# Melting temperature of water: DFT-based molecular dynamics simulations with D3 dispersion correction

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Extensive *ab initio* simulations of ice-water basal interface at seven temperatures in the range 250–400 K were performed in NVT and NPT ensembles with a collection of 389 water molecules in order to estimate the melting point of ice from direct liquid-solid two-phase coexistence. Density functional theory with the BLYP (Becke-Lee-Yang-Parr) exchange-correlation functional and the D3 dispersion correction were used in the expression of total energy. Analysis of density profiles and the evolution of the total potential, or Kohn-Sham plus D3, energy in the simulations at different temperatures resulted in an estimate for melting temperature of ice of 325 K.

## I. INTRODUCTION

Water, as the most important substance for life, has always attracted the researchers to explore and explain its numerous anomalous properties. Computer simulations, being one of the most powerful tools for the studies of atomistic structure and dynamics in condensed matter, have been intensively applied to calculations of phase diagrams of liquids, and water in particular. In the case of water a long-standing issue is the estimation (and prediction at high pressures) of phase boundaries and especially the melting points between the different modifications of ice and liquid water [1]. Different classical atomistic models of water molecules yield melting points of the hexagonal ice $I_h$ at ambient pressure [2] with a large deviation from the experimental value of 273.15 K. On the other hand, the precision of *ab initio* simulations within the density functional theory-based molecular dynamics (DFTb-MD) for the estimation of the melting point of ice $I_h$ at ambient pressure is much worse, because of much smaller simulated systems and shorter simulation times accessible than with the classical force fields.

In general, the most popular methods for the melting point estimation from computer simulations are: (i) by the thermodynamic integration for estimation of the difference in Gibbs free energy between the bulk solid and bulk liquid phases [3,4], (ii) from the direct solid-liquid coexistence [5], (iii) from the "heat-until-it-melts" approach for bulk solid [6], (iv) from the critical overheating (Z method) [7], and (v) by interface pinning [8], which consists of direct evaluation of the Gibbs free energy differences between two phases at a given temperature and pressure from a simulation of coexisting phases with a bias potential acting at the position of the interface. Among these methodologies the one that can be well utilized in *ab initio* simulations is the direct ice-water coexistence, where the melting point can be estimated either

from the analysis of density profiles [9] or from the behavior of the potential energy during the simulation [2].

Systematic studies of the ice/water interfaces with molecular dynamics (MD) simulations were started in 1987, when Karim and Haymet [5] simulated the two-phase coexistence. Their simulation was constructed of 1440 water molecules using the TIP4P model. Later the equilibrium ice/water interfaces were studied with CF1 [10], SPC/E [9,11], six-site [12] and TIP4P/2005 [13] models of water. One of the first estimations of the melting point of ice $I_h$ at ambient pressure was performed from the direct ice/water coexistence simulations at different temperatures with the SPC/E model [9,14], resulting in the melting point of $225 \pm 5$ K [14], subsequently supported by other groups [2]. Systematic calculation of the melting point of ice $I_h$ based on the evolution of the total energy in NPT simulations at different temperatures were reported in Ref. [2] with seven classical water models.

Recently *ab initio* simulations, based on DFT, were applied in order to calculate the melting point of ice $I_h$ [15,16]. In Ref. [15] the melting point was studied with the PBE [17] and BLYP [18,19] generalized gradient approximations (GGA) to the exchange-correlation functional at pressures 2.5 (PBE) and 10 kbars (BLYP) by observing ice/water coexistence in isoenthalpic-isobaric (NPH) ensemble at three temperatures 350, 400, and 450 K. These simulations resulted in melting temperatures of ice $I_h$ to be in between 400 and 450 K with these regular GGA functionals. In Ref. [16] the effect of the D2 dispersion correction [20] (an empirical van der Waals pair potential term added to the density functional energy) was explored. The simulations of ice/water coexistence with BLYP $+$ D2 correction resulted in reduction of the ice melting point down to about 360 K, in agreement with the earlier discovery of the importance of van der Waals interactions in liquid water [21].

