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# An approximation for homogeneous freezing temperature of water droplets

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In this work, based on the well-known formulae of classical nucleation theory (CNT), the temperature  $T_{N_{\rm c}=1}$  at which the mean number of critical embryos inside a droplet is unity is derived and proposed as a new approximation for homogeneous freezing temperature of water droplets. Without consideration of time dependence and stochastic nature of the ice nucleation process, the approximation  $T_{N_{\rm c}=1}$  is able to reproduce the dependence of homogeneous freezing temperature on drop size and water activity of aqueous drops observed in a wide range of experimental studies. We use the  $T_{N_{\rm c}=1}$  approximation to argue that the distribution of homogeneous freezing temperatures observed in the experiments may largely be explained by the spread in the size distribution of droplets used in the particular experiment. It thus appears that this approximation is useful for predicting homogeneous freezing temperatures of water droplets in the atmosphere.

#### 1 Introduction

Since the summary article of McDonald (1953), it has been widely observed that ice nucleation of water droplets does not occur at the equilibrium temperature (e.g. 273.15 K at 1 atm), and liquid water is frequently observed in clouds as cold as to 238 K (Rosenfeld and Woodley, 2000; Hu et al., 2010). Laboratory observations of homogeneous ice nucleation in pure water generally show that all droplets do not freeze at exactly the same temperature, and that the fraction of droplets that freeze in a given time is a function of temperature (hereafter we refer to this type of experiment as a *fraction experiment*) (e.g. Bigg, 1953; Carte, 1956; Broto and Clausse, 1976; Earle et al., 2010; Riechers et al., 2013). Riechers et al. (2013), to our knowledge uniquely among such experiments, reported information about the size distribution of the pure water droplets used in the fraction experiment, and showed that the temperature  $T_{50\%}$  when half of the population of pure water droplets are frozen has a dependence upon the mean drop

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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.

#### 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

$$N_{\text{c\_mean}}(V, a_{\text{w}}, T) = V \rho \exp\left(\frac{-\Delta F_{\text{c}}(T, a_{\text{w}})}{k_{\text{B}}T}\right)$$
 (1)

where V is the volume of the droplet,  $\rho$  is the number density of water molecules,  $k_{\rm B}$  is Boltzmann's constant, T is the temperature of the droplet, and  $\Delta F_{\rm c}(T,a_{\rm w})$  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  $\tau_{\text{freezing}}$  of a water droplet can be split conceptually into three stages – (1)  $\tau_{\rm meta\_remove}$  the time needed for the occurrence of the critical fluctuation (2)  $\tau_{\text{formation}}$  the time needed to form a critical embryo and (3)  $\tau_{\text{growing}}$  the growing time for the critical embryo expanding to the whole droplet body. These depend on  $V_{a_{\rm W}}$  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  ${\cal T}$ , the residence time of freezing experiments  $\tau_{\rm residence}$  at  ${\cal T}$  has to be longer than  $\tau_{\text{freezing}}(V, a_{\text{w}}, T)$ , resulting in a dependence of the homogeneous freezing temperature on the cooling rate  $\gamma_{
m cooling}$  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  $\exp\left(\frac{-\Delta F_{\text{c}}(T, a_{\text{w}})}{k_{\text{B}}T}\right)$  is higher or in a droplet with more molecules  $V\rho$ ;

