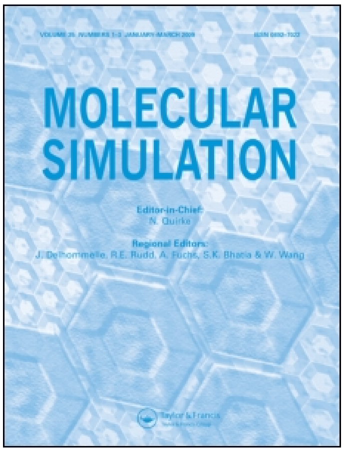

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Structural Transformations of Ice at High Pressures Via Molecular Dynamics Simulations

T. Hashimoto[a]; S. Sugawara[a]; Y. Hiwatari[a]
[a] Physics Department, Faculty of Science, Kanazawa University, Kanazawa, Japan

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STRUCTURAL TRANSFORMATIONS OF ICE AT HIGH PRESSURES VIA MOLECULAR DYNAMICS SIMULATIONS

T. HASHIMOTO*, S. SUGAWARA
AND Y. HIWATARI

Physics Department, Faculty of Science, Kanazawa University,
Kanazawa, 920-11 Japan

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A simple classical model is used for the study of the structural transformations of ice under high pressures, such as ice VIII to VII and X, via classical molecular dynamics (MD) simulation. In the present MD simulation, pair potentials of a simple form between pair of atoms and a thee-body potential representing the H-O-H angle dependence, originally developed by Kawamura *et al.*, were used. Starting with a stable ice VIII at low pressure and low temperature, we have carried out two different MD runs, one with increasing pressure keeping the temperature constant (simulation I) and the other with increasing temperature under constant pressure (simulation II). From these MD simulations we have obtained the structural transformations from ice VIII to VII for both simulations; the former was finally transformed into ice X for the simulation I. The present results are compatible with recent experiments on high pressure ices.

Keywords: Ice X; structural transformation; molecular dynamics; effective interaction for water molecules.

1. INTRODUCTION

Ice is an interesting material with various (at least 10) different stable crystalline structures [1]. They are still unknown in high pressures [2–6]. In this study we focus on the ice X and the related structures. VIII and VII, as well and the structural transformations between them. In ice X, hydrogen

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* To whom correspondence should be addressed.

atoms in this structure can be located on the mid point of the near-neighbor two oxygens, so that there is no clear picture of water "molecules" [7,8]. Ice X is obtained only at very high pressures, the transition to this phase is not accurately known because of difficulties of experiments under high pressure. Hirsch and Holzapfel have shown in their high-pressure experiment that the transition to the Ice X takes place at about 40 to 50 GPa [2,3], and Polian *et al.* have shown it at 46 GPa [4]. Recently, Pruzan *et al.* have reported their high-pressure measurements for ice, showing remarkable results at least in two points [5,6]: First, the transition from ice VIII to the high-pressure ice (VII) takes place at a significantly higher pressure (about 60 GPa) than the previous results. Secondly the transition at temperatures as low as 100 K and that at temperatures as high as 300 K have been suggested to differ by Raman spectra, *i.e.*, orientational freedoms of water molecules are key to the latter transition, while translational freedoms of hydrogen atoms along the hydrogen bonds are dominant in the former transition. The experiment by Pruzan *et al.* also reveals that upon pressuring ice VIII changes to ice VII, not to ice X, which has generally been accepted so far. The transition to ice X needs still to impose high pressures.

Under such circumstances the main purpose of the present work is to investigate the structural phase changes of ice at high pressures via a molecular dynamics simulation using recenlty developed pair and three-body effective potentials between atoms. This model differs from any rigid molecular models which are often used as models of water or ice [9,10]; it can easily be accepted that these rigid models are useless for the present work, since in high-pressure water molecules are possibly changed in their molecular structures from those of water molecule at normal pressures. In the present model the system is simply composed of two different atoms (species), H and O, without any computational condition for forming water molecules; the pair interaction and the three-body interaction between atoms, recently proposed for water and low-pressure ices by Kawamura *et al.* [11], were used. Before carrying out the MD simulation on high-pressure ices, it has first been confirmed that such model potentials give a reasonable result for ice VIII at a normal pressure in comparison with other rigid molecular models [12]. In the present MD simulation we have used the algorithm of flexible cell originally developed by Parrinello and Rahman [13,14].

Motivations of the present work are followings: (1) First, since the structures of oxygen atoms are almost unchanged through these three phases, only hydrogen atoms undergo transitions characteristic in each phase. This situation of course makes the MD computations easy. (2) Second, there are a few recent experiments on ice under high pressures, but they are unfortunately conflicted to each other due to the difficulties of the experiments at high pressures [2–6]. (3) Structures and mechanisms of the phase transition between high pressure ices are not well known. (4) Properties of defects in such high pressure ices are little known, which are supposed to play a key role in their transition region. It is known that ice usually satisfies so-called ice rules that there are two hydrogen atoms around each oxygen atom, and along each hydrogen bond there is only one hydrogen atom [15]. However, due to some reasons, such as intrinsic large fluctuations as approaching to the transition temperature and pressure, defects are generated due to thermal and mechanical effects. Defects in ice are known of the type of D or L, corresponding to either case of two hydrogen atoms on a single hydrogen bonds or no hydrogen atom. Another type of defects are ionic ones like H_3O^+ and OH^-, which can be realized by the translational movement of a hydrogen atom along a hydrogen bond.

Ice is a most typical substance with hydrogen bonds as many others like groups of KDP (most typically KH_2PO_4). The order-disorder transition of protons are well known in such hydrogen-bond materials. It is well known that the order-disorder transition takes places for KDP, driven by the translational movements of hydrogen atoms along the hydrogen bonds. Then, one may ask whether this can also be applied to pure ice , such as the transition from ice VIII to VII. We will make clear this in the present MD simulation.

