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Path-integral simulation of ice VII: Pressure and temperature effects

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ABSTRACT

The effects of pressure and temperature on structural and thermodynamic properties of ice VII have been studied by using path-integral molecular dynamics (PIMD) simulations. Temperatures between 25 and 450 K, as well as pressures up to 12 GPa were considered. Interatomic interactions were modeled by using the effective q-TIP4P/F potential for flexible water. We analyze the pressure dependence of the molar volume, bulk modulus, interatomic distances, kinetic energy, and atomic delocalization at various temperatures. Results of PIMD simulations are compared with those derived from a quasi-harmonic approximation (QHA) of vibrational modes, which helps to assess the importance of anharmonic effects, as well as the influence of the different modes on the properties of ice VII. The accuracy of the QHA for describing this high-pressure phase decreases for rising temperature, but this approximation becomes more reliable as pressure grows, since anharmonicity becomes less relevant. Comparisons with low-pressure cubic ice are presented.

1. Introduction

Over the last few decades the phase diagram of water in the high-pressure region has attracted great interest in condensed matter physics and chemistry, as well as in planetary sciences [1–4]. This is due, apart from the fundamental character of water, to the large variety of ice polymorphs which have been found under different conditions of pressure (P) and temperature (T). The phase diagram of water is currently known up to $T \sim 1000$ K and P in the order of hundreds of GPa [5].

Ice VII is generally accepted to be the stable phase of water at pressures from 2 to about 60 GPa at room temperature, although some studies predict structural variations of ice VII in this pressure range [6,7]. Oxygen atoms in ice VII form a body-centered cubic (bcc) structure, with H atoms lying between them, so that each O atom is surrounded by four H atoms, two of which covalently bonded and two H-bonded to it, according to the Bernal–Fowler rules [8]. Apart from these constraints, the H distribution is disordered over the available lattice sites [9,10]. The resulting H-bond network consists of two independent interpenetrating subnetworks not hydrogen-bonded to each other, each of them topologically equivalent to the H-bond network of cubic ice Ic [10–12].

Ice VII is believed to be present in various natural environments, such as the Earth mantle or icy planets. In this context, the thermoelastic properties of ice VII and other high-pressure polymorphs can have implications for the dynamics of cold slab subduction in the Earth lower mantle, as well as for the evolution of icy planets and satellites [7]. This high-pressure water phase has been studied by a variety of techniques, among which one finds X-ray [6,13–18] and neutron [9,19–22] diffraction, as well as vibrational spectroscopy [23–26], Brillouin scattering [7], electrical conductivity measurements [27], and several kinds of calculations [6,28–34].

At low temperatures, ice VII transforms into H-ordered ice VIII [5,25,26]. For $P < 10$ GPa, the transition temperature T_c is about 270 K, and for $P > 10$ GPa, T_c decreases for increasing pressure [26]. At $P \sim 60$ GPa, ice VII transforms into ice X, where H atoms lie on the middle point between adjacent oxygen atoms, so that the molecular nature of water is no longer preserved. This phase transition from ice VII to ice X has been found to be caused by quantum proton delocalization [35,36]. At higher pressures, other ice phases have been encountered, and some others are predicted to appear at pressures above 1 TPa [37].

Computer simulation of condensed phases of water at an atomic level date back to the 1970s [38,39]. In the last few decades, much work has been devoted to the development of empirical potentials to describe both liquid and solid H_2O phases, so that nowadays a large variety of this kind of potentials can be found in the literature [40–45]. Many of these interatomic potentials assume a rigid geometry for the water molecule, and some others allow for molecular flexibility either with harmonic or anharmonic OH stretches. In recent years, simulations of water using *ab initio* density functional theory (DFT) have been also carried out [46–48]. It has been observed, however, that a good description

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of H-bonds in condensed phases of water is a tough job with presently available energy functionals, and some properties cannot be accurately reproduced by DFT calculations [49]. Some contributions to improve the description of van der Waals interactions in water within the DFT formalism have been developed in recent years [50–54].

A limitation of *ab initio* electronic-structure calculations is that they usually deal with atomic nuclei as classical particles, without considering quantum aspects like zero-point motion. Such quantum aspects can be taken into account by using harmonic or quasiharmonic approximations for the nuclear motion, but the precision of these methods is not readily assessed when large anharmonicities are present, as may be the case for light atoms like hydrogen. To consider the quantum character of atomic nuclei, the path-integral molecular dynamics (or Monte Carlo) approach has turned out to be very useful, because in this method the nuclear degrees of freedom can be quantized in an efficient manner, including both thermal and quantum fluctuations in many-body systems at finite temperatures [55,56]. Then, a powerful method can consist in combining DFT to determine the electronic structure and path integrals to describe the quantum motion of atomic nuclei [46,48,57,58]. However, this procedure requires computer resources that may enormously reduce the number of state points that can be considered in actual simulations, as compared to the use of effective interatomic potentials.

