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Thermodynamic derivation of the energy of activation for ice nucleation

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Abstract

The activation energy 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 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 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.

1 Introduction

Ice nucleation in cloud droplets and aerosol particles leads to cloud formation at low temperature and promotes cloud glaciation and precipitation (Pruppacher and Klett, 1997). In absence of ice nuclei it proceeds by homogeneous freezing. Modeling and experimental 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, 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, $a_{\mathrm{w,eq}}$. 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 parameterizations 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. 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; 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 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 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 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 Curry, 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 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 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 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 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} 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., Spaepen, 1975; Digilov, 2004; Barahona, 2014), the phenomenological 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 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 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 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 in close proximity to the ice–liquid interface so that diffusion through the bulk of the 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),

$$J_{\mathrm{hom}} = \frac{Zf^*}{v_{\mathrm{w}}} \exp\left(-\frac{\Delta G_{\mathrm{hom}}}{k_{\mathrm{B}}T}\right), \tag{1}$$

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),

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

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),

$$\Delta G_{\mathrm{hom}} = \frac{4}{27}\frac{\left[\Gamma_{\mathrm{w}} s\left(\Delta h_{\mathrm{f}} - \Gamma_{\mathrm{w}} k_{\mathrm{B}} T \ln a_{\mathrm{w}}\right)\right]^3}{\left[k_{\mathrm{B}} T \ln\left(\frac{a_{\mathrm{w}}^2}{a_{\mathrm{w,eq}}}\right)\right]^2}. \tag{3}$$

where $\Gamma_{\mathrm{w}} = 1.46$ is the coverage of the ice-water interface, and $s = 1.105$ defines the lattice 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, 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 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 $Z_1 \approx v_{\mathrm{w}}^{-1}$ the monomer concentration.

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 D was derived from transition state theory by Turnbull and Fisher (1949) (see Sect. 2.2), who assumed that the activation energy for interface transfer is similar to that of the bulk, 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 . Since D_∞ has been measured to $T \sim 180\,\mathrm{K}$ (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. 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).

An key aspect of the transient state is that it has a higher free energy than that of bulk water, which stems from a 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 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. The work distribution in such system is governed by the fluctuation theorem (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 process between two states of a system, respectively, ΔG their equilibrium free energy difference, and W the non-equilibrium work between the two states. Equation (6) is one of the few thermodynamic relations valid in systems away from equilibrium (Bustamante et al., 2005). In writing Eq. (6) is has been assumed that the system 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).

Consider a subsystem of size n_t involved in the transfer of molecules across the ice–liquid interface. At equilibrium the molecules move freely across the interface and $\Delta G = G_{\text{liq}} - G_{\text{ice,eq}} = W = 0$, being G_{liq} and $G_{\text{ice,eq}}$ the Gibbs free energy of bulk liquid and ice, respectively (red line, Fig. 1). As the system moves away from equilibrium 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 consider the reversed process, that is, molecules spontaneously leaving the lattice into the bulk of the liquid. To move away from the ice lattice, molecules should gain energy equal to $G^* - G_{\text{ice}}$, being G^* the energy of the transient state. On the other hand, if such process could be carried out in a completely reversible manner then molecules would only need $G_{\text{liq}} - G_{\text{ice}}$ to leave the lattice. 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 $W - \Delta G = -n_t \Delta\mu_{\text{act}}$. 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 $P(W) + P(-W) = 1$. Using this Eq. (6) can be rearranged into,

$$P(W) = \left[1 + \exp\left(-\frac{W - \Delta G}{k_\mathrm{B}T}\right)\right]^{-1}. \tag{7}$$

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

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

Since dissipation comes 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 fusion of water, i.e., $\Delta\mu_\mathrm{act} \approx -\Delta\mu_\mathrm{f}$. Thus we write,

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

Using $\Delta\mu_\mathrm{f} = -k_\mathrm{B}T\ln\left(\frac{a_\mathrm{w}}{a_\mathrm{w,eq}}\right)$ into Eq. (9) we obtain

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

where $a_\mathrm{w,eq}$ is the equilibrium water activity. To complete the derivation $f(T, a_\mathrm{w})$ 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 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 $n_\mathrm{t} = 2^4 = 16$.

