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High precision determination of the melting points of water TIP4P/2005 and water TIP4P/Ice models by the direct coexistence technique

M. M. Conde,[a] M. Rovere, and P. Gallo
Dipartimento di Matematica e Fisica, Università Roma Tre, Via della Vasca Navale 84, 00146 Roma, Italy

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An exhaustive study by molecular dynamics has been performed to analyze the factors that enhance the precision of the technique of direct coexistence for a system of ice and liquid water. The factors analyzed are the stochastic nature of the method, the finite size effects, and the influence of the initial ice configuration used. The results obtained show that the precision of estimates obtained through the technique of direct coexistence is markedly affected by the effects of finite size, requiring systems with a large number of molecules to reduce the error bar of the melting point. This increase in size causes an increase in the simulation time, but the estimate of the melting point with a great accuracy is important, for example, in studies on the ice surface. We also verified that the choice of the initial ice I_h configuration with different proton arrangements does not significantly affect the estimate of the melting point. Importantly this study leads us to estimate the melting point at ambient pressure of two of the most popular models of water, TIP4P/2005 and TIP4P/Ice, with the greatest precision to date. *Published by AIP Publishing.* https://doi.org/10.1063/1.5008478

I. INTRODUCTION

One of the most active fields in science is the study of water and its solid phases. Water is the most important molecule present in nature.[1] It plays a fundamental role not only as pure water but also as a universal solvent in most of the physicochemical processes.

Although water is a simple molecule, many of its properties show anomalous behaviors.[2–5] To date, they are still not fully understood and give to the water molecule a special character. Since the pioneering work in simulation of water of Barker and Watts[6] and Rahman and Stillinger,[7] numerous studies can be found in the literature dedicated to the study of the physicochemical properties of water by computer simulation.[8–23]

The choice of a good potential model is a crucial step in the simulation studies since the results obtained depend on the force field used to describe the interactions between the molecules. A wide variety of potential models have been proposed to reproduce the properties of water. Some of the most successful models are water rigid models (SPCs,[24,25] TIPs,[26–30] and ST2[31]), flexible models (SPC/Ef,[32] q-TIP4P/F,[33] and TIP4P/2005f[34]), polarizable models (AMOEBA,[35] BK3,[36] and COS[37]), and coarse-grained type models (mW,[38] MARTINI,[39–41] primitive model,[42,43] and Mercedes-Benz[44,45]).

The description of the phase equilibrium represents a way to test the ability of water potential models. The estimate of the melting temperature (T_m) of water potential models is absolutely needed to know the phase transition of ice to liquid water in studies on pure water or in systems where water acts as a solvent. The value of the melting point of the potential models can differ markedly from the experimental melting point of water. The most popular water models (TIP3P,[26] TIP4P,[26] TIP5P,[27] SPC,[24] and SPC/E[25]) were developed in the 1980s. However, the first estimate of the melting point of these models has not been calculated until the studies of Haymet and co-workers.[46–48] Moreover, a full description of the phase diagram of these models was not published until 2004 by Vega and co-workers.[49,50] In the last decade, a new generation of water potential models have been proposed by improving the prediction of water properties: TIP4P-Ew,[28] TIP4P/2005,[29] and TIP4P/Ice.[30]

For all these water models, the error bar in the calculation of the melting point is located, in the best of cases and depending on the technique, around 2-3 K. This uncertainty is sufficient to know approximately the stability of the water phases involved in the simulation, but, unfortunately, this error bar makes it very difficult to carry out studies where a greater precision for the temperature of the phase transition of solid to liquid is required. For example, a high precision is important in studies on the existence of a liquid layer of water on a free surface, the wetting or non-wetting process, in adsorption studies of molecules on the ice surface, or the freezing point depression of water in the presence of ionic salts.

In recent years, the technique of direct coexistence has been implemented successfully to calculate the equilibrium conditions, and thus melting temperatures, in different real systems such as solid water phases,[51–54] ionic compounds,[55,56] clathrate hydrates,[57–59] or methanol.[60] This method was originally proposed by Ladd and Woodcock[61,62] for a Lennard-Jones system.

In the direct coexistence technique, the phases of interest are put in contact within the same simulation box. The implementation of this technique is simple; however, some of the

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[a] mmconde@fis.uniroma3.it

main problems to take into account are the stochastic nature and the effects of finite size.[63,64] Recently, Espinosa *et al.*[65] performed a study for a hard sphere model where they analyzed these effects. The goal of our work is twofold. First is to perform an exhaustive study of the factors that affect the technique of direct coexistence applied to a real system of liquid water and ice by computer simulation. The factors analyzed are the stochastic nature, the effects of finite size, and the importance of the initial configuration. Second is to give a most precise estimate of the melting temperature of two of the most popular water potentials that best reproduce a great number of properties of water: TIP4P/2005 and TIP4P/Ice models.

The present paper is organized as follows. In Sec. II, the water potential models used in this work are described. Section III explains the methodology followed. In Secs. IV and V, we evaluate in detail the different factors involved in the direct coexistence technique and we estimate the melting points for the TIP4P/2005 and TIP4P/Ice models. Finally, a comparison of the value of the melting point obtained by different routes and the main conclusions are discussed.

II. WATER POTENTIAL MODELS

As was said in Sec. I, there are a large number of water models in the literature which reproduce with greater or less success the properties of water. For our study, we choose two of the most popular water models: TIP4P/2005[29] and TIP4P/Ice.[30] Both models are rigid and nonpolarizable, and they are a modification of the well-known TIP4P model proposed by Jorgensen *et al.*[26]

In the TIP4P/2005 and TIP4P/Ice models, a Lennard-Jones (LJ) interaction site is located on the oxygen atom, positive charges are located on the positions of the H atoms, and the negative charge is located at a distance d_{OM} from the oxygen along the H–O–H angle bisector. Both models have the same bond geometry and the same charge distribution with a slight modification of the distance d_{OM}. The parameters of the Lennard-Jones center (σ,ϵ) as well as the positive charge of the hydrogen atom are characteristic for each model. The potential parameters for both the models are given in Table I.

These potential models have been designed to improve the description of ice and water, see, for example, Refs. 5, 66, and 67 and the references therein. Both models describe successfully the behavior of water solid phases in the phase diagram. In particular, the TIP4P/2005 model reproduces the maximum density at ambient pressure of the liquid water as a function of temperature. In fact, this model was able to predict a new ice phase[68] stable at negative pressures known as ice XVI which was later confirmed experimentally.[69] The main advantage of the TIP4P/Ice model is the excellent estimate of the density for the different water polymorphs and the melting point of the ice at ambient pressure in reasonable agreement with the experimental value.[51] These properties were not reproduced with the previous models, and this is the reason for the success of TIP4P/2005 and TIP4P/Ice.

TABLE I. Potential parameters of the TIP4P/2005 and TIP4P/Ice models. The distance between the oxygen and the hydrogen sites is d_{OH}. The angle, in degrees, formed by hydrogen, oxygen, and the other hydrogen atom is denoted by ∠H–O–H. The Lennard-Jones site is located on the oxygen with parameters σ and ϵ. The charge on the proton is q_{H}. The negative charge is placed on a point M at a distance d_{OM} from oxygen along the H–O–H bisector. Data from Refs. 29 and 30.

