Response to Comments

1 Referee 1

I thank Dr. Djikaev for the comments on the manuscript. They are adressed in detail below.

Comment by the Reviewer:
Clearly, this is much more adequate qualitative picture of ice nucleation in liquid water.However, the new approach to evaluating ΔGact , proposed by the author, is still based on some elements of the "older" CNT model. Namely, the author's approach apparently still considers the "collective rearrangement of several water molecules ... that ... facilitates" their "incorporation into the preexisting ice lattice ... " as occurring by the"...direct interface transfer" via diffusion of water molecules from the vicinal liquid to the ice crystal.

In a more realistic model the incorporation of water molecules into the ice lattice is likely to occur via both translational and orientational fluctuations in the immediate vicinity of the ice crystal. The formation of "frozen" hydrogen bonds is initially thermodynamically unfavorable, but it does occur due to collective "translational and orientational" fluctuations of vicinal water molecules (just like in "vapor-to-liquid" nucleation the initial steps of the formation of "liquid" clusters are thermodynamically unfavorable but do occur due to fluctuations). Note, that the translational fluctuation may involve a water molecule moving not only in the liquid-to-lattice" direction, but also in the "lattice-to-liquid" direction.

Response: The picture suggested by the reviewer is consistent with the proposed model. There are some limitations in using the framework of classical nucleation theory. One of them is, as the reviewer states, that the flux of water molecules is parameterized in a diffusion-like manner. However in the proposed model not only the random jump of water molecules is accounted for, but also the probability that ice-like structures are formed during those jumps. Thus although parameterized in the form of a diffusion coefficient, the proposed model contains the essential elements of the physics behind the formation of the interface, namely the fluctuation character of the vicinal molecules and the formation of "frozen" hydrogen bonds. Section 2.1 has been rewritten to emphasize this.

Comment by the Reviewer: Author's approach to the derivation of a thermodynamic expression for ΔGact (subsection 2.1) is largely based on the application of the macroscopic classical thermodynamics to microscopic subsystems (consisting of a few molecules). First of all, this must be substantiated and all the assumptions must be explicitly stated.

Response: The derivation of the activation energy is based on the fluctuation theorem (FT) which is a result non-reversible statistical thermodynamics instead of "classical macroscopic thermodynamics" as the reviewer suggests. FT relates the macropcospic response of a thermodynamic system to its microscopic dynamics under the assumption that the latter is stochastic and Markovian. These are typically valid assumptions at conditions away from the glass transition temperature. A further assumption is that of microscopic reversibility, which requires that thermodynamic potentials can be locally defined within the liquid. This assumption was also used to write the work dissipated during interface transfer. This is guaranteed near equilibrium, however in non-equilibrium conditions only holds for systems starting at equilibrium. Thus the application of FT for interface transfer is valid only if each molecule can be considered in equilibrium with its local environment within the liquid, which is again valid away from the glass transition temperature. Finally, a heuristic approach was used to write an expression for the dissipated work, which basically involves counting the minimum number of different ways in which four-coordinated water can be built. This is a simple geometric argument (akin for example to bond-counting), and is based on the result of Adam and Gibbs (1965) who showed that the transition probability within liquids is determined by the size of the smallest cooperative region. To address the reviewer's concern section 2.1 has been rewritten putting additional emphasis on the model's approximations.

Comment by the Reviewer: Secondly, the statements about the violation of the Second Law of the thermodynamics do not seem to be correct. The Second Law of Thermodynamics (as all thermodynamics) is strictly speaking applicable only to physical system in the thermodynamic limit (with the number of molecules N → ∞ and volume V → ∞ so that N/V remains finite). It does not apply to microscopic systems (a few molecules) and it does not forbid the decrease in the entropy in a non-isolated microscopic sub-system of a macroscopic system.

Response: The picture of an "apparent" violation of the second law was used as resource to describe the spontaneous organization of molecules into ice-like structures, which in a macroscopic system would be impossible (what the reviewer refers to as "thermodynamically unfavorable"), but that are possible in small systems. As mentioned above it is possible to write thermodynamic potentials for microscopic systems near the equilibrium where microscopic reversibility holds. The statements have been modified to clarify these points.

Comment by the Reviewer: In section 2, outlining the theoretical basis of the proposed model, it is assumed (as often done in CNT), that the ice crystal is formed away from the air-liquid interface so that it is not affected by surface tension effects. However, most of the experimental work on crystal nucleation in water is performed by observing the freezing of droplets...

Therefore, the conventional "semi-empirical" (page 18154) application of CNT to ice nucleation is based on empirical values of theoretical parameters (such as σ_{iw} and ΔG_{act} extracted by fitting the experimental results for the crystal nucleation rate in droplets with a CNT expression... Typical sizes of experimental (as well as atmospherically relevant) droplets allow one to assume that the formation of a single crystal nucleus in a droplet immediately leads to the crystallization of the latter, i.e., the time of growth of a crystal nucleus to

the size of the whole droplet is negligible ...

Response: A significant surface-to-volume ratio in small droplets does not guarantee a predominance of surface based nucleation. The reviewer has made several arguments in favor of a significant role of surface stimulated nucleation (SSN) in ice formation, however there are experimental results both supporting and challenging this view (Sigurbjörnsson and Signorell, 2008; Kay et al. 2003). SSN requires a germ growing in a particular orientation so that at least one its "facets" is aligned with the droplet-vapor interface. The reviewer has calculated the probability of such rare process and showed that SSN would still be thermodynamically favored over volume-based nucleation. However this result requires several assumptions that have not been shown unequivocally to hold. For example it is assumed that the exposing interface aligned with the droplet-vapor interface has a well-defined interfacial tension with a value similar to that of the bulk. Also the flux of water molecules to the nascent germ in volume and surface based processes is assumed to be the same. However this is not guaranteed as one can imagine that the water molecules between the growing ice and the droplet-vapor interface would be subject to a confinement effect reducing their mobility. Finally, as it is shown in this work, at very low temperature the nucleation rate is increasingly less controlled by thermodynamics and more dependent on the preexponential factor (e.g., the activation energy), which would limit the effect of SSN on ice formation.

It is certainly out of the scope of this work to settle the debate on the role of SSN in ice formation. To address the reviewer's concern it has been emphasized in the revisited work that all expressions are applicable to cases where ice nucleation is predominantly volume-based, and that only experimental results where nucleation rates were interpreted as volume-based are used. It is however acknowledged in the revisited work that more research is needed on this topic.

Comment by the Reviewer: The goal of the author is to derive a thermodynamic expression for the activation energy ΔGact in order to avoid considering it as an adjustable parameter in the CNT. However, the final equation (14) for ΔG_{act} contains parameters E and T_0 which are themselves adjustable parameters in the Vogel-Fulcher-Tammann equation, eq.(12). The question arises if the goal has been achieved to the full extent or not...

Response: It has, to its full extent. E and T_0 are not part of CNT, but define the bulk diffusion coefficient. They can be measured and determined independently of CNT. They are akin to constants used other correlations for physical properties like viscosity, heat of fusion, density and the like. E and To are not adjustable parameters; their values cannot be adjusted to match measured nucleation rates without losing their theoretical meaning. Moreover, E and To are related to the configuration entropy of water, and in principle also admit a thermodynamic derivation.

2 Referee 2

I thank the reviewer for the comments on the manuscript. They are addressed in detail below.

Comment by the Reviewer: My second major remark refer to the desig-

nation of the new formulation for the activation energy as a "phenomenological model". In my understanding, "phenomenological" means being based on observations. However, the author stresses that there is no empirism entering this expression (which I'm not too sure about, see below). Wikipedia gives the following definition: "A phenomenological model (sometimes referred to as a statistical model) is a mathematical expression that relates several different empirical observations of phenomena to each other, in a way which is consistent with fundamental theory, but is not directly derived from theory. In other words, a phenomenological model is not derived from first principles." - I don't think this is what describes the approach of the author, and the wording should be changed (or justified).

Response: The proposed model is phenomenological in the sense that it is derived from ascribing certain characteristics to the process of interface transfer (e.g., collective behavior, work dissipation, and a defined interface) as heuristics to reach a thermodynamic view of the ice germ growth. A true mechanistic description of the interface transfer process requires an molecular dynamics approach. The definition given by the reviewer is somehow too strict, and may stem from an older view where molecular dynamics simulations were not available and approximations to the behavior of microscopic systems were considered full mechanistic theories. To address the reviewer's concern the model is referred simply as "theoretical" in the revisited work.

Comment by the Reviewer: Thirdly, the derived expression oddly is very similar to the Zobrist et al (2007) formulation (compare equations 14 and 18). When eq. 14 is evaluated at $aw = aw_{eq}$, the two expressions differ only by the factor T=(T .. 118K). This similarity is certainly no coincidence and should be discussed further.

Response: The two expressions are fundamentally different. Equation 14 is never evaluated at $a_w = a_{w,eq}$, since it implies equilibrium conditions for which nucleation is not possible. Secondly, the apparent similarity originates because the bulk diffusion coefficient is expressed by the same relation, that is the VFT equation. However in the case of expressions like the one derived by Zobrist et al. (2007) the relation between D_∞ and ΔG_{act} is hypothesized a priori while in this work it results from the explicit consideration of the thermodynamics of interface transfer. This has been addressed in the revisited work.

Comment by the Reviewer: Furthermore, this means that the new expression contains the same empirical fit parameters (E, T0) which are criticized in the Zobrist formulation.

Response:

The criticism raised on expressions like the one formulated by Zobrist et al (2007) refers to the a priori assumtion that the activation energy for interface transfer must have the same form as that of the bulk, neglecting the dynamics of the interface, not on the usage of the diffusion coefficient. The parameters E and To describe the bulk diffusion coefficient, a physical property of water. They are not degrees of freedom of CNT and are not found by matching nucleation rate measurements. Other physical properties like the equilibrium water activity, the water density and the enthalpy of fusion also have fitted parameters. It is not a claim of this work that besides the activation energy all other physical properties of water can also be obtained from the proposed model.

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Comments by the Reviewer:

- page 18158, line 15: 'the probability of such collective arrangement is given by $f(T, a_{\mathrm{W}})$.' This is a fundamental point for the further derivations, but it is not well explained why this probability should be exactly the same as the factor in the diffusion coefficient (eq. 5).

- page 18160, line 6: Again, why is $f(T, a_{\mathrm{W}}) = P(W)$

Response: The function $f(T, a_{\mathrm{W}})$ is introduced to distinguish between the bulk diffusion coefficient D_{∞} and the diffusion coefficient across the interface, D. The latter must be taken as an "effective diffusivity", since it parameterizes procesess that are not necessarily diffusive in nature (e.g., molecular rearragement). In the view proposed in this work the breaking of hydrogen bonds is a necessary but not sufficient condition for the incorporation of water molecules into the ice germ. Molecular rearragement is required for interface transfer and requires surpassing an energy barrier. The molecules in the liquid fluctuate in different ways, some of which lead to spontaneous organization. The probability of a spontaneous process occurring in a given direction is determined by the work required for such fluctuation, W. Since interface transfer requires the spontaneous organization of water molecules into ice-like structures with probability described by $f(T, a_{\mathrm{W}})$, it follows that if W describes the work required for collective rearragement, the probability of fluctuation $P(W)$ must be equal to $f(T, a_{\mathrm{W}})$. This explanation has been added to Section 2.1.

Comments by the Reviewer: page 18163, line 24ff: As discussed here, it was shown by Ickes et al (2015) that the combination of the Z07 activation energy and the Reinhardt and Doye (2013) surface tension gives the best agreement to observations of the freezing rate, including observations at T ¡ 200K. So if this combination was used in- stead of Z07 together with the B14 surface tension, this would agree much better to observations than what is shown in Fig. 4. This figures displays an unfair comparison.

