The melting temperature of the six site potential model of water

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The calculation by computer simulation of the melting temperature and the phase diagram of different water models has been proven a stringent test of the water force field.[1,2] The ice I_h melting temperature T_m is systematically underestimated. Only a few models yield more or less satisfactory values for T_m. These are[3] TIP4P/ice[4] (270 K) and TIP5P (Ref. 5) (272 K).[3] The former model also gives a good description of the phase diagram involving solid phases. On the contrary, TIP5P fails completely in this purpose. In fact, for TIP5P, ice I_h is not thermodynamically stable at 1 bar. The actual T_m for TIP5P should then correspond to the melting temperature of ice II which is several degrees higher. Another candidate is TIP4P/2005.[6] This model accurately predicts the stability of the different ice forms and yields excellent predictions for the liquid-vapor coexistence line and critical properties.[7] TIP4P/2005 seems an excellent model for many applications, but its T_m is rather low (251 K). However, some problems (ice growth,[8,9] brine rejection from ice,[10,11] and nucleation[12]) are strongly sensitive to the degree of supercooling and, thus, require a more accurate prediction of the T_m. A first report of the T_m for the six site model of Nada and van der Eerden[13] (NvdE) was close to the experiment. However, in a recent paper Nada and Furukawa[8] arrived at a melting temperature in the range of 280–285 K. Then, before proceeding to a costly calculation of the phase diagram (which is still unknown), it seems interesting to establish more firmly the T_m for this model. This is the goal of this paper.

We have used two different methods for the calculation of the T_m for the NvdE potential. The first one is a combination of a Gibbs-Duhem integration and free energy calculations. Let us sketch here the procedure of the Gibbs-Duhem integration.[2,15–18] First, we write the intermolecular potential in terms of a reference potential and a parameter λ,

$$u = (1 - \lambda)u_{\mathrm{ref}} + \lambda u_{\mathrm{new}}. \tag{1}$$

When $\lambda = 0$, $u = u_{\mathrm{ref}}$, and for $\lambda = 1$ it follows that $u = u_{\mathrm{new}}$. Using the same procedure as that used to obtain the Clapeyron equation, one finds that[2]

$$\frac{dT}{d\lambda} = \frac{\Delta x_g}{\Delta s}, \tag{2}$$

where Δx_g, the extensive conjugate variable of λ, is given by

$$x_g = \frac{1}{N}\left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{N,p,T,\lambda}. \tag{3}$$

The technique can be used to refine the melting point of a potential.[14] It also makes possible the determination of the coexistence point of a given model from the known value for a reference one. For these reasons we denote it as "Hamiltonian" Gibbs-Duhem. In this work we use TIP4P and extended simple point charge (SPC/E) as reference models. Their melting temperatures were previously evaluated[1] by means of free energy calculations using Ewald sums and an 8.5 Å cutoff for the Lennard-Jones term (long range corrections to this term were added). The same conditions have been used in the Gibbs-Duhem simulations of this work. In Table I we display the T_m for the starting models (TIP4P and SPC/E) and the value obtained for the six site model after the Hamiltonian Gibbs-Duhem integration. The final result is almost independent on the starting model.

On the other hand, we have also calculated the NvdE melting temperature by direct coexistence.[3,19] We have performed a set of N-p-T simulations in which we put the solid and the liquid phases in contact. For the simulations we have used the molecular dynamics package GROMACS with a time step of 1 fs.[20] The initial configuration used in Madrid (864 molecules) was obtained following the algorithm of Buch *et al.*[21] for the proton disordered ice. The liquid is in contact with the secondary prismatic $\{11\bar{2}0\}$ plane. The van der Waals forces were truncated at 8.5 Å (notice that the usual long range correction cannot be applied in this case because of the different densities at both sides of the interface). For the long range forces we used the particle-mesh Ewald algorithm.[22] As regards the simulations at Purdue, the initial coordinates of the runs (1536 molecules) were taken from Hayward and Reimers.[23] The solid faces in contact are

TABLE I. Melting temperature of the NvdE model obtained by Hamiltonian Gibbs-Duhem integration using SPC/E and TIP4P as reference potentials. Column 2 are the values for SPC/E and TIP4P as obtained from free energy calculations (Ref. 1).