Model	d_{OH} (Å)	∠H–O–H	σ (Å)	ϵ/k_B (K)	q_{H} (e)	d_{OM} (Å)
TIP4P/2005	0.9572	104.52	3.1589	93.2	0.5564	0.1546
TIP4P/Ice	0.9572	104.52	3.1668	106.1	0.5897	0.1577

III. METHODOLOGY: THE DIRECT COEXISTENCE TECHNIQUE

The technique of direct coexistence is based on a simple idea: to put in contact two or more phases (in our study, one phase of ice I_h in contact with one phase of liquid water) in the same simulation box and at constant pressure to study the evolution of the system as a function of temperature and thus estimate the melting point of ice.

The solid phase of ice I_h in the initial configuration was obtained using the algorithm proposed by Buch *et al.*[70] generating an ice phase with proton disorder and almost zero dipole moment satisfying the Bernal-Fowler rules.[71] In order to equilibrate the solid, we performed anisotropic *NpT* simulations of ice I_h obtaining the correct equilibrium density of the solid. Simulations were performed for about 10 ns at ambient pressure and temperatures close to the melting point for each model used. To generate the liquid phase, we performed a *NVT* simulation for an identical phase of ice I_h at 400 K to quickly melt the ice slab in a few nanoseconds obtaining a configuration of liquid water with the same number of molecules and the same dimensions of the box simulation in both phases. Subsequently we equilibrated the liquid phase at temperatures close to the melting point for each model. During equilibration, the length of one side of the box simulation was allowed for changing to reproduce the correct equilibrium density of the liquid phase. The methodology followed was similar to that used in our previous work.[54] Finally, we put the solid in contact with the liquid phase. The plane of ice I_h exposed at the interface was the secondary prismatic plane $(1\bar{2}10)$ since it has been shown that this plane exhibits the fastest dynamics[72,73] and we equilibrated the system for a short time (20 ps) to have an equilibrated interface.

Anisotropic *NpT* simulations were performed for all coexistence simulations of our study allowing the three different sides of the simulation box to fluctuate independently to avoid stress in the solid lattice. We used the molecular dynamics package GROMACS (version 4.5.5).[74] Although the strictly correct ensemble for the study of fluid-solid equilibrium by direct coexistence should be an ensemble where the pressure is applied only in the direction perpendicular to the interface,[64] Espinosa *et al.*[65] illustrated in their work that for a large system the *NpT* ensemble provides good results.

Periodic boundary conditions were employed in the three directions of space. The geometry of the water molecules was enforced using constraints. The Lennard-Jones part of the potential was truncated at 8.5 Å. The Ewald sums were used to deal with electrostatics.[75] The real part of the

TABLE II. Number of molecules in the different phases for all systems and the water potential models studied.

Model	Ice phase	Liquid phase	Total system
TIP4P/2005	432	432	864
TIP4P/2005	1024	1024	2 048
TIP4P/2005	2000	2000	4 000
TIP4P/2005	8000	8000	16 000
TIP4P/Ice	8000	8000	16 000

Coulombic potential was truncated at 8.5 Å. The width of the mesh was 1 Å, and we used a fourth order polynomial. The temperature was fixed using the Nosé-Hoover thermostat[76,77] with a relaxation time of 2 ps. To keep the pressure constant, a Parrinello-Rahman barostat[78] was used. The relaxation time of the barostat was 2 ps. The time step used in the simulations was 2 fs.

In order to study the finite size effects of the technique, we simulated different sizes of the system (ice/liquid). The details about the number of molecules of the phases from each water model are given in Table II.

To analyze the stochastic nature in the direct coexistence technique, we simulated, for each initial configuration, five independent runs with different seed numbers in the initial velocities.

For each system studied with the same size, we performed simulations using the same initial configuration at different

TABLE III. Value of the temperature and the associated error bar for the five independent runs using different seed numbers in the initial velocity as a function of size of the system and for the largest size for three different configurations of ice for the TIP4P/2005 water model. T_{seed} is the temperature of the systems for each seed number simulated. The column on the left corresponds to the average temperature ($T_{average}$) of each simulation calculated as the average of the temperatures of different seed numbers. All temperatures are given in Kelvin (K).

System: 432 I_h + 432 liquid

$T_{average}$	$T_{seed\,1}$	$T_{seed\,2}$	$T_{seed\,3}$	$T_{seed\,4}$	$T_{seed\,5}$
251.00 ± 0.07	251.008 ± 0.035	251.006 ± 0.076	251.006 ± 0.073	250.994 ± 0.080	251.003 ± 0.085
250.01 ± 0.06	250.012 ± 0.036	250.018 ± 0.036	250.005 ± 0.068	250.013 ± 0.079	250.009 ± 0.084
249.01 ± 0.04	249.017 ± 0.035	249.014 ± 0.033	249.010 ± 0.037	249.006 ± 0.039	249.019 ± 0.037
248.01 ± 0.03	248.022 ± 0.027	248.010 ± 0.026	248.001 ± 0.031	248.020 ± 0.037	248.017 ± 0.037
247.01 ± 0.03	247.018 ± 0.035	247.017 ± 0.036	247.019 ± 0.036	246.993 ± 0.029	247.004 ± 0.032

System: 1024 I_h + 1024 liquid

$T_{average}$	$T_{seed\,1}$	$T_{seed\,2}$	$T_{seed\,3}$	$T_{seed\,4}$	$T_{seed\,5}$
250.92 ± 0.02	250.918 ± 0.015	250.927 ± 0.028	250.913 ± 0.016	250.912 ± 0.025	250.930 ± 0.015
249.92 ± 0.02	249.925 ± 0.028	249.928 ± 0.017	249.908 ± 0.022	249.947 ± 0.011	249.917 ± 0.014
248.97 ± 0.01	248.946 ± 0.012	248.994 ± 0.018	249.001 ± 0.015	248.946 ± 0.012	248.945 ± 0.012
247.97 ± 0.02	248.004 ± 0.025	247.940 ± 0.012	247.977 ± 0.021	247.957 ± 0.017	247.948 ± 0.018

System: 2000 I_h + 2000 liquid

$T_{average}$	$T_{seed\,1}$	$T_{seed\,2}$	$T_{seed\,3}$	$T_{seed\,4}$	$T_{seed\,5}$
249.913 ± 0.006	249.9160 ± 0.0065	249.9180 ± 0.0028	249.9130 ± 0.0079	249.9060 ± 0.0110	249.9120 ± 0.0043
249.423 ± 0.007	249.4140 ± 0.0049	249.4120 ± 0.0090	249.4400 ± 0.0098	249.4310 ± 0.0080	249.4200 ± 0.0041
248.934 ± 0.008	248.9330 ± 0.0069	248.9270 ± 0.0072	248.9340 ± 0.0071	248.9410 ± 0.0095	248.9330 ± 0.0096

System: 8000 I_h + 8000 liquid (configuration 1)