Response: The surface tension from B14 was used in all expressions to highlight differences due solely to the activation energy. The comparison is not unfair. Using the expression of Reinhardt and Doye (2013) leads to lower nucleation rates than when using the expression from B14. At 220 K and $a_{\mathrm{W}} = 1$, Fig 17 of Ickes et. al 2015 gives J_{hom} around 10^{23} m^{-3}s^{-1}, whereas the value shown in Fig 4 is about 10^{27} m^{-3}s^{-1} (after units conversion). The latter is closer to the experimental results. To address the reviewer's concern J_{hom} calculated using the expression of Reinhardt and Doye (2013) has been added to Fig 4.

Comments by the Reviewer: Please add more details to the caption of Fig. 1 (e.g. what are the bright and dark blue spheres? what are states 1 und 2? Why is Gice,eq higher than Gice,1 and Gice,2 ?).

Response: Figure 1 represents an idealization of the process described in this work. However I agree that the cartoon adds little to the discussion and may instead lead to confusion. It has been removed from the plot and Fig. 1 replaced with a simpler Figure.

Comments by the Reviewer: Why is the temperature dependence of the

data shown in Fig. 4b very different from the predicted temperature dependence?

Response: This is already discussed in Section 3. The theoretical reasons are unclear. However another possibility may be a slight drift in a_w during the experimental measurements. The data shown in Fig. 4b was obtained with similar techniques in which the initial a_w is set but is not controlled during the experiment (in fact in both cases the initial a_w is reported, instead of a_w at the point of freezing). It is shown in Fig. 4b and discussed in Section 3 that a decrease in a_w of 0.02 during the experiments would introduce a spurious temperature dependency and be enough to explain the discrepancy between the theory and the measurements.

However I agree that the discrepancy is troubling. Additional experimental results from Larson and Swanson, (2006) for the homogeneous freezing of ammonium sulfate were added to the Figure. They show a stronger dependency on T than the data of Alpert et al. (2011), although still lower than the predicted by the model. However the uncertainty in the temperature in the Larson and Sanwson, (2006) data is too large to establish a statistically significant difference. It is acknowledged that further research is required to elucidate this point.

Comments by the Reviewer:

- Please give units for the variables in Table 1.

- It should be mentioned that the B14 formulation of surface tension is also a fit to observations.

- page 18152, line 14: temperature → temperatures

- page 18155, line 16: into → on?

- page 18164, line 10: insert 'of' before 'Jeffery and Austin'

- page 18179, Fig. 4: Please use a distinct line style and line color instead of the minuscule crosses for 'CNT, this work'.

Response: All technical comments have been addressed in the revisited work.

3   Referee 3

I thank the reviewer for his/her assessment.

Comment by the Reviewer: The manuscript is well written throughout, except in the Activation energy section 2.1. The reviewer found this section confusing to follow and thus recommends a clearer discussion and mathematical development in the text with corresponding clarifications reflected in Figure 1. In particular, identifying and labeling the connection between the specific activation energy for interface transfer (Dmu), DG, and W.The free energies Figure: Please change energy units in Figure to kcal/mol or kJ/mol...

Response: Section 2.1 has been rewritten to clarify several points raised during this discussion. Figure 1 has been simplified to make it clearer, explicitly showing the relation between W and ΔG.

Comment by the Reviewer: ... discuss how difficult it is, from a fundamental point of view, to get the nucleation free energetics of these processes correct.

Response: This was dicussed in Section 4. It is acknowledged that the specification of water properties at very low temperature is very difficult and in general all studies use some form of thermodynamic continuation to define $a_{\mathrm{w,eq}}$ and Δh_{f} for $T < 235$ K. This point has been emphasized in the revisited paper.

Comment by the Reviewer: It would be nice to see the differences in the critical germ sizes predicted between the models as well as those deduced from experiment.

Response: The activation energy does not affect the critical germ size. The requested comparison is shown in Barahona (2014, Figure 5). The activation energy does affect the measured freezing temperature, which may translate into a different critical size estimated at the point of freezing. However this is highly dependent on the nucleation threshold chosen to calculate the freezing temperature and therefore may be misleading.

Comment by the Reviewer: Furthermore, the author can make a correspondence between the CNT interfacial free energy and the NNF formalism and plot the effective surface tension of both for comparison.

Response: This is shown in Figure 2 of Barahona (2014). The interfacial tension in NNF is not modified by the activation energy since it is obtained without fitting nucleation rates. Thus the requested figure would remain unchanged from B14.

Comment by the Reviewer: The author expresses the significance in the NNF compared to CNT, in that the former if free from the bias induced by uncertainties in the parameterization of the interfacial free energy between water and ice. However, the NNF model has expanded the number of variables (i.e., degrees of freedom) compared to CNT, and hence it isn't too surprizing that better agreement over a broad temperature range is found between prediction and experiment.

Response: The number of degrees of freedom is not increased. None of the parameters of the model presented is obtained by fitting nucleation rates and therefore are not degrees of freedom in the same sense as in CNT. Certainly the physical properties of water are not degrees of freedom either since they are determined independently. It was shown in B14 that the parameters Γ_w and s used in the definition of the interfacial energy must be restricted to narrow ranges to be physically valid. They are not found by fitting nucleation rates but instead from physical arguments. Varying them over a wider range than discussed in Section 3.5 of B14 would invalidate the theory.

Comment by the Reviewer:
The reviewer suggests the author consider a sensitivity analysis, similar to previous work by the author, of his new NNF model on the relevant variables. This will help to better constrain the parameters as well as determine which variables have the most profound influence on the homogeneous nucleation rate.

Response: The sensitivity analysis regarding the effect of uncertainty in the interfacial energy on J_{hom} was carried out in Barahona (2014). As shown in

Figure 8 of B14 the uncertainty in J_{hom} from variation in Γ_w and s is about two orders off magnitude and decreases with decreasing T since the nucleation rate becomes more dependent on ΔG_{act} and less dependent on the interfacial energy (this is emphasized in the revisited paper). Regarding the uncertainty in the activation energy, it is moslty a function of $a_{\text{w,eq}}$ and n_t. It is acknowledged that $a_{\text{w,eq}}$ may be uncertain at low T. The approximation used in this work is supported by experimental results (e.g., Koop et al . (2000)). Regarding n_t it is estimated that the preexponential factor would increase by about two orders of magnitude by a change in n_t from 16 to 15. However a plausible range of variability for n_t is hard to estimate since the characteristics of the transient state are not known. Essentially a value of n_t less than 16 would indicate that some of the rearrangement routes to form four-coordinated water are prohibited. More research is needed to elucidate this point. Another assumption that may impact the model is that of microscopic reversibility which becomes weaker at low T since water dynamics becomes slower and it cannot be always assumed that the water molecules are in equilibrium within the bulk liquid. Unfortunately giving a plausible range of variability is challenging since deviations from equilibrium are difficult to quantify, even with molecular dynamics methods. This analysis has been included in Section 3 of the revisited paper.

Comment by the Reviewer: As a minor issue, the data points represented in Figure 4 are difficult to discern. Perhaps some arrows might help?
Response: This has been corrected.

Comment by the Reviewer:
Finally, the author should provide some comments on the connection between the phenomenological thermodynamics in the new NNF and a more rigorous statistical mechanics formulation in terms of configurational partition functions of nucleating clusters from the liquid. This can aid in the identification of relevant reaction coordinates, interaction energies, fields, etc. so as to bridge the continuum and molecular scales.
Response:
Section 2.1 has been thoroughly expanded to give a better representation of the processes involved in interface transfer. However a rigorous non-equilibrium statistical mechanics formulation of the partition function is non trivial and still matter of research. Such approach would be addressed in future studies.

References

[Kay et al.(2003)Kay, Tsemekhman, Larson, Baker, and Swanson] Kay, J., Tsemekhman, V., Larson, B., Baker, M., and Swanson, B.: Comment on evidence for surface-initiated homogeneous nucleation, Atm. Chem. Phys., 3, 1439–1443, 2003.

[Larson and Swanson(2006)] Larson, B. H. and Swanson, B. D.: Experimental investigation of the homogeneous freezing of aqueous ammonium sulfate droplets, J. Phys. Chem. A, 110, 1907–1916, 2006.

[Sigurbjörnsson and Signorell(2008)] Sigurbjörnsson, Ó. F. and Signorell, R.: Volume versus surface nucleation in freezing aerosols, Physical Review E, 77, 051 601, 2008.

Thermodynamic Derivation of the Energy of Activation for Ice Nucleation

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Abstract

~~The activation energy~~Cirrus clouds play a key role in the radiative and hydrological balance of the upper troposphere. Their correct representation in atmospheric models requires an understanding of the microscopic processes leading to ice nucleation. A key parameter in the theoretical description of ice nucleation is the activation energy, which controls the flux of water molecules from the bulk of the liquid to the solid during the early stages of ice formation. In most studies it is estimated by direct association with the bulk properties of water, typically viscosity and self-diffusivity. As the environment in the ice-liquid interface may differ from that of the bulk this approach may introduce bias in calculated nucleation rates. In this work a ~~phenomenological~~ theoretical model is proposed to describe the transfer of water molecules across the ice-liquid interface. Within this framework the activation energy naturally emerges from the combination of the energy required to break hydrogen bonds in the liquid, i.e., the bulk diffusion process, and the work dissipated from the molecular rearrangement of water molecules within the ice-liquid interface. The new expression is introduced into a generalized form of classical nucleation theory. Even though no nucleation rate measurements are used to fit any of the parameters of the theory the predicted nucleation rate is in good agreement with experimental results, even at temperature as low as 190 K where it tends to be underestimated by most models. It is shown that the activation energy has a strong dependency on temperature and a weak dependency on water activity. Such dependencies are masked by thermodynamic effects at temperatures typical of homogeneous freezing of cloud droplets, however may affect the formation of ice in haze aerosol particles. The ~~phenomenological model introduced in this work~~ new model provides an independent estimation of the activation energy and the homogenous ice nucleation rate, and it may help to improve the interpretation of experimental results and the development of parameterizations for cloud formation.

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1 Introduction

Ice nucleation in cloud droplets and aerosol particles leads to cloud formation at low ~~temperature~~ <u>temperatures</u> and promotes cloud glaciation and precipitation (Pruppacher and Klett, 1997). In absence of ice nuclei, it proceeds by homogeneous freezing. Modeling and experimen-
5 tal studies suggest a significant contribution of homogeneous freezing to the formation of clouds in the upper troposphere (Barahona and Nenes, 2011; Barahona et al., 2014; Gettelman et al., 2012; Jensen et al., 2013). The parameterization of ice nucleation is critical to the proper representation of clouds in atmospheric models. In most cloud models it is done using empirical correlations (e.g., Lohmann and Kärcher, 2002; Kärcher and Burkhardt,
10 2008; Barahona et al., 2010, 2014). The most common approach uses the so-called water activity criterion (Koop et al., 2000) where the homogeneous nucleation rate, J_{hom}, is parameterized in terms of the difference between the water activity, a_{w}, and its equilibrium value, $a_{\text{w,eq}}$. The greatest advantage of the water activity criterion is that it is independent of the nature of the solute and therefore facilitates the formulation of general param-
15 eterizations of ice nucleation (Barahona and Nenes, 2008; Kärcher and Lohmann, 2002; Liu and Penner, 2005).

