Exploring an approximation for the homogeneous freezing temperature of water droplets

K. -T. O[1], R. WOOD[1]

[1] University of Washington, Department of Atmospheric Sciences, Seattle, WA, USA

Corresponding author:
Kuan-Ting O
408 Atmospheric Sciences–Geophysics (ATG) Building
Box 351640, Seattle, Washington 98195-1640
Phone (206) 543-4250 | Fax (206) 543-0308
ktoandy@u.washington.edu

Abstract

In this work, based on the well-known formulae of classical nucleation theory (CNT), the temperature $T_{N_c=1}$ at which the mean number of critical embryos inside a droplet is unity is derived from the Boltzmann distribution function and explored as an approximation for homogeneous freezing temperature of water droplets. Without including the information of the applied cooling rate $\gamma_{cooling}$ and the number of observed droplets $N_{total\_droplets}$ in the calculation, the approximation $T_{N_c=1}$ is able to reproduce the dependence of homogeneous freezing temperature on drop size V and water activity a_w of aqueous drops observed in a wide range of experimental studies for droplet diameter > 10 μm and $a_w > 0.85$, suggesting the effect of $\gamma_{cooling}$ and $N_{total\_droplets}$ may be secondary compared to the effect of V and a_w on homogeneous freezing temperatures in these size and water activity ranges under realistic atmospheric conditions. We use the $T_{N_c=1}$ approximation to argue that the distribution of homogeneous freezing temperatures observed in the experiments may be partly explained by the spread in the size distribution of droplets used in the particular experiment. It thus appears that the simplicity of this approximation makes it potentially useful for predicting homogeneous freezing temperatures of water droplets in the atmosphere.

Keywords: classical nucleation theory, homogeneous ice nucleation, freezing temperature

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 ice melting temperature (e.g. 273.15 K at 1atm), 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 and time (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). Here, experimental data of the freezing temperatures of pure water droplets from 15 independent studies over the past 60 years are collected (Fig. 1 and Table 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 K 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 Lopez, 2009; Knopf and Rigg, 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., 2003; Duft and Leisner, 2004). The unified explanations of the observed dependencies of the homogeneous freezing temperature on droplet size and water activity have been proposed by several studies based on different theoretical frameworks such as ice nucleation rate J and density fluctuation (e.g. Pruppacher 1995; Baker and Baker 2004; Khvorostyanov and Curry 2009; Barahona 2014). In our study, based on a cornerstone of classical nucleation theory (CNT), namely that a critical embryo existing in a droplet triggers ice crystal formation, we explore a simple approximation for the homogeneous freezing temperature, and seek a simpler parameterization to describe homogeneous ice nucleation process in the atmosphere. Section 2 describes the approximation; Section 3 gives the comparisons between the theoretical estimates and the experimental data; Section 4 is the discussion; Section 5 is the summary.

2. Background

2.1 The 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 defined as the i-mers having the highest formation energy 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 $\exp(\frac{-\Delta F_c(T, a_w)}{k_B T})$ (Landau and Lifshitz, 1980, P.472-473; Pruppacher and Klett, 1997), and thus the *mean number* of the critical embryos inside a water droplet in thermal equilibrium can be predicted by a Boltzmann distribution (Landau and Liftshitz, 1958, P.107; Vali, 1999),

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

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 Boltzmann distribution form of the critical embryo is derived from the partitioning function of the grand canonical ensemble, and it should be noted that the derived particle number of the Boltzmann distribution function is not a "constant" but is a "mean" number (detailed derivation and explanations can be found in Landau and Liftshitz, 1958, P.107 and Sadovskii, 2012, Chapter 3.1).

The total freezing time $\tau_{freezing}$ of a water droplet can be split conceptually into three stages – (1) $\tau_{meta\_remove}(\sim \frac{1}{J})$ the time needed for the occurrence of the critical fluctuation (2) $\tau_{formation}$ the time needed to form a critical embryo and (3) $\tau_{growing}$ 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 $\tau_{residence}$ at T has to be longer than $\tau_{freezing}(V, a_w, T)$, resulting in a dependence of the homogeneous freezing temperature on the cooling rate $\gamma_{cooling}$ of droplets in principle. According to the theoretical estimates (see Pruppacher and Klett 1997, P.678), the time scale of $\tau_{formation} + \tau_{growing}$ for 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 τ_{meta_remove}. Because τ_{meta_remove} is the time needed for the occurrence of the critical fluctuation among water molecules, τ_{meta_remove} is shorter in a larger droplet with more molecules $V\rho$ or at lower temperature when the fluctuation probability $\exp(\frac{-\Delta F_c(T, a_w)}{k_B T})$ is higher; $\tau^{-1}_{meta\_remove} \propto N_{c\_mean}(V, a_w, T)$. Embryo interaction is a stochastic process and $N_{c\_mean}(V, a_w, T)$ simply expresses the mean state, so there is always a spread of τ_{meta_remove} among droplets even in a idealized case that all the droplets used in the experiment have exactly the same V and a_w and are at exactly the same temperature T. The spread of τ_{meta_remove} can be wider when there are more observed droplets $N_{total\_droplets}$, which in principle can explain the fraction

148 experiments that some droplets with shorter τ_{meta_remove} can always be frozen at
149 higher temperature, or in shorter time for droplets at the same temperature even when
150 the droplets have a monodisperse size distribution and exactly same a_w. Hereafter we
151 refer the distribution of homogeneous freezing temperatures owing to $N_{total\_droplets}$
152 when all the droplets have exactly same V and a_w as a *stochastic feature*. Based
153 on above-mentioned principles, the homogenous freezing temperature of water
154 droplets and τ_{meta_remove} can each be written as a function of V, a_w, $\gamma_{cooling}$ and
155 $N_{total\_droplets}$, namely $T_f(V, a_w, \gamma_{cooling}, N_{total\_droplets})$ and
156 $\tau_{meta\_remove}(V, a_w, \gamma_{cooling}, N_{total\_droplets})$.

