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Citation: *The Journal of Chemical Physics* **145**, 211922 (2016); doi: 10.1063/1.4965427

View online: <http://dx.doi.org/10.1063/1.4965427>

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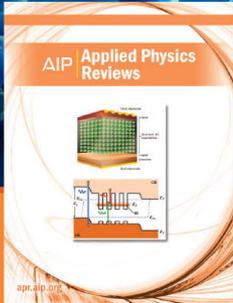
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On the time required to freeze water

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(Received 22 July 2016; accepted 4 October 2016; published online 26 October 2016)

By using the seeding technique the nucleation rate for the formation of ice at room pressure will be estimated for the TIP4P/ICE model using longer runs and a smaller grid of temperatures than in the previous work. The growth rate of ice will be determined for TIP4P/ICE and for the mW model of water. Although TIP4P/ICE and mW have a similar melting point and melting enthalpy, they differ significantly in the dynamics of freezing. The nucleation rate of mW is lower than that of TIP4P/ICE due to its higher interfacial free energy. Experimental results for the nucleation rate of ice are between the predictions of these two models when obtained from the seeding technique, although closer to the predictions of TIP4P/ICE. The growth rate of ice for the mW model is four orders of magnitude larger than for TIP4P/ICE. Avrami's expression is used to estimate the crystallization time from the values of the nucleation and growth rates. For mW the minimum in the crystallization time is found at approximately 85 K below the melting point and its value is of about a few ns, in agreement with the results obtained from brute force simulations by Moore and Molinero. For the TIP4P/ICE the minimum is found at about 55 K below the melting point, but its value is about ten microseconds. This value is compatible with the minimum cooling rate required to avoid the formation of ice and obtaining a glass phase. The crossover from the nucleation controlled crystallization to the growth controlled crystallization will be discussed for systems of finite size. This crossover could explain the apparent discrepancy between the values of J obtained by different experimental groups for temperatures below 230 K and should be considered as an alternative hypothesis to the two previously suggested: internal pressure and/or surface freezing effects. A maximum in the compressibility was found for the TIP4P/ICE model in supercooled water. The relaxation time is much smaller than the crystallization time at the temperature at which this maximum occurs, so this maximum is a real thermodynamic feature of the model. At the temperature of minimum crystallization time, the crystallization time is larger than the relaxation time by just two orders of magnitude. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4965427>]

I. INTRODUCTION

The formation of a solid phase from a metastable liquid is a process of particular interest, often occurring on the surface of small solid impurities^{1,2} contained in the supercooled liquid. In the absence of impurities, it is possible for the metastable liquid phase to survive for a long time before solid homogeneous nucleation takes place. In homogeneous nucleation a cluster of the solid phase has to reach a critical size and it requires to overcome a given free energy barrier.³⁻⁷ Once this cluster is formed, the new phase grows from this initial embryo.

Experimentally, since solids have well defined X-ray diffraction peaks, whose intensity is proportional to the amount of the solid phase, it is straightforward to determine when the system has frozen, and the time required to freeze it. τ is the time required to freeze the majority of the sample. τ depends on the supercooling (defined as the difference between the melting temperature and the temperature of interest). The value of τ is huge for temperatures slightly below the melting point and decreases significantly as the supercooling increases. However, τ is never zero. It reaches a minimum at a certain temperature and grows when increasing the supercooling. The

existence of this minimum is crucial for the understanding of the formation of glasses. If the value of τ were zero at a certain temperature then the formation of the solid phase would be unavoidable.

However, glasses are indeed often found after a fast temperature quench of the liquid phase, indicating that τ must indeed have a minimum. In a celebrated paper published in the *Journal of Chemical Physics* almost 80 years ago, Avrami^{8,9} used a theoretical treatment showing that the time required to freeze a certain fraction ϕ of a sample depends both on the nucleation rate J (i.e., the number of critical clusters formed per unit of volume and time) and on the growth rate of the solid phase u . This relation was found independently by other researches, so the Avrami relation is sometimes denoted as the Kolmogorov-Johnson-Mehl-Avrami (KJMA) relation.⁸⁻¹¹ In his paper⁹ Avrami relates the crystallization time to the (1/4) power of the inverse of the product of the nucleation rate J and the third power of the growth rate of the solid u obtaining the following (approximate) expression for the crystallization time:

$$\tau_{Avrami} = ((3\phi)/(\pi Ju^3))^{1/4}, \quad (1)$$

where ϕ is the fraction of the sample that has frozen.

Since J increases with the supercooling and u decreases with the supercooling, a minimum in the crystallization time is indeed possible. The Avrami relation is often used in material science.

A system of particular interest is water. Understanding the freezing of water from the supercooled liquid is of great interest in climate science^{12–14} (often small droplets of supercooled water are found in the clouds), microbiology,¹⁵ the food industry,^{16,17} materials science,¹⁸ and geology.¹⁹ Also, controlling the freezing of water would have an impact on cryopreservation and food science.^{20,21} For this reason, it is of interest to determine the crystallization time for water. However this still constitutes a great challenge.

Experimental nucleation rates J for water are only available for temperatures between 232 K and 245 K.^{22–33} Below 232 K J is too high to be measured experimentally. Above 245 K is too low. In the recent years it has been possible to determine J in the range from 205 K to 230 K.^{34–36} However, different results were obtained by different groups and it is difficult to understand the origin of this discrepancy. Our knowledge of u is even more limited as it has been measured only for temperatures up to 10 K below melting.^{37,38} Simulations could be useful in providing some hints as to the value of the crystallization time for water.^{39–45} However, on one hand results should be taken with care as in computer simulations one must use an approximate description of the intermolecular interactions and therefore the results do not necessarily correspond to those of real water.^{46–48} On the other hand, often τ cannot be obtained from brute force simulations since usually it is much larger than the typical maximum length of a run (hundreds of ns). An interesting exception is the mW model of water⁴⁹ for which it has been possible to determine τ using brute force simulations for homogeneous⁵⁰ and heterogeneous nucleation.^{51–54} For this model the value of τ at the minimum (at room pressure) was found to be of about a few nanoseconds. However for other water models^{55–57} the value of τ at the minimum seems to be larger as can be inferred from the fact that ice is not obtained from brute force simulations. For temperatures far from the minimum it is not possible to determine τ unless one uses rare event techniques.^{58–61} In this work our main goal is to estimate τ for the TIP4P/ICE model.⁵⁶ This model presents several advantages. It predicts rather well the phase diagram of water, especially at 1 bar.^{56,62} Its melting point is quite close to the experimental value,⁵⁶ and its melting enthalpy is only ten per cent lower than its experimental counterpart.

Estimating the crystallization time for TIP4P/ICE using Avrami's expression requires the estimation of the nucleation rate over a wide range of temperatures. We have recently used an approximate technique denoted as seeding^{63,64} to estimate J ^{65–69} showing that it provides reasonable estimates for hard spheres, LJ, NaCl, and for the mW model of water⁶⁶ as compared to the values obtained from more rigorous techniques. The origin of the seeding technique can be traced back to the papers by Li *et al.*,^{63,64} Carignano *et al.*,⁷⁰ Knott *et al.*,⁷¹ and Sanz *et al.*⁶⁵ among others. It consists in inserting a cluster of the solid phase and determining the temperature at which it becomes critical (i.e., it has a 50% probability of either growing or shrinking). After that, one uses the classical

nucleation theory^{3,72,73} to determine the free energy barrier and runs from the critical cluster to estimate the kinetic term.

In this work we shall implement the seeding technique for TIP4P/ICE. In variance with previous work, we shall increase the accuracy in determining the temperature at which the cluster is critical (by performing more runs for some temperatures and by decreasing the window size of the temperatures considered). In addition we shall incorporate into the analysis the value of the interfacial ice-water free energy at the melting temperature which can be obtained independently (and rigorously) using the recently proposed Mold Integration technique.⁷⁴ After the values of J are estimated for this model, long runs are performed to determine the growth rate at high supercooling. By combining the values of J and u , the Avrami expression will be used to estimate the crystallization time. It is found that τ_{Avrami} has a minimum for temperatures of about 215 K, and at the minimum the crystallization time as estimated from Avrami's expression is of about ten microseconds. This value is consistent with experiments showing that to form glassy water, the cooling rate should be larger than 5×10^6 K/s.^{75–77}

We also estimated the relaxation time τ_r for supercooled water at room pressure and concluded that for the temperatures considered in this work, the ratio of the crystallization and relaxation times is always a very large number except for the temperatures close to the minimum in the crystallization time where it is of the order of 100. Finally we discuss the expected variation of τ with supercooling for systems of different sizes and proposed a tentative explanation of this discrepancy in J found by different experimental groups at large supercoolings.

II. COMPUTATIONAL DETAILS

All simulations in this work were performed with Gromacs⁷⁸ using a velocity-rescaling⁷⁹ thermostat and a Parrinello-Rahman barostat⁸⁰ with a relaxation time for both of about 2 ps. The time step was always 2 fs. The LJ term of the potential was truncated at 9 Å and long range corrections were added to account for the truncation of the LJ part. Ewald sums (with the PME technique⁸¹) were used to deal with the electrostatic interactions. The real part of the electrostatic potential was also truncated at 9 Å. The algorithm used to constraint the geometry of the molecule was LINCS.

