

# The melting point of ice $I_h$ for common water models calculated from direct coexistence of the solid-liquid interface

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In this work we present an implementation for the calculation of the melting point of ice  $I_h$  from direct coexistence of the solid-liquid interface. We use molecular dynamics simulations of boxes containing liquid water and ice in contact. The implementation is based on the analysis of the evolution of the total energy along  $NpT$  simulations at different temperatures. We report the calculation of the melting point of ice  $I_h$  at 1 bar for seven water models: SPC/E, TIP4P, TIP4P-Ew, TIP4P/ice, TIP4P/2005, TIP5P, and TIP5P-E. The results for the melting temperature from the direct coexistence simulations of this work are in agreement (within the statistical uncertainty) with those obtained previously by us from free energy calculations. By taking into account the results of this work and those of our free energy calculations, recommended values of the melting point of ice  $I_h$  at 1 bar for the above mentioned water models are provided. © 2006 American Institute of Physics. [DOI: 10.1063/1.2183308]

## I. INTRODUCTION

Water is probably the molecule for which more computer simulations have been undertaken since the pioneering works of Barker and Watts and Rahman and Stillinger.<sup>1,2</sup> It is also the molecule for which more potential models have been proposed.<sup>3–6</sup> However, a literature survey shows that a few models proposed in the 1980s—TIP3P, TIP4P,<sup>7</sup> SPC,<sup>8</sup> and SPC/E (Ref. 9)—are used in the majority of the simulation studies. The parameters of these potentials were fitted to reproduce water properties at room temperature and pressure. To reduce the computational cost, the Coulombic part of the potential was truncated at about three molecular diameters. Currently, the increase of computer power allows a proper treatment of long range electrostatic forces in water as the reaction field or Ewald sums.<sup>10–16</sup> However, another type of potentials is just emerging in the last years. They were designed to reproduce not just the properties of water at ambient conditions but also other global properties. In particular, the temperature of maximum density of water has been used to fit the parameters of TIP5P (Ref. 17) [and its variant for use with Ewald sums, TIP5P-E (Ref. 13)], TIP4P-Ew,<sup>18</sup> and TIP4P/2005,<sup>19</sup> and the melting temperature of ice was used to obtain the parameters of TIP4P/ice.<sup>20</sup> In summary, even restricting to nonpolarizable, rigid models of water, the number of models of water that may be of interest is about 10.

It is interesting to know whether these popular models are able to describe the phase equilibria of water. Concerning the vapor-liquid equilibrium, the Gibbs ensemble technique<sup>21</sup> has been applied to several water models<sup>11,22–24</sup> even using first principles simulation.<sup>25</sup> For several reasons, there is a growing interest in the fluid-solid equilibria of water. Firstly, as the average temperature on earth is close to the melting temperature, the fluid-solid equilibrium is not only a com-

mon daily experience but also a question of practical interest. Secondly, water has 13 different known solid phases. To understand this complexity from a molecular point of view appears as a challenging goal. Finally, it has been suggested that water may undergo a liquid-liquid transition when supercooled,<sup>26–29</sup> so that it would be of interest to establish clearly when water is indeed below the melting point of the water model used. It is somewhat surprising that our knowledge of the fluid-solid coexistence not received a widespread attention although the interest on solid and amorphous phases of water is increasing in the last years.<sup>30–33</sup>

At the melting temperature  $T_m$ , ice and liquid water have the same chemical potential. Although  $T_m$  depends on the pressure, throughout this paper we will refer to its value at the normal pressure, 1 bar. The evaluation of the chemical potential for the fluid is relatively straightforward. But the determination of the chemical potential of the solid requires especial techniques pioneered by the work on hard spheres of Hoover and Ree.<sup>34</sup> About 20 years ago, Frenkel and Ladd proposed a new method to compute free energies of solids, the Einstein crystal method,<sup>35</sup> which has been extended to molecular (Frenkel and Mulder<sup>36</sup> and Vega *et al.*<sup>37</sup> and Vega and Monson<sup>38</sup>) and other systems as the restricted primitive model.<sup>39–41</sup> Alternatively, the difference of free energies can be calculated using the lattice-switch<sup>42</sup> and phase-switch Monte Carlo.<sup>43</sup> Free energy calculations of water in the solid phase started with the work of Báez and Clancy for SPC/E.<sup>44</sup> Since then, the technique has been applied to different water models.<sup>38,45–48</sup> More recently, in our group in Madrid, we have performed free energy calculations for the popular SPC/E and TIP4P models, not only for ice  $I_h$  but also for the rest of solid structures found experimentally in real water.<sup>49–53</sup> We have also shown that once the melting point of a model is known, the melting point of a different model can be estimated by using Hamiltonian Gibbs-Duhem

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integration.<sup>54–57</sup> However, free energy calculations of molecular fluids can be difficult. Besides, estimates of the melting point of water from different authors do not always agree. It is therefore desirable to have a different and completely independent route for the determination of the fluid-solid equilibrium.

As nucleation of ice is an activated process,<sup>58</sup> the simulation of pure liquid water below the freezing temperature usually produces supercooled liquid and not a piece of ice. Recently, Matsumoto *et al.*<sup>59</sup> have shown the nucleation of ice from water after one year of a *NVT* simulation. Shorter times—around 200 ps—are required to freeze supercooled water in the presence of a static electric field.<sup>60</sup> Experimentally, solids cannot be superheated,<sup>61</sup> but, in computer simulations of bulk solids, the absence of an interface suggests that ice can be superheated in *NpT* runs.<sup>62–65</sup> However, the existence of a fluid-solid interface removes the supercooling or superheating phenomena in computer simulations. This provides a second methodology for the determination of the fluid-solid coexistence. We shall denote this route as direct coexistence since, in this method, the fluid and solid phases are brought into contact directly. The direct coexistence method was first applied in the 1970s by Woodcock and co-workers,<sup>66–68</sup> although the computer power available at that time allowed only the simulation of small systems and short runs. Recently, Morris and Song have shown that good results can be obtained for Lennard-Jones (LJ) systems<sup>69</sup> provided that the runs are sufficiently long and the system is sufficiently large. Regarding the ice-water interface, it has been investigated during the last 15 years and estimates of the melting points for several water models have been given.<sup>70–74</sup> The direct coexistence method not only allows one to determine the melting temperature but it can also provide unique information about the dynamics of crystal growth.<sup>75,76</sup>

The goal of this paper is to use the direct simulation technique to estimate the melting temperature of the popular models SPC/E, TIP4P, and TIP5P and also for the recently proposed TIP5P-E, TIP4P-Ew, TIP4P/ice, and TIP4P/2005 models. The estimates will be compared with those obtained from free energy calculations in our group.