157 Koop et al. (1998) reported that observed homogeneous freezing temperatures do
158 not significantly depend on $\gamma_{cooling}$ of the droplets for $\gamma_{cooling}$ smaller than 20 K min^{-1}
159 (corresponding to vertical velocities 33.3 m s^{-1} in clear air). The results of Koop et al.
160 (1998) actually indicate that the slope of $\frac{\partial \tau_{meta\_remove}}{\partial T}$ is very steep at the temperature
161 when the scale of τ_{meta_remove} is close to $\tau_{residence}$ in most practical experiments and
162 realistic atmospheric conditions, resulting in the small dependence of T_f on $\gamma_{cooling}$
163 as suggested by Brewer and Palmer (1951). Based on that, in most of the practical
164 freezing experiments and realistic atmospheric conditions ($\gamma_{cooling}$ < 20 K min^{-1}), the
165 observed homogeneous freezing temperatures can be considered as a threshold
166 temperature when $\frac{\partial \tau_{meta\_remove}}{\partial T} \to \infty$. In this study, we intend to find this threshold
167 temperature directly from the information given by $N_{c\_mean}(V, a_w, T)$. The number of
168 critical embryos derived from the Boltzmann distribution is a mean value and does
169 not provide any information regarding freezing time, so it can not be used to study the

dependence of the homogeneous freezing temperature on cooling rate (i.e. time dependence) and number of droplets used in the experiments (i.e. stochastic feature). Nevertheless, since the formation of one critical embryo is required to trigger the ice nucleation process in a droplet, $T_{N_c=1}$ 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

$$N_{c\_mean} = 1 = V\rho \exp\left(\frac{-\Delta F_c(T_{N_c=1}, a_w)}{k_B T_{N_c=1}}\right) \quad (2)$$

According to the formula of $\Delta F_c(T, a_w)$, $T_{N_c=1}$ is determined by V and a_w of the droplet, namely $T_{N_c=1}(V, a_w)$. 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 $\Delta F_c(T, a_w)$ used in the calculation). It indicates that smaller droplets require lower temperatures to reach the state that $N_{c\_mean} = 1$, showing the volume dependence of $T_{N_c=1}(V, a_w)$. 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 lower temperature to reach the state that $N_{c\_mean} = 1$. This represents the solution effect on $T_{N_c=1}(V, a_w)$. The sensitivity of $T_{N_c=1}(V, a_w)$ to the variation of diameter δd and water activity δa_w of droplets can be written as

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

where d is the diameter of droplet (μm). As shown in Fig. 1, the dependence of $T_{N_c=1}$ on $\log_{10} d$ is nearly linear, so the decadal log is used here to simply derive the

linear dependence. 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 K and 2.5 K respectively over the investigated interval of water activity and drop size, which are derived numerically from 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

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

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

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 Eq. (4) and (5). As most studies suggest that the

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

215 $$\sigma_{i/w}(T,a_w)=\sigma_{i/w,e}+\frac{\partial\sigma_{i/w}}{\partial T}(T-T_0)+\frac{\partial\sigma_{i/w}}{\partial a_w}(1-a_w) \quad (6)$$

216 where $\sigma_{i/w,e}$ is the interfacial energy at the equilibrium temperature of pure ice-water,
217 and T_0 is the equilibrium temperature. The direct measurement of $\sigma_{i/w}(T,a_w)$ is
218 extremely difficult, so most of the estimations are based on combinations of CNT and
219 laboratory measurements of T_f and observed freezing rate to retrieve the values of
220 $\sigma_{i/w}(T,a_w)$ (e.g. Zobrist et al., 2007; Murray et al., 2010). These studies have shown
221 considerable diversity in the reported estimations of $\sigma_{i/w}(T,a_w)$ (Ickes et al., 2015).
222 Instead, we use values of $\sigma_{i/w,e}$ and $\frac{\partial\sigma_{i/w}}{\partial T}$ derived from a state-of-the-art molecular
223 dynamics model that explicitly simulates the molecular configurations under
224 supercooling conditions. Benet et al. (2014) gives values of $\sigma_{i/w,e}$ from the TIP4P
225 water model ($\sigma_{i/w,e}$=26.5×10^{-3} J m^{-2}), TIP4P/2005 water model ($\sigma_{i/w,e}$=27×10^{-3} J m^{-2}),
226 and TIP4P-Ew water model ($\sigma_{i/w,e}$=27.5×10^{-3} J m^{-2}), and these three values will all be
227 used in our calculations. According to Ickes et al. (2015), the values of the interfacial
228 energy used here are about the median of all the values derived from the previous
229 studies. Regarding $\frac{\partial\sigma_{i/w}}{\partial T}$, Espinosa et al. (2014) provided an average value of 0.25 ×
230 10^{-3} (J m^{-2} K^{-1}) from three different water molecular models (TIP4P/ICE, TIP4P and
231 TIP4P/2005) down to a supercooling of about 30K. Regarding $\frac{\partial\sigma_{i/w}}{\partial a_w}$, Barahona
232 (2014) proposed a new thermodynamic framework approximating the interfacial
233 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 this approximation, the solution effect on the interfacial energy can be written as