Empirical correlations provide a simple way to parameterize ice nucleation however provide limited information on the nature of ice formation. Theoretical models help to elucidate the mechanism of ice nucleation and to explain and extent experimental results.
20 Over the last decade molecular dynamics (MD) and other detailed methods have provided an unprecedented look at the microscopic mechanism of ice formation (Espinosa et al., 2014). It is known now that the formation of stable ice germs requires the cooperative rearrangement of several molecules (Matsumoto et al., 2002; Moore and Molinero, 2011) and is preceded by structural transformations within the liquid phase (Moore and Molinero, 2011;
25 Bullock and Molinero, 2013). Detailed experiments and MD simulations have shown that instead of forming a single stable structure, several metastable ice structures likely exist during the first stages of ice nucleation (Moroni et al., 2005; Malkin et al., 2012; Russo et al., 2014). There is also a profound relation between anomalies in the properties of water at

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low temperature and the formation of ice (Buhariwalla et al., 2015), and the relation between low and high density regions within supercooled water and the onset of ice nucleation is starting to be elucidated (Kawasaki and Tanaka, 2010; Singh and Bagchi, 2014; Bullock and Molinero, 2013).

Phenomenological ~~Some theoretical~~ models use mechanistic assumptions to describe the formation of ice. Although less detailed in nature than MD, they are more amenable to the development of parameterizations and to the interpretation of experimental results. The quintessential example of such models is the classical nucleation theory, CNT. According to CNT ice formation proceeds by spontaneous density fluctuations within the liquid phase forming an initial ~~stable~~ metastable ice germ, which then grows by incorporation of water molecules from an equilibrium cluster population (Kashchiev, 2000). CNT provides a framework to understand ice nucleation and has been instrumental in the development of parameterizations from experimental data (e.g., Pruppacher and Klett, 1997; Khvorostyanov and Curry, 2009; Murray et al., 2010). On the other hand, J_{hom} estimated with CNT and using independent estimates of thermodynamic parameters typically results in stark disagreement with measurements (Pruppacher and Klett, 1997; Kawasaki and Tanaka, 2010; Barahona, 2014). Thus CNT is commonly used semi-empirically, fitting several parameters of the theory, most commonly the liquid-ice interfacial tension, σ_{iw}, and the activation energy, ΔG_{act}, to measured nucleation rates (e.g., Jeffery and Austin, 1997; Khvorostyanov and 2004; Murray et al., 2010; Ickes et al., 2015).

Using CNT semi-empirically has the disadvantage that the theory cannot be decoupled from experimental measurements of J_{hom}. It has been shown that σ_{iw} obtained by fitting CNT to measured nucleation rates tends to be biased high to account for mixing effects neglected in common formulations of CNT (Barahona, 2014). Moreover, the dependency of σ_{iw} on temperature tends to depend on the value of other fitted parameters of the theory (Ickes et al., 2015). Recently Barahona (2014) (hereinafter B14) introduced a mechanistic model of the ice-liquid interface in terms of thermodynamic variables, without fitting CNT to measured nucleation rates. This was done by hypothesizing the existence of a transition layer around the germ with chemical potential defined by the entropy of the ice and

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the enthalpy of the liquid, and using the model of Spaepen (1975) to define the interface thickness. This approach was termed the negentropic nucleation framework (NNF). Recent MD simulations showing the existence of a low density region around the ice germ support the NNF model (Singh and Bagchi, 2014). Introducing NNF into CNT and correcting the

5 nucleation work for mixing effects resulted in good agreement of predicted J_{hom} with experimental results (Barahona, 2014). NNF was also shown to be consistent with the water activity criterion. On the other hand, even with the inclusion of NNF ~~into~~ in CNT, the theory predicts a maximum in J_{hom} for pure water at around 210 K. Such behavior is at odds with experimental results (Manka et al., 2012), and is ascribed to a strong increase in the

10 activation energy as temperature decreases.

The activation energy controls the flux of water molecules from the bulk of the liquid to the ice germ (Kashchiev, 2000). Most studies estimate ΔG_{act} either by direct fit of CNT to measured nucleation rates, or from bulk estimates of viscosity, self-diffusivity and dielectric relaxation time (Ickes et al., 2015). The association of bulk properties with ΔG_{act}

15 relies on the assumption that the diffusion across the liquid-ice interface is similar to the molecular diffusion in the bulk of the liquid (Kashchiev, 2000). MD results however suggest that the properties of water in the vicinity of the ice germ differ from the bulk, casting doubt into such approach (e.g., Kawasaki and Tanaka, 2010; Singh and Bagchi, 2014). Unlike for the interfacial energy where several theoretical models have been proposed (e.g.,

20 Spaepen, 1975; Digilov, 2004; Barahona, 2014), the ~~phenomenological~~ theoretical treatment of ΔG_{act} has been limited. One possible reason is that interface transfer is associated with random fluctuations near the ice-liquid interface, and therefore difficult to treat in terms of macroscopic variables. However several relations allow to describe the evolution of fluctuating systems in terms of measurable variables and their relaxation rates. Among them the

25 fluctuation-dissipation theorem that describes the relation between global and local perturbations (Jou et al., 2010), and the fluctuation theorem describing the work distribution in a fluctuating system (Crooks, 1999) have found widespread application in describing the evolution of small systems (Bustamante et al., 2005). With few exceptions (e.g., Røsjorde et al.,

2000), such relations however have not made their way into descriptions of the ice nucleation process.

In this work a ~~phenomenological~~ theoretical description of the ~~diffusional~~ process leading to the growth of ice germs during ice nucleation is advanced. The proposed model relies on a non-equilibrium view of the interface transfer and leads to the first ~~phenomenological~~ thermodynamic description of the activation energy for ice nucleation.

2 Theory

This section presents the theoretical basis of the proposed model. The ice germ is assumed to form away from the air-liquid interface so that it is not affected by surface tension effects. ~~The water molecules in the liquid phase are assumed to be~~ All the facets of the ice germ are assumed to remain within the bulk of the liquid so that surface stimulated nucleation (Djikaev, 2008) does not take place. The consequences of this assumption are discussed in Section 3. The water molecules incorporated into the ice germ are in close proximity to the ice-liquid interface ~~so that~~ and diffusion through the bulk of the liquid water can be neglected. This is justified as it is energetically more favorable to incorporate molecules close to ice germ than those far away from it. ~~Direct interface transfer is thus the dominant growth mechanism of the ice germ (Kashchiev, 2000).~~ Following these considerations the homogeneous nucleation rate can be written in general form as (Kashchiev, 2000),

$$J_{\mathsf{hom}} = \frac{Z f^*}{v_w} \exp\left(-\frac{\Delta G_{\mathsf{hom}}}{k_B T}\right), \tag{1}$$

where v_w is the molecular volume of water in the bulk, f^* is the impingement factor of the water molecules to the ice germ, and Z is the Zeldovich factor given by (Kashchiev, 2000),

$$Z = \left[\frac{\Delta G_{\mathsf{hom}}}{3\pi k_{\mathsf{B}} T \left(n^*\right)^2}\right]^{1/2}. \tag{2}$$

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where n^* ins the number of water molecules in the ice germ. Other symbols are defined in Table 1. The nucleation work is given by (Barahona, 2014),

$$\Delta G_{\text{hom}} = \frac{4}{27} \frac{\left[\Gamma_w s \left(\Delta h_f - \Gamma_w k_B T \ln a_w\right)\right]^3}{\left[k_B T \ln \left(\frac{a_w^2}{a_{w,\text{eq}}}\right)\right]^2}. \tag{3}$$

where $\Gamma_w = 1.46$ is the coverage of the ice-water interface, and $s = 1.105$ defines the lattice
5 geometry of the ice germ. The value of Γ_w results from the explicit construction of the interface following the rules: (i) maximize the density, (ii) disallow octahedral holes and (iii) preference for tetrahedral holes (Spaepen, 1975). The value of s is obtained assuming that the germ has a staggered structure lying somewhere between cubic and hexagonal ice (Malkin et al., 2012). Compared to common expressions for ΔG_{hom} derived from CNT,
10 Eq. (3) has the advantage that it does not depend on an explicit parameterization of σ_{iw}, for which there is large uncertainty. Even though it is formulated on a purely theoretical basis, application of Eqs. (1) to (3) has been shown to reproduce observed freezing temperatures (Barahona, 2014).

The impingement factor is the frequency of attachment of water molecules to the ice
15 germ. For steady state nucleation it is given by (Kashchiev, 2000),

$$f^* = \frac{\gamma D Z_1 \Omega}{d_0}, \tag{4}$$

where $\gamma \approx 1$ is the sticking coefficient, D the diffusion coefficient for interface transfer, Ω the surface area of the germ, d_0 the molecular diameter and $Z_1 \approx v_w^{-1}$, the monomer concentration. In this work D is understood as an "effective diffusivity" since it parameterizes
20 processes that are not necessarily diffusive in nature, like molecular rearrangement and reorientation, but that result in the incorporation of water molecules to the ice germ.

Uncertainty in the determination of f^* results mostly from the calculation of D, which may differ from the bulk self-diffusivity of water. The most commonly used approximation to

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D was derived from transition state theory by Turnbull and Fisher (1949) (see Section 2.3), who assumed that the activation energy for interface transfer is similar to that of the bulk liquid, however the vibration frequency is that of an elemental reaction in the gas phase. This approximation tends to underpredict the preexponential factor in Eq. (1) at low temperature (Ickes et al., 2015). Here an alternative expression is proposed assuming that D can be expressed in the form,

$$D = f(T, a_{\mathrm{w}}) D_{\infty}, \tag{5}$$

where D_{∞} is self-diffusivity of water in the bulk. The function $f(T, a_{\mathrm{w}})$ is introduced to distinguish between the bulk diffusion coefficient D_{∞} and the diffusion coefficient across the interface, D. Since D_{∞} has been measured to $T \sim 180$ K (Smith and Kay, 1999), D can be calculated provided that a suitable form $f(T, a_{\mathrm{w}})$ is known. In principle $f(T, a_{\mathrm{w}})$ can be found by fitting nucleation rate measurements. It is however desirable to obtain an expression for $f(T, a_{\mathrm{w}})$ independent of J_{hom}. To this end a heuristic approach is developed as follows.

2.1 Activation Energy

Similarly to Turnbull and Fisher (1949) it is assumed that interface transfer requires the formation of a transient state. However instead of each molecule moving independently across the interface, the formation of the transient state requires the collective rearrangement of several water molecules. The probability of such collective arrangement is given by $f(T, a_{\mathrm{w}})$. This view does not imply that water is incorporated in clusters to the ice, but rather that the rearrangement of the molecules facilitates the incorporation of each molecule into the preexisting ice lattice (Fig. 1). Such lattice is assumed to be the exposing surface of a metastable ice germ. In other words, the breaking of hydrogen bonds is a necessary but not sufficient condition for the incorporation of water molecules into the ice germ. Molecular rearrangement is required for interface transfer and requires surpassing an energy barrier.

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This view is supported by MD simulations showing the increase in the fraction of four-coordinated water prior to nucleation (e.g., Moore and Molinero, 2011; Matsumoto et al., 2002) and theoretical models where the self-diffusion of supercooled liquids is controlled by their configurational entropy (Adam and Gibbs, 1965).