## II. METHOD

In our method we carry out simulations on boxes that have ice and liquid water in contact. In order to generate the ice/liquid water initial configuration we begin by building up a box of ice of 432 molecules. This is chosen so that the system has a dipolar moment close to zero and satisfies the rules of Bernal and Fowler.<sup>77</sup> We used the algorithm of Buch *et al.*<sup>78</sup> to generate the initial configuration. Other algorithms are also available.<sup>79</sup> On the other hand, we prepared a box of liquid water of about the same size from a preexisting sample of liquid water. The resulting box contained 438 water molecules for all the systems but SPC/E for which the liquid region contained 432 molecules. We joined the ice and water boxes so the total sample size is 870 water molecules (864 for SPC/E). We put the solid in contact with the liquid oriented such that the solid face in contact is the secondary

prismatic ( $\bar{1}\bar{2}10$ ) plane. The main advantage is that it is the fastest growing face.<sup>80</sup> It is also a convenient face to make a visual monitorization of the melting or freezing processes. Then we ran either a short Monte Carlo or a molecular dynamics (MD) run to remove overlaps. In this run we kept frozen the atoms in the ice region to prevent it from melting by the generated heat. This ice/liquid water configuration is used as the starting sample in several MD simulations at temperatures close to the previously reported melting points of different water models.<sup>19,20,81,82</sup> An additional configuration containing a total of 2048 molecules was prepared to check possible sample size effects.

We perform *NpT* molecular dynamics simulations at different temperatures. Using a thermostat avoids the problem of drifts in the total energy which could be present in *NVE* runs of the length of those presented in this work (10 ns). In addition, without a thermostat the transmission of heat from the interface to the rest of the system could be the limiting rate step in the melting/freezing process. In fact, it has been reported that the velocities of crystal growth in interfaces with *NpT* simulations are several times higher than the experimental velocities, and this fact has been attributed to the artificial transmission of heat provided by the thermostat.<sup>75</sup> Although this may be a problem when the goal is to study the ice growth rate of a model and to compare it to experiment, this rapid heat transfer to the system provided by the thermostat is clearly an advantage when the goal is to establish the melting point. For this reason we believe that the presence of a thermostat increases the reliability of the results. In our simulations the temperature is fixed with a Nosé-Hoover thermostat<sup>83,84</sup> with a relaxation time of 2 ps. Using a barostat is also important for a system such as water-ice where the two coexisting phases have different densities. The use of the barostat allows the simulation box to grow or shrink during the run to adapt to changes in the relative ratio between the amounts of solid and liquid present in the simulation box. It also allows us to study the complete melting or complete freezing of the sample. To keep the pressure constant, a Parrinello-Rahman barostat<sup>85,86</sup> was used. The relaxation time of the barostat was 2 ps. The pressure of the barostat has been set to 1 bar in all the simulations. In order to adapt the cell pressure to the changes in density (recall that the ice density is roughly a 10% lower than that of liquid water) it can be convenient to allow changes in the shape of the solid region. This may favor the accommodation into the solid structure of water of molecules coming from the liquid phase or may enable to readapt the box when part of the solid melts. For this reason, the different side lengths of box were allowed to fluctuate independently. For simplicity, in accordance with the crystallographic cell of ice  $I_h$ , the orthogonality of the simulation box has been imposed (although because ice  $I_h$  is hexagonal, it is possible to choose an orthorhombic unit cell<sup>87</sup>). The typical size of the simulation box depends on the particular conditions but a typical size of the simulation box was  $23 \times 22 \times 53 \text{ \AA}^3$ , respectively. This means that the interface area between the solid and the fluid was of  $23 \times 22 \text{ \AA}^2$ . In summary, the use of the *NpT* allows, in principle, the solid to melt completely (at high temperatures) or the fluid to freeze completely (at low temperatures).

The geometry of the water molecule is enforced using constraints. This poses a problem when the water model includes massless interaction sites as is the case of TIP4P and TIP5P. These are treated specially: its position is calculated from the positions of the other sites and the force on them is redistributed on the other atoms.<sup>88</sup> The time step used in the simulations was 1 fs. The typical length of the simulations was about 10 ns ( $10 \times 10^6$  time steps). For the simulations we have used the molecular dynamics package GROMACS.<sup>89,90</sup> Let us explain the reasons for our choice. The determination of the melting temperature via computer simulations in the  $NpT$  ensemble could be performed either by the Monte Carlo technique or by the molecular dynamics technique. The results should be the same. The molecular dynamics package GROMACS was found to be more convenient in this project for at least three reasons. Firstly we wanted to estimate the melting point by using not only a completely different technique but also a completely different program (recall that our free energy results were obtained with our own Monte Carlo code). Secondly, by using molecular dynamics we could also obtain dynamic information about the speed at which ice melts or freezes for the different water models. Finally, we found GROMACS to be faster than our Monte Carlo code by a factor of about 4. This is important because it was found in this work that the determination of the melting temperature via coexistence simulations requires runs of about 10 ns if reliable results are to be obtained. The length of the runs limited also the system size that could be simulated within a reasonable time (i.e., 870 molecules). Typically it took about 8 days of CPU time on an Athlon 2.8 GHz to finish one  $NpT$  single simulation. The LJ part of the potential was truncated at 8.5 Å and a switching function was used between 7.5 and 8.5 Å. Ewald sums were used to deal with electrostatics. The real part of the Coulombic potential was truncated at 8.5 Å. The Fourier part of the Ewald sums was evaluated by using the particle mesh ewald (PME) method of Essmann *et al.*<sup>91</sup> The width of the mesh was 1 Å and we used a fourth order polynomial. As it can be seen the conditions of the molecular dynamics simulations (Ewald sums and truncation) were quite similar to those used in our previous Monte Carlo calculations.<sup>49,50,81</sup>

### III. RESULTS

In Fig. 1 the results of several  $NpT$  runs for the TIP4P/2005 model are presented. We monitor the melting or freezing by looking at the total energy (i.e., the sum of the potential and kinetic energies). If the system is above the  $T_m$  the ice region will melt whereas if the system is at a temperature below the melting point the liquid water will freeze. If the water freezes, the thermostat will take energy out of the system while if the ice melts the thermostat will give energy to the system. Figure 1 shows the typical evolution of the total energy for several runs at different temperatures using the same starting configuration. In the upper curves the system increases the energy with time, indicating that the ice is melting. After the initial equilibration period in which the interface region relaxes (lasting about 0.2 ns) the curve follows a more or less straight line. This indicates that the rate of melt-

