



On the thermodynamic and kinetic aspects of immersion ice nucleation

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Abstract. Heterogeneous ice nucleation initiated by particles immersed within droplets is likely the main pathway of ice formation in the atmosphere. Theoretical models commonly used to describe this process assume that it mimics ice formation from the vapor, neglecting interactions unique to the liquid phase. This work introduces a new approach that accounts for such interactions by linking the ability of particles to promote ice formation to the modification of the properties of water near the particle–liquid interface. It is shown that the same mechanism that lowers the thermodynamic barrier for ice nucleation also tends to decrease the mobility of water molecules, hence the ice–liquid interfacial flux. Heterogeneous ice nucleation in the liquid phase is thus determined by the competition between thermodynamic and kinetic constraints to the formation and propagation of ice. At the limit, ice nucleation may be mediated by kinetic factors instead of the nucleation work. This new ice nucleation regime is termed spinodal ice nucleation. The comparison of predicted nucleation rates against published data suggests that some materials of atmospheric relevance may nucleate ice in this regime.

1 Introduction

Ice nucleation in cloud droplets and aerosol particles leads to cloud formation and glaciation at low temperatures. It is often initiated by certain aerosol species known as ice nucleating particles (INPs) (DeMott et al., 2003; Cziczo et al., 2013; Barahona et al., 2017). These include dust, biological particles, metals, effloresced sulfate and sea salt, organic material and soot (Murray et al., 2012; Hoose and Möhler, 2012). Background INP concentrations may be influenced by

aerosol emissions (Lohmann and Feichter, 2005), altering the formation and evolution of ice clouds and leading to an indirect effect on climate. The assessment of the role of INPs in climate is challenging due to the complexity of the atmospheric processes involving ice and the limited understanding of the ice nucleation mechanism of INPs (Myhre et al., 2013). Ice formation promoted by a particle completely immersed within the liquid phase, referred as “immersion freezing”, is likely the most common cloud glaciation pathway in the atmosphere (DeMott et al., 2003; Wiacek et al., 2010). Immersion freezing is involved in the initiation of precipitation and determines, to a large extent, the phase partitioning in convective clouds (Diehl and Wurzler, 2004; Wiacek et al., 2010; Lance et al., 2011; Murray et al., 2012).

The accurate representation of immersion ice nucleation is critical for the correct modeling of cloud processes in the atmosphere (Hoose and Möhler, 2012; Murray et al., 2012; Tan et al., 2016). Field campaign data have been used to develop empirical formulations relating the INP concentration to the cloud temperature, T , and saturation ratio, S_i (e.g., Bigg, 1953; Fletcher, 1959; Meyers et al., 1992), and more recently to the ambient aerosol size and composition (e.g., DeMott et al., 2010; Niemand et al., 2012; Phillips et al., 2013). Empirical formulations provide a simple way to parameterize ice nucleation in atmospheric models (e.g., Gettelman et al., 2012; Barahona et al., 2014). However they may not be valid outside the conditions used in their development, particularly as different experimental techniques may result in a wide range of measured ice nucleation efficiencies (Hiranuma et al., 2015). Alternatively, the ice nucleation efficiency can be empirically parameterized using laboratory data, although with similar caveats (Knopf and Alpert, 2013; Murray et al., 2012).

Molecular Dynamics (MD) simulations and direct kinetic methods have been used to study ice nucleation (e.g., Taylor and Hale, 1993; Matsumoto et al., 2002; Lupi et al., 2014; Espinosa et al., 2014). However, the classical nucleation theory (CNT) is nearly the only theoretical approach employed to describe immersion freezing in cloud models (e.g., Khvorostyanov and Curry, 2004; Barahona and Nenes, 2008, 2009; Hoose et al., 2010). According to CNT, nucleation is initiated by the growth of a cap-shaped ice germ on the surface of the immersed particle (Pruppacher and Klett, 1997; Kashchiev, 2000). The geometry of the ice germ is defined by a force balance at the particle–ice–liquid interface and is characterized by the contact angle, θ . In this sense, the ice germ is assumed to “wet” the immersed particle in the same way a liquid droplet wets a solid surface (De Gennes, 1985). Low values of θ indicate a high affinity of the particle for ice and a low energy of formation of the ice germ.

Direct application of CNT in immersion freezing is thwarted by uncertainty in fundamental parameters of the theory, i.e., the ice–liquid interfacial energy, σ_{iw} , and the activation energy. Moreover, using a single θ to describe the nucleation efficiency of dust and other materials typically leads to a large discrepancy between CNT predictions and experimental measurements (e.g., Zobrist et al., 2007; Alpert et al., 2011; Broadley et al., 2012; Rigg et al., 2013). MD simulations show that an ice germ formed near a surface tends to have a complex geometry instead of the cap-shaped assumption of CNT (e.g., Lupi et al., 2014; Cox et al., 2015; Fitzner et al., 2015). Within a liquid the ice germ may not “wet” the particle but may rather exert stress on the substrate (Cahn, 1980; Rusanov, 2005), and it is not clear that this can be described as a simple function of θ (Cahn, 1980). It has also been shown that σ_{iw} obtained by fitting CNT to measured nucleation rates tend to be biased to account for the mixing effects neglected in common formulations of the theory (Barahona, 2014).

More fundamentally, CNT neglects important interactions near the immersed particle that may influence the nucleation rate. It is assumed that ice nucleation solely depends on the local geometry of the adsorbed molecules on the immersed particle (Kashchiev, 2000). This implies that the particle influences the formation of the ice germ but does not influence its adjacent water. The viscosity and density of water in the vicinity of the particle and in contact with the ice germ are assumed similar to those in the bulk (Kashchiev, 2000; Pruppacher and Klett, 1997). This is at odds with evidence of a strong effect of immersed particles on the vicinal water (Drost-Hansen, 1969; Michot et al., 2002). In fact, such an effect may be responsible for the enhancement of ice nucleation near immersed solids (Anderson, 1967).

1.1 Evidence for the formation of ordered structures near the liquid–particle interface

It has been known for some time that water near interfaces displays physicochemical properties different from those of the bulk (e.g., Drost-Hansen, 1969; Michot et al., 2002; Bellissent-Funel, 2002). By examining a wealth of reported experimental observations, Drost-Hansen (1969) concluded that vicinal water (i.e., the water immediately adjacent to the particle) may exist in an ordered state near the solid–liquid interface that may propagate over considerable distance, of the order of hundreds to thousands of molecular diameters. More recent experiments showing that hydrophilic surfaces have a long-range impact further support this conclusion (e.g., Zheng et al., 2006). The interaction between the particle and the vicinal water becomes more significant as the temperature decreases and the viscosity increases (Wolfe et al., 2002). Recent studies have shown the presence of ordered water near the interface of biological (Cooke and Kuntz, 1974; Snyder et al., 2014), metallic (Michot et al., 2002) and clay (Yu et al., 2001; Rinnert et al., 2005) particles, a notion that is also supported by molecular dynamics simulations (Lupi et al., 2014; Cox et al., 2015). In a groundbreaking work, Anderson (1967) found strong evidence of ice formation several molecular diameters away from the clay–water interface. The author concluded that ice formation does not require an ice germ attached to the substrate, but rather the nascent ice germ is stabilized by ordering in the interfacial zone. To date no quantitative theory has been developed exploiting such a view of ice nucleation.

The description of the properties of the vicinal water is still under investigation. In the supercooled region the presence of structured low-density water near solid surfaces (termed “ice-like”) has been reported for different materials (e.g., Etzler, 1983; Yu et al., 2001; Michaelides and Morgenstern, 2007; Feibelman, 2010; Snyder et al., 2014). In this region Etzler (1983) parameterized the density and enthalpy of vicinal water as a mixture of ice-like and bulk-like water. Additional experimental observations also show the modification of the mobility of water near interfaces and a higher viscosity than the bulk (Warne et al., 2000; Yu et al., 2001; Wolfe et al., 2002; Wang et al., 2006). In some cases, clays and biological systems exhibit a viscous layer of water at the particle–liquid interface that remains liquid even if the bulk has already frozen (Drost-Hansen, 1969). These effects are typically characterized as non-equilibrium, since they affect the flux of molecules to the nascent ice germ rather than the thermodynamics of ice nucleation. Li et al. (2014) found experimentally that the viscosity of interfacial water regulates the ice nucleation activity, giving support to the idea that the work of nucleation and the enhancement of the viscosity in the interfacial region are tightly linked. In fact, increased viscosity may be a necessary condition for ice nucleation, since structural ordering is not possible in a fluid with low viscosity (Anderson, 1967).

These considerations are largely missing in the theoretical description of ice nucleation. There is currently no theory that can account for the thermodynamic and kinetic effects of an immersed particle on the surrounding water, hence on ice nucleation. Such a task is undertaken in this work. Section 2 presents the theoretical description of a new approach, accounting for the thermodynamics of vicinal water (Sect. 2.3) and its relation to the work of nucleation (Sect. 2.4) and the nucleation rate (Sects. 2.5 and 2.6). These new relations are analyzed and applied to specific cases of atmospheric relevance in Sect. 3.

2 Theoretical development

The new approach is developed within the scope of the kinetic treatment of nucleation, when cluster formation is the limiting step to ice formation (Pruppacher and Klett, 1997; Kashchiev, 2000). The central result of this theory is the following well-known general expression for the nucleation rate in steady state (e.g., Kashchiev, 2000, cf. Eq. 13.33):

$$J = Z f^* C^*, \quad (1)$$

where Z is the Zeldovich factor, f^* is the attachment frequency (also called the impingement factor), and C^* is the concentration of supercritical clusters. Z corrects for the detachment of monomers from the cluster during nucleation. It can also be interpreted as the probability that a molecule reaches the ice germ following a thermally activated “random walk”. Generally,

$$Z = \left[-\frac{\left(\frac{\partial^2 \Delta G}{\partial n^2}\right)_{n=n^*}}{2\pi k_B T} \right]^{1/2}, \quad (2)$$

where ΔG is the work of cluster formation and n^* is the number of water molecules in the ice germ. If the molecular cluster size distribution can be assumed to be near equilibrium, which is the case for immersion freezing, then

$$C^* = C_0 \exp\left(-\frac{\Delta G^*}{k_B T}\right), \quad (3)$$

where ΔG^* is the work of critical germ formation and C_0 is the monomer concentration adjacent to the surface of the growing ice germ, implying that interface transfer is the dominant mechanism of cluster growth.

These expressions can be applied directly to model ice nucleation as follows. For homogeneous ice nucleation, $\Delta G^* = \Delta G_{\text{hom}}$ and $f^* = f_{\text{hom}}^*$, with $C_0 = v_w^{-1} v_w$ being the molecular volume of water (Pruppacher and Klett, 1997):

$$J_{\text{hom}} = \frac{Z f_{\text{hom}}^*}{v_w} \exp\left(-\frac{\Delta G_{\text{hom}}}{k_B T}\right). \quad (4)$$

For heterogeneous ice nucleation, $\Delta G^* = \Delta G_{\text{het}}$ and $f^* = f_{\text{het}}^*$, with $C_0 = a_0^{-1}$ being a_0 , the average cross-sectional area of a water molecule, i.e.,

$$J_{\text{het}} = \frac{Z f_{\text{het}}^*}{a_0} \exp\left(-\frac{\Delta G_{\text{het}}}{k_B T}\right). \quad (5)$$

Using $C_0 = a_0^{-1}$ is advantageous, because J_{het} is typically normalized to the particle surface area (Murray et al., 2012; Hoose and Möhler, 2012). It, however, involves the assumption that the density of water does not vary within the droplet, remaining constant even at the particle–water interface. In other words, anywhere within the liquid, the per-area molecular density should be the same. This assumption, however, does not lead to significant error, since the effect of the particle on the water density is small (e.g., Etzler, 1983), and J_{het} is linearly related to C_0 .

Equation (5) provides the basis for this work. It shows that, to predict the effect of the immersed particle on ice formation, it is necessary to understand how the presence of the particle affects ΔG_{het} and f_{het}^* . To accomplish this Sect. 2.1 provides an overview of the main assumptions of CNT, which are then contrasted with the negetropic nucleation framework (NNF) in Sect. 2.2. The latter is used in Sects. 2.3 and 2.4 to analyze the thermodynamic aspects of immersion ice nucleation and to formulate a new expression for ΔG_{het} . Section 2.5 develops an expression for f_{het}^* accounting for the effect of the particle on the mobility of water molecules. In Sect. 2.6 a new expression for the nucleation rate is formulated.