The paper is organized as follows. In section II, we describe the model for ice which was used in this work as briefly as possible. We see how the present model gives rise to a result on the thermal properties of ice VIII at a normal pressure, that is our initial configuration in the present MD simulation, compatible with those from other models. In the followng section, we will give our main results on the high-pressure ices obtained by the MD simulation. It is also discussed about a general tendency of the order-disorder transition temperature T_c on the hydrogen bond length. In section IV is given our conclusion.

2. MODEL

The potentials which we have used in the present MD simulation consist of two-body and three-body potentials as follows [11]:

$$\phi_{2\text{body}}(r_{ij}) = \frac{z_i z_j}{r_{ij}} + f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6}$$

$$+f_o D_{ij}(\exp(-2\beta_{ij}(r_{ij}-r_{ij}^0))-2\exp(-\beta_{ij}(r_{ij}-r_{ij}^0))) \quad (1)$$

and

$$\phi_{3\text{body}}(r_{ij}) = -f_k(\cos(2(\theta_{\text{HOH}}-\theta_0))-1)\sqrt{k_1 k_2}, \quad (2)$$

where

$$k_i = \frac{1}{(\exp(g_r(r_{\text{OH}i}-r_m))+1)} \quad (3)$$

In Eq. (1), the first term is the Coulomb interactions, the second term short-ranged repulsions, the third term dispersion potentials, and the fourth term covalent-bond potentials, which act only between O and H in each water molecule. On the other hand, the three-body potentials, Eq. (2), act only for each H-O-H. Values of the potential parameters which we have used in the present MD simulation are listed in Table I. The importance of the three-body potentials has been demonstrated by Kawamura *et al.*. Indeed it has been shown that thermal properties of a bulk water and ice I, II and IX under normal conditions (temperature and pressure) were able to be well reproduced with these potentials. The three-body interaction plays an important role to represent a correct angle between H-O-H of water molecules in their bulk systems.

TABLE I Values of the potentials parameters

Two body term	*O*	*H*
z	−0.8	+0.4
a(Å)	1.841	0.036
b(Å)	0.124	0.058
$c(\text{KJ}^{1/2}\cdot\text{Å}^3\cdot\text{mol}^{-1/2})$	57.28755	0.0
	O-H	
$f_0(10^{-11}\text{N})$	6.9511	
D(Å)	75.0	
$\beta(\text{Å}^{-1})$	2.74	
r^0(Å)	0.82	
Three body term	*H-O-H*	
$f_k(10^{-19}\text{J})$	1.1	
$\theta_0(^\circ)$	99.5	
r_m(Å)	1.4	
$g_r(\text{Å}^{-1})$	7.0	

In Table II, we have shown comparisons of the thermal properties for ice VIII predicted from the present model, which were computed through our NVE (microcanonical) and NPH (constant-pressure) MD simulations, with those obtained by other models (all rigid models) [12]. It is seen that the present model works for ice VIII as well, as other models do. Rigid models are useless for studying high-pressure phases of ice that is the present aim, in which molecules may change their structures. One fault of the Kawamura potentials has been pointed out that the pressure predicted by this model gives rise to a too high value. This fault of the present model should be taken into consideration when to compare with corresponding high-pressure experiments on ice, which will be discussed below in detail.

3. RESULTS

Starting with the initial configuration of ice VIII [16], we have carried out two runs, simulation I and II. Simulation I is a constant-temperature (100 K) MD calculation [17,18], pressure being increased from 5.7 GPa to 605.7 GPa at the rate of 6.0 MPa per step. One step is 0.2 fs. throughout the present MD simulations. First we present the result of the simulation I, and after that simulation II.

3.1. Simulation I

Figure 1 shows the variation of the temperature, volume and pressure in simulation steps. Figure 2 shows a comparison of the pressure vs the volume of the system calculated from the present model with experimental

TABLE II Comparison of the predictions of the present model for ice VIII with those of other models [9,10]

model	*MCY*		*SPC*		*TIP4P*		*present*	
	(NVE)	*(NPH)*	*(NVE)*	*(NPH)*	*(NVE)*	*(NPH)*	*(NVE)*	*(NPH)*
T(K)	54	57	73	74	82	85	93	107
P(kbar)	37.3	37.0	21.0	20.9	18.6	18.6	59.2	58.5
V(cm^3/mol)	12.1	12.1	12.1	12.1	12.1	12.2	12.1	12.3
a(Å)	4.85	4.91	4.85	4.78	4.85	4.79	4.85	4.75
b(Å)	4.85	4.91	4.85	4.82	4.85	4.83	4.85	5.08
c(Å)	6.85	6.68	6.85	6.99	6.85	7.00	6.85	6.76
α(deg)	90	89.9	90	90.5	90	90.5	90	89.5
β(deg)	90	89.8	90	89.4	90	88.5	90	90.2
γ(deg)	90	89.6	90	89.8	90	88.7	90	89.8