Three types of simulations were performed. (1) Simulations aimed at determining the growth rate of ice and/or the melting point were performed using 4000 molecules, located in an initial configuration consisting of 2000 molecules of ice in contact with 2000 molecules of liquid water. The dimensions of the box were approximately $3 \times 3 \times 9$ (in nm) so that the slice of ice occupies about 4.5 nm of the initial configuration. The barostat was anisotropic so that the dimensions of the simulation box L_x, L_y, L_z could be changed independently. Runs of about 200 ns were used at high temperatures, whereas runs of about 2 μ s were used at the lowest temperatures. (2) Simulations aimed at determining the diffusion coefficient of water and the relaxation time used 2000 molecules in a cubic simulation box. In this case the barostat was isotropic (i.e., the three dimensions of the box changed in the same way). Runs of about 200 ns were

used at high temperatures whereas runs of about $2 \mu\text{s}$ were used at the lowest temperatures. (3) Simulations used in the seeding technique. Three solid spherical crystalline clusters were prepared with about 8000, 3000, and 600 molecules. The inserted clusters were spherical because we have checked in previous work that cubic clusters evolve very quickly into spherical ones.⁶⁸ One possible explanation to this fact is that the shape that minimizes the ratio area/volume (interfacial energetic penalty/driving force to nucleate) is the sphere. The clusters were inserted into a supercooled liquid having about 185 000, 76 000, and 23 000 molecules, respectively. The remaining details are identical to those of our previous work.^{65,67} Simulations were performed in the NpT ensemble (using isotropic scaling). The typical length of the run was between 5 and 20 ns. To determine the temperature at which the cluster was critical, we used a temperatures grid of about 2.5 K. For some temperatures several independent runs were performed by changing the initial momenta of the particles. This is important due to the stochastic nature of the time evolution of clusters when their size is close to the critical one.

Ideally one should run as many trajectories as possible. However, the runs of the seeding technique are very expensive from a computational point of view and their number is limited. In the seeding technique we analyze the time evolution of the size of the solid cluster, identified by the q_6 proposed by Lechner and Dellago⁸² as in our previous work.⁶⁷ We used the location of the oxygen atoms to define q_6 with a cutoff distance for identifying neighboring particles of roughly 3.5 \AA corresponding to the distance of the first minimum of the oxygen-oxygen correlation function. For each molecule i we compute the value of $q_{6,i}$. When the value of $q_{6,i}$ was larger than a certain threshold value $q_{6,t}$, the molecule was labeled as solid and otherwise as liquid. Two solid particles were connected if their distance was smaller than 3.5 \AA . In this way the size of the solid cluster was obtained as the size of the largest cluster of solid particles which are connected.

In our previous work, $q_{6,t}$ was constant and set to 0.358. In this work we tune the value of $q_{6,t}$ for every temperature. We shall use the mislabeling criteria to determine $q_{6,t}$.^{66,68,69} At a given temperature we simulate bulk ice Ih and bulk water. The value of $q_{6,t}$ was obtained as that for which the percentage of mislabeled particles in bulk ice (i.e., those identified as liquid like) becomes identical to that of mislabeled particles in bulk water (i.e., those identified as ice). Typically the value of mislabeled particles at $q_{6,t}$ was about 0.5% and $q_{6,t}$ increases as the temperature decreases. This is due to the increasing tetrahedral order of the liquid phase when the temperature decreases.

III. RESULTS

To determine τ_{Avrami} , we need to determine J and u . Since we shall present the results as a function of the supercooling, an accurate determination of the melting temperature is needed.

A. Melting temperature

The melting temperature of TIP4P/ICE should be determined with accuracy and using the same conditions

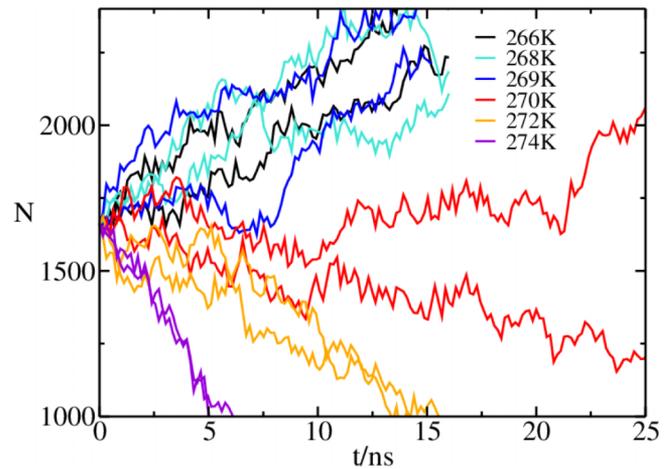


FIG. 1. Direct coexistence runs for the ice-water interface at $p=1$ bar and several temperatures of the TIP4P/ICE model. The evolution of the total number of solid particles N as a function of time (for different temperatures) is shown.

(cutoff, constraints, time step, etc.) that are used in the seeding technique. In the past we have reported a value of 272 K from free energy calculations,⁵⁶ 271 K from the melting of the free surface of ice⁸³ and of 268 K from the direct coexistence technique (using 864 particles).⁸⁴ In this work we shall determine the melting point using the direct coexistence technique with 4000 molecules.

The results are shown in Fig. 1. As can be seen, the estimated melting point is 270(1) K. This is in agreement with another recent estimate obtained also from the direct coexistence technique.⁸⁵ Notice that in our previous work dealing with the nucleation of ice for the TIP4P/ICE model, we used the value of 272 K for the melting temperature.^{65,67,68} In this work the value of 270 K will be used.

B. Growth rate

The growth rate was estimated from direct coexistence runs using the expression

$$u = L_{growth}/(2\tau_{growth}), \quad (2)$$

where L_{growth} is the length of the ice slab that grows in a time τ_{growth} . We performed runs until the entire system had frozen. In this case L_{growth} is around half of the box size in the direction perpendicular to the interface (in the initial configuration half of the sample was ice and half was liquid water). The factor of 2 accounts for the fact that we have two interfaces.

The value of u depends on the plane considered. This has been studied in detail by Rozmanov and Kusalik for TIP4P/2005.⁸⁶ The value of the growth rate is large for prismatic planes (primary and secondary have similar growth rates) and smaller for the basal plane (the value of the growth rate for the basal plane is approximately 0.6 times that of the prismatic planes). In fact we computed u for the basal plane of the TIP4P/ICE model for three temperatures (245 K, 255 K, 260 K) and found that its value was (within five per cent) 0.6 times the value of the secondary prismatic plane. In this work

TABLE I. Growth rate for the secondary prismatic plane u_{p11} as obtained in this work for the TIP4P/ICE and mW models.

Model	T/K	$u_{p11}/(\text{\AA}/\text{ns})$	Model	T/K	$u_{p11}/(\text{\AA}/\text{ns})$
TIP4P/ICE	215	0.006	mW	180	22
TIP4P/ICE	225	0.029	mW	190	60
TIP4P/ICE	235	0.169	mW	200	235
TIP4P/ICE	245	0.528	mW	210	300
TIP4P/ICE	250	0.633	mW	220	466
TIP4P/ICE	255	0.926	mW	230	512
TIP4P/ICE	257.5	0.803	mW	240	490
TIP4P/ICE	260	0.933	mW	250	375
			mW	260	266

we obtain the growth rate of the secondary prismatic plane u_{p11} (Table I and in Fig. 2).

Experimental results (only available for temperatures slightly below the melting point) are also shown.^{37,38} The agreement between simulation results for the TIP4P/ICE and experiments is very good. u has a maximum around 15° below the melting point. A similar maximum was found by Rozmanov and Kusalik for the TIP4P/2005.^{87,88} At the maximum the growth rate is about $1 \text{ \AA}/\text{ns}$.

We are interested in the value of u for spherical clusters (rather than for a planar ice-water interface). We shall estimate it as the average growth rate for the basal and the two prismatic planes, assuming that the value of the growth rate is the same for the two prismatic planes and that the value of the growth rate of the basal plane is 0.6 times the value of the prismatic planes. In practice this is equivalent to multiplying by $13/15$ the value of the growth rate of the secondary prismatic plane ($u = (u_{p11} + u_{p1} + u_{basal})/3 \approx (u_{p11} + u_{p11} + 0.6u_{p11})/3$), so that we will approximate u for the spherical cluster as $u = 13/15 u_{p11}$ (Fig. 2). We average the growth rates for these three different crystal orientations in the same way as previously done for the interfacial free energies of such planes in Refs. 89–92. For the case of the interfacial free energies, it was found that this type of average

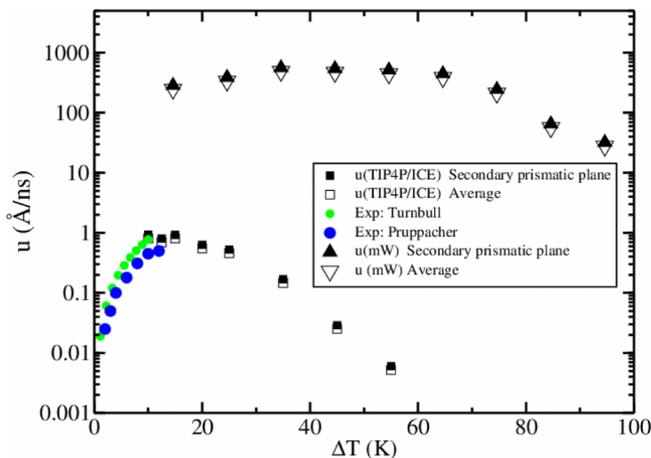


FIG. 2. u_{p11} for the secondary prismatic plane of TIP4P/ICE and mW water models (black filled symbols). The average value u (for the two prismatic and the basal planes) (open symbols) and experimental values from the work of Turnbull and Pruppacher are also shown.^{37,38}

TABLE II. Coefficients of the fit for $\ln(u/(\text{\AA}/\text{ns}))$ for the TIP4P/ICE and mW models as a function of the supercooling. For TIP4P/ICE $T_m = 270 \text{ K}$. For mW $T_m = 274.6 \text{ K}$. These fits should be used for supercoolings larger than 15 K only.