2.1 Classical nucleation theory

Since CNT is the most widely used theoretical approach in atmospheric models we start by highlighting its main characteristic. Common CNT expressions use several assumptions to simplify the description of the interaction between water and the immersed particle (e.g., Khvorostyanov and Curry, 2004; Zobrist et al., 2007; Hoose et al., 2010). Typically the particle is assumed to have a negligible effect on the mobility and the thermodynamics of the vicinal water, i.e., $f_{\text{het}}^* \approx f_{\text{hom}}^*$. The latter is calculated assuming that the formation of clusters within the liquid phase mimics a first-order reaction in an ideal gas where every molecule that randomly jumps into the ice–liquid interface is incorporated within the ice lattice. Thus f_{hom}^* is the product of the frequency factor (derived from transition state theory) and the monomer concentration at the ice–liquid interface. This leads to (Pruppacher and Klett, 1997; Kashchiev, 2000)

$$f_{\text{het,CNT}}^* = f_{\text{hom,CNT}}^* = \frac{\Omega d_0 k_B T}{v_w h} \exp\left[-\frac{\Delta G_{\text{act}}}{k_B T}\right], \quad (6)$$

where ΔG_{act} is the activation energy, i.e., the energy required for a water molecule to leave its equilibrium position in the bulk towards the vicinity of the ice germ (Pruppacher and

Klett, 1997; Zobrist et al., 2007), h is Plank's constant, Ω the surface area of the ice germ and d_0 is the molecular diameter of water.

The work of ice nucleation results from the assumption that the ice germ has a hemispherical shape. Other assumptions include no surface stress (Cahn, 1980) and negligible mixing effects during germ formation (Barahona, 2014). These considerations lead to the expression (Turnbull and Fisher, 1949)

$$\Delta G_{\text{het,CNT}} = g(\theta) \Delta G_{\text{hom,CNT}}, \quad (7)$$

where $\Delta G_{\text{hom,CNT}}$ is the homogeneous work of nucleation, given by

$$\Delta G_{\text{hom,CNT}} = \frac{16\pi\sigma_{\text{iw}}^3 v_{\text{w}}^2}{3(k_{\text{B}}T \ln S_{\text{i}})^2}, \quad (8)$$

where σ_{iw} is the ice–water interfacial energy and S_{i} is the saturation ratio with respect to ice. The effect of the immersed particle on $J_{\text{het,CNT}}$ depends on the adsorption of water molecules on individual sites, and is characterized by the contact angle, θ , in the form

$$g(\theta) = \frac{1}{4}(2 + \cos\theta)(1 - \cos\theta)^2. \quad (9)$$

Equation (9) can be extended to account for line tension, curvature and misfit effects (e.g., Khvorostyanov and Curry, 2004), which, however, requires the usage of additional unconstrained parameters. Introducing Eqs. (6) and (7) into Eq. (5) we obtain the known expression,

$$J_{\text{het,CNT}} = \frac{Z\Omega d_0}{a_0 v_{\text{w}}} \frac{k_{\text{B}}T}{h} \exp\left[-\frac{\Delta G_{\text{act}} + g(\theta)\Delta G_{\text{hom,CNT}}}{k_{\text{B}}T}\right], \quad (10)$$

where $\Omega = 4\pi r_{\text{g}}^2$, and $r_{\text{g}} = \left(\frac{3n^* v_{\text{w}}}{4\pi}\right)^{1/3}$ is the radius of the ice germ. Other symbols are defined in Table 1.

Due in part to the assumption of a negligible effect of the particle on the adjacent water the CNT framework does not provide a way to link the properties of the vicinal water to the nucleation rate. Another caveat of CNT is that fundamental parameters like ΔG_{act} , σ_{iw} and θ do not have a clear definition outside of the context of the theory. For example, ΔG_{act} is typically assumed the same as in bulk water, representing a barrier to bulk diffusion instead of interfacial transfer (Kashchiev, 2000; Barahona, 2015). Similarly σ_{iw} is not well defined for a diffuse interface, and it is difficult to measure away from equilibrium. Moreover, θ relies on a droplet-like picture of the nascent ice germ, which may not be appropriate for a germ forming within the dense liquid phase (Brukhno et al., 2008). Most studies thus treat ΔG_{act} , σ_{iw} and θ as empirical parameters, fitted to match measured nucleation rates. Many times this results in complex functional forms of T and S_{i} that may not be easily expanded to account for the modified properties of water near the immersed particle.

2.2 Negentropic nucleation framework

Some of the caveats of CNT are addressed in the negentropic nucleation framework (NNF; Barahona, 2014, 2015). In NNF simple thermodynamic arguments are used to approximate ΔG_{hom} and f_{hom} in terms of water properties that could, in principle, be independently estimated. This obviates the need for parameters that should be fitted to measured nucleation rates. At the same time, NNF is a relatively simple framework that can be easily implemented in large-scale atmospheric models and that has been shown to reproduce homogeneous freezing temperatures down to 180 K (Barahona, 2015; O and Wood, 2016). This section presents the main results of NNF for homogeneous ice nucleation.

In NNF the energy of formation of the interface, Φ_{s} , is an explicit function of the water activity and temperature in the form

$$\Phi_{\text{s}} = \Gamma_{\text{w}} s (\Delta h_{\text{f}} - \Gamma_{\text{w}} k_{\text{B}} T \ln a_{\text{w}}), \quad (11)$$

where the constants $\Gamma_{\text{w}} = 1.46$ and $s = 1.105 \text{ molec}^{1/3}$ define the coverage of the ice–water interface and the lattice geometry of the ice germ, respectively, and Δh_{f} is the latent heat of fusion of water. Other symbols are defined in Appendix A. Equation (11) results from accounting for the finite character of the ice–liquid interface and from the assumption that, in joining the ice lattice, the water molecules lose most of their entropy (Barahona, 2014). The driving force for ice nucleation, $\Delta\mu_{\text{i}}$, is given by

$$\Delta\mu_{\text{i}} = k_{\text{B}}T \ln\left(\frac{a_{\text{w}}^2}{a_{\text{w,eq}}}\right), \quad (12)$$

where $a_{\text{w,eq}}$ is the equilibrium water activity. Equation (12) accounts for the work of “unmixing” affecting the bulk of the liquid when the ice germ is formed, which is proportional to $\ln(a_{\text{w}})$ (Black, 2007). Using Eqs. (11) and (12), the critical germ size and the work of nucleation are obtained from the condition of mechanical equilibrium of the ice germ (Barahona, 2014), resulting in

$$n_{\text{hom}} = \left(\frac{2\Phi_{\text{s}}}{3\Delta\mu_{\text{i}}}\right)^3, \quad (13)$$

and

$$\Delta G_{\text{hom,NNF}} = \frac{4}{27} \frac{\Phi_{\text{s}}^3}{\Delta\mu_{\text{i}}^2} = \frac{1}{2} n_{\text{hom}} \Delta\mu_{\text{i}}. \quad (14)$$

In more recent work the kinetics of homogeneous ice nucleation have been re-examined in NNF to account for molecular rearrangement during the transfer of water molecules across the ice–liquid interface (Barahona, 2015). Within this approach f_{hom}^* is determined by the diffusion coefficient for interfacial transfer, D , in the form (Kashchiev, 2000; Barahona, 2015)

$$f^* = \frac{D\Omega}{v_{\text{w}}d_0}, \quad (15)$$

where Ω is the surface area of the ice germ. D represents contributions from purely diffusive process and from structural transformations required to incorporate water molecules into the ice germ. The latter originates because neighboring molecules need to be rearranged to accommodate new ones into the ice lattice, generating entropy and dissipating work. Using considerations from non-equilibrium thermodynamics D can be written in the form (Barahona, 2015)

$$D = D_{\infty} \left[1 + \exp\left(\frac{W_d}{k_B T}\right) \right]^{-1}, \quad (16)$$

where D_{∞} is the bulk self-diffusion coefficient of water, and W_d is the average dissipated work during interface transfer. The latter is proportional to the excess free energy of solidification of water, i.e., $W_d = -n_t \Delta\mu_s$, with $n_t = 16$, the number of possible trajectories in which individual water molecules can make four-bonded water. Equation (16) shows explicitly that bulk diffusion (i.e., D_{∞}) as well as structural rearrangement are required for ice germ growth. Introducing Eq. (16) into Eq. (15) we obtain

$$f_{\text{hom}}^* = \frac{D_{\infty} \Omega}{v_w d_0} \left[1 + \exp(-n_t \Delta\mu_s) \right]^{-1}. \quad (17)$$

Application of Eq. (17) to homogeneous ice nucleation shows agreement of J_{hom} with experimental data at very low T , where kinetic processes dominate the formation ice (Barahona, 2015).

NNF provides explicit dependencies of D and Φ_s on thermodynamic properties without depending on nucleation rate measurements. Thus it provides a suitable basis to study the thermodynamics and kinetics of ice formation in the vicinity of immersed particles. Doing so first requires building a model to describe the thermodynamics of the vicinal water.

2.3 Thermodynamics of the liquid–particle interface

The discussion presented in Sect. 1.1 suggests that the immersed particle enhances order near the particle–liquid interface, lowering the energy required to nucleate ice. The vicinal layer is thus described as a solution of hypothetical ice-like (IL) and liquid-like (LL) regions, with Gibbs free energy, given by

$$\mu_{\text{vc}} = (1 - \zeta) \hat{\mu}_{\text{LL}} + \zeta \hat{\mu}_{\text{IL}}, \quad (18)$$

where $\hat{\mu}_{\text{LL}}$ and $\hat{\mu}_{\text{IL}}$ are the chemical potentials of the LL and IL species within the solution, respectively, and ζ is the fraction of IL regions in the layer. Increased order is represented by a higher fraction of IL regions, hence higher ζ . Equation (18) can also be written in terms of the chemical potentials of the “pure” LL and IL species, μ_{LL} and μ_{IL} , respectively, in the form

$$\mu_{\text{vc}} = (1 - \zeta) \mu_{\text{LL}} + \zeta \mu_{\text{IL}} + \Delta G_{\text{mix}}, \quad (19)$$

where $\Delta G_{\text{mix}} = (\hat{\mu}_{\text{IL}} - \mu_{\text{IL}})\zeta + (1 - \zeta)(\hat{\mu}_{\text{LL}} - \mu_{\text{LL}})$ is the Gibbs energy of mixing. For a mechanical mixture of pure LL and IL species, $\Delta G_{\text{mix}} = 0$, whereas for an ideal solution, ΔG_{mix} is determined by the ideal entropy of mixing (Prausnitz et al., 1998). Reorganizing Eq. (19) we obtain,

$$\mu_{\text{vc}} = \mu_{\text{LL}} + \zeta \Delta\mu_{\text{il}} + \Delta G_{\text{mix}}, \quad (20)$$

where $\Delta\mu_{\text{il}} = \mu_{\text{IL}} - \mu_{\text{LL}}$. $\Delta\mu_{\text{il}}$ can be approximated using the equilibrium between bulk liquid and ice as a reference state (Kashchiev, 2000), making

$$\mu_{\text{IL}} = \mu_{\text{eq}} + k_B T \ln(a_{\text{IL}}), \quad (21)$$

and

$$\mu_{\text{LL}} = \mu_{\text{eq}} + k_B T \ln\left(\frac{a_{\text{w,eff}}}{a_{\text{w,eq}}}\right), \quad (22)$$

where $a_{\text{w,eff}}$ is termed the “effective water activity” and is the value of a_{w} associated with the LL regions in the vicinal water, and a_{IL} is the water activity in the IL regions. Assuming that, similarly to bulk ice, the solute does not significantly partition to the IL phase, then $a_{\text{IL}} \approx 1$. With this, and by combining Eq. (21) and Eq. (22) and rearranging, we obtain

$$\Delta\mu_{\text{il}} = -k_B T \ln\left(\frac{a_{\text{w,eff}}}{a_{\text{w,eq}}}\right). \quad (23)$$

The central assumption behind Eq. (23) is that $a_{\text{w,eq}}$ corresponds to the equilibrium water activity between liquid and ice, or in other words, that near equilibrium $\Delta\mu_{\text{il}} \approx \Delta\mu_s$. In reality $\Delta\mu_s$ corresponds to actual liquid and ice, instead of the hypothetical LL and IL substances. This difference can be accounted for by selecting a proper functional form for ΔG_{mix} , for which several empirical and semi-empirical interaction models, with varying degrees of complexity, exist (Prausnitz et al., 1998). In this work it is assumed that the vicinal water can be described as a regular solution. This is the simplest model that accounts for the interaction between solvent and solute during mixing and that is flexible enough to include corrections for the difference between $\Delta\mu_s$ and $\Delta\mu_{\text{il}}$. Using this model Holten et al. (2013) were able to approximate the chemical potential of supercooled water. The authors also showed that taking into account clustering of water molecules led to a better agreement of the estimated water properties with MD simulations and experimental results.

According to the regular solution model, modified by clustering (Holten et al., 2013, cf. Eq. 16),

$$\Delta G_{\text{mix}} = \frac{k_B T}{N} [\zeta \ln(\zeta) + (1 - \zeta) \ln(1 - \zeta)] + A_{\text{w}} \zeta (1 - \zeta). \quad (24)$$

The first term on the right-hand side corresponds to the usual definition of the ideal entropy of mixing, i.e., random ideal

mixing and weak interaction between IL and LL regions, modified to account for clustering in groups of N molecules. $N = 6$ corresponds to clustering in hexamers and is near the optimum fit between MD simulations and the solution model (Holten et al., 2013). It must be noted that Holten et al. (2013) recommended an alternative model termed “athermal solution”, where nonideality is ascribed to entropy changes upon mixing. In vicinal water some evidence points to nonideality originating from enthalpy changes near the particle (Etzler, 1983); hence a regular solution is more appropriate in this case. For $N = 6$ the difference between the two models is negligible (Holten et al., 2013).