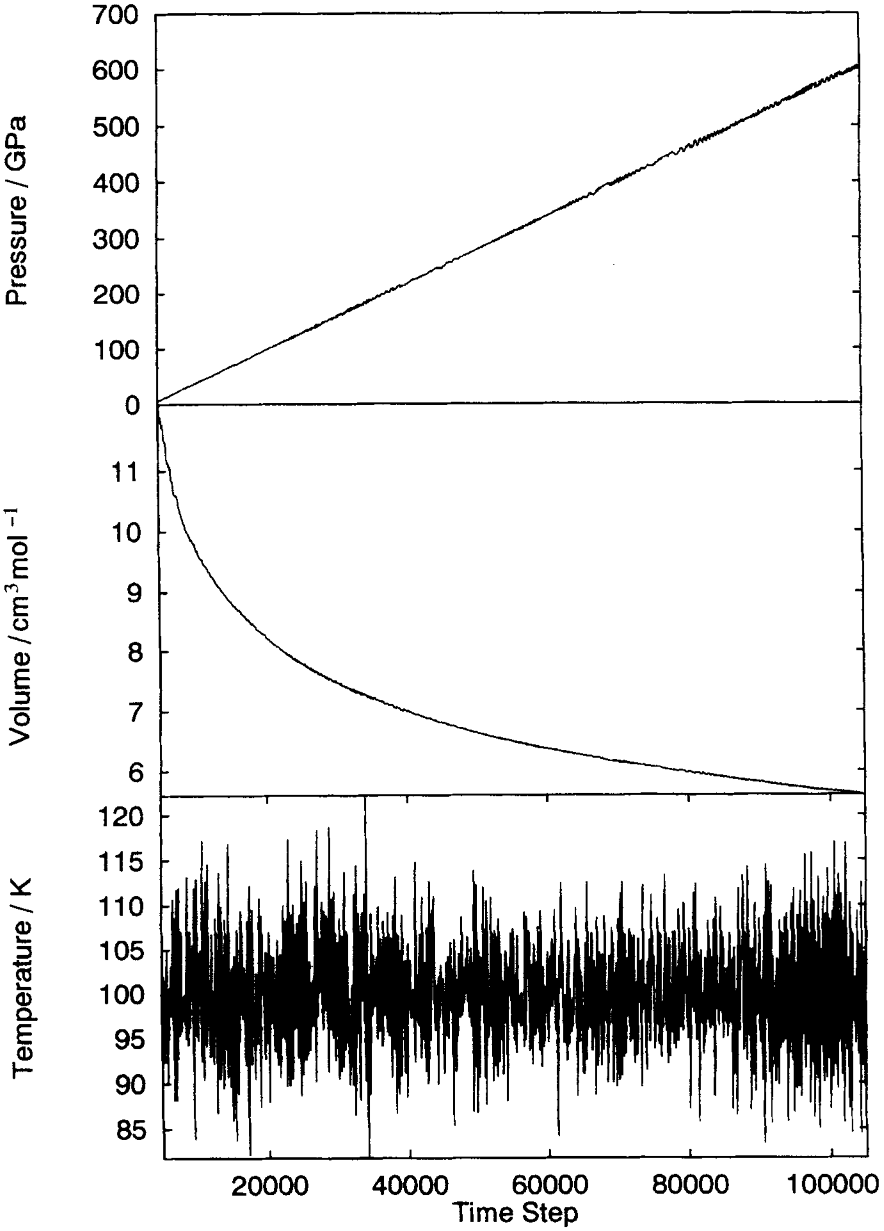

FIGURE 1 Variation of the pressure, volume and temperature vs time steps during simulation I.

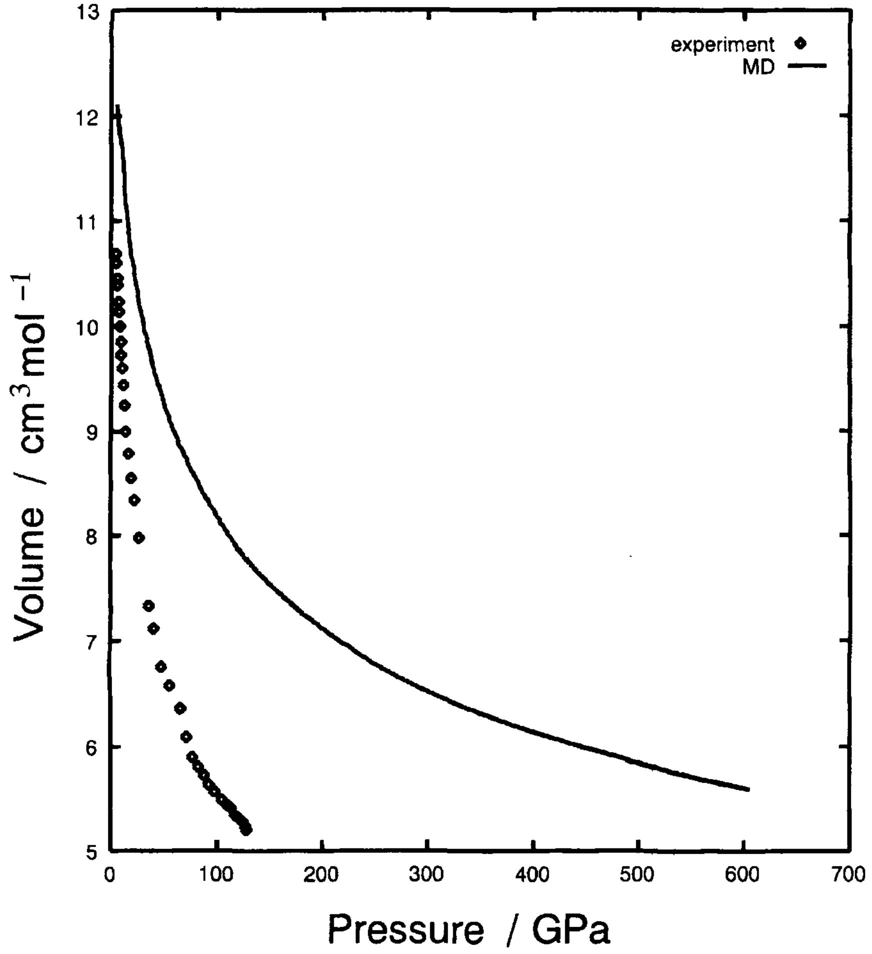

FIGURE 2 Comparison of the pressure vs volume of the system calculated from the present model (solid curve) with experimental data (circles).

data [19]. It is clearly seen that our predictions of pressure in this range of volume are too high compared with the experimental data. This implies nothing but a fault of the Kawamura potentials used in this work, the compressibility of the present model being too low. Figure 2 also shows that in both of the present model and the experiments no clear anomalous behavior is observed in the volume-pressure curve change, implying volume changes are not significantly accompanied by the phase transformation between ice VIII, VII and X, if it happens as supposed by previous experiments or even a possibility that no phase change takes place up to this pressure range. This result is inconsistent with the previously reported experiments by Hirsch and Holzapfel [2, 3] that the first-order phase transition between ice VIII and X takes place at a much lower pressure.

