Solidification of Binary Melts

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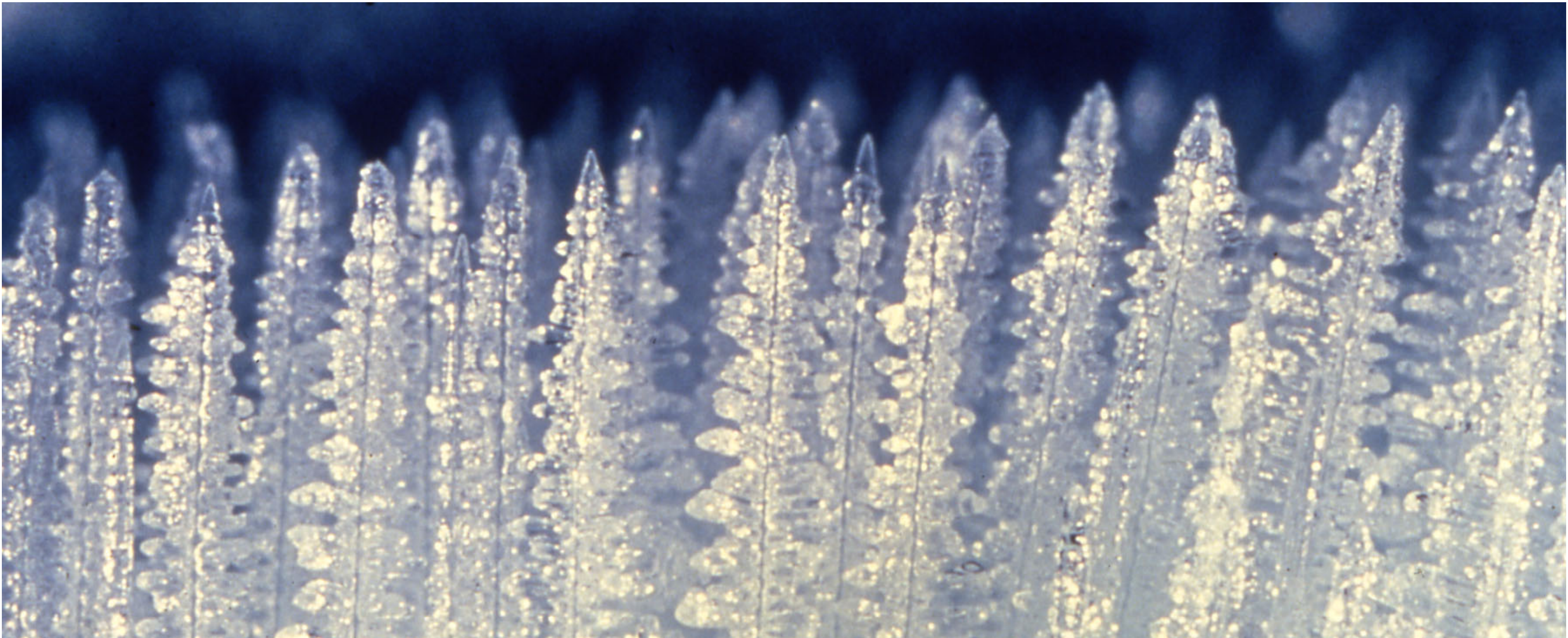
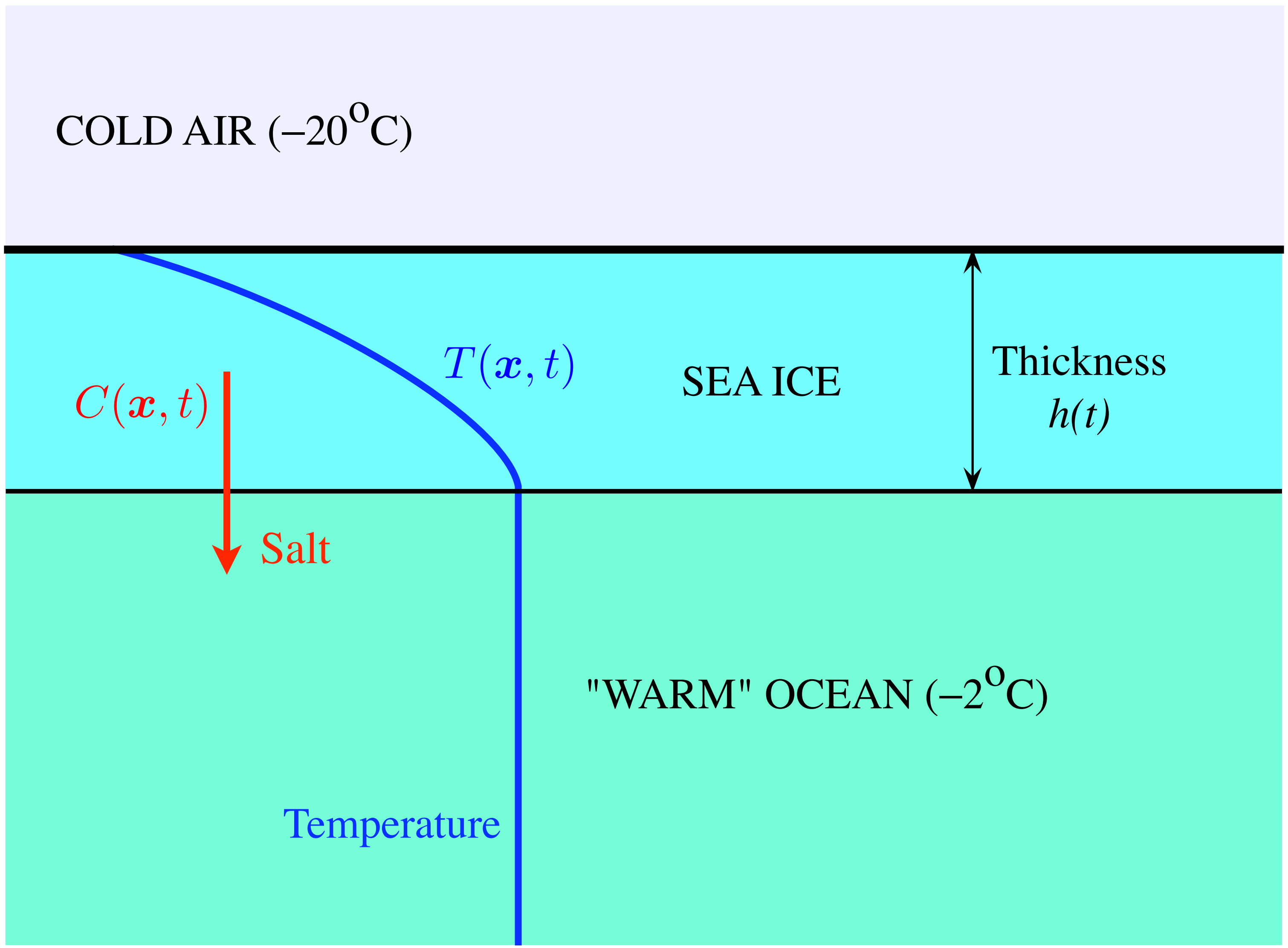
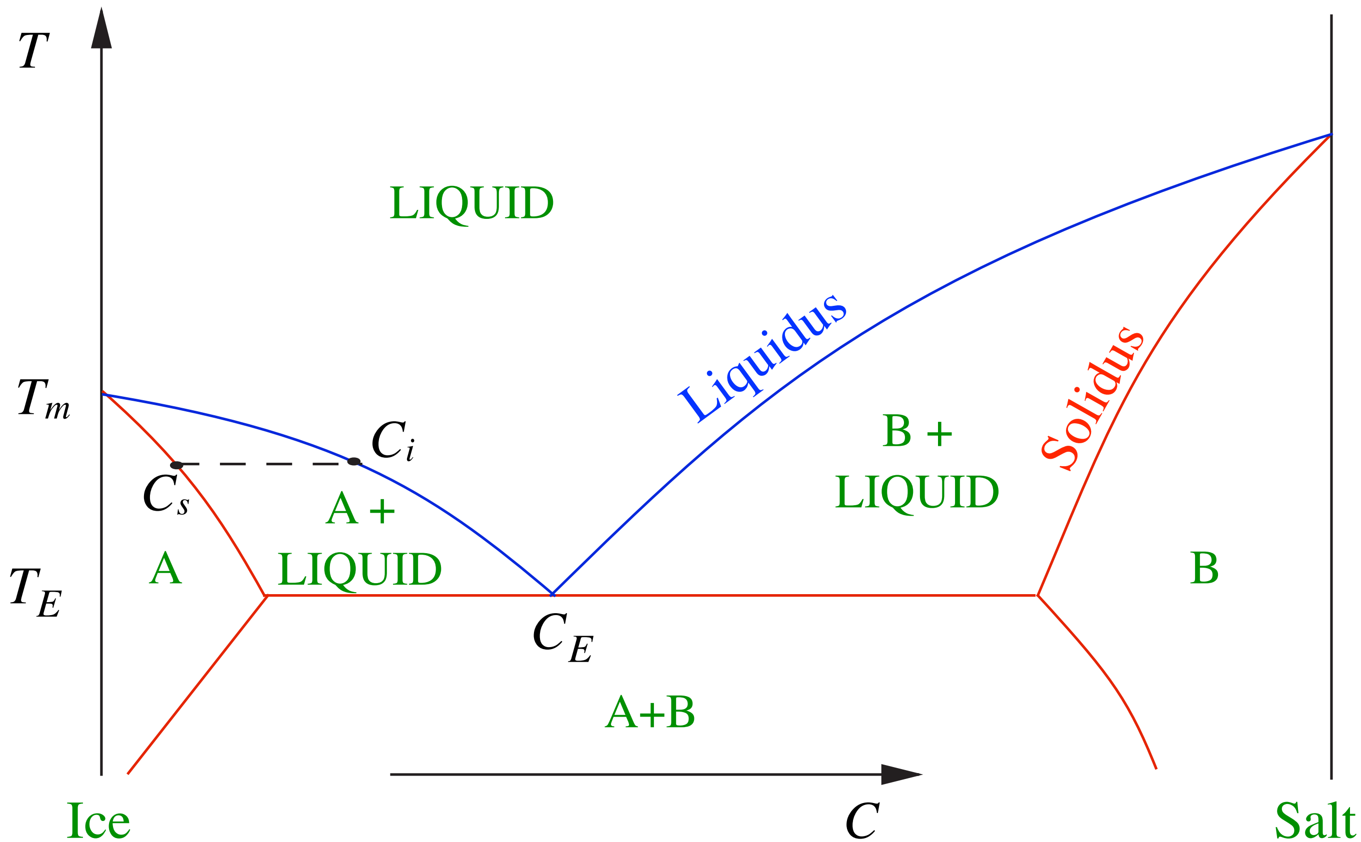