Model	C_1	C_2/K	C_3/K^2
TIP4P/ICE	-0.2597	0.028 831	-0.002 215
mW	4.1711	0.096 266	-0.001 148

corresponds to γ_0 (as can be inferred from the results of Table II of Ref. 90 and taking into account that the values of ϵ_2 and ϵ_3 are rather small as shown in Ref. 91) which is the zero order term of the expansion of γ into spherical harmonics and that the values of γ obtained from the seeding technique when extrapolated to the coexistence point yield values of γ close to γ_0 .^{90–92} In this case, we assume that the growth rate follows a similar dependence on the orientation to that of γ due to the resemblance of their trends (the growth rate and the interfacial free energies of p_{11} and p_I are quite similar and higher than those of the basal plane.) For this reason we shall also use this average to estimate the growth rate of a spherical cluster.

The values of u were fitted to the following expression (which works well for supercoolings $\Delta T = T_m - T$ larger than 15 K):

$$\ln(u/(\text{\AA}/\text{ns})) = C_1 + C_2\Delta T + C_3(\Delta T)^2, \quad (3)$$

whose coefficients of the fit are given in Table II.

We have also determined u_{p11} for the mW model of water. In this case we used the LAMMPS⁹³ package with a similar setup to that used for the TIP4P/ICE. Values of u_{p11} are presented in Fig. 2. There is a maximum in the growth rate located around 40 K below the melting point of the model (i.e., 274.6 K). The value of the growth rate at the maximum for the mW model is three orders of magnitude larger than for the TIP4P/ICE model. Also (in contrast to TIP4P/ICE) the decay of u_{p11} with temperature is very slow. For a supercooling of about 55 K , the growth rate of mW is around five orders of magnitude larger than that of TIP4P/ICE. The value of u for the spherical cluster of the mW model was also estimated as $13/15$ of u_{p11} as for the TIP4P/ICE model.

C. Diffusion coefficients and results for the room pressure isobar

In Table III the values of the densities, diffusion coefficients, and isothermal compressibilities of TIP4P/ICE are reported. The time required to diffuse one molecular diameter is also given ($\tau_r = \sigma^2/(6D) \approx 10 \text{ \AA}^2/(6D)$). This provides a rough idea of the relaxation time of the system. A more elaborate estimate of the relaxation time would be obtained from the decay of the self-intermediate scattering function.^{94–96} For instance at 230 K , Haji-Akbari and Debenedetti⁹⁶ reported a relaxation time of 0.6 ns for this model (to be compared with the one obtained here which is of about 1.5 ns). The numbers are not identical, but are of the same order of magnitude, so that they can be used as a rough guide for the relaxation time of the system.

TABLE III. Densities, diffusion coefficients, and time required to diffuse one molecular diameter τ_r , as obtained from NpT runs (for $p = 1$ bar) for the TIP4P/ICE. The length of the runs was 100 ns for temperatures above 270 K, 500 ns between 230 K and 260 K, and of the order of one or two microseconds for temperatures below 220 K. The results of the isothermal compressibility as obtained from the volume fluctuations are also shown.

T/K	$\rho_f/(g/cm^3)$	$D/(m^2/s)$	τ_r/ns	$k_T \cdot 10^{10}/(m^3/J)$
320	0.989	$2.31 \cdot 10^{-9}$	0.006	4.53
310	0.991	$1.83 \cdot 10^{-9}$	0.008	4.55
300	0.992	$1.41 \cdot 10^{-9}$	0.010	4.66
290	0.992	$1.05 \cdot 10^{-9}$	0.013	4.87
280	0.991	$7.23 \cdot 10^{-10}$	0.02	5.19
270	0.988	$4.74 \cdot 10^{-10}$	0.03	5.54
260	0.982	$2.77 \cdot 10^{-10}$	0.06	6.14
250	0.972	$1.36 \cdot 10^{-10}$	0.11	6.77
240	0.958	$4.93 \cdot 10^{-11}$	0.31	6.95
230	0.942	$9.76 \cdot 10^{-12}$	1.48	6.11
220	0.929	$1.16 \cdot 10^{-12}$	13	4.77
210	0.923	$2.13 \cdot 10^{-13}$	80	2.77
200	0.923	$2.77 \cdot 10^{-14}$	550	1.69
190	0.925	$8.60 \cdot 10^{-15}$	2020	1.63

In Fig. 3 the density of the TIP4P/ICE model along the room pressure isobar is shown. The model has a maximum in density located around 295 K (in agreement with the results obtained via Monte Carlo runs few years ago⁹⁷) and a minimum in density located at about 210 K. The density of ice Ih (and its potential energy) are always lower than those of the fluid phase. The behavior of the density curve is similar to that found⁹⁸ for TIP4P/2005 although the extrema are shifted by about 20 K. In Fig. 4 the isothermal compressibility (as obtained from volume fluctuations) along the room pressure isobar is presented and compared to experimental results.^{99–101} The agreement with experiment is quite good. As can be seen it has a maximum located at about 245 K. Again the location of the maximum is shifted by about 15–20 K with respect to the maxima obtained with the TIP4P/2005 model.^{102,103} At the temperature of the maximum, the equilibration time is of the order of half-nanosecond (i.e., the time require to diffuse one molecular diameter). Our runs lasted around 500 ns so

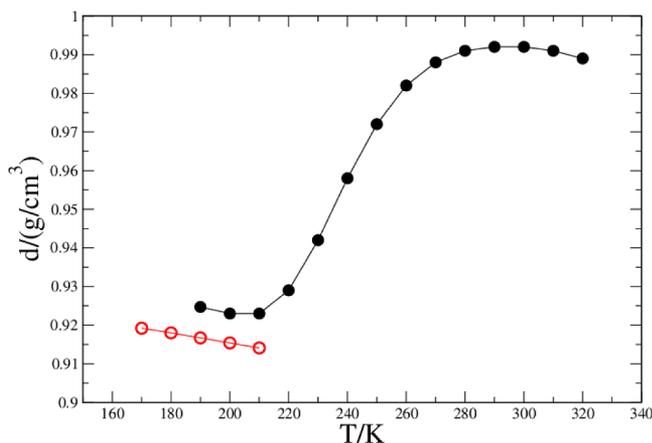


FIG. 3. Mass density (d) of the liquid (filled circles) and ice Ih (open circles) of the TIP4P/ICE model of water as obtained along the $p = 1$ bar isobar.

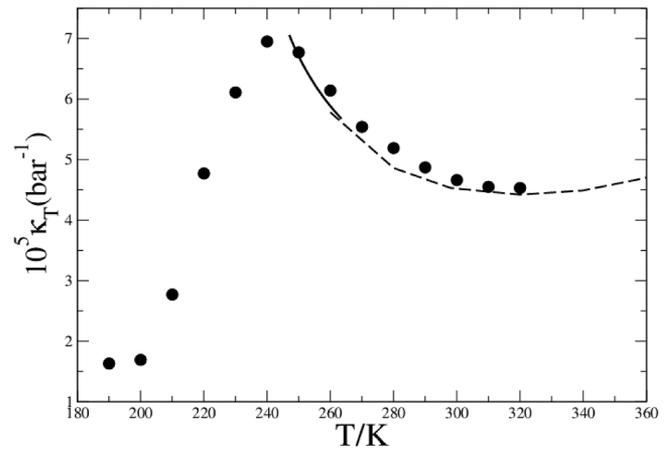


FIG. 4. Isothermal compressibility of the TIP4P/ICE along the room pressure isobar (i.e., $p = 1$ bar) as obtained from NpT simulations of the TIP4P/ICE model (symbols) and from experiments from the work of Speedy and Angell at low temperatures¹⁰⁰ and from Kell⁹⁹ and Saul and Wagner¹⁰¹ at moderate temperatures..

that each molecule moved around 1000 molecular diameters. At the temperature of the maximum in compressibility of about 245 K the crystallization time as given by the Avrami expression (see the discussion later in the paper) is of the order of hours. Therefore the maximum in compressibility (which locates a point of the Widom line) is a real equilibrium feature of the model. It has been suggested by Limmer and Chandler^{104–106} that these maxima may be due to the transient formation of ice and that generated some debate in the literature^{107–109} but it seems that this is certainly not the case for the TIP4P/ICE model.