 $au_{ ext{meta\_remove}}^{-1} \propto N_{ ext{c\_mean}}(V, a_{ ext{w}}, T)$ .  $N_{ ext{c\_mean}}(V, a_{ ext{w}}, T)$  is the mean state, so there is always a spread of  $au_{ ext{meta\_remove}}$  among droplets even though all the droplets have same V and  $a_{ ext{w}}$  and are at exactly same temperature T. The spread of  $au_{ ext{meta\_remove}}$  can be wider when there are more observed droplets  $N_{ ext{total\_droplets}}$ , causing the stochastic nature of ice nucleation process that some droplets with shorter  $au_{ ext{meta\_remove}}$  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,  $a_{\text{w}}$ ,  $\gamma_{\text{cooling}}$  and  $N_{\text{total\_droplets}}$ , namely  $\tau_{\text{meta\_remove}}(V, a_{\text{w}}, \gamma_{\text{cooling}}, N_{\text{total\_droplets}})$  and  $T_{\text{f}}(V, a_{\text{w}}, \gamma_{\text{cooling}}, N_{\text{total\_droplets}})$ . Within CNT, to derive  $\tau_{\text{meta\_remove}}$  from  $N_{\text{c\_mean}}(V, a_{\text{w}}, T)$ , 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  $J_{\text{ice}}$ . 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  $\Delta G_a$  is required for the calculation of adsorption flux, which is a highly uncertain parameter (lckes et al., 2015), and the agreements between the observed freezing temperatures and the theoretical estimates derived by CNT always rely on the fitting of  $\Delta G_a$  to data 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  $\gamma_{\text{cooling}}$  of the droplets for  $\gamma_{\text{cooling}}$  smaller than 20 K min<sup>-1</sup> (corresponding to vertical velocities 33.3 ms<sup>-1</sup> in clear air). The results of Koop

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

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

$$\delta T_{N_{c}=1} = \frac{\partial T_{N_{c}=1}}{\partial a_{w}} \delta a_{w} + \frac{\partial T_{N_{c}=1}}{\partial \log_{10} d} \delta \log_{10} d$$
(3)

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

The formation energy of the critical embryo  $\Delta F_{\rm c}(T,a_{\rm w})$  can be written as

$$\Delta F_{\rm c} = \frac{1}{3} s \sigma_{\rm i/w}(T, a_{\rm w}) r_{\rm c}^2 \tag{4}$$

$$r_{\rm c} = \frac{2\sigma_{\rm i/w}(T, a_{\rm w})v_{\rm 1}^{\rm water}}{k_{\rm B}T\ln\left(\frac{e_{\rm sw}a_{\rm w}}{e_{\rm si}}\right) + k_{\rm B}T\ln(a_{\rm w})} \tag{5}$$

where  $\sigma_{\text{i/w}}(T, a_{\text{w}})$  is the interfacial energy between liquid water and solid ice, s is the shape factor of the embryo ( $\sim$  21 by assuming the shape is hexagonal prism),  $r_{\text{c}}$  is the radius of the critical embryo,  $v_{1}^{\text{water}}$  is the volume of single water molecule,  $e_{\text{sw}}$  and  $e_{\text{si}}$  are the saturation vapor pressures over water and ice respectively (Murphy and Koop, 2005), and  $a_{\text{w}}$  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  $k_{\text{B}}T \ln(a_{\text{w}})$  in  $r_{\text{c}}$  (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-31873

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

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,  $\frac{\partial \sigma_{i/w}}{\partial a}$  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  $T_t$  and observed freezing rate to retrieve the values 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  $\sigma_{i/w}$  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  $(\sigma_{i/w, e} = 26.5 \times 10^{-3} \,\text{Jm}^{-2})$ , TIP4P/2005 water model  $(\sigma_{i/w, e} = 27 \times 10^{-3} \,\text{Jm}^{-2})$ , and TIP4P-Ew water model ( $\sigma_{i/w.e} = 27.5 \times 10^{-3} \, \mathrm{J \, m}^{-2}$ ). Regarding the temperature dependence  $\frac{\partial G_{i/w}}{\partial T}$ , Espinosa et al. (2014) provided an average value of  $0.25 \times 10^{-3}$  (J m<sup>-2</sup> K<sup>-1</sup>) from three different water molecular models (TIP4P/ICE, TIP4P and TIP4P/2005) down to a supercooling of about 30 K. Regarding the solution dependence  $\frac{\partial \sigma_{i/w}}{\partial a}$ , Barahona (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 sold matrix, which gives the relationship between  $\sigma_{i/w}$ and  $a_{\rm w}$ . Based on his approximation, the solution effect on the interfacial energy can be written as

