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Structural Properties of Water by a Flexible Water Model *

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The structural properties of water at different temperatures have been investigated using a flexible water model in the isothermal-isobaric ensemble. With decreasing temperature, the tetrahedrality of the distribution of the water molecules around the central water molecule is enhanced, and the hydrogen bonds become more linear. By means of a conjugate gradient energy minimization, dynamical configurations at various temperatures have been mapped onto nearby potential-energy minima, the $50^\circ - 60^\circ$ peak (P_1) in the distribution function of the $O-O-O$ angle of a trimer becomes far smaller. However there appears to be a small but observable temperature dependence of P_1, i.e. the higher the temperature, the higher the P_1 intensity.

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The geometry of molecules in liquid water can be investigated by means of neutron and x-ray diffractions.[1,2] However, precise quantitative results are still lacking because of the severe difficulties in extracting information from experimental data. Along this line many theoretical simulations[3] have been performed. Molecular dynamics (MD) simulations, as a powerful tool, supplement the experimental approaches. Until now, there have been many empirical potentials of water, which mainly include three kinds: (1) transferable intermolecular potential (TIP) serials (such as TIP3P,[4] TIP4P,[5] and TIP5P,[6] etc); (2) SPC[7] and its derivants;[8] (3) a flexible water model.[9] These potential models have been successfully used to study a variety of properties of liquid water. Recently much attention has been paid to the study of the temperature dependence of some physical properties of water, such as density and diffusion constant.[6] As is known, the microscopic structure of liquid water is mainly determined by H-bonds between the hydroxy groups and the oxygen atoms of neighbouring water molecules. Thus, it may be interesting to investigate the temperature dependence of H-bonds, which may help us to understand the temperature dependence of some physical properties.

The idea of resolving observable order in liquid into the vibration and the inherent structural parts offers a useful way to classify their microstructures and to discover the kinds of short-range order in many materials.[10,11] This can be reached by a minimization algorithm in computer simulation of these systems.[10,12] After the MD simulations, researchers obtained the dynamical configurations, in which there are many vibrations of an n-body system in various regions and there is one local minimum of the potential-energy surface in each corresponding region. Based on the configurations, the "inherent structure" would be reached if the conjugate gradient energy minimization was performed.

In this Letter, we present the results of a microstructure study of the flexible water model proposed by Ferguson[9] using MD simulations. The main goal of this work is to investigate the local inherent structural properties of liquid water at different temperatures.

The developed flexible water potential function is composed of

$$E(r) = \sum_{\text{bonds}} K_l(l-l^0)^2 + K_l K_{\text{cub}}(l-l^0)^3 + \sum_{\text{angles}} K_\theta(\theta-\theta^0)^2 + \sum_{vdw}\left(\frac{A}{r_{i,j}^{12}} - \frac{B}{r_{i,j}^{6}}\right) + \sum_{\text{charges}} \frac{q_i q_j}{r_{i,j}},$$

where the simple quadratic term together with the cubic function represents the bond stretching, the single quadratic term represents the angle bending, and the Lennard–Jones and Coulombic terms represent the nonbond interactive. The parameters come from Table 1 of Ref.[9]. The calculations were performed in the isothermal-isobaric ensemble at a pressure of 1 atm in the temperature range from 268 K to 378 K with a step of 10 K. The system consists of 216 water molecules with periodic boundary conditions and 8.5 Å spherical cut-offs based on OO separation, which gives a box of ∼18.6 Å for an experimental density of 0.997 g/mL at 298 K and 1 atm. The equations of motion were integrated by using the velocity Verlet algorithm with 1 fs time steps. The starting coordinates for each calculation come from a box equilibrated at either 298 K and 1 atm or under closer conditions. The structural properties of liquid water were analysed by two different methods. (1) By directly using the obtained configurations, we calculate the structure prop-

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erties at different temperatures in order to compare our results with those of experiments and the other simulations. (2) Following Stillinger and Weber,[10] we relax the system to its local minimum by a conjugate gradient energy minimization[12] and then analyse the inherent structure at different temperatures. Our results were obtained by averaging 40 configurations.

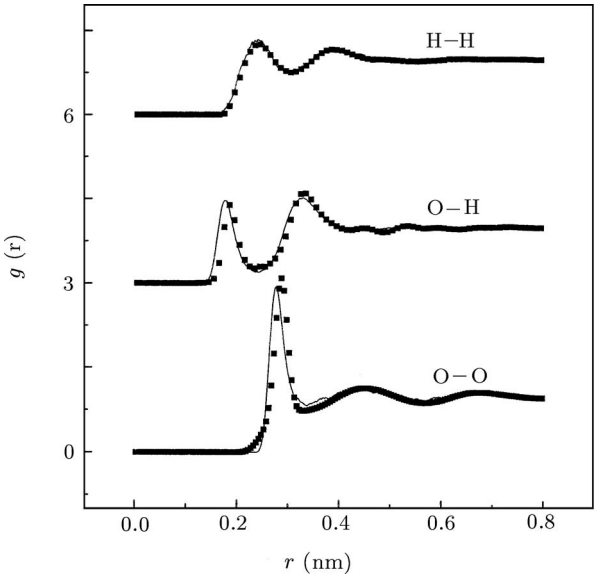

Fig. 1. O−O, O−H and H−H radial distribution functions at 298 K. The squares represent the experimental data of Ref. [2].

