Homogeneous Ice Nucleation Rate in Water

Droplets

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Abstract

To predict the radiative forcing of clouds it is necessary to know the rate with which ice homogeneously nucleates in supercooled water. Such rate is often measured in drops to avoid the presence of impurities. At large supercooling small (nanoscopic) drops must be used to prevent simultaneous nucleation events. The pressure inside such drops is larger than the atmospheric one by virtue of the Laplace equation. In this work, we take into account such pressure raise in order to predict the nucleation rate in droplets using the TIP4P/Ice water model. We start from a recent estimate of the maximum drop size that can be used at each supercooling avoiding simultaneous nucleation events [Espinosa et al. J. Chem. Phys., 2016]. We then evaluate the pressure inside the drops with the Laplace equation. Finally, we obtain the rate as a function of the supercooling by interpolating our previous results for 1 and 2000 bar [Espinosa et al. Phys. Rev. Lett. 2016] using the Classical Nucleation Theory expression for the rate. This requires, in turn, interpolating the ice-water interfacial free energy and chemical potential difference. The TIP4P/Ice rate curve thus obtained is in good agreement with most droplet-based experiments. In particular, we find a good agreement with measurements performed using nanoscopic drops, that are currently under debate. The
successful comparison between model and experiments suggests that TIP4P/Ice is a reliable model to study the water-to-ice transition and that Classical Nucleation Theory is a good framework to understand it.

To make climate change predictions it is necessary to estimate the radiative forcing (the balance between absorbed and reflected solar radiation) caused by different factors. According to reports by the Intergovernmental Panel on Climate Change (IPCC), there are large uncertainties in the radiative forcing caused by clouds. Such uncertainty is partly due to the lack of reliable predictions of the ice content in clouds. These predictions rely on estimates of the ice nucleation rate, $J$, or the number of ice embryos that proliferate per unit time and volume.

In this paper we focus on the rate of homogeneous ice nucleation from pure water, $J_{hom}$. Although ice formation in the atmosphere is thought to occur predominantly heterogeneously from aqueous solutions, the fact that clouds have been observed to supercool to very low temperatures (even below -35 °C) suggests that there is homogeneous ice nucleation from nearly pure water in clean atmospheric conditions (upper troposphere). Moreover, ice nucleation from solution and heterogeneous ice nucleation are often treated as a sophistication of the case of homogeneous ice nucleation from pure water. It is therefore relevant to fully understand and characterise the latter. Of course, predicting the freezing of clouds requires knowledge not only of the nucleation stage but also of the growth one. However, both freezing stages are sufficiently complex so as to deserve separate attention.

Experiments to measure $J_{hom}$ typically use suspended droplets ranging from microscopic to nanoscopic size to avoid heterogeneous ice nucleation on impurities. In Fig. $J_{hom}$ measurements as a function of the supercooling $\Delta T$ – the melting temperature minus temperature of interest – are reported. Green and blue symbols correspond to measurements performed with microscopic and nanoscopic droplets respectively, while orange ones correspond to droplet sizes in between both ranges. Recent measurements from 2015, downward green triangles, inspired in 2016 a new fit to $J_{hom}$ (dashed pink curve) that shows
a maximum at $\Delta T \sim 46$ K. Such fit strongly clashes with measurements performed using nanoscopic drops at deep supercooling (blue points). According to these experiments $J_{hom}$ monotonously increases with supercooling, at least up to $\Delta T = 70$ K. Clarifying such discrepancy is a very relevant issue to atmospheric and climate science for the reasons explained in the previous paragraph. Several hypothesis have been put forward to explain the discrepancy. A plausible one is a spurious overestimation of the rate in nanoscopic drops due to nucleation at the air-water interface, but this remains a controversial issue.

In a recent work we have used TIP4P/Ice, a simple yet realistic water model, to predict $J_{hom}$ with computer simulations using the Seeding and the Mold Integration techniques. Our results for 1 bar, shown with a black curve in the figure, are in better agreement with the scenario supported by the nanoscopic drops measurements. In Ref. we argue that the measurements corresponding to the downward triangles could be underestimated because the employed drops may be too large and contain many ice nuclei simultaneously growing. Then, the time needed to observe water freezing would no longer be limited by the nucleation stage, but rather by the time required for the nucleated ice embryos to grow and fill a fraction of the drop volume that enables freezing detection. Since the rate is determined under the expectation that only one ice cluster nucleates in each drop, multiple nucleation events would lead to an underestimate of the nucleation rate. This multiple nucleation aggravates as the supercooling increases because $J_{hom}$ goes up with $\Delta T$. In Fig. (a) we reproduce our results from Ref. where, by combining simulation estimates of $J_{hom}$ and of the speed of ice growth, we predicted $R_{\text{max}}(\Delta T)$, the maximum droplet radius that enables staying in the regime where drops are observed to freeze at the time required to nucleate a single critical ice cluster. As expected, $R_{\text{max}}$ goes down with $\Delta T$. Symbols in Fig. (a) have the same legend as in Fig. Downward triangles, that inspired the dashed pink fit in Fig. lie in the region where our simulations predict that many ice clusters will simultaneously grow in the droplet.

