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## **Nuclear quantum effects in solid water: new insights from computational modeling**

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## Introduction

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Solid water, commonly referred to as ice, is ubiquitous throughout the universe as a material with many unique properties. Ice plays an important role for cloud formation on earth and helping life survive on this planet. Arctic ice regulates its temperature by reflecting sunlight, and ice glaciers are an important reservoir of fresh water. Without ice, no aquatic plants and animals would survive throughout the winter months [1, 2]. Furthermore, ice under extreme conditions has received special attention in astronomy and planetary science. When searching for life on other planets, detecting ice is commonly considered to be a prerequisite. Consequently, studying ice is important for interdisciplinary research, and has been an active field in the physical sciences for many years. Since ice restructures in different phases under different temperature and pressure conditions, thermodynamic properties and their roots in chemical bonding are an interesting subject of study in the physical sciences [3].

### 1.1 Hydrogen Bond Network in Ice

Chemical bonding in ice is surprisingly complex despite the simple chemical formula of water ( $\text{H}_2\text{O}$ ). A water molecule consists of one oxygen atom covalently bound to two hydrogen atoms forming a bond angle of  $104.5^\circ$ . Since electrons are not equally

shared in these bonds, the O and the H atoms are left with slight negative and positive charges, respectively. The resulting electrostatic interaction between hydrogen and oxygen atoms of different water molecules are the most obvious cause for the existence of hydrogen bonds (HBs). In addition, HBs also share some characteristics of covalent bonding such as being directional and only involving a limited number of interaction partners. Each water molecule can form HBs with up to four other molecules: two through its hydrogen atoms and two through the two lone electron pairs of its oxygen atom [4]. In other words, each water molecule donates and accepts two HBs. The strength of HBs largely depends on the relative orientation of the contributing water molecules. Consequently, hydrogen bonds are typically 10-100 times weaker than covalent bonds but can be about ten times stronger than van der Waals (vdW) interactions [5]. HBs are thus capable of storing a lot of energy, which results in an unusual high heat capacity. This property of ice makes the climate more moderate in many parts of this planet, resulting in more stable conditions for life on earth [6, 7].

In the most common phase of ice on earth, ice Ih, the hydrogen bond network results in bond angles which come very close to the  $109.5^\circ$  found as vertex-center-vertex angle in an ideal tetrahedron. Despite the energy cost to deform the bond angle of a water molecule in gas phase (see above), the tetrahedral bond angle is favourable for the stability of ice Ih. It also implies a rather “open structure” consisting of non-planar hexagonal rings, with the oxygen atoms forming a honeycomb structure that becomes “visible” when cutting ice Ih in the basal plane. Inside those rings there is almost sufficient space for an additional  $\text{H}_2\text{O}$  molecule. This results in the density of ice Ih being 8.3% lower than the density of liquid water – and thus the famous and tremendously important property of the former floating on the latter.

While the oxygen atoms form a periodic lattice, this does not hold for the hydrogen atoms. According to the ice rules [8], each hydrogen atom is always found between precisely two oxygen atoms. In 1935 Pauling showed that these ice rules result in  $(\frac{3}{2})^N$  possible configurations for  $N$  HBs. Assuming equal likelihood for all of these configurations and thus quasi-random placement of the hydrogen atom yields a very

simple estimate for the so-called residual entropy ( $S_0 = Nk_B \ln(\frac{3}{2})$ ), which was shown to be surprisingly accurate by the experiments of Giauque and Stout in 1936. Other experiments [11, 12] suggested the existence of a hydrogen-ordered version of ice Ih, which is depicted as ice XI in Fig. 1.1. This figure also shows seven hydrogen-disordered ice phases. They can transform to hydrogen-ordered phases when being cooled to lower temperatures or by changing the pressure.