$$\frac{\partial \sigma_{i/w}}{\partial a_{w}} = -C \frac{1}{a_{w}} \tag{7}$$

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## 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  $T_{\rm f}(V,a_{\rm w}=1)$  and the approximations  $T_{N_{\rm c}=1}(V,a_{\rm w}=1)$ . 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  $T_{N_0=1}(V, a_w = 1)$  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  $T_{N_{\rm a}=1}(V,a_{\rm w}=1)$  derived by the values of  $\sigma_{\rm i/w,\,e}$  from three different water models all compare remarkably well with the experimental data (slope of Fig. 1), and different values of  $\sigma_{\rm i/w,\;e}$  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  $\gamma_{\text{cooling}}$  from 0.3 to 10 K min<sup>-1</sup> (corresponding to vertical velocities between 0.5 and 16.6 m s<sup>-1</sup> in clear air) among most of the collected data does not cause an 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 K min<sup>-1</sup> 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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slowest cooling rate (2.5 K min<sup>-1</sup>). The finding of Murray et al. (2010) will be discussed in Sect. 4. For droplets smaller than 10 µm (diameter), there are obvious deviations of observed freezing temperatures among the experimental studies, and our theoretical results can only explain parts of the data for these very small droplets. These studies do not provide enough information regarding  $\gamma_{\text{cooling}}$ ,  $N_{\text{total droplets}}$  and the spread in drop size, so we cannot evaluate what causes the disparity. We suggest that freezing experiments of pure droplets smaller than 10 µm (diameter) need more refinement and should report the potentially important dependencies.

Second, the solution effect on homogeneous freezing temperature  $T_f(V, a_w)$  is explored by changing the water activity in Eqs. (5) and (6) to derive the approximation  $T_{N_c=1}(V, a_w)$ , which will be compared with the experimental data collected in Koop et al. (2000). Size of the droplets used in the collected experimental data ranges from 1-10 µm in diameter (Koop et al., 2000, Fig. 1b), so this size range is included to calculate the approximation  $T_{N_{\rm c}=1}(V,a_{\rm w})$ . Figure 4 shows the comparison between the experimental data (Koop et al., 2000) and the approximation  $T_{N_c=1}(V, a_w)$ . Without including the cooling rate of the experiments ( $\gamma_{\text{cooling}}$  varying from 1 to 10 Kmin<sup>-1</sup>) to calculate the dependence  $\frac{\partial T_{\rm f}}{\partial \gamma_{\rm cooling}}$ , the result shows that the approximation  $T_{N_{\rm c}=1}(V,a_{\rm w})$ is in good agreement with the experimental data, and scatter of the experimental data can be mostly explained by the size range of droplets for  $a_{\rm w} > 0.9$ . For the solution droplets with high concentration ( $a_w < 0.85$ ), the observed freezing temperatures collected in Koop et al. (2000) shows considerable spread. Abbatt et al. (2006) and Swanson (2009) suggest that the disparity of the experimental data for low  $a_{\rm w}$  is caused by a variety of heterogeneous process. In addition, the formula used in the experimental studies to transform the molality to water activity of the solution droplets also has uncertainty (Clegg et al., 1998; Swanson, 2009). Future experimental study is suggested to focus on the freezing process of solution droplets with high solute concentration to clarify the causes of the disparity.

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Regarding the experimental uncertainty, Knopf and Lopez (2009) reported that the value of  $a_{\rm w}$  for supercooled aqueous solutions has the experimental uncertainty  $\delta a_{\rm w}$  of about ±0.01, which can results in the variation  $\delta T_{N_{\rm c}=1}$  of about ±2 K based on Eq. (3). Riechers et al. (2013) reported that the size of droplets produced by the microfluidic device used in their experiment has three standard deviations (99.7%) of about 18 to 33 µm in diameter, which can cause the variation  $\delta T_{N_{\rm c}=1}$  of about ±0.2 K to ±0.5 K based on Eq. (3). Therefore, the variations  $\delta T_{N_{\rm c}=1}$  caused by the experimental uncertainties  $\delta a_{\rm w}$  and  $\delta d$  can be both substantial and should not be neglected. We suggest future experimental studies should provide detailed information regarding experimental uncertainties  $\delta a_{\rm w}$  and  $\delta d$  for the purpose of better constraining the observed freezing temperatures.

