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The Melting Temperature of Liquid Water with the Effective Fragment Potential

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ABSTRACT: The direct simulation of the solid–liquid water interface with the effective fragment potential (EFP) via the constant enthalpy and pressure (NPH) ensemble was used to estimate the melting temperature ($T_m$) of ice-Ih. Initial configurations and velocities, taken from equilibrated constant pressure and temperature (NPT) simulations at $P = 1$ atm and $T = 305 K, 325 K$ and $399 K$, respectively, yielded corresponding $T_m$ values of $378 \pm 16 K$, $382 \pm 14 K$ and $384 \pm 15 K$. These estimates are consistently higher than experiment, albeit to the same degree as previously reported estimates using density functional theory (DFT)-based Born–Oppenheimer simulations with the Becke-Lee–Yang–Parr functional plus dispersion corrections (BLYP-D).

Chemistry at standard ambient temperature and pressure is ubiquitous. For this reason, the accurate description of the phase diagram of water is an important benchmark of any method, whether it is based on electronic structure or a classical description of the interaction between the water molecules. Given the fact that the melting temperature ($T_m$) of ice is just 25 K below the ambient temperature, even a small error in the description of the phase diagram of water with a particular model can result in sampling the wrong phase when performing ambient temperature simulations. Estimates of $T_m$ have previously been reported using several classical interaction potentials (cf. ref 1 for a recent review) as well as density functional theory (DFT).2–11 Whereas the reported predictions with classical potentials are generally lower than experiment (e.g., 146 K with the TIP3P potential, an exception being the TIP4P-FQ potential which predicts 303 K), the reported predictions with DFT were notably much higher than experiment.2,3 Previous DFT-based simulations with the PBE and BLYP functionals5–7 predicted $T_m$ to be 417 and 411 K, respectively.7 Dispersion corrections,8–10 when added to the BLYP functional, lowers the predicted $T_m$ to 360 K, still too high by nearly 90 K with respect to experiment.8 The DFT and DFT-D predictions for the melting temperature broadly agree with previous studies, which suggested that DFT yields an overstructured liquid at $\rho = 1$ g/cm$^3$ and ambient conditions,11–13 that a temperature of $\sim 415 K$ was necessary for the PBE functional to obtain a value for the diffusion coefficient ($D$) comparable to experiment at ambient conditions (based solely on the comparison of the value of $D$ and the corresponding radial distribution function (RDF)).14 That a distinctive transition to liquid-like diffusion occurs for the PBE functional only at an elevated temperature of 400 K,15 and that the BLYP-D functional provides a consistent description of liquid water at $T = 350 K$.16 Based on the evidence presented by those earlier results, previous studies17–20 have suggested that DFT-based molecular dynamics (MD) simulations performed at the standard ambient temperature can be interpreted as describing supercooled rather than the liquid state of water. The notion of a supercooled state at 298 K is consistent with the existence of an overstructured RDF for water produced by DFT MD simulations at the standard ambient temperature.11

For this reason, recent ambient temperature DFT-based simulations have been performed at elevated temperatures (330 K and above) to ensure that a liquid state is sampled.17,18 As noted earlier, estimates of $T_m$ have been reported using classical water interaction potentials,1,19–26 A simple point charge model, such as TIP3P, predicts a melting point of 146 K.27 TIP4P/2005, improves on TIP3P, but still predicts a too low $T_m$ of 251 K.20 The too low predicted melting point was one of the reasons that the TIP4P model has been reparametrized to more accurately predict the phase diagram of ice, resulting in TIP4P/Ice. The TIP4P/Ice model has been designed to reproduce $T_m$ by fitting the model potential parameters and predicts a value of 270 K.20 The TIP5P potential predicts an accurate value of 272 K,26 but also predicts that ice-Ih is not thermodynamically stable at 1 bar.18

With recent improvements in force field method developments,25,29–44 classical force fields can be generated from ab initio calculations as an alternative to fitting the parameters to empirical data. Examples of force fields generated by fitting parameters to ab initio calculations include iAMOEBA,25 TTM3-F,29 WHBB,41,45 and MB-Pol.43,44 The effective frag-
ment potential (EFP) method is also obtained directly from ab
initio quantum chemistry, but the EFP method contains no empirically fitted parameters.30,31 The iAMOEBA and TTM3-F
potentials predicted \( T_m \) values of 261 K and 248 K, respectively. The present study will focus on the prediction of
\( T_m \) with the EFP potential.