The second term on the right-hand side of Eq. (24) is an empirical functional form used to approximate the enthalpy of mixing, selected so that $\Delta G_{\text{mix}} = 0$ for both $\zeta = 0$ and $\zeta = 1$. A_w is a phenomenological interaction parameter, here assumed to implicitly correct the approximation $\Delta\mu_{\text{il}} \approx \Delta\mu_{\text{s}}$. Typically A_w must be fitted to experimental observations. In this work A_w is calculated using an alternative approach, as follows.

An important aspect of the regular solution model is that it predicts that μ_{vc} has a critical temperature, T_c , defined by the conditions,

$$\frac{\partial^2 \mu_{\text{vc}}}{\partial \zeta^2} = 0, \quad \frac{\partial^3 \mu_{\text{vc}}}{\partial \zeta^3} = 0. \quad (25)$$

These conditions originate because $\frac{\partial^2 \mu_{\text{vc}}}{\partial \zeta^2} = 0$ represents a stability limit for the vicinal water. A solution would split into two phases, if doing so lowers its Gibbs free energy (Prausnitz et al., 1998, cf. Sect. 6.12). For a metastable solution μ_{vc} must be minimal, hence $\frac{\partial \mu_{\text{vc}}}{\partial \zeta} = 0$. The condition $\frac{\partial^2 \mu_{\text{vc}}}{\partial \zeta^2} < 0$ indicates that any increase in ζ increases μ_{vc} (i.e., the curve μ_{vc} vs. ζ becomes concave downward), such that it is thermodynamically more favorable for the solution to split into distinct phases than to increase its concentration. The last condition, $\frac{\partial^3 \mu_{\text{vc}}}{\partial \zeta^3} = 0$, indicates that the metastable region reduces to a single point. Using Eq. (20) into Eq. (25) we obtain,

$$\frac{\partial^2 \mu_{\text{vc}}}{\partial \zeta^2} = \frac{k_B T}{N} \left(\frac{1}{\zeta(1-\zeta)} \right) - 2A_w = 0, \quad (26)$$

and

$$\frac{\partial^3 \mu_{\text{vc}}}{\partial \zeta^3} = \frac{k_B T}{N} \left(\frac{\zeta^2 - (1-\zeta)^2}{\zeta^2(1-\zeta)^2} \right) = 0. \quad (27)$$

The last expression is only valid for $\zeta = 0.5$, indicating that a single critical temperature exists for a regular solution. Using this in Eq. (26) and solving for A_w gives, for $T = T_c$,

$$A_w = \frac{2k_B T_c}{N}. \quad (28)$$

Physically, T_c represents the stability limit of the vicinal water, at which it spontaneously separates into IL and LL re-

gions. For $T < T_c$ the chemical potential of an equimolar solution of IL and LL would be larger than that of a simple mechanical mixture of the two species. Thus it is thermodynamically more favorable for the solution to split into its individual components, i.e., ice and liquid, leading to a stability limit of the system. Equation (28) thus provides an opportunity to theoretically determine A_w , since T_c should also correspond to a negligible work of nucleation. This further explained in Sect. 2.4.2.

Introducing Eqs. (23), (24) and (28) in Eq. (20), we obtain

$$\begin{aligned} \mu_{\text{vc}} = & \mu_{\text{LL}} - \zeta k_B T \ln \left(\frac{a_{\text{w,eff}}}{a_{\text{w,eq}}} \right) \\ & + \frac{k_B T}{N} [\zeta \ln(\zeta) + (1-\zeta) \ln(1-\zeta)] + \frac{2k_B T_c}{N} \zeta(1-\zeta). \end{aligned} \quad (29)$$

By defining Λ_{mix} in the form,

$$\Lambda_{\text{mix}} = \frac{1}{N} [\zeta \ln(\zeta) + (1-\zeta) \ln(1-\zeta)] + \frac{2}{N} \frac{T_c}{T} \zeta(1-\zeta), \quad (30)$$

Equation (29) can be written in the form

$$\mu_{\text{vc}} = \mu_{\text{LL}} - \zeta k_B T \ln \left(\frac{a_{\text{w,eff}}}{a_{\text{w,eq}}} \right) + k_B T \Lambda_{\text{mix}}. \quad (31)$$

Equation (31) is the equation of state of the vicinal water. It describes the properties of the vicinal water in terms of the material-specific parameter ζ and the interaction parameters N and T_c . MD simulations indicate that $N \sim 6$ (Bullock and Molinero, 2013; Holten et al., 2013). T_c is thus the only remaining unknown in Eq. (31) and is calculated in Sect. 2.4.2.

2.4 Work of germ formation

The equation of state of vicinal water can be used to link ΔG_{hom} and ΔG_{het} as follows. In immersion freezing the particle remains within the droplet long enough that equilibrium is established. This condition is mathematically expressed by the equality, $\mu_{\text{vc}} = \mu_{\text{w}}$, where μ_{w} is the chemical potential of water in the bulk of the liquid, i.e., away from the particle. Using Eq. (31) this implies that

$$\mu_{\text{w}} = \mu_{\text{LL}} - \zeta k_B T \ln \left(\frac{a_{\text{w,eff}}}{a_{\text{w,eq}}} \right) + k_B T \Lambda_{\text{mix}}. \quad (32)$$

This expression indicates that the effect of the particle on its vicinal water can be understood as an enhancement of the chemical potential of the LL regions, a consequence of the tendency of the particle to lower μ_{vc} . Since $\Delta\mu_{\text{il}} < 0$, μ_{LL} must increase to maintain equilibrium. Using the equilibrium between bulk liquid and ice as reference state so that $\mu_{\text{w}} = \mu_{\text{eq}} + k_B \ln \left(\frac{a_{\text{w}}}{a_{\text{w,eq}}} \right)$, we obtain the following after simplifying:

$$\ln(a_{\text{w}}) = \ln(a_{\text{w,eff}}) - \zeta \ln \left(\frac{a_{\text{w,eff}}}{a_{\text{w,eq}}} \right) + \Lambda_{\text{mix}}. \quad (33)$$

Or, equivalently,

$$a_w = a_{w,\text{eff}} \left(\frac{a_{w,\text{eq}}}{a_{w,\text{eff}}} \right)^\zeta \exp(\Lambda_{\text{mix}}). \quad (34)$$

Equation (34) suggests that, thermodynamically, immersion freezing can be described as homogeneous ice nucleation occurring at an enhanced water activity. This is because it is possible to create a path including homogeneous ice nucleation with the same change in Gibbs free energy as for heterogeneous freezing. Figure 1 shows that for a particle-droplet system in equilibrium, $a_{w,\text{eff}}$ satisfies the condition

$$\Delta G_{\text{het}}(a_w) = \Delta G_{\text{hom}}(a_{w,\text{eff}}). \quad (35)$$

Equation (35) represents a thermodynamic relation between ΔG_{het} and ΔG_{hom} . It has the advantage that ΔG_{het} can be obtained without invoking assumptions on the mechanistic details of the interaction between the particle and the ice germ, which are parameterized by ζ . Since a_w is typically the controlled variable in ice nucleation, $a_{w,\text{eff}}$ can be readily obtained by solving Eq. (34),

$$a_{w,\text{eff}} = \left(\frac{a_w}{\frac{\zeta}{a_{w,\text{eq}}}} \right)^{\frac{1}{1-\zeta}} \exp\left(-\frac{\Lambda_{\text{mix}}}{1-\zeta}\right). \quad (36)$$

Although ascribing ice nucleation to the LL fraction of vicinal water agrees with the decisive role of free water in the formation of ice (Wang et al., 2016), caution must be taken in considering this to be the actual mechanism of ice nucleation, which could be quite complex. Equation (35), however, establishes a thermodynamic constrain for ΔG_{het} that should be met by any ice nucleation mechanism. It is also important to analyze the behavior of $a_{w,\text{eff}}$ as $\zeta \rightarrow 1$. It can be shown that the quotient $\frac{\Lambda_{\text{mix}}}{\zeta-1}$ converges for $\zeta \rightarrow 1$ as follows. From Eq. (30) we can write

$$\frac{\Lambda_{\text{mix}}}{1-\zeta} = \frac{1}{N(1-\zeta)} [\zeta \ln(\zeta) + (1-\zeta) \ln(1-\zeta)] + \frac{2}{N} \frac{T_c}{T} \zeta. \quad (37)$$

Using $\ln(x) \rightarrow (x-1)$ for $x \rightarrow 1$, the last expression can be shown to converge to

$$\lim_{\zeta \rightarrow 1} \frac{\Lambda_{\text{mix}}}{1-\zeta} = -\frac{2\zeta}{N} + \frac{2}{N} \frac{T_c}{T} \zeta = \frac{2}{N} \left(\frac{T_c}{T} - 1 \right). \quad (38)$$

The fact that $\lim_{\zeta \rightarrow 1} \exp\left(-\frac{\Lambda_{\text{mix}}}{1-\zeta}\right) \neq 1$ for $T \neq T_c$ stems from the simple interaction model used to define ΔG_{mix} (i.e., the regular solution approximation). T_c may depend on ζ , however the regular solution approximation predicts a unique critical temperature at $\zeta = 0.5$. This, however, does not lead to uncertainty in ΔG_{hom} since for $\zeta \rightarrow 1$, the first term on the right-hand side of Eq. (36) is almost singular at $a_w = a_{w,\text{eq}}$.

Thus if $\lim_{\zeta \rightarrow 1} \exp\left(-\frac{\Lambda_{\text{mix}}}{1-\zeta}\right) < 1$, then a_w must be just above $a_{w,\text{eq}}$ to make $a_{w,\text{eff}} = 1$. In other words, for all practical purposes, $a_{w,\text{eff}} \rightarrow 1$ when the system approaches thermodynamic equilibrium.

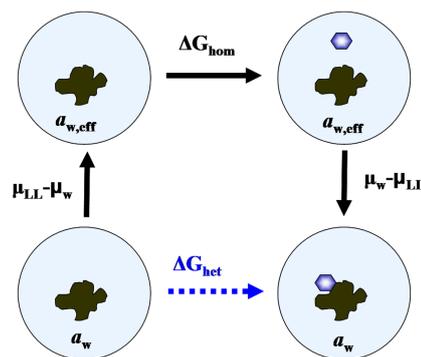


Figure 1. Diagram representing a thermodynamic path, including homogeneous ice nucleation with the same work as heterogeneous freezing.

2.4.1 Extension of the homogeneous model to the spinodal limit

In applying the homogeneous model to the heterogeneous problem in the form detailed in Sect. 2.4, caution must be taken in describing the limiting condition where the size of the ice germ becomes exceedingly small, i.e., $n_{\text{hom}} \rightarrow 1$, representing the vanishing of the energy barrier to ice nucleation. This is possible, since as $\zeta \rightarrow 1$, $a_{w,\text{eff}}$ becomes large (Eq. 36), and for $\zeta = 1$ it is only defined at thermodynamic equilibrium. Since for $n_{\text{hom}} \rightarrow 1$, thermodynamic potentials are not well defined, it is necessary to test the validity of NNF at such a limit. Moreover, in its original formulation (Sect. 2.2) NNF predicts a positive ΔG_{hom} for $n_{\text{hom}} = 1$, at odds with the notion that the formation of a monomer-sized germ should carry no work.

At the limiting condition, $n_{\text{hom}} = 1$, the work of nucleation is smaller than the thermal energy of the molecules and represents the onset of spontaneous phase separation (termed “spinodal decomposition”) during nucleation (Vekilov, 2010). Here it is argued that being a far-from-equilibrium process, ice nucleation always carries energy dissipation. When accounted for, the apparent inconsistency in NNF at $n_{\text{hom}} = 1$ vanishes, since as shown below such a condition is not accessible. This approach differs from previous treatments, where this limit is associated with a negligible driving force for nucleation (Kalikmanov and van Dongen, 1993).

