

Entropic Aspects of Supercooled Droplet Freezing*

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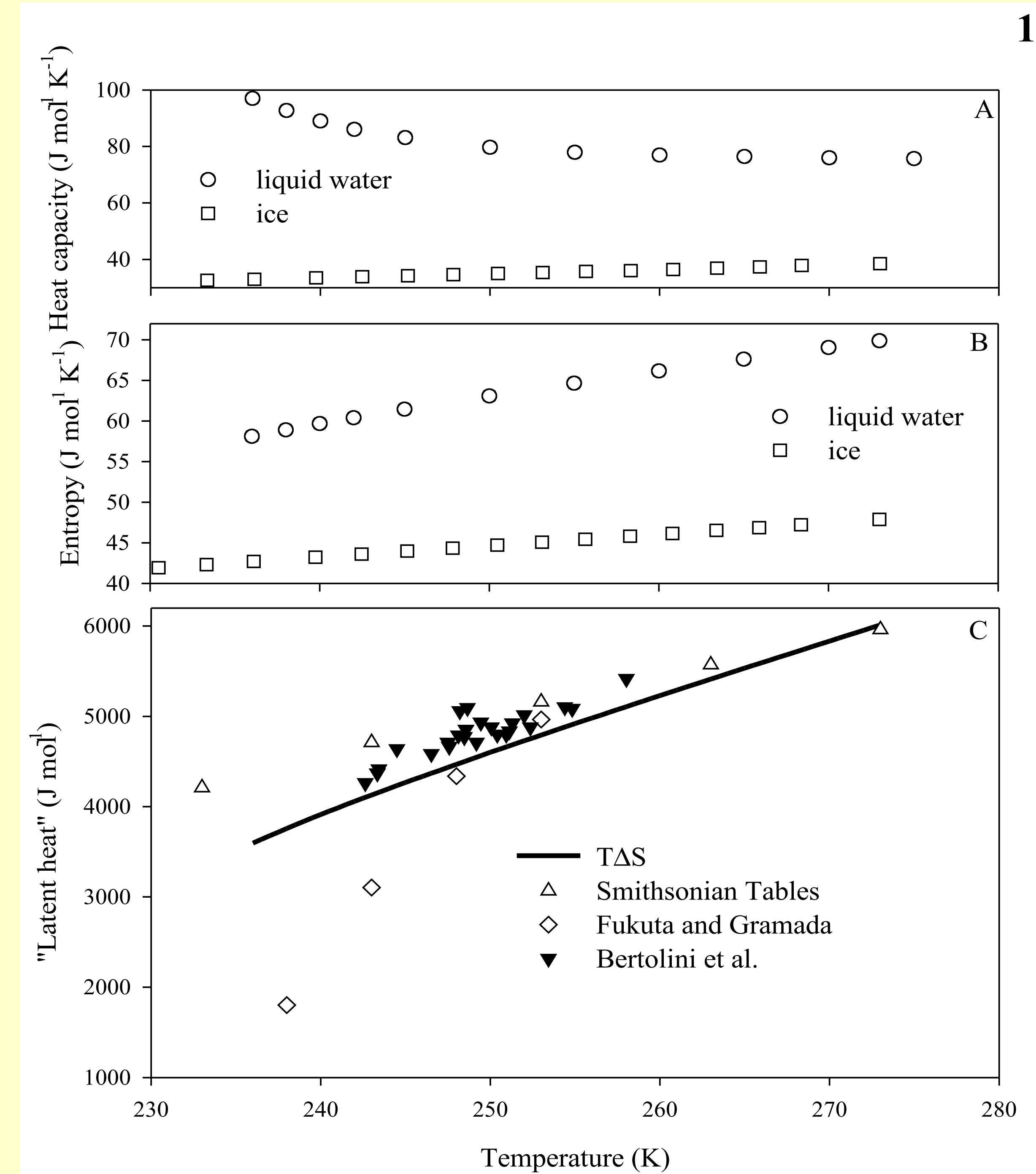
The main idea: Supercooled water is a metastable state and, therefore, the associated phase transition must be irreversible.

