



Ab initio thermodynamics of liquid and solid water

Bingqing Cheng^{a,1}, Edgar A. Engel^a, Jörg Behler^{b,c}, Christoph Dellago^d, and Michele Ceriotti^a

^aLaboratory of Computational Science and Modeling, Institute of Materials, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland; ^bUniversität Göttingen, Institut für Physikalische Chemie, Theoretische Chemie, 37077 Göttingen, Germany; ^cInternational Center for Advanced Studies of Energy Conversion, Universität Göttingen, 37073 Göttingen, Germany; and ^dFaculty of Physics, University of Vienna, 1090 Vienna, Austria

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Thermodynamic properties of liquid water as well as hexagonal (Ih) and cubic (Ic) ice are predicted based on density functional theory at the hybrid-functional level, rigorously taking into account quantum nuclear motion, anharmonic fluctuations, and proton disorder. This is made possible by combining advanced free-energy methods and state-of-the-art machine-learning techniques. The ab initio description leads to structural properties in excellent agreement with experiments and reliable estimates of the melting points of light and heavy water. We observe that nuclear-quantum effects contribute a crucial 0.2 meV/H₂O to the stability of ice Ih, making it more stable than ice Ic. Our computational approach is general and transferable, providing a comprehensive framework for quantitative predictions of ab initio thermodynamic properties using machine-learning potentials as an intermediate step.

ab initio thermodynamics | machine-learning potential | water | density functional theory | nuclear quantum effects

Liquid water and ice are ubiquitous on Earth, and their thermodynamic properties have important consequences in the climate system (1), the ocean, biological cells (2), refrigeration, and transportation systems. The solid phase that is stable at ambient pressure is ice Ih, whose hexagonal crystal structure is reflected in the sixfold symmetry of snowflakes. The cubic form, Ic, is a metastable ice phase whose relative stability with respect to ice Ih plays a central role in ice cloud formation in the Earth's atmosphere (3–5) but is extremely difficult to measure experimentally (1).

Despite the simple chemical formula, H₂O, theoretical predictions of the thermodynamic properties of liquid water and ice are extremely challenging. This is because of (i) the shortcomings of common water models including conventional force fields (6) and (semi-)local density functional theory (DFT) approaches (7–9), (ii) proton disorder in ice, and (iii) the importance of nuclear quantum effects (NQEs) (10). In particular, calculating the chemical potential difference $\Delta\mu^{\text{Ih}\rightarrow\text{Ic}} = \mu^{\text{Ic}} - \mu^{\text{Ih}}$ between Ic and Ih, which characterizes the relative stability, is extremely challenging because the zero-point configurational entropies (11), proton disorder (12), and harmonic vibrational energies of ice Ih and Ic (13) differ by <1 meV/H₂O, so that anharmonic quantum nuclear fluctuations play a decisive role.

Water and ice have been described with varying success by invoking approximations of differing severity, including simple electrostatic dipole models for the energetics of proton ordering (14), force-field-based path-integral molecular dynamics (PIMD) studies (15–18), first-principles quasiharmonic (QHA) (17, 19), and vibrational self-consistent field (VSCF) (13, 20) studies which provide an approximate upper bound for $\Delta\mu^{\text{Ih}\rightarrow\text{Ic}}$. These have greatly advanced our understanding of the nature of liquid water and ice, but also highlight the harsh trade-offs between the accuracy of the description of the potential energy surface (PES) governing nuclear motion and the associated cost of sampling relevant atomistic configurations.

In this study, we make theoretical predictions of thermodynamic properties of ice and liquid water at a hybrid DFT level of theory, taking into account NQEs, proton disorder, and anharmonicity. This is made possible by exploiting advances in

machine-learning (ML) techniques to avoid the prohibitively large computational expenses otherwise incurred by extensively sampling phase space by using first-principles methods. In particular, we use sophisticated thermodynamic integration (TI) techniques to accurately and rigorously compute the chemical potential difference between ice Ic and Ih and between ice Ih and liquid water.