5   An key aspect of the transient state is that it has a higher free energy than that of bulk water, which stems from ~~a~~ the lowering of the entropy as molecules organize into an ice-like structure and an increase of the enthalpy from the breaking of hydrogen bonds (e.g., Bullock and Molinero, 2013). ~~In a macroscopic system the spontaneous formation of such state is impossible since it violates the second law of thermodynamics. However in the~~
10 ~~microscopic system such apparent violations are compensated by energy dissipation in form of heat and the increase of entropy in other subsystems (Bustamante et al., 2005). Thus , one can think of of the liquid phase as a distribution of subsystems in which some evolve in apparent violation of the second law~~Macroscopically the formation of a transient state is thermodynamically unfavorable, however microscopically it can be reached by spontaneous
15 fluctuation. The probability of a molecule fluctuating to a given state is associated with the non-equilibrium work required to reach such state. Interface transfer requires the spontaneous organization of water molecules into ice-like structures with probability described by $f(T, a_w)$. Thus if W is the work required for collective rearrangement, $f(T, a_w)$ must be equal the work probability, $P(W)$. Molecules near the interface can fluctuate in any direction either
20 by doing work on the system or vice versa, by the system doing work on them. The work distribution is such ~~system~~ systems is governed by the fluctuation theorem (FT) (Crooks, 1999),

$$\frac{P(W)}{P(-W)} = \exp\left(\frac{W - \Delta G}{k_B T}\right), \tag{6}$$

where $P(W)$ and $P(-W)$ correspond to the work probability of the forward and reversed
25 process between two states of a system, respectively, ΔG their equilibrium free energy difference, and W the non-equilibrium work between the two states. Considering only those

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subsystems that move across the interface we assume $P(W) + P(-W) = 1$. Using this and setting $f(T, a_w) = P(W)$, Eq. (6) can be rearranged into,

$$f(T, a_w) = \left[1 + \exp\left(-\frac{W - \Delta G}{k_B T} \right) \right]^{-1}. \tag{7}$$

Equation (6) is one of the few thermodynamic relations valid in systems away from equi-
5 librium (Bustamante et al., 2005). In writing Eq. (6) ~~is~~ it has been assumed that the sys-
tem is incompressible so that ΔG approximates the Helmholtz free energy difference.
The difference $W - \Delta G$ approximates the dissipated work, W_{diss}, between the two states
(Bustamante et al., 2005; Jou et al., 2010). Equation (6) relates the macroscopic response
of a thermodynamic system to its microscopic dynamics under the assumption that the
10 latter is stochastic and Markovian. These are typically valid assumptions at conditions
away from the glass transition temperature (Crooks, 1999). A further assumption is that
of microscopic reversibility, which requires that thermodynamic potentials can be locally
defined within the liquid. This is guaranteed near equilibrium, however in non-equilibrium
tranformations only holds for systems starting at local equilibrium. Thus the application of
15 FT for interface transfer is valid only if each molecule can be considered in equilibrium with
its local environment within the liquid (Crooks, 1999). Again, this is satisfied at T higher
than the glass transition temperature, which is the case for most systems of atmospheric
interest.

~~Consider a subsystem of size n_t involved in the transfer of~~ Consider the simplified energy
20 landscape of the water molecules within the interface shown in Fig. 1. The states 1 and
3 refer to pseudoequilibirium positions (i.e., metastable states) on the liquid and the ice
side, respectively, and 2 to the transient state. We define the path $1 \rightarrow 3$ as the forward,
and $3 \rightarrow 1$ as the reversed process, respectively. At equilibrium, the forward and reversed
processes are equally probable, there is no work dissipation, and the molecules ~~across~~
25 ~~the ice-liquid interface . At equilibrium the molecules~~ move freely across the interface ~~and~~
~~$\Delta G = G_{liq} - G_{ice,eq} = W = 0$~~without the formation of a transient state. For this situation

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$\Delta G = G_{\text{liq}} - G_{\text{ice}} = W = 0$, being G_{liq} and ~~$G_{\text{ice,eq}}$~~ G_{ice} the Gibbs free energy of bulk liquid and ice, respectively ~~(red line, Fig. 1). As the system~~. For the ice germ to grow the net flux of molecules should correspond to the direction of the forward process, the path $1 \to 3$.

As water supercools it moves away from equilibrium and an energy barrier for interface transfer is created, i.e., $W > 0$ and $\Delta G < 0$ ~~(blue and black lines, Fig. 1).~~. To estimate the dissipated work ~~we~~ in this situation it is easier to consider the reversed process ~~, that is,~~ (path $3 \to 1$, Fig. 1). This corresponds to molecules spontaneously leaving the ice lattice into the bulk of the liquid. To move away from the ice lattice, molecules should pass by the transient state (path $3 \to 2$, Fig. 1) and gain energy equal to $G^* - G_{\text{ice}}$, being G^* the energy of the transient state, which is later dissipated into the bulk of the liquid. On the other hand, if such process could be carried out in a completely reversible manner ~~then~~, then a transient state does not form and molecules would only need $G_{\text{liq}} - G_{\text{ice}}$ to leave the lattice (i.e., a hypothetical path $3 \to 1$ without passing by 2, not shown). Thus for the reversed process, $W - \Delta G = G^* - G_{\text{liq}}$. ~~With this $W - \Delta G = G^* - G_{\text{liq}} = n_t \Delta\mu_{\text{act}}$, being $\Delta\mu_{\text{act}}$ the specific activation energy for interface transfer.~~ If the subsystem follows the same trajectory but in the opposite direction, i.e., the forward process ~~, then $W - \Delta G = -n_t \Delta\mu_{\text{act}}$~~ (path $1 \to 3$, Fig. 1), then $W - \Delta G = -(G^* - G_{\text{liq}})$. That is, the energy dissipated when water molecules are incorporated into the ice germ is equal to their activation energy, i.e., interface transfer is a dissipative process.

~~Considering only those subsystems that move across the interface we assume $P(W) + P(-W)$ Using this~~ Using this into Eq. (~~6)~~ can be rearranged into,

$$P(W) = \left[1 + \exp\left(-\frac{W - \Delta G}{k_{\text{B}} T} \right) \right]^{-1}.$$

~~Using $f(T, a_\mathsf{w}) = P(W)$ and $W - \Delta G = -n_\mathsf{t}\Delta\mu_{\overline{\mathsf{act}}}$ 7)~~ we obtain,

$$f(T, a_\mathsf{w}) = \left[1 + \exp\left(\frac{n_\mathsf{t}\Delta\mu_\mathsf{act}}{k_\mathsf{B}T}\frac{G^* - G_\mathsf{liq}}{k_\mathsf{B}T}\right)\right]^{-1}. \tag{8}$$

~~Since dissipation comes~~ A molecule following the forward process (path $1 \to 3$, Fig. 1) experiences a net energy change equal to $G_\mathsf{ice} - G_\mathsf{liq} = -\Delta\mu_\mathsf{f}$, being $\Delta\mu_\mathsf{f}$ the excess free energy of fusion of water. This is equal to the energy change of a molecule moving between two pseudoequilibrium positions. Thus dissipation should result mostly from collective rearrangement ~~, the subsystem can be approximated as internally reversible. This means that there is no activation energy for movement confined within the boundaries of the subsystem.Within this framework a molecule moving from the bulk of the ice to the bulk of the liquid will experience a change in chemical potential equal to the excess free energy of fusionof water, i. e. , $\Delta\mu_\mathsf{act} \approx -\Delta\mu_\mathsf{f}$. Thus we write,~~ of several molecules i.e., from the formation of the transient state. This is consistent with the assumption of internally reversibility used in Eq. (6). Moreover, it suggests that the energy barrier for transfer activation should be proportional to $\Delta\mu_\mathsf{f}$ since $\Delta\mu_\mathsf{f}$ is the minimum energy change experienced by each molecule during interface transfer.

To find the proportionality constant between $G^* - G_\mathsf{liq}$ and $\Delta\mu_\mathsf{f}$ we consider the entropy change associated with the formation of the transient state. In the ice lattice water molecules have minimal configurational entropy and can be assumed to vibrate around fixed positions. When moving towards the liquid they experience an increase in entropy that can be written in the form $\Delta S_\mathsf{f} = k_\mathsf{B}\log\omega$ being ω the number of possible configurations of the liquid, and ΔS_f the excess entropy of fusion. If there are n_t "trajectories" in in which the transient state can be formed, then the number of posible configurations at the transient state would be ω^{n_t}. Thus the change in entropy between a pseudoequilibrium position in the ice and the transient state and can be written as $k_\mathsf{B}\log\omega^{n_\mathsf{t}} = n_\mathsf{t}\Delta S_\mathsf{f}$. By extension, the change in entropy between the transient state and a pseudoequilibrium position in the liquid would be

$-n_t \Delta S_f$. Since work dissipation is proportional to the generation of entropy (Bustamante et al., 200 the work required for interface transfer must be determined by entropy changes. Thus we make $G^* - G_{\text{liq}} \approx -n_t \Delta \mu_f$, being n_t the number of possible paths in the formation of the transient state. Replacing this into Eq. (8) we obtain,

$$f(T, a_{\mathsf{w}}) = \left[1 + \exp\left(\frac{-n_t \Delta \mu_f}{k_\mathsf{B} T} - \frac{n_t \Delta \mu_f}{k_\mathsf{B} T} \right) \right]^{-1}. \tag{9}$$

Using $\Delta \mu_f = -k_\mathsf{B} T \ln\left(\frac{a_w}{a_{w,eq}} \right)$ ~~into~~ Eq. (9) ~~we obtain~~ can be written in terms of a_{w},

$$f(T, a_{\mathsf{w}}) = \left[1 + \left(\frac{a_w}{a_{\mathsf{w,eq}}} \frac{a_{\mathsf{w}}}{a_{\mathsf{w,eq}}} \right)^{n_t} \right]^{-1}, \tag{10}$$

where $a_{\mathsf{w,eq}}$ is the equilibrium water activity.

To complete the derivation of $f(T, a_{\mathsf{w}})$ it is necessary to specify ~~the size of the subsystem,~~ n_t. ~~Unlike ΔG, W is not a thermodynamic potential and therefore depends on the trajectory of the system. Thus if there are n molecules involved in interface transfer, we need to account for all possible subsets of n molecules crossing the interface.~~ MD simulations show that the onset of nucleation is accompanied by an increase in the number of four-coordinated molecules (Moore and Molinero, 2011; Matsumoto et al., 2002). In the view proposed here this means that for each molecule that is incorporated into the ice germ at least four neighboring molecules would rearrange ~~. Thus it is natural to assume the base subsystem as having four molecules, and the number of possible subsets equal to~~ into the transient state. A geometrical argument is used to count the possible number of trajectories for this process. Essentially it is assumed that at the transient state the water molecules exhibit coordination numbers between 0 and 4. Thus each molecule can be coordinated with

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zero, one, two, three or four other molecules, each combination corresponding to a different trajectory of the system. The total number of trajectories is then given by $n_t = 2^4 = 16$.