#### 3.2 Fraction of frozen pure water droplets as a function of temperature $f(T_f)$

To further examine the application of  $T_{N_c=1}(V,a_{\rm w})$  in homogeneous ice nucleation,  $T_{N_c=1}(V,a_{\rm w})$  is compared with the experimental data of the fraction experiment of Riechers et al. (2013). According to CNT, the stochastic nature of ice nucleation process can basically explain the distribution of freezing temperatures observed in the fraction experiment. However, current technology to produce water droplets for such experiments introduces a spread of sizes, and the freezing temperatures show a clear dependence on droplet volume (Fig. 1), so the spread in sizes of water droplets used in the experiments may be important for explaining the distribution  $f(T_{\rm f})$ . To test this, we incorporate the reported droplet size distribution width into the numerical calculation. Unique among such studies, Riechers et al. (2013) report both the spread of homogeneous freezing temperatures and the mean  $\mu$  and standard deviation  $\sigma$  of droplet size. According to Eq. (3), the spread in the size distribution of water droplets will result in a spread in the fraction of frozen droplets because larger droplets have higher  $T_{N_c=1}(V,a_{\rm w})$  (i.e. require less supercooling to freeze). Given the droplet size width, the distribution of the approximations  $T_{N_c=1}(V,a_{\rm w})$  of droplets can be derived from Eq. (2). Given a Gaussian distribution of drop sizes, we estimate the fraction of drops that will

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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  $T_{N_{\rm c}=1}(V,a_{\rm w})$  of the droplets with size of  $\mu$  + 3 $\sigma$  (~ the largest 0.15 % of the drops) as the theoretical onset freezing temperature  $T_{\rm f}^{\rm onset}$ ,  $T_{N_c=1}(V,a_{\rm w})$  of the droplets with size of  $\mu$  + 1.64 $\sigma$  ( $\approx$  the largest 10 % of the drops) as the theoretical estimates  $T_f^{10\%}$ ,  $T_{N_0=1}(V, a_w)$  of the droplets with mean size as the theoretical estimates  $T_{\rm f}^{50\,\%}$ , and  $T_{N_{\rm c}=1}(V,a_{\rm w})$  of the droplets with size of  $\mu$  – 1.64 $\sigma$ ( $\approx$  the smallest 10 % of the drops) as the theoretical estimates  $T_{\rm f}^{90\,\%}$ , and  $T_{N_{\rm c}=1}(V,a_{\rm w})$ of the droplets with size of  $\mu - 3\sigma$  ( $\approx$  the smallest 0.15% of the drops) as the theoretical estimates  $T_{\rm f}^{\rm end}$ . The results presented in this section only use the value of  $\sigma_{\rm i/w,\,e}$ 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  $\mu$ and  $\sigma$ . 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  $T_{\rm onset}$ ,  $T_{\rm 10\,\%}$ ,  $T_{\rm 50\,\%}$  and  $T_{\rm 90\,\%}$  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  $T_{\rm f}^{\rm onset}$  and  $T_{\rm f}^{\rm end}$  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  $T_{N_{\alpha}=1}(V, a_{w})$  based on the spread in the size distri-

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bution of droplets used in the experimental study without considering the dependency  $\frac{\partial T_{\rm f}}{\partial N_{\rm total\_droplets}}$ 

The comparison made in Sects. 3.1 to 3.2 show that the distribution of the freezing temperatures among the data can mostly be explained by the dependence of  $_{5}$   $T_{N_{c}=1}(V, a_{w})$  on V and  $a_{w}$  without considering the dependence of homogeneous freezing temperature on  $N_{\text{total droplets}}$  and  $\gamma_{\text{cooling}}$ . It suggests that in most of the practical experiments and for most atmospheric conditions, the time scale of  $au_{\rm residence}$  is shorter than  $\tau_{\text{meta remove}}$  at the temperatures higher than  $T_{N_c=1}(V, a_{\text{w}})$  (i.e.  $\tau_{\text{residence}} < 1$  $\tau_{\text{meta\_remove}}$ , when  $T > T_{N_c=1}(V, a_w)$ ), and when the temperature of the droplets is close to  $T_{N_{\rm c}=1}(V,a_{\rm w})$ , the time scale of  $au_{\rm meta\_remove}$  decreases strongly with temperature decreases and becomes shorter than  $au_{\rm residence}$  of the experiments (i.e.  $au_{\rm residence}$  >  $\tau_{\text{meta\_remove}}$  when  $T < T_{N_c=1}(V, a_{\text{w}})$ ). This leads to the result that most of the ice nucleation process can only be observed at temperatures close to  $T_{N_c=1}(V, a_{\text{w}})$  even though in principle, droplets can be frozen at any temperature.