Collecting terms into Eq. (1) we obtain,

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

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,

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

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 $a_\mathrm{w} \sim a_\mathrm{w,eq}$). Using this and substituting Eq. (12) into Eq. (11) we obtain,

$$J_\mathrm{hom} \approx \left(\frac{D_0}{v_\mathrm{w} d_0}\right)\left(\frac{Z\Omega}{v_\mathrm{w}}\right)\exp\left\{-\frac{1}{k_\mathrm{B}T}\left[\frac{k_\mathrm{B}TE}{(T - T_0)} + k_\mathrm{B}T n_\mathrm{t} \ln\left(\frac{a_\mathrm{w}}{a_\mathrm{w,eq}}\right) + \Delta G_\mathrm{hom}\right]\right\}, \tag{13}$$

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

$$\Delta G_\mathrm{act} = k_\mathrm{B}T\left[\frac{E}{(T - T_0)} + n_\mathrm{t} \ln\left(\frac{a_\mathrm{w}}{a_\mathrm{w,eq}}\right)\right]. \tag{14}$$

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,

$$J_{\mathrm{hom}} \approx \left(\frac{D_0}{v_{\mathrm{w}} d_0}\right)\left(\frac{Z\Omega}{v_{\mathrm{w}}}\right)\exp\left(-\frac{\Delta G_{\mathrm{act}} + \Delta G_{\mathrm{hom}}}{k_{\mathrm{B}}T}\right). \tag{15}$$

2.2 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 (1956) 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),

$$J_{\mathrm{hom}} = \left(\frac{N_{\mathrm{c}} k_{\mathrm{B}} T}{h}\frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{i}}}\right)\left(\frac{Z\Omega}{v_{\mathrm{w}}}\right)\exp\left(-\frac{\Delta G_{\mathrm{act}} + \Delta G_{\mathrm{CNT}}}{k_{\mathrm{B}}T}\right) = J_{0,\,\mathrm{CNT}}\exp\left(-\frac{\Delta G_{\mathrm{CNT}}}{k_{\mathrm{B}}T}\right) \tag{16}$$

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),

$$\Delta G_{\mathrm{CNT}} = \frac{16\pi\sigma_{\mathrm{iw}}^3 v_{\mathrm{w}}^2}{3(k_{\mathrm{B}}T\ln S_{\mathrm{i}})^2}, \tag{17}$$

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 Gibbs, 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 transformation 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 $a_{\mathrm{w}} = 1$ 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 activation energy. The dependency of ΔG_{act} on a_{w} is however much weaker than on T. Decreasing 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, $W_{\mathrm{diss}} = -n_{\mathrm{t}}\Delta\mu_{\mathrm{f}}$, 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 $\Delta\mu_{\mathrm{f}}$. 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 recently reviewed by Ickes et al. (2015). The authors found that the usage of the correlation 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 in B14 is used instead 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 $\Delta G_{\text{CNT}} \approx \Delta G_{\text{hom}}$ 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,

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

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 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 $\Delta G_{\text{act,Z07}}$.