~~Collecting terms~~

2.2 Nucleation Rate

5 Collecting Eqs. (2) to (5) into Eq. (1) we obtain,

$$J_{\text{hom}} = \left(\frac{Z\Omega}{v_w} \right) \frac{D_\infty f(T, a_{\text{w}})}{v_w d_0} \exp\left(-\frac{\Delta G_{\text{hom}}}{k_B T} \right) = J_0 \exp\left(-\frac{\Delta G_{\text{hom}}}{k_B T} \right), \tag{11}$$

where J_0 is referred as the preexponential factor. Since water is a glass-forming substance, the temperature dependency of D_∞ can be described by the Vogel-Fulcher-Tammann (VFT) equation,

10 $$D_\infty = D_0 \exp\left[-\frac{E}{(T - T_0)} \right], \tag{12}$$

where D_0, E and T_0 are fitting parameters (Table 1, Smith and Kay (1999)). At temperatures relevant for homogeneous ice nucleation the exponential term in Eq. (8) is expected to be much greater than one (although such is not the case when $a_{\text{w}} \sim a_{\text{w,eq}}$). Using this and ~~substituting Eq.~~ (replacing Eqs. (10) and (12) into Eq.(11) we obtain,

15 $$J_{\text{hom}} \approx \left(\frac{D_0}{v_w d_0} \right) \left(\frac{Z\Omega}{v_w} \right) \exp\left\{ -\frac{1}{k_B T} \left[\frac{k_B T E}{(T - T_0)} + k_B T n_t \ln\left(\frac{a_{\text{w}}}{a_{\text{w,eq}}} \right) + \Delta G_{\text{hom}} \right] \right\}, \tag{13}$$

Equation(13) has the form proposed by Turnbull and Fisher (1949). Thus the activation energy can be derived as,

$$\Delta G_{\text{act}} = k_B T \left[\frac{E}{(T - T_0)} + n_t \ln\left(\frac{a_{\text{w}}}{a_{\text{w,eq}}} \right) \right]. \tag{14}$$

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Equation (14) shows two contributions to the energy barrier for water transfer to the ice germ. The first term on the right hand side of Eq. (14) results from the breaking of hydrogen bonds in the liquid phase, i.e., the bulk diffusion process. The second term represents an additional energy barrier resulting from the entropy cost of molecular rearrangement within the ice-liquid interface. Substituting Eq. (14) into Eq. (13) we finally obtain,

$$J_{\text{hom}} \approx \left(\frac{D_0}{v_w d_0} \right) \left(\frac{Z\Omega}{v_w} \right) \exp\left(-\frac{\Delta G_{\text{act}} + \Delta G_{\text{hom}}}{k_B T} \right). \tag{15}$$

2.3 Common form of CNT

In most studies CNT is used in a more simplified form than presented in Eq. (1) (e.g., Khvorostyanov and Curry, 2004; Zobrist et al., 2007; Murray et al., 2010; Ickes et al., 2015). Typically, the expression of Einstein (1905) is used to relate diffusivity and viscosity and the energy of activation of water is assumed to have the same value as in the bulk (Kashchiev, 2000). Other assumptions include a semi-spherical ice germ, and negligible mixing effects during the germ formation (Barahona, 2014). These considerations lead to the commonly used CNT expression for J_{hom} (Turnbull and Fisher, 1949),

$$J_{\text{hom}} = \left(\frac{N_c k_B T}{h} \frac{\rho_w}{\rho_i} \right) \left(\frac{Z\Omega}{v_w} \right) \exp\left(-\frac{\Delta G_{\text{act}} + \Delta G_{\text{CNT}}}{k_B T} \right) = J_{0,\text{CNT}} \exp\left(-\frac{\Delta G_{\text{CNT}}}{k_B T} \right) \tag{16}$$

where N_c is the number of atoms in contact with the ice germ, and ρ_w and ρ_i are the bulk liquid water and ice density, respectively. ΔG_{CNT} is the energy of formation of the ice germ, which is commonly written in the form (Pruppacher and Klett, 1997),

$$\Delta G_{\text{CNT}} = \frac{16\pi \sigma_{\text{iw}}^3 v_w^2}{3 \left(k_B T \ln S_i \right)^2}, \tag{17}$$

15

where σ_{iw} is th ice-water interfacial energy, and S_i the saturation ratio with respect to ice. Other symbols are defined in Table 1. When using Eqs. (16) and (17), ΔG_{act} and σ_{iw} are typically considered free parameters.

3   Discussion

As temperature decreases the configurational entropy of water decreases increasing the energy required to break hydrogen bonds, thus the self-diffusivity of water decreases (Adam and G 1965). Similarly, as T decreases the energy associated with the molecular rearrangement within the interface increases, which results from a more negative excess energy of fusion. The latter can also be understood as an increase in the irreversibility of the liquid-ice trans-formation as the system moves away form thermodynamic equilibrium, therefore increasing the dissipated work, W_{diss}. As a result, ΔG_{act} increases monotonically as T decreases (Fig. 2). By definition, the rearrangement component of ΔG_{act}, W_{diss}, for $a_w = 1$ is equal to zero at $T = 273.15$ K, i.e., the equilibrium temperature the bulk ice-water system. For $T < 250$ K it corresponds to about half of ΔG_{act}.

An important aspect of Eq. (14) is that it predicts an effect of water activity on the activa-tion energy. The dependency of ΔG_{act} on a_w is however much weaker than on T. Decreas-ing a_w from 1.0 to 0.9 leads only to about 10% decrease in ΔG_{act} (Fig. 2). This is caused by a lowering in the dissipated work, $W_{diss} = -n_t \Delta \mu_f$, with decreasing a_w. Lowering a_w reduces the chemical potential of water but not that of ice as it is likely that no solute is incorporated into the ice germ during the early stages of ice formation (Barahona, 2014), therefore reducing $\Delta \mu_f$. ΔG_{hom} (Eq. 3) is much more sensitive to a_w and dominates the dependency of J_{hom} on a_w.

Empirical estimates of ΔG_{act} have been developed in several studies, and were re-cently reviewed by Ickes et al. (2015). The authors found that the usage of the ~~correlation expression~~ derived by Zobrist et al. (2007) from self-diffusivity measurements (Smith and Kay, 1999), along with the fit of Reinhardt and Doye (2013) for σ_{iw}, into Eq. (16) produced the best comparison against experimental results. Here the empirical expression for σ_{iw} ~~derived~~

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proposed in B14 ~~is used instead~~, derived from fitting Eq. 1 to the model of Koop et al. (2000), is used as it is the only available correlation that includes an explicit dependency of σ_{iw} on a_w. Usage of the B14 correlation also ensures that $\Delta G_{CNT} \approx \Delta G_{hom}$ since it empirically accounts for mixing effects. The Zobrist et al. (2007) correlation results from taking the derivative of the exponential argument of Eq. (12) in the form,

$$\Delta G_{act,Z07} = \frac{k_B T^2 E}{(T - T_0)^2}. \tag{18}$$

Equation (18) gives ΔG_{act} around the mean of common models used in the literature (see Fig. 1 of Ickes et al. (2015)). Thus the model of Zobrist et al. (2007) will be used as benchmark for comparison. However ΔG_{act} calculated using the correlation of Jeffery and Austin (1997) is also presented in Fig. 2 for reference. Although the latter is also derived from the bulk properties of water, it typically results in values of ΔG_{act} lower than $\Delta G_{act,Z07}$.

Because the contribution of the breaking of hydrogen bonds to ΔG_{act} is taken into account in both models, Eqs. (14) and (18) show similar dependencies on E and T_0, since they define D_∞. However, the two expressions are fundamentally different. In the model of Zobrist et al. (2007) the relation between D_∞ and ΔG_{act} is hypothesized a priori, while in this work it results from explicitly consideration of the thermodynamics of interface transfer. Moreover, the contribution to ΔG_{act} from molecular rearrangement, neglected in Zobrist et al. (2007), is always positive for nucleation (i.e., Eq. 14 is never evaluated at $a_w = a_{w,eq}$ since it implies equilibrium conditions for which $J_{hom} = 0$).

Figure 2 shows that $\Delta G_{act,Z07}$ increases almost quadratically as T decreases. The ~~correlation~~ expression of Jeffery and Austin (1997) results in an even stronger increase in ΔG_{act} for $T < 200$ K. This feature is common in ~~models derived from the properties of bulk water~~ empirical models (Ickes et al., 2015). In general $\Delta G_{act,Z07}$ is larger than ΔG_{act} calculated from Eq. (14). ~~Moreover, the~~ The latter increases almost linearly as T decreases instead of the quadratic increase of $\Delta G_{act,Z07}$. $\Delta G_{act,Z07}$ and Eq. (14) are the closest around $T \approx 235$ K, which is near the nominal homogeneous freezing threshold of water droplets. The difference between the two grows larger with decreasing temperature since the work dissipated

in the formation of the transient state increases (Section 2.1); at $T = 180$ K $\Delta G_{\text{act,Z07}}$ is greater than ΔG_{act} by almost a factor of two.

Figure 3 compares the preexponential factor calculated from Eq. (11) against the common CNT formulation, Eq. (16). Equation (18) was used to calculate ΔG_{act} in the latter. For
5    $T < 240$ K the factors $\left(\frac{D_0}{v_w d_0}\right)$ and $\left(\frac{N_c k_B T}{h} \frac{\rho_w}{\rho_i}\right)$ differ by less than a factor of two. Thus the difference between J_0 and $J_{0,\text{CNT}}$ is almost entirely due to ΔG_{act}. For $T > 230$ K usage of either $\Delta G_{\text{act,07}}$ or Eq. (14) introduces less than two orders of magnitude difference in J_0. However for $T < 230$ K using $\Delta G_{\text{act,07}}$ leads to a much faster decrease in J_0 than with Eq. (14), which is explained by the quadratic increase in $\Delta G_{\text{act,07}}$ as T decreases. At 180
10   K, they differ by almost 10 orders of magnitude. As expected, lowering the water activity slightly increases J_0 since ΔG_{act} is slightly reduced.

Despite the noticeable dependency of ΔG_{act} on T, J_{hom} is ~~only~~ mostly sensitive to variation in ΔG_{act} at low T. This is illustrated in Fig. 2. For $a_w = 1$ and $T > 230$ K, $\Delta G_{\text{hom}} >> \Delta G_{\text{act}}$, i.e., the nucleation rate is completely controlled by the nucleation work. As T de-
15   creases ΔG_{hom} and ΔG_{act} become comparable and for $T < 200$ K, J_{hom} is mainly controlled by ΔG_{act}. Since most experimental measurements of J_{hom} are carried out around 235 K (Fig. ~~??~~4), the lack of sensitivity of J_{hom} to ΔG_{act} at these conditions may lead to the incorrect notion that ΔG_{act} is constant. Such misconception may not be critical for the homogeneous freezing of pure water at atmospheric conditions since it rarely occurs at
20   $T < 230$ K. However it may introduce error in J_{hom} for $a_w < 1$ (Fig. 2, black lines) since ΔG_{hom} and ΔG_{act} become comparable at temperatures relevant to the formation of cirrus from haze aerosol particles (Barahona and Nenes, 2008).

As direct measurements of ΔG_{act} are not available, the skill of ΔG_{act} in reproducing experimental measurements is assessed through evaluation of J_{hom}. For common formu-
25   lations of CNT (Section 2.3) this has the caveat that such comparison is influenced by specification of other parameters of the theory. This is not the case when using the NNF formulation (Eq. 3) since it does not explicitly depend on σ_{iw}. It was shown in B14 that using $\Delta G_{\text{act,07}}$ and Eq. (3) into Eq. (16) reproduced measured J_{hom} for $T > 230$ K. The results

of B14 for $a_w = 1$ are shown in Fig. ~~??~~ 4 along with several experimental measurements, empirical correlations, and results from the formulation of CNT presented in Section 2.3.

Most of the measurements of J_{hom} are carried out using small droplets with relatively high surface-to-volume ratio. Surface stimulated nucleation (SSN) thus may take place leading

5 to values of J_{hom} higher than the volume-based theory presented here (Djikaev, 2008). However the experimental evidence for the predominance of SSN is still conflicting (Sigurbjörnsson SSN requires an ice germ growing with a particular orientation so that at least one its "facets" is aligned with the droplet-vapor interface. However it is not clear that the exposed facet would have the same interfacial tension as bulk ice (Kay et al., 2003). Moreover, SSN

10 is a thermodynamic effect, i.e., it decreases ΔG_{hom} compared to volume-based nucleation. As shown in Fig. 2 at low temperature J_{hom} is increasingly less controlled by ΔG_{hom} and more dependent on ΔG_{act}, which would limit the effect of SSN on J_{hom}. Therefore we limit the comparison in Figs. 4 and 5 to those data sets where J_{hom} is interpreted as dominated by volume-based ice nucleation.