$$\frac{\partial \sigma_{i/w}}{\partial a_w} = -\frac{\Gamma_w^2 s_{area} k_B T \frac{1}{a_w}}{(36\pi (v_1^{water})^2)^{1/3}} \quad (7)$$

where Γ_w is the surface excess of water (~1.46) (Spaepen 1975) and s_{area} is the surface area parameter (~1.105 $mol^{2/3}$) (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 approximation and the experimental data

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

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). 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 $T_f(V, a_w = 1)$ (details of the experiments are provided in Table 1) and the approximations $T_{N_c=1}(V, a_w = 1)$. For droplet diameters > 10μm, 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 most of the experimental data $T_f(V, a_w = 1)$. Using the values of $\sigma_{i/w,e}$ from TIP4P/2005 and TIP4P-Ew leads to a shift downward of about 1~2 K of $T_{N_c=1}(V, a_w = 1)$. There is one study regarding the time dependence 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 K min^{-1} to 10 K min^{-1} corresponds to a

256 shift of 0.5 K to 1 K in observed freezing temperatures of pure water droplets, and our
257 best agreement estimates $T_{N_c=1}(V, a_w = 1)$ can only explain the experimental data with
258 slowest cooling rate (2.5 K min^{-1}). The finding of Murray et al. (2010) will be
259 discussed in Sect. 4. For droplets smaller than 10 μm (diameter), there are obvious
260 deviations of observed freezing temperatures among the experimental studies. These
261 studies do not provide enough information regarding $\gamma_{cooling}$, $N_{total\_droplets}$ and the
262 spread in drop size, so we cannot evaluate what causes the disparity. We suggest that
263 freezing experiments of pure droplets smaller than 10 μm (diameter) need more
264 refinement and should report the potentially important dependencies such as applied
265 cooling rate, size distribution of droplets and number of observed droplets used in
266 experiments.

267 Second, the solution effect on homogeneous freezing temperature $T_f(V, a_w)$ is
268 explored by changing the water activity in Eq. (5) and (6) to derive the approximation
269 $T_{N_c=1}(V, a_w)$, which will be compared with the experimental data collected in Koop et
270 al. (2000), Knopf and Lopez (2009) and Knopf and Rigg (2011). Size of the droplets
271 used in the collected experimental data ranges from 1μm to 10 μm in Koop et al.
272 (2000), from 10μm to 80μm in Knopf and Lopez (2009) and from 20μm to 80μm in
273 Knopf and Rigg (2011), and these sizes are included to calculate the approximation
274 $T_{N_c=1}(V, a_w)$. Figure 4 shows the comparison between the experimental data and the
275 approximation $T_{N_c=1}(V, a_w)$. Without considering the time dependence ($\gamma_{cooling}$
276 varying from 1 K min^{-1} to 10 K min^{-1} among all the experiments) and the stochastic
277 feature (i.e. $N_{total\_droplets}$), the result shows that the approximation $T_{N_c=1}(V, a_w)$ is in
278 good agreement with the experimental data for $a_w > 0.85$. The scattering of the

experimental data between the theoretical estimates for $a_w > 0.85$ (i.e. $T_{N_c=1}$ for d =1 to 80 μm) suggests that the spread of droplet size applied in the experiments may play an important role in the spread of homogeneous freezing temperatures. For the solution droplets with high concentration ($a_w < 0.85$), the observed freezing temperatures show considerable spread. Abbatt et al. (2006) suggests that the disparity of the experimental data for low a_w can be partly attributed to a variety of heterogeneous process, which can result in the higher observed freezing temperatures. In addition, as suggested by knopf and Lopez (2009), the deviations at low water activity may be most likely due to our incomplete understanding of a_w for certain aqueous solutions and the corresponding uncertainties. Future experimental study is suggested to focus on the freezing process of solution droplets with high solute concentration ($a_w < 0.85$) to clarify the causes of the disparity.

Regarding the experimental uncertainty, Knopf and Lopez (2009) reported that the value of a_w for supercooled aqueous solutions has the experimental uncertainty δa_w of about ± 0.01, which can results in the variation in $T_{N_c=1}$ 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 μm to 33 μm in diameter, which can cause the variation in $T_{N_c=1}$ of about ± 0.2 K to ± 0.5 K based on Eq. (3). Therefore, the variation in $T_{N_c=1}$ caused by the experimental uncertainties δa_w and δd can be both substantial and should not be neglected. We suggest future experimental studies should provide detailed information regarding experimental uncertainties δa_w and δd 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 $T_{N_c=1}(V,a_w)$ in homogeneous ice nucleation, $T_{N_c=1}(V,a_w)$ is compared to the experimental data of the fraction experiment of Riechers et al. (2013). According to CNT, the stochastic feature of the ice nucleation process can basically explain the distribution of freezing temperatures observed in the fraction experiment (Pruppacher and Klett, 1997, Eq. (7-71); Koop et al., 1998; Niedermeier et al., 2011). 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 $f(T_f)$. In other words, the size distribution of droplets used in a given experiment may be an important factor governing the observed spread of freezing temperatures (i.e. dotted line shown in Fig. 1). 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 μ and standard deviation σ 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 $T_{N_c=1}(V,a_w)$ (i.e. require less supercooling to freeze). Given the droplet size width, the distribution of the approximations $T_{N_c=1}(V,a_w)$ of droplets can be derived from Eq. (2). Given a Gaussian distribution of drop sizes, we estimate the fraction of drops that will freeze at a given temperature *solely by assuming that the spread in freezing temperatures arises from the spread in droplet sizes* based on Eq. (3). For example, we estimate