Recently we reported a study [22] of static structure and collective dynamics of water and $D_2O$ at 323.15 K with and without the D3 dispersion correction. One of the findings was the change from slow stretched relaxation of density-density
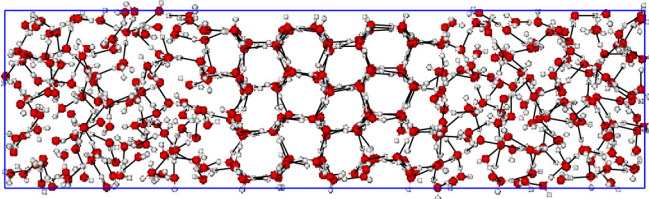
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FIG. 1. Snapshot of equilibrated two-phase system used in *ab initio* simulations at $T = 325$ K. Oxygen and hydrogens are drawn as red and gray spheres, respectively, and the dashed black lines indicate hydrogen bonds.



FIG. 2. Oxygen density profiles in the last 5 ps at the seven different simulated temperatures.

time correlation functions typical for supercooled liquids to regular exponential relaxation when the D3 dispersion correction was turned on. This finding indirectly implied that the melting point of ice $I_h$ would undergo significant reduction due to the application of the D3 dispersion correction. The importance of D3 correction for a qualitatively correct description of water structure in DFTb-MD simulations has been recognized [23] and highlighted in a recent review [24]. Its effect on the ice melting point, however, has not been discussed.

Very recently there appeared a study of the application of neural-network potentials (NNPs) to estimation of the ice melting point [25]. The NNPs were fitted to initial *ab initio* simulations with BLYP, BLYP + D3, RPBE, RPBE + D3 exchange-correlation approximations, and subsequently applied in classical MD simulations in larger systems, using for the estimation of the melting point via the interface pinning methodology [8,26]. The application of NNPs for BLYP exchange correlation resulted in $T_m = 323 \pm 3$ K of ice, and significant reduction to $283 \pm 2$ K was observed when BLYP + D3 was used. Overall the study confirmed the earlier conclusions drawn about the importance of the van der Waals interactions in water [21,27].

Hence, the aim of this study is the estimation of the melting temperature of ice from *ab initio* simulations with the D3 dispersion correction. To achieve this goal we apply NPT and NVT ensembles in two-phase ice-water coexistence MD simulations of a large system of 389 molecules, using an analysis of density and dipole profiles and of behavior of potential energy at different temperatures.

The rest of this article is organized as follows: in the next section we give the details of the *ab initio* simulations and of the procedure of analyses. Results from our simulations are reported in Sec. III, a critical discussion of the present results in relation to earlier studies conducted in Sec. IV, and conclusions drawn from the present study are given in the last section.

## II. SIMULATION SETUP

We prepared the two-phase ice $I_h$/water system of 389 water molecules for the *ab initio* simulations from classical MD simulations with the SPC/E water model [28] (for details see the Supporting Material [29]). The bulk ice phase $I_h$ in Ref. [28] was constructed as described in Ref. [30]. A snapshot of the DFTb-MD simulations at $T = 325$ K at the end of the simulated trajectory is shown in Fig. 1.
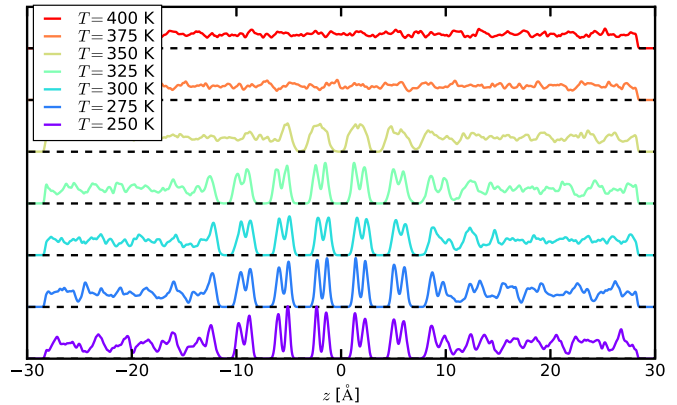
In our simulations we used the QuickStep module in the CP2K package [31]. We employed the Gaussian-plane wave (GPW) method with the TZV2P basis set for the Kohn-Sham orbitals and 600 Ry for expanding the electron density in the plane wave (PW) basis, and norm-conserving pseudopotentials. We used the NVT ensemble with the same density at seven temperatures in the temperature range 250–400 K in the simulations. We expect the error due this approach to be small, as we are close to the maximum of the density, thus variations in the density with reasonable changes in temperature would be small. We used thermostat chains and a time step of 0.5 fs and we deuterated the hydrogen atoms. Furthermore, we performed the NPT simulations at 1 bar at the same temperatures with a cut-off energy of 1200 Ry in the PW expansion of the density. The length of the trajectories is from 40 to 90 ps, with the shorter ones at temperatures where the melting or freezing of the sample is soon obvious. In general, we discarded the initial 10 ps into the simulations as a period of equilibration.