To account for the finite, albeit small, amount of work dissipated from the generation of entropy during spontaneous fluctuation, a simple approach is proposed. It involves writing the work of cluster formation in the form

$$\Delta G = -n \Delta \mu_i + n^{2/3} \Phi_s + W_{\text{diss}}, \quad (39)$$

where W_{diss} represents work dissipation, assumed independent of the germ size, since it results from spontaneous fluctuations occurring in the liquid phase. Equation (39) is the typical expression for ΔG (Barahona, 2014, cf. Eq. 15) with

an additional term accounting for irreversibility. The nucleation work is defined for $n = n_{\text{hom}}$ in the form

$$\Delta G_{\text{hom}} = -n_{\text{hom}} \Delta \mu_i + n_{\text{hom}}^{2/3} \Phi_s + W_{\text{diss}}, \quad (40)$$

where n_{hom} is obtained from the mechanical stability condition, $\frac{\partial \Delta G}{\partial n} = 0$, and is still given by Eq. (13), since W_{diss} is assumed independent of n . W_{diss} is then obtained from the conditions

$$\Delta G_{\text{hom}}|_{n_{\text{hom}}=1} = 0, \quad \frac{\partial^2 \Delta G_{\text{hom}}}{\partial n_{\text{hom}}^2}|_{n_{\text{hom}}=1} = 0. \quad (41)$$

The first condition expresses the fact that the formation of a monomer-sized ice germ carries no work. The second condition establishes that $n_{\text{hom}} = 1$ should correspond to a stability limit of the system where nucleation and spontaneous separation are analogous. This is referred as the spinodal point. From Eq. (40) we obtain

$$\frac{\partial^2 \Delta G_{\text{hom}}}{\partial n_{\text{hom}}^2} = -\frac{2}{9} n_{\text{hom}}^{-4/3} \Phi_s = 0. \quad (42)$$

Since n_{hom} only attains positive values, then only the trivial solution $\Phi_s = 0$ satisfies Eq. (42), i.e., the energy barrier to the formation of the ice germ vanishes at the spinodal. Using $\Phi_s = 0$ and $\Delta G_{\text{hom}}|_{n_{\text{hom}}=1} = 0$, Eq. (40) can be solved for W_{diss} in the form

$$W_{\text{diss}} = \Delta \mu_i. \quad (43)$$

Thus the minimum amount of work dissipated during nucleation corresponds to a fluctuation relaxing $\Delta \mu_i$. Replacing this expression within Eq. (40), we obtain

$$\Delta G_{\text{hom}} = -\Delta \mu_i (n_{\text{hom}} - 1) + n_{\text{hom}}^{2/3} \Phi_s \quad (44)$$

Using Eq. (13) in Eq. (44) gives, after rearranging, the work of germ formation by homogeneous ice nucleation:

$$\Delta G_{\text{hom}} = \frac{1}{2} \Delta \mu_i (n_{\text{hom}} + 2). \quad (45)$$

Equation (45) only differs from the NNF expression, Eq. (14), on the right-hand side, where it is implied that nucleation in a solution requires the coordination of at least two molecules, a condition that has been observed experimentally in the crystallization of proteins (Vekilov, 2010). It also suggests that dissipation effects are negligible for typical homogeneous nucleation conditions, i.e., $\Delta G_{\text{hom}} \approx \Delta G_{\text{hom,NNF}}$, since $n_{\text{hom}} \sim 200$ (Barahona, 2014). Moreover, the fact that $\Delta G_{\text{hom}} > 0$ even when $n_{\text{hom}} \rightarrow 0$ implies that ice nucleation always requires some work. Using Eq. (35) the heterogeneous work of nucleation can be readily written as

$$\Delta G_{\text{het}}(a_w) = \left[\frac{1}{2} \Delta \mu_i (n_{\text{hom}} + 2) \right]_{a_w, \text{eff}}. \quad (46)$$

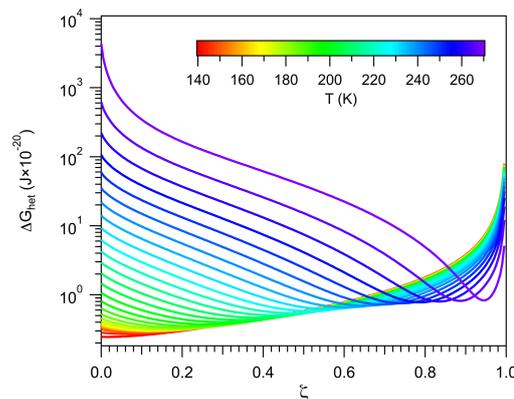


Figure 2. Work of heterogeneous ice nucleation. Color indicates different temperatures.

Equation (46) also suggests an operational definition for the critical ice germ in immersion freezing in the form

$$n_{\text{het}} = (n_{\text{hom}} + 2) a_{w, \text{eff}}. \quad (47)$$

The results of Eqs. (45) and (46) require further explanation, since in principle, an ice germ with only two molecules does not exist. Thus Eq. (45) must be interpreted in a different way. As $\zeta \rightarrow 1$, or in deeply supercooled conditions, the fraction of ice-like regions in the vicinal water becomes large. Under such a scenario the reorientation of only two molecules may be enough to initiate ice nucleation. In other words, beyond the spinodal point ice nucleation is controlled by molecular motion within already formed ice-like regions. For homogeneous ice nucleation this would require extreme supercooling ($T \sim 140$ K, Fig. 2). In immersion ice nucleation it may occur at higher T , since the formation of a high fraction of ice-like regions in the vicinal water is facilitated by efficient INPs. This is further explored in Sect. 3.

NNF carries the assumption that thermodynamic potentials can be defined for the ice germ. In other words n_{hom} should be large enough that it represents a statistical ensemble of molecules. Of course this is not the case for $n_{\text{hom}} = 1$, and it may cast doubt on the application of Eq. (39) to such limits. This possibility is, however, mitigated in two ways. Unlike CNT, which is based on the interfacial tension, the NNF framework is robust for small germs. Size effects impact ΔG mostly through Φ_s , since $\Delta \mu_i$ does not change substantially with the size of the system. In NNF the product $\Gamma_{w,s} \Delta h_f$ in Eq. (11) remains constant, and Φ_s is relatively insensitive to n . This is because Δh_f decreases with n as the total cohesive energy of the germ is inversely proportional to the number of molecules within the ice–liquid interfacial layer (Zhang et al., 1999; Johnston and Molinero, 2012). At the same time, the product $\Gamma_{w,s}$, i.e., the ratio of the number of surface to interior molecules in the germ (Barahona, 2014; Spaepen, 1975), should increase for small ice germs, offsetting the decrease in Δh_f . Such behavior is supported

by MD simulations (Johnston and Molinero, 2012). Equation (11) thus remains valid for small germs. A second mitigating factor is discussed in Sect. 3.1, where it is shown that conditions leading to $n_{\text{het}} \rightarrow 1$ are rare in the atmosphere, and J_{het} is largely independent of n_{het} for very small germs.

2.4.2 Critical temperature

To complete the thermodynamic description of ice nucleation near the particle–liquid interface it is necessary to specify the critical separation temperature defined in Eq. (28). The criterion used to find T_c is that the reversible work of nucleation, that is, without accounting for the dissipation term, becomes negligible. W_{diss} is not included, since the definition of ΔG_{mix} (Eq. 24), does not account for such effects.

An analysis of Eqs. (44) and (46) reveals that ΔG_{hom} (hence ΔG_{het}) is at a minimum when the reversible work becomes negligible. As T decreases, $\Delta\mu_i$ increases, decreasing n_{hom} and ΔG_{hom} . However, as $n_{\text{hom}} \rightarrow 0$, the tendency is reversed, since $\Delta G_{\text{hom}} \sim W_{\text{diss}}$. In this regime dissipative effects dominate, and ΔG_{hom} and ΔG_{het} become proportional to $\Delta\mu_i$ (Fig. 2). Thus the minimum in ΔG_{het} signals $n_{\text{hom}} \rightarrow 0$ and $n_{\text{het}} \rightarrow 2$. If no dissipation or kinetic effects were present (for example at low supercooling), then phase separation would ensue, since the work of nucleation would be smaller than the thermal energy of the water molecules. This limit should also correspond to the stability limit of the vicinal water where IL and LL species separate spontaneously; hence it can be used to find T_c . It must be noted that this criterion does not mean that $\Delta G_{\text{het}} = 0$ at $T = T_c$ but rather that such would be the case for a thermodynamically reversible nucleation process.

In the regular solution model the interaction parameter A_w is defined for T_c at $\zeta = 0.5$ (Sect. 2.3). Thus to find T_c we look for the temperature that would produce a minimum in ΔG_{het} at $\zeta = 0.5$. Mathematically, this is the temperature that simultaneously satisfies the conditions described in Eqs. (25) and (41). Figure 2 shows that this occurs around $T \sim 211$ K for $\zeta = 0.5$. Since both ΔG_{het} and $a_{w,\text{eff}}$ depend on T_c , we can iteratively solve Eqs. (36) and (46) to find $T_c = 211.473$ K. Figure 2 also suggests that when T remains constant there is a critical value of ζ that marks the transition between two thermodynamic regimes. This is analyzed in Sect. 3.1.

2.5 Kinetics of immersion freezing

Almost every theoretical approach to describe the effect of INPs on ice formation focuses on the thermodynamics of ice nucleation. However as discussed in Sect. 1.1, increased molecular ordering increases the viscosity of vicinal water, implying that the immersed particle modifies the flux of water molecules to the nascent ice germ, hence the kinetics of ice nucleation (Etzler, 1983; Feibelman, 2010). Since these structural changes are also related to modifications in

the chemical potential of the vicinal water, it is likely that the same mechanism that decreases ΔG_{het} also controls the mobility of water molecules in the environment around the particle. Such a connection between the water thermodynamic properties and its molecular mobility is well established (Adam and Gibbs, 1965; Debenedetti and Stillinger, 2001; Scala et al., 2000), but it is generally neglected in nucleation theory (e.g., Pruppacher and Klett, 1997; Ickes et al., 2017). In this section a heuristic model is proposed to account for such effects.

Kinetic effects modify the value of the impingement factor, f_{het}^* , which controls the flux of water molecules to the ice germ. In general the ice germ grows by diffusion and rearrangement of nearby water molecules across the ice–liquid interface, characterized by the interfacial diffusion coefficient, D . Increased ordering is characterized by a higher IL fraction, hence higher ζ . Thus, in immersion freezing, D must be a function of ζ . Using Eq. (15) this can be expressed in the form

$$f_{\text{het}}^* = \frac{\Omega}{v_w d_0} D(\zeta). \quad (48)$$

Assuming that within the vicinal layer the ice germ grows following a similar mechanism as in the bulk of the liquid, then Eq. (16) can be applied to the heterogeneous process in the form

$$D(\zeta) = D_{\infty}(\zeta) \left\{ 1 + \exp \left[\frac{W_d(\zeta)}{k_B T} \right] \right\}^{-1}. \quad (49)$$

The last expression indicates that ice–liquid interfacial transfer requires a diffusional and a rearrangement component. $D_{\infty}(\zeta)$ characterizes purely diffusional processes occurring within the particle–liquid interface. Molecular rearrangement during ice germ growth within the vicinal layer is determined by $W_d(\zeta)$. Since only molecules in the LL fraction of the vicinal water would rearrange to join the ice lattice then the latter is given by

$$W_d(\zeta) = W_d(1 - \zeta) = -n_t \Delta\mu_s(1 - \zeta). \quad (50)$$

Introducing the last expression in Eq. (49) we obtain

$$D(\zeta) = D_{\infty}(\zeta) \left[1 + \exp \left(\frac{-n_t \Delta\mu_s(1 - \zeta)}{k_B T} \right) \right]^{-1}. \quad (51)$$

This expression is consistent with the thermodynamic model presented in Sect. 2.3, since as ζ increases, the vicinal water has a larger “ice” character, and fewer molecules need to rearrange to be incorporated into the growing ice germ.

2.5.1 Diffusion within the particle–liquid interface

The diffusional component of D corresponds to the random jump of water molecules across the ice–liquid interface. For $\zeta \rightarrow 0$ there is no interaction between the particle and

the adjacent water, hence diffusion must proceed as in the bulk of the supercooled water. At the opposite limit, $\zeta \rightarrow 1$ and $D_\infty(\zeta) \rightarrow 0$, which simply states that interfacial transfer vanishes when no net driving force exists across the ice–liquid interface, i.e., the system is in equilibrium. To model this behavior the well-known relaxation theory proposed by Adam and Gibbs (1965) is employed (hereinafter, AG65). According to AG65, relaxation and diffusion in supercooled liquids require the formation of cooperative regions (CRs). The average transition probability and the timescale of diffusion are determined by the size of the smallest CR. Following a statistical mechanics treatment and assuming that each CR interacts weakly with the rest of the system, the authors derived the following expression for the average transition probability:

$$\bar{W} \propto \exp\left(-\frac{A}{TS_c}\right), \quad (52)$$

where A represents the product of the minimum size of a CR in the liquid and the energy required to displace water molecules from their equilibrium position in the bulk, and S_c is the configurational entropy. Since A is approximately constant, the mobility of water molecules is controlled by S_c , which has been confirmed in molecular dynamics simulations and experimental studies (e.g., Scala et al., 2000; Debenedetti and Stillinger, 2001). The self-diffusivity of water is proportional to the transition probability and can be expressed in the form $D_\infty \sim D_0 \bar{W}$, where D_0 is a constant. Using Eq. (52) this suggests the relationship

$$\frac{D_\infty(\zeta)}{D_\infty} = \frac{\bar{W}(\zeta)}{\bar{W}(\zeta=0)} = \exp\left[-\frac{A}{TS_{c,0}}\left(\frac{S_{c,0}}{S_c} - 1\right)\right], \quad (53)$$

where $D_\infty = D_\infty(\zeta=0)$ and $S_{c,0} = S_c(\zeta=0)$ represent values in the bulk of the liquid. Equation (53) implies that the flux of molecules to the ice germ during immersion freezing is controlled by the configurational entropy of vicinal water. The usage of Eq. (53) thus requires developing an expression for S_c , which is approximated in the form

$$S_c = (1 - \zeta)S_{c,LL} + \zeta S_{c,IL}, \quad (54)$$

where $S_{c,LL}$ and $S_{c,IL}$ are the configurational entropies of the LL and IL fractions, respectively. The term $S_{c,LL}$ in Eq. (54) dominates S_c , since diffusion is controlled by molecules mobile enough to be incorporated in CRs (Stanley and Teixeira, 1980), although $S_{c,IL}$ determines S_c when $\zeta \rightarrow 1$.