$T_{average}$	$T_{seed\,1}$	$T_{seed\,2}$	$T_{seed\,3}$	$T_{seed\,4}$	$T_{seed\,5}$
249.910 ± 0.006	249.9090 ± 0.0078	249.9090 ± 0.0065	249.9090 ± 0.0079	249.9100 ± 0.0057	249.9140 ± 0.0042
249.659 ± 0.007	249.6600 ± 0.0071	249.6560 ± 0.0096	249.6620 ± 0.0051	249.6550 ± 0.0058	249.6630 ± 0.0061
249.425 ± 0.005	249.4100 ± 0.0053	249.4130 ± 0.0032	249.4280 ± 0.0044	249.4360 ± 0.0058	249.4360 ± 0.0046
249.181 ± 0.005	249.1820 ± 0.0044	249.1750 ± 0.0037	249.1840 ± 0.0064	249.1800 ± 0.0043	249.1820 ± 0.0048
248.934 ± 0.005	248.9320 ± 0.0050	248.9330 ± 0.0036	248.9340 ± 0.0063	248.9370 ± 0.0072	248.9320 ± 0.0039

System: 8000 I_h + 8000 liquid (configuration 2)

$T_{average}$	$T_{seed\,1}$	$T_{seed\,2}$	$T_{seed\,3}$	$T_{seed\,4}$	$T_{seed\,5}$
249.908 ± 0.007	249.9130 ± 0.0063	249.9070 ± 0.0072	249.9090 ± 0.0056	249.9030 ± 0.0083	249.9060 ± 0.0086
249.660 ± 0.005	249.6560 ± 0.0061	249.6610 ± 0.0043	249.6610 ± 0.0031	249.6640 ± 0.0046	249.6580 ± 0.0084
249.428 ± 0.005	249.4350 ± 0.0051	249.4330 ± 0.0058	249.4350 ± 0.0065	249.4110 ± 0.0054	249.4280 ± 0.0031

System: 8000 I_h + 8000 liquid (configuration 3)

$T_{average}$	$T_{seed\,1}$	$T_{seed\,2}$	$T_{seed\,3}$	$T_{seed\,4}$	$T_{seed\,5}$
249.908 ± 0.006	249.9090 ± 0.0055	249.9040 ± 0.0068	249.9060 ± 0.0058	249.9120 ± 0.0051	249.9080 ± 0.0056
249.661 ± 0.005	249.6620 ± 0.0053	249.6640 ± 0.0036	249.6590 ± 0.0053	249.6570 ± 0.0093	249.6630 ± 0.0037
249.425 ± 0.004	249.4320 ± 0.0051	249.4270 ± 0.0038	249.4270 ± 0.0048	249.4120 ± 0.0053	249.4290 ± 0.0032

temperatures and ambient pressure to estimate the melting point of the model. In addition, for the TIP4P/2005 model in the largest system, we used different initial configurations to study the influence of the configuration of ice I_h on the determination of the melting point.

The length of each simulation depends on the size of the system and the temperature selected.

IV. TIP4P/2005 MELTING POINT

To determine the melting point of a water model by direct coexistence, we monitor the potential energy as a function of time. The potential energy presents two different behaviors depending on the temperature. When the temperature is above the melting point, the solid phase melts until the system transforms completely into a liquid phase. This phase transition is associated with a marked increase in potential energy. On the contrary, at temperatures below the melting point, the potential energy decreases continuously. This decrease in energy reveals the growth of the ice phase until the total freezing of the system is reached. Thus, the melting point of the system at ambient pressure is estimated as the average between the lowest temperature for which the solid phase melts, T_1, and the highest temperature for which the solid phase grows, T_2. The error bar associated with the melting temperature is given by the maximum error (δ_{max}) of the lowest temperature and the highest temperature following the formula

$$\delta_{\text{max}} = \frac{(T_1 + \delta_1) - ((T_2 - \delta_2))}{2}, \tag{1}$$

where T_1 and T_2 are the lowest and the highest temperatures close to the melting point and δ is the error associated with each temperature, respectively.

A. Systems with different sizes and same initial configuration

Several factors may affect the precision in the determination of the melting point obtained by direct coexistence. One of them is the stochastic nature of the technique. When the simulations are performed by direct coexistence, it is possible to find for the same temperature two simulations with opposite behaviors. That is to say that, near the melting point for the same temperature in the same system, it is possible to find a simulation where the ice melts and another where the ice grows.

To evaluate the effect of the stochastic nature of direct coexistence, we perform for the same system size and for each temperature selected five independent simulations with different seed numbers in the initial velocity. In our study to control the temperature, we chose the Nosé-Hoover thermostat.[76,77] Along the simulation, the temperature can fluctuate slightly varying its final value from the initial value. Consequently, the five independent runs with different seed numbers present slightly different values of temperature. Each

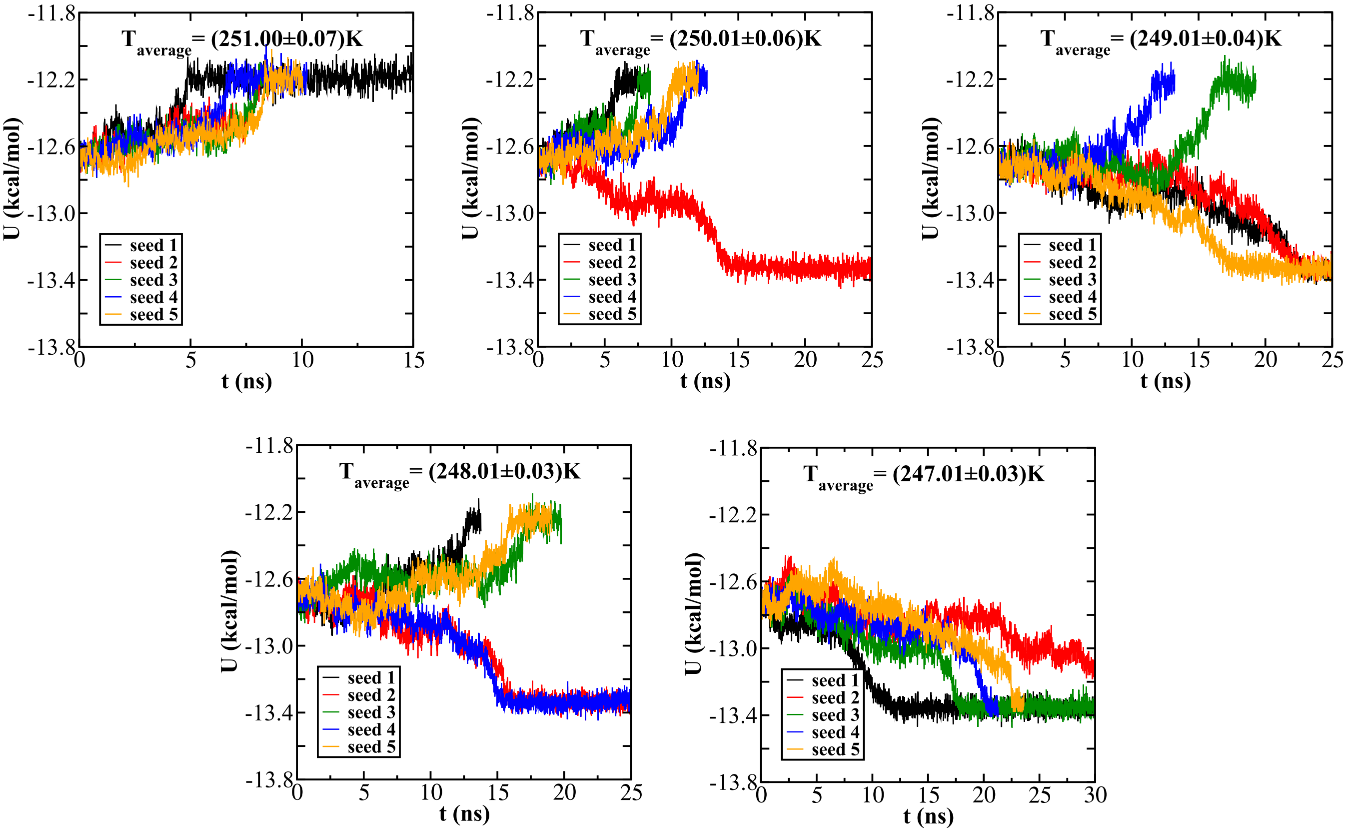

FIG. 1. Evolution of the potential energy as a function of time for a system formed by 432 molecules of ice I_h and 432 molecules of liquid water at different temperatures and at ambient pressure for the TIP4P/2005 model. Five independent runs for the same initial configuration and different seed numbers in the initial velocity are shown for each average temperature.

