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Molecular dynamics study of ice structural evolution*

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Molecular dynamics simulation is employed to study the structural evolution of low density amorphous ice during its compression from one atmosphere to 2.5 GPa. Calculated results show that high density amorphous ice is formed at an intermediate pressure of ∼1.0 GPa; the O–O–O bond angle ranges from 83° to 113°, and the O–H···O bond is bent from 112° to 160°. Very high density amorphous ice is obtained by quenching to 80 K and decompressing the ice to ambient pressure from 160 K/1.3 GPa or 160 K/1.7 GPa; and the next-nearest O–O length is found to be 0.310 nm, just 0.035 nm beyond the nearest O–O distance of 0.275 nm.

Keywords: molecule dynamics, amorphous ice, phase transition
PACC: 6120J, 6470, 8130H, 6170A

1. Introduction

The dynamical and structural properties of amorphous ice have attracted considerable attention because of its importance for the study of ice forms in astrophysics and for its wide practical applications in cryobiology, as well as for a better understanding of unusual behaviour of water in its liquid state. Different forms of amorphous ice with or without trapped impurities play an important role in astrophysics, because ice in space exists mostly in the form of low-temperature deposit.[1]

There are many different forms of amorphous ice. Their structures and densities vary with both the formation condition and the sample preparation procedure. They are mainly divided into three types, low-density amorphous (LDA) ice, high-density amorphous (HDA) ice and very high-density amorphous (VHDA) ice. The structural properties about these amorphous forms have been studied for a long time by x-ray, electron and neutron diffractions (for reviews see Refs.[2–4]). It is widely believed that all forms of LDA ices are the same or very similar to each other; while HDA ice probably has many metastable states and they cannot interconvert at 80 K due to free energy barriers for re-bonding.[5] VHDA ice is thought to be a more stable form of HDA ice and is an amorphous ice of quenched high-density liquid (HDL).[6]

HDA ice can be prepared in different ways. That with a density of 1.31 g/cm^3 can be produced by pressing a crystalline hexagonal ice (ice Ih) to a high-pressure (> 1.2 GPa) at 77 K. Its density can be reduced to 1.17 g/cm^3 at a temperature below its glass transition (usually < 100 K) by releasing the pressure.[7] HDA ice can also be produced from high-pressure phase of ices at low temperatures (< glass transition temperature ∼100 K) and ambient pressure, otherwise it will transform to LDA ice. For example, the high-pressure phase of ice VIII can be transformed to HDA ice by releasing the pressure at 77 K and slowly warming it to 130 K.[8] By further slow heating, the recovered HDA ice will transform to LDA ice (0.94 g/cm^3).[7] However, recent results show that the HDA to LDA transformation could occur at a lower temperature of 113.4K.[9]

VHDA ice (1.25 g/cm^3) can be obtained by pressing ice Ih to 1.34 GPa at liquid nitrogen temperature, keeping the pressure for 16 min then reducing it to 1.15 GPa while heating the ice to 160 K.[4] Heating is needed because molecules need activation energy to overcome the transition barriers. Very recent research shows that two distinct density changes are observable corresponding to LDA → HDA → VHDA conversions on compressing LDA ice at 125 K up to 1.6 GPa,[10] which means that they are first-order transitions. As for their structural differences, VHDA ice has the double occupancy of the interstitial molecules located in a shell whose distance from a typical central molecule is larger than the direct hydrogen bonded

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neighbours by 0.01–0.02 nm.[4] In this paper, by using molecular dynamics (MD) simulation, we provide more detailed information about structural evolutions during compressing LDA ice up to 2.5 GPa at 125 and 160 K,[11] separately. Then dropping temperature down to 80 K and releasing the pressure at different stages, such as 125 K/0.5 GPa, 125 K/0.9 GPa, 125 K/1.3 GPa, 125 K/1.7 GPa, 160 K/0.5 GPa, 160K/0.9 GPa, 160 K/1.3 GPa and 160 K/1.7 GPa.