In the EFP method, each water molecule is represented as a
fragment with fixed internal geometry. The EFP method contains five interaction energy terms that represent the
fundamental types of intermolecular interactions:

\[
E_{\text{EFP}} = E_{\text{Coul}} + E_{\text{pol}} + E_{\text{exrep}} + E_{\text{disp}} + E_{\text{CT}}
\]  

(1)

In eq 1, \( E_{\text{Coul}} \) is the Coulombic interaction, expressed as a
distributed multipole expansion. \( E_{\text{pol}} \) is the polarization
interaction, which is expressed in terms of localized molecular
orbital (LMO) polarizability tensors and is iterated to self-
consistency. The polarizability term accounts for the many-
body interactions via this iterative process. \( E_{\text{exrep}} \) represents the exchange repulsion interaction and is expressed in a power
series of the intermolecular overlap. Because of the use of
localized orbitals, the series is successfully truncated at the
quadratic term. \( E_{\text{disp}} \) is the dispersion interaction, expressed in
terms of LMO frequency-dependent polarizabilities, integrated
over the imaginary frequency range. \( E_{\text{CT}} \) is the charge transfer
interaction, obtained in terms of the interaction between the
occupied orbitals on one fragment and the virtual orbitals on
the second fragment. Details regarding these terms can be
obtained from the original references. Using coupled cluster CCSD(T)
calculations as a reference, it has been demonstrated that the EFP predictions of interaction energies for a wide range of interaction types,
including water clusters, are comparable in accuracy to that of
second order perturbation theory (MP2), while requiring orders of magnitude less computational resources.36

The melting temperature can be calculated in at least two
ways: by a Gibbs–Duhem integration of the free energy \(^47\) or by
direct simulation of the solid–liquid interface.\(^48\)–\(^50\) At the
melting point,

\[
G_{\text{liq}}(P, T)_{T=T_m} = G_{\text{solid}}(P, T)_{T=T_m}
\]  

(2)

so the determination of \( T_m \) by Gibbs–Duhem integration
requires the nontrivial determination of the Gibbs free energy
for both the ice and liquid states. Additional information about
the relative benefits and drawbacks of Gibbs–Duhem integration and direct coexistence simulations in different
ensembles can be found in a recent review.\(^51\) An alternative
approach, adopted in the present study, is to calculate \( T_m \) by
direct coexistence simulations of the ice–water interface. The
direct coexistence simulations can be performed using different
ensembles. The present study uses the constant pressure and
enthalpy \( (\text{NPH}) \) ensemble, since this allows the temperature of
the system to adjust spontaneously to \( T_m \) where eq 2 is
satisfied. Unlike the \( (\text{NVE}) \) ensemble, which also allows the
temperature to spontaneously adjust, the \( (\text{NPH}) \) ensemble also
allows the pressure to be maintained during the simulation.
During the simulation of the ice–water coexistence system with
the \( (\text{NPH}) \) ensemble, if the initial temperature of the system is
lower than the melting point, \( T < T_m \) then the chemical
potential of the liquid phase will be higher than the one of ice
and water molecules from the liquid phase will release heat by
freezing onto the ice surface. Likewise, if the initial temperature of the system is higher than the melting point, \( T > T_m \) then the
chemical potential of the ice phase will be higher than the one
for the liquid phase and water molecules from the ice phase will
absorb heat and melt (become liquid-like) from the ice surface.
The coexisting solid–liquid phase approach has been previously
used in conjunction with DFT simulations to estimate \( T_m \) for
metals such as Al,\(^52\) Ta,\(^53\) Si,\(^54\) MgO,\(^55\) and water under high
pressure.\(^4\)