15   Compared to the formulation of B14, J_{hom} from Eq. (11) only differs in the specification of J_0 which mainly depends on ΔG_{act}. As expected, for $T > 230$ and $a_w = 1$ the formulation of B14 and Eq. (11) produce similar J_{hom}, and within experimental variability and model uncertainty (typically about 3 orders of magnitude) of measured values. Notably J_{hom} predicted by NNF is very close to the data of Riechers et al. (2013) who used a microfluidic

20 device to obtain an accurate estimation of T. For $T < 230$ K, J_{hom} from B14 is much lower than measured values (by up to 9 orders of magnitude), which is also the case for the CNT formulation, Eq. (16), when using $\Delta G_{act,07}$. In both formulations J_{hom} decreases for T below 210 K, which results from an strong increase in $\Delta G_{act,07}$ and a decrease in J_0. Using the fit of Reinhardt and Doye (2013) for σ_{iw} and $\Delta G_{act,07}$ also leads to underestimation of

25 J_{hom} at low T, consistent with the results of Ickes et al. (2015). At the same conditions, Eq. (11) predicts a higher J_{hom} and within experimental uncertainty of measurements. Using Eq. (14) within the CNT formulation, Eq. (16), leads to a similar result. Thus the higher J_{hom} and the better agreement with the experimental measurements at low T results from the usage of the formulation of ΔG_{act} presented here.

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Most experimental measurements of J_{hom} have been carried out for $a_{\text{w}} = 1$. However homogeneous freezing for $a_{\text{w}} < 1$ is ~~likely~~ important for the formation of cirrus at low T (e.g., Koop et al., 2000). Figure **?? (right panel)** 5 shows J_{hom} for $a_{\text{w}} = 0.9$ from Eqs. (16) and (11), and using $\Delta G_{\text{act,07}}$ and Eq. (14) to compute the activation energy. The correlation derived by Koop et al. (2000) is also reproduced along with available experimental data (Alpert et al., 2011; Knopf and Rigg, 2011). For the latter only data reported for $T < 221$ K is shown to avoid heterogeneous freezing effects. The expression for J_{hom} in $(NH_4)_2SO_4$ solutions derived by Larson and Swanson (2006) is also presented in Fig. 5. For the latter the solution equilibrium model of Clegg et al. (1998) was used to relate a_{w} to the mass fraction of $(NH_4)_2SO_4$.

For $T > 218$ K and and $a_{\text{w}} = 0.9$, J_{hom} from all formulations agree within three orders of magnitude, and within experimental uncertainty (Alpert et al., 2011; Larson and Swanson, 2006) of the measured rates. ~~However for~~ For $T < 216$ K, ~~calculated~~ the models tend to predict higher than measured nucleation rates. Experimental measurements also show a weaker dependency of J_{hom} ~~is higher than the experimental results. This would indicate that J_{hom} is less sensitive to~~ on T at $a_{\text{w}} = 0.9$ than at $a_{\text{w}} = 1.0$. ~~Another possibility may be a slight decrease in a_{w} during the experiments.~~ This is evident in the data of Alpert et al. (2011) and less evident for the correlation of Larson and Swanson (2006). For the latter the authors report a T uncertainty of about 1 K which may account for the observed difference. Alpert et al. (2011) reports an uncertainty in initial a_{w} of 0.01 which explains the scatter of the data around $T \sim 218$ K. ~~However~~ The authors however do not report measurements of a_{w} at the point of freezing. Knopf and Rigg (2011), who used a similar technique, discuss the possibility of a slight decrease in a_{w} of their test solutions as T decreases. ~~Figure ?? (right panel)shows~~, which would indicate a higher uncertainty in a_{w} than reported by Alpert et al. (2011). Similarly Larson and Swanson (2006) carried measurements at constant mass fraction and variation in a_{w} during their experiments cannot be ruled out. To demonstrate the effect of a drift towards lower a_{w} values, J_{hom} was recalculated at $a_{\text{w}} = 0.88$ (Fig. 5). It was found that a decrease of 0.02 in a_{w} ~~during the experiments would be enough to~~ with respect to the initial setting (assumed to be $a_{\text{w}} = 0.9$) would explain the observed J_{hom}. It is

however remarkable that two different experimental techniques (Larson and Swanson, 2006; Alpert results consistent with a lower sensitivity of J_{hom} to T than predicted by theoretical models, indicating that such discrepancy may not result solely from experimental artifacts. More research and further experimentation is required to clarify this point.

5   At low temperature ($T < 210$ K) the usage of Eq. (14) leads to a higher J_{hom} than when $\Delta G_{\text{act,07}}$ is used, for both formulations of CNT. For $a_{\text{w}} < 1$ Eq. (16) and Eq. (11) do not overlap as is the case for $a_{\text{w}} = 1$, which results from the different sensitivity to a_{w} of both formulations (Fig. 5). Interestingly, for $a_{\text{w}} = 1$ and $a_{\text{w}} = 0.9$, J_{hom} reaches similar values at $T = 180$ K, being just about an order of magnitude higher in the latter due to the sensitivity

10 of ΔG_{act} to a_{w}. This shows that a low T, J_{hom} is mainly controlled by J_0, hence ΔG_{act}.

    Finally it is important to dicuss the effect of variation in the parameters of the proposed theory on J_{hom}. It was concluded in B14 (c.f., Fig. 8) that the uncertainty in J_{hom} from variation in Γ_w and s (used in Eq. 3) is about two orders off magnitude and decreases with decreasing T since J_{hom} becomes more dependent on ΔG_{act} and less dependent on the

15 interfacial energy. Uncertainty in ΔG_{act} results mostly from uncertainty in $a_{\text{w,eq}}$ and n_t. The specification of the thermodynamic properties of water at very low T is challenging since several combinations of parameters can lead to thermodynamically consistent solutions. Several studies (e.g., Johari et al., 1994; Koop and Zobrist, 2009) have used some form of thermodynamic continuation below $T \sim 235$ K to define $a_{\text{w,eq}}$ and Δh_{f}, which is also used in

20 this work. This approximation is indirectly supported by experimental results (Koop and Zobrist, 20 may lead to uncertainty. It is estimated that the preexponential factor would increase about two orders of magnitude by a change in n_t from 16 to 15. Essentially a value of n_t less than 16 would indicate that some of the rearrangement routes to form the transient state are prohibited. Another assumption that may impact the model is that of microscopic reversibility

25 used in the derivation of $f(T, a_{\text{w}})$ (Section 2), which becomes weaker at low T since water dynamics becomes slower and it cannot be always assumed that the water molecules are in equilibrium with their local environment. Unfortunately it is challenging to estimate a plausible range of uncertainty in J_{hom} associated with these approximations. Deviations from thermodynamic equilibrium are difficult to quantify, even with molecular dynamics

methods, and the characteristics of the transient state are not known. Progress in MD and further experimentation may shed light on these issues.

4 Conclusions

This work advances a ~~phenomenological~~ theoretical description of the process of interface
transfer of water molecules from the liquid phase to the ice during the early stages of nu-
cleation. Unlike previous approaches, the model presented here does not assume that the
water properties in the liquid-ice interface are the same as those of the bulk. Instead a the-
oretical approach is proposed where the interaction of several water molecules is required
for interface transfer. Application of this model resulted in a thermodynamic definition of
ΔG_{act}. As D_{∞} and σ_{iw} can also be defined on a thermodynamic basis (Adam and Gibbs,
1965; Barahona, 2014), this work gives support to the assertion of Koop et al. (2000) that
the ice nucleation rate can be determined entirely by thermodynamics.

The approach proposed here elucidates two contributions to the activation energy. The
first one is the self-diffusion process in the bulk water, that is, the breaking of hydrogen
bonds in the liquid phase. The second is the work dissipated during interface transfer, as-
sociated with the rearrangement of the water molecules within the ice-liquid interface. The
commonly used model of Turnbull and Fisher (1949) neglected the latter. However since
homogeneous ice nucleation occurs away from equilibrium, interface transfer implies an
energy cost to the system. At temperatures relevant for homogeneous ice nucleation it rep-
resents about half of ΔG_{act}.

It was shown that at low temperature interface transfer has the largest effect on the nucle-
ation rate. For such conditions $\Delta G_{act} \sim \Delta G_{hom}$ and variations in the preexponential factor
may dominate the variation in J_{hom}. On the other hand moderate variation in ΔG_{act} will
have a limited effect on J_{hom} for pure water droplets since they typically freeze at $T > 230$
K where $\Delta G_{hom} >> \Delta G_{act}$. However ΔG_{act} may have a marked influence for the homo-
geneous freezing of haze aerosol which occurs at very low temperature. Also ΔG_{act} may

impact the nucleation rate when the same formulation is used for heterogeneous ice nucleation as the nucleation work is typically lower than in the homogeneous case.

For $T > 230$ K the formulation of ΔG_{act} presented here predicts values close to those obtained using empirical correlations, particularly that of Zobrist et al. (2007). However for $T < 230$ K, Eq.(14) predicts a linear increase in ΔG_{act} with decreasing T, and differs from the nonlinear tendency typically found when ΔG_{act} is assumed to be determined solely by self-diffusivity of bulk water (Ickes et al., 2015). As a result, at low T the preexponential factor, hence the nucleation rate, predicted using empirical formulations of ΔG_{act} tends to be lower than found in this work.

Introducing the new formulation of ΔG_{act} into a generalized form of CNT (Eq. 1) and using the NNF framework to define ΔG_{hom}, resulted in good agreement of J_{hom} with observations, even at very low T where it is underestimated by most models. This is remarkable since no parameters of the theory were found by fitting nucleation rates. Introducing Eq. (14) into a common formulation of CNT and with σ_{iw} constrained as in B14 also led to a good agreement of J_{hom} with measured values. For $a_{\mathrm{w}} = 0.9$ and $T > 218$ K predicted J_{hom} is in ~~agreeement~~ agreement within experimental uncertainty with reported experimental values, however it tends to be higher than measurements at lower T. It is not clear whether systematic deviation in a_{w} during the experiments, or ~~unkown~~ unknown factors not considered in the theoretical models are the source of this discrepancy and more research is needed to elucidate this point. The NNF model, which can be independently constrained and evaluated, may be more suitable to investigate such differences between theory and measurements than common formulations of CNT where ΔG_{act} and σ_{iw} must be fitted to measured J_{hom}.

This work centers on the activation energy as a fundamental parameter. Equation (15) however suggests that the flux of water molecules from the bulk to the ice may be better understood in terms of the bulk self-diffusivity of water and the probability of interface transfer, $f(T, a_{\mathrm{w}})$. These two quantities have a more specific physical meaning than ΔG_{act}. D_{∞} has been independently measured (e.g., Smith and Kay, 1999), whereas $f(T, a_{\mathrm{w}})$ is

related to the work dissipated during ice nucleation and can in principle be obtained from MD simulations.