## III. RESULTS

Density profiles are the standard tools in studies of structural features in the two-phase systems. The equilibrium ice-water interface at the melting point is characterized by a density profile that remains stable over time, while melting obviously leads to smearing-out of the atomistic planes in the density profile, whereas at temperatures below the melting point a very slow sharpening of initially smeared atomistic planes in the interfacial region is observed [9]. Another quantity enabling estimation of the melting point is the total potential energy [2], evolution of which during the simulation can contain an increase with time (melting, i.e., the system is above the melting point) or decrease (the system is below the melting point); at the melting point, i.e., at a stable ice-water interface, the total potential energy fluctuates around a constant value during the MD simulation.

The profiles of the oxygen density toward the end of the seven simulations are shown in Fig. 2 and their time evolution in Fig. S1 in the Supplemental Material [29]. The melting occurs very fast at the temperatures 400 K (within 5 ps of production period of the simulation) and 375 K (within 20 ps).
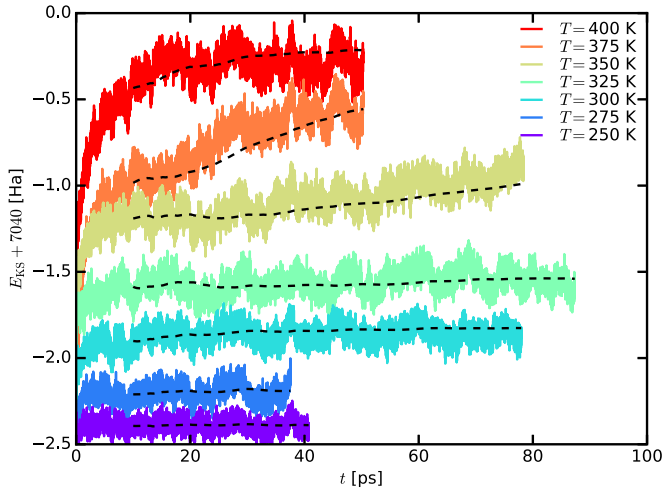
FIG. 3. Evolution of the potential energy and its cumulative average (dashed lines) at seven temperatures in NVT ensemble.

At 350 K, which would be below the reported melting point with BLYP + D2 [16], undergoes complete melting during the simulation of ∼60 ps. At $T = 325$ K and below we observed stable ice-water interfaces. It is still impossible to study the nucleation of ice at the ice-water interface with *ab initio* simulations below the melting temperature because extremely long simulations and large system sizes are required [32]. Therefore we made use of the evolution of the total energy in order to discriminate the two-phase systems at temperatures below the melting one.

In Fig. 3 we present the evolution of the potential energy in the NVT simulations. One can see that the potential energy increases rapidly at $T = 350$ K and above. At lower temperatures in NVT ensemble the energy fluctuates near an average value without showing a clear tendency with the decreasing temperature. The simulations in NPT ensemble allow more realistic insight into the evolution of the total potential energy (Kohn-Sham energy plus the D3 correction), its two-phase coexistence. At $T = 350$ K and above we observed the same increase of the potential energy as in
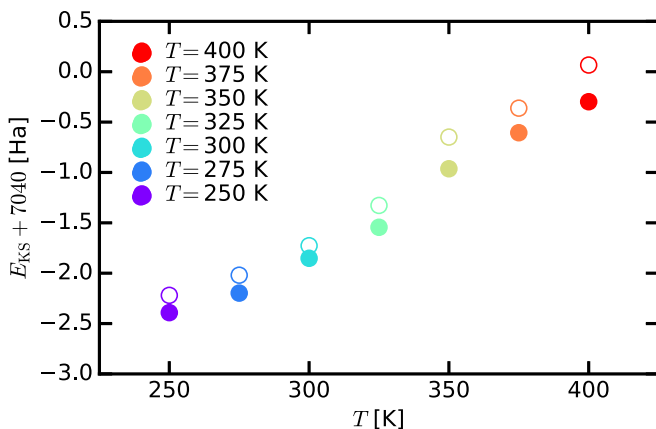