2. Simulation

There were 576 water molecules in our MD simulation unit-cell and the four-site classic potential TIP4P[12] was used to describe water intermolecular interactions. Rigid water molecule model was adopted, i.e. the bond length of O–H was set to 0.09572 nm, ∠HOH was 104.52°, and the M site was separated from oxygen atom 0.015 nm along the molecular symmetry axis. Fortran code MDCSPC4[13] was used during the whole of the simulations. The simulations were carried out in an isobaric—isothermal (NPT) ensemble and 1fs (10^{-15} second) was set for the simulation step. The non-bonded H_2O–H_2O interactions were truncated at 1.5 nm and the summation was made using Ewald techniques.[13] The initial velocities assigned to the individual atoms were chosen from a Maxwell–Boltzmann distribution corresponding to the desired simulation temperature.

Ice Ih primitive unit-cell included four water molecules.[14] Because its hydrogen arrangement was disordered, the simulation cell should be chosen as big as possible. We used a Random Walk program[15] to set hydrogen atoms, i.e. first taking one hydrogen atom out and then allowing this hydrogen vacancy to move randomly throughout the whole lattice but with the ice rules being obeyed.[16] After that, the lattice was compressed up to 1.2 GPa at 77 K, the density was increased from 0.94 g/cm^3 up to 1.33 g/cm^3 and the lattice was compressed to that of HDA ice.[17] Then the pressure was reduced to the ambient and the system was heated separately to 125 K and 160 K at a rate of 2×10^{12} K/s (5 K/2500 steps). The LDA simulation system was obtained at the densities of 1.000 g/cm^3 and 0.998 g/cm^3 for different heating temperatures of 125 and 160 K, respectively. They were not far from ρ=0.94 g/cm^3 experimentally prepared at P=0 and 80K or ρ=0.98 g/cm^3, 1.04 g/cm^3 prepared by simulations.[5] Finally, the simulation systems were compressed to 2.5 GPa, during which the pressure was added by 0.1GPa within 50 ps so the compression rate was 0.002 GPa/ps. The rates of reduction of temperature (2×10^{12}K/s) and pressure (0.002GPa/ps) were the same as those of increasing.

3. Result and discussion

Figure 1 shows the evolutions of intermolecular energy and density of the system during compression at temperatures of 125 and 160 K, separately. Triangle-solid lines in the figure represent the processes of decreasing temperature to 80 K followed by

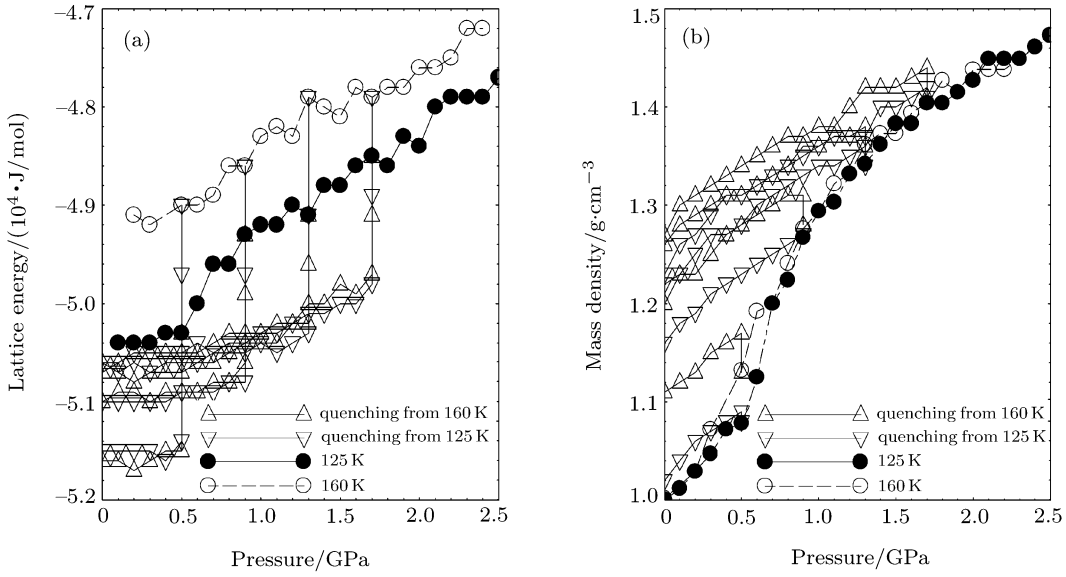


Fig.1. Variation of the simulated amorphous system with compressing pressure at different temperatures of 125 K and 160 K (a) lattice energy of the system; (b) mass density.

the pressure release. From these recovered densities at 80 K we can approximately estimate that the transform pressures of LDA → HAD range from 0.7 to 1.1 GPa, which agrees well with experimental result of 0.9 GPa.[10] A pressure > 1.3 GPa at 160 K is necessary for the formation of VHDA, which is also in agreement with the experimental result –1.34GPa, and then it is reduced to 1.15 GPa when the system is heated to 160 K.[4] But by investigating these curves, We find that the samples heated to 125 K cannot be transformed to VHDA even under 1.7 GPa.

