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## Entropic Aspects of Supercooled Droplet Freezing

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### ABSTRACT

The freezing of supercooled water droplets in the atmosphere, with an emphasis on the entropic aspects of the problem, is examined. Supercooled water is a metastable state and, therefore, the associated phase transition must be irreversible. Temperature-dependent heat capacities of supercooled water and ice are used to calculate the entropy difference. That difference is then used to establish a lower bound on the amount of latent heat that can be liberated by the freezing droplets. The calculation is compared with tabulated values of the latent heat of fusion with surprising results. Based on a novel physical picture of the freezing process, the authors suggest a simple estimate for the effective latent heat that is suitable for heat budget calculations of glaciating clouds. In addition, the authors arrive at a quadratic dependence on supercooling,  $(\Delta T)^2$ , for the irreversible contribution to heat exchange during the freezing process. The proportionality factor is estimated as  $-0.3 \text{ J mol}^{-1} \text{ K}^{-2}$ .

### 1. Introduction

Despite its ubiquity in our environment (clouds and fogs) and practical importance (aircraft icing), supercooled water remains enigmatic. For example, the heat capacity of water at normal pressure varies by less than 1% over the entire range between the melting and boiling points. However, within  $36^\circ$  below the melting point, it increases by 35%, from  $75.9$  to  $102.7 \text{ J mol}^{-1} \text{ K}^{-1}$  (Angell et al. 1982). The latent heat of fusion of supercooled water is also known to depend on temperature. Given the wide range of supercooling observed in atmospheric clouds, the corresponding variation in the latent heat exchanged with the atmosphere may be substantial, possibly reaching 30% at extreme supercooling, according to Fukuta and Gramada (2003).

The temperature dependence of the latent heat of fusion impacts not only our fundamental understanding of clouds but also their representation in climate models. Hence, it is important to estimate the amount of heat released to the atmosphere by freezing droplets as a function of ambient temperature. There is a microphysical motivation as well—latent heat appears in the exponent of the expression for the ice nuclea-

tion rate (see, e.g., Landau and Lifshitz 1980, p. 535); a small change in the expression for latent heat may result in a large change in the corresponding nucleation rate.

Measurements of the latent heat of fusion as a function of temperature are difficult and remain scarce. We have been able to locate only three studies—Fukuta and Gramada (2003), the *Smithsonian Meteorological Tables* (List 1951), and Bertolini et al. (1985). In the two atmospherically motivated studies—Fukuta and Gramada (2003) and the *Smithsonian Meteorological Tables* (List 1951)—the latent heat values were obtained by using measured vapor pressures<sup>1</sup> and then using the Clausius–Clapeyron equation as well as the triple-point identity for the latent heats of sublimation, vaporization, and fusion to extract the latent heat of fusion. Thus, the latent heat measurements are not direct and, as argued below, involve assumptions whose validity, while unquestionable for phase equilibrium, is not clear in the supercooled (metastable) domain (see appendix A). Therefore, our second goal is to employ entropic considerations in order to facilitate an interpretation of difficult experiments and constrain the measurements.

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<sup>1</sup> Fukuta and Gramada (2003) used measured values of the vapor pressure of supercooled water, while values in the *Smithsonian Meteorological Tables* (List 1951) are extrapolated from measurements above the melting point.

## 2. The entropy constraint

We regard a supercooled droplet as a thermodynamic system and the ambient air as the heat reservoir. Initially, both are at temperature  $T_i < T_{\text{melting}}$ , corresponding to a metastable equilibrium of the supercooled water. Upon freezing at that temperature,  $L(T_i)$  is given off to the atmosphere by the droplet. From the outset, we note that the notion of latent heat is freely extended to the supercooled domain throughout the literature, despite being originally developed for a reversible phase equilibrium. For example, the relationship  $L(T_i) = T_i \Delta S$ , where  $S$  is entropy and  $\Delta S \equiv S_{\text{water}} - S_{\text{ice}}$  has been used [Jeffery and Austin 1997, p. 2750, Eq. (3c)]. It is also implied in the identity  $L_{\text{sublim}} = L_{\text{vapor}} + L_{\text{fusion}}$ , a relation used extensively in the literature, for example, by Fukuta and Gramada (2003) and the *Smithsonian Meteorological Tables* (List 1951). However, the relationship  $L_{\text{fusion}}(T) = T \Delta S$  is valid only at the melting point; reversibility is the key requirement.

Indeed, recall that the Clausius definition of entropy  $dS = dQ/T$  requires reversibility. On the other hand, the supercooled water cannot undergo a reversible freezing transition because it is in a metastable equilibrium so that the process is unidirectional; that is, supercooled water can turn into ice but not vice versa. This observation suggests the following question: How does the irreversibility, inevitably associated with supercooled water freezing, affect the amount of latent heat given off to the atmosphere?

We begin to answer this question by examining Fig. 1a, which is a plot of the heat capacity of supercooled water (Angell et al. 1982; Archer and Carter 2000) and ice (Haida et al. 1974) as a function of temperature. We then use the data as input to calculate the entropy of supercooled water and ice via

$$S(T) = S(T_m) - \int_T^{T_m} \frac{c(T')}{T'} dT', \quad (1)$$

where  $c$  stands for heat capacity of water or ice. Our results are displayed in Fig. 1b.

The next step in this chain of reasoning is to calculate the latent heat at constant (atmospheric) pressure via the previous equation and

$$L(T) = T \Delta S = T[S_{\text{water}}(T) - S_{\text{ice}}(T)], \quad (2)$$

which is valid for reversible processes. Throughout this work,  $T_i$  denotes the initial temperature of the super-

cooled water, which is not to be confused with  $c_i$  denoting heat capacity of ice. The results of the calculation as well as values from Fukuta and Gramada (2003), the *Smithsonian Meteorological Tables* (List 1951), and Bertolini et al. (1985) are shown in Fig. 1c.