The regular model proposed in Sect. 2.3 suggests a weak interaction between IL and LL regions, since ΔG_{mix} is small compared to μ_{vc} . Thus we can approximate that $S_{c,LL} \approx S_{c,0}$. Unfortunately equating $S_{c,IL}$ to the configurational entropy of bulk ice (which can be deduced from geometrical arguments; Pauling, 1935) would violate the requirement that $D \rightarrow 0$ at thermodynamic equilibrium. To estimate $S_{c,IL}$ we assume instead that water molecules in the IL regions should

be displaced from their equilibrium position (essentially “diffusing” into the LL regions) to be incorporated into the ice lattice. During this process they gain an amount of energy equal to $-\Delta\mu_s$ which is returned to the system upon entering the ice–liquid interface. Since this energy exchange results mostly from configurational rearrangement we can approximate that $S_{c,IL} \approx -\Delta\mu_s/T$ (Barahona, 2014; Spaepen, 1975). With this, and using $\Delta\mu_s = -k_B T \ln\left(\frac{a_w}{a_{w,\text{eq}}}\right)$, Eq. (54) can be rewritten in the form

$$S_c = S_{c,0}(1 - \zeta) + \zeta k_B \ln\left(\frac{a_w}{a_{w,\text{eq}}}\right). \quad (55)$$

By introducing this expression into Eq. (53) and rearranging, we obtain

$$\frac{D_\infty(\zeta)}{D_\infty} = \exp\left[-\frac{A}{TS_{c,0}}\frac{\zeta\sigma_E}{(1 - \zeta\sigma_E)}\right], \quad (56)$$

where $\sigma_E = 1 - S_{c,0}^{-1}k_B \ln\left(\frac{a_w}{a_{w,\text{eq}}}\right)$. Using $D_\infty = D_0 \bar{W}$, an equivalent expression to Eq. (56) can be written in the form

$$D_\infty(\zeta) = D_\infty \left(\frac{D_\infty}{D_0}\right)^{\frac{\zeta\sigma_E}{1 - \zeta\sigma_E}}. \quad (57)$$

Equation (57) represents the effect of the immersed particle on the rate of growth of the ice germ. For $\zeta = 0$, the particle does not affect the flux of water molecules to the nascent ice germ and $D_\infty(\zeta) = D_\infty$. However as $\zeta \rightarrow 1$, $D_\infty(\zeta) \propto \exp\left(-\frac{1}{1 - \zeta\sigma_E}\right)$, and interface transfer becomes severely limited, particularly near equilibrium, since $\sigma_E \rightarrow 1$. This effect is much stronger than the reduction in the dissipated work from an increased ζ (Sect. 2.5) and dominates D .

Introducing Eqs. (51) and (57) into Eq. (48) and rearranging, we obtain

$$f_{\text{het}}^* = \frac{D_\infty \Omega}{v_w d_0} \left(\frac{D_\infty}{D_0}\right)^{\frac{\zeta\sigma_E}{1 - \zeta\sigma_E}} \left[1 + \left(\frac{a_w}{a_{w,\text{eq}}}\right)^{n_i(1 - \zeta)}\right]^{-1}, \quad (58)$$

where $\Delta\mu_s = -k_B T \ln\left(\frac{a_w}{a_{w,\text{eq}}}\right)$ was used.

2.6 Nucleation rate

The results of Sects. 2.3 to 2.5 provide the basis for writing an expression for the ice nucleation rate of droplets by immersion freezing. Before completing such a description we need to provide an expression for Z . The application of Eq. (2) typically leads to the known expression (Pruppacher and Klett, 1997)

$$Z = \left(\frac{\Delta G_{\text{het}}}{3\pi k_B T n_{\text{het}}^2}\right)^{1/2}. \quad (59)$$

On the other hand using Eq. (46) in Eq. (2), we obtain

$$Z_d = \left[\frac{\Delta G_{\text{het}}(n_{\text{het}} - 2)^{1/3}}{3\pi k_B T n_{\text{het}}^{7/3}}\right]^{1/2}, \quad (60)$$

where the subscript “d” indicates that energy dissipation is taken into account. For $n_{\text{het}} > 3$ it is easily verifiable that $Z_d \approx Z$. Indeed the discrepancy between Z_d and Z is only 30 % for $n_{\text{het}} = 3$, and it is much smaller for larger ice germs. However for $n_{\text{het}} = 2$, $Z_d = 0$. This issue is rather fundamental and may represent the breaking of the assumption that each germ grows by the addition of a single molecule at a time. Hence Eq. (59) will be used keeping in mind that for very small ice germs, it represents only an approximation.

With the above considerations it is now possible to substitute Eqs. (46), (47), (58) and (59) into Eq. (5) to obtain the heterogeneous ice nucleation rate

$$J_{\text{het}} = \frac{2ZD_{\infty}\Omega}{3v_w^2} \left(\frac{D_{\infty}}{D_0}\right)^{\frac{\zeta\sigma_E}{1-\zeta\sigma_E}} \left[1 + \left(\frac{a_w}{a_{w,\text{eq}}}\right)^{n_i(1-\zeta)}\right]^{-1} \exp\left(-\frac{n_{\text{het}}\Delta\mu_i|_{a_{w,\text{eff}}}}{2k_B T}\right), \quad (61)$$

where $d_0 = (6v_w/\pi)^{1/3}$ and $a_0 = \pi d_0^2/4$ were used, and $\Omega = \Gamma_w n_{\text{het}}^{2/3} a_0$ is the surface area of the ice germ. Other symbols and values used are listed in Appendix A.

2.7 The role of active sites

There is evidence that in dust and other INPs, ice is formed preferentially in the vicinity of surface patches, commonly referred as active sites. The existence of active sites has been established experimentally for deposition ice nucleation (i.e., ice nucleation directly from the vapor phase; Kiselev et al., 2017), and they may be also important for immersion freezing (e.g., Murray et al., 2012). In the classical view active sites have the property of locally reducing ΔG_{het} , increasing J_{het} . In the so-called singular hypothesis each active site has an associated characteristic temperature at which it nucleates ice. Current interpretation assigns $J_{\text{het}} \rightarrow \infty$ at each active site at its characteristic temperature, with some variability due to “statistical fluctuations” in the germ size (Vali, 2014). Some CNT-based approaches to describe immersion freezing account for the existence of active sites by assuming a distribution of contact angles for each particle. Hence each active site is assigned a characteristic contact angle instead of a characteristic temperature (e.g., Zobrist et al., 2007; Ickes et al., 2017).

The view of the role of active sites as capable of locally decreasing ΔG_{het} relies heavily on an interpretation of immersion freezing that mimics ice nucleation from the vapor phase (Fig. 3a). Such a description is, however, too limited for ice formation within the liquid phase. For example, it is implicitly assumed that the active site brings molecules together, similar to an adsorption site. However a particle immersed within a liquid is already surrounded by water molecules (Fig. 3b). In fact, nascent ice structures are associated with low-density regions within the liquid (Bullock and Molinero, 2013). Thus in the classical view the active site should be

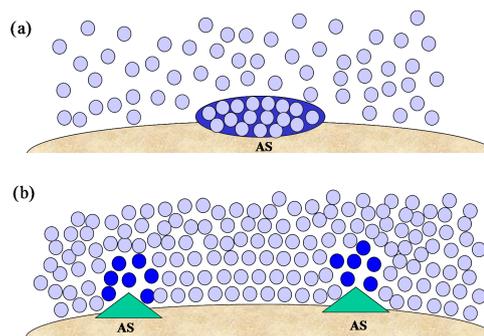


Figure 3. Different representations of immersion freezing. (a) an ice germ (dark blue) forming on an active site (AS) by random collision of water molecules (light blue). (b) low-density regions (dark blue) forming in the vicinity of active sites within a dense liquid phase (light blue).

able to “pull molecules apart” instead of bringing them together. This creates a conceptual problem. To locally reduce ΔG_{het} active sites should be able to permanently create low-density regions within the liquid, which would require a large amount of energy. In other words, active sites would have the unusual property of creating a thermodynamic barrier maintaining their surrounding water in a non-equilibrium state. Such situation is unlikely in immersion freezing.

The concept of a local nucleation rate also presents some difficulties. In the strict sense J_{het} is the velocity with which the size distribution of molecular clusters in an equilibrium population crosses the critical size (Kashchiev, 2000; Seinfeld and Pandis, 1998). In immersion freezing the domain of such a distribution is the whole volume of the droplet. Thus only a single value of J_{het} can be defined for a continuous liquid phase, independently of where the actual nucleation process is occurring, since no permanent spatial gradients of T or concentration exist within equilibrium systems. Having otherwise implies that parts of the system would need to be maintained in a non-equilibrium state, having their own cluster size distribution. This requires the presence of non-permeable barriers within the liquid, a condition not encountered in immersion freezing. Similarly, the characteristic temperature of an active site is an unmeasurable quantity, since a system in equilibrium has the same temperature everywhere. Hence it would be impossible to distinguish whether the particle as a whole or only the active site must reach a certain temperature before nucleation takes place.

These difficulties can be reconciled if, instead of promoting nucleation through a thermodynamic mechanism, active sites provide a kinetic advantage to ice nucleation. A way in which this can be visualized is shown in Fig. 3b. The vicinal water is in equilibrium with the particle and exhibits a larger degree of ordering near the interface. Since in immersion freezing the formation of ice in the liquid depends on molecular rearrangement, the active site should produce a transient structural transformation that allows the propa-

gation of ice. These sites would be characterized by defects where templating is not efficient, allowing greater molecular movement, hence facilitating restructuring. Their presence is guaranteed, since particles are never uniform at the molecular scale. In this view active sites create ice by promoting fluctuation instead of by locking water molecules in strict configurations. It implies that for uniform systems (e.g., a single droplet with a single particle) ΔG_{het} depends on the equilibrium between the particle and the vicinal water, and active sites enhance fluctuation around specific locations. This obviates the need for the hypothesis of a well-defined characteristic temperature for each active site. It, however, does not mean that active sites are transient. They are permanent features of the particle and should have a reproducible behavior, inducing ice nucleation around the same place in repeated experiments (e.g., Kiselev et al., 2017).

Within the framework presented above, there can only be one J_{het} defined in the droplet volume. The presence of active sites introduces variability in J_0 instead of ΔG_{het} . The latter is determined by the thermodynamic equilibrium between the particle and its vicinal water. Although the theory presented here does not account for internal gradients in the droplet–particle system, in practice it is likely that the observed J_{het} corresponds to the site promoting the largest density fluctuations. Variability in J_{het} would be introduced by fluctuation in the cluster size distribution in the liquid and from the multiplicity of active sites in the particle population. In this sense the proposed view is purely stochastic.

3 Discussion

3.1 Ice nucleation regimes

A consequence of the linkage between the properties of vicinal water and ΔG_{het} is the existence of distinct nucleation regimes. This was mentioned in Sect. 2.4.1, and here it is explored in detail. Recall from Fig. 2 that for a given temperature, ΔG_{het} passes by a minimum defined by the condition $\frac{\partial^2 \Delta G_{\text{het}}}{\partial n_{\text{het}}^2} = 0$. Figure 4b depicts a similar behavior when varying T . It shows that for a given ζ there is a temperature T_s at which ΔG_{het} is minimum. For $T > T_s$, ΔG_{het} increases with increasing T because n_{het} increases (Fig. 4a). This is the typical behavior predicted by the classical model (e.g., Khvorostyanov and Curry, 2005), hence such regime will be termed “germ-forming”, since ΔG_{het} is determined by the formation of the ice–liquid interface.