Figure 2 shows that $\Delta G_{\text{act,Z07}}$ increases almost quadratically as T decreases. The correlation 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 (Ickes et al., 2015). In general $\Delta G_{\text{act,Z07}}$ is larger than ΔG_{act} calculated from Eq. (14). Moreover, the latter increases almost linearly as T decreases instead of the quadratic increase of $\Delta G_{\text{act,Z07}}$. $\Delta G_{\text{act,Z07}}$ 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; 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 $T < 240$ K the factors $(\frac{D_0}{v_{\text{w}} d_0})$ and $(\frac{N_{\text{c}} k_{\text{B}} T}{h} \frac{\rho_{\text{w}}}{\rho_{\text{i}}})$ 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 $\Delta G_{\mathrm{act},07}$ leads to a much faster decrease in J_0 than with Eq. (14), which is explained by the quadratic increase in $\Delta G_{\mathrm{act},07}$ as T decreases. At 180 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 sensitive to variation in ΔG_{act} at low T. This is illustrated in Fig. 2. For $a_{\mathrm{w}} = 1$ and $T > 230$ K, $\Delta G_{\mathrm{hom}} \gg \Delta G_{\mathrm{act}}$, i.e., the nucleation rate is completely controlled by the nucleation work. As T decreases 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 $T < 230$ K. However it may introduce error in J_{hom} for $a_{\mathrm{w}} < 1$ (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 formulations of CNT (Sect. 2.2) 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 $\Delta G_{\mathrm{act},07}$ and Eq. (3) into Eq. (16) reproduced measured J_{hom} for $T > 230$ K. The results of B14 are shown in Fig. 4 along with several experimental measurements, empirical correlations, and results from the formulation of CNT presented in Sect. 2.2.

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 $a_{\mathrm{w}} = 1$ 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 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 $\Delta G_{\mathrm{act},07}$. In both formulations J_{hom} decreases for T below 210 K, which results from an strong increase in $\Delta G_{\mathrm{act},07}$ and a decrease in J_0. 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 results from the usage of the formulation of ΔG_{act} presented here.

Most experimental measurements of J_{hom} have been carried out for $a_{\mathrm{w}} = 1$. However homogeneous freezing for $a_{\mathrm{w}} < 1$ is likely important for the formation of cirrus at low T (e.g., Koop et al., 2000). Figure 4 (right panel) shows J_{hom} for $a_{\mathrm{w}} = 0.9$ from Eqs. (16) and (11), and using $\Delta G_{\mathrm{act},07}$ 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. For $T > 218$ K, J_{hom} from all formulations agree within three orders of magnitude, and within experimental uncertainty of the measured rates. However for $T < 216$ K, calculated J_{hom} is higher than the experimental results. This would indicate that J_{hom} is less sensitive to T at $a_{\mathrm{w}} = 0.9$ than at $a_{\mathrm{w}} = 1.0$. Another possibility may be a slight decrease in a_{w} during the experiments. 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 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 4 (right panel) shows that a decrease of 0.02 in a_{w} during the experiments would be enough to explain the observed J_{hom}. More research and further experimentation is required to clarify this point.

At low temperature ($T < 210$ K) the usage of Eq. (14) leads to a higher J_{hom} than when $\Delta G_{\mathrm{act},07}$ is used, for both formulations of CNT. For $a_{\mathrm{w}} < 1$ Eqs. (16) and (11) do not overlap as is the case for $a_{\mathrm{w}} = 1$, which results from the different sensitivity to a_{w} of both formulations. Interestingly, for $a_{\mathrm{w}} = 1$ and $a_{\mathrm{w}} = 0.9$, J_{hom} reaches similar values at $T = 180\,\mathrm{K}$, being just about an order of magnitude higher in the latter due to the sensitivity of ΔG_{act} to a_{w}. This shows that a low T, J_{hom} is mainly controlled by J_0, hence ΔG_{act}.

4 Conclusions

This work advances a phenomenological description of the process of interface transfer of water molecules from the liquid phase to the ice during the early stages of nucleation. 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 theoretical 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, associated 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 represents about half of ΔG_{act}.

It was shown that at low temperature interface transfer has the largest effect on the nucleation rate. For such conditions $\Delta G_{\mathrm{act}} \sim \Delta G_{\mathrm{hom}}$ 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 $T > 230\,\mathrm{K}$ where $\Delta G_{\mathrm{hom}} \gg \Delta G_{\mathrm{act}}$. However ΔG_{act} may have a marked influence for the homogeneous 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 $T > 230\,\mathrm{K}$ 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 $T < 230\,\mathrm{K}$, 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 the 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 $T > 218\,\mathrm{K}$ predicted J_{hom} is in agreeement within experimental uncertanity 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 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}.

