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An approximation for homogeneous freezing temperature of water droplets

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volume as suggested by Bigg (1953). Here, experimental data of the freezing temperatures of pure water droplets from 15 independent studies over the past 60 years are collected (Fig. 1), showing a clear dependence of freezing temperature upon drop volume across different experiments. Over the investigated size interval (1–1000 μm diameter), observed freezing temperatures range from 232 to 240 K. The range of freezing temperatures and the volume dependence in Fig. 1 are consistent with the experimental data reviewed in Pruppacher (1995).

On the other hand, solutes, at sufficiently high concentrations, can suppress the homogeneous freezing temperature of water droplets. Koop et al. (2000) showed that the depression of freezing temperature strongly depends on the water activity a_w of the solution droplet, which has been confirmed in several independent experimental studies (e.g. Knopf and Rigg, 2011; Alpert et al., 2011). In this paper, two aforementioned features of homogeneous ice nucleation observed in the experimental data are examined – (1) the volume and water activity dependence of homogeneous freezing temperatures of water droplets $T_f(V, a_w)$, (2) the distribution of homogeneous freezing temperatures observed in fraction experiments $f(T_f)$. In this paper, we describe only volume-based nucleation and do not include the droplet surface effects on homogeneous ice nucleation as there remains considerable uncertainty about the importance of surface nucleation (Kay et al., 2001; Duft and Leisner, 2004). Based on a cornerstone of classical nucleation theory (CNT), namely that a critical embryo existing in a droplet triggers ice crystal formation, we propose a new approximation for the homogeneous freezing temperature, and seek a unified explanation of $T_f(V, a_w)$ and $f(T_f)$ observed in the experimental studies. Section 2 describes the new approximation; Sect. 3 gives the comparisons between the theoretical estimates and the experimental data; Sect. 4 is the discussion; Sect. 5 is the summary.

2 Background

2.1 The new approximation $T_{N_c=1}(V, a_w)$

According to CNT, the formation of a critical embryo inside a droplet can trigger the freezing process in the droplet. The critical embryo is formed by the critical fluctuation in orientation of hydrogen bonds (e.g. density fluctuation) (Baker and Baker, 2004), which is large enough to provide the formation energy of the critical embryo $\Delta F_c(T, a_w)$ and remove metastability of supercooled water. The probability of occurrence of the critical fluctuation is $\exp\left(\frac{-\Delta F_c(T, a_w)}{k_B T}\right)$ (Landau and Lifshitz, 1980; Pruppacher and Klett, 1997), and thus the *mean number* of the critical embryos inside a water droplet is given by

$$N_{c_mean}(V, a_w, T) = V\rho \exp\left(\frac{-\Delta F_c(T, a_w)}{k_B T}\right) \quad (1)$$

where V is the volume of the droplet, ρ is the number density of water molecules, k_B is Boltzmann's constant, T is the temperature of the droplet, and $\Delta F_c(T, a_w)$ is the formation energy of the critical embryo in the droplet with water activity a_w at T , which will be discussed in detail in Sect. 2.2.

The total freezing time τ_{freezing} of a water droplet can be split conceptually into three stages – (1) $\tau_{\text{meta_remove}}$ the time needed for the occurrence of the critical fluctuation (2) $\tau_{\text{formation}}$ the time needed to form a critical embryo and (3) τ_{growing} the growing time for the critical embryo expanding to the whole droplet body. These depend on V, a_w and T of the droplet (Pruppacher and Klett, 1997; Bauerecker et al., 2008). To observe freezing of droplets with volume V and water activity a_w occurring at temperature T , the residence time of freezing experiments $\tau_{\text{residence}}$ at T has to be longer than $\tau_{\text{freezing}}(V, a_w, T)$, resulting in a dependence of the homogeneous freezing temperature on the cooling rate γ_{cooling} of droplets in principle. According to the theoretical estimates (see Pruppacher and Klett, 1997, p. 678), the time scale of $\tau_{\text{formation}} + \tau_{\text{growing}}$ for

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the size of the droplets investigated here is short compared with the typical residence times in the laboratory studies. Thus, the dominant factor determining the homogeneous freezing temperatures is $\tau_{\text{meta_remove}}$. Because $\tau_{\text{meta_remove}}$ is the time needed for the occurrence of the critical fluctuation, it is shorter at cooler temperature when the fluctuation probability $\exp\left(\frac{-\Delta F_c(T, a_w)}{k_B T}\right)$ is higher or in a droplet with more molecules $V\rho$;

