Modeling the polymorphic transformations in amorphous solid ice

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ABSTRACT

The description of various amorphous phases of ices has been performed on a molecular level in order to study the nature of amorphous polymorphism in a water system. The models of very high-, high- and low-density amorphous (VHDA, HDA and LDA, respectively) ices have been constructed. The molecules are located in their equilibrium states and the structure of the networks is characterized by the absence of long-range atomic order, but short-range order is still present. The thermodynamic properties of VHDA, HDA and LDA ices have been determined using the molecular dynamics and lattice dynamics methods. It has been found that at low temperatures the transformation LDA → HDA is a real phase transition in the classical sense. In the case of HDA → VHDA, the same transition has been found only in negative pressure regions. At positive pressure the transformation from the metastable phase HDA to the thermodynamically stable phase VHDA can be classified as a continuous one.

1. Introduction

Polymorphism, i.e. the presence of more than one amorphous state or phase in amorphous solids and liquids, is of fundamental importance in solid state chemistry and physics, geology, materials science [1]. Amorphous ice can also exist as more than one solid structure. There have been discoveries involving the pressure-induced transformation of hexagonal (I_h) ice to high-density amorphous (HDA) ice, the transformation of HDA into low-density amorphous (LDA) ice warmed to about 120 K at ambient pressure [2—4] and the HDA transformation into very-high-density amorphous (VHDA) ice by isobaric heating to about 160 K at a constant pressure of 1.15 GPa [5]. Many investigations related to polymorphism have been performed in other amorphous substances as well: water (for reviews see Ref. [6]), silica [7], silicon [8,9], chalcogenide glasses [10] and metallic glass [11].

Experimental and theoretical studies on VHDA, HDA and LDA ices have raised questions regarding the nature of the transformation between the amorphous forms of ice. One of the main questions is whether the amorphous ices are thermodynamically continuously connected with liquid states and can be regarded as

vitrified liquids (glassy states) or distorted crystalline phases (crystal-like states) [12].

Polymorphism in supercooled liquid water continues to be a topic of intensive study (see most recently [13—22]). This is connected with the substantiation of the hypothesis of a first-order thermodynamic liquid—liquid transformation in the highly supercooled liquid and the existence of a phase boundary line between two distinct phases of liquid water. This boundary ends at a second critical point located from measurements of the LDA—HDA transformation to be at ~1 kbar and 220 K [23—25]. The scenario of two supercooled liquid phases has been questioned by the discovery of VHDA ice [5] and the existence of two distinct density steps, LDA → HDA and HDA → VHDA at 125 K up to 1.6 GPa [26].

Neutron experiments, x-ray experiments [27] and MD simulations [28] of the transition between LDA and HDA ices at ambient pressure show the presence of an intermediate form of amorphous ice (the relaxed structures of the high-density amorphous (RHDA)) formed between 95 and 105 K at atmospheric pressure during the HDA → LDA ice transformation. Thus, the transformation of HDA to LDA ice is not a first-order thermodynamic transition and may occur in series between metastable states, with each metastable state representing an intermediate state between HDA and LDA. This is also not agreement with the scenario of two supercooled liquid phases.

These experimental and theoretical studies have raised

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important questions that are related to nature of polymorphism:

a) Are the intermediate phases between HDA and LDA ices true thermodynamic metastable states or glassy states?
b) Are the transformations of HDA to LDA and HDA to VHDA ices true thermodynamic phase transitions or kinetic densification processes?
c) Are VHDA, HDA and LDA ices unique phases?

In most cases, classical molecular dynamics (MD) simulations are able to reproduce qualitatively many of the transformations between ice, amorphous ice, and liquid water observed in experiments [16—18]. However, amorphous ices are quantum systems and therefore the zero-point vibration free energy is large and it should be taken into account in calculations. At low temperatures, the significance of this term for ice is known but there is no direct procedure to include this effect in free energy calculations using the MD method [29].

The models of HDA and LDA solid ices were built including zero-point vibration free energy [30—33]. It was shown that quantum corrections have a profound effect on the thermodynamic properties as well as the location of important thermodynamic points in the water phase diagram. The combination of molecular dynamics and conjugate-gradient and lattice dynamics methods was applied in conjunction with experimental data and a detailed reconstruction of the networks of hydrogen bonds of VHDA, HDA and LDA solid ices was obtained [34]. In this approach, the amorphous structure was constructed using the MD method and the final configurations were compared with experiment using paired correlation functions. The dynamically stable structures of different amorphous solid ices were obtained by additional optimization using the conjugate gradient method and verified by frequency calculations using the lattice dynamics (LD) approach. Thus, the vibrational spectra have been calculated directly with less computational time.