Figure 2 shows the evolutions of O–O radial distribution functions (RDFs) during the compressing procedure at 125 K and 160 K. The second peak in Fig.2(a) (125 K) shifts much less than that in Fig.2(b) (160K) under low pressure (< 0.8 GPa), which may be due to low kinetic energy of the molecules. When the pressure is larger than 1.0 GPa, different temperatures do not cause obvious differences in structures. Unlike the first stable peak (from 0.269 nm at 0.2GPa back to 0.264 nm at 2.4 GPa), the second peak for 125 K moves from 0.420 nm (at 0.2 GPa) through 0.326 nm (1.0 GPa) to 0.309 nm (2.4 GPa) and that for 160 K is back from 0.430 nm (0.2 GPa) through two peaks –0.310 nm, 0.340 nm (1.0 GPa) to 0.310 nm (2.4 GPa). This means that the next-nearest oxygen–oxygen length is located at a shell of radius ∼0.310 nm, which is about 0.035 nm longer than the nearest O–O distance of 0.275 nm. The third peak displaces in the way similar to the second peak.

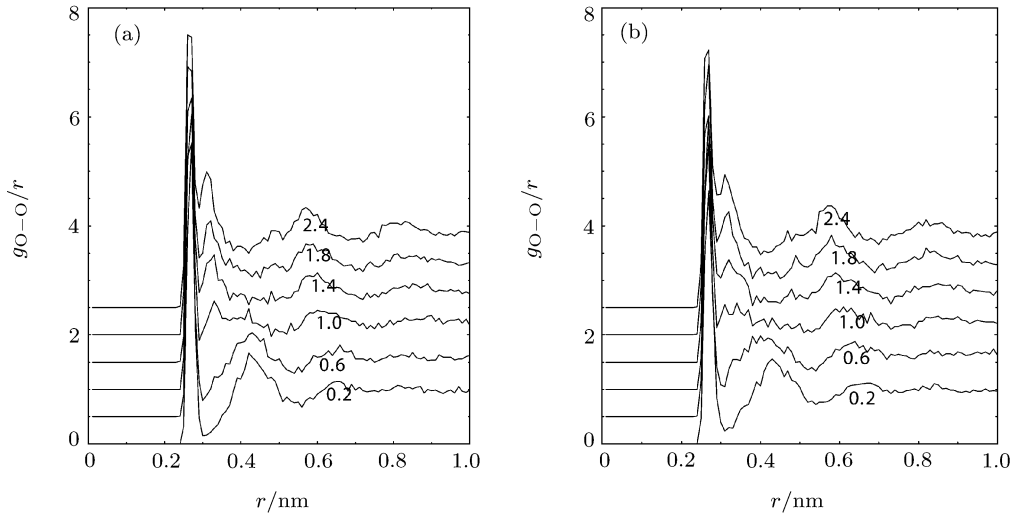


Fig.2. Evolution of the O–O radial distribution function with compressing pressure from 0.2 up to 2.4 GPa at different temperatures (a) 125 K; (b) 160 K.

Figure 3 shows the evolutions of O–O–O angle distribution functions (ADF). The ADF at lower temperature evolves with pressure from single Gaussian peak located at 106° (0.2 GPa) through two Gaussian peaks located at 86°, 113° (1.0 GPa) to two peaks at 70°, 106°(2.4 GPa). The ADF at higher temperature shows the same evolution tendency: from 104° (0.2 GPa) through 80°, 112° (1.0 GPa) to wider ranges of 75°, 96°, 119° (2.4 GPa).