5 $\tau_{\text{meta_remove}}^{-1} \propto N_{\text{c_mean}}(V, a_w, T)$. $N_{\text{c_mean}}(V, a_w, T)$ is the mean state, so there is always a spread of $\tau_{\text{meta_remove}}$ among droplets even though all the droplets have same V and a_w and are at exactly same temperature T . The spread of $\tau_{\text{meta_remove}}$ can be wider when there are more observed droplets $N_{\text{total_droplets}}$, causing the stochastic nature

10 of ice nucleation process that some droplets with shorter $\tau_{\text{meta_remove}}$ can always be frozen at higher temperature, or in shorter time for droplets at the same temperature.

Based on above-mentioned principles, the homogenous freezing temperature of water droplets and $\tau_{\text{meta_remove}}$ can each be written as a function of V , a_w , γ_{cooling} and $N_{\text{total_droplets}}$, namely $\tau_{\text{meta_remove}}(V, a_w, \gamma_{\text{cooling}}, N_{\text{total_droplets}})$ and $T_f(V, a_w, \gamma_{\text{cooling}}, N_{\text{total_droplets}})$. Within CNT, to derive $\tau_{\text{meta_remove}}$ from $N_{\text{c_mean}}(V, a_w, T)$, and thereby include the stochastic nature of ice nucleation process, the kinetic adsorption/desorption flux system of molecule is applied to derive the ice nucleation rate J_{ice} . To simplify the ice nucleation model, CNT assumes that the adsorption/desorption process of molecules can represent the formation process of the embryo, and the embryo can only grow via bonding with monomolecules (Defour and Defay, 1963). The activation energy for the transfer of a water molecule across the water–ice boundary ΔG_a is required for the calculation of adsorption flux, which is a highly uncertain parameter (Ickes et al., 2015), and the agreements between the observed freezing temperatures and the theoretical estimates derived by CNT always rely on the fitting of ΔG_a to data

20 such as that in Fig. 1 (e.g. Pruppacher, 1995).

Koop et al. (1998) reported that observed homogeneous freezing temperatures do not significantly depend on γ_{cooling} of the droplets for γ_{cooling} smaller than 20 K min^{-1} (corresponding to vertical velocities 33.3 ms^{-1} in clear air). The results of Koop

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et al. (1998) actually indicated that the slope of $\frac{\partial \tau_{\text{meta_remove}}(V, a_w, T)}{\partial T}$ is very sharp at the temperature when the scale of $\tau_{\text{meta_remove}}(V, a_w, T)$ is close to $\tau_{\text{residence}}$ in most practical experiments and realistic atmospheric conditions, resulting in the small dependence of T_f on γ_{cooling} as suggested by Brewer and Palmer (1951). Based on that, in most of the practical freezing experiments and realistic atmospheric conditions ($\gamma_{\text{cooling}} < 20 \text{ Kmin}^{-1}$), the observed homogeneous freezing temperatures can be considered as a threshold temperature when $\frac{\partial \tau_{\text{meta_remove}}(V, a_w, T)}{\partial T} \rightarrow \infty$. In this study, without using the kinetic adsorption/desorption flux as in CNT, we intend to find this threshold temperature directly from the information given by $N_{\text{c_mean}}(V, a_w, T)$. Since the formation of one critical embryo is required to trigger the ice nucleation process in a droplet, $T_{N_{\text{c}}=1}$ may be a good approximation for the threshold temperature, the temperature at which the mean number of the critical embryos inside a droplet is unity, which can be given by

$$N_{\text{c_mean}} = 1 = V \rho e^{-\frac{\Delta F_{\text{c}}(T_{N_{\text{c}}=1}, a_w)}{k_{\text{B}} T_{N_{\text{c}}=1}}} \quad (2)$$