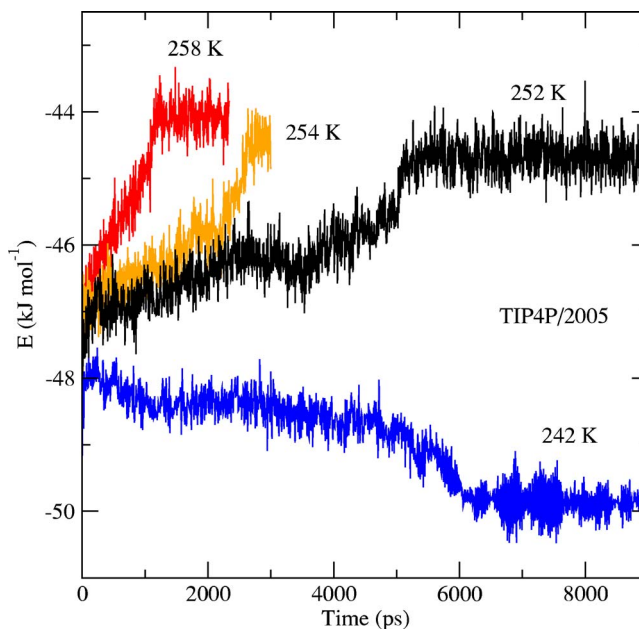


FIG. 1. Evolution of the total energy (per mole of molecules) in  $NpT$  simulations of a box containing ice and liquid water at 1 bar for the TIP4P/2005 model. The temperatures of the three upper curves are (from left to right) are 258, 254, and 252 K, respectively. The lower curve corresponds to a temperature of 242 K.

ing is approximately constant with time. After a sudden increase in the slope of the curves the energy remains constant for the rest of the simulation. The existence of a plateau at the end of the curves clearly denotes the complete melting of the ice present in the box. The sudden change of slope seen in the steps previous to the plateau seems to indicate that the rate of melting increases when only remain at the interface one or two layers of ice. The above description of the melting process is somehow schematic as it can be seen in Fig. 1 which shows a small plateau in the middle part of the curve at 252 K. Leaving aside these irregularities (more evident at temperatures close to the coexistence temperature) the same behavior has been observed in all the systems. By visual inspection of the movies of the simulation runs we have confirmed that the beginning of the final plateau in the curves corresponds exactly to the time for which the last layer of ice melts. In the same manner we have confirmed that the rate of melting for the last ice layers is considerably larger than for the rest of the ice, thus confirming this as the reason for the sudden increase of the energy previous to the final plateau. Figure 2 shows snapshots of the starting configuration and the final ones for the TIP4P/2005 model at two different temperatures. It is evident that the final configuration at 252 K corresponds to a homogeneous liquid, indicating that the ice has completely melted.

It is interesting to check whether the energy difference between the initial and final states is in accordance with the enthalpy of melting  $\Delta_m H$  of the model. We have calculated the mean value of the energy along the final plateau of the melting curves in Fig. 1. On the other hand, we have fitted the initial energies to a straight line and extrapolated the value at zero time (the fit is needed because the initial configuration is not completely relaxed at the interface and the

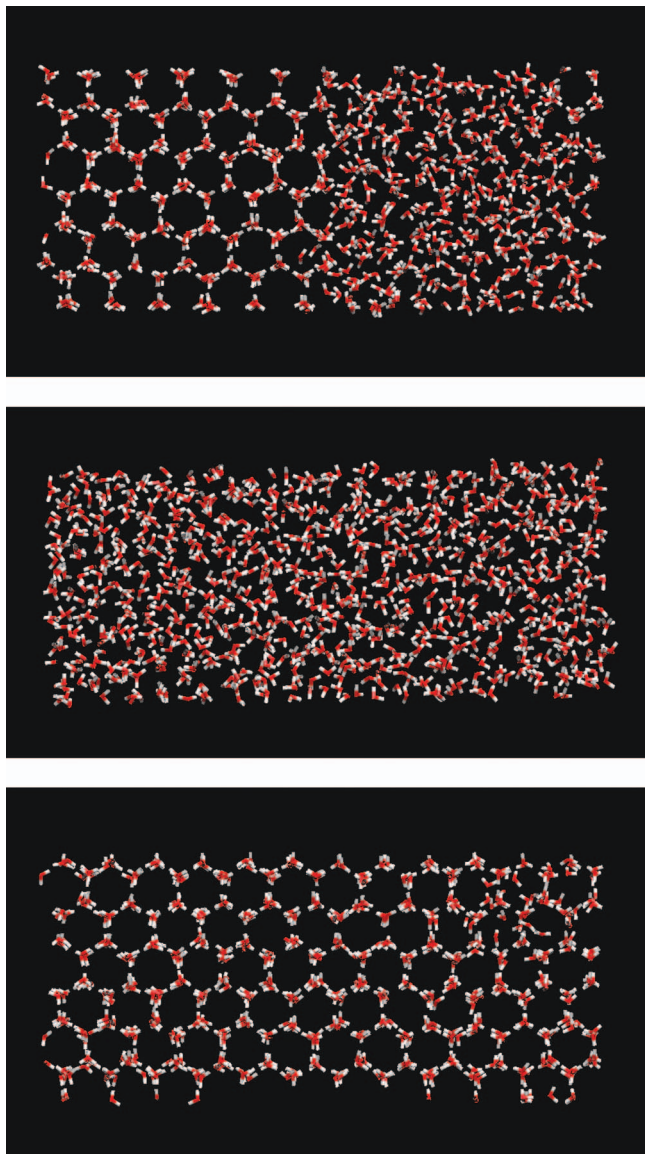


FIG. 2. (Color) Snapshots of initial (top) and final configurations of the simulations of a box containing ice and liquid water at 1 bar for the TIP4P/2005 model at 252 K (middle) and 242 K (bottom). The view is from the basal plane (0001) and the solid plane in contact with the liquid is the secondary prismatic ( $1\bar{2}10$ ) plane.

energy fluctuates very much in the initial steps). By subtracting both values and taking into account that the enthalpy difference corresponds to the heat released by the melting of 432 molecules of ice in a system of 870 water molecules, we have estimated the melting enthalpies as 5.32, 4.93, and 4.84 kJ/mol, for the temperatures of 258, 254, and 252 K, respectively. The value at 252 K is very close to the reported result of  $\Delta_m H = 4.85$  kJ/mol for the TIP4P/2005 model.<sup>19</sup> The agreement is excellent but an extrapolation of the results at 254 and 258 K indicates that it is a bit fortuitous. The extrapolation of the value at 258 K using the Kirchoff equation with  $C_p(\text{liquid water}) = 0.092 \text{ J mol}^{-1} \text{ K}^{-1}$  (taken from Ref. 19) and assuming that  $C_p(\text{ice}) \sim C_p(\text{liq})/2$  gives  $\Delta_m H = 5.05$  kJ/mol at 252 K. The same extrapolation for the result at 254 K gives again  $\Delta_m H = 4.84$  kJ/mol at 252 K. The mean value obtained from the three simulation runs is  $\Delta_m H$