We can now use $R_{\text{max}}(\Delta T)$ in conjunction with the Laplace equation, $\Delta P = 2\gamma_{lv}/R_{\text{max}}$, where $\gamma_{lv}$ is the surface tension of ice-water.
Figure 1: Ice nucleation rate at a function of supercooling, $\Delta T$ (difference between melting temperature and temperature of interest). Solid symbols correspond to experimental measurements in drops. Green squares, correspond to micron sized drops from Refs.; downward green triangles are also micron sized drops but from Ref. blue symbols correspond to nanoscopic drops; orange symbols correspond to drops in between the nanoscopic and the microscopic regime. Empty symbols correspond to measurements of the nucleation rate in thin films. Dashed pink curve is a fit proposed in Ref. inspired by the publication of the data represented by the downward green triangles. Solid lines correspond to simulation estimates using the TIP4P/Ice water model obtained with Seeding. The black line corresponds to the rate estimate at 1 bar (from Ref.). In the red curves (this work) the effect of the Laplace pressure inside the drops is taken into account in the simulation rate estimate. Solid red corresponds to the rate measured in the largest possible drop where there is a single nucleation event, while dashed red corresponds to the rate in drops of size typically used in experiments.

...to estimate the pressure inside the largest drops that can be used if simultaneous nucleation events are to be avoided ($\gamma_{lv}$ is the liquid-vapor surface tension). To do such estimate we have used the $\gamma_{lv}$ temperature dependence given in Ref. which we linearly extrapolated outside the reported measurement range (below -25°C). The smooth variation of $\gamma_{lv}$ with temperature justifies such extrapolation. Using $\gamma_{lv}$ for a flat interface could be inappropriate...
when dealing with curved drop surfaces. However, using a Tolman length of 1Å—larger than the values typically reported\textsuperscript{36–38} to correct for curvature effects only yields changes of less than 2 mN/m for the smallest drops considered. We therefore neglect any curvature effects in $\gamma_{lv}$. The results for the pressure inside the drops as a function the corresponding supercooling are shown in Fig. 2(b), solid curve. For supercooling larger than $\sim 50$ K the pressure sharply goes up. Therefore, rate measurements using drops can no longer be performed at 1 bar for $\Delta T > 50K$, which is an interesting conclusion of our analysis. This has to be taken into account when comparing simulation estimates with droplet based experimental measurements of the nucleation rate. This issue has been disregarded in the black curve shown in Fig. 1 which entirely corresponds to 1 bar (in simulations the rate is not computed inside drops but in the bulk thanks to periodic boundary conditions).

The main aim of this paper is to provide a simulation prediction of $J_{hom}(\Delta T)$ that can be directly compared with drop based measurements. This has been recently attempted in an experimental work, but only rough estimates were provided.\textsuperscript{24}

Figure 2: (a) Droplet radius as a function of the supercooling. The solid red curve corresponds to the maximum radius that enables measuring ice nucleation rates avoiding the simultaneous growth of several nuclei, $R_{max}$.\textsuperscript{24} The red dashed curve, $R_{exp}$, corresponds to a fit to the experimental data, excluding those given by downward green triangles. Symbols correspond to the experiments indicated in the legend of Fig. 1. (b) Solid (dashed): Laplace pressure inside drops of radius $R_{max}$ ($R_{exp}$) as a function of the supercooling.