According to the formula of $\Delta F_{\text{c}}(T, a_w)$, $T_{N_{\text{c}}=1}$ is determined by V and a_w of the droplet, namely $T_{N_{\text{c}}=1}(V, a_w)$. Figure 2 shows the mean number of critical embryos inside a pure water droplet ($a_w = 1$) at different temperatures using Eq. (1) (see next section for details of $\Delta F_{\text{c}}(T, a_w)$ used in the calculation). It indicates that smaller droplets require cooler temperatures to reach the state that $N_{\text{c_mean}} = 1$, showing the volume dependence of $T_{N_{\text{c}}=1}(V, a_w)$. Figure 3 shows the mean number of critical embryos inside a solution droplet with different values of water activity. The result indicates that more concentrated solution droplets (lower a_w) need cooler temperature to reach the state that $N_{\text{c_mean}} = 1$. This then represents the solution effect on $T_{N_{\text{c}}=1}(V, a_w)$. The sensitivity of $T_{N_{\text{c}}=1}(V, a_w)$ to the variation of diameter δd and water activity δa_w of droplets can be written as

$$\delta T_{N_{\text{c}}=1} = \frac{\partial T_{N_{\text{c}}=1}}{\partial a_w} \delta a_w + \frac{\partial T_{N_{\text{c}}=1}}{\partial \log_{10} d} \delta \log_{10} d \quad (3)$$

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where d is the diameter of droplet (μm). The values of $\frac{\partial T_{N_c=1}}{\partial a_w}$ and $\frac{\partial T_{N_c=1}}{\partial \log_{10} d}$ are about 216 and 2.5 K respectively over the investigated interval of water activity and drop size, and may explain the observed dependence of homogeneous freezing temperatures on a_w and V respectively. To test our approximation, we aim to compare the observed $T_f(V, a_w)$ and $f(T_f)$ with $T_{N_c=1}(V, a_w)$ derived using the constraint in Eq. (2).

2.2 Formation energy of the critical embryo $\Delta F_c(T, a_w)$

The formation energy of the critical embryo $\Delta F_c(T, a_w)$ can be written as

$$\Delta F_c = \frac{1}{3} s \sigma_{i/w}(T, a_w) r_c^2 \quad (4)$$

$$r_c = \frac{2 \sigma_{i/w}(T, a_w) v_1^{\text{water}}}{k_B T \ln \left(\frac{e_{sw} a_w}{e_{si}} \right) + k_B T \ln(a_w)} \quad (5)$$

where $\sigma_{i/w}(T, a_w)$ is the interfacial energy between liquid water and solid ice, s is the shape factor of the embryo (~ 21 by assuming the shape is hexagonal prism), r_c is the radius of the critical embryo, v_1^{water} is the volume of single water molecule, e_{sw} and e_{si} are the saturation vapor pressures over water and ice respectively (Murphy and Koop, 2005), and a_w is the water activity of the solution droplet (see detailed derivations of Eq. (4) in Defour and Defay, 1963 and Pruppacher and Klett, 1997). It should be noted that the term $k_B T \ln(a_w)$ in r_c (Eq. 5) is the *entropy of unmixing* which originates from the change of the Gibbs free energy of the bulk solution during freezing, and is usually neglected in the previous theoretical studies (Bourne and Davey, 1976; Black, 2007). Barahona (2014) pointed out that although this term is small for dilute solution, it should not be neglected when applying to high concentration solution droplets (see Eq. 8 in Barahona, 2014).

The value of interfacial energy between liquid water and solid ice $\sigma_{i/w}(T, a_w)$ is needed for our calculation of Eqs. (4) and (5). As most of the studies suggest that the tempera-

ture dependence of $\sigma_{i/w}(T, a_w)$ should be linear (Ickes et al., 2015), and that increasing the concentration of the solution droplet increases the value of $\sigma_{i/w}(T, a_w)$ (Jones and Chadwick, 1971; Alpert et al., 2011), $\sigma_{i/w}(T, a_w)$ can be written as

$$\sigma_{i/w}(T, a_w) = \sigma_{i/w, e} + \frac{\partial \sigma_{i/w}}{\partial T}(T - T_0) + \frac{\partial \sigma_{i/w}}{\partial a_w}(1 - a_w) \quad (6)$$

5 where $\sigma_{i/w, e}$ is the interfacial energy at the melting temperature of pure ice-water (equilibrium temperature), $\frac{\partial \sigma_{i/w}}{\partial T}$ is the temperature dependence, $\frac{\partial \sigma_{i/w}}{\partial a_w}$ is the solution dependence and T_0 is the equilibrium temperature. The direct measurement of $\sigma_{i/w}(T, a_w)$ is extremely difficult, so most of the estimations are based on combinations of CNT and laboratory measurements of T_f and observed freezing rate to retrieve the values