value of the temperature has associated an estimated error. In systems with a small number of molecules, the error of the technique of direct coexistence is larger than the error in the thermostat so this last can be negligible. However, for estimates with a great accuracy, the error in the temperature controlled by the thermostat cannot be neglected. We estimate the average temperature of the system as the arithmetic mean of the five runs. The temperature values, their error bars, and the average temperature for each system are shown in Table III.

Figure 1 shows the evolution of the potential energy as a function of time for a system composed of 432 molecules of ice and 432 molecules of liquid water for the temperatures T = 251.00 K, 250.01 K, 249.01 K, 248.01 K, and 247.01 K. At T = 251.00 K, the five independent simulations reveal the clear melting of the system due to the considerable increase in potential energy in a few nanoseconds. At T = 250.01 K, it can be observed that in four out of five simulations with different seeds the potential energy increases indicating that the system melts and it is situated above the melting point. Only one of the simulations shows a decrease in potential energy revealing the ice growth. This stochastic nature of the system becomes more evident for the other two following temperatures studied. At T = 249.01 K and T = 248.01 K, it is observed how the energy of the system increases or decreases in a random way as a function of the seed number used. However, at T = 247.01 K, that stochastic nature disappears and the five independent simulations show the ice growth clearly.

In Table IV, we can see the results obtained for this system for temperatures from 251.00 K to 247.01 K depending on whether the system melts or grows. Thus, for this system size (432 ice I_h/432 liquid), the melting point is at T = 249 K ± 2 K. This result is identical to that obtained by Fernandez *et al.*[51] using the same technique and the same size of the system. However, this error bar is still insufficient to perform studies where a greater precision is required.

In order to check if an increase in the number of simulations with different seed numbers would improve the error bar in a temperature selected, we analyzed ten different seed numbers for this size of system at T = 249.01 K. The error bar obtained for that temperature using ten seeds was identical to that obtained, analyzing half of the trajectories. Thereby, five different seed numbers are enough to study the stochastic nature of the direct coexistence technique in water/ice systems.

TABLE IV. Melting (M) or growth (G) for each average temperature ($T_{average}$) studied as a function of seed number used for systems with different sizes and different initial configurations using the TIP4P/2005 model.

System: 432 I_h + 432 liquid					
$T_{average}$ (K)	seed1	seed2	seed3	seed4	seed5
251.00 ± 0.07	M	M	M	M	M
250.01 ± 0.06	M	G	M	M	M
249.01 ± 0.04	G	G	M	M	G
248.01 ± 0.03	M	G	M	G	M
247.01 ±0.03	G	G	G	G	G
System: 1024 I_h + 1024 liquid					
$T_{average}$ (K)	seed1	seed2	seed3	seed4	seed5
250.92 ± 0.02	M	M	M	M	M
249.92 ± 0.02	M	G	M	G	M
248.97 ± 0.01	M	M	G	G	G
247.97 ± 0.02	G	G	G	G	G
System: 2000 I_h + 2000 liquid					
$T_{average}$ (K)	seed1	seed2	seed3	seed4	seed5
249.913 ± 0.006	M	M	M	M	M
249.423 ± 0.007	M	M	G	M	G
248.934 ± 0.008	G	G	G	G	G
System: 8000 I_h + 8000 liquid (configuration 1)					
$T_{average}$ (K)	seed1	seed2	seed3	seed4	seed5
249.910 ± 0.006	M	M	M	M	M
249.659 ± 0.007	M	M	M	M	M
249.425 ± 0.005	G	G	G	G	G
249.181 ± 0.005	G	G	G	G	G
248.934 ± 0.005	G	G	G	G	G
System: 8000 I_h + 8000 liquid (configuration 2)					
$T_{average}$ (K)	seed1	seed2	seed3	seed4	seed5
249.908 ± 0.007	M	M	M	M	M
249.660 ± 0.005	M	M	M	M	M
249.428 ± 0.005	G	G	G	M	G
System: 8000 I_h + 8000 liquid (configuration 3)					
$T_{average}$ (K)	seed1	seed2	seed3	seed4	seed5
249.908 ± 0.006	M	M	M	M	M
249.661 ± 0.005	M	M	M	M	M
249.425 ± 0.004	G	G	G	M	G

Another important factor that can affect the precision of the technique is the effect of the system size on the prediction of the melting point. To analyze the impact of this factor, we simulate different sizes of the system and compare the values obtained for the melting point. We increase the size of the previous system to a system containing 1024 molecules of ice and 1024 molecules of liquid water, and we study the same temperatures in order to capture the melting point with a greater precision. The results of the potential energy for this system are collected in Fig. 2 and in Table IV. At T = 250.92 K in all the simulations studied, the system melts resulting in an increase in the potential energy. At T = 249.92 K and T = 248.97 K, we continue to observe the stochastic nature of the technique obtaining simulations for the same temperature where the system melts or grows depending on the initial seed number. However, at T = 247.97 K, the behavior of the system is clearly constant. All the simulations for this temperature reveal the growth of the solid phase until the complete freezing of the system is reached. The value of the melting point for this system size is 249.5 K ± 1.5 K.

If we continue to increase the size of the system to a system formed by 2000 molecules of ice and 2000 molecules of liquid water, we observe now how the time required for the complete melting or growth of the ice increases progressively as a function of the number of molecules of the system