325 $T_{N_c=1}(V,a_w)$ of the droplets with size of μ+3σ (~ the largest 0.15% of the drops) as
326 the theoretical onset freezing temperature T_f^{onset}, $T_{N_c=1}(V,a_w)$ of the droplets with
327 size of μ+1.64σ (≈ the largest 10% of the drops) as the theoretical estimates $T_f^{10\%}$,
328 $T_{N_c=1}(V,a_w)$ of the droplets with mean size as the theoretical estimates $T_f^{50\%}$, and
329 $T_{N_c=1}(V,a_w)$ of the droplets with size of μ-1.64σ (≈ the smallest 10% of the drops) as
330 the theoretical estimates $T_f^{90\%}$, and $T_{N_c=1}(V,a_w)$ of the droplets with size of μ-3σ (≈
331 the smallest 0.15% of the drops) as the theoretical estimates T_f^{end}. The results
332 presented in this section only use the value of $\sigma_{i/w,e}$ from the TIP4P water model,
333 which has the best agreement with the experimental data shown in Sect. 3.1 (Fig. 1).

334 There are five experimental results from Riechers et al. (2013), each with
335 different μ and σ. The comparisons (Fig. 5 and Table 2) show that our estimates
336 match the experimental data fairly well. The slope of the freezing fraction versus
337 temperature in the theoretical results is driven entirely by the reported spread in the
338 size distribution of drops and matches fairly well with the observed slope, although
339 across the experiments the theoretical slope is somewhat greater (observed values are
340 shifted to the right of the blue curve at the higher temperatures but mostly to the left at
341 the lower temperature), which might be attributable to the stochastic feature of the ice
342 nucleation process. That said, the observational uncertainties in the experimental
343 values of T_{on-set}, $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ more or less span the theoretical values
344 derived from Eq. (2). Riechers et al. (2013) also reported that during cooling, the
345 majority of the droplets are frozen over a temperature interval of 0.84-0.98 K, which
346 is consistent with the range between the theoretical estimates T_f^{onset} and T_f^{end} derived
347 here, namely 0.42-1.06 K from five different droplet size distributions, suggesting the

spread in droplet size (i.e. a disperse distribution) may be an important factor governing the spread of the homogeneous freezing temperatures observed in a given fraction experiment.

The comparison made in Sect. 3.1 to 3.2 shows that the distribution of the freezing temperatures among the data can mostly be explained by the dependence of $T_{N_c=1}(V,a_w)$ on V and a_w for droplet diameter > 10 μm and a_w > 0.85 without considering the dependence of homogeneous freezing temperature on $N_{total\_droplets}$ and $\gamma_{cooling}$ in the calculations. It suggests that in most of the practical experiments and for most atmospheric conditions, the time scale of $\tau_{residence}$ is shorter than τ_{meta_remove} at the temperatures higher than $T_{N_c=1}(V,a_w)$ (i.e. $\tau_{residence} < \tau_{meta\_remove}$, when $T > T_{N_c=1}(V,a_w)$), and when the temperature of the droplets is close to $T_{N_c=1}(V,a_w)$, the time scale of τ_{meta_remove} decreases strongly with temperature decreases and becomes shorter than $\tau_{residence}$ of the experiments (i.e. $\tau_{residence} > \tau_{meta\_remove}$ when $T < T_{N_c=1}(V,a_w)$). This leads to the result that most of the homogeneous ice nucleation process can only be observed at temperatures close to $T_{N_c=1}(V,a_w)$ even though in principle, droplets can be frozen at any temperature.

4. Discussion

As mentioned in Sect. 2, the observed freezing temperatures with $\gamma_{cooling}$ ~ 2.5 K min^{-1} reported in Murray et al. (2010) can be well described by $T_{N_c=1}(V,a_w)$, but it also showed there is a shift of 0.5 K to 1 K in observed freezing temperatures when varying the cooling rate from 2.5 K min^{-1} to 10 K min^{-1}. One possibility is that the total freezing time $\tau_{freezing}$ needed to freeze a droplet at $T_{N_c=1}(V,a_w)$ is longer than

the time scale of $\tau_{residence}$ when $\gamma_{cooling}$ is higher than 2.5 K min^{-1}, which may be attributed to τ_{meta_remove}, $\tau_{formation}$ or $\tau_{growing}$. Without considering the experimental uncertainty associated with the thermal equilibrium time $\tau_{thermal}$, these 0.5K to 1K shifts corresponds to 3s to 6s shifts (for $\gamma_{cooling}$ = -10 K min^{-1}), which may be partly caused by $\tau_{formation} + \tau_{growing}$. 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 supercooled water to completely freezing) using an infrared camera. The results of Ba08 showed that for the droplet sized 3mm (diameter), $\tau_{growing}$ is around 20s and $\tau_{thermal}$ is around 60s. 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 $\tau_{growing}$ 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 τ_{meta_remove}, $\tau_{formation}$ and $\tau_{growing}$ observed in the experiments. On the other hand, Koop et al. (1998) suggested that when the cooling rate is smaller than about 2K min^{-1}, 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 $\frac{\partial T_f}{\partial \gamma_{cooling}}$, potential biases at high cooling rate and the shift caused by $\tau_{formation} + \tau_{growing}$ should