#### **Discussion**

As mentioned in Sect. 2, the observed freezing temperatures with  $\gamma_{\rm cooling} \sim 2.5\,{\rm K\,min}^{-1}$ reported in Murray et al. (2010) can be well described by  $T_{N_a=1}(V, \tilde{a_w})$ , but it also showed there is a shift of 0.5 to 1 K in observed freezing temperatures when varying the cooling rate from 2.5 to 10 K min<sup>-1</sup>. One possibility is that the total freezing time  $\tau_{\text{freezing}}$ needed to freeze a droplet at  $T_{N_c=1}(V,a_{\rm w})$  is longer than the time scale of  $\tau_{\rm residence}$ when  $\gamma_{\text{cooling}}$  is higher 2.5 Kmin<sup>-1</sup>, which may be attributed to  $\tau_{\text{meta\_remove}}$ ,  $\tau_{\text{formation}}$ or  $\tau_{arowing}$ . Without considering the experimental uncertainty associated with the thermal equilibrium time  $\tau_{\text{thermal}}$ , these 0.5 to 1 K shifts corresponds to 3 to 6 s shifts (for  $\gamma_{\rm cooling}$  = -10 K min  $^{-1}$ ), which may be partly caused by  $\tau_{\rm formation}$  +  $\tau_{\rm growing}$ . Bauerecker et al. (2008) (hereafter Ba08) explored an advanced method providing time series of water droplet temperature during the entire cooling and freezing process (from super15, 31867–31889, 2015

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cooled water to completely freezing) using an infrared camera. The results of Ba08 showed that for the droplet sized 3 mm (diameter),  $\tau_{\text{growing}}$  is around 20 s and  $\tau_{\text{thermal}}$ is around 60 s. The droplet used in Ba08 is much larger than the size normally used in the freezing experiments because of the limitation of IR camera sensitivity. If  $au_{
m growing}$ linearly depends on drop radius, we may expect it to be several tenths of a second for the drops sized 10–100 µm in diameter. We suggest that the infrared camera technique should be used more widely in the future experimental studies of ice nucleation with smaller droplets, which can add significant insights into the time dependence study of ice nucleation, and clarify the importance of  $\tau_{\rm meta\ remove}$ ,  $\tau_{\rm formation}$  and  $\tau_{\rm growing}$  observed in the experiments. On the other hand, Koop et al. (1998) suggested that when the cooling rate is smaller than about 2 Kmin<sup>-1</sup>, mass transport of water can take place between the frozen ice particles and supercooled droplets, but if the cooling rate is too large, it can cause an offset between the measured temperature and the actual temperature of the drops, which can both cause a bias of the observed freezing temperatures. Therefore, we suggest that in future experimental studies, in order to precisely measure the dependence  $\frac{\partial T_{\rm f}}{\partial V_{\rm cooling}}$ , potential biases at high cooling rate and the shift caused by  $\tau_{\text{formation}} + \tau_{\text{growing}}$  should be better constrained. Since Koop et al. (1998) and Murray et al. (2010) showed different dependencies of homogeneous freezing temperatures on  $\gamma_{\text{cooling}}$ , future experiments should reexamine and perform the same experiments for  $\gamma_{\text{cooling}} > 2.5 \,\text{K}\,\text{min}^{-1}$ .