Evolution of Sea Ice



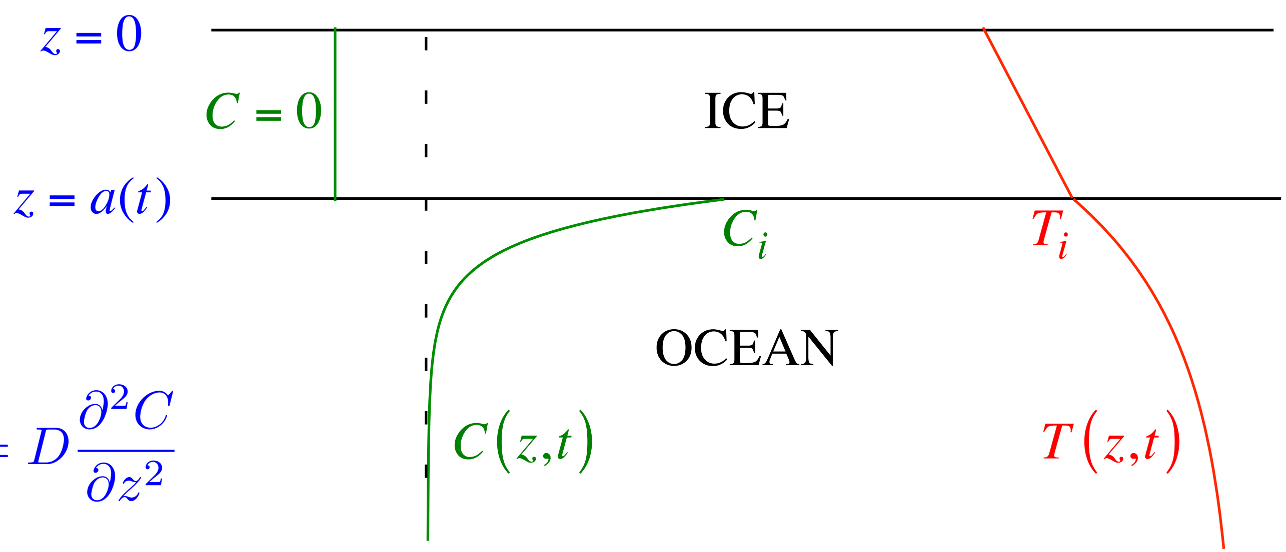
Binary Mixtures: Equilibrium Phase Diagram



Freezing temperature (liquidus) is a function of composition $T_L(C)$

Solid that forms has a different composition (given by the solidus) than the liquid

Ice Growth from a Salt Solution



$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2}$$

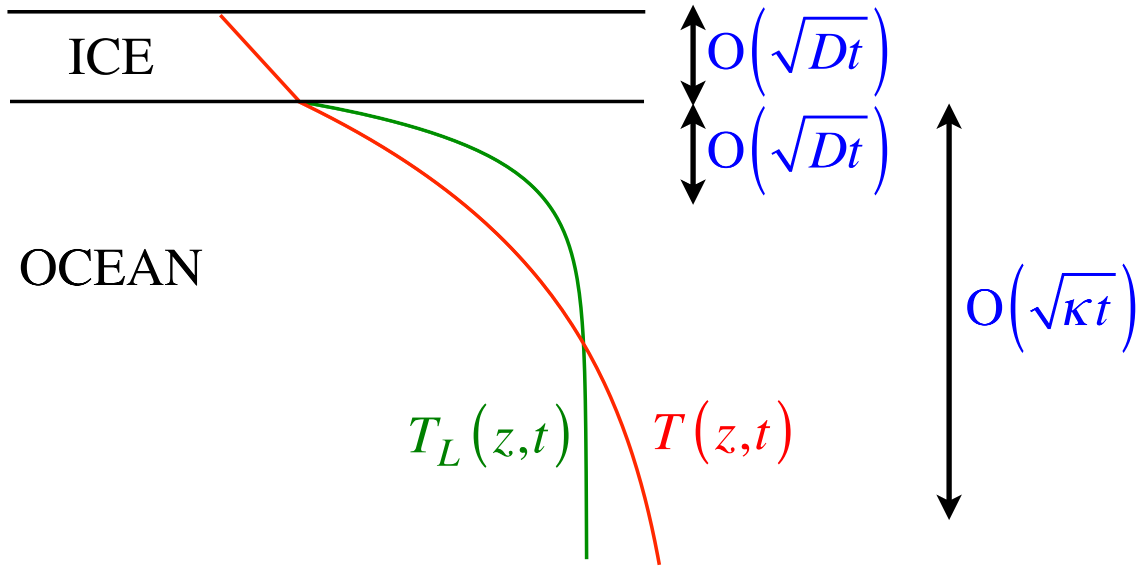
$$\frac{\partial T}{\partial t} = \kappa\frac{\partial^2 T}{\partial z^2}$$

Additional boundary conditions

$$T_i = T_L(C_i) \approx T_m - mC_i$$

$$C_i\frac{da}{dt} = -D\frac{\partial C}{\partial z}\bigg|_{z=a+}$$

Ice Growth from a Salt Solution



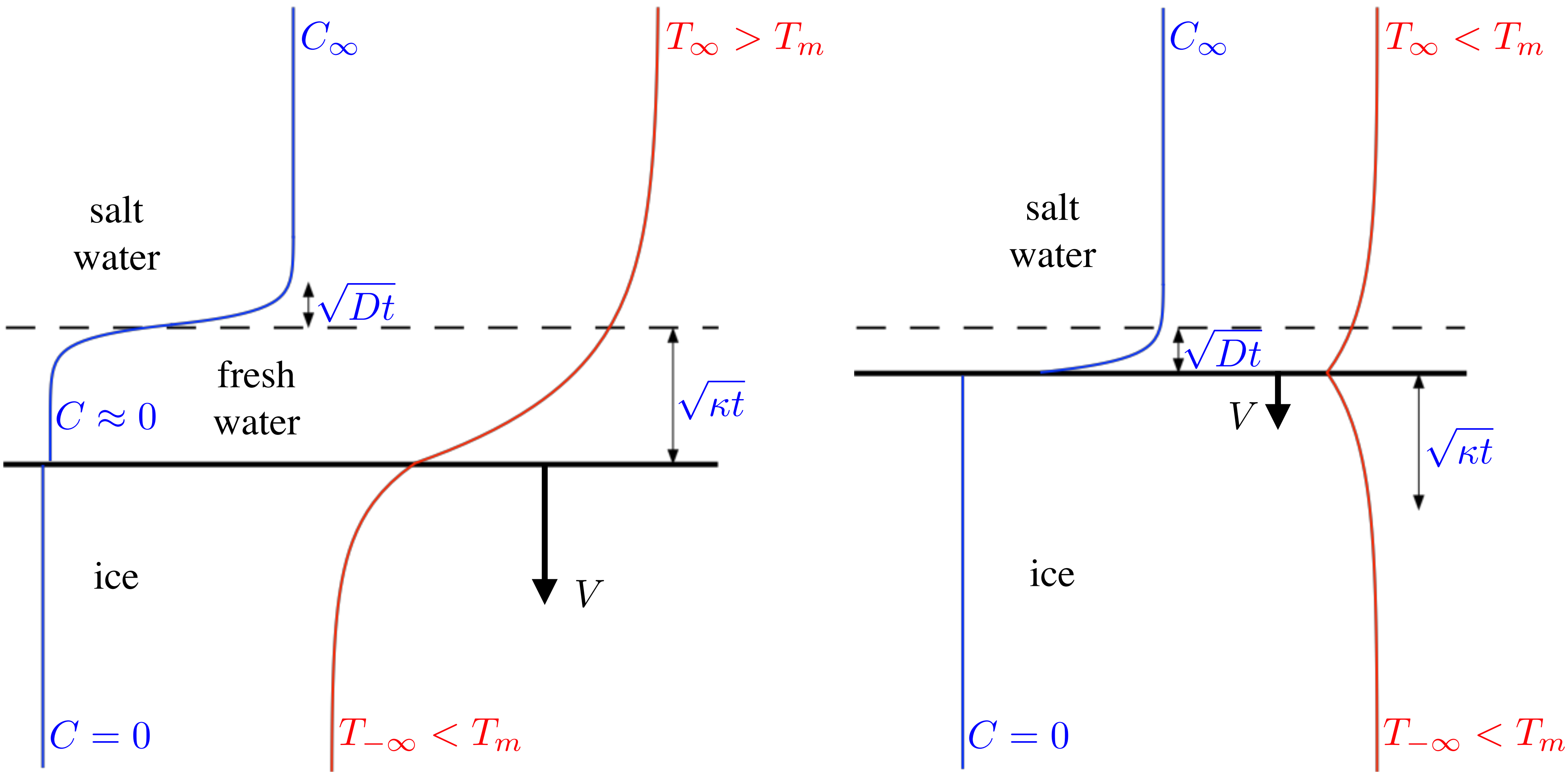
$$C = C_\infty + \left(C_i - C_\infty\right)\mathrm{erfc}\left(z/2\sqrt{Dt}\right)/\,\mathrm{erfc}\left(a/2\sqrt{Dt}\right)$$

