Melting points of water models: current situation

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By using the direct coexistence method we have calculated the melting points of Ice Ih at normal pressure for three recently proposed water models, namely TIP3P-FB, TIP4P-FB and TIP4P-D. We obtained T_m=216 K for TIP3P-FB, T_m=242 K for TIP4P-FB and T_m=247 K for TIP4P-D. We revisited the melting point of TIP4P/2005 and TIP5P obtaining T_m=250 and 274 K respectively. We summarize the current situation of the melting point of ice Ih for a number of water models and conclude that no model is yet able to simultaneously reproduce the melting temperature of ice Ih and the temperature of the maximum in density at room pressure. This probably points towards our both still incomplete knowledge of the potential energy surface of water and the necessity of incorporating nuclear quantum effects to describe both properties simultaneously.

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When simulating water a force field is needed and it is common to use a simple rigid non-polarizable force field. Usually positive charges are located on the hydrogen atoms and a Lennard-Jones center is located on the oxygen. In three center models (3C) the negative charge is located on the oxygen atom as in the TIP3P[50], SPC[51] and SPC/E[52], models proposed by the groups of Jorgensen and Berendsen respectively. In the four center models (4C) the negative charge is located along the bisector of the H-O-H angle[53] leading to the popular TIP4P model[50]. In this first wave of water models (80's) the density and vaporization enthalpy were used as target properties (although in the case of SPC/E only when including the self energy correction[52]). Water, at constant pressure, has a temperature at which the density reachs a maximum (TMD). Recognizing the importance of that led to the second wave (2000-2010) of potential models where the TMD was used as a target property. Two different approaches to achieve this goal were used. In the first approach the negative charge was located in the position of the lone pair electrons as in the TIP5P[54] (a geommetry also used in the old ST2 model[55]) resulting in five center models (5C). In the second approach the TIP4P geometry was kept but the vaporization enthalpy was sacrificed as a target property (unless the self energy correction is included) in favour of the TMD as in the TIP4P-Ew[56] and TIP4P/2005 models[57]. Over the last ten years some additional non polarizable models have been proposed. Some of then using a 3C geometry as OPC-3[58] or TIP3P-FB[59] and some of them using a 4C geometry as TIP4P-FB[59], TIP4P-ϵ[60],TIP4P-D[61] or OPC[62]. In general the aim of these models was to improve the description of the dielectric constant of liquid water (but not in ices) with respect to TIP4P-Ew and TIP4P/2005 models although in general the improvement was made at the cost of deteriorating the predictions for another property (see Ref.[63] for a general discussion on the role of the dielectric constant in water simulations). If we focus on polarizable models we can also find three new and interesting force fields such as the BK3[64], i-AMOEBA[65], MB-Pol[66] or HBP[67] models which add polarization to a 4C geometry. Not only the TMD (at 1 bar) is an interesting property of water but also the melting point of ice Ih (also at 1 bar). In fact one of the properties which one can study to validate a water force field is the melting point of ice I_h. For most of the models proposed up to 2012 the melting point of ice is well known.[68,69] For some of the models proposed over the last ten years we know now the melting point, as for instance for OPC and OPC-3[70] and for TIP4P-ϵ[60]. However the melting point of ice Ih for three popular recently proposed water models, namely TIP3P-FB[59], TIP4P-FB[59] and TIP4P-D[61] is unknown. The goal of this work is to determine their melting temperatures and to summarize the current situation of force fields with respect to their capacity to predict the melting point of ice and the TMD. We will use the direct coexistence method[68,71], where a solid phase consisting of 2000 molecules of ice Ih (proton disordered configuration was obtained using the algorithm of Buch et al.[72]) is placed in contact with 2000 molecules of liquid water. The ice plane exposed at the interface is the secondary prismatic one ($1\bar{2}10$). We have performed anisotropic NpT simulations with GROMACS package[73] with a time step of 2 fs. Temperature and pressure were kept constant by using the Nosé-Hoover thermostat[74] and Parrinello-Rahman barostat[75] both with a coupling constant of 2 ps. For electrostatics and Van der Waals interactions the cut-off radii was fixed at 1.0 nm and long-range corrections to the LJ part of the potential in the energy and pressure were applied. We used PME[76] to account for the long-range electrostatic forces and LINCS[77] for constraints.