10 of $\sigma_{i/w}(T, a_w)$ (e.g. Zobrist et al., 2007; Murray et al., 2010). These studies have shown considerable diversity in the reported estimations of $\sigma_{i/w}(T, a_w)$ (Ickes et al., 2015). Therefore, we use values of $\sigma_{i/w, e}$ and $\frac{\partial \sigma_{i/w}}{\partial T}$ derived from a state-of-the-art molecular dynamics model that explicitly simulates the molecular configurations under supercooling conditions. Benet et al. (2014) gave values of $\sigma_{i/w, e}$ from the TIP4P water model

15 ($\sigma_{i/w, e} = 26.5 \times 10^{-3} \text{ Jm}^{-2}$), TIP4P/2005 water model ($\sigma_{i/w, e} = 27 \times 10^{-3} \text{ Jm}^{-2}$), and TIP4P-Ew water model ($\sigma_{i/w, e} = 27.5 \times 10^{-3} \text{ Jm}^{-2}$). Regarding the temperature dependence $\frac{\partial \sigma_{i/w}}{\partial T}$, Espinosa et al. (2014) provided an average value of $0.25 \times 10^{-3} \text{ (Jm}^{-2} \text{ K}^{-1})$ from three different water molecular models (TIP4P/ICE, TIP4P and TIP4P/2005) down to a supercooling of about 30 K. Regarding the solution dependence $\frac{\partial \sigma_{i/w}}{\partial a_w}$, Barahona

20 (2014) proposed a new thermodynamic framework approximating the interfacial energy of ice-solution by assuming the interface between solid ice and liquid water is made of liquid molecules trapped by the solid matrix, which gives the relationship between $\sigma_{i/w}$ and a_w . Based on his approximation, the solution effect on the interfacial energy can be written as

$$\frac{\partial \sigma_{i/w}}{\partial a_w} = -C \frac{1}{a_w} \quad (7)$$

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where C is the parameter derived from the surface property of water (see Barahona, 2014 for details). The values of $\sigma_{i/w}(T, a_w)$ estimated from above studies are used to derive the numerical result $T_{N_c=1}(V, a_w)$ presented here.

3 Results – comparison between the theoretical results and the experimental data

3.1 Volume and water activity dependence of $T_f(V, a_w)$

First, $T_{N_c=1}(V, a_w = 1)$ of pure water droplet is derived. Figure 1 shows the comparison between the experimentally determined homogeneous freezing temperatures $T_f(V, a_w = 1)$ and the approximations $T_{N_c=1}(V, a_w = 1)$. Over the investigated size interval, the theoretical values of $T_{N_c=1}(V, a_w = 1)$ derived by the value of $\sigma_{i/w, e}$ from TIP4P water model agree very well with the experimental data $T_f(V, a_w = 1)$. The theoretical results $T_{N_c=1}(V, a_w = 1)$ derived by the values of $\sigma_{i/w, e}$ from TIP4P/2005 and TIP4P-Ew are about 1–2 K lower than the experimental data $T_f(V, a_w = 1)$. The volume dependence of $T_{N_c=1}(V, a_w = 1)$ derived by the values of $\sigma_{i/w, e}$ from three different water models all compare remarkably well with the experimental data (slope of Fig. 1), and different values of $\sigma_{i/w, e}$ only lead to a shift up and downward of the theoretical estimates $T_{N_c=1}(V, a_w = 1)$. From the comparison made in Fig. 1, as suggested by Koop et al. (1998), the varying of $\gamma_{cooling}$ from 0.3 to 10 Kmin⁻¹ (corresponding to vertical velocities between 0.5 and 16.6 ms⁻¹ in clear air) among most of the collected data does not cause a significant variation in $T_f(V, a_w = 1)$ and after considering the uncertainty and the freezing ranges (dotted lines in Fig. 1) of the experiments, most of the data are in good agreement with $T_{N_c=1}(V, a_w = 1)$. However, there is one exception that should be mentioned. The laboratory observation of Murray et al. (2010) (black triangle in Fig. 1) showed that varying of cooling rate from 2.5 to 10 Kmin⁻¹ corresponds to a shift of 0.5 to 1 K in observed freezing temperatures of pure water droplets, and our best agreement estimates $T_{N_c=1}(V, a_w = 1)$ can only explain the experimental data with