Does the irreversibility associated with freezing of supercooled water constrain the data? Indeed, the second law of thermodynamics can be stated as (e.g., Fermi 1936, p. 77)

$$dS_{\text{sys}} \geq dQ/T_i, \quad (3)$$

where  $Q$  is the heat exchanged with the environment and the equality is attained in reversible processes. In our case,  $dS_{\text{sys}} < 0$  (entropy decreases upon freezing) and  $dQ = L(T_i) < 0$  (heat is given off). Thus, for magnitudes, in our case the entropy inequality implies

$$|L(T_i)| \geq |T_i \Delta S|. \quad (4)$$

Equation (4) shows that the magnitude of the latent heat must equal or exceed the magnitude of  $T_i \Delta S$ . Furthermore, it is only for a reversible process that the limiting expression,  $T_i \Delta S$ , can be achieved. For the reader's convenience, magnitudes of all quantities are shown in Fig. 1c. Whereas data from Bertolini et al. (1985) and the *Smithsonian Meteorological Tables* (List 1951) are above the lower bound, the data from Fukuta and Gramada (2003) fall below it (see appendix A for the likely reasons for this discrepancy).

## 3. Effective latent heat of freezing for supercooled water: A useful approximation

While supercooled water droplets do not freeze slowly and reversibly in the atmosphere, this need not prevent one from finding a physically realizable reversible path that links the same initial and final states. Given that energy and entropy are state functions, such a path can be used to calculate heat exchange between droplets and the atmosphere, thereby establishing an expression for effective latent heat of supercooled water versus temperature. This is probably the motivation behind the notion, occasionally found in the physical chemistry literature, for defining the latent heat as an enthalpy difference between supercooled water and ice. [See, e.g., Franks (1982, p. 252); Metz (1989, p. 77); Bertolini et al. (1985). A related discussion in the atmospheric science literature is given in Tsonis (2002, p. 88).] The enthalpy difference is

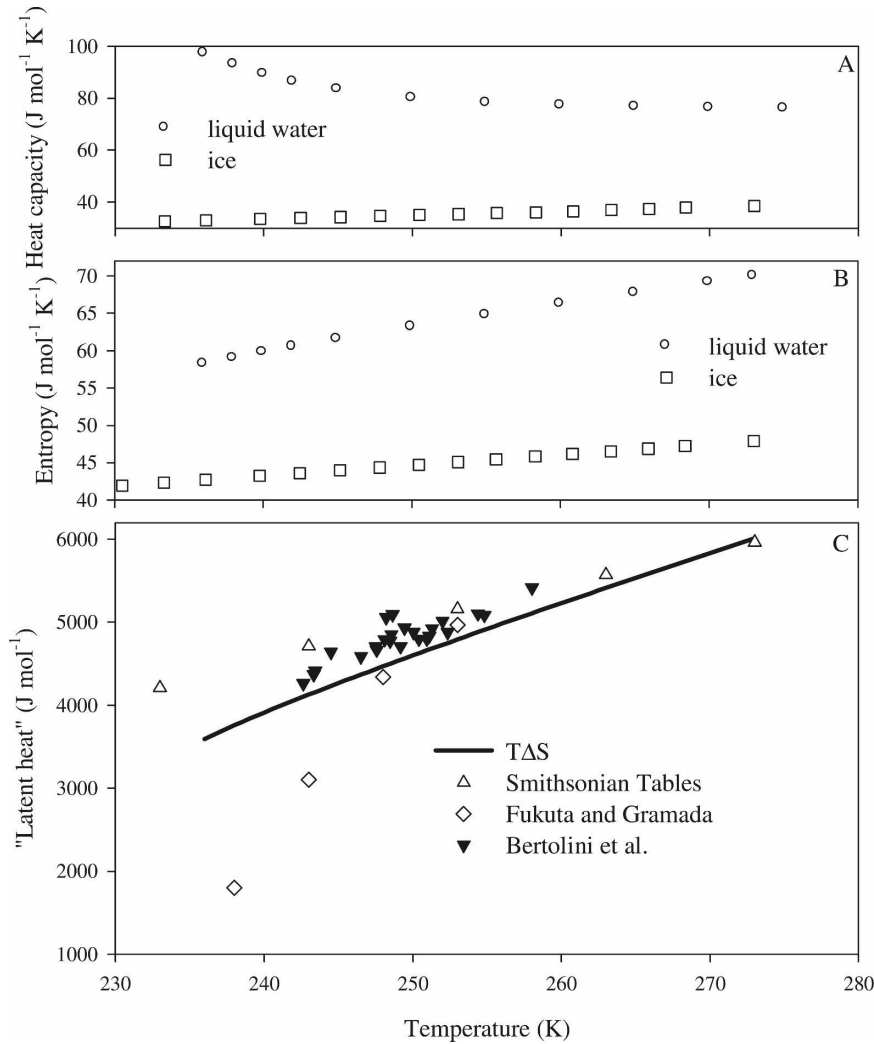


FIG. 1. Chain of reasoning leading to the lower bound for the amount of latent heat released at a given temperature  $T$ . (a) Heat capacity vs temperature for supercooled water at constant pressure (Angell et al. 1982; Archer and Carter 2000) and ice (Haida et al. 1974). (b) The results of our calculations for entropy of supercooled water vs temperature via

$$S(T) = S(T_m) - \int_T^{T_m} \frac{c(T')}{T'} dT',$$

where  $c$  denotes the heat capacity of water or ice, taken from (a). (c) Values of the latent heat of fusion from the *Smithsonian Meteorological Tables* (List 1951), Fukuta and Gramada (2003), and Bertolini et al. (1985), as well as  $L = T\Delta S$ , with  $\Delta S$  as input from (b). The  $T\Delta S$  curve is not the lowest (see appendix A).

$$L' = L_m - \int_{T_i}^{T_m} [c_w(T) - c_i(T)] dT \quad (5)$$

and involves only the reversible latent heat at the melting point and specific heat data for supercooled water and ice.