First-Principles Thermodynamics

As the underlying electronic structure description, we use the hybrid revPBE0 (21–23) functional with a Grimme D3 dispersion correction (24, 25), which has been demonstrated to accurately predict the structure, dynamics, and spectroscopy of liquid water in molecular dynamics (MD) and PIMD simulations (26). revPBE0-D3 predicts a difference in lattice energy between the most stable proton-ordered forms of ice Ic and Ih of $U^{\text{Ic}} - U^{\text{Ih}} = -0.3 \text{ meV/H}_2\text{O}$ (see *SI Appendix* for further details), which is consistent with diffusion Monte Carlo predictions of $U^{\text{Ic}} - U^{\text{Ih}} = -0.4 \pm 2.9 \text{ meV/H}_2\text{O}$ (12) and two different random-phase approximation predictions of $-0.2 \text{ meV/H}_2\text{O}$ and $0.7 \text{ meV/H}_2\text{O}$ (27).

Since thorough sampling of the phase space of water at the revPBE0-D3 level of theory is prohibitively expensive, we sample the phase space using a surrogate ML PES, U_{ML} . We then exploit the fact that the Gibbs free energy of the surrogate systems, G_{ML} , can be promoted to the revPBE0-D3 level of theory by using free-energy perturbation

Significance

A central goal of computational physics and chemistry is to predict material properties by using first-principles methods based on the fundamental laws of quantum mechanics. However, the high computational costs of these methods typically prevent rigorous predictions of macroscopic quantities at finite temperatures, such as heat capacity, density, and chemical potential. Here, we enable such predictions by marrying advanced free-energy methods with data-driven machine-learning interatomic potentials. We show that, for the ubiquitous and technologically essential system of water, a first-principles thermodynamic description not only leads to excellent agreement with experiments, but also reveals the crucial role of nuclear quantum fluctuations in modulating the thermodynamic stabilities of different phases of water.

Author contributions: B.C., J.B., C.D., and M.C. designed research; B.C. performed research; B.C. and E.A.E. analyzed data; and B.C., E.A.E., J.B., C.D., and M.C. wrote the paper.

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Data deposition: The NN potential has been deposited on GitHub and is available at <https://github.com/BingqingCheng/ab-initio-thermodynamics-of-water>.

¹To whom correspondence should be addressed. Email: bingqing.cheng@epfl.ch.

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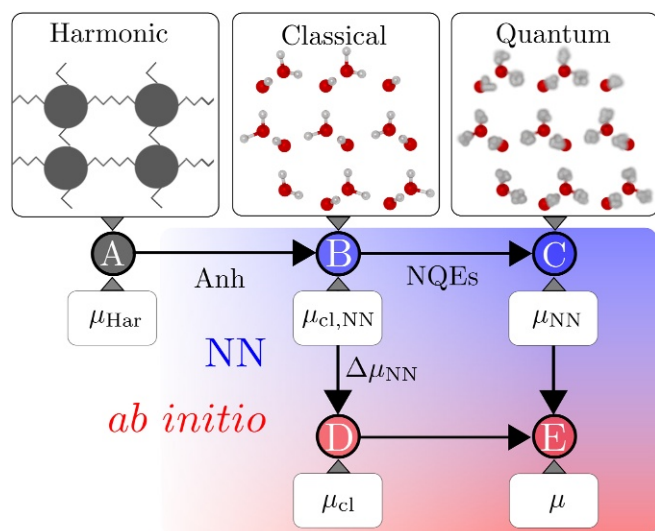


Fig. 7. A schematic of the TI workflow, which starts from a harmonic reference crystal, uses a NN description as an intermediate step, and finally arrives at the underlying ab initio level. The chemical potentials indicated here are related to the absolute Gibbs free energy of the systems by $\mu \equiv G/N$.

Conclusions

We show that a revPBE0-D3 description of the electronic structure predicts properties for ice Ih, ice Ic, and liquid water that are in excellent quantitative agreement with experiment. This is made possible by using a ML potential as an intermediate surrogate model and by using advanced free-energy techniques. We not only rigorously compute but also quantitatively analyze the individual contributions from NQEs, proton disorder, and anharmonicity.

This study demonstrates that it is possible to achieve a sub-millielectronvolt level of statistical accuracy in predicting the thermodynamic properties of a complex system such as water at a hybrid DFT level of theory. The idea of using ML potentials as sampling devices significantly broadens the applicability and prowess of electronic-structure approaches, making it affordable to use them in the accurate computations of free energies and other thermodynamic properties. The overall framework and the free-energy methods described here provide a general, accurate, and robust way for first-principles predictions of thermodynamic properties of a plethora of physical systems, such as pharmaceutical compounds, hydrogen storage materials, hydrocarbons, and metallic alloys.