The EFP method was used to describe the waters in all MD
simulations, using the electronic structure program GAMESS.\(^56\)

Since no information exists about the EFP phase diagram for
water, the EFP liquid-ice coexistence boundary must first be
identified. Note that there is no liquid-ice coexistence boundary
below the pressure at the triple point.\(^57\) To confirm the use of a
pressure of 1.0 atm in the EFP simulations described below, a
NVT MD simulation was performed with 216 water molecules
at \( T = 300 \) K and a density of 1 g/cm\(^3\), to make sure that the
EFP pressure of water is not close to the triple point. This MD
simulation was performed with a step size of 0.25 fs, the
velocity–Verlet algorithm, and a cubic simulation cell with edge
length of 18.62 Å. After 2 ps of equilibration, the next 2 ps was
used to calculate the average pressure of the system to be \( -200 \) atm.
Hence, the use of a pressure of 1.0 atm is reasonable for the
calculation of the melting temperature for the molecular
dynamic simulations in the \( (\text{NPH}) \) ensembles as the liquid-ice
coexistence should be stable at this pressure. For comparison,
analogous calculations using DFT with the BLYP (PBE)
functional finds 10000 atm \( (25000 \) atm).\(^2\)

To calculate \( T_{\text{m}} \), an ice-liquid system of 192 water molecules
was prepared in a simulation cell of 27.32 \( \times \) 15.61 \( \times \) 14.72 Å. A representative geometry of the ice-liquid system is shown in
Figure 1. For the initial configuration of the ice-liquid system,
96 of the water molecules were assumed to be ice-I\(_h\)-like (top
half of Figure 1) and were arranged according to the Bernal–
Fowler rules such that the ice phase has a net zero dipole
moment.\(^58\) The remaining 96 waters (bottom half of Figure 1)
were assumed to be liquid-like and were prepared from a

![Figure 1. A representative configuration of the ice–water system with 96 ice-I\(_h\)-like and 96 liquid-like water molecules.](image)
(NVT) equilibration at $T = 300$ K for 100 ps with a step size of 0.25 fs using the velocity–Verlet algorithm in a simulation cell of $13.52 \times 15.61 \times 14.72$ Å. The ice-liquid system in the present study is the same size and prepared in a similar manner as the one used in previous DFT calculations$^{2,3}$ of $T_m$ to allow the direct comparison of $T_m$ between the EFP method and the previous DFT simulations.

The predicted $T_m$ is apparently not converged with respect to system size for a simulation cell of 192 waters. Previous studies$^{27}$ with the TIP4P potential have suggested that the calculated $T_m$ via the (NVE) ensemble increases with system size, rising from ~200 K with a simulation cell of 192 molecules to $229 \pm 1$ K with a simulation cell of 12,288 water molecules. The previous DFT studies,$^{2,3}$ upon which the present work is based, estimated $T_m$ using a simulation cell of 192 water molecules. The authors of these previous studies assumed that the change of $T_m$ as a function of simulation cell size was qualitatively similar for TIP4P and DFT, and therefore their calculated $T_m$ with DFT was most likely a lower bound. This assumption is made in the present work as well. Additionally, nuclear quantum effects have been shown to be important for a correct theoretical description of water at this temperature range.$^{58}$ The inclusion of nuclear quantum effects in previous studies$^{59,60}$ suggested a downward shift of the temperature range by about 30 K. As in the previous DFT studies,$^{2,3}$ on which this work is based, nuclear quantum effects are not considered in this study.