FIG. 4. Average potential energy at different temperatures: NVT simulations—full circles, NPT—open circles.
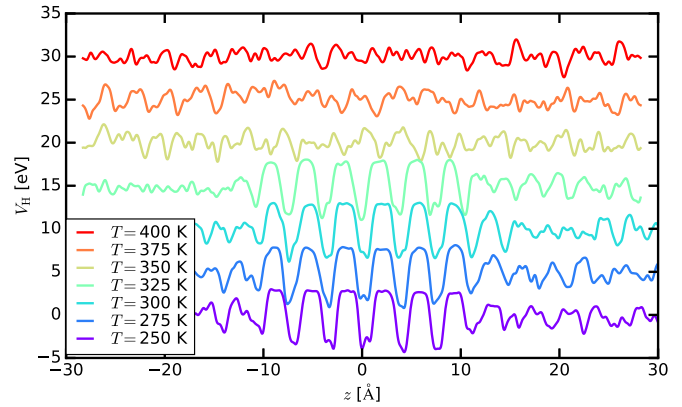


FIG. 5. Profile of the Hartree potential at the different temperatures in a single snapshot configuration.

NVT simulations (see Fig. S2). Only the system at 325 K shows a stable potential energy during the simulation, while temperatures 300 K and below show very slow decrease of the average potential energy with time. This can be an evidence that only the system at 325 K is kept close to the melting point.

Figure 4 contains the temperature dependence of the average total potential energy averaged over the production period of the simulations in NVT and NPT ensembles. A noticeable kink occurs between the temperatures 350 and 325 K, both in the NVT and NPT simulations. This supports the conclusion that the estimated melting point of ice with the BLYP + D3 approach should be close to 325 K.

In addition to the mass density, charge density, and tetrahedrality profiles [14] that can characterize the order parameter in the two-phase ice-water systems [9], here we introduce two further profiles which can be obtained from *ab initio* simulations: The first one is the dipole moment profile (see Fig. S3), that is, the instantaneous dipole moments of the water molecules as a function of the position of the molecule, calculated via the localization of the Kohn-Sham orbitals onto Wannier functions on the molecules [29]. One can see that at stable interfaces the ice phase's average dipole is about 3.34 D, while in the liquid phase the water molecules have on average a dipole moment of 2.84 D. At $T = 350$ K and above these interfaces melted and the dipole density profile showed values of molecular dipoles typical for the liquid state.

Another profile accessible from *ab initio* simulations is the one of the Hartree potential (i.e., Coulomb potential profile) shown in Fig. 5. At the stable ice-water interfaces we obtained a stable charge separation with pronounced atomic planes with positive charge of ions and distribution of the Coulomb potential arising from the distribution of electron density. At temperatures which led to melting of the interfaces the profile of the Hartree potential does not show a stable separation of charge densities but quite noisy potential profile, with an average value of the Hartree potential typical for liquid state.

## IV. DISCUSSION

The previous *ab initio* calculations of the melting point suffer from several factors which should be taken into account: the $I_h$ bulk region should be relatively large and must be

TABLE I. Scaling of the melting temperature of SPC/E model with the system size estimated from two-phase ice-water equilibrium simulations.

| $N_{mol}$ | $T_m^{SPC/E}$ (K) |
| --- | --- |
| 389 | $203 \pm 3$ |
| 485 | $208 \pm 3$ |
| 581 | $217 \pm 3$ |
| 766 | $220 \pm 3$ |
| 1920[a] | $225 \pm 5$ |
| 2304[b] | $225 \pm 5$ |

[a]Reference [9].
[b]Reference [28].

prepared very carefully in order to reproduce well the proton-disordered phase; the ice/water system itself must be quite large so as to contain bulk $I_h$ and bulk water regions together with two interfaces, taking into account that the "10-90" width of each interface is $\sim$9–11 Å [9].