To interpret this physically, consider the reversible path associated with Eq. (5). Imagine slowly warming a supercooled droplet from the initial state at  $T_i$  to the melting point, freezing it *reversibly*, and then cooling

the resulting ice back down to  $T_i$ .<sup>2</sup> Thus, the entire process is reversible. During the first stage, the super-

<sup>2</sup> In most of this work we shall set the initial temperature  $T_i = T_{\text{final}}$  in order to render the notion of  $L(T_i)$  unambiguous and to mimic experimental conditions. The implication is that atmospheric temperature does not change during droplet freezing, which is reasonable for a single droplet and a reservoir (the atmosphere), but the temperature of the real atmosphere may, of course, rise if billions of droplets freeze. Later, we account for atmospheric warm up.

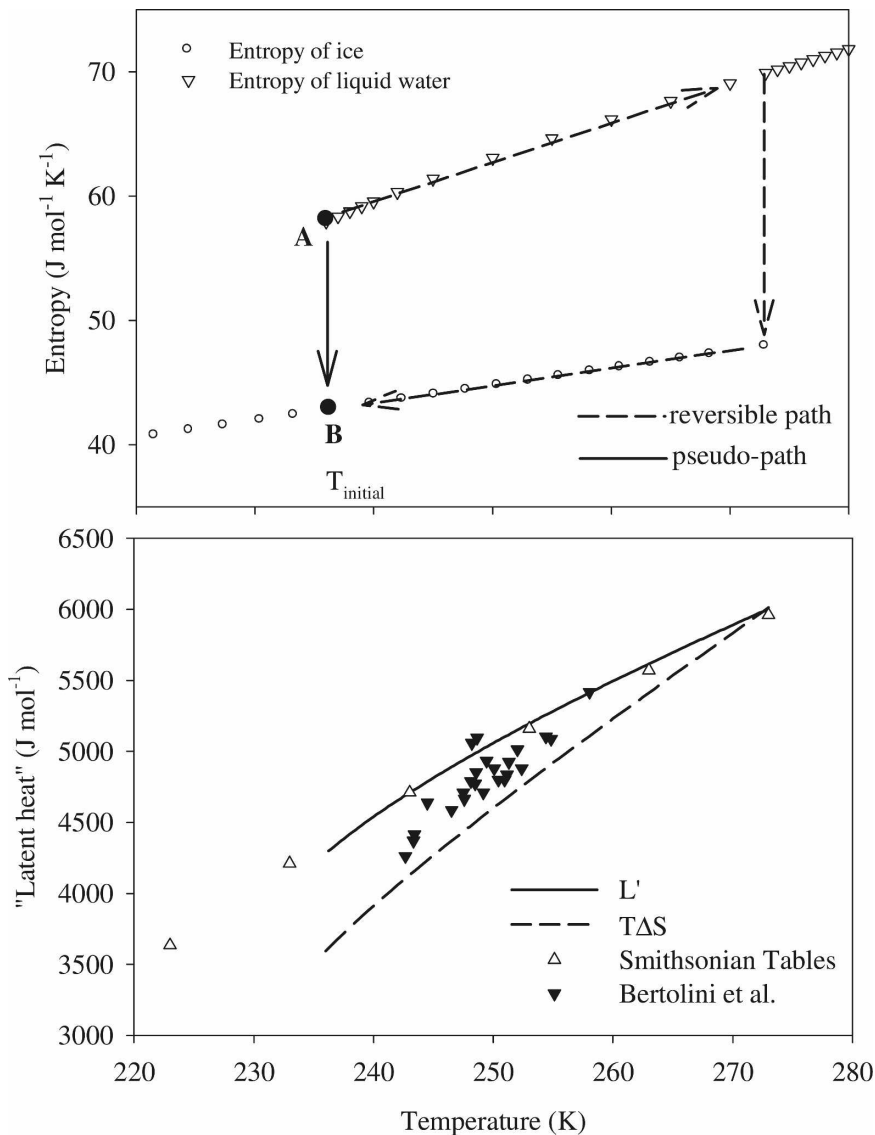


FIG. 2. An approach to a reversible approximation for the effective latent heat of supercooled water. (top) Two ways of freezing supercooled water on an entropy vs temperature plot. The vertical path is loosely implied by the phrase “supercooled droplet freezes at  $T_i$ .” The reversible path consists of warming the supercooled water slowly to the melting point (succession of metastable equilibrium states), with the subsequent phase transition at the melting temperature. The resulting ice is then cooled to the initial temperature. (bottom) Here  $L'(T) \equiv L'(T_i) = L_m - \int_{T_i}^T [c_w(T) - c_i(T)] dT$  is computed using the heat capacity data of Fig. 1a and the results are compared to data and to  $T\Delta S$ .

cooled droplet gains an amount of heat  $Q_1 = \int_{T_i}^{T_m} c_w(T) dT$ , reaches the melting point, and then freezes so that an amount of heat  $L_m$  is released (per unit mass, and  $m$  indicates that the transition takes place at the melting point). Finally, the droplet cools back to  $T_i$ , releasing  $Q_2 = \int_{T_i}^{T_m} c_i(T) dT$ . The magnitude of net heat exchange is then  $L'(T_i)$ . This process is indicated by the dashed lines in the upper panel of Fig. 2. Unlike the vertical “drop” from A to B, dashed lines constitute a path

insofar as each point represents an equilibrium state (albeit a metastable one) with the same  $T$  throughout the droplet and the reservoir (see, e.g., Zemansky 1981, p. 183).

The arguments for  $L'$  appear eminently reasonable, but there is a subtle flaw, which is the assumption that the final state of ice is identical for reversible and irreversible changes. Atmospheric pressure and temperature do not determine the thermodynamic state of ice

(a solid) uniquely; one needs to specify stress components and final volume as well (see appendix B for details). Also, rapid freezing may result in ice filled with defects, while reversibly made ice is relatively defect free (crystal growers slow down solidification in order to produce high quality crystals).<sup>3</sup> It turns out (see below) that the irreversibility correction is relatively small, so Eq. (5) may still be a good approximation to the actual heat exchange.

To compare  $L'$  to the available data, we calculated  $L'(T_i) \equiv L_m - \int_{T_i}^{T_m} [c_w(T) - c_i(T)] dT$  using the heat capacity data of Fig. 1. The results are shown in the lower panel of Fig. 2 along with the entropic bound and two datasets. As expected,  $L' > T\Delta S$  in magnitude throughout the supercooled region.