Materials and Methods

Simulation Details. The density isobar in Fig. 1 is computed by using both classical MD and PIMD simulations in the NPT ensemble for ice Ic, ice Ih, and liquid water systems of 64 molecules. We confirm that the equilibrium density computed with 64 water molecules in classical MD simulations is consistent with the values obtained for systems with $\sim 2,000$ molecules. All MD simulations and PIMD simulations that use 56 beads are performed by

using the i-PI code (60) in conjunction with LAMMPS (61) with a NN potential implementation (62, 63).

Interface Pinning. The interface pinning simulations (56) are performed by using the PLUMED code (64) on an ice-liquid system containing 5,760 molecules at temperatures ranging from 250 to 300 K and pressure 1 bar, using the NN potential.

Accounting for NQEs. NQEs on the chemical potential difference between ice Ic and ice Ih at 200, 250, 273, and 300 K are taken into account by integrating the quantum centroid virial kinetic energy $\langle T_{CV} \rangle$ with respect to the fictitious atomic mass \bar{m} from the classical mass (i.e., infinity) to the physical masses of oxygen and hydrogen atoms (18, 65–67)—that is,

$$\Delta\mu_{NN}^{\text{Ih} \rightarrow \text{Ic}} - \Delta\mu_{\text{cl,NN}}^{\text{Ih} \rightarrow \text{Ic}} = \int_m^\infty d\bar{m} \frac{\langle T_{CV}^{\text{Ic}}(\bar{m}) \rangle - \langle T_{CV}^{\text{Ih}}(\bar{m}) \rangle}{\bar{m}}, \quad [3]$$

where m are the physical masses of the elements. In practice, a change of variable $y = \sqrt{m/\bar{m}}$ is applied to reduce the discretization error in the evaluation of the integral (65), and the integrand is evaluated by using PIMD simulations for $y = 1/4, 1/2\sqrt{2}, 1/2, 1/\sqrt{2}, 1$ —that is,

$$\Delta\mu_{NN}^{\text{Ih} \rightarrow \text{Ic}} - \Delta\mu_{\text{cl,NN}}^{\text{Ih} \rightarrow \text{Ic}} = 2 \int_0^1 \frac{\langle T_{CV}^{\text{Ic}}(1/y^2) \rangle - \langle T_{CV}^{\text{Ih}}(1/y^2) \rangle}{y} dy. \quad [4]$$

To evaluate this integral, we perform a PIMD simulation that uses 56 beads at the NPT ensemble for systems containing 64 molecules. For the case of ice Ih and liquid water, the treatment is similar.

Workflow for Computing $\Delta\mu^{\text{Ih} \rightarrow \text{Ic}}$. Here, we describe the workflow for computing absolute Gibbs free energy and thereby the chemical potential of an ice system. The first step is a TI from a harmonic reference to a classical ice system ($A \rightarrow B$ in Fig. 7). We closely follow the methods described in ref. 51: First integrate from a Debye crystal to classical ice at 25 K in the NVT ensemble, then transition to the NPT ensemble, and, finally, evaluate the temperature dependence of the Gibbs free energy by using MD simulations in the NPT ensemble at temperatures between 25 and 300 K. Subsequently, to reach the ab initio description of classical ice from the NN description ($B \rightarrow D$ in Fig. 7), the correction term $\Delta\mu_{NN}$ (Fig. 3) computed by using the free energy perturbation expression in Eq. 1 is included. Finally, to describe ab initio ice with quantum-mechanical nuclei ($D \rightarrow E$ in Fig. 7), NQEs are included by integrating from the infinite atomic mass to the physical masses (Eq. 3). As an alternative strategy, one can also follow the TI route $A \rightarrow B \rightarrow C \rightarrow E$, but this requires reweighting the whole ring-polymer system in PIMD simulations by using Eq. 1, which is more costly.

Datasets. The NN potential for water based on revPBE0-D3, the training set for the potential, and all necessary simulation input files are included in *SI Appendix* and are available at <https://archive.materialscloud.org/2018.0020/v1>.

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