$$T = T_\infty + \left(T_i - T_\infty\right)\mathrm{erfc}\left(z/2\sqrt{\kappa t}\right)/\,\mathrm{erfc}\left(a/2\sqrt{\kappa t}\right)$$

$$a = 2\mu\sqrt{Dt} \qquad \sqrt{\pi}\mu e^{\mu^2}\mathrm{erfc}\mu \approx \mathcal{C}^{-1} \qquad \mathcal{C} = \frac{C_0}{\Delta C} \qquad \mathrm{erfc}\,\mu = 1 - \mathrm{erf}\,\mu$$

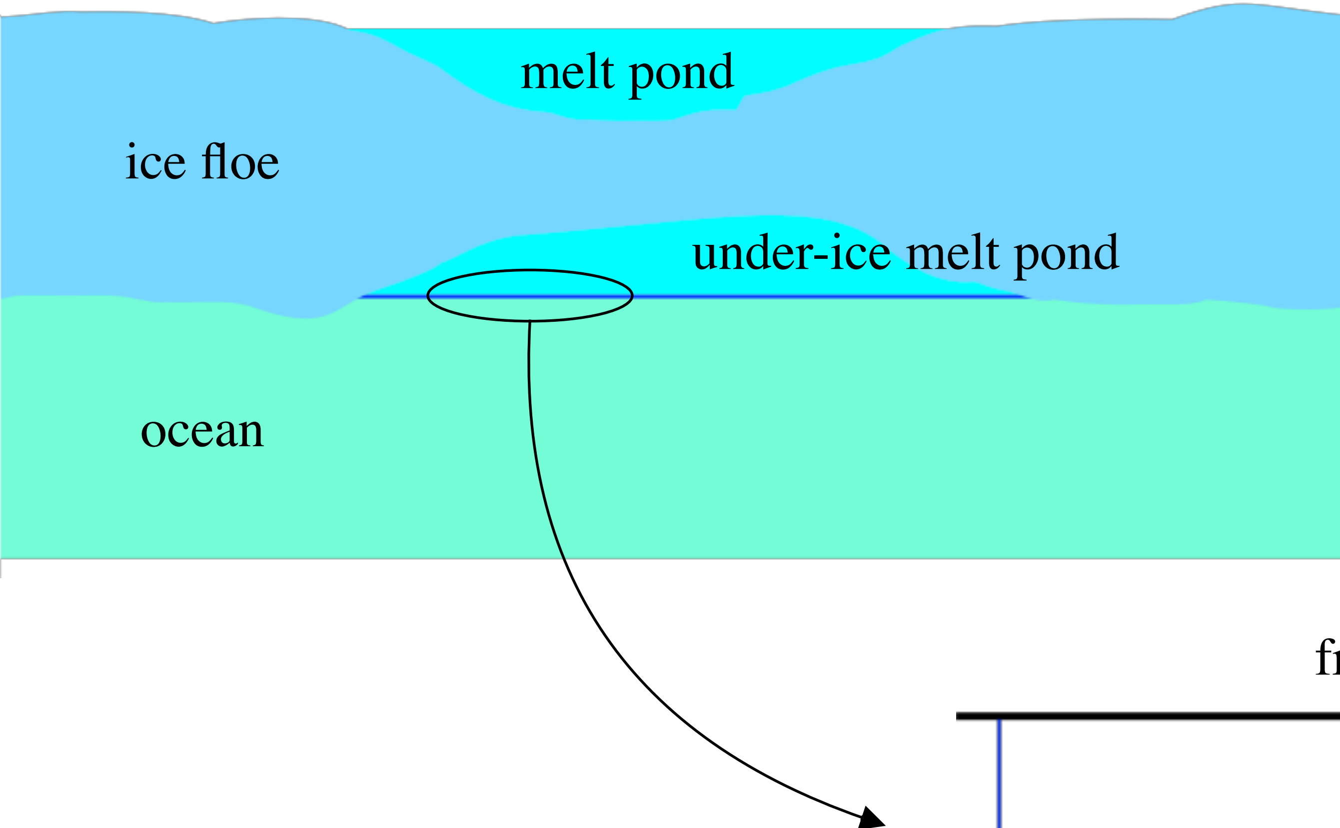
The growth rate of a planar solid–liquid interface is limited by the rate of removal of solute.

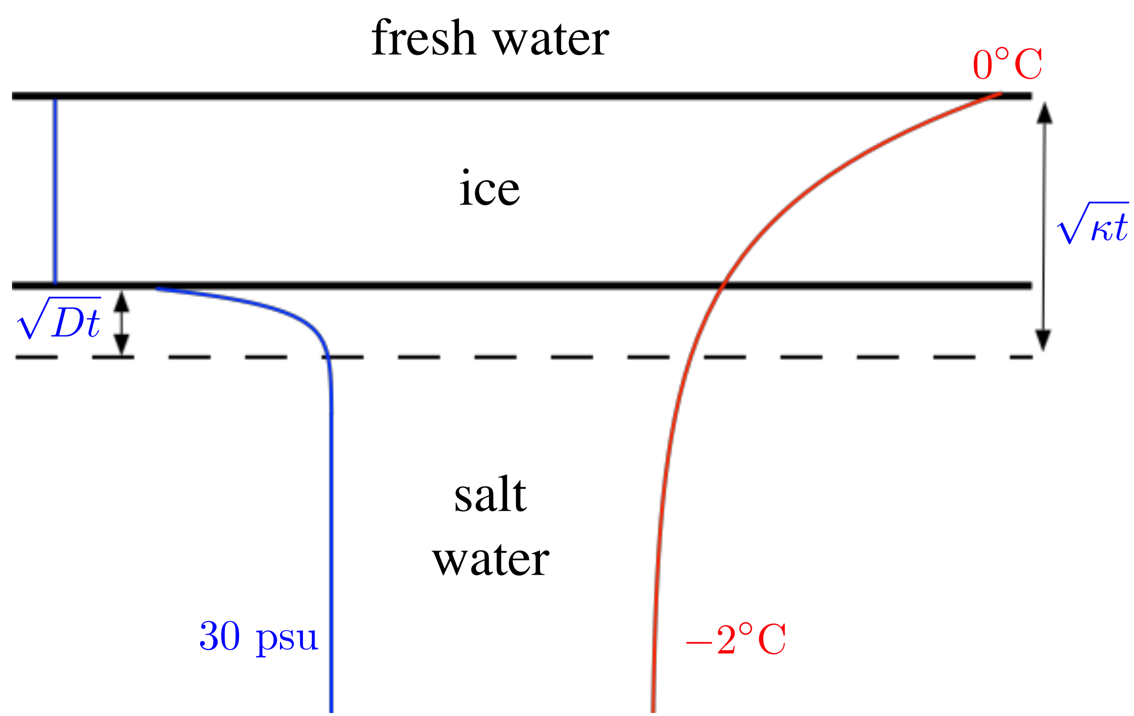
Melting versus Dissolving



Melting $\propto \sqrt{\kappa t}$ $\quad \frac{D}{\kappa} \approx 10^{-2}$ $\quad$ Dissolving $\propto \sqrt{Dt}$