be better constrained. Since Koop et al. (1998) and Murray et al. (2010) showed different dependencies of homogeneous freezing temperatures on $\gamma_{cooling}$, future experiments should reexamine and perform the same experiments for $\gamma_{cooling} >$ 2.5 K min^{-1}. The results shown in Fig. 1 and Fig. 4 suggest that the time consideration may be more important when droplet volume and water activity are low where the experimental data show considerable inconsistency (i.e. $a_w < 0.85$ and d <10μm), and future experiments are suggested to emphasize these droplet size and water activity ranges.

5. Summary

The limitation of our method proposed here is that the time dependence and the stochastic feature of homogeneous freezing temperature cannot be considered because the Boltzmann distribution applied here is a average distribution and does not provide any information regarding time. Combining the well-known Boltzmann distribution function for the mean number of critical embryos $N_{c\_mean}(V,a_w,T)$ and their formation energy $\Delta F_c(T,a_w)$ from CNT formulae, $T_{N_c=1}(V,a_w)$ is derived as a function of volume and water activity of water droplets. With the comparison made in Sect. 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 applied cooling rate (i.e. time dependence) and the number of droplets used in the experiment (i.e. stochastic feature) for d > 10μm and a_w > 0.85. Future experimental study is suggested to focus on the homogeneous freezing process of droplets with high solute

concentration ($a_w < 0.85$) and small volume (d < 10μm). The experimental spread in homogeneous freezing temperatures of water droplets may be partly explained by the size distribution of droplets used in the experiments. The advantage of our approximation in the cloud modeling is "the temperature history" of droplets is not required to calculate the homogeneous freezing temperature as it is when using the ice nucleation rate (i.e. Eq. (7-71) in Pruppacher and Klett, 1997). When using the ice nucleation rate $J(T(t))$, the complete temperature history of droplets is needed to calculate the integration of $J(T(t))$ with respect to time in order to consider the time dependence and the stochastic feature, which can introduce considerable complexity in cloud modeling. However, based on the experimental studies of homogeneous freezing temperature collected and discussed in our study, we suggest in most of the practical experiments and realistic atmospheric conditions (i.e. $\gamma_{cooling}$ < 20 K min^{-1}), the time dependence and the stochastic feature of homogeneous freezing temperature may be a secondary factor compared to the effect of volume and water activity for droplet diameter > 10 μm and a_w > 0.85. The approximation proposed here is relatively simpler to be implemented into cloud models and may improve the representation of homogeneous ice nucleation in the atmosphere.

Acknowledgements

The authors gratefully appreciate helpful discussion with Marcia Baker, Daniel Cziczo and Sarvesh Garimella who provided important insight and guidance for this study. Two anonymous reviewers are thanked for providing important feedback that helped to improve the paper. The authors thank Thomas Koop for his help in supplying the data in Figure 4.

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References	Diameter (μm)	T_f (K)	Diameter Range (μm)	Range of freezing temperatures (K)	Cooling rate	Uncertainty (K)
Pound et al. (1953)	30^{+}	233.15^{a}	[10 50]	[231.15 235.15]	n/a	n/a
Mossop (1955)	530^{+}	238.65^{a}	[220 840]	[238.65 242.15]	0.5K/ min	0.2
Carte (1956)	15^{+}	236.25^{a}	[10 20]	[235.15 237.15]	1K/min	0.2
	231.3^{d}	238.45^{b}	n/a	n/a	0.5K/min	0.2
	279.4^{d}	238.55^{b}	n/a	n/a	0.5K/min	0.2
	292.9^{d}	238.35^{b}	n/a	n/a	0.5K/min	0.2
	321.9^{d}	238.45^{b}	n/a	n/a	0.5K/min	0.2
	362.2^{d}	238.55^{b}	n/a	n/a	0.5K/min	0.2
	427.3^{d}	238.65^{b}	n/a	n/a	0.5K/min	0.2
	469.7^{d}	238.55^{b}	n/a	n/a	0.5K/min	0.2
	498.2^{d}	238.95^{b}	n/a	n/a	0.5K/min	0.2
	567.3^{d}	238.95^{b}	n/a	n/a	0.5K/min	0.2
	623.6^{d}	238.85^{b}	n/a	n/a	0.5K/min	0.2
	718.5^{d}	238.85^{b}	n/a	n/a	0.5K/min	0.2
	818.1^{d}	238.95^{b}	n/a	n/a	0.5K/min	0.2
	965.2^{d}	239.15^{b}	n/a	n/a	0.5K/min	0.2
	1179.8^{d}	239.45^{b}	n/a	n/a	0.5K/min	0.2
	1408.4^{d}	239.65^{b}	n/a	n/a	0.5K/min	0.2
Langham and Mason (1958)	66.1^{d}	237.35^{a}	n/a	n/a	0.33K/min	n/a
	92.3^{d}	237.65^{a}	n/a	n/a	0.33K/min	n/a
	115.3^{d}	238.15^{a}	n/a	n/a	0.33K/min	n/a
	144^{d}	238.25^{a}	n/a	n/a	0.33K/min	n/a
	171.8^{d}	238.15^{a}	n/a	n/a	0.33K/min	n/a
	270.5^{d}	238.55^{a}	n/a	n/a	0.33K/min	n/a
Hoffer (1961)	110^{+}	236.55^{a}	[100 120]	[235.65 238.15]	1K/min	0.5
	130^{+}	237.25^{a}	[125 145]	[235.65 238.15]	1K/min	0.5
Kuhns and Mason (1967)	1^{d}	233.05^{a}	n/a	n/a	6K/min	0.1
	5^{d}	234.65^{a}	n/a	n/a	6K/min	0.1
	8^{d}	235.15^{a}	n/a	n/a	6K/min	0.1
	10^{d}	235.45^{a}	n/a	n/a	6K/min	0.1
	20^{d}	236.15^{a}	n/a	n/a	6K/min	0.1
	30^{d}	236.75^{a}	n/a	n/a	6K/min	0.1