The results of the diffusion coefficient are shown in Fig. 5 for both the TIP4P/ICE and mW models. TIP4P/ICE underestimates the experimental¹¹⁰ value of the diffusion coefficient (typically by a factor of two at moderate supercooling and by a factor of 4 at high supercooling) and mW overestimates it by 2–3 orders of magnitude. The value of D for the mW is hardly affected by the temperature whereas that of the TIP4P/ICE decreases significantly. The results of TIP4P/ICE are well described for temperatures

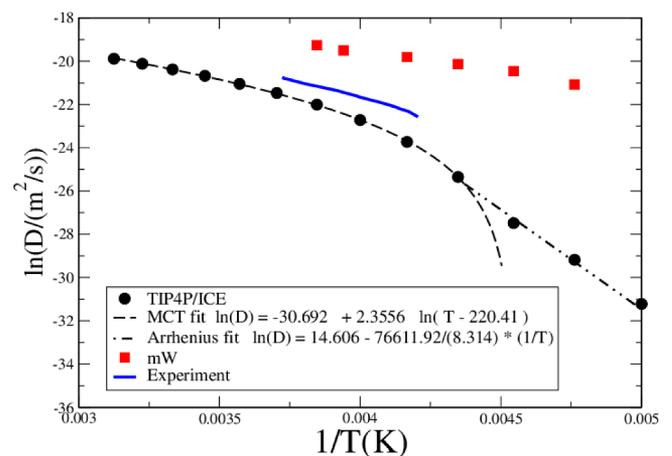


FIG. 5. Diffusion coefficient D (in m^2/s) for the TIP4P/ICE and mW models of water. Experimental results have also been included.¹¹⁰

up to 230 K by mode coupling theory $D = D_0(T - T_{MCT})^\alpha$. The values obtained for T_{MCT} and α , 220.4 K and 2.35, are in reasonable agreement with the experimental values, 221 K and 2.2 respectively. The value of T_{MCT} for TIP4P/ICE is about 12 K above that obtained for TIP4P/2005.¹¹¹ For temperatures below 230 K the results are better described by an Arrhenius expression $D = D^* \exp(-E_a/RT)$. This change in the variation of D with temperature is sometimes denoted as the fragile-strong transition.¹¹² For TIP4P/ICE this change seems to be located at 230 K. The fragile to strong transition for supercooled water for TIP4P/2005 has been studied in detail recently by de Marzio *et al.*⁹⁴ and by Wong, Jahn, and Giovambattista.¹¹¹ The parameters of the fit for D of TIP4P/ICE (both for temperatures above 230 K and for temperatures below) are shown in the inset of Fig. 5.

D. Estimating the nucleation rate J

The nucleation rate J will be estimated from the treatment of Becker and Doring⁷³ (often used when implementing the umbrella sampling technique^{113–115})

$$J = \rho_f Z f^+ \exp(-\Delta G_c / (k_B T)), \quad (4)$$

where (ρ_f) is the number density of the fluid phase, Z is the Zeldovich factor, ΔG_c is the free energy barrier for the formation of the critical cluster, and f^+ the attachment rate of particles to the critical cluster. The Zeldovich factor³ is related to the curvature of the free energy surface on the top of the free energy barrier whose classical nucleation theory expression is $Z = \sqrt{|\Delta\mu| / (6\pi k_B T N_c)}$, where $\Delta\mu$ is the difference in chemical potential between the fluid and the solid phases at the temperature of interest. f^+ can be computed as a diffusion coefficient of the cluster size at the top of the barrier. We have recently shown that for a number of different systems (including water), f^+ is well described by the CNT expression^{66,67,116}

$$f^+ = \frac{24D(N_c)^{2/3}}{\lambda^2}, \quad (5)$$

where N_c is the number of molecules of the critical cluster (so that $N_c^{2/3}$ is proportional to the number of molecules at the cluster's surface) and $\lambda^2 / (6D)$ is the time required for a molecule to diffuse a given length λ (D being the self-diffusion coefficient of the supercooled liquid). Using a value of λ of the order of one molecule diameter gives a good estimate of f^+ . Following our previous work⁶⁷ we use a value of λ of 3.8 Å for TIP4P/ICE and of 2.5 Å for the mW model of water. The values of the diffusion coefficient were obtained from this work (for TIP4P/ICE) and from our previous work for mW.⁶⁷

The value of ΔG_c obtained using the seeding technique is

$$\Delta G_c = N_c |\Delta\mu(T_c)| / 2. \quad (6)$$

The value of $\Delta\mu$ is obtained by using thermodynamic integration¹¹⁷ and the condition $\Delta\mu = 0$ at the melting point (270 K for the TIP4P/ICE) model. For the TIP4P/ICE at 230 K we obtained $\Delta\mu = 0.146$ kcal/mol, in good agreement with the value 0.147 kcal/mol reported by Haji-Akbari and Debenedetti.⁹⁶

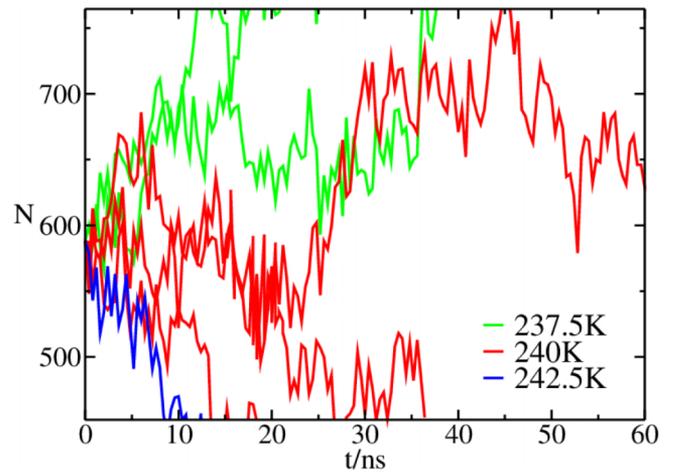


FIG. 6. Time evolution of ice Ih cluster with 588 molecules for several temperatures. Different lines with the same color indicate trajectories with different initial velocities.

Finally, it is also possible to estimate the interfacial free energy γ from the expression (obtained from CNT),

$$\gamma^3 = N_c \frac{3\rho_s^2 |\Delta\mu|^3}{32\pi}, \quad (7)$$

where ρ_s is the number density of the solid phase. In Refs. 65–68 we have already presented all possible sources of errors coming from applying the seeding technique.

To compute N_c we considered three clusters having approximately 8000, 3000, and 600 molecules inserted in the supercooled liquid. Results of the NpT runs for these three clusters for the TIP4P/ICE model are presented in Figs. 6–8 and in Table IV.

The values of γ (as obtained from Eq. (7)) are presented in Fig. 9 and Table IV together with γ for the planar interface at coexistence obtained using the mold integration technique^{74,92} (the value presented corresponds to the average obtained for the two prismatics and the basal planes). Fitting the values of γ to a straight line, we find a slope of about -0.27 mJ/(m² K), similar to the slope used in Ref. 118,

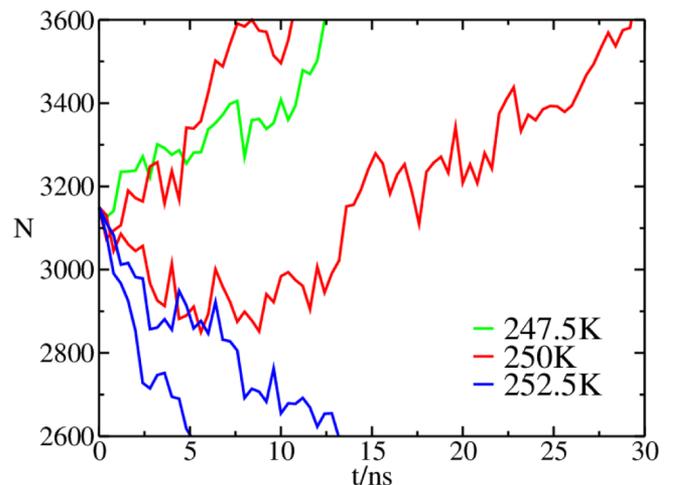


FIG. 7. Time evolution of ice Ih cluster with 3150 molecules. Details as in Fig. 6.