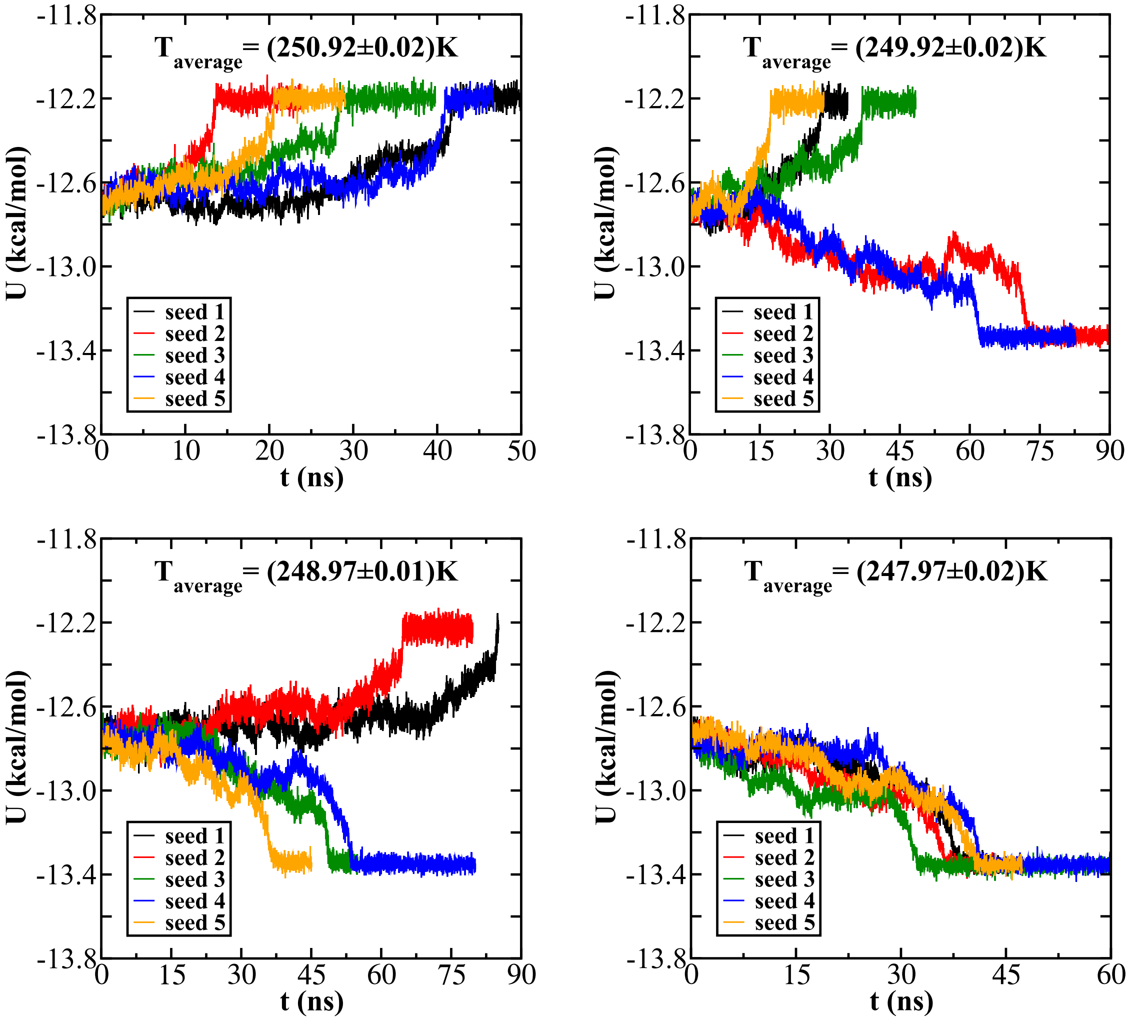

FIG. 2. Evolution of the potential energy as a function of time for a system formed by 1024 molecules of ice I_h and 1024 molecules of liquid water at different temperatures and at ambient pressure for the TIP4P/2005 model. Five independent runs for the same initial configuration and different seed numbers in the initial velocity are shown for each average temperature.

and the stochastic effects disappear for the average temperatures 249.913 K and 248.934 K. As it can be seen in Fig. 3 and Table IV, the melting point of this system is located at $T = 249.4 \pm 0.5$ K. Increasing the size of the system by a factor 5 with respect to the initial size leads to a considerable reduction of the error bar although the simulation time increases by a factor 8.

When the system is small, the melting temperature can be estimated from the derivative of the potential energy as a function of time at short times close to zero, that is,

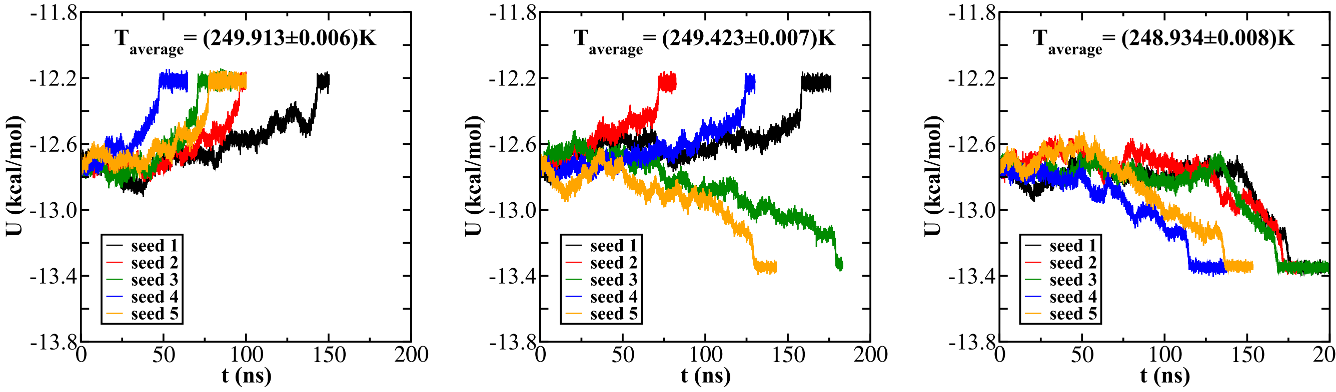

FIG. 3. Evolution of the potential energy as a function of time for a system formed by 2000 molecules of ice I_h and 2000 molecules of liquid water at different temperatures and at ambient pressure for the TIP4P/2005 model. Five independent runs for the same initial configuration and different seed numbers in the initial velocity are shown for each average temperature.

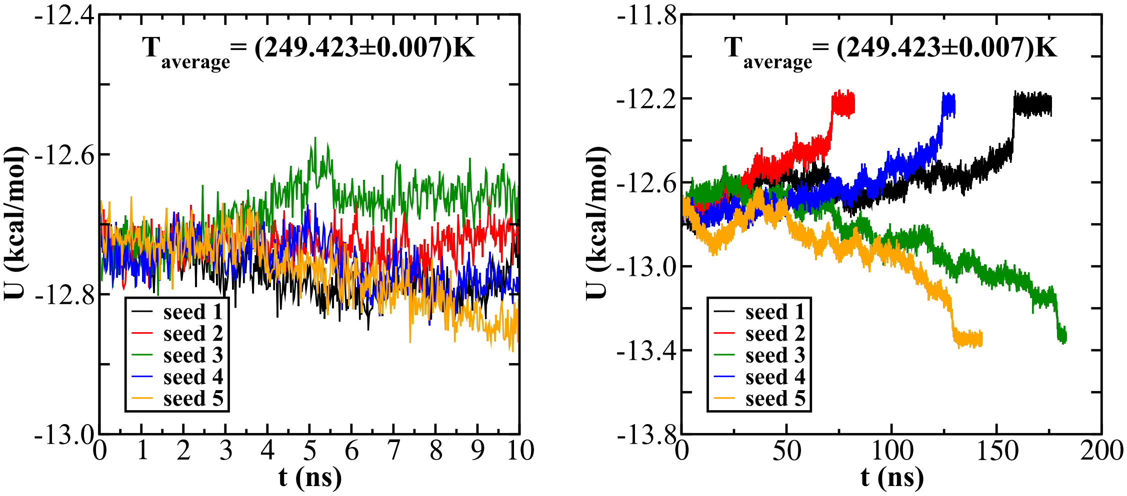

FIG. 4. Evolution of the potential energy for the same system and the same temperature *T* = 249.423 K at short times (left) and long times (right). The system is formed by 2000 molecules of ice I_h and 2000 molecules of liquid water for the TIP4P/2005 model. Five independent runs for the same initial configuration and different seed numbers in the initial velocity are shown.

analyzing the tendency of the slope of the potential energy if the energy increases or decreases at short times. But when the system is larger, the potential energy behavior can change the trend during the simulation, for example, increasing the potential energy during the first 10 ns and then decreasing it. An example of this issue is shown in Fig. 4. As it can be seen very clearly at *T* = 249.423 K for seed3, the slope of the energy at short times shows the tendency of the system to melt. Conversely, when the system continues at longer times, this behavior is reversed resulting in the growth of the solid phase and therefore a decrease in the potential energy.