In Figure 1 the time evolution of the potential energy of the system at several temperatures for TIP4P-FB and TIP4P-D force fields is shown. For the TIP4P-FB model ice melts (i.e energy grows) for all temperatures above 243 K. Ice grows at all temperatures below 241 K. Thus, we can conclude that the melting temperature for the TIP4P-FB model is T_m = 242(1) K (not surprisingly similar to that of TIP4P/ϵ T_m = 240(1) K taking into account the similarity of the parameters of both models). Following the same procedure, we estimate that the melting temperature of TIP4P-D force field is T_m = 247(1) K. To evaluate the impact of the cutoff on the calculations we repeated for TIP4P-D the calculations using a larger cutoff (i.e 1.2 nm) obtaining again T_m = 247(1) K.

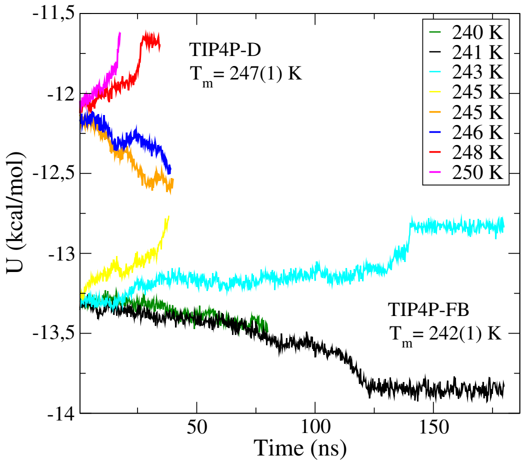

FIG. 1. Evolution of the potential energy as a function of time for the NpT runs of TIP4P-D (top) and TIP4P-FB (bottom) models at 1 bar and different temperatures. The energies of TIP4P-D water model are shifted 1.3 kcal/mol for better visualization of the reader.

We have also recalculated the melting point of TIP4P/2005 and TIP5P using the same system size obtaining 250(1) and 274(1) K respectively (see Supp. Mat.). The melting point of TIP4P/2005 is in excellent agreement with the result reported by Conde et al.[78] Finally, we also evaluated the melting point of the TIP3P-FB obtaining (see supplementary material) $T_m = 216(4)$ K (the larger error bar is due to the slow dynamics at such low temperatures). We have also determined the melting enthalpy at the melting temperature for TIP3P-FB, TIP4P-FB, OPC, TIP4P-D and TIP5P obtaining 0.63, 0.99, 1.07, 1.11 and 1.78 kcal/mol respectively, compared with the result obtained for TIP4P-2005 (i.e 1.13 kcal/mol) and the experimental value (i.e 1.44 kcal/mol). Let us now present a more general discussion. In Figure 2 the results of the melting point of water models are presented. In Table I we also show the numerical results for the melting points, the TMD of the models and the difference in temperature between the TMD and the melting temperature (ΔT = TMD - T_m). As can be seen in Fig. 2, 3C models yield a poor description of the melting temperature of ice Ih (the average being located around 220 K). In short, 3C are not recommended to study the freezing of water (in addition ice Ih may not be the most stable phase at room pressure for these models[79]). 4C models improve the description, the average melting temperature being around 245 K. As can be seen the melting points of TIP4P-FB and TIP4P-D are below that of TIP4P/2005. Polarizable models using a TIP4P geometry improve the description of the melting point, the average being located around 255 K but still below the experimental value. The only models reproducing the experimental value are those of the 5C geometry, the coarse grained mW[80], the TIP6P[81] and the special purpose model TIP4P/Ice.[82] In general the melting point increases with the value of the quadrupole moment of the model.[83]

It is interesting to analyze the performance of the models with respect to the TMD. In Fig. 2, models with a small deviation (4 K or less from the experimental value) are represented as blue squares, models with a moderate deviation (i.e between 5 and 10 K) are represented by empty squares and models with a large deviation from experiment (more than 10 K) are represented by black squares. As can be seen models that reproduce well the melting point do not reproduce well the TMD and viceversa. For most of the models the difference in temperature between the TMD and the melting temperature is too large, ranging from 11 to 50 K when compared to the experimental value which is only 4 degrees (the only exceptions are the MB-Pol and HBP models for which this difference is almost 0 and 7 K respectively).