Figure 3 shows the partial pair distribution functions g_{OO}, g_{OH}, and g_{HH} for the simulation I (constant temperature MD) at various different time steps (pressures). Here, g_{AB} means the partial pair distribution function of the species (atoms) B at the distance r from an atom of the species A. Running coordination numbers (dashed curves) are also shown in the figure. The transition from ice VIII (hydrogen-ordered state) to VII (disordered state) takes place at when the O-O distance becomes 2.47 Å, while the transition from VII to X takes place at 2.32 Å. Comparison of the O-O distance with other hydrogen-bonded substances that exhibit a similar order-disorder transition and the relation between the O-O distance and the transition temperature are discussed below. In both ice VIII and VII, two hydrogen atoms are still occupied around each oxygen atom, as seen from the behavior of the g_{OH}.

Figure 4 shows the variation of the distortion parameter δ at different (time steps) pressures which yield 0.05 Å in the crystalline structure of the ice VIII, denoting a degree of mismatch of two equivalent sublattices adopted in the initial configuration of the present MD simulation. It turns out that the distortion parameter vanishes after about 50000 time steps, indicating the order (VIII)-disorder (VII) change takes place around the corresponding pressure (275 GPa) and volume (6.64 cm^3/mol).

We have monitored two nearest-neighbor hydrogen atoms around each oxygen atom during the run of the simulation I, and analyzed if they are the same as the hydrogen atoms at the initial configuration. The ordinate in Figure 5 indicates the average probability occupied by the same hydrogen atoms as the initial ones. In this computation, we have put 1 when nearest-neighbor atoms are the same as the initial ones, otherwise put 0. It is found that after the transition to the disordered phase only about one hydrogen atom per an oxygen atom is the same as one of the initial two hydrogen atoms. We note that after the transition to ice X (beyond 80000 time steps) this analysis becomes meaningless, because the coordination number (hydrogen atoms) around each oxygen atom is four, not two.

Figure 6 shows the probability that the average coordination number of hydrogen atoms within a distance of 1.2 Å around each oxygen atom is 1, 2, 3 and 4. It turns out that well before 50000 time steps, *i.e.*, the transition from ice VIII to VII, the probability of the average coordination number being 1 and 3 becomes significant, with that of two remarkably decreased.

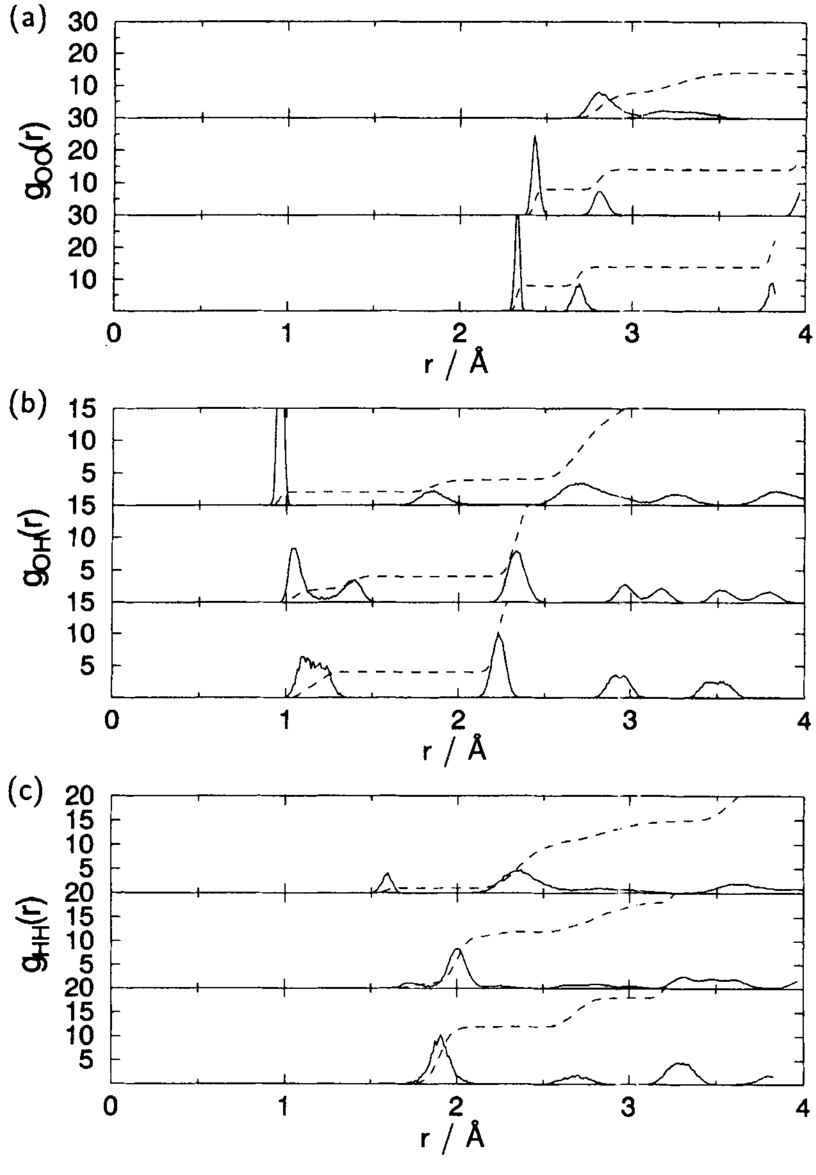

FIGURE 3 Partial pair distribution functions g_{OO}, g_{OH} and g_{HH} for the simulation I. The dashed curves are the corresponding running coordination number. (a) g_{OO} when pressure is 5.7 GPa (ice VIII, upper), 245.7 GPa (ice VII, middle), and 485.7 GPa (ice X, lower). (b) and (c) g_{OH} and g_{HH} whose pressures correspond to those of (a).

