding inherent structures suggests that P_1 in the ordinary structures originates mainly from thermal fluctuations. The presence of the added-H_2O molecules (which, to be presented in the following paragraph, are the nearest-neighbours of the central molecule but not hydrogen-bonded to it) in the inherent structure is the origin of the small P_1 in the inherent structure, which is implied by the two facts: (1) the first minimum of O–O RDFs is about 0.32–0.35nm in the ordinary structure at different temperatures and 0.31nm in the inherent structure; (2) the water molecules with more than 4 nearest neighbours are much less in the inherent structure than in the ordinary structure, for example, the probability of molecules with 5 nearest-neighbours is 28% in the ordinary structure and 7% in the inherent structure.

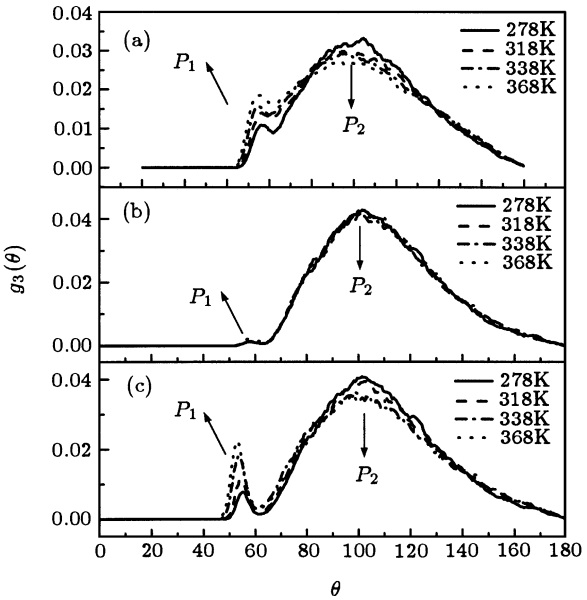


Fig.1. O–O–O angle distribution function $g_3(\theta)$ for the ordinary (a) and inherent (b) and (c) structures. The cutoff distance in (a) and (b) is the first minimum of the corresponding O–O RDFs. Note that (c) is for the inherent structures but the cutoff distance used in (c) is the same as in (a).

The hydrogen bond between a pair of water molecules is commonly analysed in terms of the O–H RDF: a pair of water molecules are defined to be hydrogen-bonded when their O–H separation (note that O and H atoms belong to different water molecules) is less than the first minimum of the O–H RDF, and integrating its first peak gives the number of hydrogen bonds per water molecule. From the ordinary O–H RDFs, we find that the number of hydrogen bonds per water molecule decreases with temperature, whereas from the inherent RDFs it is nearly temperature independent. Now we turn our attention to the introduced-H_2O effect on the hydrogen bond in its neighbouring molecules by investigating, as a function of the coordination number, (i) the hydrogen-bond probability of the central water molecule and (ii) the hydrogen-bond number between the neighbouring water molecules of the central water molecule, which are denoted respectively as P(HB) and NN(HB). P(HB) is defined as the ratio of the number of hydrogen-bond pairs (between the central water molecule and its neighbouring water molecules) to the total number of pairs (which in fact is equal to the coordination number of the central water molecule). In the perfect tetrahedral configurations akin to those in ice Ih, P(HB)=1 and NN(HB)=0. Figure 2 shows that the hydrogen-bond probability (P(HB)) of the central water molecule as a function of coordination number (N), here 2(a) and (b) are obtained from the ordinary and the inherent structure configurations respectively. According to Fig.2 for the coordination number equal to or less than 4, the probability is close to 1 and does not change with the coordination number. For a coordination number greater than 4, the probability decreases with the coordination number and, the product of probability and coordination number nearly keeps constant ∼4 or 4 plus. A comparison of Figs.2 (a) and (b) indicates that, these two features is a little distorted due to the thermal noise. Thus, for the water molecules, even though they may have five or more nearest-neighbouring molecules by means of the O–O RDF, they are usually hydrogen-bonded with only four of their nearest neighbours. In Fig.3 we display the hydrogen-bond number (NN(HB)) between the neighbouring water molecules of the central water molecule as a function of coordination number (N). For the coordination number equal to or less than 4, NN(HB) is about 0. For the coordination number greater than 4, NN(HB) is almost increased by one with N being increased by one. So the added nearest neighbours (denoted as added-H_2O) are hydrogen-bonded to one molecule of the original nearest-neighbours of the central water molecule, but not hydrogen-bonded to the central molecule. This result, along with the presence of 60° peak in the O–O–O angle distribution, indicates that some water

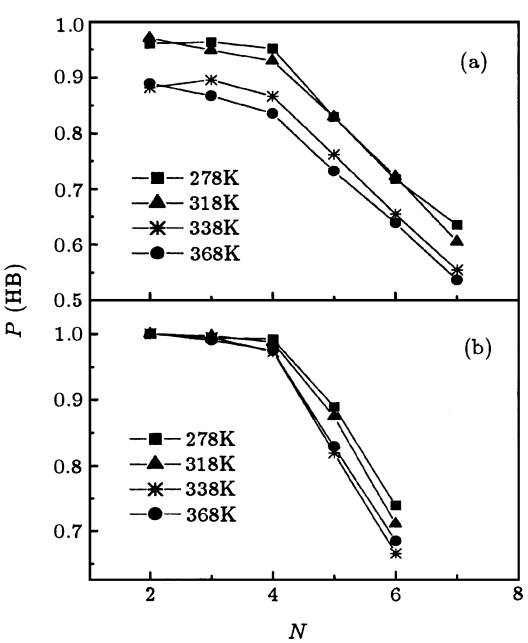


Fig.2. The hydrogen-bond probability (P(HB)) of the central molecule as a function of its coordination number (N) for the ordinary (a) and inherent (b) structures.

molecules (in the second shell) move toward the central molecule through the bending of hydrogen bonds and even become first-shell molecules of the central molecule due to the variation of O–O distance but not first-shell molecules in the sense of the hydrogen bond, because the ideal first-shell should be hydrogen-bonded to the central molecule.