We estimate a lower bound on the amount of latent heat liberated by freezing droplets. Based on a physical picture of the freezing process, we arrive at an estimate for the effective latent heat (calculated along a reversible path), suitable for heat budget calculations of glaciating clouds. In addition, we arrive at a quadratic dependence on supercooling for the irreversible contribution to heat exchange during the freezing process. The proportionality factor is estimated as $-0.3 \text{ J mol}^{-1} \text{ K}^{-2}$.

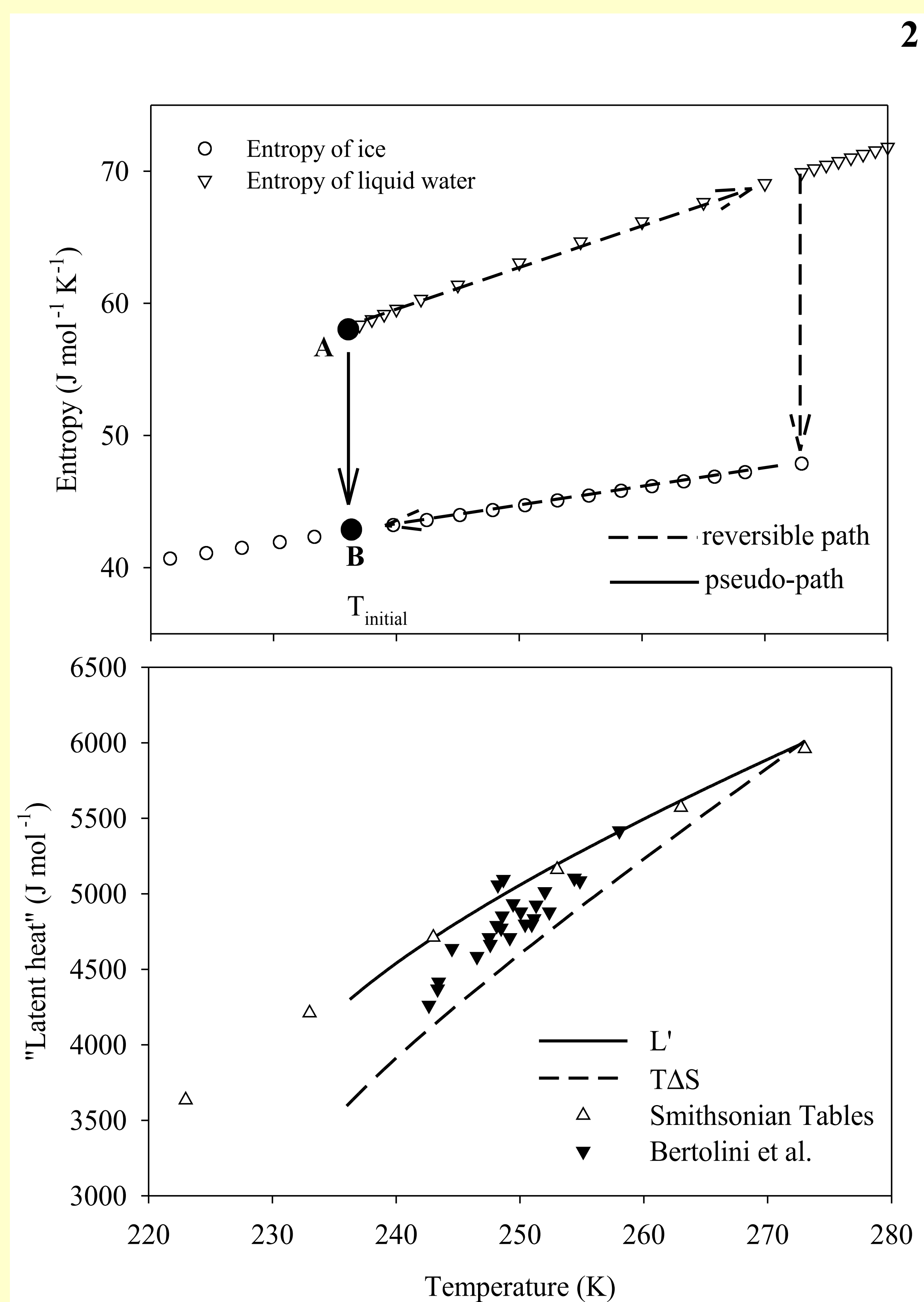
Does the irreversibility associated with the freezing of supercooled water constrain the data?