Guided by MD results, it was assumed that a molecule crossing the interface would interact with four other molecules, so that $n_{\mathrm{t}} = 16$. This is expected at low T since the water structure becomes more ice-like, however n_{t} may be a function of the temperature. 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 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 $T \sim 235\,\mathrm{K}$ to define $a_{\mathrm{w,eq}}$ 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. Progress in MD and further experimentation may shed light on these issues.

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, $f(T, a_{\mathrm{w}})$. 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.

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 formulation presented here may be more amenable to testing and expansion. In turn, a physically-based definition of the parameters 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.

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Table 1. List of symbols.

a_w	Activity of water
$a_\mathrm{w,eq}$	Equilibrium a_w between bulk liquid and ice (Koop and Zobrist, 2009)
E, T_0	Parameters of the VFT equation, 892 and 118 K, respectively (Smith and Kay, 1999)
D	Diffusion coefficient for interface transfer
D_∞	Self-diffusion coefficient of bulk water
D_0	Fitting parameter, $3.06 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$(Smith and Kay, 1999)
d_0	Molecular diameter of water
$f(T, a_\mathrm{w})$	Interface transfer probability
f^*	Impingement factor
G	Gibbs free energy
G^*	Gibbs free energy of the transient state
$G_\mathrm{liq}, G_\mathrm{ice}$	Gibbs free energy of liquid and ice, respectively
J_0, $J_\mathrm{0,CNT}$	Pre-exponential factor calculated from Eqs. (11) and (16), respectively
J_hom	Nucleation rate
k_B	Boltzmann constant
n^*	Critical germ size
N_c	Number of atoms in contact with the ice germ, $5.85 \times 10^{18}\,\mathrm{m^{-2}}$(Pruppacher and Klett, 1997)
n_t	Number of configurations of a subsystem, 16
$p_\mathrm{s,w}$, $p_\mathrm{s,i}$	Liquid water and ice saturation vapor pressure, respectively (Murphy and Koop, 2005)
s	Geometric constant of the ice lattice, $1.105\,\mathrm{mol}^{2/3}$(Barahona, 2014)
S_i	Saturation ratio with respect to ice
T	Temperature
v_w	Molecular volume of water in ice (Zobrist et al., 2007)
W	Non-equilibrium work
W_diss	Dissipated work
Z	Zeldovich factor
ΔG_act	Activation energy for ice nucleation
ΔG_hom	Nucleation work, NNF framework
ΔG_CNT	Nucleation work, CNT framework
Δh_f	Heat of fusion of water (Barahona, 2014; Johari et al., 1994)*
Δa_w	$a_\mathrm{w} - a_\mathrm{w,eq}$
$\Delta \mu_\mathrm{f}$	Excess free energy of water
$\Delta \mu_\mathrm{act}$	Specific activation energy for interface transfer
Γ_w	Molecular surface excess of at the interface, 1.46 (Barahona, 2014; Spaepen, 1975)
ρ_w, ρ_i	Bulk density of liquid water and ice, respectively (Pruppacher and Klett, 1997)
σ_iw	Ice–liquid interfacial energy (Barahona, 2014)
Ω_g	Ice germ surface area

* A change in enthalpy of 50 ($\mathrm{J\,mol^{-1}}$) was assumed for the transition between cubic and hexagonal ice.