The apparent agreement between  $L'$  and the *Smithsonian Meteorological Tables* (List 1951) is not particularly surprising; the values are based on reversible “tools” such as Kirchoff’s relation,  $dL/dT = \Delta c_p$ , which is satisfied by  $L'$  (see appendix A). More significant is the comparison of  $L'$  with the data from Bertolini et al. (1985), obtained from a direct calorimetric experiment. The data are within a few percent of  $L'$  and this closeness suggests the following questions: Are the thermodynamic state and entropy of actual ice very near the ones of the reversibly prepared ice? Why is the data mostly below the  $L'$  curve? The answer to the second question is that the “hurriedly” made irreversible ice has higher entropy; we shall examine this in detail in a later section. For now, we focus on the first question.

Why should  $L'$  be a reasonable estimate to actual freezing of supercooled droplets in the atmosphere? In other words, does the actual freezing mimic, in some way, the reversible path shown in the upper panel of Fig. 2? To that end, in the next section we shall consider heat transfer within the supercooled droplet because heat transfer and measurements of latent heat are inextricably intertwined. Seemingly simple questions such as “at what temperature is ice produced?” or “what is the temperature of ice/water interface?” are more subtle than would appear at a first glance.

#### 4. Heat transfer within a supercooled water droplet and a proposed picture of irreversible freezing

Consider a supercooled water droplet suspended in air at, say,  $-30^\circ\text{C}$ , and examine the phrase “droplet

freezes at  $-30^\circ\text{C}$ ” more closely. Does it mean that all of the droplet water freezes at  $-30^\circ\text{C}$ ? If not, at what temperature does a supercooled water droplet freeze? Let us separate the freezing event into the following main stages:

- 1) Nucleation occurs and the ice/water interface is created. (Whether the nucleation is homogeneous or heterogeneous is immaterial in this paper.)
- 2) The interface advances, accompanied by the release of latent heat of fusion. Temperature gradients are established within the droplet.
- 3) The entire droplet freezes, latent heat is conducted away into the surrounding atmosphere, and the newly created ice particle cools back down to the ambient temperature of  $-30^\circ\text{C}$ .

What is the fate of latent heat in this chain of events? Once the formation of a critical embryo initiates bulk freezing,  $\sim 10^{-20} \text{ J} \approx 0.06 \text{ eV}$  per molecule must be dissipated. If spent on the embryo molecules only (i.e., used to heat the newly created ice), a temperature increase of  $\Delta T = L_{\text{fusion}}/c_{\text{ice}} \approx 170 \text{ K}$  results! Hence, the latent heat must be conducted away immediately and raise the temperature of matter adjacent to the interface. The latent heat of fusion corresponds to a warm up of some  $80^\circ\text{C}$  for liquid water ( $\Delta T = L_{\text{fusion}}/c_{\text{water}} = 80 \text{ K}$ ), causing steep temperature gradients to develop. The temperature is highest at the advancing ice–water interface (source of heat). We argue, therefore, that the advancing interface is at the usual melting point and that the excess heat is conducted into the remaining supercooled water. In our picture, ice is always created at  $T_m$ , so the intrinsic latent heat released always equals  $L(T_m)$ . Our physical picture is illustrated schematically in Fig. 3. Despite spatial temperature gradients and regardless of supercooling magnitude, the actual freezing always occurs at the same (melting) temperature.

Thus, because of the continuous heat production within the droplet and the associated temperature gradients, there is no single temperature characterizing the droplet during the conversion of supercooled liquid water to ice. Yet, the temperature at which the liquid water is actually converted to ice and at which latent heat is released is the melting point,  $T_m$ . Therefore, ice is always created at the melting point, and the heat flux at any point of the advancing and possibly complicated (dendritic) ice–water interface is directed outward against the temperature gradients and from ice to supercooled water as schematically illustrated in Fig. 3.<sup>4</sup>

<sup>3</sup> Also note that at the moment of nucleation, the ice embryo is under higher pressure than is water because of the Laplace pressure. Hence, enthalpy difference is not quite appropriate as the two phases are under different pressures.

<sup>4</sup> This physical picture is further illustrated for the adiabatic stage in appendix C, along with a comparison to prior work.