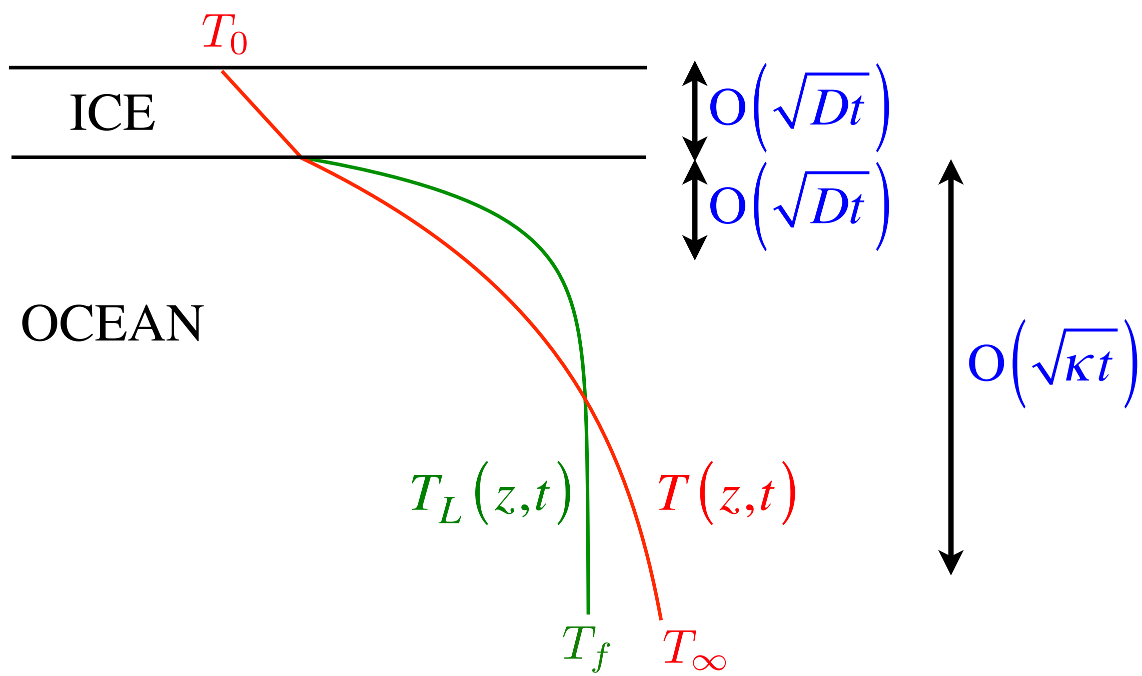
Evolution of Under-ice Melt Ponds





“False bottom” freezes at the top while dissolving at the bottom. Appears to migrate upwards.

Constitutional Supercooling



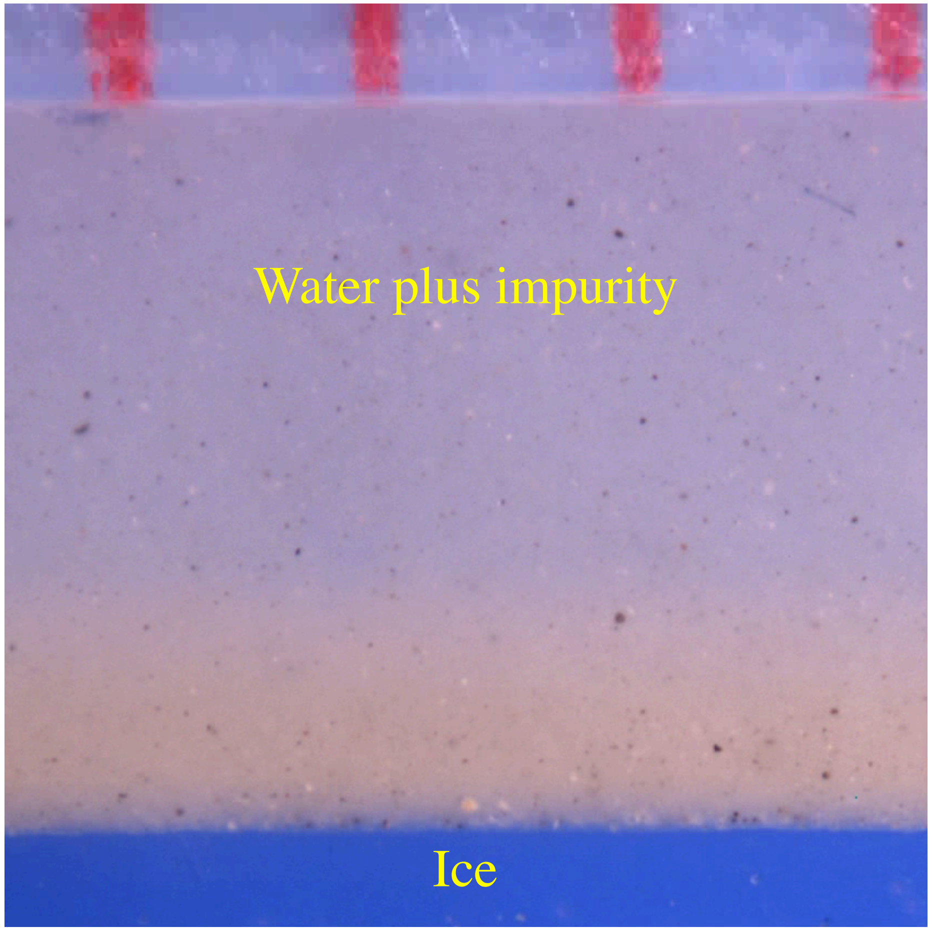
Slow salt diffusion relative to heat diffusion causes constitutional supercooling

Constitutional supercooling if $$\frac{\partial T}{\partial z} < \frac{\partial T_L}{\partial z} = -m\frac{\partial C}{\partial z}$$

From similarity solution, if $$\frac{T_f - T_0}{T_\infty - T_0} \gtrsim \sqrt{\frac{D}{\kappa}}\mathrm{e}^{\mu^2}$$

Segregation

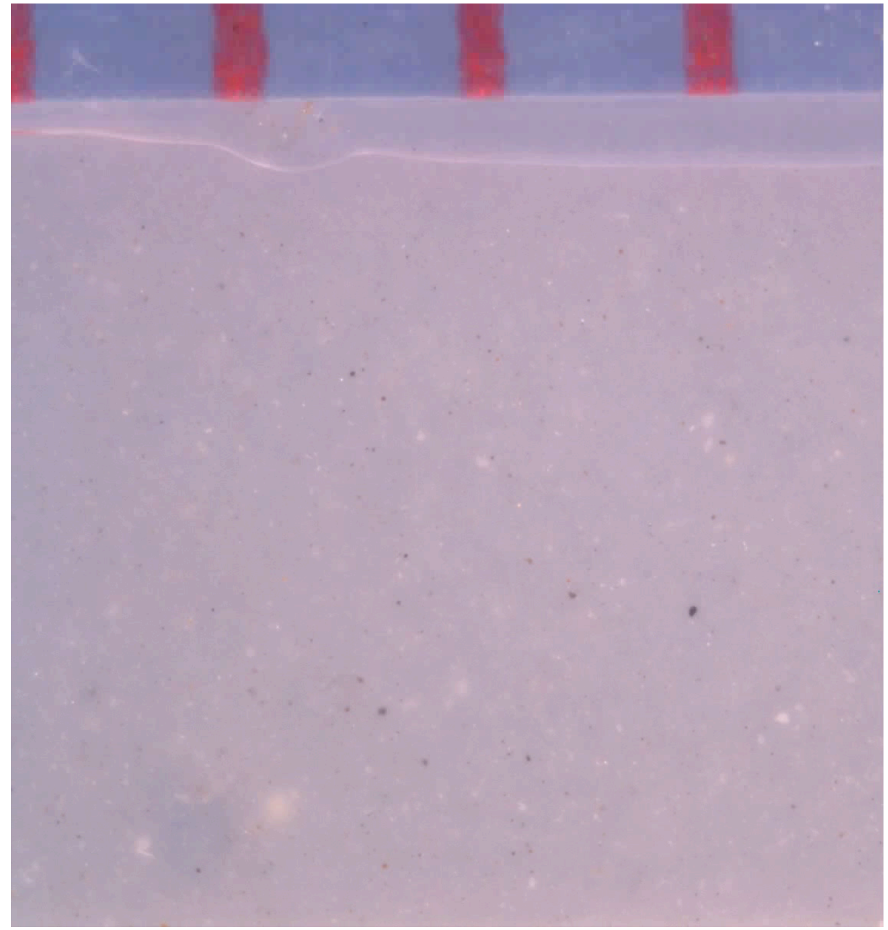
Single ice lens



30 minutes real time

Solute expelled from continuous solid phase

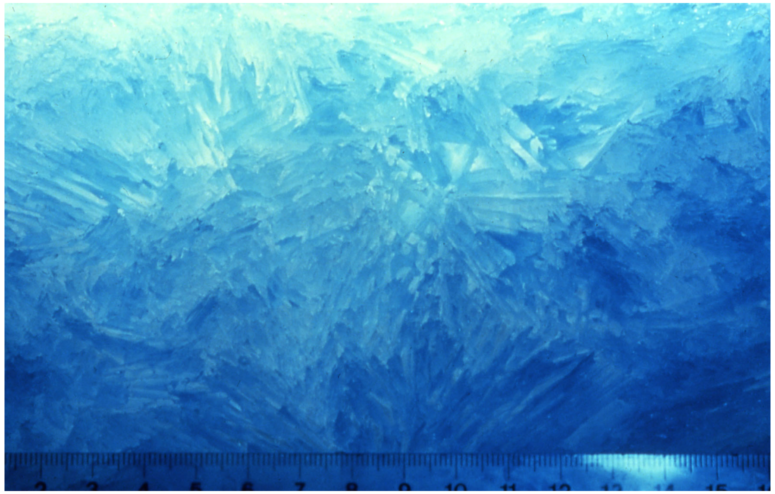
Mushy layer



10 minutes real time

Solute concentrated in interstices

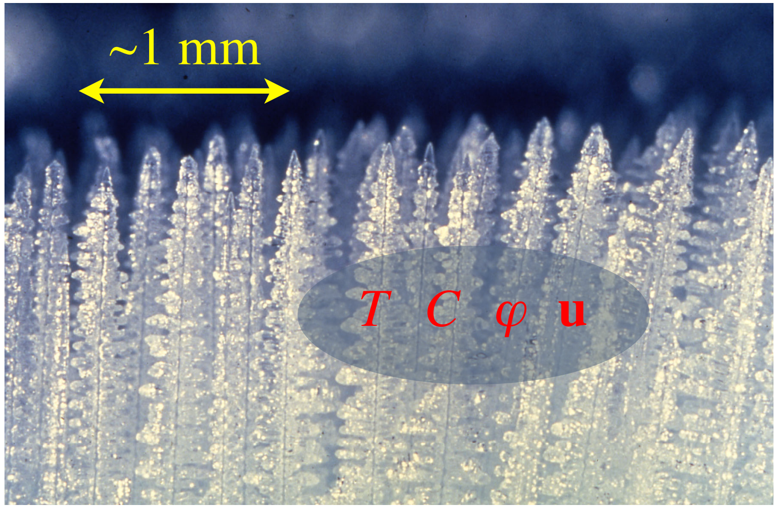
Sea Ice is a Mushy Layer



Two phase (solid + liquid)