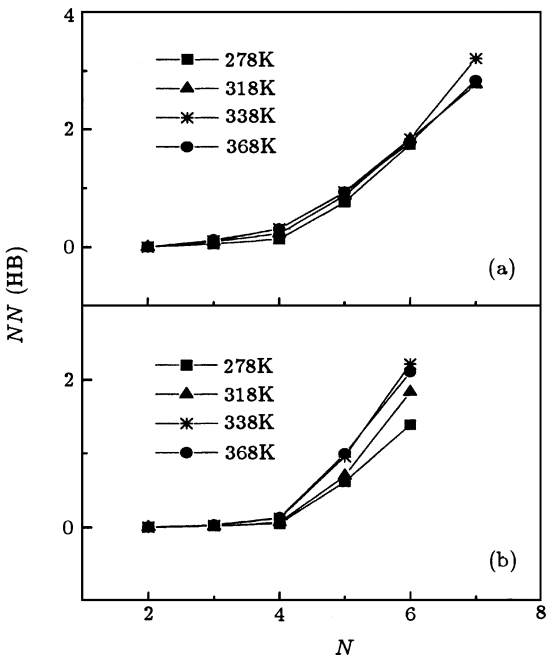


Fig.3. The hydrogen-bond number (NN(HB)) between the neighbouring water molecules of the central water molecule as a function of the coordination number (N) for the ordinary (a) and inherent (b) structures.

We now turn our attention to the pressure effects on the O–O RDFs at 298K, which are illustrated in Fig.4, where (a) and (b) are respectively obtained from the ordinary and inherent structures. From Fig.4 (a) we can observe two remarkable changes in O–O RDFs with the pressure. First of all, an obvious lowering of the peak at 0.45nm is observed as pressure increases. As mentioned above, each molecule of water may join four nearest molecules by hydrogen bonds and the four nearest molecules form a tetrahedral configuration akin to those in ice Ih. The pairs of molecules at the vertices of the tetrahedron separated by a mean distance of about 0.45nm compose the second coordination sphere, whereas the pairs formed by the central molecule with those localized in the tetrahedral vertices represent the first coordination sphere, which corresponds to the first peak of the pair correlation function at 0.28nm. So the decrease of the correlation at 0.45nm apparently indicates the weakening of tetrahedral nearest ordering as a result of compression. The other striking change of the O–O RDFs shown in Fig.4(a) is the shoulder at about 0.32nm being clearly observed with increasing pressure. These two changes with increasing pressure, the lessening of the second peak at 0.45nm and the strengthening of the shoulder on the right-hand side of the first peak, indicate a correlation between the first and the second coordination spheres. Interestingly, in contrast with Fig.4(a) we see from Fig.4(b) that the first peak is nearly independent of the pressure; the position of the second peak moves from 0.45 to 0.32nm as the pressure is increased from 1×10^5Pa to 1×10^9Pa. The behaviour of the second peak is a signature of local tetrahedral structures decreasing as the pressure is increased. This particularly evident pressure effect gives a positive evidence of the two-state outer-neighbour mixture model.

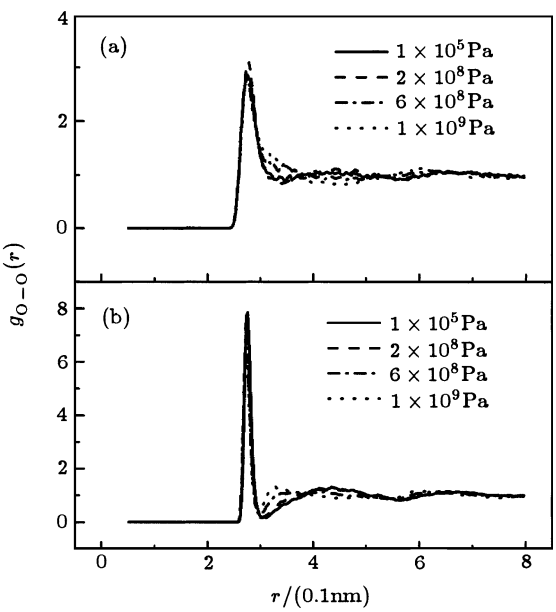


Fig.4. Pressure dependence of O–O radial distribution function at 298K for the ordinary (a) and inherent (b) structures.

4. Conclusions

Using a flexible water model and the inherent structure mechanism we have performed MD study on the structural properties of water at different temperatures and pressures. We found, through the analysis of the local geometry picture and the hydrogen-bond probability, that some water molecules (in the second shell) move toward their central molecule through the bending of hydrogen bonds and even become first-shell molecules of the central molecule due to the variation of O–O distance but not first-shell molecules in the sense of the hydrogen bond. The O–O radial distri-

bution functions in the inherent structures obtained at different pressures show that, the first peak is almost independent of the pressure; the position of second peak moves from 0.45 to 0.32nm as the pressure is increased from 1×10^5Pa to 1×10^9Pa. This particularly evident pressure effect, the constant nearest-neighbours and the transformation of outer-neighbour on the basis of O–O distance, together with the presence of 60^o peak in the O–O–O angle distribution function and the behaviours of the hydrogen bonds in the first shell at different temperatures, provide an evidence in favor of the two-state outer-neighbour mixture model.

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