$dS_{\text{system}} \geq \frac{dQ}{T}$ In the case of freezing, $dS_{\text{system}} < 0$ ($S_{\text{ice}} < S_{\text{water}}$ for any given T) and $dQ = L(T) < 0$.

Thus: $|L(T)| \geq |T\Delta S|$. In other words, between two specified states (e.g. supercooled water at some p, T and ice at the same p, T), the latent heat released by the freezing water must exceed $T\Delta S$. Caveat: specifying p and T does not fully specify the thermodynamic state of a solid. (See below)



Chain of reasoning leading to an estimate of the lower bound for the amount of latent heat released at a given temperature T . **Panel 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). **Panel B:** The results of our calculations for entropy of supercooled water vs temperature via $S(T) = S(T_m) - \int_{T_m}^T c(T)/T' dT'$, where $S(T_m)$ is the entropy at the melting point, c denotes the heat capacity of water or ice, taken from panel A, and the limits of the integral run from the melting point to the temperature, T . **Panel C:** Values of the latent heat of fusion from the Smithsonian Meteorological Tables (1951), Fukuta and Gramada (2003), and Bertolini et al. (1985) as well as $L = T\Delta S$, with ΔS as input from panel B.



An approximation to the effective latent heat of freezing

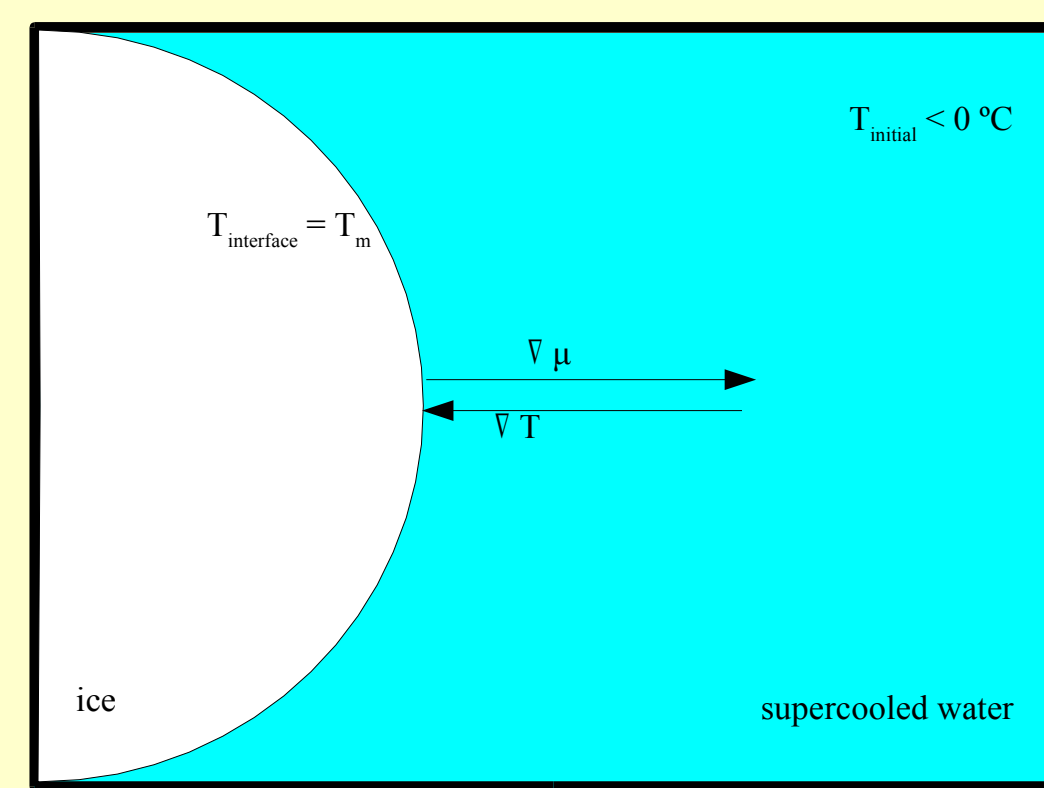
While supercooled water droplets do not freeze slowly and reversibly in the atmosphere, this need not prevent one from finding a physically realizable reversible path that links the same initial and final states. Given that energy and entropy are state functions (see caveat below), such a path can be used to calculate heat exchange between droplets and the atmosphere, thereby establishing an expression for effective latent heat of supercooled water vs. temperature. The enthalpy difference is: $L' = L_m - \int [c_{\text{water}}(T) - c_{\text{ice}}(T)] dT$ and involves only the reversible latent heat at the melting point, L_m , and specific heat data for supercooled water and ice. The path described here corresponds to the dashed line in the upper panel of Figure 2 (bottom left). Note that the path corresponding to the solid line (vertical drop) is not a succession of equilibrium states.