#### 5 Summary

The experimental studies of homogeneous freezing temperature show that in most of the practical experiments and under realistic atmospheric conditions, the observed homogeneous freezing temperatures can be regarded as the threshold temperature when  $\frac{\partial \tau_{\text{meta\_remove}}(V, a_{\text{w}}, T)}{\partial T} \rightarrow \infty$ , and we propose  $T_{N_{\text{c}}=1}(V, a_{\text{w}})$  is a useful approximation for this threshold temperature. Combining well-known CNT formulae for the mean number of

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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  $T_{N_0=1}(V, a_w)$  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  $T_{N_{c}=1}(V,a_{\mathrm{w}})$  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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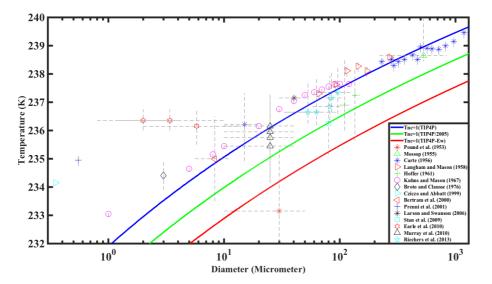
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**Figure 1.** Freezing temperatures of pure water droplets: comparison between the approximations  $T_{N_c=1}(V,a_{\rm w}=1)$  and the collected experimental data. Experimental data: the uncertainties and ranges of the drop size and the freezing temperatures are presented by the dotted line if information is provided by the studies. The approximations  $T_{N_c=1}(V,a_{\rm w}=1)$ : 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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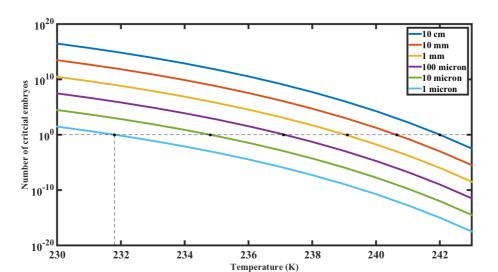
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**Figure 2.** Mean number of critical embryos  $N_{\text{c\_mean}}$  (by Eq. 1) in a pure water droplet ( $a_{\text{w}} = 1$ ) with different size (diameter) as a function of temperature. Solid circle: the approximations  $T_{N_{c}=1}(V,a_{\text{w}})$  derived by Eq. (2) (using  $\sigma_{\text{i/w},e}$  from TIP4P model).

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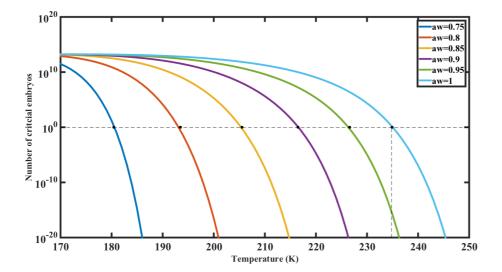
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**Figure 3.** Mean number of critical embryos  $N_{\text{c\_mean}}$  (by Eq. 1) in a solution droplet (diameter = 1 µm) with different water activity as a function of temperature. Solid circle: the approximations  $T_{N_{\text{c}}=1}(V, a_{\text{w}})$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

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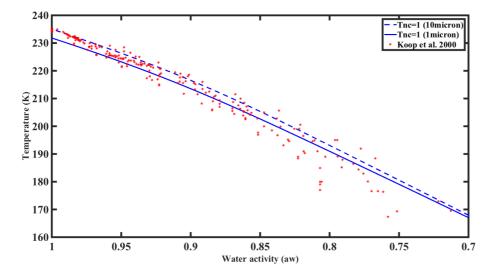
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**Figure 4.** Comparison between the experimental data of freezing temperatures of solution droplets (Koop et al., 2000) and the approximation  $T_{N_c=1}(V, a_w)$ . Solid line (1 µm) and dotted line (10 µm) show the size range of droplets used in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

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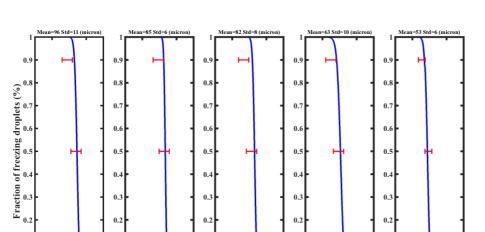
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**Figure 5.** Comparison between the experimental results of the fraction experiment from Riechers et al. (2013) and the theoretical estimates derived here. Red line: experimental results with uncertainties from Riechers et al. (2013). Blue line: theoretical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

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Temperature (K)

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