	40[d]	237.05[a]	n/a	n/a	6K/min	0.1
	50[d]	237.25[a]	n/a	n/a	6K/min	0.1
	60[d]	237.35[a]	n/a	n/a	6K/min	0.1
	70[d]	237.45[a]	n/a	n/a	6K/min	0.1
	80[d]	237.55[a]	n/a	n/a	6K/min	0.1
	90[d]	237.65[a]	n/a	n/a	6K/min	0.1
	100[d]	237.65[a]	n/a	n/a	6K/min	0.1
	120[d]	237.65[a]	n/a	n/a	6K/min	0.1
Broto and Clausse (1976)	3[d]	234.35[a]	n/a	n/a	1.25K/min	0.5
Cziczo and Abbatt (1999)	0.35[d]	234.15[d]	n/a	n/a	n/a	n/a
Bertram et al. (2000)	8.3[+]	235[a]	[5.6 11.0]	n/a	10k/min	1.5
Prenni et al. (2001)	0.6[+]	234.95[d]	n/a	n/a	1K/increment	0.2
Larson and Swanson (2006)	40[+]	237.15[a]	[30 50]	n/a	n/a	n/a
Stan et al. (2009)	80 [d]	236.25[a]	n/a	[235.35 237.15]	2~100K/sec	0.21
Earle et al. (2010)	2[+]	236.35[a]	[0.8 4]	[236 236.75]	n/a	n/a
	3.4[+]	236.35[a]	[1.2 10]	[236 236.75]	n/a	n/a
	5.8[+]	236.15[a]	[2 14]	[235.5 236.75]	n/a	n/a
Murray et al. (2010)	25[+]	236.25[a]	[10 40]	[235.9 236.7]	2.5K/min	0.6
	25[+]	236.05[a]	[10 40]	[234.75 237.75]	5K/min	0.6
	25[+]	235.75[a]	[10 40]	[236.45 237.75]	7.5K/min	0.6
	25[+]	235.51[a]	[10 40]	[234.45 237.75]	10K/min	0.6
Riechers et al. (2013)	53[m]	236.65[c]	[35 71]	[236.55 237.44]	1K/min	0.3
	63[m]	236.65[c]	[33 93]	[236.49 237.5]	1K/min	0.3
	82[m]	236.85[c]	[58 106]	[236.67 237.63]	1K/min	0.3
	85[m]	237.15[c]	[67 103]	[236.93 237.77]	1K/min	0.3
	96[m]	237.35[c]	[63 129]	[236.89 237.91]	1K/min	0.3

Table 1. Information regarding the details of the homogeneous ice nucleation experiments used in the comparison, including the size, the freezing temperature, as well as the cooling rate and uncertainty of the experiments. Homogeneous freezing temperature T_f, <a>: freezing temperature when half of the water droplets freezing $T_{50\%}$, <b>: freezing temperature when 95% of the water droplets freezing $T_{95\%}$, <c>: freezing temperature when most of the droplets freezing (peak signal) T_{Mode}, and <d>: not defined or provided by the experiments. Diameter of water droplets used in the experiments, <+> median size, <m> mean size, and <d> not provided by the

experiments.

Diameter μ±σ	**96±11(μm)**		**85±6 (μm)**		**82±8 (μm)**	
	Experiment values (K)	$T_{N_c=1}$ (K)	Experiment values (K)	$T_{N_c=1}$ (K)	Experiment values (K)	$T_{N_c=1}$ (K)
T_f^{onset}	237.91± 0.2	237.74	237.77± 0.2	237.53	237.63± 0.2	237.55
$T_f^{10\%}$	237.87± 0.2	237.59	237.76± 0.2	237.43	237.63± 0.2	237.42
$T_f^{50\%}$	237.4± 0.3	237.46	237.28± 0.3	237.34	237.13± 0.3	237.31
$T_f^{90\%}$	236.89± 0.3	237.31	236.93± 0.3	237.25	236.67± 0.3	237.18
T_f^{end}	N/A	237.05	N/A	237.11	N/A	236.97
Diameter μ±σ	**63±10 (μm)**		**53±6 (μm)**			
	Experiment values (K)	$T_{N_c=1}$ (K)	Experiment values (K)	$T_{N_c=1}$ (K)		
T_f^{onset}	237.50± 0.2	237.43	237.44± 0.2	237.17		
$T_f^{10\%}$	237.46± 0.2	237.23	237.40± 0.2	237.02		
$T_f^{50\%}$	236.94± 0.3	237.05	236.94± 0.3	236.88		
$T_f^{90\%}$	236.49± 0.3	236.83	236.55± 0.3	236.72		
T_f^{end}	N/A	236.4	N/A	236.46		

Table 2. Comparison between the experimental results of the fraction experiment from Riechers et al. (2013) and the theoretical estimates $T_{N_c=1}$ derived here.