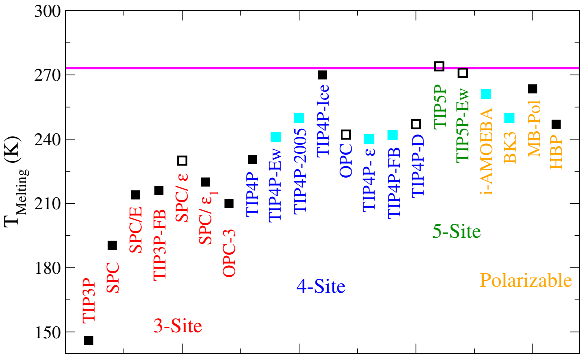

FIG. 2. Melting points of ice I_h of different water models at 1 bar. Blue filled squares: Models which provide (at 1 bar) a good estimation of the TMD (maximum of 4 K of deviation from the experiment). Empty squares: Models which provide a fair estimation of the TMD (maximum of 5-10 K of deviation from the experiment). Black filled squares: Models with a bad estimation of the TMD (more than 10 K deviation from the experiment).

To summarize, in this work we have determined the melting points of three recently proposed rigid and non polarisable water models (TIP4P-FB, TIP4P-D and TIP3P-FB) with the goal of analyzing if they could reproduce simultaneously the melting point and the TMD. The answer is negative and their melting points are similar (although a few degrees lower) than that of TIP4P/2005. The main conclusion is that in 2022 we do not have yet any model of water (polarizable or not) able to reproduce simultaneously both the melting point of ice Ih and the TMD. Further work is needed to determine whether this is a deficiency in the description of the potential energy surface of water (PES) of all force fields proposed so far, or to the necessity of incorporating nuclear quantum effects to describe both properties at the same time accurately.[96–98] If this were the case then even an accu-

TABLE I. Melting temperature of ice I_h (T_m) and temperature of the maximum in density (TMD) both at 1 bar for different water models as calculated in this work or taken from the literature. We also show the difference between the TMD and the T_m (ΔT). TMD uncertainty is tipically 2 K.

Model	T_m (K)	TMD (K)	ΔT (K)
Expt.	273	277	4
TIP3P	146(5)[69]	182[84]	36
SPC	190.5(5)[69]	228[84]	37.5
SPC/E	214(3)[68]	241[84]	27
TIP3P-FB	216(4) This work	261[59]	45
SPC-ϵ	230(2)[85]	270[85]	40
SPC-ϵ_2	220(2)[85]	250[85]	30
OPC-3	210(10)[70]	260[58]	50
TIP4P	229(9)[86]	253[84]	24
TIP4P-FQ	303(8)[87]	253[88]	-50
TIP4P-Ew	241(1)[70]	274[56]	33
TIP4P-2005	250(1) This work	277[89]	27
TIP4P-Ice	270(3)[68]	295[84]	25
OPC	242.2(0.9)[70]	272[62]	29.8
TIP4P-ϵ	240(2)[60]	276[60]	36
TIP4P-FB	242(1) This work	277[59]	35
TIP4P-D	247(1) This work	270[61]	23
TIP5P	274(1) This work	285[90]	11
TIP5P-EW	271(3)[68]	282[91]	11
ST2	299(2)[92]	323[93]	24
TIP6P	274.5(1.5)[81]	290[81]	15.5
mW	273(1.5)[94]	251[94]	-22
i-AMOEBA	261(2)[65]	277[65]	16
BK3	250(3)[64]	275[64]	25
MB-Pol	263.5(1.5)[66]	263[95]	-0.5
HBP	247(3)[67]	254[67]	7

rate PES could not reproduce both properties simultaneously when using classical simulations.

See the Supplementary Material for aditional figures of the melting point of the models studied in this work and for the comparison of different properties such as melting enthalpy and densities of ice and liquid water for each model.

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I. CONFLICT OF INTEREST

The authors have no conflicts to disclose.

II. DATA AVAILABILITY

The data that support the findings of this study are available within the article and in the Supp. Mat.

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