The description of the structure of a liquid is basically provided by the pair correlation functions. Figure 1 presents the oxygen–oxygen, oxygen–hydrogen and hydrogen–hydrogen radial distribution functions (RDFs) at 298 K along with the experimental data.[2] The calculated results of the RDF are in good agreement with the experimental findings. Compared with the experimental data, the first peak of the O−O RDF is slightly shifted toward a denser packing of the neighbours, so it is the first peak of the O−H RDF. The first peak of the H−H RDF in height is slightly higher than the experimental data. This is not shown here, however the expected reduction in structure with decreasing temperature is perceptible. The inherent RDFs were also calculated, represented in Figs 2(a)−2(c). These were obtained from the corresponding configurations at potential minima resulting from the conjugate gradient energy minimization (CGEM). Comparing Fig. 1 with Figs. 2(a)−2(c), respectively, it is immediately obvious that the mapping[10] onto nearby potential-energy minima enhances structural features that are otherwise largely obscured by thermal motions. Figures 2(a)−2(c) show that the inherent RDFs, with some discrepancy of the order of expected statistical error for our finite sampling, are independent of the temperature. This result is in agreement with that in the Ni–P system and the single-component fcc and bcc models.[10]

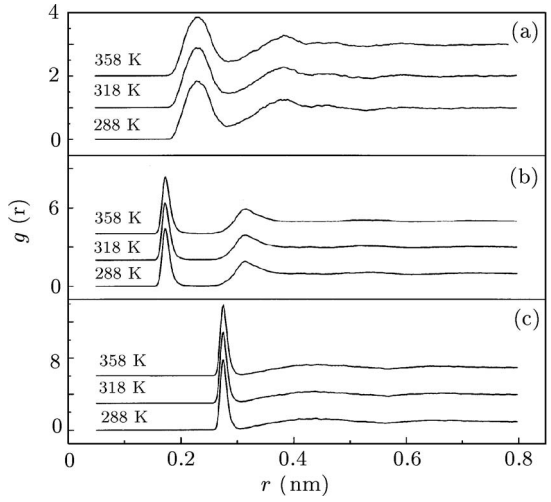

Fig. 2. O−O (*a*), O−H (*b*) and H−H (*c*) RDFs of the inherent structures at different temperatures.

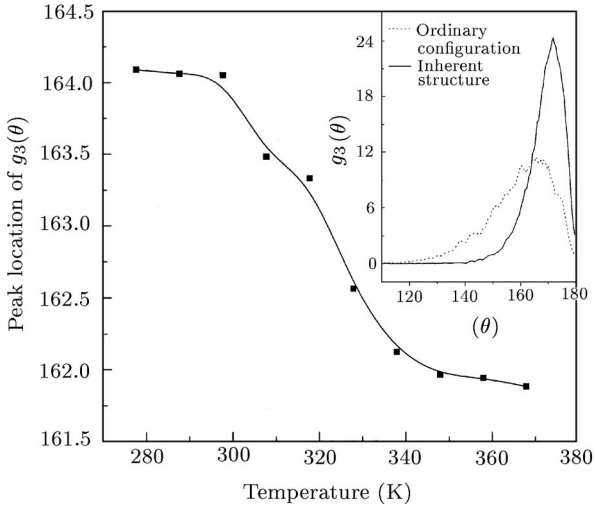

Fig. 3. Peak location of O−H···O angle distribution functions versus temperature. The inset shows O−H···O angle distribution functions $g_3(\theta)$ at 298 K.

The hydrogen bond between a pair of water molecules is commonly analysed in terms of the O–H RDF. Integrating the RDF in the first peak gives the number of hydrogen bonds per water molecule. Based on Figs. 1 and 2(b) and the RDFs of the other temperatures, we can obtain that the number of hydrogen bond per water molecule from the general RDFs is increased as the temperature is lowered, whereas from the inherent RDFs it is temperature independent. The orientational correlation in a neighbouring pair of water molecules is further characterized in terms of the O−H···O angle distribution in the pair, in which the O−H···O angle is denoted by θ. The calculated probability distribution functions at different temperatures, shown in Fig. 3 and its inset,

indicate that the hydrogen bonds become more linear ($\theta \rightarrow 180°$) and the distribution for θ becomes narrower with decreasing temperature. Whereas this temperature dependence of the probability distribution functions for θ nearly disappears when based on the inherent structural configurations.