A different behavior is found for $T < T_s$, where ΔG_{het} decreases with increasing T . In this regime n_{het} remains almost constant at very low values, ΔG_{het} is small and results mostly from the dissipation of work. Ice nucleation is not limited by the formation of the ice–liquid interface but rather by the propagation of small fluctuations in the vicinity of preformed ice-like regions. Therefore it is controlled by the diffusion of water molecules to such regions rather than by ΔG_{het} . This is

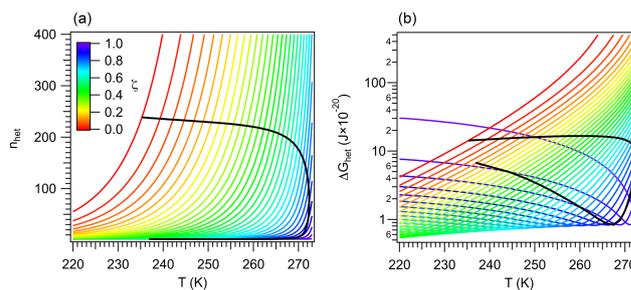


Figure 4. Critical germ size (a) and work of heterogeneous ice nucleation (b) for different values of ζ (color). Black lines correspond to constant $J_{\text{het}} = 10^6 \text{ m}^{-2} \text{ s}^{-1}$.

akin to a spinodal decomposition process (Cahn and Hilliard, 1958) and will be termed “spinodal ice nucleation”. It is, however, not truly spinodal decomposition, since it requires a finite, albeit small, amount of work to occur.

Since for each value of ζ there is a minimum in ΔG_{het} (Fig. 4), theoretically all INPs are capable of nucleating ice in both regimes. In practice spinodal ice nucleation would only occur if T_s lies within the $233 \text{ K} < T < 273 \text{ K}$ range, where immersion freezing occurs. For example, for $\zeta = 0.1$, Fig. 4b shows that the minimum in ΔG_{het} occurs at $T < 220 \text{ K}$. Since homogeneous ice nucleation should occur above this temperature, INPs characterized by $\zeta = 0.1$ will not exhibit spinodal ice nucleation. These particles always nucleate ice in the classical germ-forming regime ($T > T_s$). The situation is, however, different for $\zeta = 0.9$, since $T_s \approx 270 \text{ K}$. These INPs are capable of nucleating ice in both the spinodal ($T < T_s$) and the germ-forming ($T > T_s$) regimes. For the spinodal regime, ΔG_{het} is low and decreases slightly with increasing T , indicating that the thermodynamic barrier to nucleation is virtually removed. Ice formation is therefore almost entirely controlled by kinetics.

The existence of the spinodal nucleation regime signals the possibility of an interesting behavior in freezing experiments, where the same ΔG_{het} may correspond to two very different INPs. To show this the values of ΔG_{het} and n_{het} corresponding to $J_{\text{het}} = 10^6 \text{ m}^{-2} \text{ s}^{-1}$ are depicted in Fig. 4 with black lines. These lines form semi-closed curves when plotted against temperature indicating that the same ΔG_{het} may correspond to two different values of ζ . The upper branch (with high ΔG_{het}) corresponds to the germ-forming regime and the lower branch to the spinodal regime. This picture may be convoluted by the fact that high ζ also implies strong kinetic limitations during ice nucleation and is further discussed in Sect. 3.3.

3.2 Pre-exponential factor

Kinetic effects on ice nucleation are typically analyzed in terms of the pre-exponential factor, which is proportional to

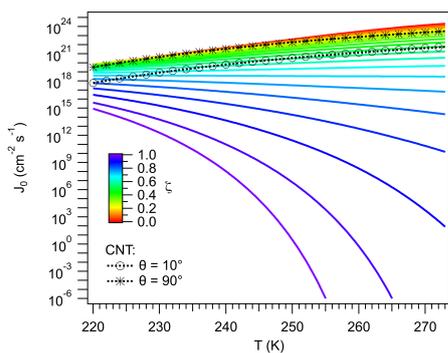


Figure 5. Pre-exponential factor. Colored lines indicate different values of ζ . Black lines correspond to results calculated using CNT for different values of the contact angle, θ .

f_{het}^* in the form

$$J_0 = \frac{Z f_{\text{het}}^*}{a_0}. \quad (62)$$

J_0 expresses the normalized flux of water molecules to the ice germ, corrected by Z . Figure 5 shows J_0 calculated using Eqs. (58) and (59). Results from CNT (Eq. 6) are also shown. In general J_0 varies with T and ζ . The sensitivity of J_0 to T is determined by D_∞ (Barahona, 2015), with J_0 increasing with T , since water molecules increase their mobility. Also, at higher T , less work is dissipated during interface transfer. These effects dominate the variation in J_0 for $\zeta < 0.5$, suggesting that the particle has a limited effect on the mobility of vicinal water. Ice nucleation around these particles would be reasonably well described by assuming a negligible effect of the particle on J_0 , as done in CNT. This is evidenced by the CNT-derived values for $\theta = 10^\circ$ and $\theta = 90^\circ$, which represent particles with high and low particle–ice affinity, respectively, and correspond to the range of expected variability in CNT. The $\theta = 90^\circ$ and $\zeta \sim 0$ lines in Fig. 5 are within 1 order of magnitude of each other and are in agreement with homogeneous nucleation results (Barahona, 2015). The $\theta = 10^\circ$ line is also close to the $\zeta \sim 0.5$ curve. In both cases J_0 increases by about 2 orders of magnitude between 220 K and 273 K and decreases by about 2 orders of magnitude from $\zeta = 0.0$ to $\zeta = 0.5$, or from $\theta = 90^\circ$ to $\theta = 10^\circ$ in CNT. This reflects the effect of variation in Z on J_0 .

The behavior of J_0 for $\zeta > 0.5$ dramatically differs from CNT. For $\zeta > 0.5$, and particularly for $\zeta > 0.8$, J_0 decreases strongly with increasing T . This is because as $\zeta \rightarrow 1$ and $T \rightarrow 273$ K, the driving force for interfacial transfer, i.e., the separation of μ_{vc} from thermodynamic equilibrium, vanishes. As the system moves near these conditions D becomes very small. This is the result of the high IL fraction of the vicinal water limiting the number of configurations available to form cooperative regions, required to induce water mobility (Sect. 2.5.1). Such behavior cannot be reproduced by CNT, since no explicit dependency of D on the properties of

the vicinal layer is accounted for. For $\zeta > 0.99$ J_0 decreases by more than 30 orders of magnitude from 220 K to 273 K; molecular transport nearly stops. Ice nucleation may not be possible at such an extreme, despite the fact that these particles very efficiently reduce ΔG_{het} (Fig. 4); water may remain in the liquid state at very low temperatures. Such an effect has been experimentally observed in some biological systems (Wolfe et al., 2002).

3.3 Nucleation rate

The interplay between kinetics and thermodynamics determines the complex behavior of J_{het} in immersion ice nucleation. Particles highly efficient at decreasing ΔG_{het} also decrease the rate of interfacial diffusion to the point where they may effectively prevent ice nucleation. On the other hand, INPs with low ζ do not significantly affect J_0 but have a limited effect on ΔG_{het} . This is confounded with the presence of two thermodynamic nucleation regimes, one in which ΔG_{het} may be large and increases with T (“germ-forming”), and another in which ΔG_{het} is very small and decreases as T increases (“spinodal nucleation”). This picture can be simplified, since within the range $233 \text{ K} < T < 273 \text{ K}$, where immersion freezing is relevant for atmospheric conditions, INPs with $\zeta > 0.7$ are, at the same time, more likely to nucleate ice in the spinodal regime and to exhibit strong kinetic limitations. Similarly for $\zeta < 0.6$ the transition to spinodal nucleation occurs below 233 K (Fig. 2). These INPs tend to nucleate ice in the germ-forming regime without significantly affecting J_0 . Thus the thermodynamic regimes introduced in Sect. 3.1 loosely correspond to kinetic regimes. Roughly, ice nucleation in the spinodal regime is controlled by kinetics, and in the germ-forming regime, it is controlled by thermodynamics. This is a useful approximation, but it should be used with caution. Even in the germ-forming regime the particle affects the kinetics of ice–liquid interfacial transfer to some extent. Similarly, in the spinodal regime ΔG_{het} is small, but finite.

Figure 6 shows the behavior of J_{het} as T increases for different values of ζ . J_{het} in the germ-forming regime resembles the behavior predicted by CNT. J_{het} increases steeply with decreasing T and increasing ζ . Similarly for CNT, J_{het} increases for decreasing T and θ . This is characteristic of the thermodynamic control on J_{het} , where ΔG_{het} and $\frac{d\Delta G_{\text{het}}}{dT}$ are large (Fig. 4), and J_0 is relatively unaffected by the particle. In this regime it is always possible to find a contact angle (typically between 10 and 100°) that results in close agreement of J_{het} between CNT and NNF predictions (Fig. 6), particularly for $J_{\text{het}} < 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$, which covers most values of atmospheric interest. This is also true for $a_w = 0.9$ (Fig. 6), although the approximation to the equilibrium temperature signals a steeper behavior in CNT peaking at higher values than NNF. Since $\frac{dJ_{\text{het}}}{dT}$ is large, J_{het} may show threshold behavior, characteristic of ice nucleation mediated by some dust species like Chlorite and Montmorillonite (Atkin-

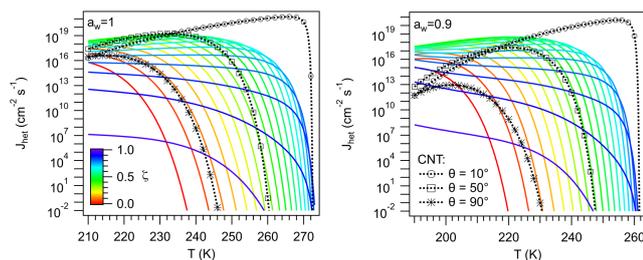


Figure 6. Ice nucleation rate calculated using Eq. (61) for different values of ζ (color). Black lines were calculated using CNT for different values of the contact angle, θ .

son et al., 2013; Murray et al., 2012; Hoose and Möhler, 2012).

There is, however, no value of θ that would lead to overlap between CNT and NNF for $\zeta > 0.7$. These conditions largely correspond to spinodal ice nucleation. J_{het} is kinetically controlled, since ΔG_{het} is small, and J_0 varies widely with T (Fig. 5). As in the germ-forming regime J_{het} also reaches significant values but increases more slowly with decreasing T (Fig. 6). Higher ζ leads to J_{het} becoming significant at higher T . But unlike in the germ-forming case, curves with higher ζ tend to plateau at progressively lower values of J_{het} , since they become kinetically limited by their approximation to the thermodynamic equilibrium. For $\zeta \sim 0.7$ some of the curves of Fig. 6 also display germ-forming behavior at high T and are characterized by a sudden decrease in $-\frac{dJ_{\text{het}}}{dT}$ as T decreases. The sudden change of slope corresponds to the region around the minimum ΔG_{het} (Fig. 4) and signals the transition from germ-forming to spinodal ice nucleation. Such behavior has been observed in some INPs of bacterial origin (Murray et al., 2012).

Figure 6 also indicates that nucleation regimes cannot be assigned based on the values of J_{het} or on the observed freezing temperature, T_f . In both regimes, J_{het} may reach substantial values, hence T_f may cover the entire range $233 \text{ K} < T < 273 \text{ K}$. What is striking is that J_{het} curves with $\zeta > 0.7$ tend to cross those with $\zeta < 0.7$. This means that two INPs characterized by very different ζ can have the same freezing temperature. This result thus challenges the common notion that INPs with higher freezing temperatures are intrinsically more active at nucleating ice, or in other words, that by measuring T_f alone, it is possible to characterize the freezing properties of a given material. In reality, to discern whether the observed T_f corresponds to a good (in the thermodynamic sense) INP acting in the spinodal regime or a less active INP acting in the germ-forming regime, it is necessary to measure $\frac{dJ_{\text{het}}}{dT}$ along with T_f .

3.4 Application to the water activity-based nucleation rate

If a droplet is in equilibrium with its environment then a_w is a function of the relative humidity. Thus the relationship between a_w and the freezing temperature, T_f , conveys important information about the potential of a particle to catalyze the formation of ice and can be used to generate parameterizations of immersion ice nucleation for cloud models (Kärcher and Lohmann, 2003; Koop and Zobrist, 2009; Barahona and Nenes, 2009). A widely used class of parameterizations is based on the so-called water activity criterion (Koop et al., 2000; Koop and Zobrist, 2009), the condition that for a given material the water activity at which heterogeneous ice nucleation is observed, $a_{w,\text{het}}$, is related by a constant to $a_{w,\text{eq}}$ (Koop et al., 2000; Koop and Zobrist, 2009). Here it is shown that the two-state thermodynamic model proposed in Sect. 2.3 implies the water activity criterion as a purely thermodynamic constraint to freezing.