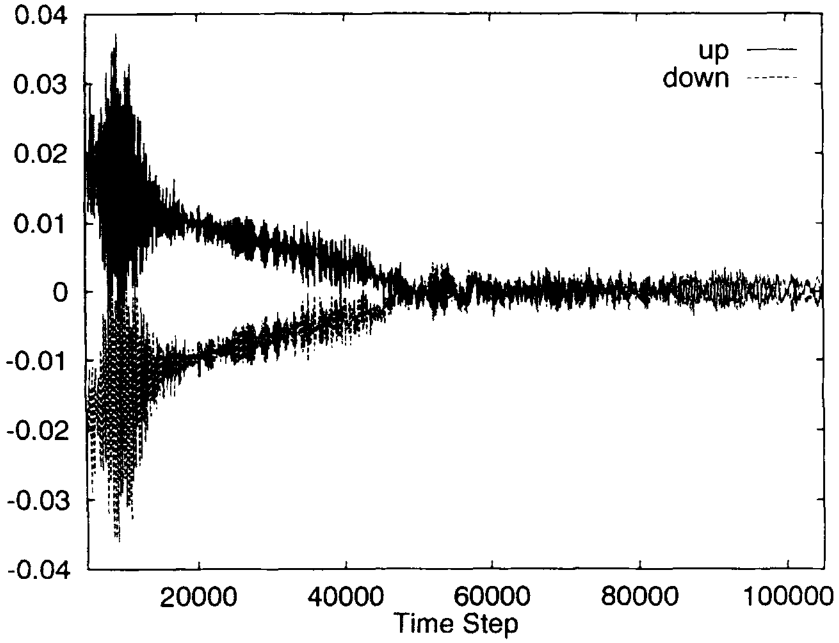

FIGURE 4 Variation of the distortion parameter δ vs time steps for the simulation I. "up" and "down" correspond to the two oxygen sublattices initially displaced upwards and downwards, respectively.

This result indicates that a significant amount of defects are brought as approaching the transition.

3.2. Simulation II

Molecular dynamics simulation II has been carried out at a constant pressure (5.7 GPa), heated from 100 K to 400 K at a rate of 0.01 K per step, followed by a constant-temperature and constant pressure MD simulation for 70000 time steps. Figure 7 shows the variation of the temperature, volume and pressure of such an MD run. In Figure 8 are shown the partial pair distribution functions g_{OO}, g_{OH} and g_{HH} for the simulation II. It turns out that all these functions do not show essential change during the run (heating process); only some quantitative changes are observed, which are remarkable contrast to those obtained for the simulation I. We note that the first coordination number of hydrogen atoms around each oxygen atom is always two.

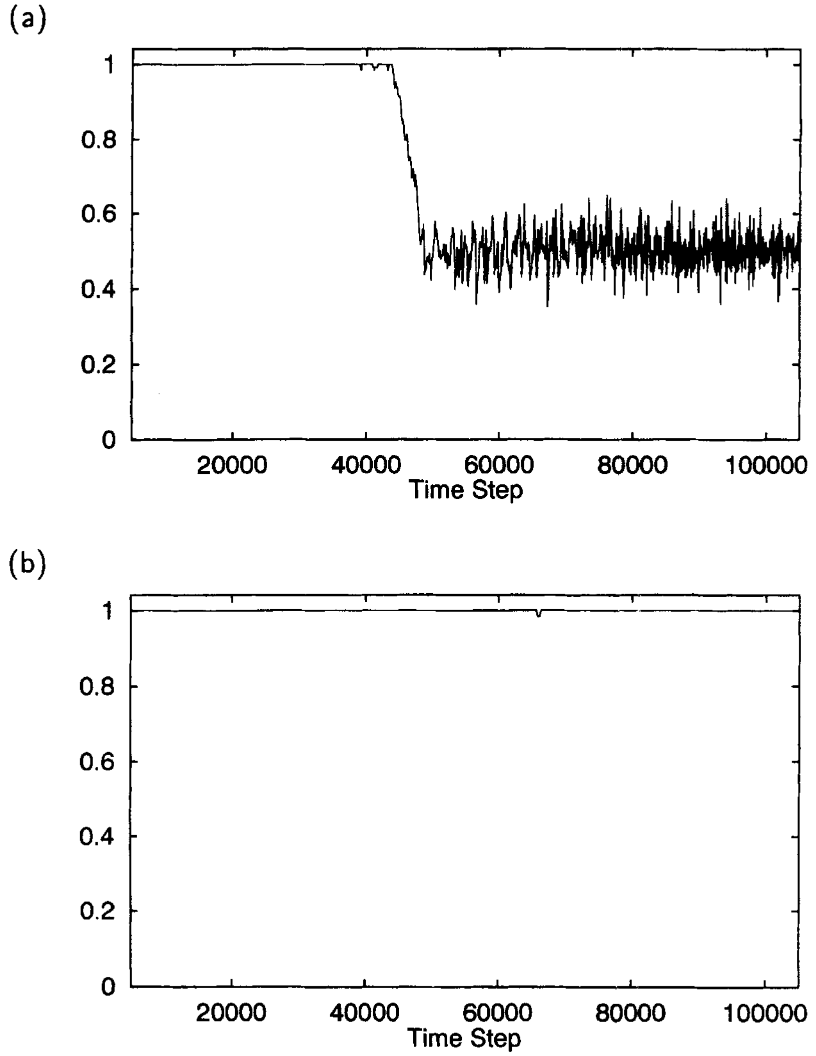

FIGURE 5 Probability occupied by the same H atoms as the initial ones vs time steps for the simulation I (a) and the simulation II (b).