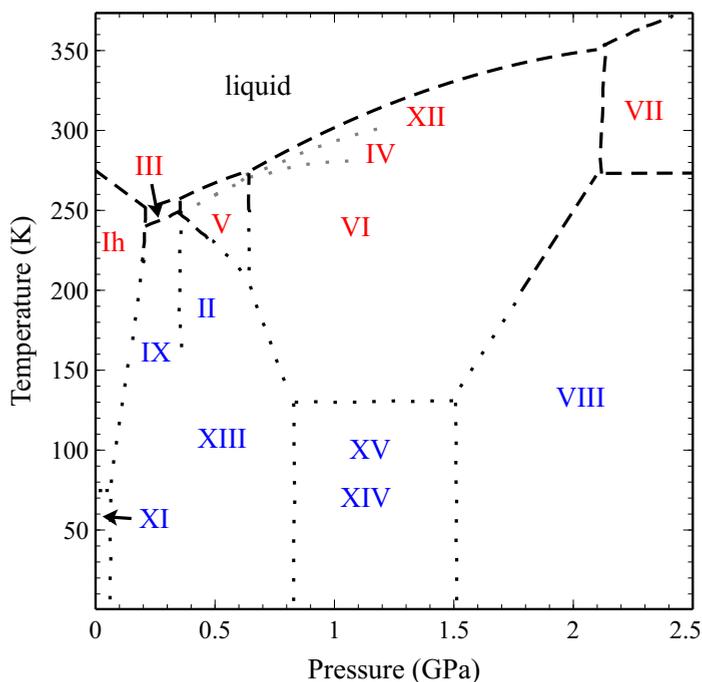


Figure 1.1: Phase diagram of water and ice as function of pressure and temperature Salzmann [13]. Hydrogen-disordered and hydrogen-ordered ice phases are indicated by red and blue labels, respectively. Measured (extrapolated) phase boundaries are shown by black dashed (dotted) lines. Gray dotted lines show phase boundaries for metastable phases, e.g. IV and XII.

## 1.2 Modeling Ice Properties

For a long time, experimental techniques have been the only way to obtain scientific insights about structural and thermodynamic properties of ice. X-ray or neutron scattering experiments for example have provided significant insights to understand how the water molecules are arranged in different ice phases and thus allowed to unravel the importance of hydrogen bond networks. Remarkably, it was Pauling's theoretical work that proposed for the first time that four water molecules are connected in a tetrahedral arrangement in ice Ih [7, 9]. This structural model was confirmed by a neutron diffraction scattering experiment afterwards [14]. Nowadays, the knowledge obtained from computational modeling and experiments is considered complementary to each other. Ideally, calculations allow to quantitatively understand measurements and thus provide insights as well as stimulate new experiments. The improvement of computational facilities and algorithms used for computational modeling during the last decades has increased the scope for the latter, which allows to address questions like the structure of ice under extreme conditions. For instance, studying the enormous geophysical pressure produced by planetary cores demands considerable efforts in real experiments, while calculations can easily take a  $pV$ -term into account in a thermodynamic context [15, 16].

For any atomistic computational modeling, an interaction potential is mandatory to calculate properties of ice. In the simplest case, such a potential only depends on the nuclear coordinates and relies on empirically motivated and parametrized expressions for different contributions to the bonding. Interatomic pair potentials with fixed atomic charges are the prime example of this approach [17–19]. More accurate models have been developed by accounting for (atomic or molecular) polarizability [20–22], which is particularly relevant for long-range electrostatic interactions that play an important role in ice. In so-called first-principles approaches, electrons are explicitly included in the description of the inter- and intramolecular interactions of water molecules. The electron structure thereby implicitly mitigates all different kind of (molecular) many-body effects among the nuclei. For extended systems like ice, density functional

theory (DFT) is often the only viable computational option to model sufficiently large unit cells. Although DFT is in principle exact, any practical calculation requires an approximation for the so-called exchange-correlation (xc) functional. In the context of hydrogen bond networks, accurate accounting for long-ranged van der Waals (vdW) interactions in the context of DFT requires special attention.