In this work the thermodynamic properties (equation of states, Helmholtz and Gibbs free energies) of VHDA, HDA and LDA phases of amorphous solid ices have been calculated. The lines of the structural solid-solid classical first-order transition in the amorphous solid ices on the *P-T* phase diagram have been defined.

2. Theory and computational details

The Helmholtz free energy, $-F_{qh}(V,T)$, of a given system can be calculated at temperature T using the following formula:

$$F_{qh}(V,T) = U + E_o + F_{vib}(T), \qquad (1)$$

where U is the potential energy, E_0 is the zero-point vibration energy and $F_{vib}(T)$ is the temperature dependent vibrational contribution, respectively,

$$E_0 = \frac{1}{2}\sum_{j\,\vec{q}} \hbar\omega_j(\vec{q}) \text{ and } F_{vib} = k_B T \sum_{j\,\vec{q}} \ln\left(1 - e^{-\hbar\omega_j(\vec{q})/k_B T}\right). \quad (2)$$

and $\omega_j(\vec{q})$ is the *j*th lattice vibrational frequency.

The equations of state of VHDA, HDA and LDA solid ices can be determined from the derivatives at constant temperature T:

$$p(V) = -\left(\partial F_{qh}(V,T)/\partial V\right)_T \qquad (3)$$

where V is the volume of the solid.

The Gibbs free energy, $G(p,T)$, or chemical potential of a one-component system, $\mu(p,T)$, can be expressed from the Helmholtz

free energy free energy, F_{qh} (V, T), using the equation of state p(V):

$$G(p,T) = \mu(p,T)N = F_{qh}(V(p),T) + PV(p) \qquad (4)$$

where N is the number of molecules.

Here, the quasiharmonic lattice dynamics (QLD) method has been applied to estimate the free energy, Gibbs functions, phase diagram and equations of state of VHDA, HDA and LDA solid ices. In the quasiharmonic approximation, the free energy of a crystal has the same form as in the harmonic approximation but the structural parameters at fixed volume and temperature are determined self-consistently by minimization of the free energy. The details of this approach can be found elsewhere [35—37].

For the description of amorphous solid ice the model of a crystal with a large unit cell (supercell) has been used. The supercell consists of 512 water molecules. The simulation was performed within the framework of the modified simple point charge-extended (SPCE) water-water interaction potential [38]:

$$V_{mm'} = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right] - \frac{Z_m Z_{m'}}{R} \qquad (5)$$

with modified parameters $\varepsilon = 0.65053$ kJ/mol and $\sigma = 0.31556$ nm. The charges on the oxygen and hydrogen atoms are $Z_O = -0.8476|e|$ and $Z_H = 0.4238|e|$, respectively, where $|e|$ is the elementary charge, which remains the same as in the original SPCE potential [39]. The long-range electrostatic interactions have been computed by the Ewald method [40].

The structures of LDA, HDA, and VHDA ices were obtained using a procedure that includes isothermal compression/decompression and isochoric heating that was described previously [22]. First, the structure of the HDA ice supercell was obtained by multiple compressions and expansions of the initial crystal lattice of ice I_c at 77 K using MD simulations implemented in the LAMMPS code [41]. Then the HDA structure was decompressed down to a density of 0.94 g/cm^3 and isochoric heated up to 140 K. The obtained LDA structure was compressed up to a density of 1.25 g/cm^3 and heated up to 150 K. The MD simulations of all intermediate processes were performed for 6 ns with a time step of 1 fs. After the MD runs were completed the LDA, HDA, and VHDA structures were additionally optimized by the conjugate-gradient method in order to obtain the potential energy minima with a dynamically stable configuration for each amorphous phase. The importance of this effect for liquid water systems has been shown previously [42]. Finally, the dynamic and thermodynamic properties of the VHDA, HDA, LDA, and I_h ices were estimated using the lattice dynamics (LD) calculations [43,44].

3. Results and discussion

Structural analysis shows that the obtained structures of the LDA, HDA and VHDA phases have no long range ordering but the local order still contains 4 nearest neighbors having a hydrogen bonding connection with the distorted tetrahedral configuration as shown in Fig. 1a—c. The average length of such bonds is about ~2.7 Å. For HDA and VHDA ices there are also one and two additional neighbors, respectively, which are located at longer distances to the central atom without hydrogen bonds. These additional neighbors are placed within the range ~3.2 Å — 3.5 Å. This peculiarity of amorphous ices agreed well with earlier obtained experimental results [45,46]. The proposed approach reproduced the oxygen-oxygen radial distribution functions $G_{OO}(R)$ (see Fig. 1d) of the amorphous structures in agreement with experimental data [45,46]. The first coordination shell for LDA ice gives a well-defined peak characterizing the formation of hydrogen-bond networks