3.4.1 Water activity shift

By definition the thermodynamic path shown in Fig. 1 operates between two equilibrium states. The relation between ΔG_{het} and ΔG_{hom} is therefore independent of the way the system reaches $a_{w,\text{eff}}$. In the absence of any kinetic limitations to the germ growth, Eq. (35) also represents a direct relationship between J_{hom} and J_{het} . (Kärcher and Lohmann, 2003; Marcolli et al., 2007; Koop and Zobrist, 2009; Knopf and Alpert, 2013). Thus one can imagine two separate experiments in which the environmental conditions are set to either a_w or $a_{w,\text{eff}}$, the former resulting in heterogeneous freezing and the latter in homogeneous ice nucleation. Under these conditions Eq. (34) implies that when heterogeneous ice nucleation is observed at $a_{w,\text{het}} = a_w$ there is a corresponding homogeneous process that would occur at $a_{w,\text{hom}} = a_{w,\text{eff}}$. Thus we can write an equivalent expression to Eq. (34), but in terms of $a_{w,\text{het}}$ and $a_{w,\text{hom}}$, in the form

$$a_{w,\text{het}} = a_{w,\text{hom}} \left(\frac{a_{w,\text{eq}}}{a_{w,\text{hom}}} \right)^\zeta \exp(\Lambda_{\text{mix}}). \quad (63)$$

Eq. (63) can be rewritten as

$$\ln(a_{w,\text{het}}) = (1 - \zeta) \ln(a_{w,\text{hom}}) + \zeta \ln(a_{w,\text{eq}}) + \Lambda_{\text{mix}}. \quad (64)$$

Subtracting $\ln(a_{w,\text{eq}})$ from each side of Eq. (64) gives

$$\begin{aligned} \ln(a_{w,\text{het}}) - \ln(a_{w,\text{eq}}) = \\ (1 - \zeta) [\ln(a_{w,\text{hom}}) - \ln(a_{w,\text{eq}})] + \Lambda_{\text{mix}}. \end{aligned} \quad (65)$$

Using the approximation $\ln(x) \approx x - 1$ for $x \sim 1$, Eq. (65) can be linearized in the form

$$\Delta a_{w,\text{het}} = \Delta a_{w,\text{hom}} (1 - \zeta) + \Lambda_{\text{mix}}, \quad (66)$$

where $\Delta a_{w,\text{hom}} = a_{w,\text{hom}} - a_{w,\text{eq}}$ and $\Delta a_{w,\text{het}} = a_{w,\text{het}} - a_{w,\text{eq}}$ are the homogeneous and heterogeneous water activity shifts,

respectively. $\Delta a_{w,\text{hom}}$ has been found to be approximately constant for a wide range of solutes (Koop et al., 2000); therefore Eq. (66) suggests that $\Delta a_{w,\text{het}}$ should be approximately constant, since $\Lambda_{\text{mix}} \sim 0.02$ and only depends on T . Thus, the two-state model presented in Sect. 2.3 implies the so-called water activity criterion (Koop et al., 2000) for heterogeneous ice nucleation, giving support to the hypothesis that increasing order near the particle surface drives ice nucleation.

Equations (63) to (66) are fundamental thermodynamic relationships of the system and can be used to analyze the effect of the immersed particle on ice formation independently of kinetic effects. To do so $a_{w,\text{hom}}$ must be determined entirely by thermodynamics. This is because if $a_{w,\text{hom}}$ is defined at some J_{hom} threshold then it (and by extension $a_{w,\text{het}}$) would also depend on the freezing kinetics. Fortunately, a thermodynamic definition of $a_{w,\text{hom}}$ has been achieved by Baker and Baker (2004). The authors showed that, on average, freezing occurs below the temperature at which the compressibility of water reaches a maximum. At this point density fluctuations are wide enough to allow for structural transformations that facilitate the formation of ice-like regions within the droplet volume. Such a criterion does not depend on measured freezing rates and can be extended to the freezing of water solutions, coinciding with the results of Koop et al. (2000). Bullock and Molinero (2013) also derived a pure thermodynamic criterion for $a_{w,\text{hom}}$ using the equilibrium between low-density regions and the bulk solution. Within these frameworks $a_{w,\text{hom}}$ can be defined without reference to a J_{hom} threshold. By extension, Eq. (64) guarantees that $a_{w,\text{het}}$ can be determined entirely by the thermodynamic properties of the system.

Equation (64) also implies that for a given $a_{w,\text{hom}}$ there is a temperature for which $a_w = a_{w,\text{het}}$, referred as the “thermodynamic freezing temperature”, T_{fit} . Formally, T_{fit} represents the solution of

$$\ln(a_w) - (1 - \zeta) \ln[a_{w,\text{eq}}(T_{\text{fit}}) + \Delta a_{w,\text{hom}}] - \zeta \ln[a_{w,\text{eq}}(T_{\text{fit}})] - \Lambda_{\text{mix}}(T_{\text{fit}}) = 0, \quad (67)$$

or in the linearized form,

$$a_w - a_{w,\text{eq}}(T_{\text{fit}}) - \Delta a_{w,\text{hom}}(1 - \zeta) - \Lambda_{\text{mix}}(T_{\text{fit}}) = 0. \quad (68)$$

Since $\Delta a_{w,\text{hom}}$ is considered a thermodynamic property of the system (Baker and Baker, 2004), T_{fit} does not depend on the freezing kinetics. Thus T_{fit} can be interpreted as the highest temperature where it is likely to observe ice nucleation for a given thermodynamic state (determined by a_w , ζ and the system pressure).

Figure 7 shows the $T_{\text{fit}}-a_w$ relationship defined by Eq. (67), calculated using $\Delta a_{w,\text{hom}} = 0.304$ (Koop et al., 2000; Barahona, 2014; Baker and Baker, 2004). As expected, the figure resembles experimental results found by several authors (e.g., Koop and Zobrist, 2009; Zuberi et al., 2002; Zobrist et al., 2008; Alpert et al., 2011; Knopf and Alpert, 2013),

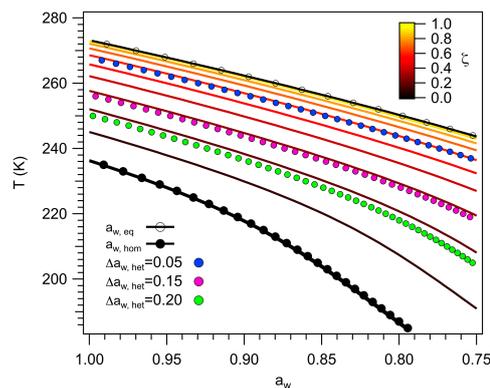


Figure 7. Thermodynamic freezing temperature as a function of water activity. Colored lines correspond to $T_{\text{fit}}(a_w = a_{w,\text{het}})$ for different values of ζ . Also shown are the water activities at equilibrium and at the homogeneous freezing threshold, $a_{w,\text{eq}}$ and $a_{w,\text{hom}}$, respectively, and lines drawn applying constant water activity shifts, $\Delta a_{w,\text{het}}$, of 0.05, 0.15 and 0.20.

where curves for $\zeta > 0$ align with constant water activity shifts to $a_{w,\text{eq}}$. To make this evident, lines were drawn using constant values of $\Delta a_{w,\text{het}} = 0.05, 0.15$ and 0.20 , which coincide with lines corresponding to $\zeta = 0.2, 0.3$ and 0.7 , respectively. This shows that Eq. (66) is a good approximation to Eq. (63) and constitutes a theoretical derivation of the water activity criterion. The fact that such behavior can be reproduced by Eq. (63) validates the regular solution approximation used in Sect. 2.3 and supports the idea that the effect of the immersed particle on ice nucleation can be explained as a relative increase in the ice-like character of the vicinal water.

It must be emphasized that T_{fit} only establishes the potential of an INP to induce freezing at $a_w = a_{w,\text{het}}$, regardless of whether a measurable J_{het} can be experimentally realized. Physically, it is plausible that as the particle increases the ice-like character of the vicinal water, it also increases the probability of wide density fluctuations. As a result low-density regions, wide enough to accommodate the ice gem, exist at higher T than in homogeneous ice nucleation. Following the argument of Baker and Baker (2004) this would also imply that the compressibility of water near the particle reaches a maximum at higher T than in the bulk. More research however is needed to elucidate this point. The presence of a spinodal regime would also mean that the observed freezing temperature may differ from T_{fit} , since at such a limit nucleation, it is no longer controlled by thermodynamics. This is illustrated in the next section.

3.4.2 Freezing by humic-like INPs

$\Delta a_{w,\text{het}}$ has been determined in several studies and has been used to predict and parameterize J_{het} in atmospheric models (e.g., Zobrist et al., 2008; Knopf and Alpert, 2013). Thus it

is useful in analyzing the conditions under which ζ (hence J_{het}) can be estimated using measured $\Delta a_{\text{w,het}}$ values. Rearranging Eq. (66) we obtain

$$\Delta a_{\text{w,het}} - \Delta a_{\text{w,hom}}(1 - \zeta) - \Lambda_{\text{mix}} = 0. \quad (69)$$

If $\Delta a_{\text{w,hom}}$ and $\Delta a_{\text{w,het}}$ are known, ζ can be estimated iteratively by solving Eq. (69). Note that Λ_{mix} is temperature dependent (Eq. 34), implying a slight dependency of ζ on T when $\Delta a_{\text{w,het}}$ is constant. However since Λ_{mix} is also typically small, ζ is almost equal to $1 - \frac{\Delta a_{\text{w,het}}}{\Delta a_{\text{w,hom}}}$.

To test Eq. (69) the data for leonardite (LEO) and Pahokee peat (PP) particles (humic-like substances) obtained by Rigg et al. (2013) are used. The authors reported $\Delta a_{\text{w,het}} = 0.2703$ for LEO and $\Delta a_{\text{w,het}} = 0.2466$ for PP. These values are assumed to be independent of a_{w} and T , with an experimental error in $\Delta a_{\text{w,het}}$ of 0.025. The average J_{het} obtained from different samples and from repeated freezing and melting experiments for both materials is depicted in Fig. 8. Applying Eq. (69) over the $T = 210 \text{ K} - 250 \text{ K}$ range and using $\Delta a_{\text{w,hom}} = 0.304$ results in $\zeta = 0.049 - 0.058$ for LEO and $\zeta = 0.096 - 0.121$ for PP. Within this temperature range these values correspond to the germ-forming regime, hence J_{het} is thermodynamically controlled. A comparison against the experimentally determined J_{het} for three different values of a_{w} is shown in Fig. 8. Within the margin of error there is a reasonable agreement between the modeled and the experimental J_{het} .

The top panels of Figure 8, however, reveal that even if J_{het} becomes significant around the values predicted by Eq. (69), $-\frac{d \ln J_{\text{het}}}{dT}$ is overestimated, particularly for PP. This may indicate that these INPs nucleate ice in the spinodal regime. To test this hypothesis J_{het} was fitted to the reported measurements by varying ζ within the range where spinodal nucleation would be dominant. To avoid agreement by design a single ζ was used for all experiments for each species resulting in $\zeta = 0.949$ for PP and $\zeta = 0.952$ for LEO (Fig. 8, bottom panels). For PP, J_{het} and $-\frac{d \ln J_{\text{het}}}{dT}$ agree better with the experimental values, whereas for LEO the agreement improves at high T but worsens at low T . In this regime J_{het} seems to be slightly overestimated by the theory at the lowest a_{w} tested. This may be due to small uncertainties in a_{w} that play a large role in J_{het} (for example, the assumption of a T -independent a_{w} ; Alpert et al., 2011). There is the possibility that the humic acid present in PP may slightly dissolve during the experiments (Daniel Knopf, personal communication, 2017), which would impact not only a_{w} but also may modify the composition of the particles, hence ζ .

The exercise above suggests that ice nucleation in PP may follow a spinodal mechanism. Using a single value of $\Delta a_{\text{w,het}}$ to predict ζ , as expressed mathematically by Eq. (69), seems to work for LEO. Since Eq. (69) represents a thermodynamic relation between $\Delta a_{\text{w,hom}}$ and $\Delta a_{\text{w,het}}$, it is expected to work well when nucleation is thermodynamically controlled, i.e., the germ-forming regime. However it

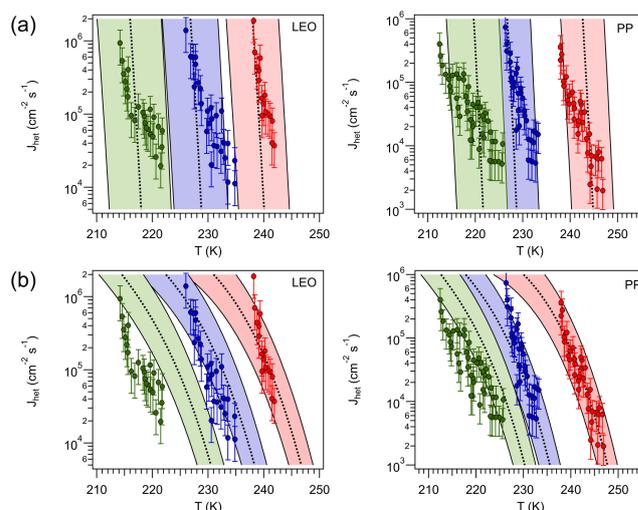


Figure 8. (a) Heterogeneous ice nucleation rate calculated using a constant shift in a_{w} (black, dotted, lines) for leonardite (LEO, $\Delta a_{\text{w,het}} = 0.2703$) and Pahokee peat (PP, $\Delta a_{\text{w,het}} = 0.2466$). Red, blue and green colors correspond to a_{w} equal to 1.0, 0.931 and 0.872, respectively, for LEO, and 1.0, 0.901 and 0.862 for PP. Shaded area corresponds to $\Delta a_{\text{w,het}} \pm 0.025$. Markers correspond to experimental measurements reported by Rigg et al. (2013); error bars represent an order of magnitude deviation from the reported value. (b) J_{het} calculated for constant $\zeta = 0.949$ for LEO and $\zeta = 0.952$ for PP. The shaded area corresponds to $a_{\text{w}} \pm 0.01$ and $\zeta \pm 0.0015$.

may fail for spinodal ice nucleation, since it does not consider the effect of the particle on J_0 . $\Delta a_{\text{w,het}}$ however carries important information about J_{het} (Knopf and Alpert, 2013), but for spinodal ice nucleation, the relationship between $\Delta a_{\text{w,het}}$ and ζ must be more complex than predicted by Eq. (69), since kinetic limitations play a significant role. Figure 8 also shows that similar T_{f} can be obtained by either high or low ζ . The particular regime in which an INP nucleates ice determines $-\frac{d \ln J_{\text{het}}}{dT}$, hence the sensitivity of the droplet freezing rate to the particle size and to the cooling rate.