Caveat: There is an implicit assumption that the final state of ice is the same for reversible and irreversible changes. Pressure and temperature do not fully determine the thermodynamic state of ice. The final volume, strain, and stress enter. See discussion of irreversibility below.

L' is compared to available data in Figure 2. As expected, L' exceeds $T\Delta S$ everywhere except at the melting point. The apparent agreement between the Smithsonian Tables and L' is not surprising since values in the Smithsonian Tables are based on "reversible" tools like the triple point identity and Kirchoff's relation, $dL/dT = c_{p,\text{water}} - c_{p,\text{ice}}$. (Note that L' satisfies the relation at constant pressure.) More significant is the comparison of L' with the data from Bertolini et al., obtained from a direct calorimetric experiment. The data suggest the following questions:

Are the thermodynamic state and entropy of actual ice nearly those of the reversibly prepared ice?

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 Figure 2? Consider heat transfer within the supercooled droplet.



Freezing of supercooled water droplet:

A schematic illustration of the proposed physical picture. Latent heat of fusion, liberated during the superfreezing, is conducted from the advancing interface into the supercooled water (heat flux to air is neglected at this stage). The advancing interface (source of heat) is at the melting point, T_m , and a temperature gradient, normal to the interface, is set up throughout the aqueous part of the droplet. The corresponding gradient in the chemical potential is in the opposite direction. 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 $L'(T) = L_m - \int [c_{\text{water}}(T) - c_{\text{ice}}(T)] dT$ when the ambient air temperature remains constant. For the more general case of air temperature T_f at the end of freezing, ($T_{\text{initial}} < T_f < T_m$), the effective latent heat expression we propose is:

$$L'_{\text{general}}(T_{\text{initial}}, T_f) = L_m - \int_{T_{\text{initial}}}^{T_m} c_{\text{water}}(T) dT + \int_{T_f}^{T_m} c_{\text{ice}}(T) dT - \beta(\Delta T)^2$$

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 outwards against the temperature gradients and from ice to supercooled water.

Why is the calorimetric data mostly below L' ? Answer: Irreversibly made ice has a higher entropy

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, δs_{irr} , as the production of the relevant relaxation time and entropy production. This results in:

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

where k is the thermal conductivity of water, d is the diameter of the droplet, α is the thermal diffusivity of water, ρ is the density of water, and c_p is the heat capacity (of the liquid).