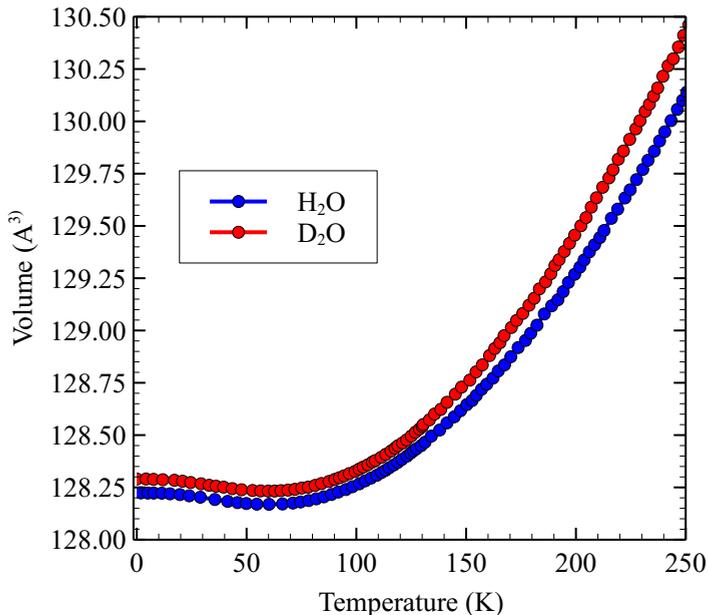


Figure 1.2: Measured unit cell volume of ice Ih comprised of H<sub>2</sub>O (blue) and D<sub>2</sub>O (red) molecules as a function of temperature based on high-precision neutron scattering experiments [23].

Apart from the interaction potential, modeling ice can also be challenged by having to take nuclear quantum effects (NQE) into account [24–30]. NQEs result from the fact that in particular the hydrogen atoms behave more like quantum mechanical rather than classical particles. Likewise, vibrational modes are better described by quantum mechanical rather than classical (harmonic) oscillators, which immediately gives rise to zero-point energy (ZPE). Without NQEs, ice would have considerable smaller heat

capacity. It would thus take much less energy to melt ice [31] – with obvious consequences for everyday life. Figure 1.2 depicts two other (subtle) manifestations of NQEs in ice: negative thermal expansion (NTE) and the volume isotope effect (VIE). Normal materials expand their volume upon increasing the temperature. Ice Ih on the other hand is anomalous in this respect and keeps shrinking for (increasing) temperatures between 0 to 50 K (for both H<sub>2</sub>O and D<sub>2</sub>O isotopologues), which is referred to as NTE. Most materials show a normal VIE, which means substitution with heavier isotopes results in a smaller volume at temperatures approaching the absolute zero. Handwavingly, in a classical picture, this can be rationalized by the smaller vibrational amplitude ascribed to a heavier nucleus experiencing the same chemical interaction potential at the same temperature. For instance, the lattice vector of <sup>22</sup>Ne is by 0.6% smaller than <sup>20</sup>Ne at 0 K [32]. Quite the opposite, although Ne and H<sub>2</sub>O have the very similar masses, the volume of H<sub>2</sub>O isotopologue of ice Ih is 0.1% smaller than D<sub>2</sub>O (see Fig. 1.2) [24, 33, 34]. As seen in Fig. 1.2, this difference persists and even increases further up to the boiling point [35, 36]. The fact that ice features this anomalous VIE illustrates that the aforementioned rationalization is too simple and demands more elaborate computational modeling.

### 1.3 Aims and Scope of this Thesis

The following questions are being addressed in this thesis:

1. How important is the contribution of zero-point energy to thermodynamical properties of ice phases?
2. How accurately do available interaction potentials allow to model (small) difference in H<sub>2</sub>O and D<sub>2</sub>O ices related to nuclear quantum effects?
3. Do interaction potentials need to be improved when nuclear quantum effects in ice are taken into account?

**Chapter 2** It summarizes the theoretical background of the methods used in this thesis. Starting from the Born-Oppenheimer approximation, interaction potentials used for modeling ice in the following are grouped into two categories: DFT and force fields. In the DFT section, a brief description of xc functionals is given, including special attention to vdW corrections because of their important role in modeling hydrogen-bond networks in ice. The force field section describes a set of particular interaction potentials ranging from simple fixed-charge pair potentials to accounting for many-body contributions by including polarizability at atomic sites and for entire H<sub>2</sub>O molecules as well as additional short-range effects. This chapter concludes with a concise description of phonons and their relevance for thermodynamic properties in the harmonic and quasi-harmonic approximation (QHA).

**Chapter 3** To set the stage for subsequent chapters, the importance of zero-point energy is quantified for crystalline ice phases using several commonly used fixed-charge pair potentials in comparison to several state-of-the-art exchange-correlation functionals within DFT.