$= 4.91$  kJ/mol which differs less than 0.1 kJ/mol from the reported value<sup>19</sup> for this model at 252 K. In summary, the procedure accounts approximately for the melting enthalpy of the TIP4P/2005 model. The importance of this result is to confirm once again that the final plateau of the upper curves in Fig. 1 is clearly indicative of a complete melting of the ice. Notice that this method of calculating  $\Delta_m H$  was used only to get a rough estimate of the melting enthalpy at the melting point and is not rigorous. The best way to compute the enthalpy of melting at  $T_m$  is to simulate pure ice at the melting temperature, to simulate pure water at the melting temperature, and to subtract both enthalpies as was done in our previous work.<sup>81</sup>

In regard to the lower curve in Fig. 1, it is evident that it corresponds to a temperature (242 K) below the melting point. Figure 2 depicts the final configuration of this run. It indicates that the system has crystallized almost perfectly. However, in the top-right part one can see a small number of molecules not accommodated into the crystal structure. In addition, there should be an equal number of structural vacancies and these defects should lower somewhat the melting enthalpy. In fact, the extrapolation of  $\Delta_m H$  to 252 K following the above commented procedure gives the result of 4.55 kJ/mol. It is indeed smaller than the reported value—4.85—for this model<sup>19</sup> and that the mean value—4.91—obtained from the melting curves. The monitorization of the run indicates that the beginning of the final plateau is indeed the point at which the system freezes completely with the exception of the small number of defective molecules. Figure 3 shows the density profiles of the TIP4P/2005 model calculated along 100 ps for the 242 K (after 8 ns) and the 252 K (after 2.5 ns) runs. For comparison, the density profile of the starting configuration is also plotted. The density profile at 252 K corresponds unequivocally to a liquid system while that at 242 K denotes a crystal.

The velocity at which the interface boundary moves as a function of deviations from the equilibrium melting temperature is usually termed the interface response function. The Wilson-Frenkel theory predicts that the interface response function is given by<sup>92-94</sup>

$$v = (Da/\Lambda^2)[1 - e^{\Delta\mu/kT}], \quad (1)$$

where  $D$  is the self-diffusion coefficient,  $a$  is the thickness of the adjacent liquid layer,  $\Lambda$  is the mean free path for this process, and  $\Delta\mu$  is the difference in chemical potential between the crystal and the metastable liquid at the interface. It is usually assumed that  $a \approx \Lambda \approx d$  (the particle radius). Since  $\Delta\mu = \Delta_m H \Delta T / T_m$ , for small  $\Delta T$  the equation can be simplified to

$$v = \frac{D \Delta_m H}{d k T_m^2} \Delta T. \quad (2)$$

Figure 1 shows that at 258 K the whole ice region disappears at about 1 ns while it needs 2.5 ns for a complete melting at 254 K and 5 ns at 252 K. This suggests a proportionality between the melting velocity and the departure from a melting temperature around 250 K (we will see below that the melting temperature is indeed close to this value) which is in agreement with Eq. (2). The analysis of the rate of freezing is

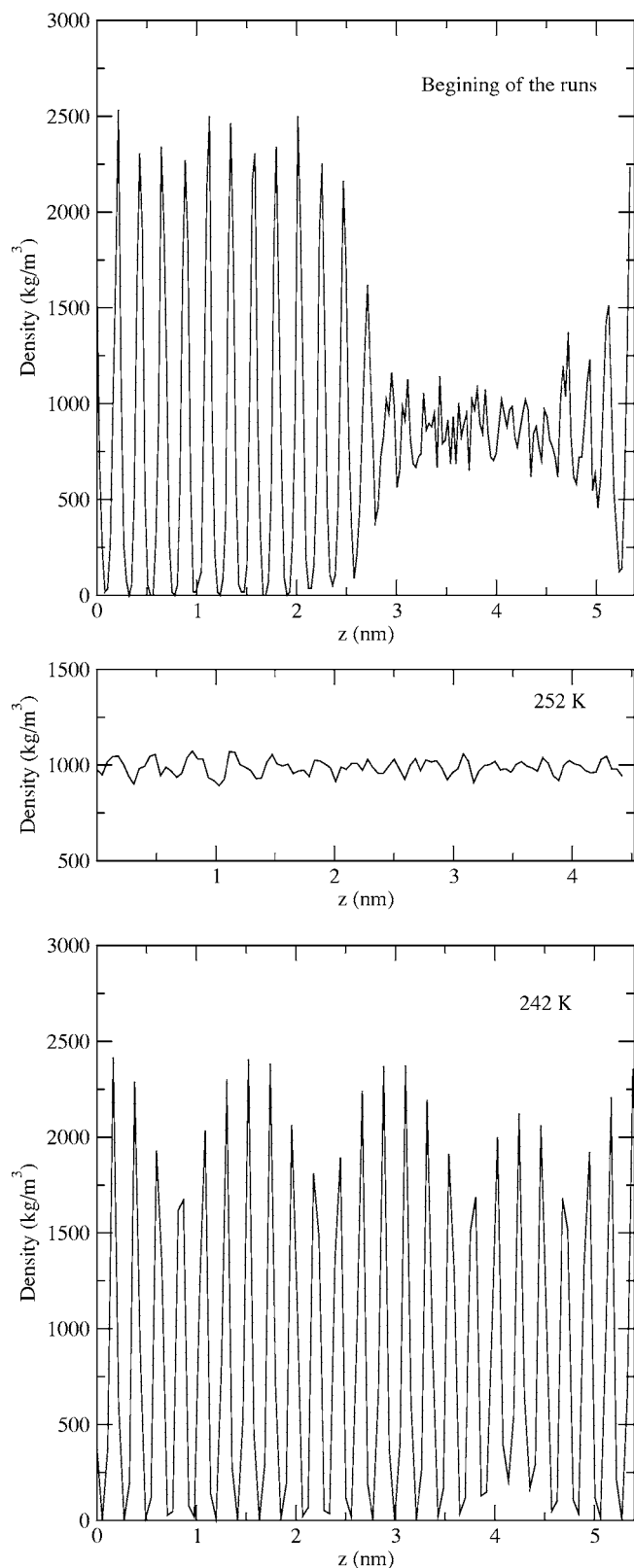


FIG. 3. Mean values of the density profiles for the TIP4P/2005 model along 100 ps. Top: Initial configuration, middle: at 252 K, after 2.5 ns, and bottom: at 242 K after 8 ns.