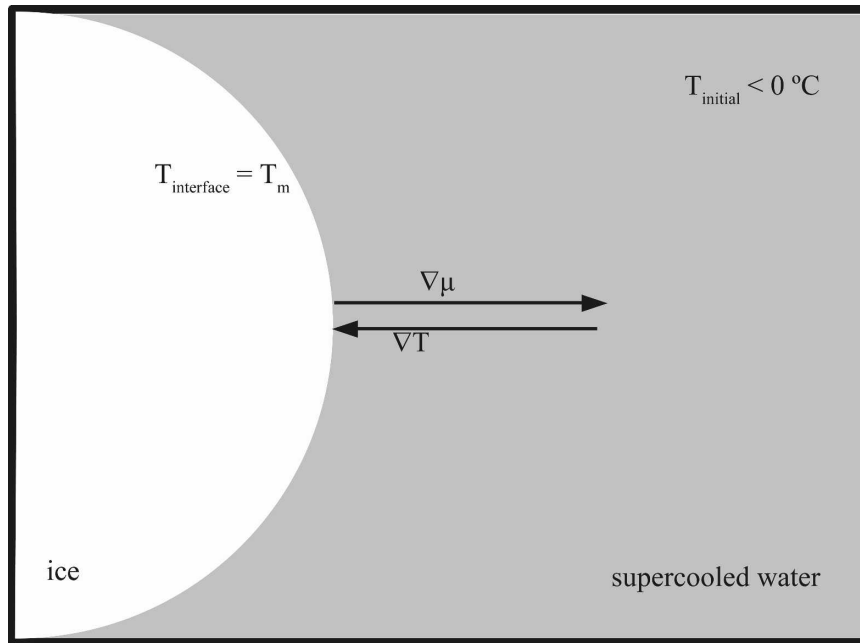


FIG. 3. Freezing of the supercooled water droplet: a schematic illustration of the proposed physical picture. Latent heat of fusion, liberated during the freezing, is conducted from the advancing interface into the supercooled water (heat flux to air is neglected at this stage; see appendix C). The advancing interface (source of heat) is at the melting point ( $T_m$ ) and a temperature gradient, normal to the interface, is setup throughout the aqueous part of the droplet. The corresponding gradient in the chemical potential is in the opposite direction ( $d\mu = -sdT, p = \text{const}$ ). Thus, the ice is always created at  $T_m$ , latent heat is always liberated at  $T_m$  and, at the advancing interface, the following boundary conditions hold:  $\mu_{\text{ice}} = \mu_{\text{water}}$  and  $T_{\text{ice}} = T_{\text{water}} = T_m$ . The water is warmed up in a thin “boundary layer” near the interface, one fluid filament at a time, so that the effective latent heat can be reasonably approximated by  $L'(T) \equiv L'(T_i) = L_m - \int_{T_i}^{T_m} [c_w(T) - c_i(T)] dT$  when the ambient air temperature remains constant at  $T_i$ . For the more general case of air temperature  $T_f$  at the end of freezing ( $T_i < T_f < T_m$ ), the effective latent heat expression we propose is  $L'_{\text{gen}}(T_i, T_f) = L_m - \int_{T_i}^{T_m} c_w(T) dT + \int_{T_f}^{T_m} c_{\text{ice}}(T) dT - \beta(\Delta T)^2$  (see text).

Each fluid element is continually warmed from  $T_i$  to  $T_m$ , reminiscent of the reversible path shown in the upper panel of Fig. 2. Can  $L'(T) = L_m - \int_{T_i}^{T_m} (c_w - c_i)(T) dT$  serve as a useful approximation for the heat exchanged between the droplet and the environment? To that end, we proceed to estimate the impact of irreversibility on the entropy budget.

The phase transition at  $T_m$  is reversible and does not generate *net total* entropy, but temperature gradients do. We estimate the magnitude of the contribution from heat conduction using an expression for entropy production  $\delta s_{\text{irr}} \approx s\tau$  from Zemansky (1981, p. 204); see, also, de Groot 1951; Prigogine 1955). Taking  $\tau$  as the droplet’s thermal relaxation time,  $\tau = d^2/\alpha$ , where  $d$  is the diameter of the droplet,  $\alpha$  is the thermal diffusivity of water,  $k/(\rho c_p)$ , and  $k$  is the thermal conductivity of water, the rate of entropy production  $s$  can be estimated as  $s = I_Q(\Delta T)/T^2$  (Zemansky 1981, p. 204), where  $I_Q$  is the heat “current.” Collecting the terms we

obtain for the irreversible entropy (area  $A \propto d^2$ ;  $I_Q \propto kA\nabla T$ ):

$$\delta s_{\text{irr}} \approx s\tau \sim kd^2 \left( \frac{\Delta T}{d} \right) \left( \frac{\Delta T}{T^2} \right) \left( \frac{d^2}{\alpha} \right) = (\rho c_p d^3) \left( \frac{\Delta T}{T} \right)^2. \quad (6)$$

Note that entropy and heat capacity have the same units and that the term  $\rho c_p d^3 = mc_p$  is for the entire system (droplet). To obtain a specific estimate, we normalize the result by the reversible entropy  $\delta s_{\text{rev}} = L/T_m$ , where  $L$  is the latent heat released by the entire droplet. We obtain

$$\frac{\delta s_{\text{irr}}}{\delta s_{\text{rev}}} \approx \left( \frac{c_p \Delta T}{l} \right) \left( \frac{\Delta T}{T_m} \right), \quad (7)$$

where  $l$  is the specific latent heat of fusion. The result suggests a very small correction at small supercooling (small gradients) but on the order of 10% at extreme

supercooling of  $\Delta T \approx 40$  K. The quadratic dependence on  $\Delta T$  can be tested in future experiments. The plausible conjecture that the “hurriedly” made irreversible ice has higher entropy than the reversible one is in excellent agreement with the data of Bertolini et al. (1985).<sup>5</sup> We therefore suggest the following simple expression for the effective latent heat to be used in practice:

$$\begin{aligned} L_p &= L_m - \int_{T_i}^{T_m} [c_w(T) - c_i(T)] dT - \beta(\Delta T)^2 \\ &\equiv L' - \beta(\Delta T)^2, \end{aligned} \quad (8)$$

with  $\beta = 0.3 \text{ J mol}^{-1} \text{ K}^{-2}$  being a result of a simple fit to data of Bertolini et al. (1985), subject to improvements by future experiments.

## 5. Implications at microscopic scales

In this section we examine the implications of our model from the molecular point of view. Insofar as a temperature can be assigned at every point within the drop [ $T = T(\mathbf{x}, t)$ ], local thermodynamic equilibrium (LTE) is implied (e.g., Pruppacher and Klett 1997; Landau and Lifshitz 1987) and “point” refers to a volume that is large compared with molecular dimensions, yet small compared with the characteristic length of temperature variation. In particular, this means that the ice–water interface is a geometric “line” that, nevertheless, spans many molecular layers.

The LTE assumption [frequently employed in solidification studies; see, e.g., the opening paragraph of Glicksman et al. (1994)] can also be justified kinetically if the conversion of liquid to ice is relatively rapid in comparison with the speed of the advancing interface (Ma 1985). According to Kurz and Fisher (1989, p. 134), LTE holds at a well-defined interface as long as the interface’s rate of advance does not exceed the diffusion rate across the interface. Setting  $a^2/D = a/u$ , where  $a$  is the thickness of the interface,  $D$  is the diffusion coefficient of water, and  $u$  is the critical interface speed, yields  $u \sim D/a$ . Taking a conservative estimate of  $a = 10^{-9}$  m and  $D = 1.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for water near the freezing point gives the critical speed  $u \approx 1.3 \text{ m s}^{-1}$ . This value is considerably larger than even the maximal measured ice–water interface speed of about  $20 \text{ cm s}^{-1}$  (Pruppacher and Klett 1997, p. 673), recorded in the very beginning of the semiadiabatic stage of freezing.