**Chapter 4** Calorimetric experiments for the ice II to ice Ic phase transition have revealed a surprising isotope effect. The concomitant transition enthalpy is endothermic for H<sub>2</sub>O and exothermic for D<sub>2</sub>O, albeit with only a small difference of about 180 J mol<sup>-1</sup>. Such a sign change upon isotope substitution is unprecedented in ice research, and I have accepted the challenge to rationalise this finding by computational modeling.

**Chapter 5** The original single center multipole expansion (SCME) model [37, 38], a physically motivated force-field including molecular polarizability (up to the quadrupole-quadrupole level), does not allow to describe intramolecular vibrations. Shifts of the latter due to the interaction with other water molecules cannot be accounted for, making it impossible to properly describe zero-point energy-related effects. Motivated by the results of Chapter 3, SCME is extended to “self-consistently” include ZPE in the parametrization procedure.

**Chapter 6** The anomalous volume isotope and non-thermal expansion effects are investigated by making use of the extended SCME model from the previous chapter and compared to other force field and density-functional theory-based results. Both of these nuclear quantum effects are very challenging for computational modeling: the former could so far be obtained when using particular exchange-correlation functionals [39].

## 1.4 Main Results

The main scientific results of Chapters 3 to 6 are summarized here:

**Chapter 3** : Importance of ZPE for crystalline ice phases

A systematic comparison for seven hydrogen-ordered crystalline ice phases (Ih, IX, II, XIII, XIV, XV, VIII) between many commonly-used fixed-charge pair potentials and density functional theory based on various exchange-correlation functionals is presented. The latter includes some recently developed meta-GGA functionals and accounting for vdW interactions. Starting from space-group-constrained relaxed structures for all ice phases, highly-accurate phonon calculations within the QHA are carried out. The resulting zero-point energies have a much stronger effect on the cohesive energies and equilibrium volumes for the force fields than for DFT and result in better agreement with experimental data for the former. When including ZPE the force fields yield equilibrium volumes and cohesive energies that are in better agreement with experimental data than most density functionals. This is further analyzed in detail by i) a decomposition of the cohesive energies into intramolecular deformation, electrostatic and vdW contributions and ii) a comparison of O–H-stretching-mode shifts due to volume changes to available experimental data from Raman spectroscopy.

**Chapter 4** : Calorimetric Signature of Deuterated Ice II

The transition enthalpy of ice II to ice Ic are measured by calorimetry as  $+40 \text{ J mol}^{-1}$  for  $\text{H}_2\text{O}$  and  $-140 \text{ J mol}^{-1}$  for  $\text{D}_2\text{O}$ , resulting in an isotope effect of about  $180 \text{ J mol}^{-1}$ . A hierarchy of theoretical expressions for the transition enthalpy is used to account

for more and more (subtle) contributions. Apart from zero-point energy, also the usually neglected configurational entropy is ultimately taken into account because ice II is a hydrogen-order and ice Ic is a hydrogen-disordered phase. The expressions are evaluated computationally using two force fields, q-TIP4P/F and MB-pol, that are known to perform well for calculating the cohesive energy and vibrational properties of different ice phases. To that end, highly-accurate phonon calculations in the QHA are carried out. Considering the fact that the measured transition enthalpies are one to two order of magnitude smaller than what is commonly considered as chemical accuracy ( $4 \text{ kJ mol}^{-1}$ ) in computational modeling, it is not surprising that the sign change cannot be reproduced. However, both force fields yield the isotope effect due to (dominantly) the zero-point energy differences between the  $\text{H}_2\text{O}$  and corresponding  $\text{D}_2\text{O}$  ice phases in reasonable agreement with the measurements: q-TIP4P/F is able to account for about 3/4 of the isotope effect, while MB-pol only catches about 1/3.