Effective potential models for condensed phases of water usually treat H_2O molecules as well-defined unbreakable entities, connected by H-bonds. This prevents their use to study high-pressure phases such as ice X, including symmetric O–H–O bonds. This shortcoming does not affect *ab initio* potentials, where in principle any bonding configuration or geometry can be studied. In this line, Benoit et al. [59,60] investigated the influence of nuclear quantum motion in proton ordering and H-bond symmetrization in high-pressure phases of ice, by carrying out path-integral molecular dynamics (PIMD) simulations with an interatomic interaction given by DFT calculations. More recently, the momentum distribution of protons in ice X was studied by Morrone et al. [61] using also *ab initio* PIMD.

Nuclear quantum effects become more relevant for light atomic masses, and are expected to be especially important in the case of hydrogen. Then, we consider the question of how quantum motion of the lightest atom can influence the structural properties of a solid water phase such as ice VII, and in particular if these effects are relevant or detectable for the solid at different densities, i.e. under different external pressures. This refers to the crystal volume and interatomic distances, but also to the thermodynamic properties of ice. In this respect, it is interesting to estimate the effect of nuclear quantum motion on the stability range of the different ice phases. Thus, it is known that quantum effects change the melting temperature T_m of hexagonal ice Ih at ambient pressure by some degrees, as manifested by the isotope effect on T_m [62].

In this paper we study ice VII by PIMD simulations at several pressures and temperatures, in order to analyze its structural and thermodynamic properties. Interatomic interactions are described by the flexible q-TIP4P/F model, which was used earlier to carry out PIMD simulations of liquid water [63], ice Ih [62,64,65], and high-density amorphous ice [66]. This potential model has been found to yield a reasonable description of the phase diagram of water up to pressures in the order of 10 GPa [67]. The use of a rather accurate effective potential allows us to carry out long PIMD simulation runs, and to obtain a good convergence of structural and thermodynamic variables in the $P-T$ region under consideration. The q-TIP4P/F potential model was found to yield reliable results for low-pressure phases such as ice Ih [64,65,68], and it is a goal of the present work to analyze its capability to describe high-pressure phases as ice VII. A different goal consists in evaluating the reliability of applying a QHA to study these phases, by comparing its predictions with results of PIMD simulations. Such an approximation has been used earlier to study low-pressure water phases such as ices Ih, II, and III [69].

The paper is organized as follows. In Section 2, we describe the computational methods and the model used in our calculations. Our results are presented in Section 3, dealing with the pressure and temperature dependence of molar volume, bulk modulus, O–H interatomic distance, kinetic energy, and atomic delocalization in ice VII. Section 4 gives a summary of the main results.

2. Computational method

2.1. Path-integral molecular dynamics

We use the PIMD method to obtain equilibrium properties of ice VII at various temperatures and pressures. This method is based on an isomorphism between the real quantum system and a fictitious classical one, that appears after a discretization of the quantum density matrix along cyclic paths [70,71]. Such an isomorphism translates in practice into replacing each quantum particle by a ring polymer consisting of L (Trotter number) classical particles, which are connected by harmonic springs with temperature- and mass-dependent force constant. This isomorphism is exact for $L \to \infty$, so that a numerical error is introduced by using a finite L, which may be corrected by adequate extrapolation of the results to infinite L (see below). Details on this simulation technique can be found elsewhere [55,56,72]. The dynamics considered in the PIMD method is artificial, and does not correspond to the actual quantum dynamics of the real particles under consideration. It is, however, useful for effectively sampling the many-body configuration space, giving precise results for the equilibrium properties of the quantum system. An alternative way to obtain equilibrium properties is Monte Carlo sampling, but this procedure requires for our present problem more computer resources (CPU time) than the PIMD method. In particular, for the latter procedure the codes can be more readily parallelized, which is an important factor for efficient use of modern computer architectures.

Ice VII has a body-centered cubic structure with space group *Pn3m* and two water molecules per unit cell [9]. For the simulations we generated cubic supercells including $N = 432$ water molecules with periodic boundary conditions. In these supercells, hydrogen-disordered ice structures were generated by a Monte Carlo procedure, in such a way that each oxygen atom had two covalently bonded and two H-bonded hydrogen atoms (Bernal–Fowler rules [8]). It was also imposed that the electric dipole moment of the generated supercells were close to zero [73]. To quantify the influence of hydrogen disorder on the results presented below, we carried out PIMD simulations for six different hydrogen arrangements. We found that the dispersion of the results found for the different H configurations was smaller than the statistical error bars obtained from simulations for a single H arrangement. This was taken as an indication that the supercell size considered here was enough to adequately represent the proton disorder in ice VII, in accord with earlier results for this ice phase [67].

Interatomic interactions have been modeled here by the point charge, flexible q-TIP4P/F model, which was applied earlier to study liquid water [63,68], ice [62,64,65], and water clusters [74]. Several empirical potentials previously used for simulations of condensed phases of water treat H_2O molecules as rigid bodies [75–77]. This may be convenient for computational efficiency, giving reliable results for various properties of liquid water and ice, but they disregard the contribution of molecular flexibility in the structure and dynamics of condensed phases of water [63], aspects which may be relevant for our present purposes. In particular, a