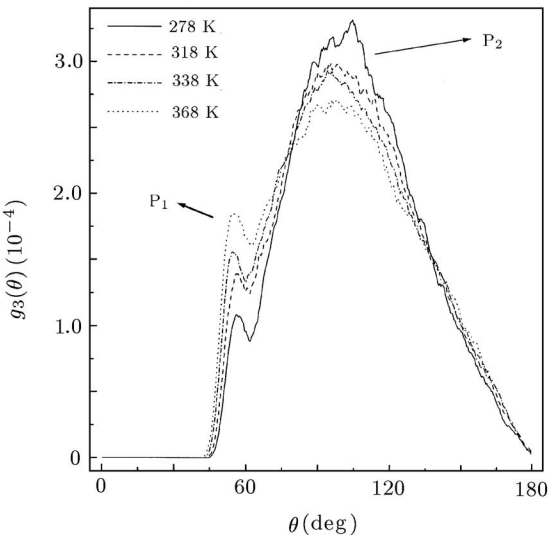

Fig. 4. O−O−O angle distribution functions $g_3(\theta)$ at different temperatures.

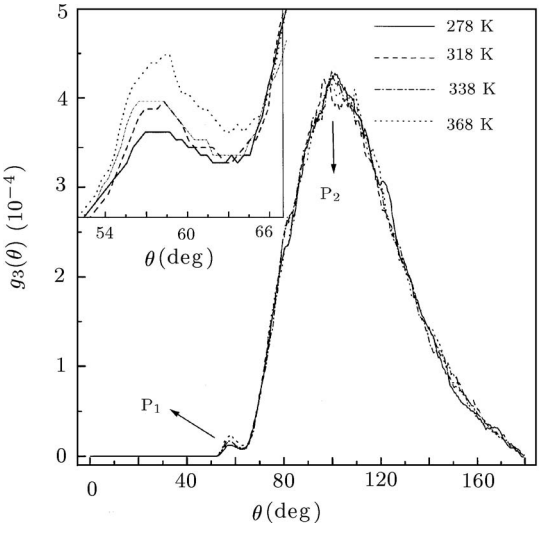

Fig. 5. O−O−O angle distribution functions $g_3(\theta)$ of the inherent structures at different temperatures.

Not surprisingly, the constant-density CGEM procedure causes the correlation RDF and O−H···O angle distribution function to change to a much more structured function. However it is interesting that at constant density both are substantially independent of temperature, which prevails in the thermodynamically stable liquid before the CGEM procedure. Thus as an uncompleted result it appears that the liquid water statistically possesses a temperature-independent inherent structure and that the temperature dependence of the correction functions reflects only a variable extent of thermal excitation in the inherent structure. Especially, the mean number of hydrogen bonds and the O−H···O angle distribution in the pair, which both reflect the characters of H-bonds, are substantially different from each other for the ordinary structure, perhaps inducing us to conclude that the "structures" of the cool and the hot water are rather distinct. Furthermore, both appear to quench to essentially the same inherent structures. The differences are primarily due to the degree of vibrational excitation within the regions around H-bond minima, not to thermally induced population shifts among some other regions. Furthermore, it can be said that the vibration may be anharmonic, which can be indirectly inferred by the left shift of the peak of the O−H···O angle distribution function from the one of inherent structure: from 172° to about 160°. Generally, to obtain the inherent structure means a method to partition the dynamical configurations into different characterized configurations. Therefore, we can conclude that these "bound-by-H-bonds" pairs are in the same inherent configurations.

By considering the tetrahedral nature of water, the triplet correlations are a particularly important function to analyse the short-range order. 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 joins a central oxygen atom with two nearest oxygen neighbours. The $g_3(\theta)$ values at different temperatures are shown in Fig. 4 (for clarity, only results at four different temperatures are presented). From this figure, it is seen that there are two peaks around 50° – 60° and 100° denoted by P_1 and P_2, respectively, which are in good agreement with the results of Ref. [14]. The P_1 peak reflects the presence of mismatching water molecules in the neighbouring shell or reveals the occurrence of non hydrogen bond interactions in the first shell.[13,14] The P_2 peak represents the tetrahedral ordering of water. With the temperature elevated, the height of P_1 is increased while the height of P_2 is lowered. Thus the tetrahedrality of the distribution of the water molecules around the central water molecule is weakened with the increasing temperature. Figure 5 exhibits $g_3(\theta)$ of the inherent structure at different temperatures. From Figs. 4 and 5, it is clear that P_1 of the inherent structure become far smaller than that of the ordinary structure. This indicates that the mapping onto nearby potential-energy minima enhances tetrahedral features that are otherwise largely obscured by thermal motions. From the inset of Fig. 5, we can also see that there is a small but observable temperature dependence of P_1, i.e. the higher the temperature, the higher the P_1. This may come from the fact that the higher the temperature, the more the fluctuation in local density. It is believable that the CGEM proce-

dure is so effective that the system is never able to surmount a potential energy barrier. This partition method is so sensitive and reliable to probe that the inherent local structure of water has a small change (a substantial transition) with the variation in temperature. A fifth even more order mismatching molecule appears in the neighbouring shell.

In summary, we have studied the structural properties of water with a flexible model. With decreasing temperature, the hydrogen bonds become more linear and the far smaller $50^{o} - 60^{o}$ peaks after the CGEM procedure have a perceptible reduction. Furthermore, some meaningful points can be inferred. (1) the "bound-by-H-bonds" pairs are in the same inherent configurations. (2) H-bonds and the global water structure, which are reflected by all RDFs, are independent of temperature. (3) There are also some mismatching water molecules in the first shell, which are enhanced with the increasing temperature.

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