Because of the LTE, the chemical potentials of the two coexisting phases must be equal at the advancing interface. Therefore, the interface must be at  $T_m$  since that is the only temperature on the ice–water coexistence curve such that  $\mu_{\text{ice}} = \mu_{\text{liquid}}$  at atmospheric pressure. Thus, water freezes and ice is produced at  $T_m$ . Consequently, it is the supercooled water that is constantly being warmed (see appendix C).

These implications appear likely to cause resistance and it may be helpful to examine typical objections, encountered during numerous discussions with colleagues not only within the atmospheric sciences but also with physical chemists and materials scientists. Invariably, we are asked: If the chemical potentials are equal, why does the interface move? A slightly different phrasing is: What is the driving force for the advancement of the interface?

To that end, note that the equality of chemical potentials at the advancing interface does not imply equality throughout the drop. As described above, the chemical potentials cannot be spatially uniform while the droplet is freezing because the latent heat is released continuously at the boundary.

Spatial gradients in chemical potential are directed away from the interface while the temperature gradients are directed toward it. Thus, the interface advances because the driving force is the gradient in the chemical potential  $\nabla\mu$ .<sup>6</sup>

Also, note that our model does not contradict the idea of a jump in the chemical potential  $\Delta\mu$ , as long as one introduces a molecular jump distance  $a$  (e.g., Frenkel 1955) so that  $\Delta\mu \approx a\nabla\mu$ . In a similar manner we can resolve the controversy related to the question: What is the temperature of the interface? (See appendix D for further details.) Across  $a$ ,  $\Delta T \equiv a\nabla T$  for the temperature jump  $\Delta T$  across the interface. This is consistent with the experimental evidence (see appendix D), although the latter is somewhat ambiguous in that it is restricted to plane-parallel interfaces between ice and water (i.e., slow growth at modest supercooling) and relies heavily upon the assumed solution of the heat conduction equation. The experiments show that the interface temperature is within a few tenths of a degree of the melting point (see Hobbs 1974, 584–585 and references therein). Indeed, for  $a$  comparable to molecular dimensions,  $\Delta T = a\nabla T$  results in a small fraction of a degree for typical experiments (see appendix D for details).

<sup>5</sup> This is particularly because maximal deviations are on the order of 10% and Bertolini et al. (1985) were skeptical about the two points above the  $L'$  curve, associated with weak signals.

<sup>6</sup> This is somewhat analogous to diffusion problems, for example, where  $\nabla\mu$  “drives” the flux of matter. Also, in the Stokes–Einstein relation, the driving force ( $\nabla\mu$ ) balances the viscous force (friction), yielding constant “velocity,” that is, mobility.



## 6. Concluding remarks

Measurements of latent heat as a function of temperature in a supercooled domain are difficult and scarce. Beginning with the observation that supercooled water freezing cannot be a reversible process, we have reexamined the problem from an entropy-based perspective. We have suggested a simple approximate expression for the effective latent heat, based on a proposed reversible path between supercooled water at  $T_i$  and the resulting ice as well as an irreversibility correction, whose quadratic dependence on  $\Delta T$  can be tested in future experiments.

The proposed expression is  $L'(T_i) = L_m - \int_{T_i}^{T_m} [c_w(T) - c_i(T)] dT$  for the case of constant ambient temperature and the correction is  $-\beta(\Delta T)^2$ , with  $\beta = 0.3 \text{ J mol}^{-1} \text{ K}^{-2}$  based on the data of Bertolini et al. (1985). The expression for  $L'$  can be extended to an arbitrary final ambient temperature  $T_f$ , attained at the end of the freezing process ( $T_i < T_f < T_m$ ) as follows:

$$L'_{\text{gen}}(T_i, T_f) = L_m - \int_{T_i}^{T_m} c_w(T) dT + \int_{T_f}^{T_m} c_{\text{ice}}(T) dT - \beta \Delta T^2.$$

This expression can be used to solve for  $T_f$  when examining the heat budget of glaciating clouds. Also,  $L_p(T_i)$  can be inserted in the expression for nucleation rate, critical nucleus dimension, etc., with implications in nucleation theory.

The expression for  $L'$  led us to scrutinize the question “At what temperature does supercooled water freeze?” This led to a model of freezing in which ice, and therefore latent heat, is always produced at the melting point. Temperature gradients do, however, cause the irreversibility correction, which we interpret as “hurriedly made” ice with entropy somewhat higher than that of reversible ice. While the latter has an equilibrium concentration of defects at a given  $T$ , the former may have a higher concentration yet, at least for some time. This raises interesting questions about possible effects of metastable freezing on optical and mechanical properties of the resulting ice.

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## APPENDIX A

### Some Misconceptions in Thermodynamic Interpretation of Supercooled Water Measurements

Here we briefly examine prior work with an emphasis on the importance of irreversibility. In particular, what assumptions are likely responsible for the rather low latent heat values reported in Fukuta and Gramada (2003)? In our opinion, the vapor measurements for supercooled water reported in Fukuta and Gramada (2003) are accurate, but getting from the measured vapor pressure data to latent and specific heats involves three doubtful steps (see Fukuta and Gramada 2003, p. 1873). These steps are by no means unique to Fukuta and Gramada but originate much earlier (e.g., see McDonald 1953) and are common in the literature (e.g., Pruppacher 1995). We shall discuss each of the three briefly.

