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

In the case of freezing, $dS_{\text{f}} = 0$. (Given any T and p), and $dQ = L(T) \, dT$.

Thus: $L(T) \geq \text{TAS}$. 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 TAS. Cautions: specifying p and T does not fully specify the thermodynamic state of a solid. (See below)

$\int_{T_0}^{T_1} L(T) \, dT$ is the amount of latent heat required for a transformation from the initial temperature to the melting point. $L'$ is an estimate of the effective latent heat of freezing assuming that the rate of heat exchange during the freezing process is negligible.

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 for the conversion of supercooled liquid water to ice.

A schematic illustration of the proposed physical picture. Latent heat of fusion is always created at 0 ºC. 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 for the conversion of supercooled liquid water to ice.

$p$ and $T$ do not fully specify the thermodynamic state of a solid. (See below)


**References**


Kostinski and Cantrell for an approximation of $\beta$.

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 TAS 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" tests like the triple point and Kirchoff's relation, $\Delta L(T) = \int_{T_0}^{T_1} c_p \, dT$. When the ambient temperature remains constant. For the most general case of air temperature $T_2$, at the end of freezing, $T_m \rightarrow T_2$, the effective latent heat expression we propose is:

$\int_{T_0}^{T_2} L(T) \, dT = \int_{T_0}^{T_2} c_p \, dT \delta L(T)$

where $L$ is the latent heat released by the entire drop. Thus: $\int_{T_0}^{T_2} L(T) \, dT = \int_{T_0}^{T_2} c_p \, dT \delta L(T)$

The effective latent heat is then: $L'(T) = L - \int_{T_0}^{T_2} c_p \, dT \delta L(T)$

The effective heat exchange between droplets in a glaciating cloud and the atmosphere can be approximated using $L_{\text{pseudopath}}$ (given above). (See Kostinski and Cantrell for an approximation of $\beta$.) 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, $S^c$, and $L$ are the number of defects, the former need not depend exponentially on supercooling.

An approximation 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 TAS". The reversible path consists of warming the supercooled water slowly to the melting point of supercooled equilibrium states, with the subsequent phase transition at the melting point.

$\delta L(T)$ 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.

Lower panel: $L_{\text{pseudopath}} = \int_{T_0}^{T_2} c_p(T) \, dT$ is computed using the heat capacity data of panel A of Figure 1 and the results are compared to data and to TAS. $L_{\text{p}}$ 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.

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 TAS". The reversible path consists of warming the supercooled water slowly to the melting point of supercooled equilibrium states, with the subsequent phase transition at the melting point. The resulting ice is then cooled to the initial temperature.

Lower panel: $L_{\text{pseudopath}} = \int_{T_0}^{T_2} c_p(T) \, dT$ is computed using the heat capacity data of panel A of Figure 1 and the results are compared to data and to TAS. $L_{\text{p}}$ 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.