More work is needed to estimate the range of validity of the approximations introduced in Section 2. Guided by MD results, it was assumed that a molecule crossing the inter-face would interact with four other molecules, so that $n_\text{t} = 16$. This is expected at low T since the water structure becomes more ice-like, however n_t may be a function of the tem-perature. For example, the size of cooperative regions in water is known to be a function of the configurational entropy and therefore of temperature (Adam and Gibbs, 1965). It is not clear whether that should also be the case for interface transfer. ~~Another source of uncertainty has to do with the specification of~~ The role of surface stimulated nucleation (Djikaev, 2008) and the effect of deviations from microscopic reversibility on ΔG_act and J_hom must be further investigated. The estimation of water properties at ~~very~~ low T ~~.~~ ~~Several studies (e.g., Johari et al., 1994; Koop and Zobrist, 2009) have used some form of thermodynamic continuation below $T \sim 235$ K to define $a_\text{w,eq}$ and Δh_f, which is also used in this work. These functions are not unique since several combinations of parameters can lead to thermodynamically consistent solutions.~~ is also challenging and still uncertain. Progress in MD and further experimentation ~~may shed light on~~ are required to address these issues. Understanding ΔG_act as a thermodynamic function, instead of a fundamental property of water may help setting up a road map for further research.

~~This work centers on the activation energy as a fundamental parameter. Equation (15) however suggest that the flux of water molecules from the bulk to the ice may be better understood in terms of the bulk self-diffusivity of water and the probability of interface transfer, $f(T, a_\text{w})$. These two quantities have a more specific physical meaning than ΔG_act. D_∞ has been independently measured (e.g., Smith and Kay, 1999), whereas $f(T, a_\text{w})$ is related to the work dissipated during ice nucleation and can in principle be obtained from MD simulations.~~

From their analysis of different models Ickes et al. (2015) concluded that at low T either σ_iw is thermodynamically undefined or the temperature dependency of ΔG_act reverses. Such predictions are mistaken. This work shows that both ΔG_act and σ_iw can be defined

on a thermodynamic basis. The work of Ickes et al. (2015) however shows the difficulties in ascribing physical behavior to the parameters of CNT by fitting experimental results. The independent ~~phenomenological~~ theoretical formulation presented here may be more amenable to testing and expansion. In turn, a physically-based definition of the parameters
5 of CNT may improve the development of parameterizations of ice formation in cloud models, and lead to a better understanding of ice processes in the atmosphere.

References

10 Adam, G. and Gibbs, J. H.: On the temperature dependence of cooperative relaxation properties in glass-forming liquids, J. Chem. Phys., 43, 139–146, 1965.

Alpert, P., Aller, J., and Knopf, D.: Ice nucleation from aqueous NaCl droplets with and without marine diatoms, Atm. Chem. Phys., 11, 5539–5555, 2011.

Barahona, D.: Analysis of the effect of water activity on ice formation using a new ther-
15 modynamic framework, Atm.Chem. Phys., 14, 7665–7680, doi:10.5194/acp-14-7665-2014, http://www.atmos-chem-phys.net/14/7665/2014/, 2014.

Barahona, D. and Nenes, A.: Parameterization of cirrus formation in large scale models: Homogeneous nucleation, J. Geophys. Res., 113, D11 211, doi:10.1029/2007JD009355, 2008.

Barahona, D. and Nenes, A.: Dynamical states of low temperature cirrus, Atmos. Chem. Phys., 11,
20 3757–3771, doi:10.5194/acp-11-3757-2011, 2011.

Barahona, D., Rodriguez, J., and Nenes, A.: Sensitivity of the global distribution of cirrus ice crystal concentration to heterogeneous freezing, J. Geophys. Res., 15, D23 213, doi:10.1029/2010JD014273, 2010.

Barahona, D., Molod, A., Bacmeister, J., Nenes, A., Gettelman, A., Morrison, H., Phillips, V., and
25 Eichmann, A.: Development of two-moment cloud microphysics for liquid and ice within the NASA Goddard Earth Observing System Model (GEOS-5), Geosc. Model Dev., 7, 1733–1766, doi:10.5194/gmd-7-1733-2014, http://www.geosci-model-dev.net/7/1733/2014/, 2014.

Bartell, L. and Chushak, Y.: in: Water in confining geometries, Springer Science & Business Media, 2003.

25

Buhariwalla, C. R., Bowles, R. K., Saika-Voivod, I., Sciortino, F., and Poole, P. H.: Free energy of formation of small ice nuclei near the Widom line in simulations of supercooled water, arXiv preprint arXiv:1501.03115, 2015.

Bullock, G. and Molinero, V.: Low-density liquid water is the mother of ice: on the relation between mesostructure, thermodynamics and ice crystallization in solutions., Faraday Discuss., doi:10.1039/C3FD00085K, 2013.

Bustamante, C., Liphardt, J., and Ritort, F.: The nonequilibrium thermodynamics of small systems, Phys. Today, 58, 43–4, doi:10.1063/1.2012462, 2005.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system H+-NH4+-SO42–NO3–H2O at tropospheric temperatures, J. Phys. Chem. A, 102, 2137–2154, 1998.

Crooks, G. E.: Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences, Physical Review E, 60, 2721, doi:http://dx.doi.org/10.1103/PhysRevE.60.2721, 1999.

Digilov, R. M.: Semi-empirical model for prediction of crystal–melt interfacial tension, Surface Sci., 555, 68–74, 2004.

Djikaev, Y. S.: Effect of the surface-stimulated mode on the kinetics of homogeneous crystal nucleation in droplets, J. Phys. Chem. A, 112, 6592–6600, 2008.

Einstein, A.: Investigations on the theory of Brownian movement, Ann. der Physik, 1905.

Espinosa, J., Sanz, E., Valeriani, C., and Vega, C.: Homogeneous ice nucleation evaluated for several water models, J. Chem. Phys., 141, 18C529, 2014.

Gettelman, A., Liu, X., Barahona, D., Lohmann, U., and Chen, C.: Climate impacts of ice nucleation, J. Geophys. Res., 117, doi:10.1029/2012JD017950, 2012.

Hagen, D. E., Anderson, R. J., and Kassner Jr, J. L.: Homogeneous condensation-freezing nucleation rate measurements for small water droplets in an expansion cloud chamber, J. Atmos. Sci., 38, 1236–1243, 1981.

Ickes, L., Welti, A., Hoose, C., and Lohmann, U.: Classical nucleation theory of homogeneous freezing of water: thermodynamic and kinetic parameters, Phys. Chem. Chem. Phys., 17, 5514–5537, doi:10.1039/C4CP04184D, 2015.

Jeffery, C. and Austin, P.: Homogeneous nucleation of supercooled water: Results from a new equation of state, J. Geophys. Res., 102, 25 269–25 279, 1997.

Jensen, E. J., Diskin, G., Lawson, R. P., Lance, S., Bui, T. P., Hlavka, D., McGill, M., Pfister, L., Toon, O. B., and Gao, R.: Ice nucleation and dehydration in the Tropical Tropopause Layer, Proc. Nat. Acad. Sc., 110, 2041–2046, 2013.

Johari, G., Fleissner, G., Hallbrucker, A., and Mayer, E.: Thermodynamic continuity between glassy and normal water, J. Phys. Chem., 98, 4719–4725, 1994.

Jou, D., Casas-Vázquez, J., and Lebon, G.: Extended irreversible thermodynamics, Springer, 4th edn., 2010.

Kärcher, B. and Burkhardt, U.: A cirrus scheme for global circulation models, Q. J. R. Meteorol. Soc., 134, 1439–1461; doi:10.1002/Qj.301, 2008.

Kärcher, B. and Lohmann, U.: A parameterization of cirrus cloud formation: homogeneous freezing including effects or aerosol size, J. Geophys. Res., 107, 4698, doi:10.1029/2001JD001 429, 2002.

Kashchiev, D.: Nucleation: basic theory with applications, Butterworth Heinemann, 2000.

Kawasaki, T. and Tanaka, H.: Formation of a crystal nucleus from liquid, Proc. Nat. Acad. Sci., 107, 14 036–14 041, 2010.

Kay, J., Tsemekhman, V., Larson, B., Baker, M., and Swanson, B.: Comment on evidence for surface-initiated homogeneous nucleation, Atm. Chem. Phys., 3, 1439–1443, 2003.

Khvorostyanov, V. and Curry, J.: Critical humidities of homogeneous and heterogeneous ice nucleation: Inferences from extended classical nucleation theory, J. Geophys. Res., 114, D04 207, doi:10.1029/2008JD011 197, 2009.

Khvorostyanov, V. I. and Curry, J. A.: Thermodynamic theory of freezing and melting of water and aqueous solutions, J. Phys. Chem. A, 108, 11 073–11 085, 2004.

Knopf, D. A. and Rigg, Y. J.: Homogeneous ice nucleation from aqueous inorganic/organic particles representative of biomass burning: Water activity, freezing temperatures, nucleation rates, J. Phys. Chem. A, 115, 762–773, 2011.

Koop, T. and Zobrist, B.: Parameterizations for ice nucleation in biological and atmospheric systems, Phys. Chem. Chem. Phys., 11, 10 839–10 850, 2009.

Koop, T., Luo, B., Tslas, A., and Peter, T.: Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, Nature, 406, 611–614, 2000.

Larson, B. H. and Swanson, B. D.: Experimental investigation of the homogeneous freezing of aqueous ammonium sulfate droplets, J. Phys. Chem. A, 110, 1907–1916, 2006.

Liu, X. and Penner, J.: Ice nucleation parameterization for global models, Meteorol. Z., 14, 499–514, 2005.

Lohmann, U. and Kärcher, B.: First interactive simulations of cirrus clouds formed by homogeneous freezing in the ECHAM general circulation model, J. Geophys. Res., 107, 4105, doi:10.1029/2001JD000 767, 2002.

27

Malkin, T. L., Murray, B. J., Brukhno, A. V., Anwar, J., and Salzmann, C. G.: Structure of ice crystallized from supercooled water, PNAS, 109, 1041–1045, 2012.

Manka, A., Pathak, H., Tanimura, S., Wölk, J., Strey, R., and Wyslouzil, B. E.: Freezing water in no-man's land, Phys. Chem. Chem. Phys., 14, 4505–4516, 2012.

Matsumoto, M., Saito, S., and Ohmine, I.: Molecular dynamics simulation of the ice nucleation and growth process leading to water freezing, Nature, 416, 409–413, 2002.

Moore, E. B. and Molinero, V.: Structural transformation in supercooled water controls the crystallization rate of ice, Nature, 479, 506–508, 2011.

Moroni, D., Ten Wolde, P. R., and Bolhuis, P. G.: Interplay between structure and size in a critical crystal nucleus, Physical review letters, 94, 235 703, 2005.

Murphy, D. and Koop, T.: Review of the vapour pressures of ice and supercooled water for atmospheric applications, Q. J. R. Meteorol. Soc., 131, 1539–1565, 2005.

Murray, B., Broadley, S., Wilson, T., Bull, S., Wills, R., Christenson, H., and Murray, E.: Kinetics of the homogeneous freezing of water, Phys. Chem. Chem. Phys., 12, 10 380–10 387, 2010.

Pruppacher, H.: A new look at homogeneous ice nucleation in supercooled water drops, J. Atmos. Sci., 52, 1924–1933, 1995.

Pruppacher, H. and Klett, J.: Microphysics of clouds and precipitation, Kluwer Academic Publishers, Boston, MA, 2nd edn., 1997.

Reinhardt, A. and Doye, J. P.: Note: Homogeneous TIP4P/2005 ice nucleation at low supercooling, J. Chem. Phys., 139, 096 102, 2013.

Riechers, B., Wittbracht, F., Hütten, A., and Koop, T.: The homogeneous ice nucleation rate of water droplets produced in a microfluidic device and the role of temperature uncertainty, Phys. Chem. Chem. Phys., 15, 5873–5887, 2013.

Røsjorde, A., Fossmo, D., Bedeaux, D., Kjelstrup, S., and Hafskjold, B.: Nonequilibrium molecular dynamics simulations of steady-state heat and mass transport in condensation: I. Local equilibrium, J. Colloid Interface Sci., 232, 178–185, 2000.