Given the vapor pressure of water as a function of temperature (below the melting point), it is tempting to use the equality  $L_s = L_f + L_v$  ( $L_s$  denotes the latent heat of sublimation;  $L_v$  denotes the latent heat of vaporization) to deduce the latent heat of fusion ( $L_f$ ) as a function of temperature at a fixed pressure. However, this step can be taken only when all three phase transitions may be accomplished reversibly—a requirement fulfilled only at the triple point. Then and only then, substituting  $L = T\Delta S$  for all three latent heats yields an identity  $S_{\text{vapor}} - S_{\text{ice}} = (S_{\text{water}} - S_{\text{ice}}) + (S_{\text{vapor}} - S_{\text{water}}) = S_{\text{vapor}} - S_{\text{ice}}$ . However, as discussed above,  $L_f$  does not equal  $T\Delta S$  because the phase transition from supercooled water to ice is not a reversible one.<sup>A1</sup>

The remaining two difficulties both involve the use of the Kirchhoff relation, used often in the atmospheric science literature (e.g., McDonald 1953, p. 423; Prup-

<sup>A1</sup> Much of the literature including atmospheric physics texts is quite misleading on this point. For example, Fleagle and Businger (1980, p. 113) write, “It follows from the conservation of energy that at the triple point  $L_s = L_f + L_v$ .” While the statement is correct, the reason given is not because the requirement of reversibility is ignored. See Tsonis (2002, p. 88 versus p. 167) as well: Table A.3 implies reversibility for the supercooled state.

pacher 1995, p. 1928). At first sight, the relation suggests an alternative to a direct measurement of the latent heat as a function of temperature along the following lines: deduce  $L_f$  at one point on the phase boundary, and then use the difference in the heat capacities of the liquid and solid to calculate further values through the Kirchhoff relation

$$\frac{dL}{dT} = \Delta c_p. \quad (\text{A1})$$

There are several difficulties: The approximation leading to the Kirchhoff relation as stated above is valid only for sublimation or evaporation; see Denbigh (1966, 200–201) or Iribarne and Godson (1981, p. 28, 69). Most importantly, the Kirchhoff relation describes the variation of the reversible latent heat along the phase boundary but not the variation of the latent heat of a metastable phase at a fixed pressure as a function of temperature. Note that differentiating the reversible approximation

$$L'(T_i) = L_m - \int_{T_i}^{T_m} [c_w(T) - c_i(T)] dT$$

w.r.t. to  $T_i$  and using the fundamental theorem of calculus results in the Kirchhoff relation.

Irreversibility renders all measurements, for example, vapor pressure of supercooled water, fundamentally stochastic because spontaneous freezing during the measurement is always a possibility. For illustration, consider “slow, quasi-steady reversible” warming of supercooled water. Slow warming implies that the duration of the experiment  $t_{\text{expt}}$  must be much longer than the thermal relaxation time  $\tau_{\text{relax}} \approx d^2/\alpha$ , where  $d$  is the droplet diameter and  $\alpha$  is the thermal diffusivity, which is on the order of  $10^{-3} \text{ cm}^2 \text{ s}^{-1}$  for water. On the other hand, for a given degree of supercooling  $\Delta T$ , the nucleation rate  $J(\Delta T)$  yields an average lifetime of a supercooled droplet  $t = (JV)^{-1} \propto (Jd^3)^{-1}$ . Thus, experiments must satisfy the condition  $d^2/\alpha \ll t_{\text{expt}} \ll (Jd^3)^{-1}$ . When  $d^2/\alpha = (Jd^3)^{-1}$ , reversible warming is not possible for  $d_{\text{cr}} \sim (\alpha/J)^{0.2}$ , yielding  $d < 100 \text{ }\mu\text{m}$  for the nucleation rate of  $10^8 \text{ cm}^{-3} \text{ s}^{-1}$ , corresponding to  $\Delta T \approx 36.5 \text{ K}$ .

## APPENDIX B

### Thermodynamic Equivalence on the $TS$ Diagram

In section 3 we argued that the two paths on Fig. 2 are not thermodynamically equivalent for two reasons. First, the “vertical drop” is not really a path as it does not consist of a succession of thermodynamic equilibrium states. The actual transition is not quasi static, and

does not result in the same final state of ice as that for a reversible transition. The purpose of this appendix is to elaborate on the fact that the  $S$  versus  $T$  plot does not provide enough information to fully specify the thermodynamic state of ice.

Indeed, the final thermodynamic state of ice is not determined entirely by the final volume and the (atmospheric) pressure, but also by stress components [Landau and Lifshitz (1959, section 3), thermodynamics of deformation equations (3.2) and (3.2a); see also Frederick and Chang (1965, p. 129)]. Therefore, once some ice is present in the droplet, the differential work element is no longer given by  $PdV$  (valid only for hydrostatic systems) but, rather, by  $\sigma_{ik}du_{ik}$  (stress and strain tensors, respectively) and reduces to the hydrostatic expression only for the special case of uniform compression. This means that freezing the same mass of supercooled liquid water may result in slightly different states (e.g., volumes), depending on the degree of supercooling. This could result, for example, from defects and dislocations in the ice structure produced by rapid dendritic growth. Thus, the final “state” is path dependent, though the ice may eventually anneal, approaching the minimum of the free energy. Conversely, the same value of entropy on the  $S$  versus  $T$  plot may correspond to different final volumes, depending on supercooling.

## APPENDIX C

### The Adiabatic Case and Complete Freezing

The heat conduction coefficient ( $k$ ) for air is much smaller than that of water, so the heat flux ( $\propto k\nabla T$ ) to air is weak compared to that from ice to water. Hence, most of the released latent heat remains within the droplet during this initial semiadiabatic stage (see e.g., Pruppacher and Klett 1997, p. 674). Pruppacher and Klett (1997) write the energy balance as follows [Eqs. (16)–(18) on p. 674]:

$$Lm_i = (m_i c_i + m_w c_w) \Delta T, \quad (\text{C1})$$

where  $\Delta T = T_m - T_{\text{initial}}$  and  $m_i$  and  $m_w$  denote masses of the ice and water fractions, respectively. This equation implies that heat released during freezing is spent on warming both the water and ice. In contrast, there is no warming of ice in our picture. Yet, the energy budget depends on the physical picture of supercooled water freezing.