Finally, to estimate the melting point with an error bar as small as possible, we study a system consisting of 8000 molecules of ice and 8000 molecules of liquid water. The results are shown in Fig. 5 and Table IV. A noticeable increase in the size of the system reduces considerably the finite

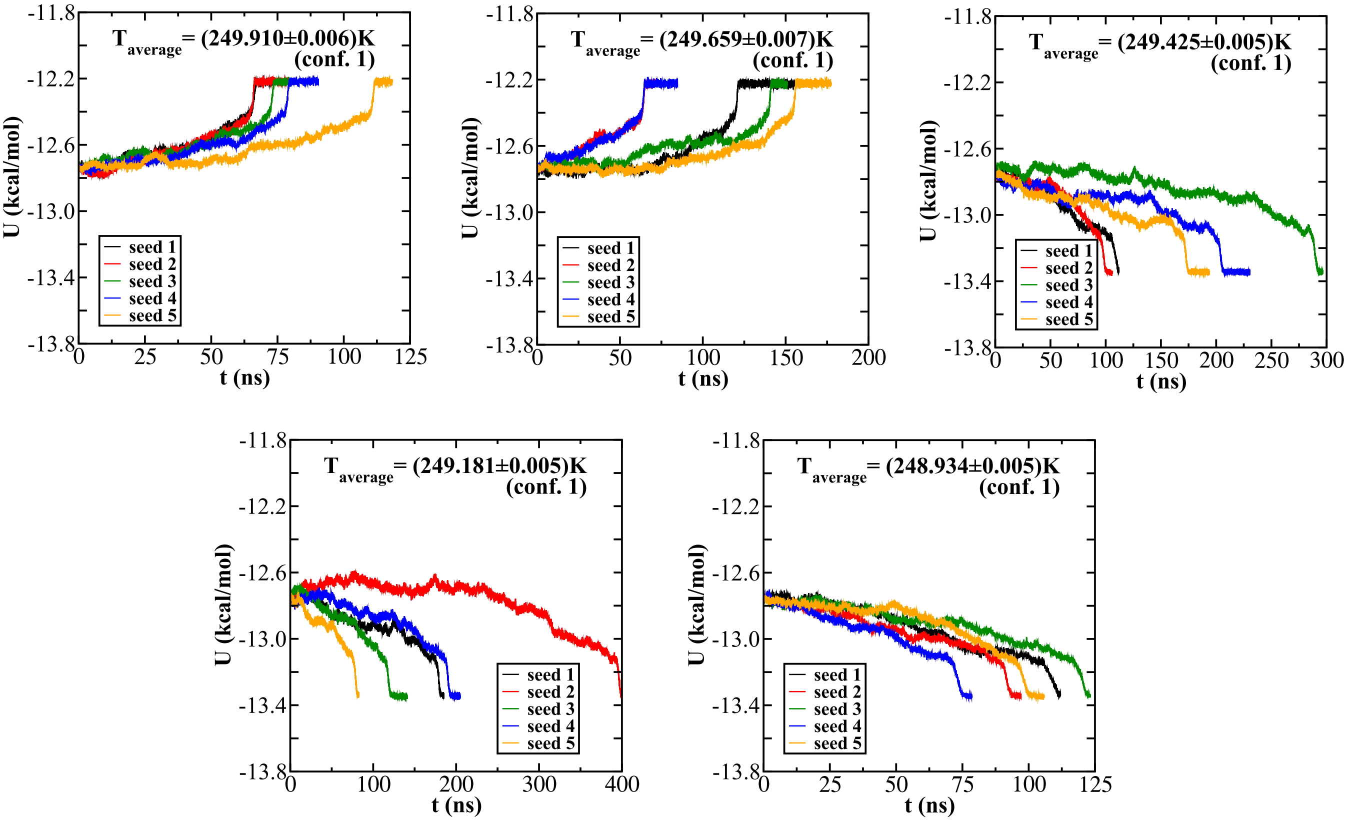

FIG. 5. Evolution of the potential energy as a function of time for a system formed by 8000 molecules of ice I_h and 8000 molecules of liquid water at different temperatures and at ambient pressure for the TIP4P/2005 model. Five independent runs for the same initial configuration (configuration 1) and different seed numbers in the initial velocity are shown for each average temperature.

TABLE V. Melting points T_m for the TIP4P/2005 water model for different size systems at ambient pressure obtained using the direct coexistence technique.

System	T_m
432 ice I_h + 432 liquid	249 ± 2
1024 ice I_h + 1024 liquid	249.5 ± 1.5
2000 ice I_h + 2000 liquid	249.4 ± 0.5
8000 ice I_h + 8000 liquid	249.5 ± 0.1

size effects and the stochastic nature of the technique. At $T = 249.910$ K, the five independent simulations show a clear increase in potential energy. The same behavior is observed at $T = 249.659$ K indicating that we are at temperatures above the melting point. At $T = 249.425$ K, 249.181 K, and 248.934 K, the energy of the system decreases obtaining the complete freezing of the system for the five seed numbers. For this system size, no evidence of stochastic behavior in the simulations was observed. The melting point of the model TIP4P/2005 is situated between 249.659 K and 249.425 K with an error bar of one order of magnitude less than that in the case of the smaller system.

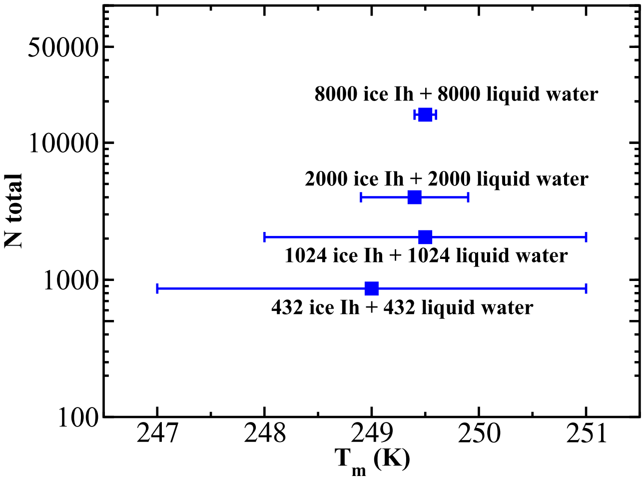

FIG. 6. Dependence of the system size (Ntotal) on the calculation of the melting point (T_m) for the systems studied using the TIP4P/2005 model. The blue squares are simulation results of the melting point from this work and the blue lines refer to the error obtained for each system.