We have simulated a relatively large two-phase ice-water system of 389 water molecules. Before, the *ab initio* simulations of ice-water coexistence with BLYP exchange correlation [15] with and without the D2 dispersion correction [16] performed on a system of 192 molecules resulted in a reduction of the ice melting point down to about 360 K due to the inclusion of the D2 dispersion correction. Our two-phase system was prepared with several requirements on the ice-water coexistence: at least one 96-molecule block of proton-disordered ice phase with zero net dipole in order to correctly represent the bulk ice region, and a quite large size of the $z$ side of the MD box able to fully contain both ice-water interfaces each of $\sim$10 Å wide [9] in addition to pure ice and pure water regions. In that sense our setup with the ice-water coexistence for *ab initio* simulations in a cell with the length of 56.58 Å is much more correct than in the previously employed, smaller systems.

In order to have an estimate of how the finite size of the MD box affects the observed melting temperature in the *ab initio* simulations one would have to perform similar simulations with larger sizes of the ice-water system. This is not a realistic task because even the actual *ab initio* simulations of the interface with 389 molecules require huge computational efforts. Therefore we have tried to obtain a rough estimate of the scaling of the ice-water melting using the classical MD simulations with the SPC/E model. We used four different sizes of the ice-water coexistence from 389 to 766 molecules in NPT and NVT ensembles for equilibration and production, respectively (see Table I), and those results were complemented with the earlier values in much larger cells [9,28].

We can conclude that the estimated $T_m^{SPC/E}$ in an ice-water system of 389 SPC/E molecules is $\approx$10% lower than in the very large systems. In general the melting temperature increases with the system size reaching at 766 molecules (within the

error bars) the same value as in the larger systems. It is, however, not to be expected that the scaling curve of the melting temperature from *ab initio* simulations will be the same as with the oversimplified, rigid SPC/E model of water molecules. Yet qualitatively it would probably look quite similar, with an increase of the $T_m$ with the system size.

An important technical issue in the previous DFTb-MD simulations [15,16] is the too small a basis set (280 Ry) used to expand the electron density with PWs with the CP2K/QuickStep package. As shown in Ref. [23] a minimum cut-off energy of 400 Ry is needed for a reasonable convergence, in fixed cell (NVT ensemble) and the evaluation of the pressure tensor requires even higher values [27]. Therefore the results in Refs. [15,16] should be considered with some suspicion.

The melting point for BLYP-based NNPs in Ref. [25] was about 100 K lower than the reported one from direct ice-water coexistence in *ab initio* simulations with 192 molecules [16].

Direct simulations of the solid-liquid coexistence usually result in lower $T_m$ than the ones obtained by the thermodynamic integration approach [2]. To date the source of this discrepancy between the two methodologies is not clear. Future application of the BLYP + D3 *ab initio* simulations with the interface pinning methodology in systems of different sizes is highly desirable in order to clarify the discrepancy in the reported values of melting point between the actual two-phase ice-water simulations and the NNP-based calculations [25].

We further note that the quantum effects were found to reduce the melting temperature of water in ring-polymer molecular dynamics simulations [33] by 8 K with the q-TIP4P/F water model (22 K with the q-SPC/Fw model). The quantum effects would thus decrease our melting temperature with the BLYP + D3 approach, bringing the value to somewhat better agreement with the experiments ($T_m^{expt} = 273.15$ K).

## V. SUMMARY

We simulated the ice-water coexistence at seven temperatures in the range 250–400 K in NVT and NPT ensembles. At temperatures 350 K and above we observed total melting of the ice-water interface in both NVT and NPT simulations with BLYP + D3. At temperatures 325 K and below we observed quite stable ice-water coexistence, while the behavior of potential energies, especially in NPT simulations, allowed us to estimate the ice melting point to be close to 325 K. Another interesting feature, a kink in the temperature dependence of the average potential energy, supports this value.

## ACKNOWLEDGMENTS

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