Two component (water + salt)

Reactive porous medium



We seek an averaged description of local

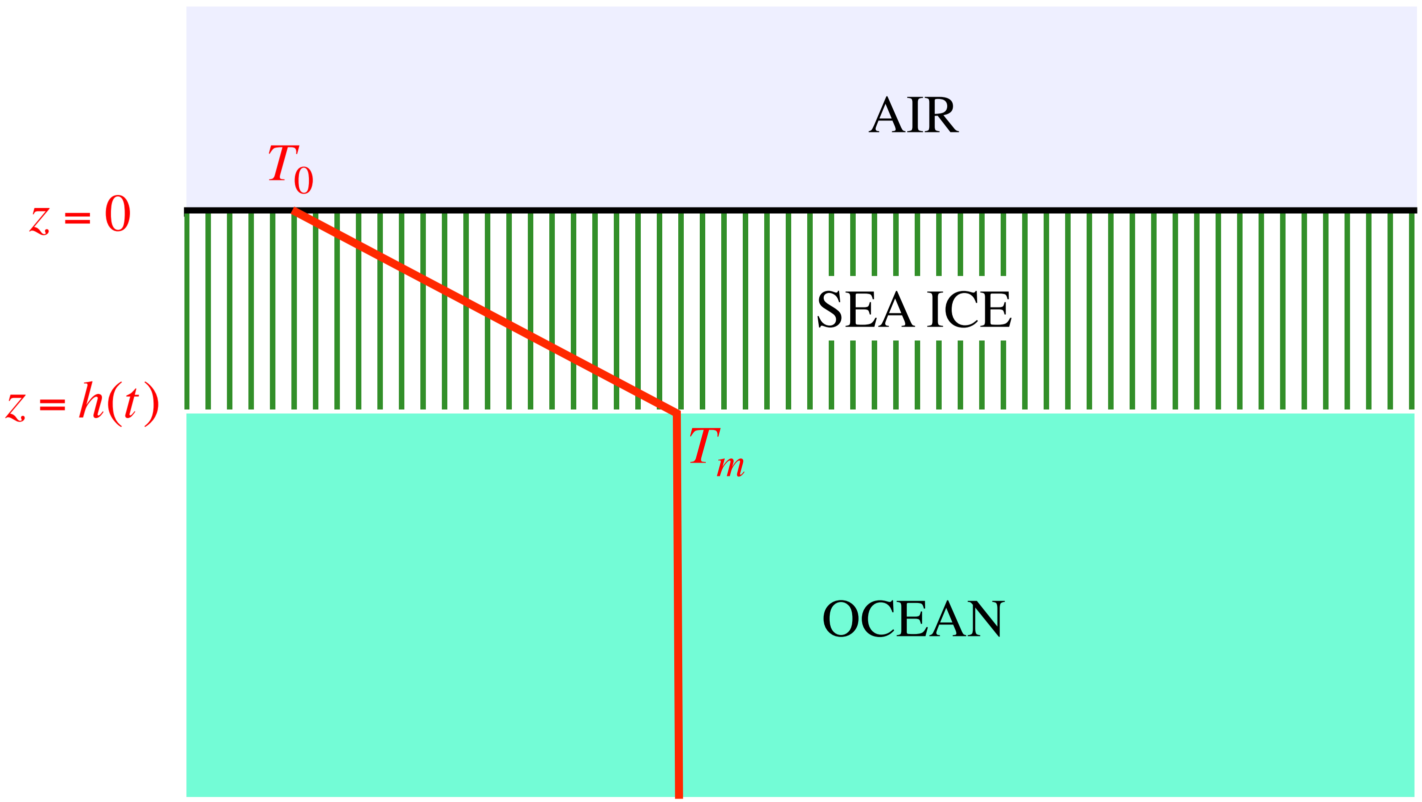
Mean temperature $T(x,t)$

Mean interstitial concentration $C(x,t)$

Solid fraction $\varphi(x,t)$

Darcy velocity $\mathbf{u}(x,t)$

Zero-Layer Semtner Model



$$\rho L \varphi \frac{dh}{dt} = \bar{k}(\varphi)\frac{T_m - T_0}{h}$$

$$\bar{k}(\varphi) = \varphi k_s + (1-\varphi) k_l$$

$$h = \sqrt{\frac{2\bar{k}(\varphi)(T_m - T_0)}{\rho L \varphi} t}$$

Thermodynamic Models of (quiescent) Sea Ice

Heat equation $$\overline{\rho c_p}\frac{\partial T}{\partial t} = \nabla \cdot \left(\bar{k}\nabla T\right) + \rho_s L \frac{\partial \phi}{\partial t}$$

Liquidus relates interstitial concentration to temperature $$T = T_L(C) \approx T_m - mC$$

Bulk concentration $$C_B = (1-\phi)C$$ so $$\phi = 1 - \frac{C_B}{C}$$

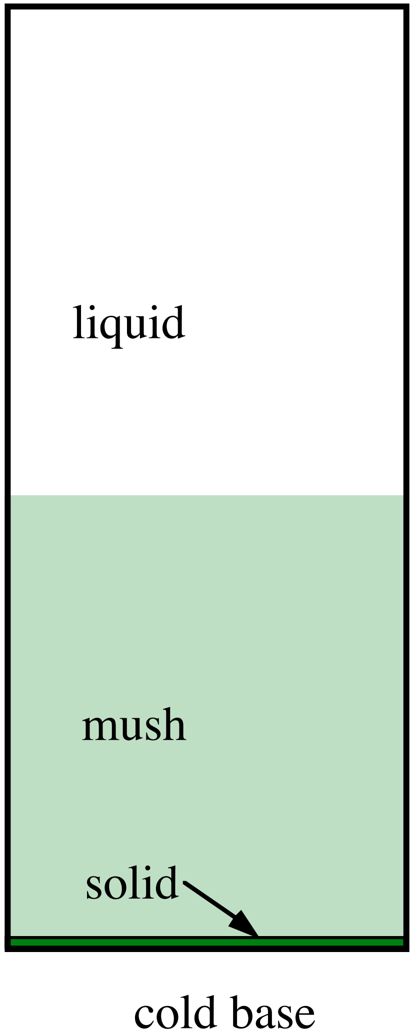
If $\frac{\partial C_B}{\partial t} \equiv 0$ so that $C_B = C_B(\mathbf{x})$ then $$\frac{\partial \phi}{\partial t} = \frac{C_B}{C^2}\frac{\partial C}{\partial t} = -\frac{1}{m}\frac{C_B}{C^2}\frac{\partial T}{\partial t}$$

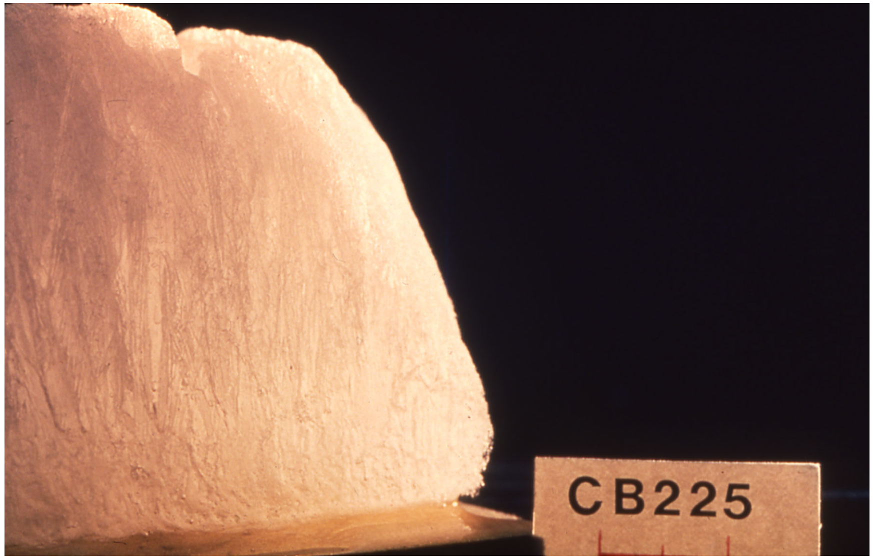
$$\left[\overline{\rho c_p} + \rho_s L \frac{m C_B}{(T_m - T)^2}\right]\frac{\partial T}{\partial t} = \nabla \cdot \left(\bar{k}\nabla T\right)$$