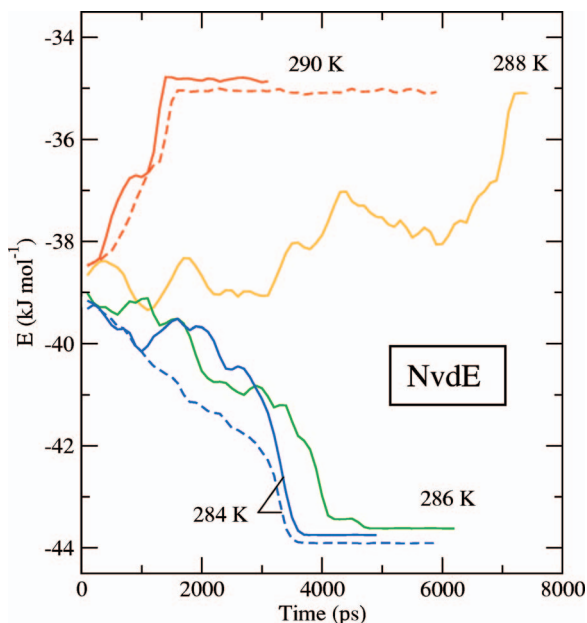| Reference model	Starting T_m (K)	Six site model (K)
TIP4P	232	290
SPC/E	215	291

FIG. 1. (Color) Total energy along the N-p-T runs for the six site model (averaged over 20 ps simulation blocks). Solid lines: 864 molecules and dashed lines: 1536 molecules.

FIG. 2. The velocity of freezing for the primary prismatic and basal planes for the system with 1536 molecules.

either the basal {0001} or the primary prismatic {10$\bar{1}$0} planes. The cutoff is now 10 Å for both the Lennard-Jones (LJ) potential and the electrostatic interactions. As in the original paper for the six site model,[13] no long range correction is applied for the electrostatic interactions. As can be seen in Fig. 1 the energy changes along the N-p-T simulation runs because, depending on the temperature of the system, the solid (liquid) phase melts (freezes) at the interface. Once the phase change is completed the energy remains constant. We may then assign the T_m to the mean value of the closest temperatures for which melting and freezing are observed.[3] Two different runs are plotted for the systems at 290 and 284 K. These correspond to the different sample sizes and starting configurations. According to the curves of Fig. 1 the direct coexistence method yields $T_m=287$ K for the smaller system. Notice that neither the starting configuration nor the sample size influences significantly the results. In fact, the large system also froze at 286 K (results not shown in Fig. 1) and did not show a definite evidence of melting or freezing at 288 K, so we may assign this value as the T_m of the larger system. This value is slightly higher than that reported by Nada and Furukawa[8] using a similar technique. The difference in the T_m calculated with the free energy/Gibbs-Duhem route and the direct coexistence method is around 3 K which is the same as that obtained for other water models.[3] In summary, averaging the results obtained with both methods we propose 289 K as the recommended T_m of the model.

Finally, Fig. 2 shows the results for the freezing process in three independent runs at 284 K when the primary prismatic and the basal planes of ice I_h are facing the liquid. Although the growth rate shows a wide variation along different runs for a given plane, it is clear that the freezing is faster when the prismatic plane is in contact with the liquid.
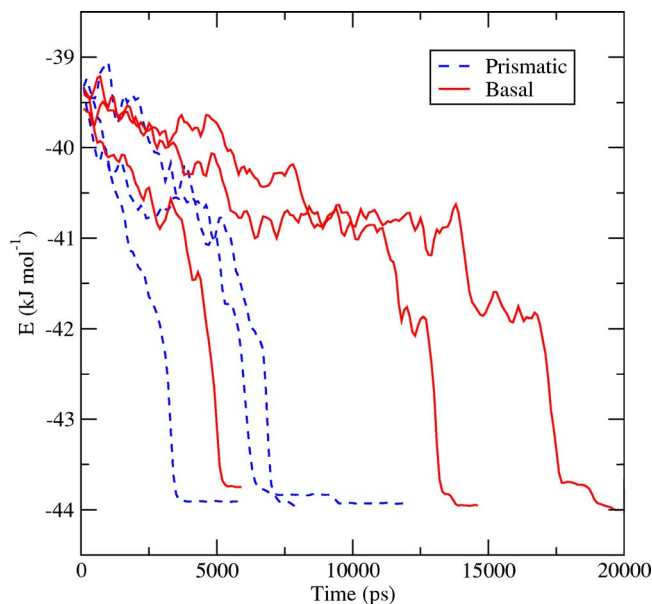
This confirms previous observations[8,9] which also suggest a different growth mechanism for the basal and prismatic planes.

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