

Latent heat of freezing in glaciating clouds

A. Kostinski and W. Cantrell

Michigan Technological University

Question: Does the fact that a supercooled droplet suspended in air freezes at $-20\text{ }^\circ\text{C}$ imply that latent heat is released at the same temperature? Our answer is **No**.

Question: What does it mean in those circumstances to say, “a droplet freezes at $-20\text{ }^\circ\text{C}$.”?

Answer: Freezing of a droplet can be separated into the following sequence of events:

- > Nucleation
- > Conversion of liquid water to ice, release of latent heat establishing temperature gradients within the droplet
- > Entire droplet frozen, cooling back to environmental temperature

Question: What is the temperature of the droplet?

Answer: Initial and final temperatures can be defined and are uniform at $-20\text{ }^\circ\text{C}$.

Intermediate stages are characterized by strong temperature gradients so no single temperature characterizes the droplet.

The importance of gradients has been overlooked in the literature to date. Gradients exist because latent heat is released at the advancing ice-water interface. *Therefore, the interface must be the hottest point in the system* (e.g. local application of the Dirichlet maximum principle).

Question: What happens to the latent heat of nucleation?

Answer: Latent heat is approximately 10^{-20} J per molecule ($10^{-20}\text{ J} \sim 3kT \sim 0.06\text{ eV}$) or $(170\text{K})c_i \sim (80\text{K})c_w$ [c_i = heat capacity of ice; c_w = heat capacity of water.]

No heat has been exchanged with the environment. The newly created ice is not superheated. Some latent heat goes to warm ice to the melting point and the excess energy goes into warming the surrounding liquid. (See Fig. 2)

Question: What are the conditions at an advancing ice-water interface?

Answer: Measured rates of growth are slow compared to molecular time scales and therefore, the interface is in local thermodynamic equilibrium.

Question: What does local thermodynamic equilibrium imply?

Answer: The equality of chemical potentials at the advancing interface, $\mu_{\text{ice}} = \mu_{\text{water}}$.

Question: Why does freezing proceed if $\mu_{\text{ice}} = \mu_{\text{water}}$ at the interface?

Answer: The gradient in chemical potential is the “driving force” for the advancing interface just as gradient in temperature is the “driving force” for heat flux or concentration gradient drives mass flux.

(see Figure 2: next column)

Motivation: How much latent heat (due to freezing) is released to the atmosphere by glaciating clouds?

6012 J mol^{-1} , or $L(T=273\text{ K})$. This is contrary to the current view in the field as illustrated in Figure 1. The discrepancy in heat released to the atmosphere can be as high as 30%.