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freeze at a given temperature *solely by assuming that the spread in freezing temperatures arises from the spread in droplet sizes* and without considering the stochastic nature of ice nucleation process. We estimate $T_{N_c=1}(V, a_w)$ of the droplets with size of $\mu + 3\sigma$ (\sim the largest 0.15 % of the drops) as the theoretical onset freezing temperature T_f^{onset} , $T_{N_c=1}(V, a_w)$ of the droplets with size of $\mu + 1.64\sigma$ (\approx the largest 10 % of the drops) as the theoretical estimates $T_f^{10\%}$, $T_{N_c=1}(V, a_w)$ of the droplets with mean size as the theoretical estimates $T_f^{50\%}$, and $T_{N_c=1}(V, a_w)$ of the droplets with size of $\mu - 1.64\sigma$ (\approx the smallest 10 % of the drops) as the theoretical estimates $T_f^{90\%}$, and $T_{N_c=1}(V, a_w)$ of the droplets with size of $\mu - 3\sigma$ (\approx the smallest 0.15 % of the drops) as the theoretical estimates T_f^{end} . The results presented in this section only use the value of $\sigma_{i/w, e}$ from the TIP4P water model, which has the best agreement with the experimental data shown in Sect. 3.1 (Fig. 1).

There are five experimental results from Riechers et al. (2013), each with different μ and σ . The comparisons (Fig. 5) show that our estimates match the experimental data fairly well. The slope of the freezing fraction vs. temperature in the theoretical results is driven entirely by the reported spread in the size distribution of drops and matches fairly well with the observed slope, although across the experiments the theoretical slope is somewhat greater (observed values are shifted the right of the blue curve at the higher temperatures but mostly to the left at the lower temperature), which might be attributable to the stochastic nature of ice nucleation process. That said, the observational errors in the experimental values of T_{onset} , $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ more or less span the theoretical values derived from Eq. (2). Riechers et al. (2013) also reported that during cooling, the majority of the droplets are frozen over a temperature interval of 0.84–0.98 K, which is consistent with the range between the theoretical estimates T_f^{onset} and T_f^{end} derived here, namely 0.42–1.06 K from five different droplet size distributions. From the comparison made in Fig. 4, the often-termed “stochastic” feature of there being a distribution of freezing temperatures observed in the fraction experiments can instead largely be explained by $T_{N_c=1}(V, a_w)$ based on the spread in the size distri-

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critical embryos $N_{c_mean}(V, a_w, T)$ and their formation energy $\Delta F_c(T, a_w)$, $T_{N_c=1}(V, a_w)$ is derived as a function of volume and water activity of water droplets. With the comparison made in Sects. 3.1 to 3.2, it can be summarized that under most atmospheric conditions, homogeneous freezing temperatures can be well described by the new approximation $T_{N_c=1}(V, a_w)$ proposed here without considering information of the cooling rate (updraft velocity) and the total number of droplets. The experimental spread in homogeneous freezing temperatures of water droplets may largely be explained by the size distribution of droplets used in the experiments. It suggests that the theoretical estimate of $T_{N_c=1}(V, a_w)$ is a good approximation for the homogeneous freezing temperatures of water drops in the atmosphere and can explain much of the experimental data of homogeneous ice nucleation in terms of $T_f(V, a_w)$ and $f(T_f)$.

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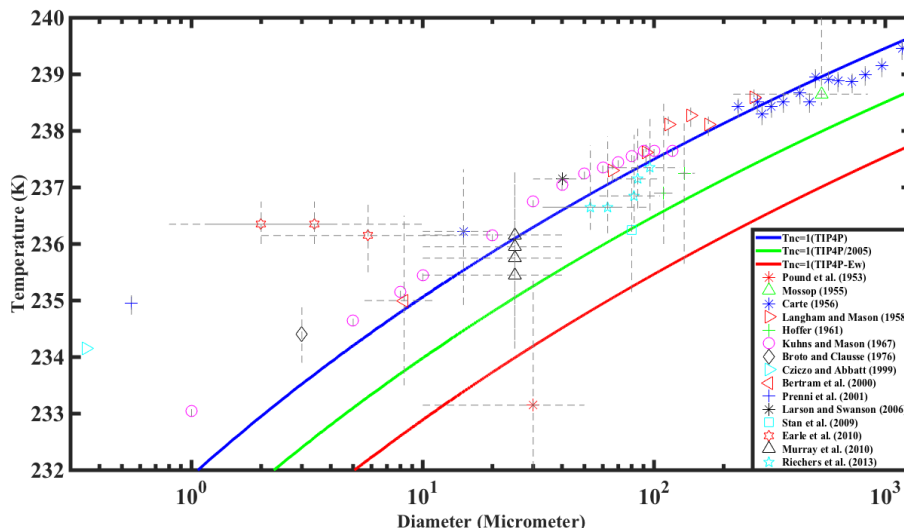