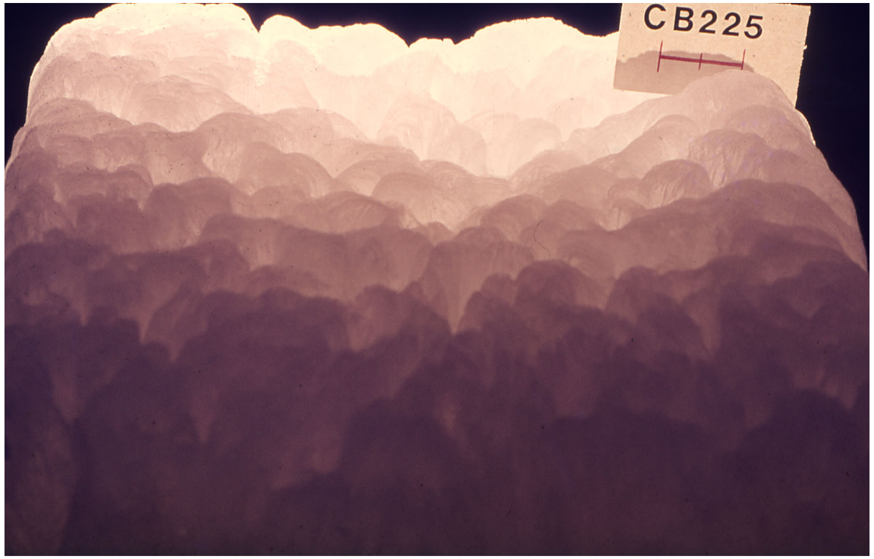
The thermal inertia (specific heat capacity) of sea ice is dominated by the internal release of latent heat.

“Sea Ice”
with no convection

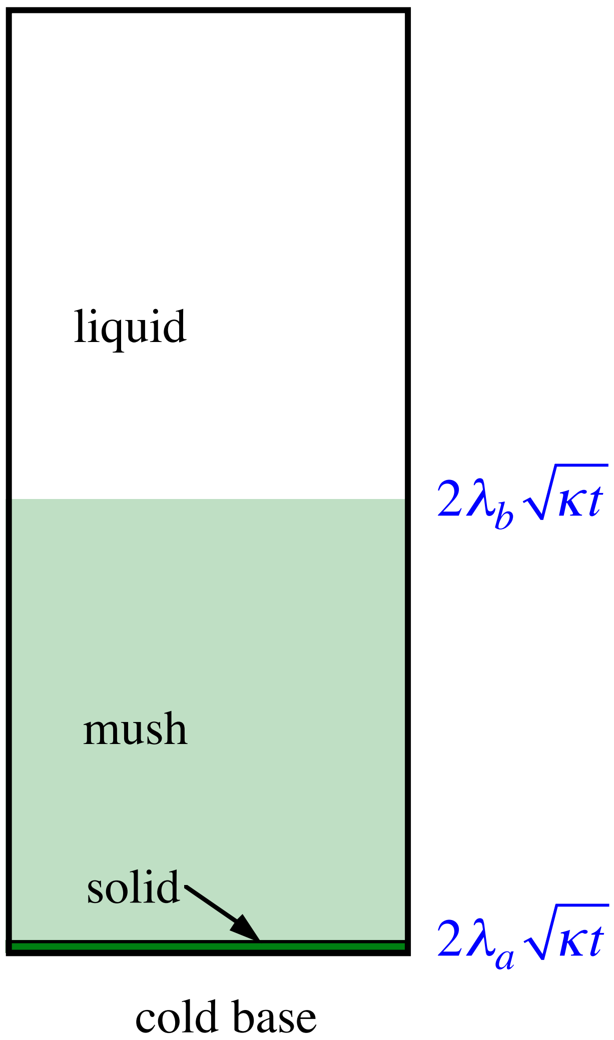
$C_B = C_0$ (constant and uniform)

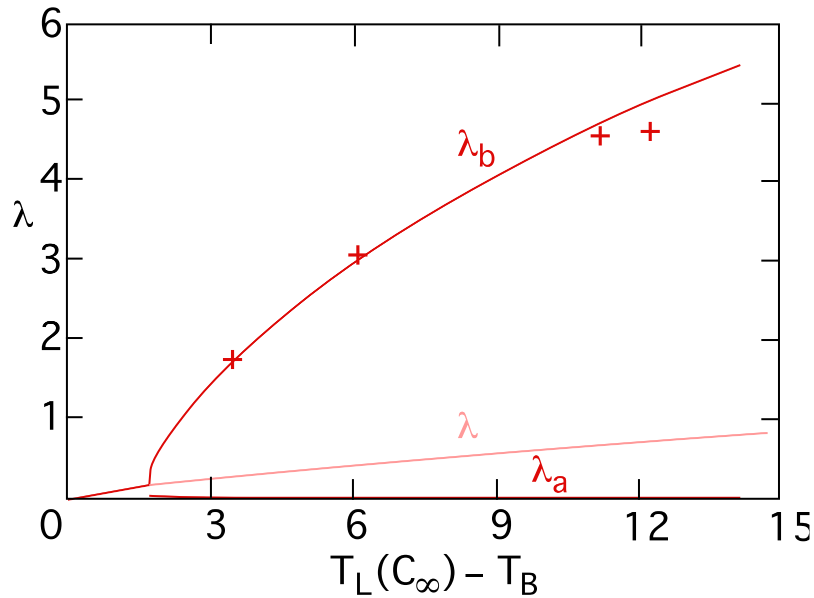


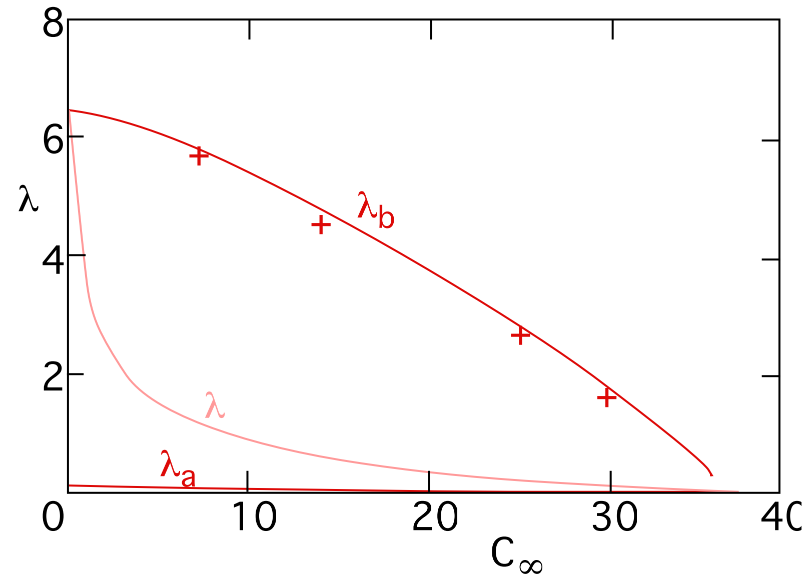




Thickness of a Mushy Layer — Experiments versus Theory







Summary

Thermal-diffusion-controlled solidification has length scales proportional to $\sqrt{\kappa t}$

Rate of solidification of a mixture at a planar solid–liquid interface is limited by rate of transport of rejected solute with length scales proportional to $\sqrt{Dt}$

But rejected solute causes local constitutional supercooling and morphological instability ...

... leading to the development of a mushy layer, with length scales again proportional to $\sqrt{\kappa t}$

Sea ice is a mushy layer.

Mathematical models of mushy layers give accurate predictions of their evolution once their salinity is known,

What determines the salinity of sea ice?