Computation of δ during the run of the simulation II is shown in Figure 9. This clearly indicates a change of crystalline structure from the sublattice structure of ice VIII to a single lattice with vanishing distortion δ, *i.e.*, the change from the ordered phase to the disordered phase at about 60000 time steps. On the other hand, it turns out that the probability of the

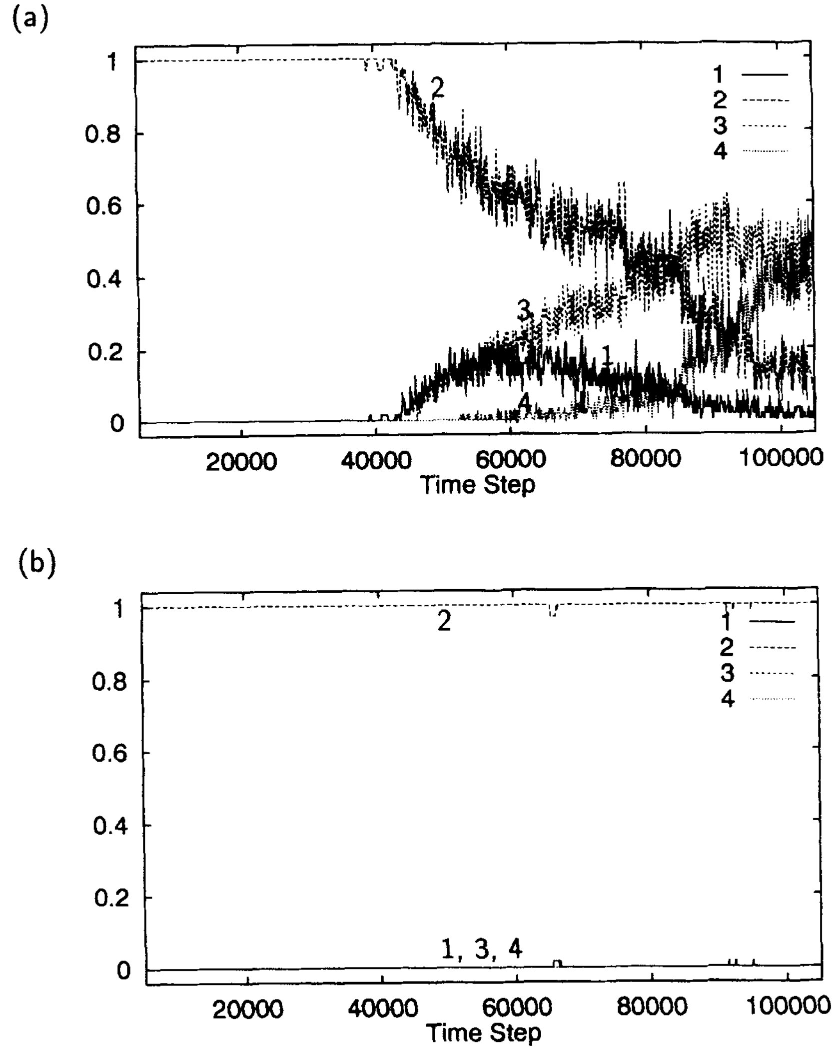

FIGURE 6 Probability of average number of H around each O being 1, 2, 3, and 4 vs time steps for the simulation I (a) and the simulation II (b).

two nearest-neighbor hydrogen atoms around each oxygen atom at any time being the same as those at the initial time is almost one except for very rare cases (Fig. 5(b)), and that the number of the hydrogen atoms within a distance of 1.2 Å around each oxygen atom is almost always two (Fig. 6(b)), contrast to that for the simulation I shown in Figure 6(a). These results