difficult for a number of reasons. Firstly, the rate of crystallization in our simulations is not as constant with time as the melting process. Sometimes, freezing proceeds in steps with intervals of time at which the energy is constant. It is tempt-

ing to relate this to the formation of successive new layers of ice but the visual inspection of the run movies did not allow us to make a precise correlation between the evolution of the total energy and the formation of new ice layers. It seems that crystallization is even more stochastic than melting. In this sense only by performing a number of different trajectories can firm conclusions be established about the rate of freezing. Notice also that the self-diffusion coefficient is usually represented by the Arrhenius equation  $D=D_0 \times \exp(-Q/kT)$ , and, thus, it strongly decreases at low temperatures. There are two competing factors determining the rate of crystal growth, namely, the diffusion coefficient and the degree of supercooling. As a result the interface response function is not monotonous on  $\Delta T$  but it reaches a maximum and then decreases.<sup>94-97</sup> It is outside the scope of the paper to make a deep analysis of the kinetics of the interface for water so we have not analyzed this question in detail. However, it is interesting to point out that the curve exhibiting complete freezing in Fig. 1 corresponds to a temperature (242 K) which differs from our first rough estimate for  $T_m$  (250 K) by the same amount as the melting curve at 258 K. But the interface response functions are quite different because the melting process took 1 ns and the freezing required 6 ns. Such a difference is an indication of the strong influence of the self-diffusion coefficient. In summary, our results are consistent with the fact that the melting velocity is a monotonous function of the degree of superheating but that the crystal growth may indeed get a maximum velocity when the effect of lower temperatures in supercooling decreases noticeably the value of  $D$ . This has also been noted by Carignano *et al.*<sup>76</sup> Notice finally that an important methodological consequence emerges from this picture: the calculation of  $T_m$  is much feasible by approaching from high temperatures than from low temperatures.

Until now we have analyzed the results for temperatures at which complete melting or freezing is observed. For TIP4P/2005 (Fig. 1), the interval between the lower temperature at which complete melting is observed (252 K) and the highest at which the water freezes completely (242 K) is 10 K. The interval depends on the time window used for the runs so an attempt to reduce the interval eventually becomes unaffordable in computer time. But, notice that it is not strictly necessary to wait for the complete melting (or freezing of the system). It suffices to see a consistent increase (or decrease) of the system energy to ensure that system is melting (i.e., above  $T_m$ ) or freezing (below  $T_m$ ). As mentioned above, the melting process seems more reliable than crystallization. Thus, in our procedure we begin by establishing a first interval of temperatures for which complete melting/freezing is observed. Then we run a simulation of 2–3° below the upper limit of the interval and observe whether the energy of the system increases along the simulation. If so, we reduce again the temperature until, for a given value, the energy of the system decreases along the simulation. We assign the mean value of these latter temperatures as the  $T_m$  of the system.

In Fig. 4 we show some of the curves obtained for several TIP4P models: TIP4P/ice,<sup>20</sup> TIP4P/2005,<sup>19</sup> TIP4P-Ew,<sup>18</sup> and the original TIP4P.<sup>7</sup> To facilitate the presentation we

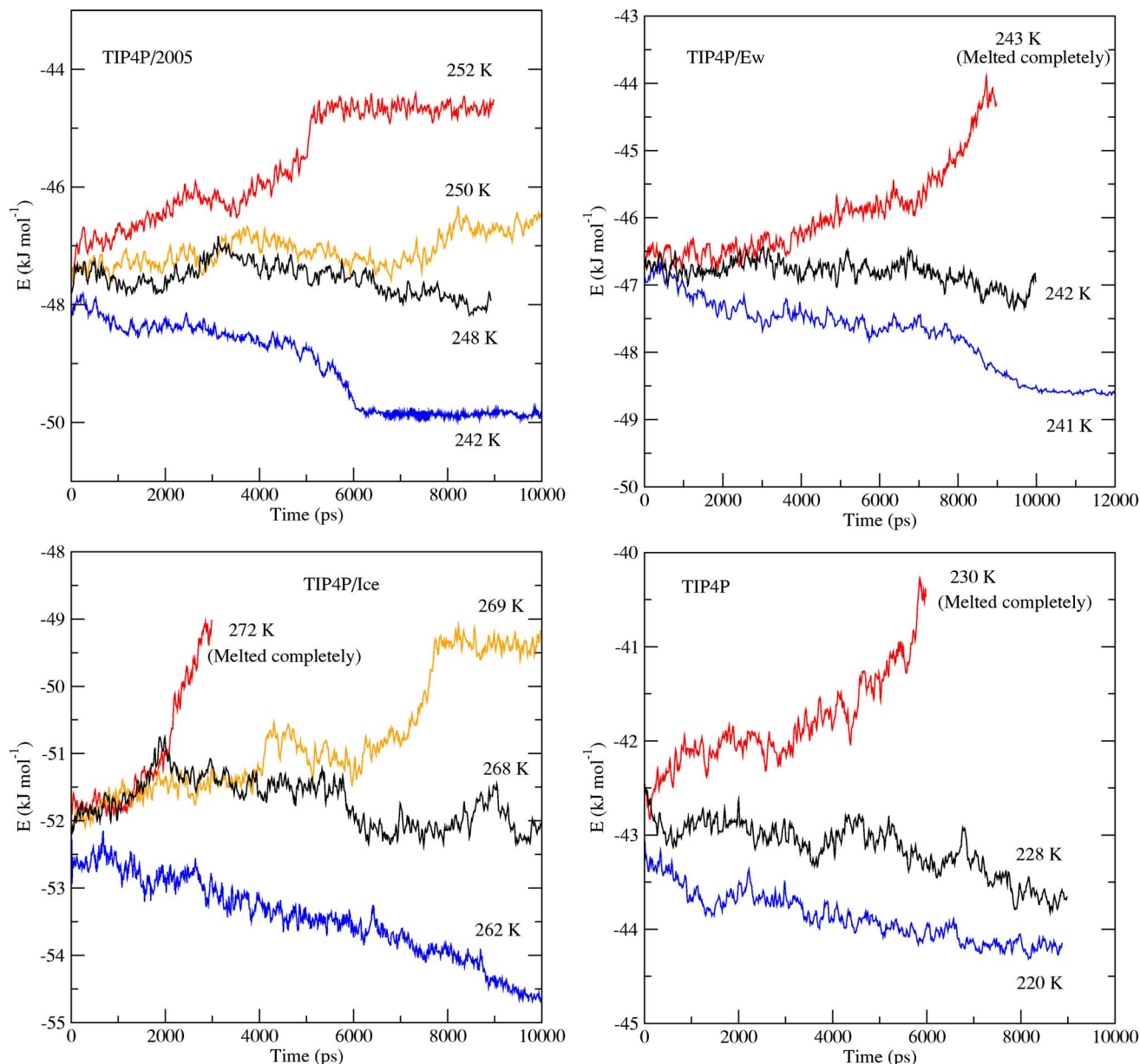


FIG. 4. Evolution of the total energy along the  $NpT$  runs for several TIP4P-type potential models. The values represented are the running averages over 25 ps. There is a plot for each of the water model (TIP4P/2005, TIP4P/ice, TIP4P-Ew, and the original TIP4P). The labels of the water model are given within the plots. The curves are also labeled to indicate the temperature of the corresponding run. The pressure was fixed to 1 bar. The sample size is 870 molecules for all the systems.

have displayed the running averages of the total energy along 25 ps. Let us now examine the plot for TIP4P/2005. The curves at 252 and 242 K correspond to temperatures for which complete melting or freezing is observed and, thus, they already appeared in Fig. 1. It may be seen that the intermediate curves at 250 and 248 K are somehow oscillatory although the net drift of the first one shows a slight increase of the energy and the latter one a slight decrease. Thus, our final value for the melting temperature with this method is 249 K. For the TIP4P/2005 case, the uncertainty in the determination of the  $T_m$  would be around  $2^\circ$  if one takes solely into consideration this source of error. Longer simulations could reduce the uncertainty but it should be stressed that the simulation presented in this work is probably among the longest performed so far for a solid-liquid

interface of water. Moreover other factors may affect the value of the melting point by the same amount (1–3 K) as, for instance, the initial solid configuration (ice  $I_h$  presents proton disorder and for this reason there is not a unique initial solid configuration), system size, the value of the truncation of the LJ potential, and the use of a switching function. For this reason it seems reasonable to analyze the impact of each of these factors on the melting point before attempting an extremely precise determination of the melting point for a certain choice of simulation conditions.