Desalination Processes of Sea Ice

Interfacial fractionation

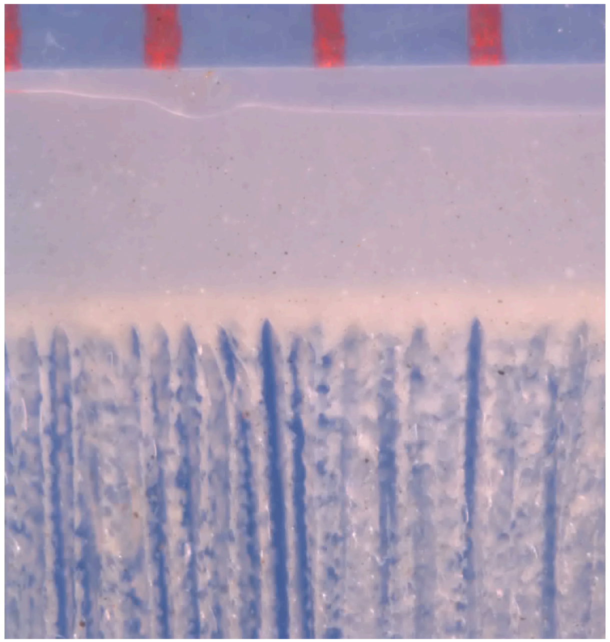
Brine expulsion

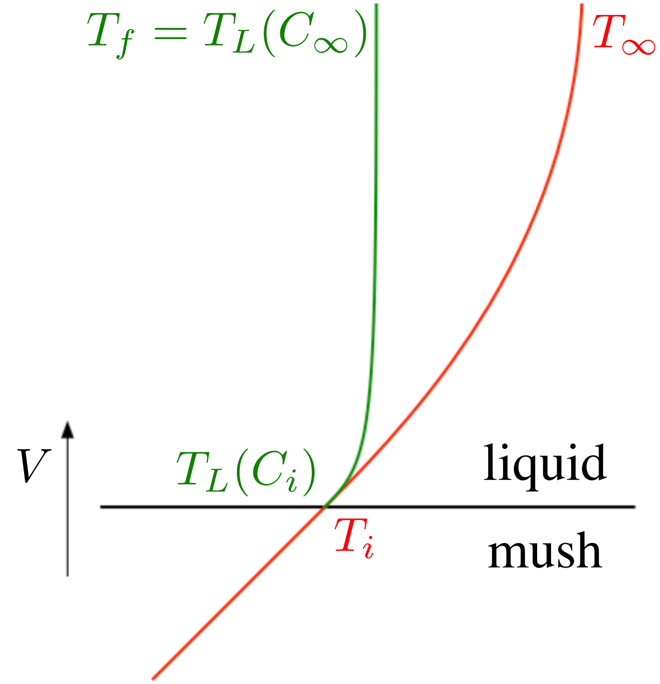
Brine pocket migration

Brine drainage

Flushing

Interfacial Fractionation





$$T = T_\infty + (T_i - T_\infty)\mathrm{e}^{-Vz/\kappa}$$

$$C = C_\infty + (C_i - C_\infty)\mathrm{e}^{-Vz/D}$$

Marginal equilibrium
$$\left.\frac{\partial T}{\partial z}\right|_i = \left.\frac{\partial T_L}{\partial z}\right|_i = -m\left.\frac{\partial C}{\partial z}\right|_i$$

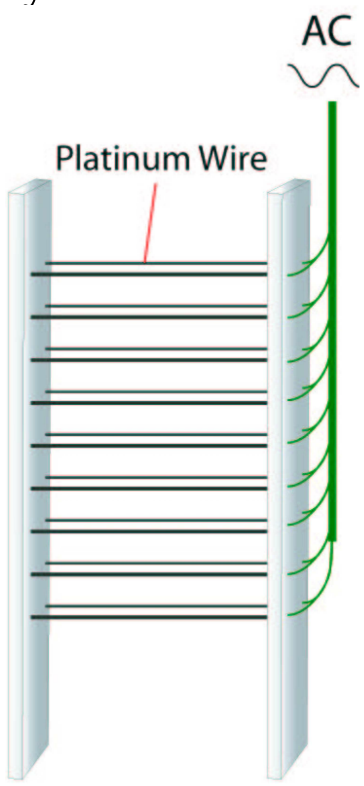
Fractionation
$$C_i - C_\infty = \frac{\epsilon}{1-\epsilon}\frac{T_\infty - T_f}{m} = \mathrm{O}(\epsilon) \qquad \epsilon = \frac{D}{\kappa}$$

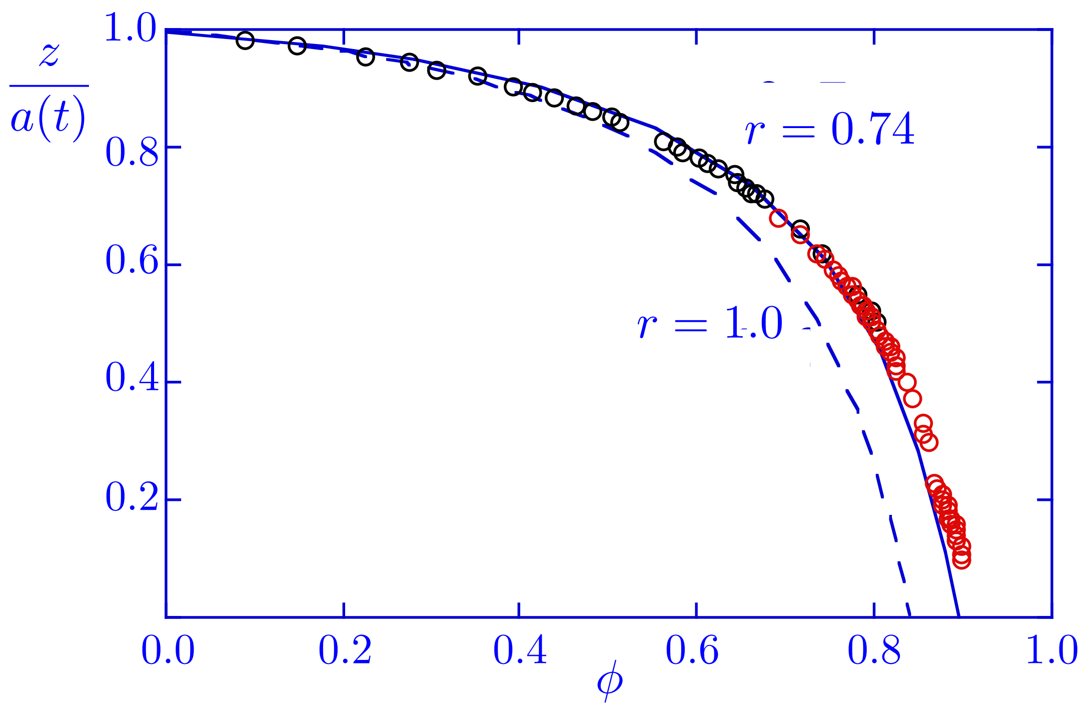
Brine Expulsion

Mass conservation $$\frac{\partial}{\partial t}\left[\phi\rho_s + (1-\phi)\rho_l\right] + \nabla\cdot(\rho_l \mathbf{u}) = 0$$

Darcy flux $$\nabla\cdot\mathbf{u} = \left(1 - \frac{\rho_s}{\rho_l}\right)\frac{\partial\phi}{\partial t}$$

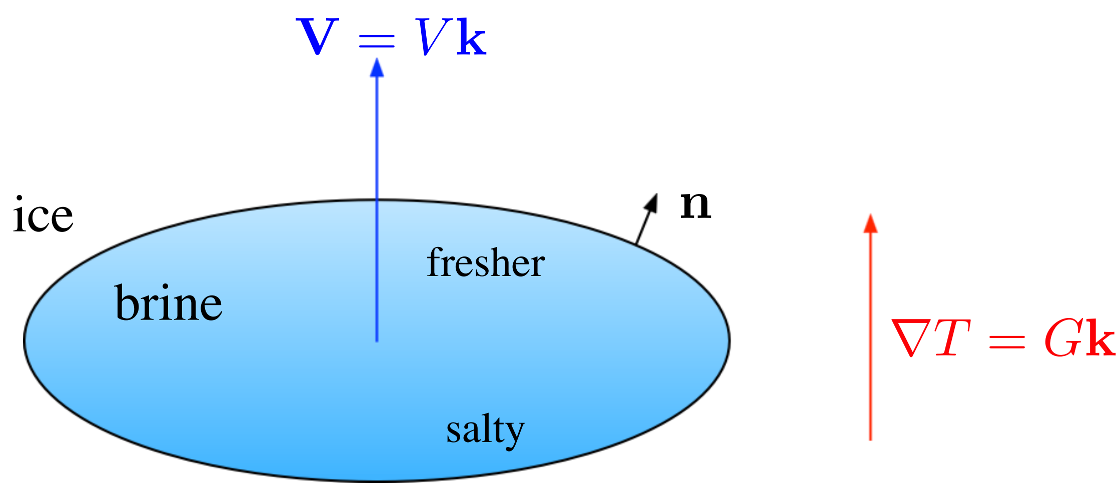
$$r = \frac{\rho_s}{\rho_l}$$





Redistributes brine and thickens mushy layer but doesn’t cause brine to leave layer

Brine Pocket Migration



Temperature $$T = T_0 + G\mathbf{k}.\mathbf{x}$$

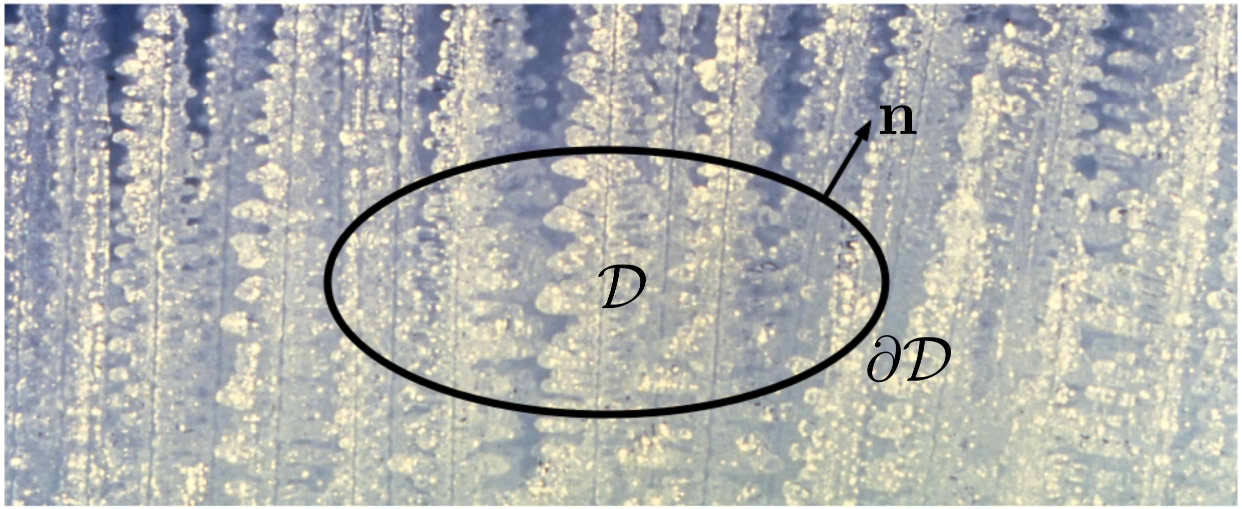
Liquidus gives salinity $$C = \frac{1}{m}(T_m - T_0 - G\mathbf{k}.\mathbf{x})$$