To obtain an estimate in a non-dimensional form, we normalize by the reversible entropy, $\delta S_{\text{rev}} = L/T_m$,

where L is the latent heat released by the entire drop. Then: $\frac{\delta s_{\text{irr}}}{\delta S_{\text{rev}}} = \left(\frac{c_p \Delta T}{l} \right) \left(\frac{\Delta T}{T_m} \right)$ where l is the specific latent heat of fusion. For an extreme supercooling of $\sim 40 \text{ K}$, the correction would be a few percent.

Our conjecture that "hurriedly" made ice has a higher entropy (and therefore releases less latent heat) is in agreement with Bertolini et al.'s data, which is consistently below L' . Note that the magnitude of the discrepancy between their data and L' increases with supercooling.

Concluding remarks

- Reversible tools such as $L = T\Delta S$, the triple point identity, Kirchoff's rule, and even the Clapeyron equation must be applied with caution to phase transitions involving metastable phases.
- The proposed model predicts that the ice-water interface is at the normal melting point - i.e. at atmospheric pressure, ice is always created at 0°C .
- The effective latent heat is then: $L'(T) = L_m - \int [c_{\text{water}}(T) - c_{\text{ice}}(T)] dT$. The effective heat exchange between droplets in a glaciating cloud and the atmosphere can be approximated using L'_{general} (given above). (See Kostinski and Cantrell for an approximation of β .)
- The irreversibility correction is quadratic in supercooling. (We are attempting to confirm this experimentally.)
- While the effect of irreversibility on the latent heat is likely to be (only) a few percent, the implications for the structural and optical properties may be profound. For instance, recall that configurational entropy, $S \sim \ln(M)$, where M is the number of defects. Thus, the number of defects in irreversibly made ice may depend exponentially on supercooling.

* See A. Kostinski and W. Cantrell, Entropic aspects of supercooled droplet freezing. *J. Atmos. Sci.*, in press. See also Cantrell et al., Measurements of the vapor pressure of supercooled water using infrared spectroscopy. *J. Atmos. Oceanic Technol.*, in press.

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References

- Angell, C., M. Oguni, and W. Sichina, 1982: Heat-capacity of water at extremes of supercooling and superheating. *J. Phys. Chem.*, **86**, 998-1002.
 Archer, D. and R. Carter, 2000: Thermodynamic properties of NaCl + H₂O system. 4. Heat capacities of H₂O and NaCl(aq) in cold-stable and supercooled states. *J. Phys. Chem. B*, **104**, 8563-8584.
 Bertolini, D., M. Cassettari, and G. Salvetti, 1985: Anomalies in the "latent heat" of solidification of supercooled water. *Chem. Phys. Lett.*, **119**, 553-555.
 Fukuta, N. and C. Gramada, 2003: Vapor pressure measurement of supercooled water. *J. Atmos. Sci.*, **60**, 1871-1875.
 Haida, O., T. Matsuo, H. Suga, and S. Seki, 1974: Calorimetric study of the glassy state X. enthalpy relaxation at the glass-transition temperature of hexagonal ice. *J. Chem. Thermodynamics*, **6**, 815-825.
 List, R., ed., 1951: Smithsonian Meteorological Tables. Smithsonian Institution, 6th edition, 527 pp.

Figure Caption

An approach to a reversible approximation for the effective latent heat of supercooled water. **Upper panel:** 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_{initial} ". 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. **Lower panel:** $L'(T) = L_m - \int [c_{\text{water}}(T) - c_{\text{ice}}(T)] dT$ is computed using the heat capacity data of panel A of Figure 1 and the results are compared to data and to $T\Delta S$. L_m is the latent heat of melting at the normal melting point, and the limits on the integral run from the initial temperature to the melting point.