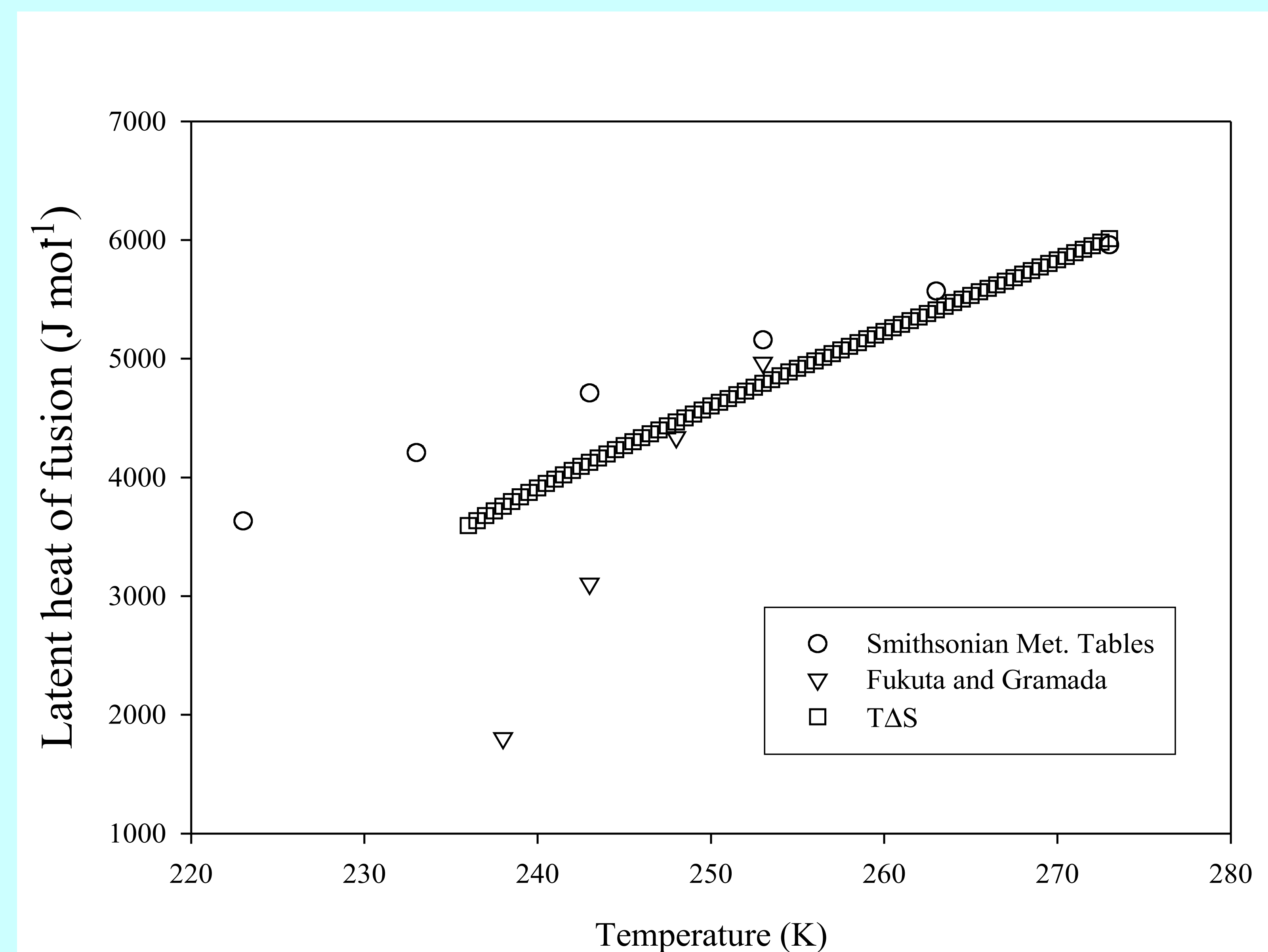


Figure 1. “Latent heat of fusion” for supercooled water as a function of temperature. Both the Smithsonian Meteorological Tables and Fukuta and Gramada (2003) use the vapor pressure of liquid water, in conjunction with the Clausius-Clapeyron Equation, to derive a value for L_f . (Values of the vapor pressure are extrapolated from above the melting point in the case of the Meteorological Tables. Fukuta and Gramada’s vapor pressures are measured.) Our computed points, labeled TAS, are derived from the entropies of liquid water and ice, which in turn are calculated via:

$$S(T) = \int_{T_0}^T \frac{c_p(T)dT}{T}$$

where $S(T)$ is the entropy of ice or water and $c_p(T)$ is the measured heat capacity. (We question the validity of all three curves for $T < T_m$, since latent heat is defined only for a reversible process.)

Question: What is the temperature of the interface?

Answer: The melting point, T_m . The heat source (*i.e.* release of latent heat at the advancing interface) is the hottest point in the system and the temperature there is mandated by the equality of the chemical potentials. Ice is always created at the melting point.

Compare our answers to the previous two questions with Pruppacher and Klett “...nor is it (the interface) exactly the equilibrium temperature... or there would be no driving force for freezing.”