Figure 1. Freezing temperatures of pure water droplets: comparison between the approximations $T_{N_c=1}(V, a_w = 1)$ and the collected experimental data. Experimental data: the uncertainties and ranges of the drop size and the freezing temperatures are presented by the dotted line if information is provided by the studies. The approximations $T_{N_c=1}(V, a_w = 1)$: blue line – $\sigma_{i/w, e}$ from TIP4P model, green line – $\sigma_{i/w, e}$ from TIP4P/2005 model and red line – $\sigma_{i/w, e}$ from TIP4P-Ew model.

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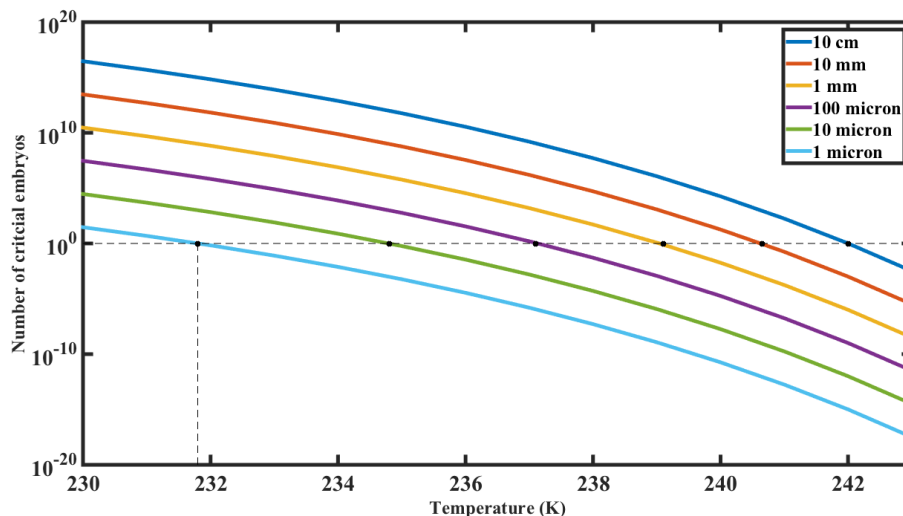


Figure 2. Mean number of critical embryos $N_{c,\text{mean}}$ (by Eq. 1) in a pure water droplet ($a_w = 1$) with different size (diameter) as a function of temperature. Solid circle: the approximations $T_{N_c=1}(V, a_w)$ derived by Eq. (2) (using $\sigma_{i/w,e}$ from TIP4P model).

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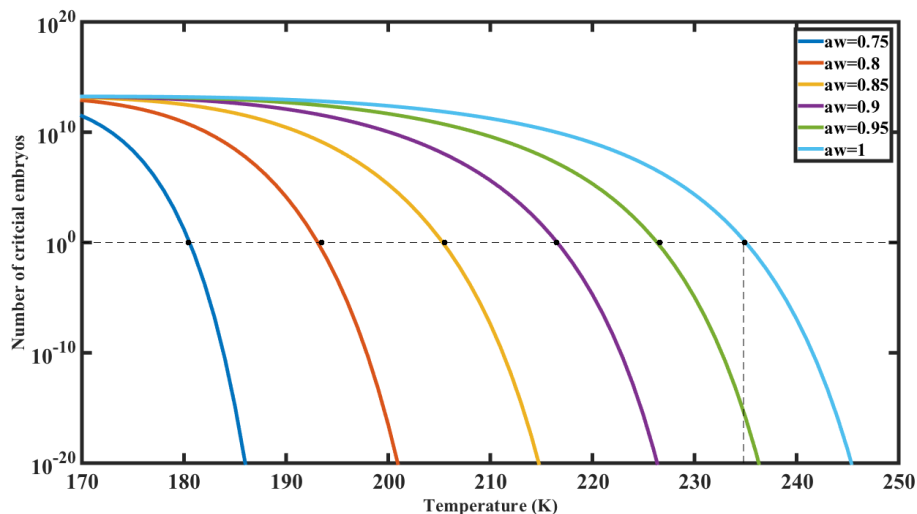


Figure 3. Mean number of critical embryos N_{c_mean} (by Eq. 1) in a solution droplet (diameter = 1 μm) with different water activity as a function of temperature. Solid circle: the approximations $T_{N_{c=1}}(V, a_w)$ derived by Eq. (2) (using $\sigma_{i/w, e}$ from TIP4P model).