The time of simulation clearly depends on the number of molecules in the system. When the number of molecules is larger, the computational cost is higher. The rate of melting or growth depends on the temperature simulated, being a slower process that consequently takes longer simulation time when the temperature is closer to the melting point. The difference

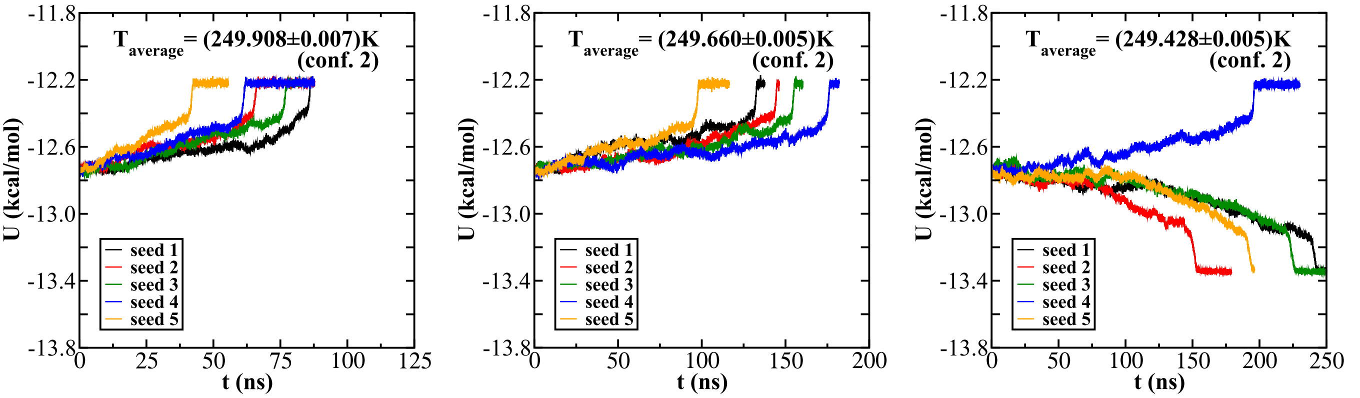

FIG. 7. Evolution of the potential energy as a function of time for a system formed by 8000 molecules of ice I_h and 8000 molecules of liquid water at different temperatures and at ambient pressure for the TIP4P/2005 model. Five independent runs for the same initial configuration (configuration 2) and different seed numbers in the initial velocity are shown for each average temperature.

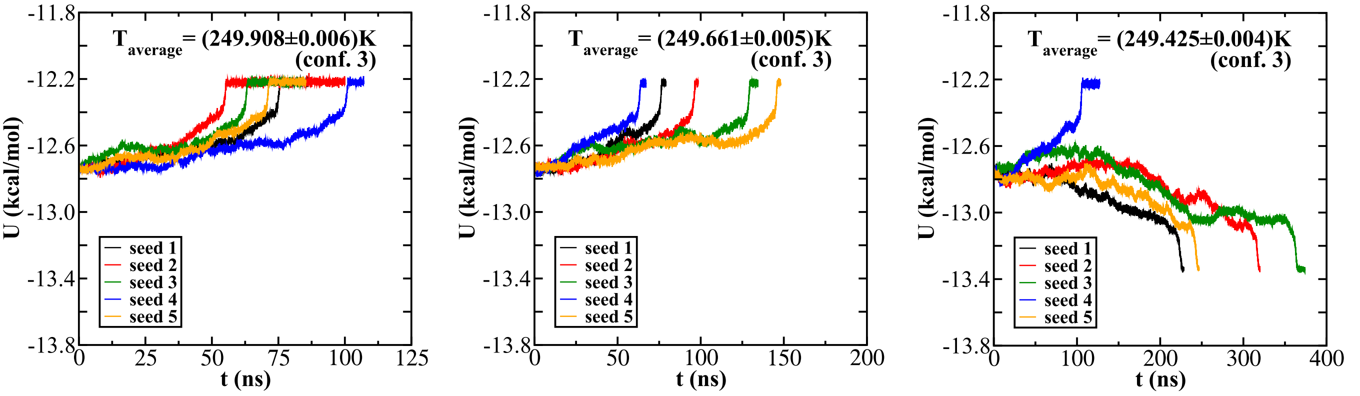

FIG. 8. Evolution of the potential energy as a function of time for a system formed by 8000 molecules of ice I_h and 8000 molecules of liquid water at different temperatures and at ambient pressure for the TIP4P/2005 model. Five independent runs for the same initial configuration (configuration 3) and different seed numbers in the initial velocity are shown for each average temperature.

TABLE VI. Value of the temperature and the associated error bar for the five independent runs using different seed numbers in the initial velocity as a function of size of the system for the TIP4P/Ice water model. The column on the left corresponds to the average temperature ($T_{average}$) of each simulation calculated as the average of the temperatures of the different seed numbers. All temperatures are given in Kelvin (K).

System: 8000 I_h + 8000 liquid					
$T_{average}$	T_{seed1}	T_{seed2}	T_{seed3}	T_{seed4}	T_{seed5}
269.896 ± 0.005	269.8910 ± 0.0059	269.8910 ± 0.0049	269.8920 ± 0.0066	269.8940 ± 0.0035	269.9110 ± 0.0041
269.662 ± 0.006	269.6610 ± 0.0035	269.6670 ± 0.0074	269.6590 ± 0.0050	269.6560 ± 0.0047	269.6680 ± 0.0078
269.413 ± 0.005	269.4200 ± 0.0051	269.4120 ± 0.0038	269.4130 ± 0.0048	269.4090 ± 0.0053	269.4130 ± 0.0032

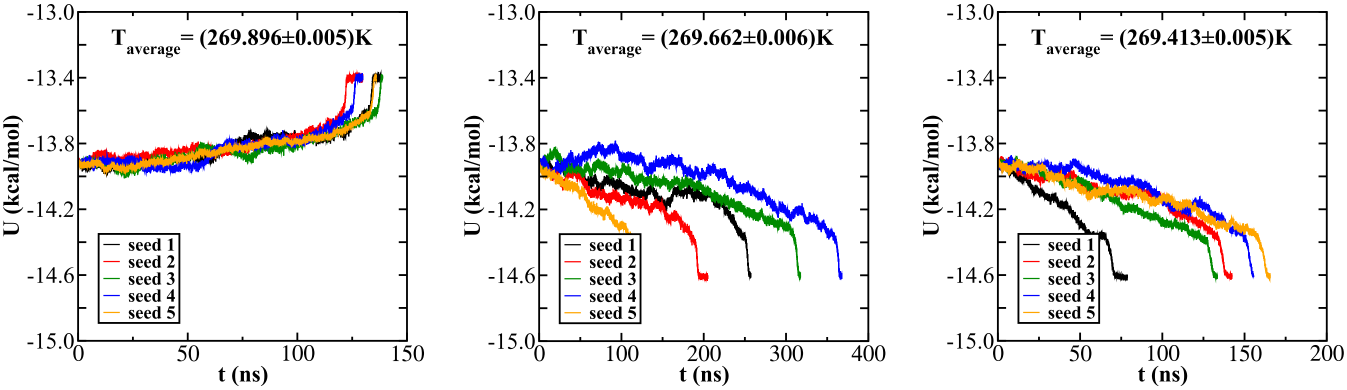

FIG. 9. Evolution of the potential energy as a function of time for a system formed by 8000 molecules of ice I_h and 8000 molecules of liquid water at different temperatures and at ambient pressure for the TIP4P/Ice model. Five independent runs for the same initial configuration and different seed numbers in the initial velocity are shown for each average temperature.

between the initial energy and the final energy remains constant for all system sizes studied. For the melting process, this difference is about 0.5 kcal/mol, and when the system freezes, the difference is around 0.7 kcal/mol. These differences in the potential energy can give us an approximate estimate of the enthalpy of the processes.