3.5 Limitations

It is important to analyze the effect of several assumptions introduced in Sect. 2 on the theory presented here. One of the limitations of the approach used in deriving Eq. (61) is that it employs macroscale thermodynamics in the formulation of the work of nucleation. The effect of this assumption is, however, minimized in several ways. First, unlike frameworks based on the interfacial tension, NNF is much more robust to changes in ice germ size, since the product $\Gamma_{\text{w}} s \Delta h_{\text{f}}$ remains constant (Sect. 2.4). Second, in the spinodal regime ΔG_{het} is independent of n_{het} , and only for $T > 268 \text{ K}$ and in the germ-forming regime, the approach presented here may lead to uncertainty (Sect. 3.1). Thus Eq. (61) remains

valid for most atmospheric conditions, although caution must be taken when $T_f > 268$ K. Alternatively the framework presented here could be extended to account explicitly for the effect of size on Δh_f and Γ_w (e.g., Zhang et al., 1999).

Further improvement could be achieved by implementing a more sophisticated equation of state of the vicinal water. Here a two-state assumption has been used, such that μ_{vc} is a linear combination of ice-like and liquid-like fractions. Such approximation has been used with success before (Etzler, 1983; Holten et al., 2013). However it is known that the structure of supercooled water represents an average of several distinct configurations (Stanley and Teixeira, 1980). These are, in principle, accounted for in the proposed approach, since ζ represents a relative, not an absolute, increase in the IL fraction. However there is no guarantee that such an increase can be linearly mapped in the way described in Sect. 2. Fortunately this would only mean, in practice, that the value of ζ for a given material is linked to the particular form of the equation of state used to describe the vicinal water.

Equation (61) is also blind to the surface properties of the immersed particle. The implicit assumption is that the effect of surface composition, charge, hydrophilicity and roughness on J_{het} can be parameterized as a function of ζ . The example shown in Sect. 3.4 suggests that this is indeed the case. Making such relations explicit must, however, lie at the center of future development of the proposed approach. Similarly, a heuristic approach was used to study the effect of irreversibility on the nucleation work. This can be improved substantially by making use of a generalized Gibbs approach (Schmelzer et al., 2006), which unfortunately may also increase the number of free parameters in the model. None of these limitations is expected to change the conclusions of this study, however they may affect the values of ζ fitted when analyzing experimental data. The approach proposed here, however, has the advantage of being a simple, one-parameter approximation that can be easily implemented in cloud models.

4 Summary and conclusions

Immersion freezing is a fundamental cloud process, and its correct representation in atmospheric models is critical for accurate climate and weather predictions. Current theories rely on a view that mimics ice formation from the vapor, neglecting several interactions unique to the liquid. This work develops, for the first time, a comprehensive approach to account for such interactions. The ice nucleation activity of immersed particles is linked to their effect on the vicinal water. It is shown that the same mechanism that lowers the thermodynamic barrier for ice nucleation also tends to decrease the mobility of water molecules, hence limiting interfacial transfer and ice germ growth. The role of the immersed particle in ice nucleation can be understood as increasing order

in the adjacent water, facilitating the formation of ice-like structures. Thus, instead of being purely driven by thermodynamics, heterogeneous ice nucleation in the liquid phase is a process determined by the competition between thermodynamic and kinetic constraints to the formation and propagation of ice.

In the new approach the properties of vicinal water are approximated using a regular solution between high and low-density regions, with composition defined by an material specific parameter, ζ , which acts as a “templating factor” for ice nucleation. This results on an identity between the homogeneous and the heterogeneous work of nucleation (Eq. 35), implying that by knowing an expression for ΔG_{hom} , ΔG_{het} can be readily written. This is advantageous, as homogeneous ice nucleation is far better understood than immersion ice nucleation and, because it avoids a mechanistic description of the complex interaction between the particle, the ice and the liquid. To describe ΔG_{hom} the NNF framework (Barahona, 2014) was employed. This approach was extended to include non-equilibrium dissipation effects.

A model to describe the effect of the immersed particle on the mobility of water molecules, hence on the kinetics of immersion freezing, was also developed. This model builds upon an expression for the interfacial diffusion flux that accounts for the work required for water molecules to accommodate in an ice-like manner during interface transfer. Here this expression is extended to account for the effect of the particle on the molecular flux to the ice germ. It was shown that J_0 strongly decreases as the system moves towards thermodynamic equilibrium.

The model presented here suggests the existence of a spinodal regime in ice nucleation where a pair of molecules with orientation similar to that of bulk ice may be enough to trigger freezing. Ice nucleation in the spinodal regime requires a highly efficient templating effect by the particle, however also tends to be strongly limited by the kinetics of the ice–liquid interfacial transfer. Compared to the classical germ-forming regime, nucleation by a spinodal mechanism is much more limited by diffusion and exhibits a more moderate increase in J_{het} as temperature decreases. The existence of two nucleation regimes and the strong kinetic limitations occurring in efficient INPs imply that the freezing temperature is an ambiguous measure of ice nucleation activity. This is because, for a given T , two INPs characterized by different ζ may have the same J_{het} , although with very different sensitivity to surface area and cooling rate.

The relationship between the measured shift in water activity $\Delta a_{w,het}$ and ζ was analyzed. It was shown that the proposed model leads directly to the derivation of the so-called water activity criterion for heterogeneous ice nucleation. The concept of “thermodynamic freezing temperature” was introduced and defined as the highest temperature at which it is likely to observe ice nucleation for a given thermodynamic state. T_{ft} is useful in analyzing how changes in the thermody-

dynamic environment around the droplet affect ice nucleation, independently of the freezing kinetics.

The theory presented here was tested using data for humic-like substances. It was found that assuming a fixed water activity shift to predict J_{het} could be appropriate for low ζ , as found in leonardite (the germ-forming regime); however this may lead to overprediction of $-\frac{d \ln J_{\text{het}}}{dT}$ for the high ζ characterizing Pahokee peat INPs. This is because the water activity criterion represents a thermodynamic relation between a_w and T_f but does not account for kinetic limitations, which may be significant in spinodal ice nucleation.

Immersion freezing research has seen a resurgence during the last decade (DeMott et al., 2011). A wealth of data is now available to test theories and new approaches to describe ice formation in atmospheric models. To do so effectively, it is necessary to develop models that realistically capture the complexities of the liquid phase. Further development of the approach presented here will look to better describe the non-reversible aspects of nucleation as well as to establish a more complete description of the properties of the vicinal water. The application to the freezing of atmospheric aerosol requires the definition of the ice nucleation spectrum, which will be pursued in a future work. Nevertheless, the present study constitutes, for first the time, an approximation to the modeling of ice nucleation that links the modifications of the properties of vicinal water by immersed particles with their ice nucleation ability. The approach presented here may help with expanding our understanding of immersion ice nucleation and facilitating the interpretation of experimental data in situations where current models fall short. The application of these ideas in cloud models will allow for the elucidation of the conditions under which different nucleation regimes occur in the atmosphere.

Data availability. Supplementary material includes data used in generating Figs. 4–6. Fortran subroutines with the full implementation of the theory are available upon request.

Appendix A: List of symbols.

a_0	Cross-sectional area of a water molecule, $\pi d_0^2/4$, m ²
A_w	Phenomenological interaction parameter
a_w	Activity of water
$a_{w,eff}$	Effective water activity
$a_{w,eq}$	Equilibrium a_w between bulk liquid and ice (Koop and Zobrist, 2009)
$a_{w,het}$	Thermodynamic freezing threshold for heterogeneous ice nucleation
$a_{w,hom}$	Thermodynamic freezing threshold for homogeneous ice nucleation
C_0	Monomer concentration, m ⁻²
E, T_0	Parameters of the Vogel–Fulcher–Tammann equation defining D_∞ , 892 and 118 K (Smith and Kay, 1999)
D	Diffusion coefficient for interface transfer, m ² s ⁻¹
D_∞	Self-diffusion coefficient of bulk water (Smith and Kay, 1999), m ² s ⁻¹
D_0	Fitting parameter, 3.06×10^{-9} m ² s ⁻¹ (Smith and Kay, 1999)
d_0	Molecular diameter of water, $(6v_w/\pi)^{1/3}$, m
f_{het}^*	Impingement factor for heterogeneous ice nucleation, s ⁻¹
f_{hom}^*	Impingement factor for homogeneous ice nucleation, s ⁻¹
G	Gibbs free energy, J
h	Planck's constant, Js
J_0	Pre-exponential factor m ⁻² s ⁻¹
J_{het}	Heterogeneous nucleation rate, m ⁻² s ⁻¹
k_B	Boltzmann constant, JK ⁻¹
N	Number of clustering molecules in LL and IL regions, 6 (Holten et al., 2013)
n	Number of molecules in an ice cluster
n^*	Critical germ size
n_{het}	Critical germ size for heterogeneous ice nucleation
n_{hom}	Critical germ size for homogeneous ice nucleation
n_t	Number of formation paths of the transient state, 16 (Barahona, 2015)
$p_{s,w}, p_{s,i}$	Liquid water and ice saturation vapor pressure, respectively, Pa (Murphy and Koop, 2005)
s	Geometric constant of the ice lattice, 1.105 molec ^{1/3} (Barahona, 2014)
S_i	Saturation ratio with respect to ice
$S_{c,0}$	Configuration entropy of water*
S_c	Configuration entropy of vicinal water
T	Temperature, K
T_c	Critical separation temperature, 211.473 K
v_w	Molecular volume of water in ice (Zobrist et al., 2007), m ⁻³
$v_{w,0}$	Molecular volume of water at 273.15 K
\bar{W}	Average transition probability in water
W_{diss}	Work dissipated during cluster formation, J
W_d	Work dissipated during interface transfer, J
Z	Zeldovich factor
$\Delta a_{w,het}$	$a_{w,het} - a_{w,eq}$
$\Delta a_{w,hom}$	$a_{w,hom} - a_{w,eq}$, 0.304 (Koop et al., 2000; Barahona, 2014)
ΔG	Work of cluster formation, J
ΔG_{act}	Activation energy for ice nucleation, J
ΔG_{hom}	Nucleation work for homogeneous ice nucleation, J
ΔG_{het}	Nucleation work for heterogeneous ice nucleation, J
Δh_f	Heat of solidification of water, J mol ⁻¹ (Barahona et al., 2014; Johari et al., 1994)
$\Delta \mu_s$	Excess free energy of solidification of water, J
$\Delta \mu_i$	Driving force for ice nucleation, J
Λ_{mix}	Dimensionless mixing parameter, defined in Eq. (30)
Φ	Energy of formation of the ice–liquid interface, molec ^{1/3} J
Γ_w	Molecular surface excess at the interface, 1.46 (Barahona et al., 2014; Spaepen, 1975)
μ_w, μ_s, μ_{vc}	Chemical potential of water, ice and vicinal water, respectively J
ρ_w, ρ_i	Bulk density of liquid water and ice, respectively, Kg m ⁻³ (Pruppacher and Klett, 1997)
σ_E	Dimensionless residual entropy
σ_{iw}	Ice–liquid interfacial energy J m ⁻² (Barahona et al., 2014)
θ	Contact angle
ζ	Templating factor
Ω_g	Ice germ surface area, m ⁻²

* From the data of Scala et al. (2000), the following fit was obtained: $S_{c,0} = k_B v_w / v_{w,0} (-7.7481 \times 10^{-5} T^2 + 5.5160 \times 10^{-2} T - 6.6716)$ (JK⁻¹) for T between 180 and 273 K.

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