The rest of the TIP4P-type models behave in a similar way to that already described for the TIP4P/2005 model. A 2 K interval is more than enough to bracket the  $T_m$  for TIP4P-Ew. Notice that total melting is observed for the system at 243 K and that the system at 241 K crystallizes com-

pletely. As the slope of the energy of the 242 K system is essentially null we may assign this temperature as the  $T_m$ . For TIP4P/ice the systems melt at 269 K and the energy is constant (or perhaps with a very small negative drift) at 268 K, so that the melting point is between these two temperatures, probably closer to the latter one. Finally, the  $T_m$  for the original TIP4P is somewhere between 230 K (for which the complete melting occurred in 6 ns) and 228 K (that shows an energy curve with a net negative slope with time). In summary, the methodology employed has allowed the determination of the melting temperature within an interval of  $2^\circ$  or less in simulation runs of 10 ns maximum. We recall that the  $2^\circ$  interval corresponds exclusively to the uncertainty of the methodology employed in this work as there are other intrinsic sources of error in the determination of  $T_m$ .

The comments made for the interface response functions of TIP4P/2005 are confirmed for the rest of TIP4P models. An inspection of Fig. 4 indicates that, as a general rule, a complete melting of the sample is expected in less than 8 ns for temperatures of  $2^\circ$  or more above  $T_m$  (the required time obviously depends on the width of the solid and liquid regions). But the same assertion cannot be stated for the freezing process. Since—for the same deviation from  $T_m$ —freezing in general requires longer times than melting, the cost effective way of determining  $T_m$  is by running simulations at *successively* lower temperatures until the drift of the total energy is negative (or about zero) in a long enough run. The corresponding energy-time plots for TIP5P-type<sup>13,17</sup> and the SPC/E models are presented in Figs. 5 and 6, respectively. They show patterns similar to those for TIP4P models. The estimated melting temperatures are 271 K for the original TIP5P, 270 K for TIP5P-E, and 214 K for SPC/E. It is to be noticed that both melting and freezing are quite fast for the TIP5P models. It seems a general rule that, for a given departure  $\Delta T$  from the melting temperature, melting is faster for models with higher  $T_m$ . TIP4P/ice, TIP5P, and TIP5P-E (all of them with a  $T_m$  around 270 K) melted completely in less than 3 ns for temperatures of 2–4 K above  $T_m$  while SPC/E (for which  $T_m$  is about 215 K) did not achieve complete melting in 10 ns for a temperature  $7^\circ$  over  $T_m$ . Notice that the dependence of the velocity on  $T_m$ —Eq. (2)—is opposed to that of the diffusion coefficient. In particular, the experimental self-diffusion coefficient of water drops by more than one order of magnitude<sup>98</sup> for a change in temperature similar to the range of  $T_m$  calculated for the water models in this work. In summary, high  $T_m$  values imply high diffusivities and this has a greater effect on the melting velocities than any other factor. Similar trends are observed in general for freezing. Fast crystallizations have been observed for both TIP5P models. According to what is expected, the only systems for which complete freezing was not observed within 10 ns are just those with lower  $T_m$ : TIP4P and SPC/E. However, it seems not so obvious to explain that complete freezing occurred in TIP4P-Ew only  $1^\circ$  below  $T_m$  despite that its melting temperature is some 30 K lower than that for TIP4P/ice and TIP5P. In contrast, TIP4P/ice required 10 ns 7 K below  $T_m$  which is a longer time than that required by TIP4P/2005 at identical  $\Delta T$  but with a significantly lower melting temperature. Since the time and length scale our

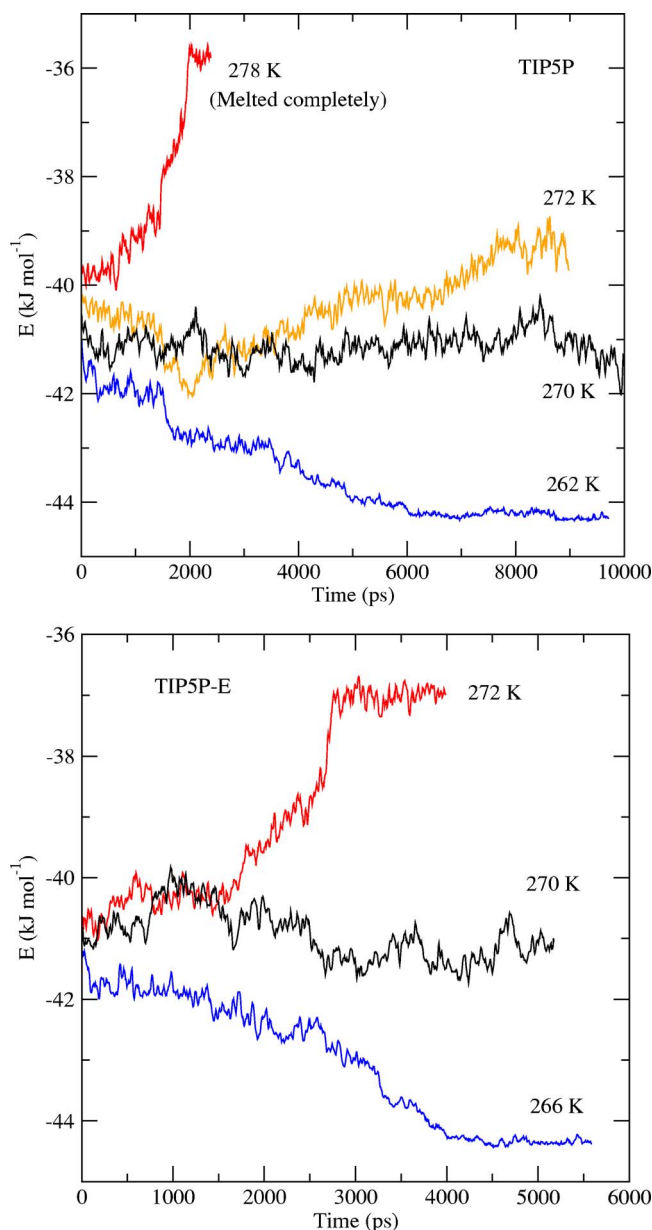


FIG. 5. Evolution of the total energy along the  $NpT$  runs for the original TIP5P and the TIP5P-E potential models. The values are the running averages over 20 ps. The pressure was fixed to 1 bar. The sample size is 870 molecules for both systems.

simulations are not sufficient to establish firm conclusions; it seems that further work is needed to better understand the kinetics of freezing.