In Table V, the value of the melting point for the TIP4P/2005 water model is collected as a function of size of the system. All values obtained are consistent within the error bar. The dependence of the system size on the calculation of the melting point is illustrated in Fig. 6. It is noticeable that how an increase in the size of the system reduces considerably the error bar in the value of the melting point to an order of magnitude. This increase in system size is associated with a marked increase in computational cost.

B. Systems with the same size and different initial configurations

The choice of the initial solid configuration of ice I_h may affect the value of the melting point obtained by direct coexistence. Ice I_h presents proton disorder in its structure. There are many possible configurations for ice I_h, depending on the arrangement of the protons in the solid lattice. We use three different proton configurations for the solid phase of ice I_h to study the influence of this factor in the direct coexistence technique.

The results of the evolution of the potential energy as a function of time for the three different initial configurations of the system formed by 8000 molecules of ice and 8000 molecules of liquid water are given in Figs. 5, 7, and 8. As it can be seen, although the simulation times to complete the melting or growth of the system are different depending on the initial configuration and the seed number used, the three systems lead to the same estimate of the melting point situated at $T = 249.5 \pm 0.1$ K. The increase of the size of the system reduces considerably the finite size effects, and the choice of the initial solid configuration with different proton arrangements is not significant in the estimate of the melting point. Zaragoza *et al.*[79] performed several independent calculations of the free energy of ice I_h and I_c using different proton disordered configurations. They also found negligible differences in the value of the free energy with respect to the proton arrangements in agreement with the behavior observed in our work for the technique of direct coexistence.

V. TIP4P/ICE MELTING POINT

After estimating the melting point for the TIP4P/2005 model, we extend the study for the TIP4P/Ice model. This

TABLE VII. Melting (M) or growth (G) for each average temperature ($T_{average}$) studied as a function of seed number used for a system formed by 8000 molecules of ice I_h and 8000 molecules of liquid water using the TIP4P/Ice model.

System: 8000 I_h + 8000 liquid					
$T_{average}$ (K)	seed1	seed2	seed3	seed4	seed5
269.896 ± 0.005	M	M	M	M	M
269.662 ± 0.006	G	G	G	G	G
269.413 ± 0.005	G	G	G	G	G

TABLE VIII. Melting points T_m of the TIP4P/2005 and TIP4P/Ice water models as obtained from different methodologies (free energy calculations and direct coexistence technique).

Model	T_m (free energy)[80]	T_m (solid-liquid)[51]	T_m (solid-free surface)[52]	T_m (this work)
TIP4P/2005	252 ± 6	249 ± 2	249 ± 3	249.5 ± 0.1
TIP4P/Ice	272 ± 6	268 ± 2	271 ± 1	269.8 ± 0.1

model predicts the melting point of the ice I_h at ambient pressure in good agreement with the experimental value. We note here that most water potential models present a melting point considerably away from the experimental value.

We analyze the potential energy for a system containing 8000 molecules of ice and 8000 molecules of liquid water using the TIP4P/Ice water model. In this case, we use a single initial ice configuration since, as we observed in the previous case for the TIP4P/2005 model, the estimate of the melting point is not affected by the choice of the initial configuration.

In Table VI, the average temperatures of the different seed numbers for the system studied are given. Figure 9 and Table VII show the results for the evolution of the potential energy and the estimate of the melting point obtained for the TIP4P/Ice model. As it can be seen, the value of the melting point is situated between 269.896 K and 269.662 K. In particular, we obtain a value of the melting point for the TIP4P/Ice model of 269.8 ± 0.1 K. By using a large system, we have reduced the error bar by an order of magnitude compared to previous studies with smaller systems. This model has a temperature of only 3.35 K below the experimental value of the water located at $T = 273.15$ K. Likewise this model is an excellent candidate for simulations where similar conditions of melting to the experimental value are required.

As in the study of the TIP4P/2005 model, the energy difference in the melting process is about 0.5 kcal/mol and around 0.7 kcal/mol for the process of growth. These results reveal that the differences in potential energy are independent of the models used in this work. It is not surprising since both models have very similar potential parameters. The simulation time as in the previous case depends on the temperature studied being longer at temperatures close to the melting point.

VI. COMPARISON OF MELTING POINT BY DIFFERENT TECHNIQUES

The value of the thermodynamic properties of a system should be independent of the technique used. To confirm this issue, we compare the value of the melting point obtained in different studies found in the literature with the value obtained in this work for the two models used. The techniques chosen are the calculation of free energies,[80] the direct coexistence technique for solid-liquid systems,[51] and the study of ice in presence of a free surface.[52] This comparison is collected in Table VIII. As it can be seen, all the values of the melting point are in agreement within the statistical uncertainty of each calculation, confirming the independence of the technique in the calculation of melting points.

It is remarkable how the error bar in the calculation of free energies is greater due to its complexity. For this method, it is in fact necessary to determine first the free energies of all the phases present in the equilibrium and later to perform a Gibbs-Duhem integration to estimate the melting point. For the direct coexistence technique, the error bar is reduced increasing the system size up to an order of magnitude as demonstrated in this work, where we obtain the value of the melting point for the TIP4P/2005 and TIP4P/Ice models with the greatest precision to date.

VII. CONCLUSIONS

In this work, we performed an exhaustive study by molecular dynamics to analyze the factors that enhance the precision of the technique of direct coexistence for a system of ice and liquid water. The factors analyzed are the stochastic nature, the effects of finite size, and the importance of the initial configuration. To describe the water molecules, we chose two of the most popular water models: TIP4P/2005 and TIP4P/Ice.

Our results show that the precision of estimates obtained through the technique of direct coexistence is markedly affected by the effects of finite size, requiring systems with a large number of molecules to reduce the error bar of the melting point. This increase in size causes an increase in the simulation time, but the estimate of the melting point with a great accuracy is important, for example, in studies on the ice surface or to evaluate the freezing point depression of water in the presence of different concentrations of ionic salts.

The stochastic nature of the technique is observed especially in small systems and at temperatures close to the melting point where it is possible to find simulations where the solid phase melts or grows at the same temperature. However, these stochastic effects disappear considerably increasing the size of the system.

We also verified that the estimate of the melting point is not significantly affected by the choice of the initial ice I_h configuration with different proton arrangements.

Finally, we estimated the melting point at ambient pressure of the TIP4P/2005 and TIP4P/Ice water models with the greatest precision to date. For the TIP4P/2005 model, we calculated the melting point for different system sizes obtaining different error bars as a function of size. For large systems where the finite size effects and the stochastic nature of the technique can be negligible, the value of the melting point is 249.5 ± 0.1 K. For the TIP4P/Ice model, the melting point obtained is 269.8 ± 0.1 K. In both the models, the error bar is reduced to an order of magnitude with respect to previous studies. The values of the melting point obtained in this work are in agreement with those obtained by other techniques within the statistical uncertainty confirming the ability of the techniques in the calculation of melting points.

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