#### **Chapter 5** : Transferable Potential Function for Flexible $\text{H}_2\text{O}$

The single center multipole expansion (SCME) model [37, 38] is extended towards flexible water molecules, resulting in a new model called SCME/f. To that end, the coordinate dependence of the quadrupole moment tensor of a single  $\text{H}_2\text{O}$  molecule needs to be fitted to high-level quantum-chemistry calculations for small water cluster. Other parameters from the original SCME formulation are readjusted as well to incorporate ZPE corrections for lattice energies of ice Ih – enabling a proper incorporation of experimental data. This requires to carry out computationally demanding phonon calculations within the quasi-harmonic approximation “on-the-fly” for the reparametrization candidates in an iterative procedure. The resulting best fit is a significant improvement over the original SCME potential function – as evidenced also by comparing the energetics of “rigid” water cluster structures. Finally, the importance of accurately describing the variation of the quadrupole moment tensor with molecular structure is analyzed by comparison to simpler models.

#### **Chapter 6** : Volume Isotope Effect of Ice Ih

This chapter demonstrates that a polarizable force field is able to model the anomalous

VIE of ice Ih, which has hitherto been deemed impossible. The state-of-the-art MB-pol force field also describes the NTE more accurately than most DFT-based approaches. In the subsequent analysis, the short-range three-body contributions (involving three water molecules) as described by MB-pol are found to play a very important role for the proper description of the VIE, whereas they are of minor importance e.g. for the cohesive energy. This could be a reason for why the SCME/f model performs slightly worse. Furthermore, a phonon mode decomposition of the so-called zero-point pressure ( $P_{ZP}$ ) illustrates that the librational and stretching are the most important phonon modes responsible for the anomalous VIE, which could be verified by future experiments.

## 1.5 Outlook

In all chapters included in this thesis NQEs have been explicitly included in the computational modeling of different ice phases. Obviously, measurements always implicitly include these effects. Whalley has already estimated and emphasized in his pioneering work in the 1950s that they can have a very sizeable influence on “intermolecular forces” [40, 41]. Parameters for many interaction potentials have been obtained by fitting “extrapolated” experimental data with ZPE contributions semi-empirically removed. However, the ZPE given by the semi-empirical correction and directly obtained from the interaction potential “a posteriori” do then not necessarily agree. Fitting to the “raw” data requires to calculate ZPEs during the parametrisation procedure and thus comes with a significantly higher computational effort. In Chapter 5 it is demonstrated this is possible nowadays, resulting in an improved SCME model. Therefore, the same strategy could also be applied to other interaction potentials for water in the future.

Apart from using NQEs to systematically improve the quality of the interaction potentials, the accuracy of the quasi-harmonic approximation employed in this work also deserves further attention. This holds in particular for Chapter 4, where very small energy scales ( $\text{J mol}^{-1}$ ) are relevant for the transition enthalpy of ice II to ice Ic.

Path-integral molecular dynamics (PIMD) allows to include anharmonic effects in the modeling of NQEs. Although PIMD comes at much higher computational cost than the quasi-harmonic approximation, it would be very interesting to carry out PIMD simulations for the same interaction potentials and investigate whether this could yield better agreement with the absolute transition enthalpies reported in Chapter 4 – ideally reproducing the water-isotopologue-related sign change.

In both Chapter 3 and Chapter 6 the experiments by Minceva-Sukarova *et al.* [42] are being invoked. The authors of that study have measured Raman spectra of different ice phases as a function of temperature and pressure. Since the latter is related to expansion and compression of the unit cell volume of an ice crystal, it can be compared to the corresponding predictions vibrational frequency shifts (and concomitant changes of the phonon density of state) obtained from calculations with different interactions potentials. These frequency shifts are crucial in the context of ZPE and the VIE as detailed in Chapter 3 and Chapter 6, respectively. The aforementioned experiments only report results for stretching modes of different water isotopologues. It would be very important to also have experimental data for the other modes (translation, librational and bending) in the future, because this is the only way to verify whether interaction potentials for water can predict NQEs (like the VIE and NTE in particular) accurately and for the right reason – and thus provide fundamentally important insights about the latter.

Ultimately, intriguing vibrational properties of ice (Ih) do not stop in the bulk, but have also been observed for ice surfaces. For example, low-energy electron diffraction and helium scattering experiments have suggested largely enhanced vibrational amplitudes related to water molecules at the surface [43–45] and dispersionless surface phonon bands [45]. It remains to be seen whether future work that builds on the calculations carried out in this thesis might elucidate those enigmatic vibrational features of ice surfaces.

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