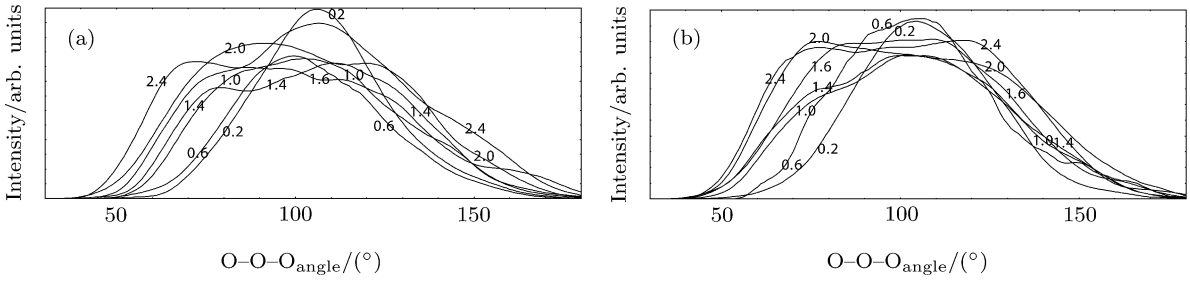


Fig.3. The evolution of O–O–O angle distribution function with compressing pressure at different temperatures (a) 125 K; (b) 160 K.

Figure 4 shows O–H RDF evolutions. The locations of the first peak (0.179 nm) and the second peak (0.304 nm for 125 K and 0.311 nm for 160 K) remain stable. The second peak height increases dramatically and the third peak disappears, so we believe that the peak for the third nearest neighbours (0.445 nm) have merged with that for the second nearest neighbours. A new third peak appears after 1.0 GPa and it is located at about 0.57 nm.

Figure 5 illustrates the structural O–O and O–H RDFs of 80 K quenching from 160 K/1.3 GPa, 160 K/1.7 GPa, 125 K/1.3 GPa and 125 K/1.7 GPa. It can be easily found that the samples quenching from 160 K/1.3 GPa and 160 K/1.7 GPa are VHDA ice, however, the VHDA ice cannot be obtained from 125 K even at a pressure as high as 1.7 GPa.

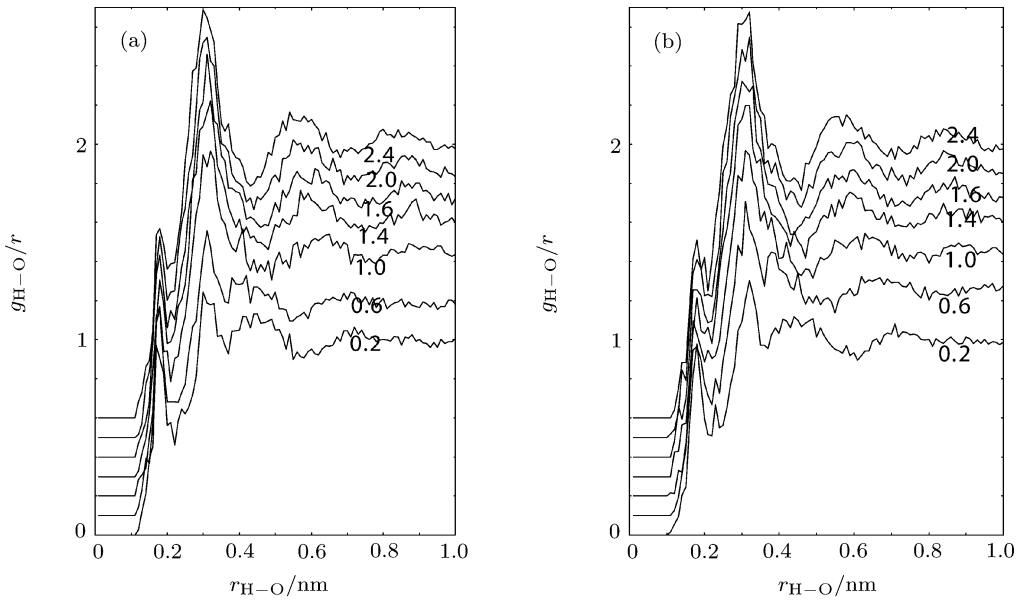


Fig.4. The evolution of O–H radial distribution function with compressing pressure at different temperatures (a) 125 K; (b) 160 K.