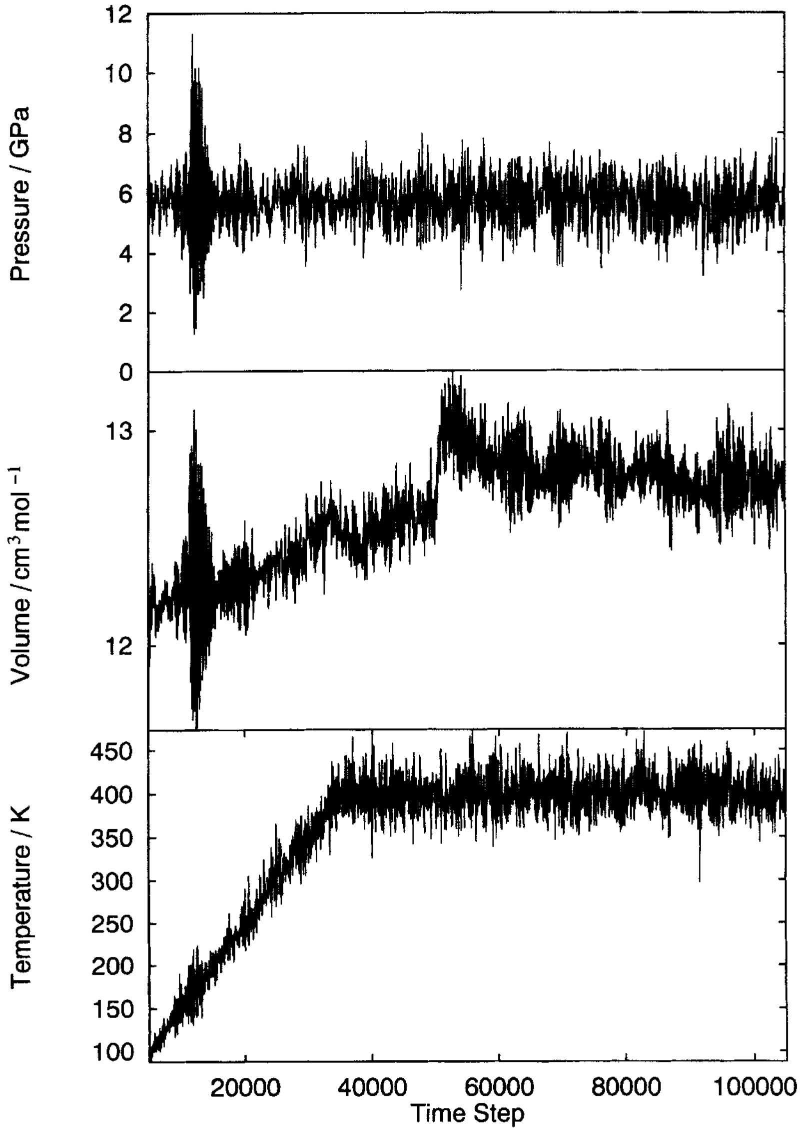

FIGURE 7 Variation of pressure, volume and temperature during the simulation II.

obtained from the simulation II indicate that water molecules do not give rise to changes of their form during the run on heating, being in marked contrast to the case of the simulation I on pressuring.

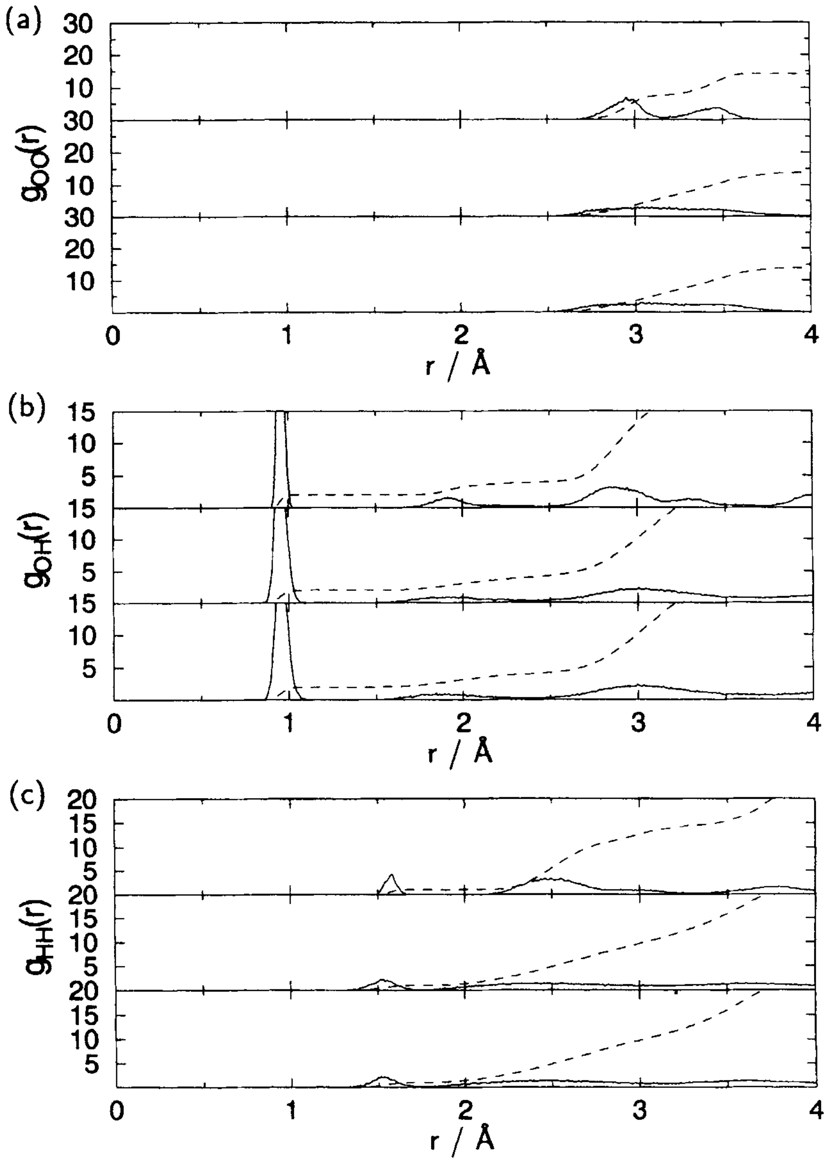

FIGURE 8 Partial pair distribution functions g_{OO}, g_{OH} and g_{HH} for the simulation II. The dashed curves are the corresponding running coordination number. (a) g_{OO} when time step is 5 000 (upper), 45 000 (middle), and 85 000 (lower). (b) and (c) g_{OH} and g_{HH} whose time steps correspond to those of (a).

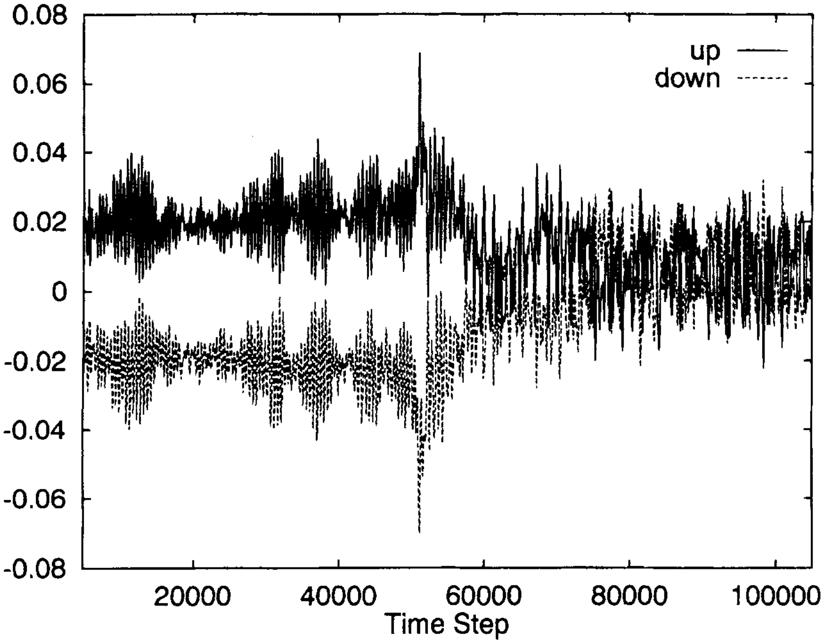

FIGURE 9 Variation of the distortion parameter δ vs time steps for the simulation II."up" and "down" denote the same meaning as that of Figure 4.