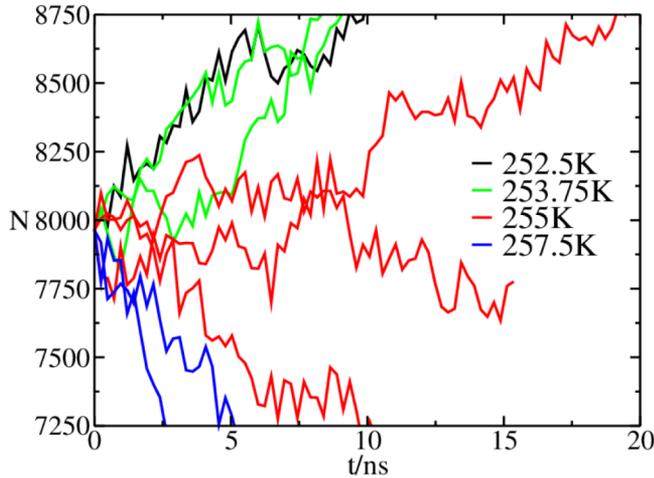


FIG. 8. Time evolution of ice Ih cluster with 7964 molecules. Details as in Fig. 6.

to reproduce the experimental values of J and consistent with the slope presented in Figure 10 of Ref. 22. Fig. 9 also represents the values of γ obtained from the seeding technique (for temperatures below the melting point) and from the mold integration technique for the mW model: they are larger than those of the TIP4P/ICE model and their decrease with the supercooling is less pronounced (the slope is $-0.14 \text{ mJ}/(\text{m}^2 \text{ K})$). For the TIP4P/2005 model Reinhard and Doye¹¹⁹ reported a value for the slope of $-0.18 \text{ (mJ}/(\text{m}^2 \text{ K}))$ which is between the values obtained here for the TIP4P/ICE and mW models.

Now it is possible to obtain values of J for a wide range of temperatures by making use of a fit of the densities of the solid and fluid phases, a fit of the diffusion coefficient of liquid water, a fit of $\Delta\mu$, and a fit of γ as a function of T . The results of J for the TIP4P/ICE are shown in Fig. 10, together with results for the mW model obtained from the seeding technique in our previous work.⁶⁶ The values of J for a given supercooling are higher for TIP4P/ICE than for mW. Although the attachment rate f^+ is higher for mW (by about two to three orders of magnitude), its higher interfacial free energy causes a lower value of J .

Our results are qualitatively consistent with the results of Debenedetti and coworkers who computed J using forward flux sampling¹²⁰ for a supercooling of about 30 K for both models.^{96,121} They found that the nucleation rate of TIP4P/ICE at 230 K was about seven orders of magnitude larger than the

TABLE IV. Results for TIP4P/ICE model of water. N_c is the size of the solid cluster inserted in the liquid. N_{H_2O} is the total number of molecules of water used in the simulation, T_c is the temperature at which the cluster is critical, $q_{6,t}$ is the threshold value of the order parameter⁸² used to distinguish liquid and solid particles (using the mislabeling criterion), and γ is the interfacial ice Ih-fluid free energy as obtained from Eq. (7).

N_c	N_{H_2O}	T_c/K	$q_{6,t}$	$\gamma/(\text{mJ}/\text{m}^2)$
588	22712	238.75	0.372	21.4
3150	76781	251.25	0.364	24.2
7964	182585	255.0	0.361	26.9

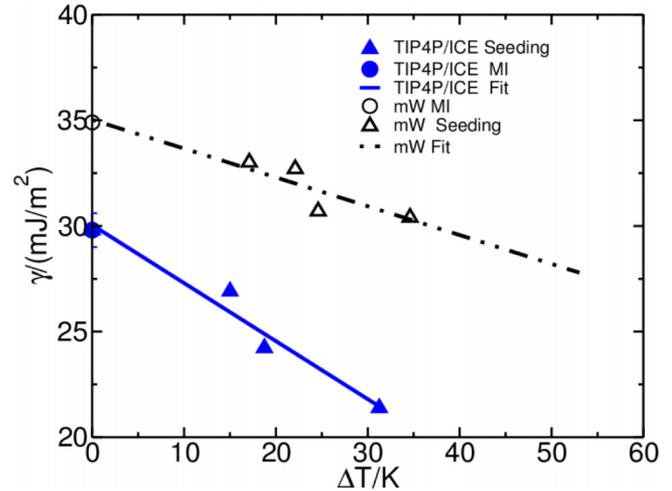


FIG. 9. γ versus supercooling for the TIP4P/ICE and mW models of water as obtained from seeding (for temperatures below melting) and from mold integration (at the melting point). The fit to the results for the mW model is given by $\gamma \text{ (mJ}/\text{m}^2) = 35.028 - 0.13648(274.6 - T)$. The fit for TIP4P/ICE model is $\gamma \text{ (mJ}/\text{m}^2) = 30.044 - 0.27477(270 - T)$.

nucleation rate of mW at 235 K. However from a quantitative point of view the agreement is not so good, as the values of J for TIP4P/ICE at 230 K from this work are about 14 orders of magnitude larger than those obtained by Haji-Akbari and Debenedetti from the more rigorous FFS technique. This certainly points out the approximate character of the seeding technique. However the deviation with respect to the results of Geiger and Dellago¹²² goes in the opposite direction as in this case our work predicts a free energy barrier for nucleation at 235 K of $56 k_B T$ which is higher than the value of $35 k_B T$ reported by Geiger and Dellago¹²² at this temperature. Certainly further work is needed to clarify these discrepancies. In previous work^{66,116} deviations of about 3-4 orders of magnitude between the predictions from seeding and

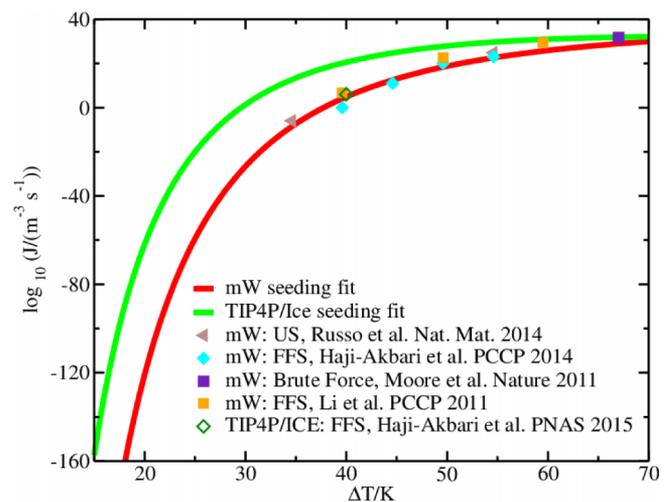


FIG. 10. Values of the nucleation rate J for the TIP4P/ICE and mW models of water as obtained from seeding (solid lines). Results for seeding of TIP4P/ICE are from this work. Results for seeding of mW are from our previous work.⁶⁶ Results obtained from other works (symbols): mW by Russo *et al.*,⁶¹ Haji-Akbari *et al.*,¹²¹ Moore *et al.*,⁵⁰ and Li *et al.*,⁶⁰ TIP4P/ICE obtained from FFS by Haji-Akbari *et al.*⁹⁶

those obtained from more rigorous techniques were found at high supercooling for systems as varied as hard spheres, LJ, NaCl, and the mW model of water. The deviations found here for the TIP4P/ICE model are larger. Since there is only one result reported for J of the TIP4P/ICE obtained from the FFS technique and only one estimate of the free energy barrier, it would be useful to have more values to compare with. This is especially relevant as, for the mW model, the values of J at 235 K obtained from FFS may be as different as $10^{-1}/(\text{m}^3 \text{ s})$ ¹²¹ and $10^6/(\text{m}^3 \text{ s})$.⁶⁰ It is also interesting to point out that even for the well studied hard spheres system the values of J at moderate saturation (i.e., reduced pressure of 15) from FFS are about 2-3 orders of magnitude lower than those obtained from umbrella sampling.^{114,123}

In Fig. 11 we compare our values of J both for mW and TIP4P/ICE to the experimental results. The agreement of TIP4P/ICE with experiments is quite reasonable. The mW model seems to underestimate the experimental nucleation rate due to its large value of γ .

The agreement of the TIP4P/ICE model may be fortuitous as the seeding technique may be overestimating the nucleation rate of the TIP4P/ICE model (and this issue should be clarified in future work). One reason to support the idea that the TIP4P/ICE cannot reproduce the experimental results is the fact that its melting enthalpy (1.29 kcal/mol) is about ten per cent lower than the experimental value of 1.44 kcal/mol. Thus one may expect that the values of $\Delta\mu$ for the model (at a certain supercooling) may be about ten per cent lower. Since the driving force for nucleation in the model is lower than in experiments that would lead to lower nucleation rates. However $\Delta\mu$ is not the only variable that plays a role. The interfacial free energy γ also plays an important role.¹²⁴⁻¹²⁷ According to the Turnbull rule the interfacial free energy at the melting point is correlated with the melting enthalpy. In fact for the TIP4P models (TIP4P, TIP4P/2005 and TIP4P/ICE)

we have found that the value of γ increases with the melting enthalpy of the model. Thus it is possible that the value of γ for real water is higher than for the TIP4P/ICE model. Experimental values of γ between 26 and 35 mJ/m² have been reported,^{128,129} so this hypothesis cannot be discarded. The free energy barrier for nucleation (from CNT) at a certain temperature is given by

$$\Delta G_c = \frac{16\pi\gamma^3}{3\rho_s^2|\Delta\mu|^2}. \quad (8)$$

Therefore the free energy barrier for nucleation for real water could be ten per cent higher than that found for the TIP4P/ICE model (notice that γ appears to the third power and $\Delta\mu$ to the second power). This could yield values of J for the model larger than in experiments even though the melting enthalpy of the model is lower. This tentative explanation could justify why the values of J for the TIP4P/ICE model is slightly higher than those found in experiments as shown in Fig. 11.