Russo, J., Romano, F., and Tanaka, H.: New metastable form of ice and its role in the homogeneous crystallization of water, Nature materials, 13, 733–739, 2014.

Sigurbjörnsson, Ó. F. and Signorell, R.: Volume versus surface nucleation in freezing aerosols, Physical Review E, 77, 051 601, 2008.

Singh, R. S. and Bagchi, B.: Correlation between thermodynamic anomalies and pathways of ice nucleation in supercooled water, J. Chem. Phys., 140, 164 503, 2014.

Smith, R. S. and Kay, B. D.: The existence of supercooled liquid water at 150 K, Nature, 398, 788–791, 1999.

Spaepen, F.: A structural model for the solid-liquid interface in monatomic systems, Acta Metallurgica, 23, 729–743, 1975.

5 Taborek, P.: Nucleation in emulsified supercooled water, Physical Review B, 32, 5902, 1985.

Turnbull, D. and Fisher, J. C.: Rate of nucleation in condensed systems, J. Chem. Phys., 17, 71–73, 1949.

Zobrist, B., Koop, T., Luo, B., Marcolli, C., and Peter, T.: Heterogeneous ice nucleation rate coefficient of water droplets coated by a nonadecanol monolayer, J. Phys. Chem. C, 111, 2149–2155, 2007.

Table 1. List of symbols.

a_w	Activity of water
$a_{w,eq}$	Equilibrium a_w between bulk liquid and ice (Koop and Zobrist, 2009)
E, T_0	Parameters of the VFT equation, 892 K and 118 K, respectively (Smith and Kay, 1999)
D	Diffusion coefficient for interface transfer, $m^2 s^{-1}$
D_∞	Self-diffusion coefficient of bulk water, $m^2 s^{-1}$
D_0	Fitting parameter, $3.06 \times 10^{-9} m^2 s^{-1}$ (Smith and Kay, 1999)
d_0	Molecular diameter of water, m
$f(T, a_w)$	Interface transfer probability
f^*	Impingement factor, s^{-1}
G	Gibbs free energy, J
G^*	Gibbs free energy of the transient state, J
G_{liq}, G_{ice}	Gibbs free energy of liquid and ice, respectively, J
$J_0, J_{0,CNT}$	Pre-exponential factor calculated from Eqs. (11) and (16), respectively, $m^{-3} s^{-1}$
J_{hom}	Nucleation rate, $m^{-3} s^{-1}$
k_B	Boltzmann constant, $J K^{-1}$
n^*	Critical germ size
N_c	Number of atoms in contact with the ice germ, $5.85 \times 10^{18} m^{-2}$ (Pruppacher and Klett, 199
n_t	Number of ~~configurations of a subsystem~~formation paths of the transient state, 16
$p_{s,w}, p_{s,i}$	Liquid water and ice saturation vapor pressure, respectively, Pa (Murphy and Koop, 2005)
s	Geometric constant of the ice lattice, $1.105 \, mol^{2/3}$ (Barahona, 2014)
S_i	Saturation ratio with respect to ice
T	Temperature, K
v_w	Molecular volume of water in ice (Zobrist et al., 2007), m^{-3}
W	Non-equilibrium work, J
W_{diss}	Dissipated work, J
Z	Zeldovich factor

ΔG_{act}	Activation energy for ice nucleation, J
ΔG_{hom}	Nucleation work, NNF framework, J
ΔG_{CNT}	Nucleation work, CNT framework, J
Δh_{f}	Heat of fusion of water, $J\,mol^{-1}$, J (Barahona,
Δa_{w}	$a_{\text{w}} - a_{\text{w,eq}}$
$\Delta \mu_{\text{f}}$	Excess free energy of water, J
~~$\Delta \mu_{\text{act}}$ Specific activation energy for interface transfer~~ Γ_{w}	Molecular surface excess of at the interface, 1.
ρ_{w}, ρ_{i}	Bulk density of liquid water and ice, respectivel
σ_{iw}	Ice–liquid interfacial energy $J\,m^{-2}$ (Barahona,
Ω_{g}	Ice germ surface area m^{-2}

* A change in enthalpy of 50 ($J\,mol^{-1}$) was assumed for the transition between cubic and hexagonal ice.
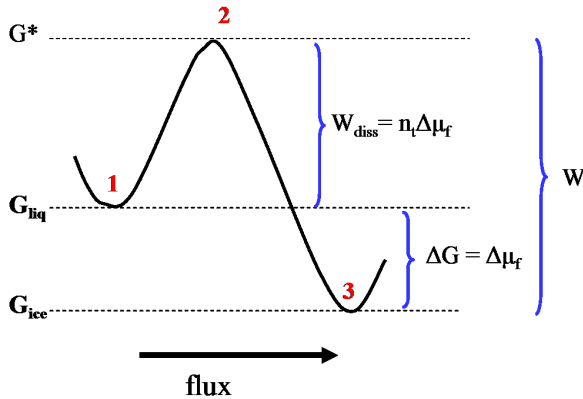
Figure 1. ~~Scheme~~ Simplified energy landscape of ~~the transfer of~~ water molecules ~~to a metastable ice germ~~in the ice-liquid interface during interface transfer. ~~Red lines~~ States 1 and 3 correspond to ~~situations close to thermodynamic equilibirium whereas blue and black lines represent conditions progressively away from~~ metastable equilibrium ~~(subscripts 1~~ positions in the liquid and ~~2~~ice, respectively~~)~~, and 2 to the transient state. ~~G_{ice}, G_{liq}~~ G_{ice}, G_{liq} and G^* correspond to the Gibbs free energy of ice, liquid and the transient state, respectively. ~~The cartoon at~~ W and W_{diss} are the ~~top of~~ total non-equilibrium work and the ~~graph~~ dissipated work, respectively. $\Delta\mu_f$ is ~~a visualization~~ the excess free energy of water and n_t is defined in Section 2. The bold arrow represents the ~~interaction direction~~ of net flux of water molecules during ~~interface transfer~~the growth of the ice germ.
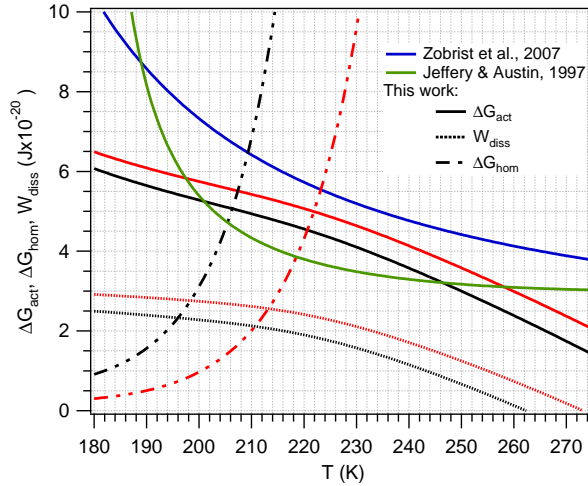
Figure 2. Energy of activation represented by several models. Also presented are the dissipated work, W_{diss}, and the work of nucleation ΔG_{hom}. Red lines and black lines correspond to $a_{\text{w}} = 0.9$ and $a_{\text{w}} = 1$, respectively.
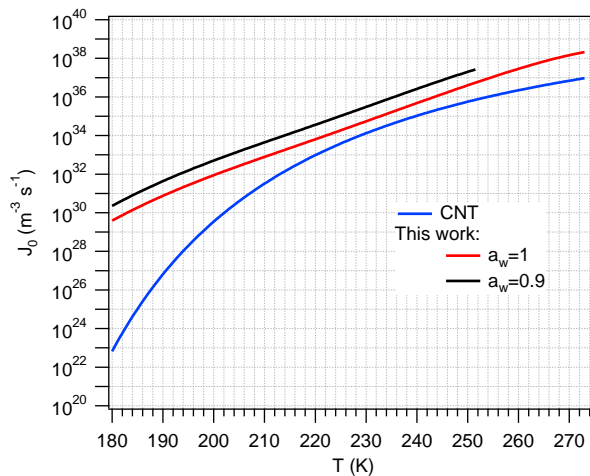
Figure 3. Preexponential factor using the common form of CNT (Section 2.3) and the model presented in this work, Eq. (11). For CNT the correlation of Zobrist et al. (2007) was used to calculate ΔG_{act}.
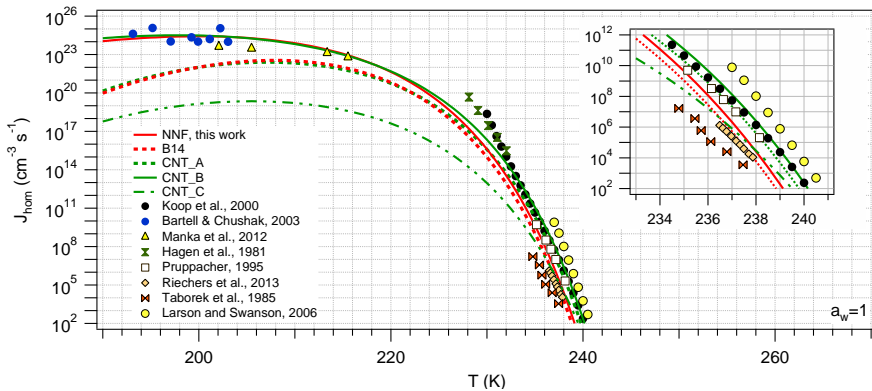
Figure 4. Homogeneous ice nucleation rate calculated using Eq. (16) (label "CNT") and Eq. (11) (label "NNF"). For CNT_A ΔG_{act} was defined as in Zobrist et al. (2007) and for CNT_B it was calculated using Eq.(14); in both cases the empirical expression for σ_{iw} from Barahona (2014) was used. For the model of Koop et al. (2000) $a_{w,eq}$ was defined as in Koop and Zobrist (2009). Also presented are experimental results and empirical correlations obtained from the literature.
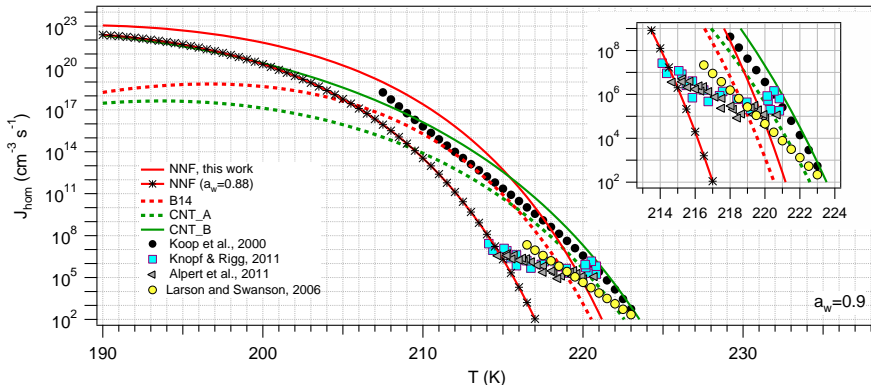
Figure 5. Homogeneous ice nucleation rate calculated using Eq. (16) (label "CNT") and Eq. (11) (label "NNF"). For CNT_A ΔG_{act} was defined as in Zobrist et al. (2007) and for CNT_B it was calculated using Eq.(14); in both cases the empirical expression for σ_{iw} from Barahona (2014) was used. For the model of Koop et al. (2000) $a_{w,eq}$ was defined as in Koop and Zobrist (2009). Also presented are experimental results and empirical correlations obtained from the literature.