To achieve this goal, one needs to compute for each $\Delta T$ the rate at the pressure given by
Figure 3: TIP4P/Ice predictions for the chemical potential difference between water and ice, (a), and the ice-water interfacial free energy, (b), as a function of supercooling. Black curves correspond to 1 bar, solid red corresponds to the largest drops that can be used while avoiding simultaneous nucleation events, and dashed red to drops with sizes typically used in the experiments. In order to parametrise the nucleation rate we use the following fits for the red solid curves: $|\Delta \mu| = 0.0012522 + 0.0044213 \Delta T - 1.6401 \cdot 10^{-5} \Delta T^2 - 1.259 \cdot 10^{-7} \Delta T^3$ and $\gamma_{iw} = 30.157 - 0.3219 \Delta T + 0.0042643 \Delta T^2 - 0.0001333 \Delta T^3 + 1.3504 \cdot 10^{-6} \Delta T^4$ and these for the red dashed ones: $|\Delta \mu| = 0.00035032 + 0.0046013 \Delta T - 2.3187 \cdot 10^{-5} \Delta T^2 - 6.9536 \cdot 10^{-8} \Delta T^3$ and $\gamma_{iw} = 29.986 - 0.25559 \Delta T - 0.0010465 \Delta T^2 + 4.6503 \cdot 10^{-6} \Delta T^3 + 2.9065 \cdot 10^{-7} \Delta T^4$.

$p(\Delta T)$ in Fig. 2. We have recently published $J_{hom}$ at 1 and 2000 bar for TIP4P/Ice. Here, we interpolate our results to obtain $J_{hom}$ at the desired pressure. We compute $J_{hom}$ by plugging parameters obtained by simulations into the expressions given by Classical Nucleation Theory (CNT), a combination we call Seeding. The CNT rate is given by:

$$J_{hom} = A \exp \left( - \frac{C \gamma_{iw}^3}{k_B T \rho_s^2 |\Delta \mu|^2} \right)$$  \hspace{1cm} (1)

Where $C$ is a constant that depends on the shape of the critical nucleus (here, $16\pi/3$ for spherical clusters), $A$ is a kinetic pre-factor, $k_B$ is the Boltzmann constant, $\rho_s$ is the solid density, $\gamma_{iw}$ is the ice-water interfacial free energy and $|\Delta \mu|$ is the chemical potential difference between the bulk water and ice phases. $|\Delta \mu|$ is computed with thermodynamic integration and $\gamma_{iw}$ with Mold Integration and Seeding for coexistence and supercooled conditions, respectively. The $\gamma_{iw}$ thus obtained has proven to give correct values for the nucleation rate when combined with Classical Nucleation Theory. Therefore, the $\gamma_{iw}$ we use for spherical critical clusters at supercooled conditions implicitly includes curvature.
and temperature corrections to that of a flat interface at coexistence.

As shown in Fig. 3 of Ref. 31, neither $A$ nor the solid density significantly change with pressure. Therefore, we use the values of $A$ and $\rho_s$ corresponding to 1 bar for any supercooling. To parametrise the rate we use the following fits for $A$ and $\rho_s$: 

$$\ln \left( \frac{A}{(m^{-3} s^{-1})} \right) = 91.656 - 0.11729 \Delta T - 0.00081401 \Delta T^2 ; \rho_s/(g/cm^3) = 0.906 + 0.14 \cdot 10^{-3} \Delta T.$$ 

The chemical potential difference can be easily obtained by thermodynamic integration from coexistence. In Ref. 31 we showed that $|\Delta \mu|$ does not strongly change from 1 to 2000 bar. The smooth variation of $|\Delta \mu|$ with pressure enables us to obtain it by interpolation at the required pressure for each supercooling. The results are shown in Fig. 3(a), where we compare $\Delta \mu(\Delta T)$ at 1 bar (black curve) with that at the pressure given by $p(\Delta T)$ in Fig. 3(b). Both curves are obviously the same up to $\Delta T \sim 50K$ where, according to Fig. 2(b), the pressure inside the drops is the atmospheric one. Beyond that supercooling $|\Delta \mu|$ is lower for the drops, which will contribute to lower $J_{hom}$ with respect to the bulk value ($|\Delta \mu|$ goes in the denominator of the exponential in Eq. 1).

We can also interpolate $\gamma_{iw}$ between our previously published values for 1 and 2000 bar. The results are shown in Fig. 3(b). Again, there is a noticeable effect at large supercooling: $\gamma_{iw}$ increases due to the fact that, in virtue of the Laplace equation, the pressure inside the drops exceeds the atmospheric one (as we have recently shown, the ice-water interfacial free energy increases with pressure). From Eq. 1 it is clear that an increase of $\gamma_{iw}$ entails a decrease of the nucleation rate.