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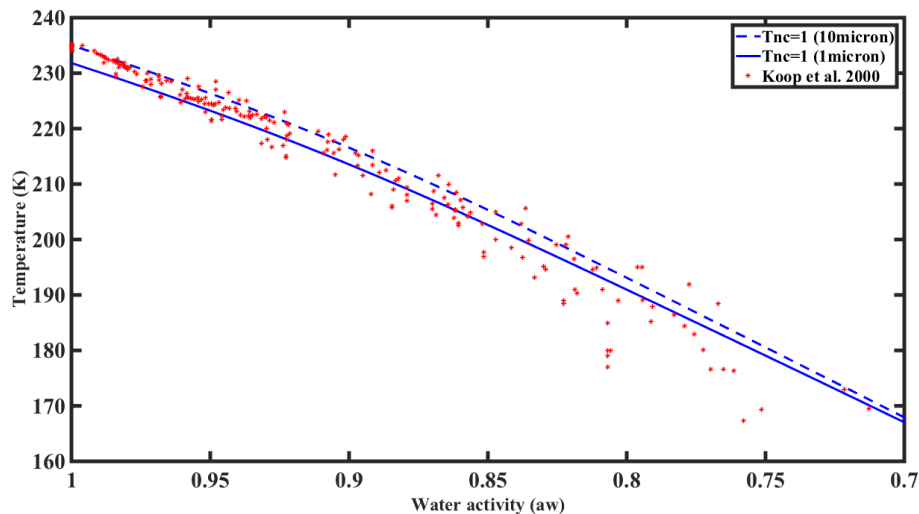


Figure 4. Comparison between the experimental data of freezing temperatures of solution droplets (Koop et al., 2000) and the approximation $T_{N_c=1}(V, a_w)$. Solid line (1 μm) and dotted line (10 μm) show the size range of droplets used in the experiments.

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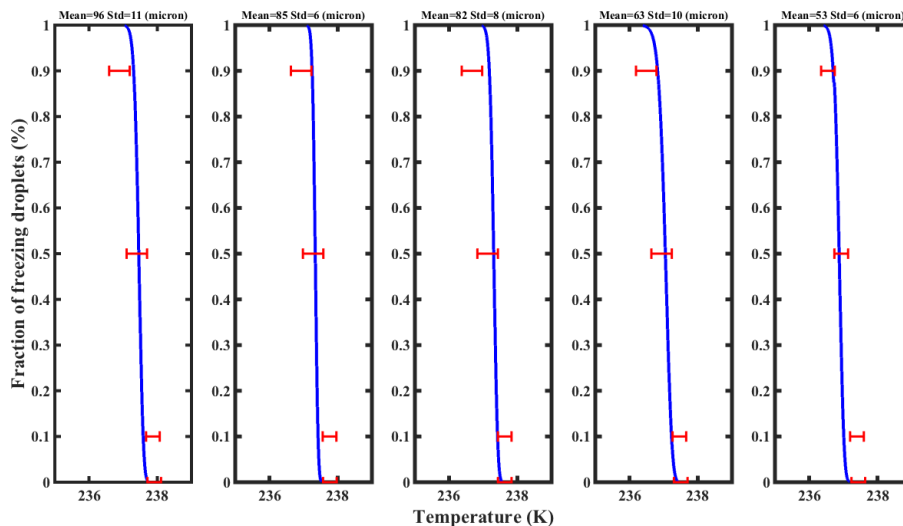


Figure 5. Comparison between the experimental results of the fraction experiment from Riechers et al. (2013) and the theoretical estimates derived here. Red line: experimental results with uncertainties from Riechers et al. (2013). Blue line: theoretical estimates ($\sigma_{i/w, e}$ from TIP4P model).

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