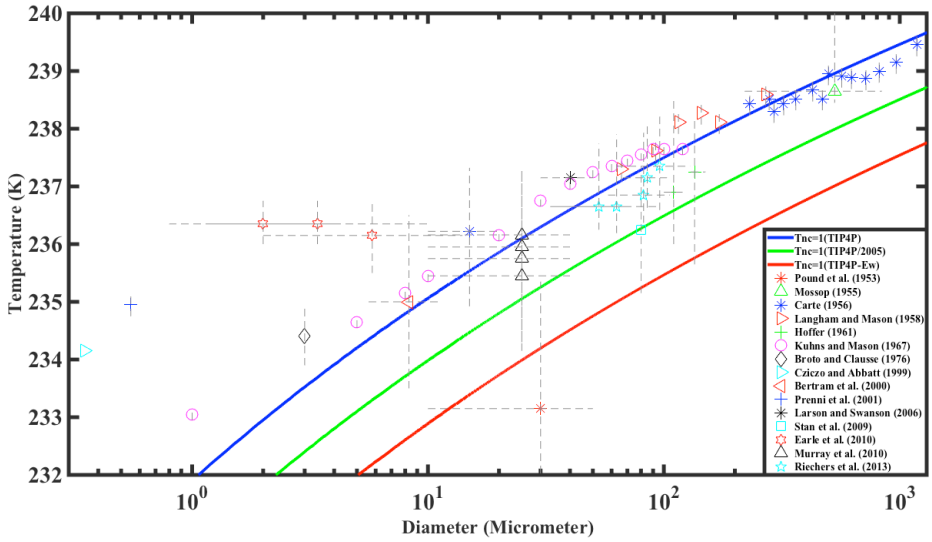


Figure 1. Freezing temperatures of pure water droplets: comparison between the approximations $T_{N_c=1}(V, a_w = 1)$ and the collected experimental data. Experimental data: the uncertainties and ranges of the drop size and the freezing temperatures are presented by the dotted line if information is provided by the studies (details in Table 1). 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.

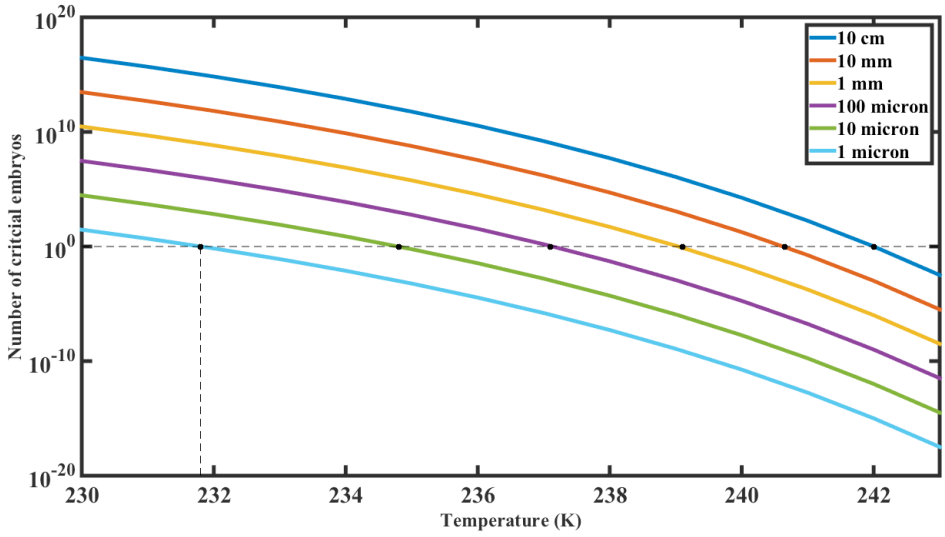
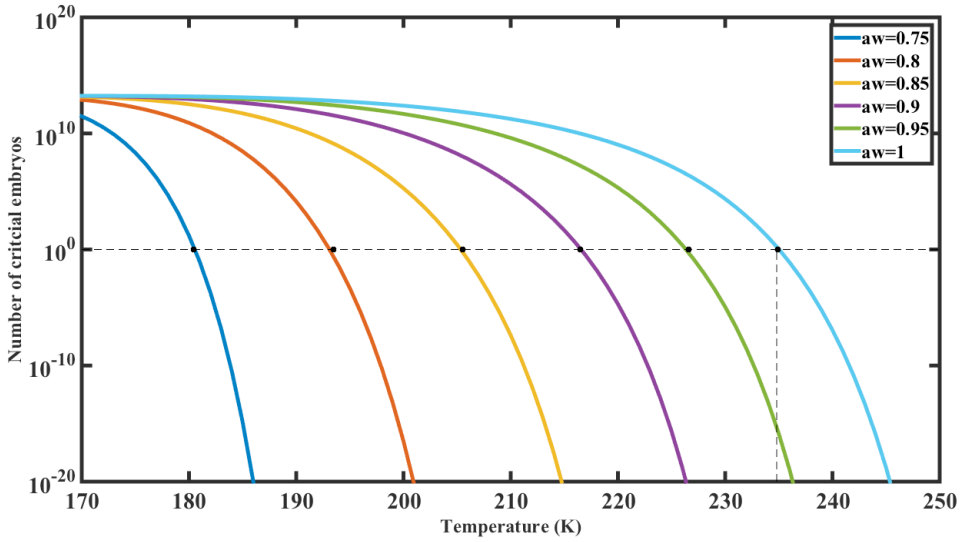