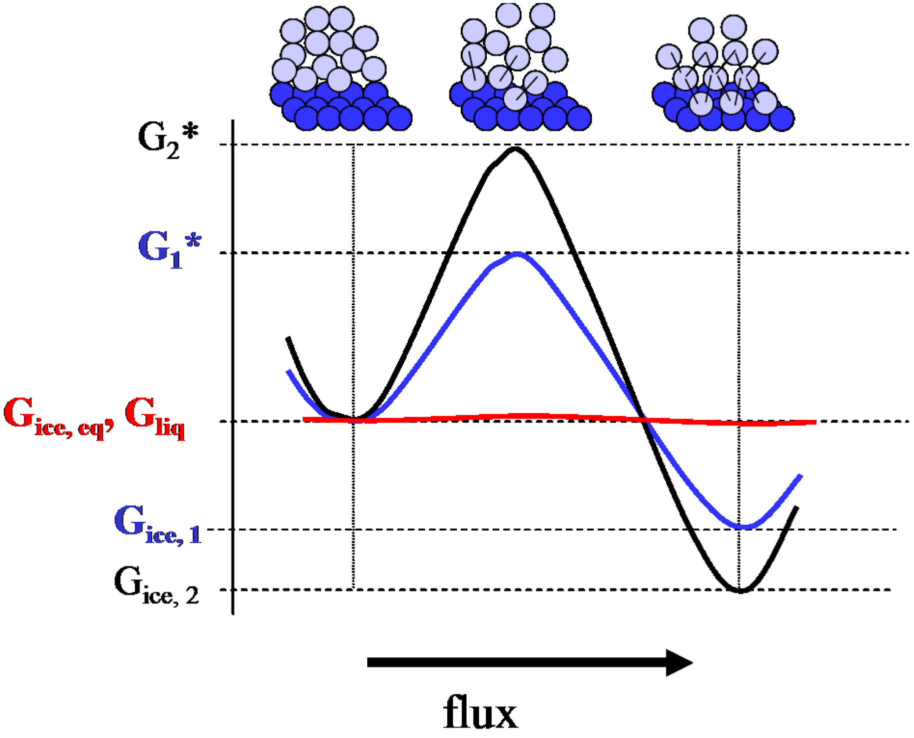

Figure 1. Scheme of the transfer of water molecules to a metastable ice germ. Red lines correspond to situations close to thermodynamic equilibirium whereas blue and black lines represent conditions progressively away from equilibrium (subscripts 1 and 2, respectively). G_{ice}, G_{liq} and G^* correspond to the Gibbs free energy of ice, liquid and the transient state, respectively. The cartoon at the top of the graph is a visualization of the interaction of water molecules during interface transfer.

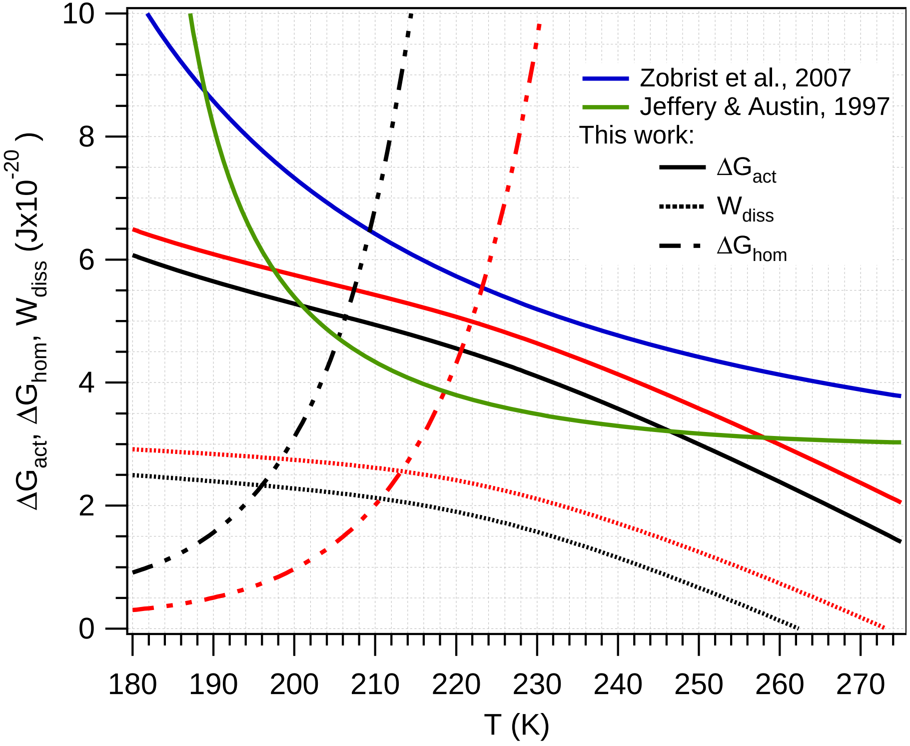

Figure 2. Energy of activation represented by several models. Also presented are the dissipated work, W_{diss}, and the work of nucleation ΔG_{hom}. Red lines and black lines correspond to $a_w = 0.9$ and $a_w = 1$, respectively.