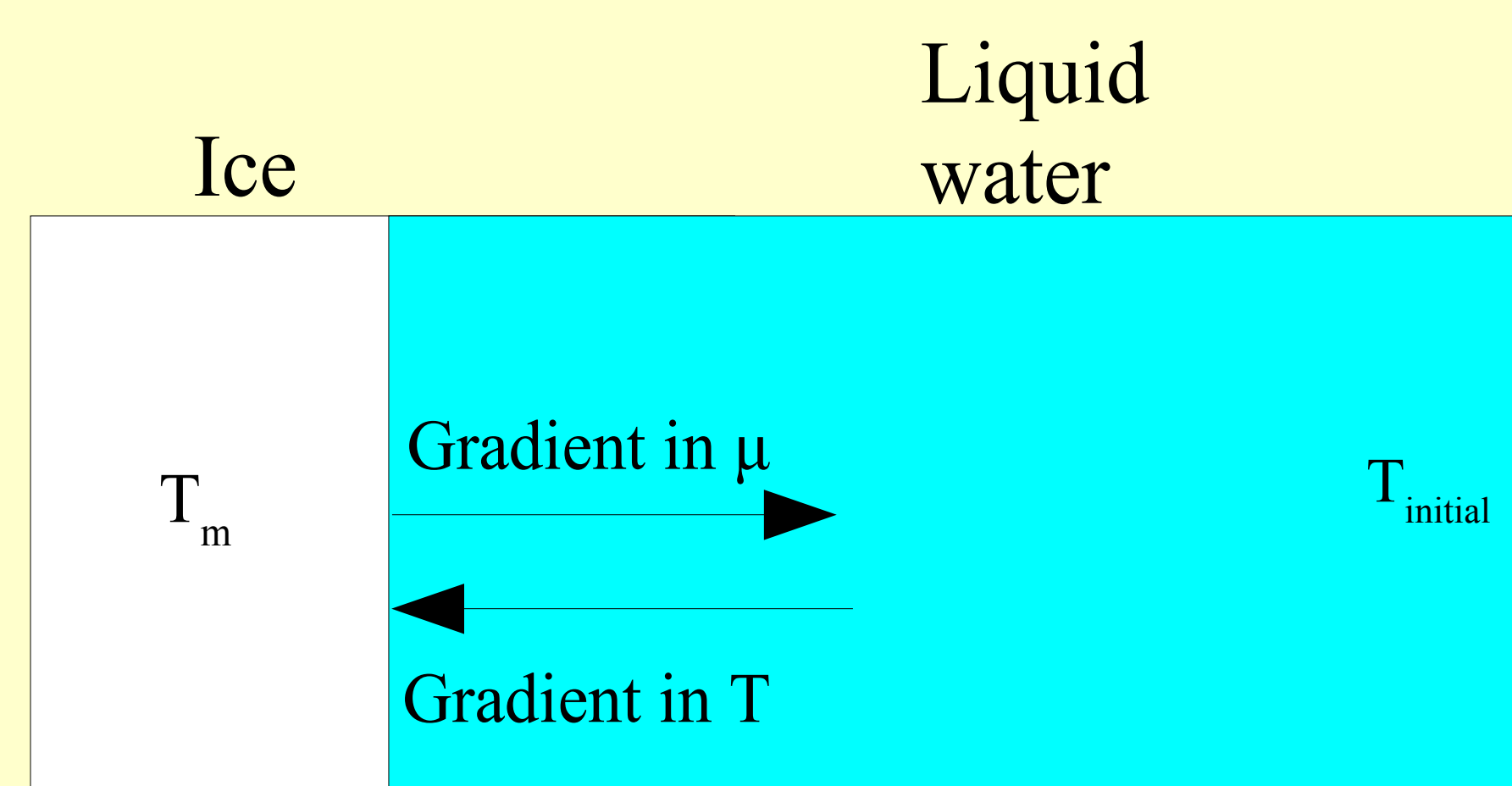


Figure 2. Schematic of the ice-water interface. The boundary conditions at the interface are $\mu_{\text{ice}} = \mu_{\text{water}}$ and $T_{\text{ice}} = T_{\text{water}} = T_m$.

A thought experiment – Adiabatic freezing

A supercooled droplet at initial temperature T_i freezes without exchanging heat with the environment. The final temperature must be T_m , the melting point.

Heat balance:

Latent heat of freezing always goes into warming liquid water since ice is created at $0\text{ }^\circ\text{C}$ in our picture.

$$mxL = m(1-x)c_w\Delta T + mx c_w\Delta T = mc_w\Delta T$$

m = mass of system, x = fraction frozen, $\Delta T = T_m - T_i$

In words, latent heat is spent warming all of the water to the melting point. Complete adiabatic freezing can occur when the latent heat released exactly balances the energy needed to warm water to the melting point. The supercooling required in that case is:

$$\Delta T = \frac{L}{c_w} \approx 80\text{ K}$$

Contrast this result with the conventional formulation (P&K):

$$Lm_i = \Delta T(c_i m_i + c_w m_w)$$

m_i = mass of ice, c_i = heat capacity of ice, etc...

Note that latent heat is expended on warming the liquid water *and* ice at every stage of the process in contrast to our model where only water is warmed because ice is created at the melting point..

Complete adiabatic freezing occurs when $m_w = 0$ or for an initial supercooling of:

$$\Delta T = \frac{L}{c_i} \approx 170\text{ K}$$

Note that this expression has no memory of the properties of liquid water.

Conclusion: In our model ice is always created at the melting point, so the latent heat released to the atmosphere is always $L(T_m) = 6012\text{ J mol}^{-1}$.

Acknowledgments: This work was supported by the National Science Foundation, grants ATM01-06271, ATM05-54670, and CHE-0410007. ABK also acknowledges the Weizmann Institute of Science (Rehovot, Israel) for support via the Weston visiting professorship. Several fruitful discussions with G. Ryskin and B. Conant as well as helpful comments from D. Lamb and R. Shaw are greatly appreciated.

References:

Pruppacher, H. and J. Klett, **Microphysics of Clouds and Precipitation**, Kluwer Academic, 1997, 2nd ed., 954 pp.
Fukuta, N. and C. Gramada, Vapor pressure measurement of supercooled water. *J. Atmos. Sci.*, **60**, 1871-1875, 2003.
List, R., **Smithsonian Meteorological Tables**. Smithsonian Institution, 1951, 6th ed., 527pp.