Figure 2. Mean number of critical embryos N_{c_mean} (by Eq. (1)) in a pure water droplet ($a_w = 1$) with different size (diameter) as a function of temperature. Solid

645 circle: the approximations $T_{N_c=1}(V,a_w)$ derived by Eq. (2) (using $\sigma_{i/w,e}$ from TIP4P

646 model).



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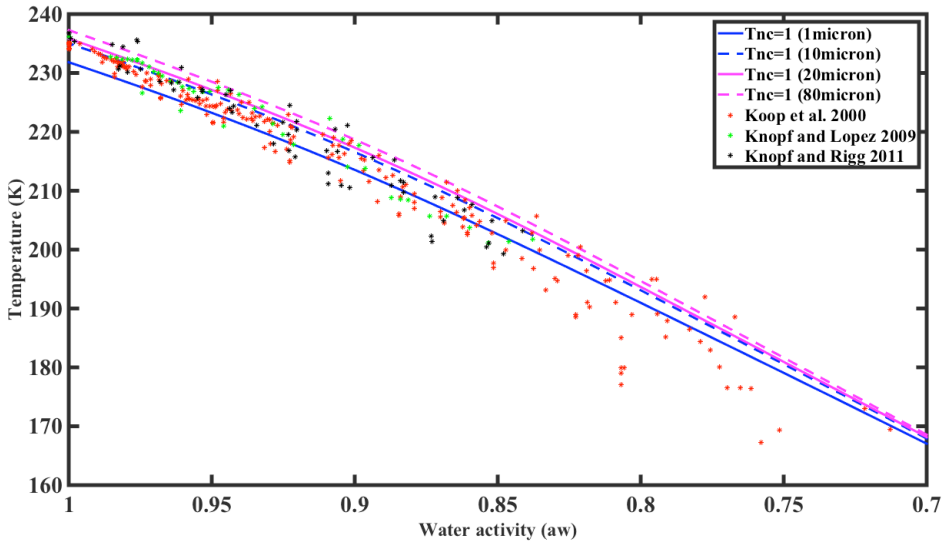
648 Figure 3. Mean number of critical embryos N_{c_mean} (by Eq. (1)) in a solution droplet

649 (diameter=1μm) with different water activity as a function of temperature. Solid circle:

650 the approximations $T_{N_c=1}(V,a_w)$ derived by Eq. (2) (using $\sigma_{i/w,e}$ from TIP4P

651 model).



652

653 Figure 4. Comparison between the experimental data of freezing temperatures of

654 solution droplets (Koop et al., 2000; Knopf and Lopez, 2009; Knopf and Rigg, 2011)

and the approximation $T_{N_c=1}(V, a_w)$.

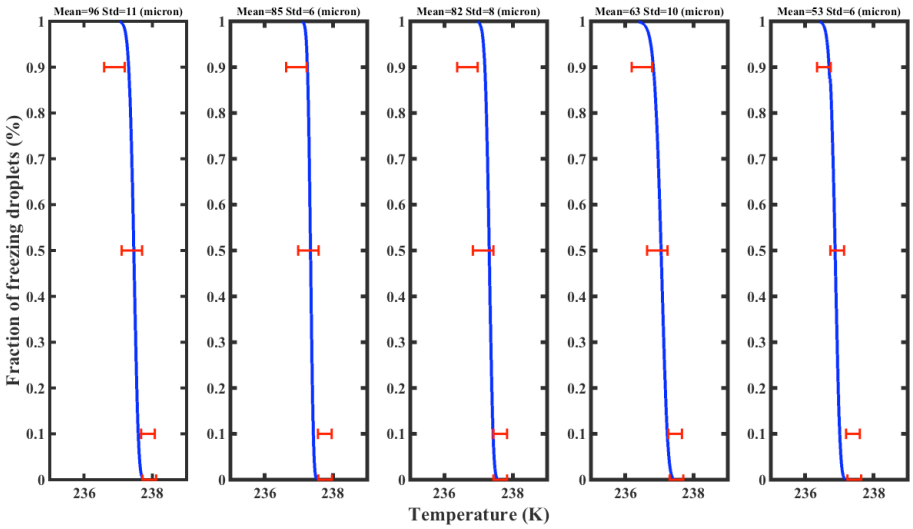


Figure 5. Comparison between the experimental results of the fraction experiment from Riechers et al. (2013) and the theoretical estimates derived here. Red: experimental results with uncertainties from Riechers et al. (2013). Blue: theoretical estimates ($\sigma_{i/w,e}$ from TIP4P model).