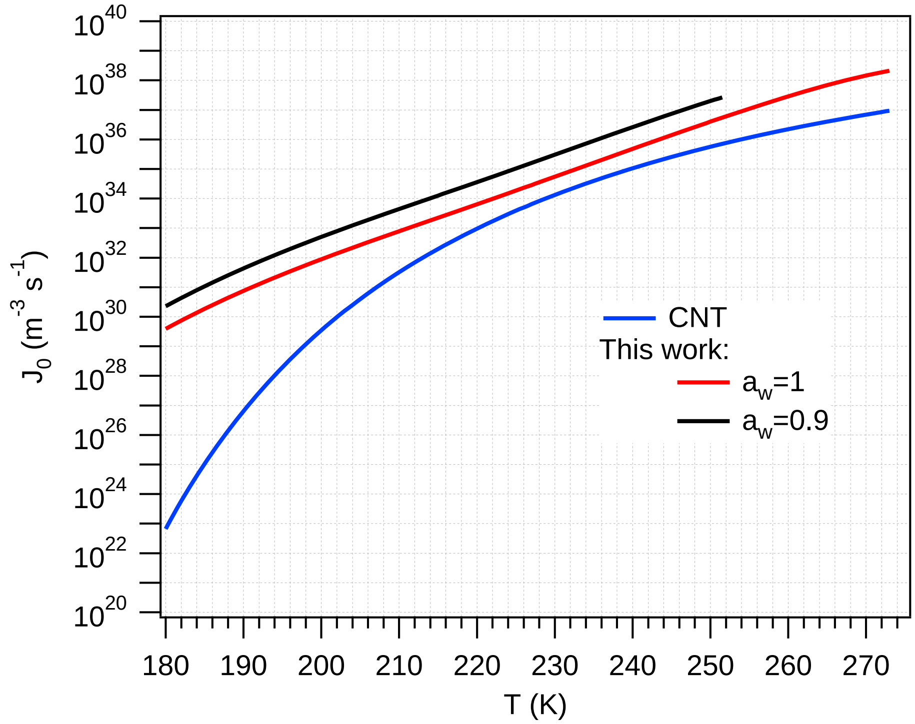

Figure 3. Preexponential factor using the common form of CNT (Sect. 2.2) and the model presented in this work, Eq. (11). For CNT the correlation of Zobrist et al. (2007) was used to calculate ΔG_{act}.

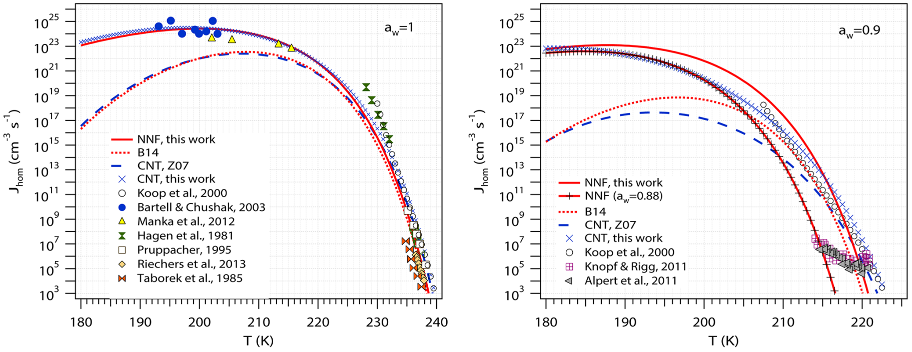

Figure 4. Homogeneous ice nucleation rate calculated using Eq. (16) (label "CNT") and Eq. (11) (label "NNF"). ΔG_{act} was defined as in Zobrist et al. (2007) (Z07) and using Eq. (14) (this work). Also presented are experimental results and empirical correlations obtained from the literature.