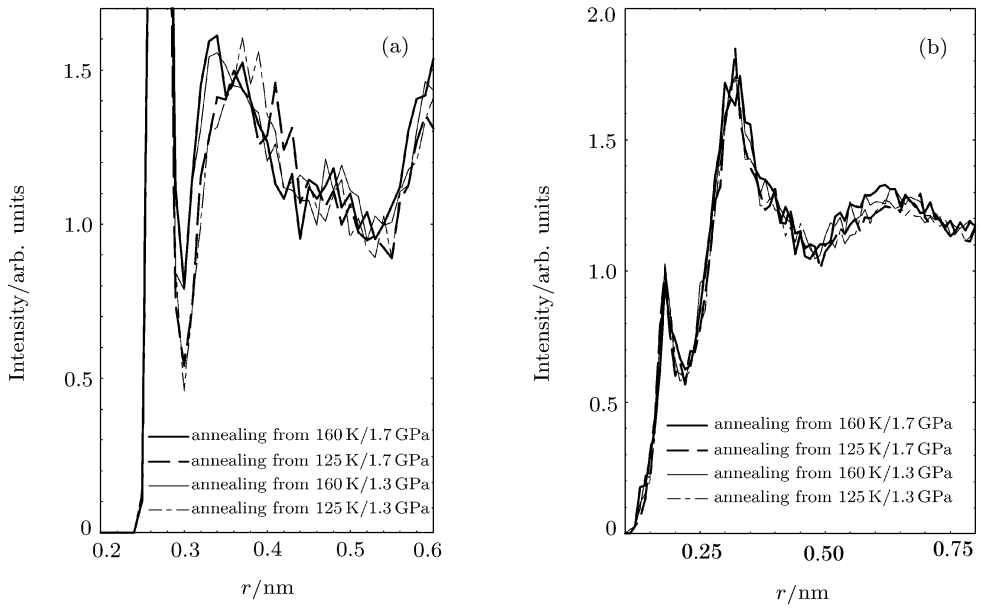


Fig.5. The radial distribution function comparisons obtained by quenching to 80 K and ambient pressure from different temperatures (125 K and 160 K) and pressures (0.5 and 1.3 GPa).(a) O–O; (b) O–H.

It is found that the angle of O–O–O varies from 105° in LDA ice through 75°–122° in HDA ice to 66°–124° in VHDA ice and that of O–H$\cdots$O varies from 160° in LDA ice to 110°–150° in VHDA ice. Similar simulations have been carried out in Ref.[5] but here we have obtained a different structural evolution showing that the increase of amorphous ice density comes from the bendings of O–O–O and O–H$\cdots$O that make the O–O next nearest-neighbour and O–H the third nearest-neighbour close together. In Fig.3 no small O–O–O angles appear and in Fig. 4 the first peak does not rise up sharply, so it can be concluded that the five nearest oxygen configurations cannot be formed during compression. In Figs.2, 3 and 4 all variations are slow so we conclude that amorphous ice structures are similar and undergo no abrupt changes such as from one lattice to two interpenetrated sublattices like ice VI or VIII.

As mentioned earlier, all LDA ices have very similar structures but HDA ices vary in forms. From Fig.1 it can be seen that the two amorphous structures with almost the same energy have two obviously different densities, which means that these HDA ices have different structures. There is indeed a gap between the densities of HDA and VHDA at 80 K, which is due to the existence of the second critical point.[6,18] In the future, much attention should be paid on VHDA structural evolution during compressing.

4. Summary

LDA ice was compressed from ambient pressure to 2.5 GPa at 125 K or 160 K. No obvious difference between the molecules at different temperatures could be found when the pressure was higher than 1.0 GPa; but if the pressure was less than 0.8 GPa, the water molecules at 125 K were inactive. In other words, 125 K was too low for molecules to overcome the energy barriers. VHDA ice was obtained by quenching from 160 K/1.3 GPa and 160 K/1.7 GPa, whereas they cannot be obtained from the 125 K sample even at 1.7 GPa, which is inconsistent with the experimental results.[10] Interstitial molecules were formed and they appeared to be in the 0.310 nm shell, which was about 0.03 $\sim$0.04 nm beyond the typical nearest O–O distance of 0.275 nm.

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