Then, both $|\Delta \mu|$ and $\gamma_{iw}$ contribute to lower the nucleation rate inside the drops. With Eq. 1 the red curves in Fig 3 and the kinetic pre-factor previously obtained we can correct the black curve in Fig. 1 to account for Laplace pressure effects. The result is the red curve in Fig. 1 which is now in very good agreement with nanoscopic drop data (blue symbols). In fact, the red curve is in good agreement with all drop-based rate measurements (solid symbols in Fig. 1) except from those that inspired the fit with a maximum at $\Delta T = 46K$ (dashed pink). To obtain the solid red curve in Fig. 1 one needs to combine in Eq. 1 the
fits to the solid red curves of $\Delta \mu$ and $\gamma_{iw}$ given in the caption to Fig. 3 with those to $A$ and $\rho_s$ given above.

The red curve in Fig. 1 corresponds to the nucleation rate in the largest possible drop that can be used for each supercooling avoiding multiple nucleation events (one with radius $R_{\text{max}}(\Delta T)$). However, the droplets employed in experiments need not be of radius $R_{\text{max}}$. In fact, in Fig. 2(a) one can see that the experimental droplet sizes typically lie below $R_{\text{max}}$. It is therefore interesting to compute the nucleation rate for the droplet sizes typically used in the experiments, given by a radius $R_{\text{exp}}$. We estimate $R_{\text{exp}}(\Delta T)$ by fitting the experimental values given in Fig. 2(a), excluding the downward green triangles because they lie in the multiple nucleation events region. The $R_{\text{exp}}(\Delta T)$ fit is given by the dashed red curve in the figure. Given that $R_{\text{exp}} < R_{\text{max}}$, the pressure inside drops of radius $R_{\text{exp}}$ is larger than that inside drops of radius $R_{\text{max}}$ (see Fig. 2(b)). In fact, as shown in Fig. 2(b), now the pressure departs from the atmospheric one at milder supercooling, $\Delta T = 45$ instead of 50 K. Since a larger pressure causes a lower nucleation rate, the red dashed curve in Fig. 1, corresponding to $R_{\text{exp}}$, lies below the solid red one, corresponding to drops with radius $R_{\text{max}}$. In fact, the $R_{\text{max}}$ curve in Fig. 1 is an estimate of the highest possible rate that can be measured using drops and avoiding multiple nucleation events. The $R_{\text{exp}}$ curve in Fig. 1 fits the experiments even better than the $R_{\text{max}}$ one, which further supports the reliability of the predictions given by our model. To obtain the dashed red curve in Fig. 1 one needs to combine in Eq. 1 the fits to the dashed red curves of $\Delta \mu$ and $\gamma_{iw}$ given in the caption to Fig. 3 with those to $A$ and $\rho_s$ given above.

The experiments with thin films (empty diamonds in Fig. 1) are carried out at atmospheric pressure (with a flat air-water interface). Therefore, they should be compared with the simulation predictions for 1 bar, black line in Fig. 1. The comparison is not entirely satisfactory and further work is required to clarify this issue. Furthermore, the comparison of thin film experiments with droplet experiments in a supercooling regime where drops are expected to be at nearly atmospheric pressure ($\Delta T < 45$ K) does not look satisfactory.
either (as discussed in this work, for supercooling larger than 50 K thin film and droplet experiments cannot be compared because the latter are carried out at a higher pressure).

In summary, we have recently argued that there is a maximum droplet size that can be used at each supercooling to measure the rate without having many ice nuclei simultaneously growing. Such size goes down with supercooling and, for supercooling larger than \( \sim 50 \text{ K} \), the pressure inside the drop departs from the atmospheric one due to curvature effects (Laplace pressure). When the pressure of the liquid where ice nucleates increases, the nucleation rate decreases, mainly due to an increase of the interfacial free energy.\(^{31}\) Taking this into account we provide simulation estimates of the homogeneous nucleation rate in droplets and we find a good agreement with most droplet-based experimental measurements in a wide supercooling range. The agreement is even better if drops with radius typically used in the experiments are considered (in this case a Laplace pressure correction to the rate is noticeable for supercooling larger than 45 K). Such a good agreement has several implications: (i) the data obtained at deep supercooling using nanoscopic drops (blue point in Fig. 1) are supported by our simulations, while those recently obtained with microscopic drops (downward green triangles in Fig. 1) that inspired a fit to the nucleation rate with a maximum at a supercooling of 46 K (dashed pink line in Fig. 1) are not; (ii) TIP4P/Ice seems to be a good model to investigate both the thermodynamics and the kinetics of the water-to-ice transition; (iii) Classical Nucleation Theory seems to be a solid framework to understand ice nucleation.

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