Table I reports the values of the melting temperatures obtained in this work. The results are in excellent agreement with those obtained by us in free energy calculations.<sup>81</sup> We have already mentioned that the estimated uncertainty of the  $T_m$  from the methodology of this work (without including other sources of error as system size, initial solid configuration, and distance of truncation for the LJ potential) is of about  $2^\circ$ . Let us comment briefly on the estimated uncertainty of the column labeled “free energy.” The estimated uncertainty in the melting temperature of the SPC/E and TIP4P models obtained from free energy calculations is about 4 K (including the uncertainty in the equation of state

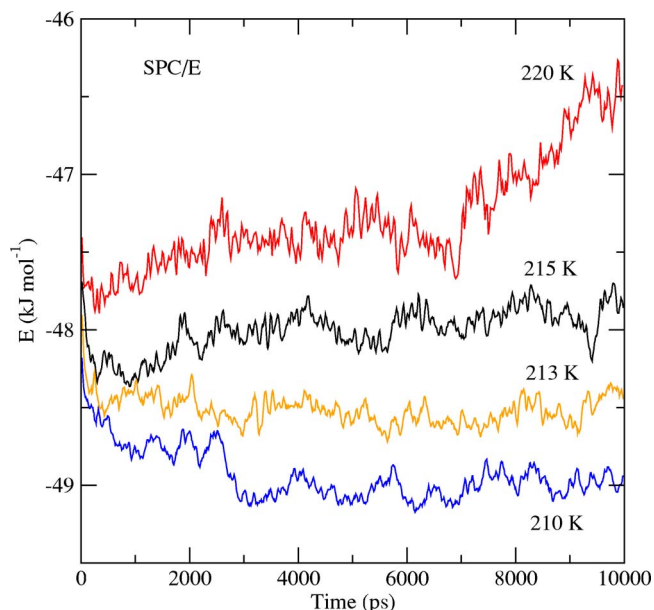


FIG. 6. Evolution of the total energy along the  $NpT$  runs for SPC/E at 1 bar. The values are the running averages over 25 ps and the sample size is 864 water molecules in this case.

of the solid, of the fluid, and the free energy calculations of the fluid and solid phases). The melting point of TIP4P/ice, TIP4P/2005, TIP4P-Ew, TIP5P, and TIP5P-E was not obtained from free energy calculations but rather from Hamiltonian Gibbs-Duhem integration. In the Hamiltonian Gibbs-Duhem integration<sup>56</sup> the melting point of a certain model of water is obtained from the melting point of another model.<sup>81</sup> The estimated uncertainty of the integration is about 2 K. We typically used the TIP4P model as the initial model. Therefore, the typical uncertainty of the melting temperature of models obtained from Hamiltonian Gibbs-Duhem is about 6 K. In summary, the uncertainty of the melting point for TIP4P and SPC/E is about 4 K whereas for the other models is about 6 K. By looking again at Table I it can be clearly stated that the melting temperature as obtained from these

TABLE I. Melting points obtained in this work by coexistence of a solid-liquid interface compared to the results from free energy calculations and/or Hamiltonian Gibbs-Duhem integration of our group (Refs. 19, 20, 81, and 82). The results for SPC/E and TIP4P were obtained from free energy calculations and the estimated uncertainty of  $T_m$  is about 4 K. The results for the rest of the models were obtained from Hamiltonian Gibbs-Duhem integration starting from the TIP4P model so that their total uncertainty is about 6 K [a free energy calculation by Koyama *et al.* (Ref. 48) for TIP5P has been included for comparison]. In the last column the recommended values of the melting point of ice  $I_h$  for the different models are presented.

Model	This work	Free energy	Recommended
TIP4/ice	268(2)	272(6)	270(3)
TIP4/2005	249(2)	252(6)	250.5(3)
TIP4P-Ew	242(2)	245.5(6)	244(3)
TIP4P	229(2)	232(4)	230.5(3)
TIP5P	271(2)	274(6)	272(3)
		268(6) <sup>a</sup>	
TIP5P-E	270(2)	271.5(6)	271(3)
SPC/E	213(2)	215(4)	214(3)

<sup>a</sup>Reference 48.

three different routes (free energy calculations, Hamiltonian Gibbs-Duhem integration, and direct fluid-solid coexistence) is in agreement and the deviations are well within the typical uncertainties. This means that the two routes proposed by Ladd and Woodcock more than 20 years ago—the direct coexistence simulations<sup>67</sup> and the Einstein crystal free energy calculations<sup>35</sup>—can be brought into mutual agreement even for a relatively complex system as water.

Table I illustrates the fact that melting temperatures obtained from free energy calculations and from direct simulations should not disagree by more than about 4 K. A larger difference is probably not acceptable. Until this work it was not clear whether larger differences could be obtained by using these two different techniques. The only point that deserves further comment is the fact that, in general, the melting temperature of the direct fluid-solid equilibrium is around 3 K below that of free energy calculations. The deviation seems to be systematic. The origin of this small discrepancy is not clear. The same initial ice configuration (with 432 molecules) was used for all the calculations of this work. Also, the same initial ice configuration (with 288 molecules) was used for all the free energy calculations of our previous work. Hence, the different initial solid configurations of both sets could be the origin of the discrepancy. Another possibility is that our free energy calculations overestimated the melting point of TIP4P by about 3 K, and this error of the initial reference model was transmitted to the melting point of the other models when using the Hamiltonian Gibbs-Duhem integration. Another aspect that may affect the results is that LJ dispersion forces were treated in a slightly different way in this work (switched potential) and in our free energy calculations (truncated potential with added long range corrections). Finally, the possibility that the direct fluid-solid simulations could exhibit system size effects should also be considered. The system size effects could be due to the fact that the interface may perturbate the relative stability of solid and liquid phases in small systems. It has been pointed out that the cutoff distance may affect coexistence properties when obtained from direct interface simulations.<sup>99,100</sup> This is clearly true for the vapor-liquid equilibrium though the effect should be smaller in the fluid-solid equilibria where the density of the two phases is rather similar.