Initial MD simulations for 500 fs with a 0.25 fs step size were carried out in the (NPT) ensemble at $P = 1.0$ atm with the velocity–Verlet algorithm at temperatures between 300 and 400 K on the merged ice-liquid systems to allow the ice-liquid system to relax. The (NPT) simulations at 300, 350, and 400 K produced configurations at 305, 325, and 399 K, which were the initial starting conditions for each of the (NPH) simulations during which the $T_m$ was estimated. The (NPH) simulations used a 0.25 fs step size, a pressure of 1.0 atm, and were performed using the velocity–Verlet algorithm. For the (NPH) simulations with initial temperatures of 325 and 399 K, the simulations were assumed to converge after 10 ps, and the next 10 ps were used to determine the value and corresponding error bars. For the (NPH) simulation with an initial temperature of 305 K, the simulation was assumed to converge after 25 ps and the next 10 ps were used to determine the value and corresponding error bars. The $T_m$ value was obtained as the average of the individual steps of the last 10 ps of $T$ values after the (NPH) simulation had been assumed to converge and the error bars were calculated as the standard deviation of those individual steps in the last 10 ps.

Periodic boundary conditions were imposed with the minimum image convention during all MD simulations. For the periodic boundary conditions, a switching function that gradually drops the fragment–fragment interactions from full strength to a value SWR1 to zero at a value SWR2 was used. For all MD simulations, SWR2 was half the smallest box dimension, while SWR1 was $0.8 \times$ SWR2.

The temperature versus the MD simulation time for the three (NPH) simulations starting at $T = 305$ K (green), 325 K (blue) and 399 K (red) is shown in Figure 2. The three simulations (starting from the above three different initial conditions) converge to the values of $378 \pm 16$ K, $382 \pm 14$ K, and $384 \pm 15$ K, respectively. The $T_m$ estimates from the three simulations lie within the error bars of one another.

A summary of the $T_m$'s predicted by the EFP method compared to other predictions reported with DFT and classical potentials is presented in Table 1. The estimate of $T_m$ with the EFP method is substantially higher than experiment, smaller than the predictions with the BLYP and PBE functionals (~400 K) and similar to the one predicted by BLYP-D. The agreement between the EFP and DFT methods (especially BLYP-D) is not entirely surprising, since the EFP method is also derived from first-principles and includes a dispersion term. In contrast, most classical potentials seem to produce values that are smaller than experiment. Based on the current results and the ones with previous DFT-based simulations, it appears that electronic state based methods systematically overestimate $T_m$ by ~100 K, though it should be noted that the previous DFT studies have been performed with generalized gradient approximation functionals and not with more modern meta-hybrid functionals. Additionally, the inclusion of nuclear quantum effects is expected to decrease this difference by ~30 K or more. However, this decrease maybe offset in part by the expected increase in the melting temperature due to the size effect of the simulation box.

The fact that the EFP method currently relies on the use of rigid monomers should not be a significant source of error in the estimation of $T_m$ (even though the liquid water and ice internal geometries are different).$^{62}$ Issues related to the rigid monomer geometry and its influence on the estimate of $T_m$ will be addressed in future studies using the effective fragment molecular orbital (EFMO) method,$^{52,63}$ which is based on flexible fragments. It is possible that the EFP method is
mimicking what the MP2 melting point of water would be if one performed MP2 MD simulations (excluding nuclear quantum effects) with internally frozen geometries. This possibility will be analyzed once MP2 MD simulations become feasible either by conventional MP2 or via the use of fragmentation methods such as the fragment molecular orbital method.84

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

K.R.B. was supported by a Computational Science Graduate Fellowship from the Department of Energy. M.S.G. was supported by a U.S. National Science Foundation Software Infrastructure (SI2) grant (ACI — 1047772). S.S.X. acknowledges support from the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences. Pacific Northwest National Laboratory (PNNL) is a multiprogram national laboratory operated for DOE by Battelle.

■ REFERENCES

(23) Nässon, Å.; Pettersson, L. G. Perspective on the Structure of Liquid Water. Chem. Phys. 2011, 389, 1—34.