In any case, and even admitting that the good agreement with experiments shown by TIP4P/ICE can be due to a fortuitous cancellation of errors (i.e., underestimates $\Delta\mu$ and γ), it is gratifying to see that a molecular approach can reproduce the experimental results so well over a broad range of temperatures. In contrast to empirical correlations of J ,^{22,130} where it is difficult to test the validity of each term of the fit, here we present a molecular (although admittedly still incomplete) perspective.

Finally there is another issue that should be discussed. The experimental values for J shown in Fig. 11 are quite similar for all temperatures above 232 K. Below this temperature they are grouped into two families: the one with the results of Manka *et al.*³⁴ and Hagen *et al.*,³¹ and the ones with the results of Laksmono *et al.*¹³¹ We shall return to this issue later in this paper.

E. Determining τ_{Avrami}

Once the values of u and J for the TIP4P/ICE and mW models have been determined, it is time to determine τ_{Avrami} using Eq. (1). Eq. (1) is the linearized version of a more sophisticated expression that reads

$$\phi = 1 - \exp\left(\frac{-\pi J u^3 \tau_{Avrami}^4}{3}\right). \quad (9)$$

For long times ϕ should go to one, and this is the case for the non-linearized version of the Avrami equation. In this work values of τ_{Avrami} will be obtained using $\phi = 0.7$. For this volume fraction, the differences in τ_{Avrami} between both expressions are very small.

In Fig. 12, τ_{Avrami} for the TIP4P/ICE and mW models of water is shown. The value of τ_{Avrami} decreases as the supercooling increases, reaches a minimum, and then increases again.¹³² The reason is that J increases slowly at high supercoolings (even reaching a maximum) and u decreases very quickly. The fast decrease in u with the supercooling provokes the increase in τ_{Avrami} . For the mW model the minimum in τ_{Avrami} is about one nanosecond. A comparison with the brute force simulations of Moore and Molinero⁵⁰ for

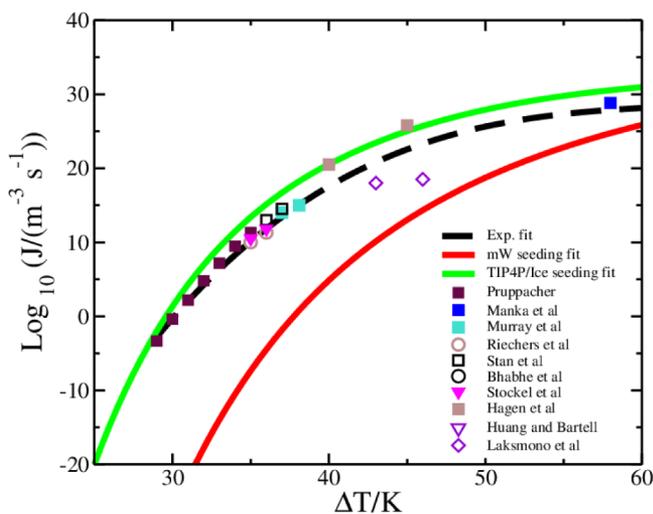


FIG. 11. Values of logarithm of J for the TIP4P/ICE and for the mW model as obtained in this work from the seeding technique (solid lines) and from experimental results^{22,24,25,29-32,34-36,131} (symbols). The experimental results (for $\log_{10}(J/(\text{m}^{-3}/\text{s}))$) were fitted to the following expression $-154.59 + 8.5035\Delta T - 0.13304(\Delta T)^2 + 0.00070129(\Delta T)^3$ where $\Delta T = 273.15 - T$ and they are shown as a dashed line. All experimental results (symbols) shown in this figure were included in the experimental fit.

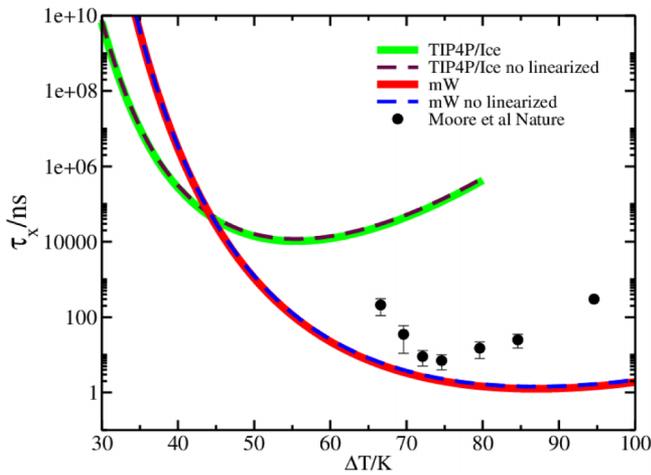


FIG. 12. Crystallization time for $\phi = 0.7$ (lines) for mW and TIP4P/ICE models of water as obtained from the Avrami equation (both for the linearized Eq. (1) and for non-linearized (9) expression). These plots are also denoted as time-temperature-transformation (TTT). The results of the seeding technique were used to estimate J . The growth rates were taken from this work. Simulations results (symbols) for τ from brute force simulations of Moore and Molinero⁵⁰ for the mW model of water (with about 4000 molecules and $\phi = 0.7$) are also shown.

τ is also shown in Fig. 12. The minimum crystallization time found by Moore and Molinero is of about ten nanoseconds. The agreement although not perfect is reasonable. The Avrami expression is rather flat around the minimum when compared to the simulation results.⁵⁰ At the left of the minimum this can be explained taking into account that for the system size studied by Moore and Molinero, the crystallization time corresponds to the nucleation time (this issue will be discussed more deeply in Subsection III F when presenting the results of Fig. 13). However, we do not have an explanation about

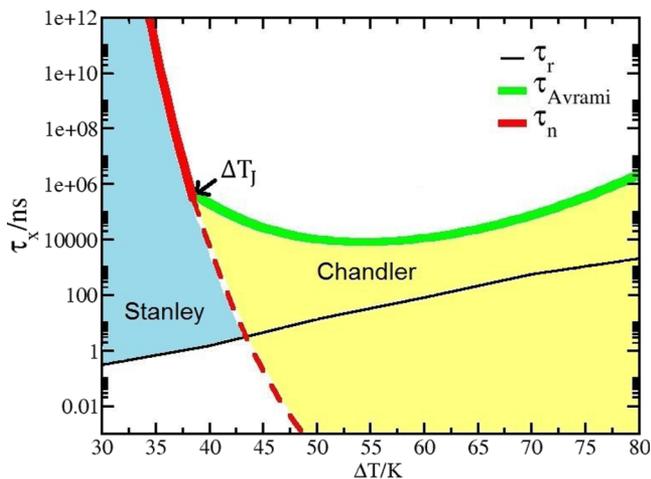


FIG. 13. Crystallization time τ_x as defined in the main text (thick solid lines) as predicted for the TIP4P/ICE model of water for system containing the same number of water molecules as a droplet of water with a radius of $5 \mu\text{m}$. At high supercoolings τ_x is given by the Avrami expression (i.e., Eq. (1) with $\phi = 0.7$). At low supercoolings the crystallization is controlled by nucleation and τ_x is given by τ_n (i.e., we neglect the time required for the growth of the solid phase after a critical cluster is formed). The black thin solid curve is the relaxation time τ_r , which was estimated as the time required for the molecules to move one molecular diameter. For the definition of the region of Chandler and Stanley, see the main text. ΔT_J is the supercooling at which the crossover from nucleation to growth controlled crystallization occurs.

the origin of the discrepancies on the right hand side of the minimum. Certainly further work is needed to clarify this issue. Most likely our estimates of J at these temperatures may have large errors since they were obtained by extrapolating the results obtained at moderate supercooling. It would also be interesting to test the validity of the assumptions behind the Avrami expression performing simulations for larger system sizes.¹³³ In any case the Avrami's expression used in this work is able to describe to within one order of magnitude the minimum of the crystallization time found by Moore and Molinero in their brute force simulations. For the TIP4P/ICE model, the minimum in τ_{Avrami} is of about ten microseconds, four orders of magnitude higher than for mW.

To avoid the crystallization of the sample, one should cross the region around the minimum (say 50 K) in less than about 1/10 of the time of the minimum. For the mW model that yields a cooling rate of $50 \text{ K}/(1 \text{ ns}) = 5 \times 10^{10} \text{ K/s}$. This is comparable with the cooling rate of 10^{10} K/s used by Moore and Molinero⁵⁰ for the mW model to avoid crystallization and to obtain a glass.⁵⁰ For TIP4P/ICE the results of this work suggest a minimum cooling rate of $50 \text{ K}/(1 \mu\text{s}) = 5 \times 10^7 \text{ K/s}$ to obtain the glass. In real water the minimum cooling rate⁷⁵⁻⁷⁷ to avoid crystallization is of about 10^7 K/s in good agreement with the predictions of this work for TIP4P/ICE. The main reason for the difference of τ_{Avrami} at the minimum between mW and TIP4P/ICE is the large difference in u for both models which seems to be the dominant factor as it appears to the power minus three-fourths in Avrami's expression as compared to J that appears to the power minus one fourth.