In order to investigate the possible effect of the sample size we have carried out additional simulations of the TIP4P/ice model for a system of 2048 molecules (1024 ice and 1024 water molecules). In these simulations, the cutoff for the van der Waals forces and for the real part of the electrostatic contributions has been increased to 10 Å. The size of the simulation box is now  $30 \times 31 \times 69$  Å. Results of the runs for this larger system are presented in Fig. 7. The melting temperature of this system is 270 K which is 2° higher than the result obtained for the smaller system made of 870 molecules. The difference is still within the uncertainty of the procedure so the sample size dependence has a minor effect on the final calculations. Interestingly, the possible effect goes in the direction to correct the already small difference between our interfacial and free energy melting temperatures. For the time being we believe that the best estimate of the melting point of the water models with the



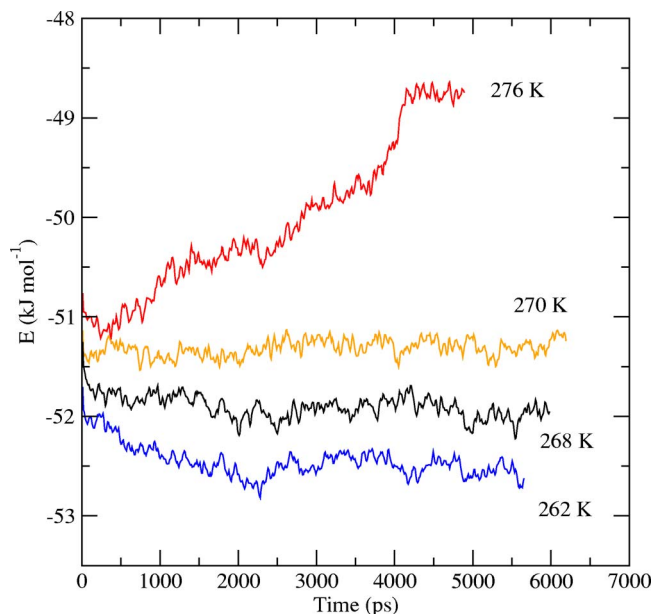


FIG. 7. Evolution of the total energy along the  $NpT$  runs for TIP4P/ice at 1 bar for a 2048 molecule system. The values are the running averages over 25 ps.

information available so far is probably to take an average of the values of the two methodologies presented in Table I and to assign an uncertainty of about 3 K. The recommended values are given in Table I.

Finally, it is of interest to compare the results of this work with recent estimates of the melting point obtained by other authors. In particular, our values of  $T_m$  for TIP4P and TIP5P are very similar to those of Koyama *et al.*,<sup>48</sup> namely, 229(9) and 268(6) K, respectively, which were obtained with free energy calculations. They are also in close agreement with the results of Wang *et al.*<sup>74</sup> for TIP4P and TIP5P, namely, 229(1) and 272(1) K, respectively, using an interface solid-liquid and the  $NpH$  ensemble instead of  $NpT$ . Thus, for TIP4P and TIP5P the effort of different groups and techniques is converging to the same value. For TIP4P-Ew and TIP5P-E Wang *et al.* reported 257 and 254 K, respectively,<sup>74</sup> by using interface solid-liquid simulations with runs of about 0.3 ns. These results differ by about 15 K from those presented in Table I (although in one case our  $T_m$  is lower and in other case is higher than their values). Further work is needed to clarify this discrepancy although runs of 0.3 ns are probably not sufficient to determine precisely the melting point. For the SPC/E model, also with a solid/liquid interface, Bryk and Haymet have reported a melting temperature of  $225 \pm 5$  K (Ref. 72) by using runs of 1 ns or less. This result is not too far from our estimate but the difference is larger than the statistical uncertainty. The origin of the difference from our results is not clear. We have shown that the dynamics of the SPC/E is very slow in the proximities of the melting point so that it is likely that longer runs are also required for this model. It should be mentioned that we have also employed the free energy result for the melting point of SPC/E ( $T_m=215$ K) to estimate the melting temperature of TIP4P by using Hamiltonian Gibbs-Duhem integration.<sup>81</sup> The result for TIP4P was 232 K, the same obtained in inde-

pendent free energy calculations and in line with the value reported in this work. It is also worth noting that our result is coincident with that from independent direct coexistence simulations at the same conditions.<sup>101</sup>

#### IV. CONCLUSIONS

In this work we have presented an implementation for the calculation of the melting point of ice  $I_h$  from direct coexistence of the solid-liquid interface. The method based on  $NpT$  simulations of the interface has robustness as its main advantage. If the trial temperature is considerably higher than the  $T_m$ , the solid region melts quickly and the drift of the total energy is positive. The temperature is then reduced until, for a given value, the drift of the total energy along the simulation is null or negative. The uncertainty in the determination of the melting temperature is strongly dependent on the simulated time. We have shown that in order to reduce the uncertainty to about  $2^\circ$  the simulations should be of the order of 10 ns long. The same time (or even more) would be required in the  $NpH$  ensemble (first proposed by Andersen<sup>102</sup>) where, in addition to the usual system fluctuations, the heat generated at the interface by the melting of ice should be dissipated to the rest of the system.

We have compared the direct coexistence results with our own  $T_m$  determinations using a free energy route. We have found a very good agreement between the results of both methodologies, the differences being around  $3^\circ$  for a number of water models: SPC/E, TIP4P, TIP5P, TIP5P-E, TIP4P-Ew, TIP4P/2005, and TIP4P/ice. These results demonstrate that the calculation of the melting point by  $NpT$  simulations of the liquid-solid interface is a reliable technique that gives results consistent with those of free energy calculations in similar conditions. An advantage is that the calculations can be performed with standard molecular dynamics packages in contrast to free energy calculations which require homemade programs. In contrast, the method is computationally more expensive than the free energy route.

A reliable estimate of the melting point is needed for other studies dealing with the fluid-solid equilibria as, for instance, studies on the rate of nucleation of ice from liquid water or the dynamics and speed of crystal growth. These two kinds of studies require the knowledge of the melting point of the model, which as it can be seen in Table I is not always coincident with the experimental melting point of real water. We hope that the estimates provided in Table I for  $T_m$  will encourage research along these lines which are both of practical and theoretical interests. However, it is important to stress that one cannot simply decide on the relative merits of models based on the melting temperature alone. Even restricting to the solid-liquid equilibria the situation is not as simple as it could appear. Perhaps the most extreme case is that of TIP5P. Although it gives an excellent prediction for the  $T_m$ , the results for the coexistence densities are quite poor. As a result, the slope of the  $p$ - $T$  melting curve is five times larger than the experimental one.<sup>81</sup> Moreover, for TIP5P (and also SPC/E) ice II is the stable phase at 1 bar instead of ice  $I_h$ .<sup>49,81</sup> Less dramatic but still not satisfactory is

the TIP4P-Ew case. Although ice  $I_h$  is the stable polymorph at 1 bar, ice II takes over the region of intermediate pressures and makes ice III a metastable form and reduces that of ice V to an almost insignificant interval of pressures.<sup>19</sup>

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