4. CONCLUSION AND DISCUSSION

We have carried out two MD simulations, simulation I upon pressuring at a constant temperature and simulation II on heating at a constant pressure, either of which has started with the configuration of ice VIII, and obtained the following results of interest: (1) Through simulation I we have obtained the transition from ice VIII (proton ordered state) to VII (proton disordered state), which was transformed to ice X on further pressuring. In ice X, protons are occupied on the mid points of each O-O distance along a hydrogen bond, and therefore each oxygen atom occupy four hydrogen atoms. The transitions from the proton-ordered state with two different sublattices, which are distorted in the *c*-direction, to the disordered state (single lattice) was confirmed by monitoring the distortion parameter δ (see Fig. 4). Thus, the present result show that ice VII intervenes between ice VIII and X on an appropriate range of high pressures, in disagreement with the hypothetical phase diagram in which the phase transition from ice VIII to X upon pressuring is shown to take place directly [2,3]. (2) Through the simulation II we have also obtained the transition to ice VII. However, it has been made clear that the behaviors on the transitions associated with the processes of both simulations were based on the essentially different mechanisms. During the structural transformation from ice VIII to ice X on applying pressure (simulation I), ice VII appears. The structure of ice VII thus obtained differs from that of ice VII obtained by heating of VIII at a normal pressure (simulation II). The latter is accompanied by the defects induced by rotation of water molecules (orientational defects), while the former contains the defects by exchange of two stable sites of a hydrogen-bond atom between two near-neighbor oxygen atoms (ionic defects). (3) The values of pressures obtained by the simulation is remarkably higher than the corresponding experimental values [3]. This is nothing but to show that the present model is not sufficiently good to the pressure prediction. Since the pressure is proportional to the derivative of the total energy with respect to the volume of the system, it should be rather sensitive to tails of weak potentials, which are very difficult to know in general. The model potentials which we have used in the

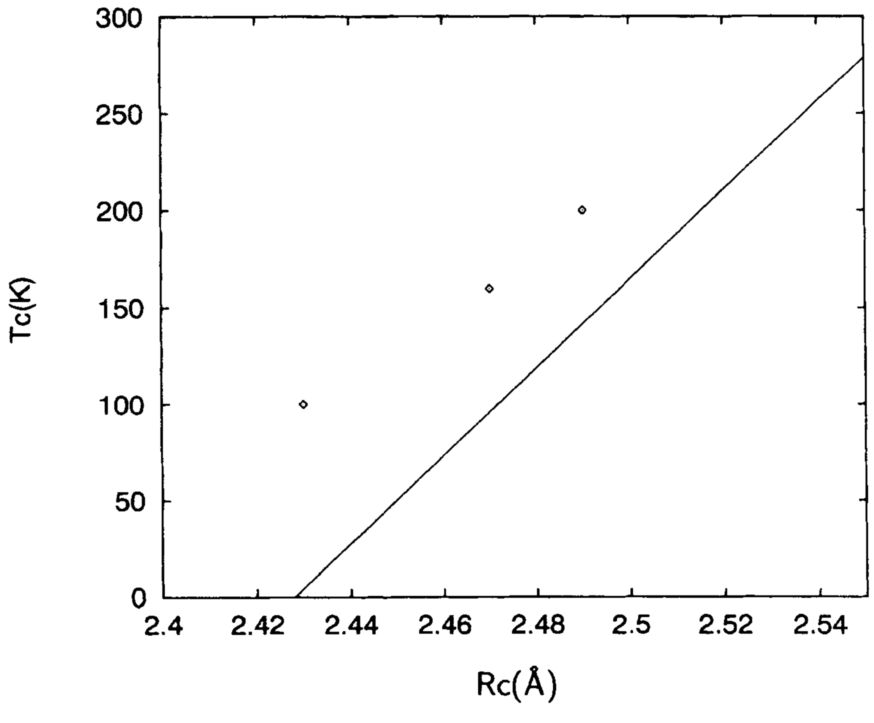

FIGURE 10 The transition temperature T_c vs O-H···O length R_c (solid line: Least-square fit of the experimental data, dots: our result).

present work are also possible to apply to other structural transformations of ice. We will discuss about this in a forthcoming paper.

It is interesting to note the O-O distance of the hydrogen bonds at which the order-disorder phase transition takes place. Figure 10 shows such O-O distances (R_c) vs the transition temperature (T_c) for various hydrogen-bonded substances [20]. It is notable that T_c is increased linearly as R_c is increased. Similar behavior is also found for the present one, which is shown in Figure 10. In the present model, R_c was roughly estimated by the curves shown in the previous sections which indicate the transition in different runs with different temperatures. Therefore the value is not very accurate.

Finally we comment on quantum corrections for the transitions which we have studied in this paper. The hydrogen atom has to be treated as a quantum atom at low temperatures and/or high pressures. The main corrections are due to a zero-point vibration at low temperatures and tunneling effects at high pressures. In the present classical molecular dynamics simulation we have neglected such quantum effects. The tunneling effect may cause the transition from ice VIII to VII and X lead to a lower value of pressure than that predicted by the classical theory.

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