F. Nucleation versus Avrami time

Another interesting issue is that τ_{Avrami} as given by the Avrami expression (linearized or not) depends only on the intensive variables J and u . Therefore, the time required to freeze a certain fraction of a system does not depend on the system size. Could this be the case? Quite often to form the solid phase, one must wait for a long time before a critical nucleus is formed: after that the growth of the solid phase is very fast. In this case τ is not given by the Avrami expression but rather by the nucleation time τ_n ,

$$\tau = \tau_n = 1/(JV). \quad (10)$$

When τ is controlled by nucleation, it depends on the system size. The larger the system, the lower the time one has to wait to freeze a certain fraction of the sample. How to conciliate both descriptions (i.e., the Avrami expression τ_{Avrami} which does not depend on the system size and τ_n which depends on the system size)? Berg and Dubey¹³⁴ (among others^{135,136}) addressed this issue some time ago. To illustrate the problem we shall present both τ_{Avrami} and τ_n for a system having the same number of water molecules as a spherical droplet with a radius of $5 \mu\text{m}$ (a typical size in experiments). It should be pointed out that in our simulations we do not have droplets with a free surface since we are using periodic boundary conditions but there is no reason why we could not estimate τ_n for the TIP4P/ICE model for a system having a similar number of water molecules as that found in droplets of $5 \mu\text{m}$ of radius in real water.

In Fig. 13 τ_{Avrami} and τ_n are presented for this droplet. As can be seen, τ_n decreases very quickly as the supercooling increases and at a certain temperature which we shall denote as $\Delta T_J(N)$, it crosses the crystallization time given by the Avrami expression. An approximate picture of the problem is that for supercoolings smaller than $\Delta T_J(N)$, the crystallization is controlled by nucleation and τ can be approximated by τ_n , and for supercoolings larger than $\Delta T_J(N)$ the crystallization is controlled by the ice growth and τ is given approximately by τ_{Avrami} (even when using the Avrami expression the value of J matters, but since u appears to the power minus three-fourths it plays a crucial role so that it seems adequate to call this region the growth-controlled region). The notation $\Delta T_J(N)$ reminds us that the supercooling at which the crossover from nucleation-controlled to growth-controlled occurs depends on the system size. Let us now define τ_x as

$$\tau_x = \max(\tau_{Avrami}, \tau_n). \quad (11)$$

From the definition, τ_x is given by τ_n for supercoolings up to ΔT_J and by τ_{Avrami} for higher supercoolings. τ_x is plotted in Fig. 13 as thick solid lines. Therefore we suggest to approximate the crystallization time of water τ as

$$\tau \simeq \tau_x. \quad (12)$$

At this point it is pertinent to introduce a remark: the transition from the nucleation to the growth-controlled regime does not occur in an abrupt manner. Rather one should expect a smooth transition from τ_n to τ_{Avrami} for temperatures around $\Delta T_J(N)$ (some empirical suggestion has been proposed for obtaining such a smooth transition in Eq. (26.42) in the book by Kashchiev,¹³⁵ in Eq. (16) in the review of Li and Rutledge,¹³⁶ or in the work of Berg and co-worker¹³⁴).

However, and even taking into account that the transition from nucleation to growth-controlled crystallization should be smooth, our picture indicating that the transition should occur around $\Delta T_J(N)$ is qualitatively correct. From the results of this work for TIP4P/ICE (with J estimated from the seeding approach and u determined from direct coexistence simulations) it is clear that the transition from nucleation to growth-controlled crystallization for a droplet of 5 μm occurs for a supercooling located around forty degrees. It is interesting to mention that $\Delta T_J(N)$ will move to lower/higher supercoolings as the size of the system becomes larger/smaller.

G. Can one use τ to estimate J ?

We wish to propose an interesting question. Experimentally one determines τ which is the time required to freeze the majority of a sample. The question arises whether one can use τ to determine the nucleation rate J .

The answer to this question is affirmative when for the conditions considered (system size and supercooling) crystallization is controlled by nucleation, but it is negative when the crystallization is controlled by crystal growth (one could in principle use Avrami's equation in this case but since the experimental value of u is in general completely unknown one cannot determine J).

Of course the problem is that in general from experiments one simply gets τ but has no *a priori* information on whether

one is in the nucleation or in the growth controlled regime. However, there is a simple experiment to test this. One could repeat the experiment using a system with say half the size of the initial sample. If one is in the nucleation-controlled regime, the crystallization time τ should increase by a factor of two. If this is the case, one can indeed determine J from τ and besides J will be independent of the system size. Conversely, if the crystallization time does not change when the size of the system decreases, one may suspect that one is in the growth-controlled regime.

Another physical interpretation is that τ is given by Avrami's expression whenever for the system size considered there is already a critical cluster in the system for times much smaller than τ_{Avrami} .

H. Crossover from nucleation to growth-controlled crystallization

Let us now obtain a mathematical expression for the crossover radius, R as a function of ΔT_J . This is easily done by equating τ_n and τ_{Avrami} . We shall assume that we have a spherical droplet so that V is given by $4/3\pi R^3$. Then one obtains

$$R = \left(\frac{3}{4}\right)^{1/3} \left(\frac{1}{3\phi}\right)^{1/12} \left(\frac{u(\Delta T)}{\pi J(\Delta T)}\right)^{1/4} = 0.64 \left(\frac{u(\Delta T)}{J(\Delta T)}\right)^{1/4}, \quad (13)$$

where we used $\phi = 0.7$ in the last expression.

We could implement this expression for the results of the TIP4P/ICE model. However since our aim is to provide a guide to experimentalist, we shall use a hybrid approach. The value of J will be obtained from a fit to the experimental results of J , as shown in Fig. 11 as a dashed line. For u we shall use the values obtained for the TIP4P/ICE model. After all they seem to agree well with experimental values, at least for small supercoolings.

In Fig. 14 the value of R as a function of the supercooling ΔT is shown. For each supercooling τ is controlled by nucleation for a radius smaller than $R(\Delta T_J)$ and by growth for a radius larger than $R(\Delta T_J)$. Also one can state that for each radius there is a maximum supercooling where the crystallization is controlled by nucleation. Up to this temperature it is correct to assume that τ is given by τ_n and to compute J from Eq. (10). For supercoolings larger than this, τ will be given by the Avrami expression, and it is necessary to use the value of u to compute J correctly. In Fig. 14, we have included the radius and supercoolings considered in different experimental works. As can be seen, all of them fall into the nucleation controlled regime. The only exception is the results of Laksmono *et al.*¹³¹ that fall into the growth controlled regime. As can be seen in the figure for a droplet of a radius of 5 μm (which is roughly the size considered by Laksmono *et al.*¹³¹) the maximum supercooling where crystallization is controlled by nucleation is about 41 K, which corresponds to a temperature of about 232 K. We would like to point out that we are by no means questioning the experiments nor the values reported for τ by Laksmono *et al.*¹³¹ We are just suggesting that their results may fall into the growth controlled regime so that it may not be possible to directly determine J from τ . That was already

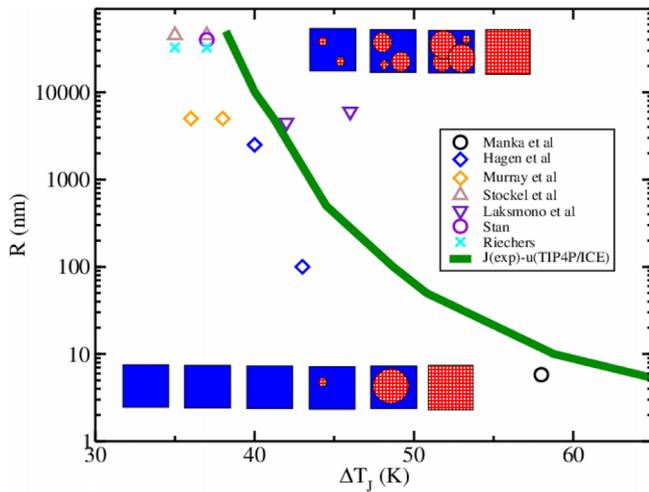


FIG. 14. Radius R of the droplet where the crossover from nucleation to growth controlled crystallization occurs for a certain supercooling as given by Eq. (13) using a fit to the experimental values of J and the values of u for the TIP4P/ICE model obtained in this work. The snapshots illustrate the two different mechanisms for crystallization. On the left side of the solid line, once a critical cluster is formed the system freezes very quickly since the growth rate of ice is very fast. On the right hand side critical clusters (which grow slowly) are formed steadily. (See Ref. 50 for an example of this in mW water model at 180 K.)

suggested by Laksmono *et al.* in the supplementary material of Ref. 131.