Salt conservation $$CV\mathbf{k}\cdot\mathbf{n} = -D\mathbf{n}\cdot\nabla C\big|_{\text{boundary}} = \frac{DG}{m}\mathbf{n}\cdot\mathbf{k}$$

Migration speed $$V \approx \frac{DG}{T_m - T_0} \quad \text{if} \quad \text{pocket size} \ll \frac{T_m - T_0}{G}$$

$$\sim \frac{D}{\kappa} \times \text{ growth rate of mushy layer}$$

Temperature Gradient Zone Migration



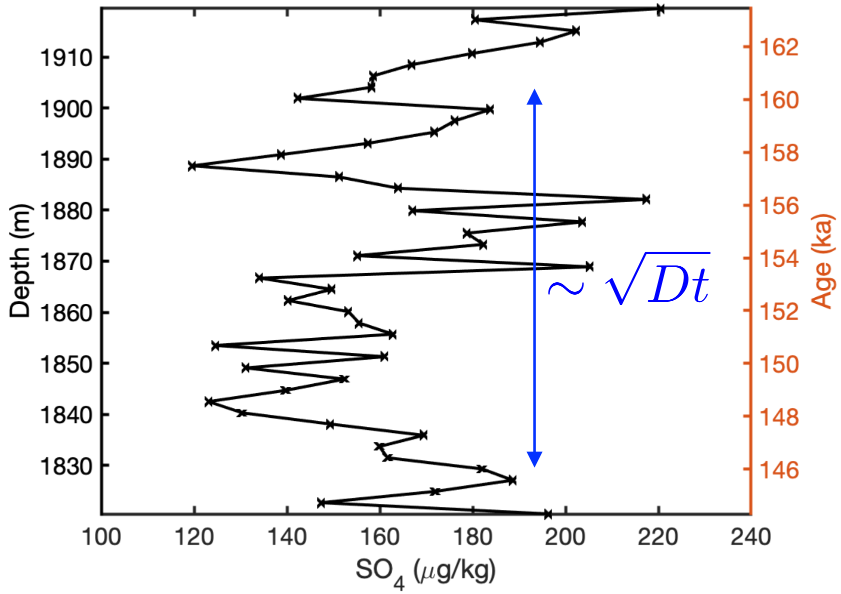
Salt conservation

$$\frac{d}{dt}\int_{\mathcal{D}}(1-\phi)C\,dV = -\int_{\partial\mathcal{D}}\mathbf{n}\cdot[\mathbf{u}C - D(1-\phi)\nabla C]\;dS$$

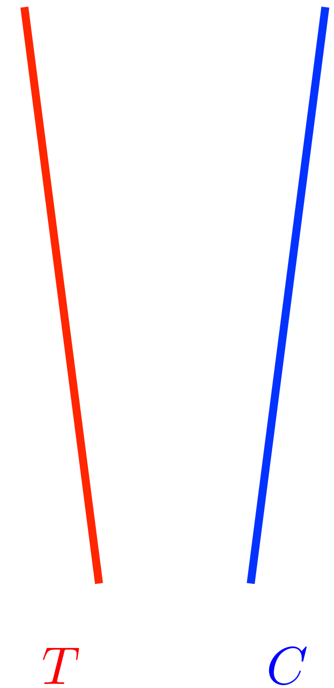
$$(1-\phi)\frac{\partial C}{\partial t} + \mathbf{u}\cdot\nabla C = D\nabla\cdot[(1-\phi)\nabla C] + C\frac{\partial \phi}{\partial t}$$

$$\frac{\partial C_B}{\partial t} = -\frac{1}{m}\nabla\cdot[D(1-\phi)\nabla T] + \frac{1}{m}\mathbf{u}\cdot\nabla T$$

Migration of Climate Signals



$C_B \propto 1 - \phi$



$$\frac{\partial C_B}{\partial t} = -\frac{1}{m}\nabla \cdot [D(1-\phi)\nabla T] + \frac{1}{m}\mathbf{u}\cdot\nabla T$$

$$\frac{\partial C_B}{\partial t} + \nabla \cdot \left[D\frac{\nabla T}{C}C_B\right] = 0 \qquad \frac{\partial C_B}{\partial t} + \nabla \cdot \left[\frac{D\nabla T}{T_m - T}C_B\right] = 0$$

Bulk salinity **migrates** with ‘velocity’ $\mathbf{V} = \dfrac{D\nabla T}{T_m - T}$

Summary

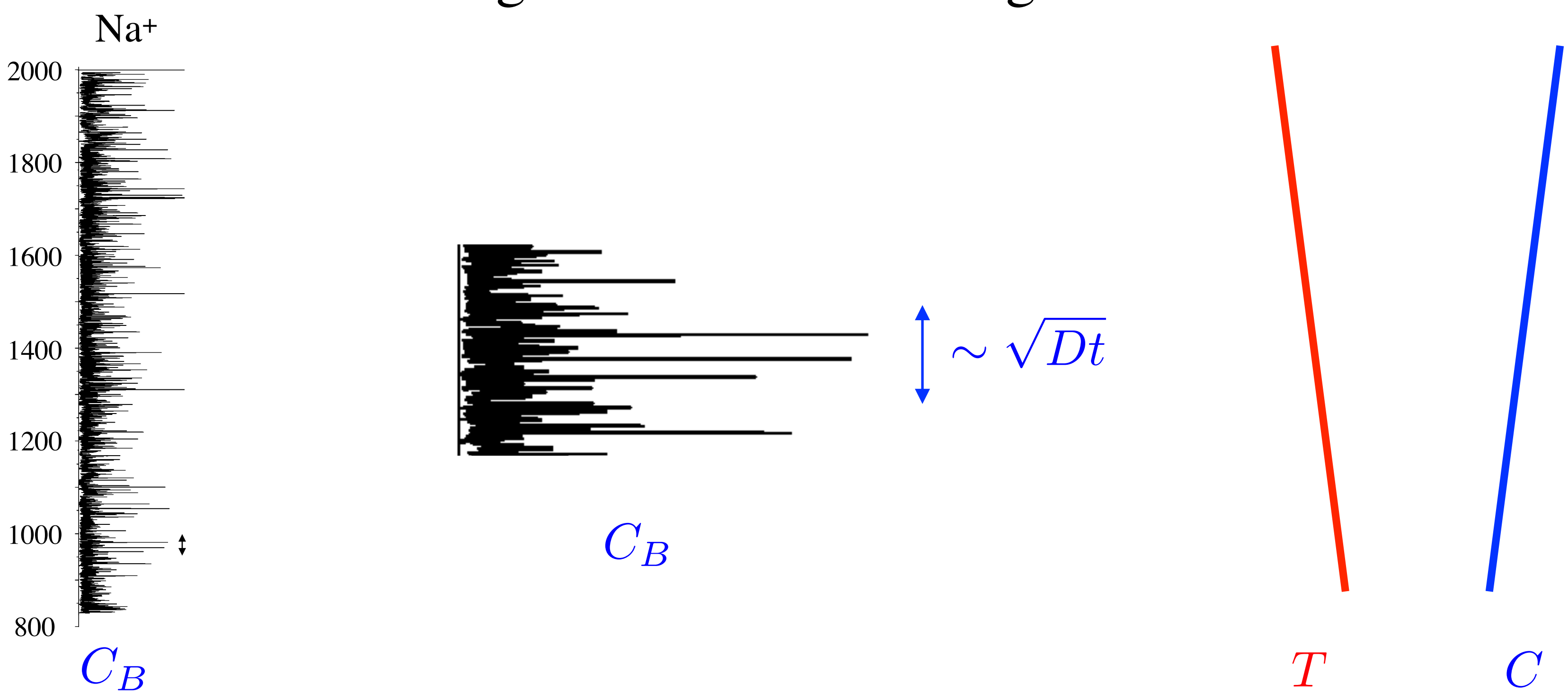
Interfacial fractionation is negligible $\mathrm{O}\left(\frac{D}{\kappa}\right)$

Brine ‘expulsion’ (velocity induced by density change) doesn’t expel

Brine-pocket migration is negligible $\mathrm{O}\left(\frac{D}{\kappa}\right)$ during growth

Bulk-salinity signal does not diffuse but is advected by thermal gradients

Migration of Climate Signals



$$\frac{\partial C_B}{\partial t} = -\frac{1}{m}\nabla \cdot [D(1-\phi)\nabla T] + \frac{1}{m}\mathbf{u} \cdot \nabla T$$

$$\frac{\partial C_B}{\partial t} + \nabla \cdot \left[D\frac{\nabla T}{C} C_B \right] = 0$$

$$\frac{\partial C_B}{\partial t} + \nabla \cdot \left[\frac{D\nabla T}{T_m - T} C_B \right] = 0$$

Bulk salinity **migrates** with ‘velocity’ $\mathbf{V} = \frac{D\nabla T}{T_m - T}$