We maintain that there is always a temperature gradient within the drop as it freezes because the advancing ice–water interface is maintained at the melting point. Consequently, the latent heat is spent on warm-

ing water since all ice is created at the melting point. This is expressed as

$$mxL = mx \int_{T_i}^{T_m} c_w(T) dT + m(1-x) \int_{T_i}^{T_m} c_w(T) dT, \quad (C2)$$

where  $m$  is the mass of the droplet and  $x$  is the fraction frozen. The first term in the rhs of this equation corresponds to warming water that eventually froze, while the second corresponds to water that warmed to the melting point but did not freeze. The lhs represents total heat released: all spent on warming the water as the rhs amounts to  $m \int_{T_i}^{T_m} c_w(T) dT$ .<sup>C1</sup> For the limit of complete adiabatic freezing,  $x = 1$ , yielding

$$L = \int_{T_{\text{initial}}}^{T_m} c_w(T) dT. \quad (C3)$$

In words, the total latent heat released during freezing ( $Q = Lm_{\text{ice}}$ ) is spent on warming all of the supercooled water from the initial temperature up to the melting point [ $Q = m_{\text{water}} \int_{T_{\text{initial}}}^{T_m} c_w(T) dT$ ], where mass conservation and the complete freezing condition  $m_{\text{ice}} = m_{\text{water}}$  was used.

For illustration, let us consider the degree of supercooling, required for complete freezing and take, for simplicity,  $c_i$  and  $c_w$  as constants (with values at the melting point). Then Eq. (C1) yields  $\Delta T = L/c_i = 170$  K, completely (and somewhat surprisingly) eliminating the heat capacity of water from consideration. On the other hand, Eq. (C3) reduces to  $\Delta T = L/c_w = 80$  K, rendering the heat capacity of ice irrelevant.<sup>C2</sup>

## APPENDIX D

### Conflicting Opinions in the Literature Concerning Temperature of the Crystallization Front: Proposed Resolution

What is the temperature of the ice–water interface? The perceived importance of the latter question is such that it reached semipopular literature. For example, Knight (1967, p. 63) writes, “Interface temperature emerges as the most important parameter in crystal

growth from pure melts. . . The difficulty of determining interface temperature is one of the major frustrations. . .” Consulting the literature on this issue reveals a surprising diversity of often contradictory opinions. Some state that the temperature of the interface separating the growing crystal from its melt is the normal melting point (Frenkel 1955; Tamman 1925; Glicksman et al. 1994), while others insist that the interface must be at a temperature below the normal melting point, though no one specifies just what that temperature is (Hallett 1964; Macklin and Payne 1967, 1968; Prupacher and Klett 1997; Frenkel 1955).

Those in the lower-than-melting-point camp make statements exemplified by “The condition for freezing, however, is that the interface temperature should be equal to, or slightly lower than, the thermodynamic freezing point. It follows that the liquid just ahead of the interface must have a still lower temperature. . .” [Cottrell (1955, p. 210); see also Chalmers (1959, p. 232)]. On the other hand, Haasen (1978, p. 59) states “it can be assumed that the temperature of the interface is always  $T_m$ ,” and Porter and Easterling (1981, p. 205) concur, stating “solid/liquid interface remains isothermal at essentially  $T_m$ .”

Curiously, Frenkel (1945, 1955) is cited by both camps. In the Russian edition of his classical monograph, *Kinetic Theory of Liquids*, he states (p. 375, translation by ABK) “. . . because of the release of the latent heat of crystallization, the temperature near the crystal–solution boundary remains at a steady level, corresponding to the usual melting point.” However, the English translation, appearing only a year later, states (Frenkel 1955, p. 417) “the temperature near the boundary surface between the liquid and the crystal is raised, owing to the evolution of the latent heat of crystallization, being determined by the rate of flow of heat away from this surface.” We have been unable to establish whether Frenkel changed his mind or whether the translators, Sir Neville Mott and R. S. Sack, “corrected the error.”

Because the ice–water interface moves slowly (see section 5), the conflicting opinions may be reconciled via the relation  $\Delta T = l \nabla T$ , connecting the microscopic and macroscopic descriptions. To estimate the temperature gradient, consider heat conduction limited advancement of the ice–water interface. The scaling is  $u \propto \Delta T / \Delta l$ , where  $u$  is the interface speed and  $\Delta T$  is the temperature gradient between the ice and supercooled liquid over the distance  $\Delta l$ . More precisely, the heat loss from an area  $A$  is  $kA \nabla T$ . The heat supply is  $dQ/dt = A \rho L_{\text{fusion}} u$ . Steady state yields  $\nabla T = \rho L_{\text{fusion}}^{-1} u$ .

Inserting values for the density of water,  $k = 0.6$  W m K<sup>-1</sup> and  $L_{\text{fusion}} = 0.33 \times 10^6$  J kg<sup>-1</sup> and using ob-

<sup>C1</sup> There is a possibility that a solid crystalline mass at a temperature  $T_f < T_m$  is a net result of isenthalpic solidification as was observed by Glicksman and Schaefer (1966) for deeply supercooled phosphorus. Gentler supercooling did result in a phosphorus “slush” similar to freezing of supercooled water.

<sup>C2</sup> A similar difference of opinion occurred in the literature of physical metallurgy and solidification. See, for example, Glicksman and Schaefer (1966, p. 2368).

served interface speeds in the range of 1–10 cm s<sup>-1</sup> (Pruppacher and Klett 1997, p. 669) gives the range of  $\nabla T \approx 5\text{--}50 \text{ K } \mu\text{m}^{-1}$ . This should be considered an upper bound as forced convection, caused by the movement of dendrites, is likely to soften the gradients.<sup>D1</sup> Another simple estimate of  $\nabla T$  is to take supercooling of, say, 30° and divide it by 3  $\mu\text{m}$  (representing distance from a random nucleation site to the cloud-droplet surface). This still results in 10 K  $\mu\text{m}^{-1}$ , so the two estimates are not far apart. Setting the “molecular jump length” to 10 Å yields the temperature difference across the “interface” of about 0.02°C. This is in agreement with a “fraction of a degree” often reported in the literature (Pruppacher and Klett 1997, p. 673), especially if the “jump length” is increased to mimic the conditions of the various experiments.<sup>D2</sup>

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<sup>D1</sup> Natural convection is not likely to occur. The Rayleigh number, the ratio of convection-causing buoyancy to resistance by diffusion and viscosity, is on the order of 10<sup>-5</sup> for a 10- $\mu\text{m}$  droplet.

<sup>D2</sup> The argument can also be used in reverse, to justify the heat transfer limited regime by observation of interface speed on the order of several centimeters per second.