I. Possible role of the internal pressure versus heterogeneous nucleation in the small droplets

Since the value of J for a certain temperature should be unique it is necessary to provide an explanation of why different experimental values of J have been reported for the same supercooling (see the symbols in Fig. 11). This is a problem for the entire community studying the nucleation of supercooled water.

The tentative hypothesis of this work is that for droplets of radius of $5 \mu\text{m}$ it is possible to identify τ with τ_n only for temperatures up to 232 K. For lower temperatures (i.e., higher supercoolings) we suggest that one may fall into the growth controlled regime so that it may not be possible to obtain J from τ . However there are other possible explanations.

The first is that for small droplets (of size less than a few hundreds of nm) the internal pressure is high so that the results obtained do not correspond to room pressure. This is certainly true. However it is unlikely that this is sufficient to explain the large differences between the results of Laksmono¹³¹ and those of Hagen *et al.*³¹ and Manka *et al.*³⁴ First, the internal pressure is never too large (about 500 bars for the smallest drop of Manka *et al.*,³⁴ which we included in Fig. 11 and 15 bars for the drops of Hagen *et al.*³¹). Secondly, applying pressure should reduce J (and not to increase it) since the melting point of ice decreases with pressure so that for a certain value of T the supercooling would be lower. Besides this, the experimental results of Kanno, Speedy, and Angell¹³⁷ show that pressure makes nucleation more difficult since the homogeneous nucleation temperature is more distant from the melting curve when pressure is applied and we have provided recently an explanation for that.⁶⁹ The results of Johnston

and Molinero for nanometer droplets are also consistent with the idea that pressure decreases the nucleation rate.¹³⁸ In summary, if pressure were responsible, one should expect that the values of J of Hagen *et al.*³¹ and Manka *et al.*³⁴ should be lower than those of Laksmono.¹³¹

The second possibility is that for small droplets the nucleation starts at the surface and that enhances the value of J in small droplets with respect to large droplets (i.e., large surface to volume ratio). This is an interesting hypothesis that could indeed explain the discrepancies. If this were the case then the surface would dramatically enhance the nucleation rate. However Haji-Akbari *et al.*¹²¹ have found for the mW model that the nucleation rate J in a system with a planar interface are slightly lower than those of a system without an interface. Vrbka and Jungwirth¹³⁹ found some indirect evidence of the opposite for a different water model although nucleation rates were not reported. The results obtained from seeding for the TIP4P/ICE model (for a system having no vapor-liquid interface) for J seem to be consistent with those obtained for small droplets suggesting that neither pressure nor surface play a dramatic role.

For the time being it is difficult to conclude which is the correct explanation for the origin of the discrepancies in J from different groups (internal pressure, surface freezing, or the crossover suggested in this work). Further work is needed to unravel this issue.

J. Can we equilibrate a liquid before it freezes?

An interesting question raised by Limmer and Chandler is if the liquid can be equilibrated before it freezes.^{104,106} In Fig. 13 the relaxation time τ_r (as given by the diffusion criteria) is also shown. As can be seen τ_x is always larger than τ_r . The difference is of many orders of magnitude at moderate supercooling and of just two orders of magnitude in the region where τ_x is minimum (in the Avrami region).

However we should distinguish two regions in this plot. In the so-called “Chandler” region, critical solid nuclei are formed steadily and they keep growing slowly. The system is indeed transient and it is not possible to determine the properties of the supercooled liquid in this region. Whereas in the so-called “Stanley” region no critical cluster is formed before the liquid equilibrates (although certainly some subcritical clusters will be formed^{140,141} from time to time that could indeed be regarded as equilibrium fluctuations of the fluid phase), and since the crystallization time is much larger than the equilibration time, it seems possible to determine the thermodynamic properties of the supercooled liquid.

These two regimes (Stanley’s and Chandler’s) are visible in the mean first passage time¹⁴² plots of Moore and Molinero.⁵⁰ Notice that the sizes of the Stanley’s and Chandler’s regions depends on the system size as their border is given by ΔT_j which indeed depends on the system size (Eq. (10)). The red line shown in Fig. 13 will move to the right for smaller systems and to the left for larger ones (the green and black lines in principle are not affected by the size of the system).

The reader may wonder how we estimated (in Fig. 13) the relaxation time in the Chandler’s region where the system

is transient for droplets of 5 μm of radius. The explanation is that to estimate τ_r , we used simulation results for a system having 2000 molecules of water so that for this small size the system is still in the Stanley's regime and is not transient. We also assume that the relaxation time is not size dependent (at least in the absence of critical solid clusters). The reason why the system is transient in the Chandler region of Fig. 13 is not because the molecules do not have enough time to diffuse before they freeze but rather that critical clusters are formed in times comparable to the time required to diffuse. Notice also that all our seeding runs, were obtained in the region controlled by nucleation (i.e., the Stanley region) so that the system was also not transient under these conditions.

Strictly speaking in the thermodynamic limit ΔT_f will go to zero. Thus the Chandler region will dominate all the behavior of the supercooled fluid. In fact in the thermodynamic limit the supercooled liquid is transient as there will always be critical solid clusters formed steadily and the system would evolve slowly to the solid phase.^{143,144} However, often experimentalists are able to measure thermodynamic properties of supercooled liquids.¹⁴⁵ This is so because real systems are always of limited size, so there will always be a Stanley region. The only way to push the Stanley region to the right (i.e., to high supercoolings) is to decrease the size of the system. Not surprisingly and due to the extraordinary small system size used in computer simulations (by experimental standards) it was in computer simulations where it was possible to push the Stanley region to temperatures never explored before in experimental work and to learn about the extraordinary anomalous behavior of water in this region.^{107,146–149}

IV. CONCLUSIONS

In this work the seeding methodology is applied to the study of homogeneous nucleation of TIP4P/ICE water. We improved the accuracy of the calculations by using several runs for each temperature, using a smaller grid of temperatures and correcting the temperature of the melting point. The growth rate was also determined for the TIP4P/ICE and mW models to estimate the time required to freeze water. The main conclusions of this work can be summarized as follows:

- The values of the interfacial free energy γ obtained from seeding extrapolated to the melting point are consistent with those obtained from the rigorous mold integration technique. The value of γ of the mW model of water is higher than that of the TIP4P/ICE, even though both models have similar melting temperatures and enthalpies.
- Values of J for the mW model are lower than those of the TIP4P/ICE due to its higher interfacial free energy. The differences are higher at moderate supercooling and become smaller at high supercooling where the faster dynamics of the mW model (reflected in a higher attachment rate) partially compensate the higher interfacial free energy.
- The experimental values of J are located between those of the TIP4P/ICE and those of the mW models although they seem to be closer to those of the TIP4P/ICE model.

- The growth rate u of the mW model is between 3 (at moderate supercooling) and 5 (at high supercooling) orders of magnitude higher than that of TIP4P/ICE (when compared at the same supercooling). The growth rate obtained for the TIP4P/ICE is in reasonable agreement with the experimental results, at least for the temperatures at which it was possible to determine it experimentally.
- The minimum in the crystallization time obtained from the Avrami equation for mW is about a few ns, in agreement with the results obtained from brute force simulations.⁵⁰ For the TIP4P/ICE this minimum is of about ten microseconds. This value is consistent with the minimum cooling rate required to avoid crystallization and to form a glass phase in experiments.^{75–77} The main reason for this difference in the minimum time for crystallization is the growth rate, since the differences in the values of J for these two models are not so large at high supercoolings.
- The compressibility of the TIP4P/ICE model for supercooled water presents a maximum. The relaxation time is much smaller than the crystallization time at the temperature at which this maximum occurs so that this maximum is a real thermodynamic feature of the model. The relaxation time increases with supercooling and it is always smaller than the crystallization time. However for the temperature at which the crystallization time reaches a minimum the difference is of only two orders of magnitude.
- Although the TIP4P/ICE is a simplification of water interactions and the seeding technique is an approximate route to J , we obtain a good overall description of the nucleation rates of real water. This may or may not be due to fortuitous cancellation of errors (approximate model and approximate technique).
- There is a system-size dependent crossover in the crystallization time from the region where it is controlled by nucleation to the region where it is controlled by growth. That could be at the origin of the discrepancies in the values of J reported by different experimental groups although other possibilities such as internal pressure or surface nucleation should not be discarded.

There has been significant progress in our understanding of the nucleation of ice in the recent years. This paper aims to show that simulations can be useful in interpreting the experimental results. However it is obvious that further work is needed. We hope that some of the issues raised in this paper can be clarified in the near future.

ACKNOWLEDGMENTS

This work was funded by Grant No. FIS2013/43209-P of the MEC, and by the Marie Curie Integration Grant. No. COSAAC-FP7-PEOPLE-2012-CIG. C. Valeriani and E. Sanz acknowledge financial support from a Ramon y Cajal Fellowship. J. R. Espinosa acknowledges financial support from the FPI Grant No. BES-2014-067625. Calculations were carried out thanks to the supercomputer facility Tirant in

the Spanish Supercomputing Network (RES) (through Project No. QCM-2015-1-0028). We thank Professor Molinero for providing us with the input files to perform runs of the mW model of water using LAMMPS. We thank Dr. McBride for a critical reading of the manuscript and Professor Abascal for helpful discussions.

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