Fundamentals of Solidification

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Advection–Diffusion Equation

(conservation of heat)

Specific enthalpy H is heat per unit mass at constant pressure

Conservation $$\frac{\partial}{\partial t}(\rho H) + \nabla \cdot \mathbf{q} = 0$$

Heat flux $$\mathbf{q} \quad = \quad \rho H \mathbf{u} \quad - k \nabla T$$

advection Fickian diffusion

$$\rho \frac{\partial H}{\partial t} + H \frac{\partial \rho}{\partial t} + H \nabla \cdot (\rho \mathbf{u}) + \rho \mathbf{u} \cdot \nabla H = \nabla \cdot (k \nabla T)$$

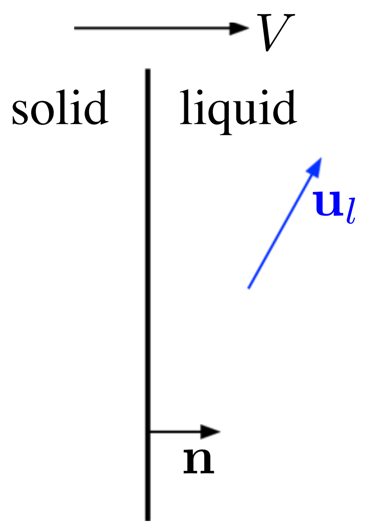
Specific heat capacity $$c_p = \left. \frac{\partial H}{\partial T} \right|_p$$

$$\frac{DH}{Dt} = \rho c_p \frac{DT}{Dt} = \nabla \cdot (k \nabla T)$$

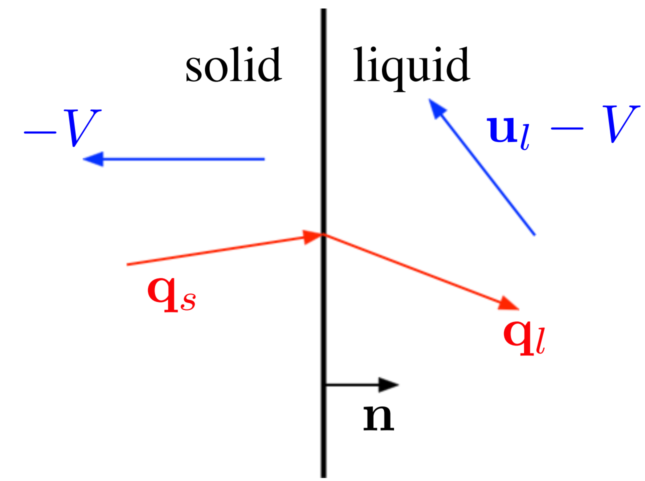
Stefan Condition

(conservation of heat)

frame fixed in solid



frame fixed with interface



$$\mathbf{n}\cdot\mathbf{q}_s = \mathbf{n}\cdot\mathbf{q}_l$$

$$\rho_s H_s(-V) - k_s\mathbf{n}\cdot\nabla T_s = \rho_l H_l\left(\mathbf{u}_l\cdot\mathbf{n} - V\right) - k_l\mathbf{n}\cdot\nabla T_l$$

$$\rho_s(-H_s + H_l)V - H_l\left[\rho_s V + \rho_l(\mathbf{u}_l\cdot\mathbf{n} - V)\right] = k_s\mathbf{n}\cdot\nabla T_s - k_l\mathbf{n}\cdot\nabla T_l$$

$$\rho_s L V = k_s\mathbf{n}\cdot\nabla T_s - k_l\mathbf{n}\cdot\nabla T_l \qquad L = H_l - H_s$$

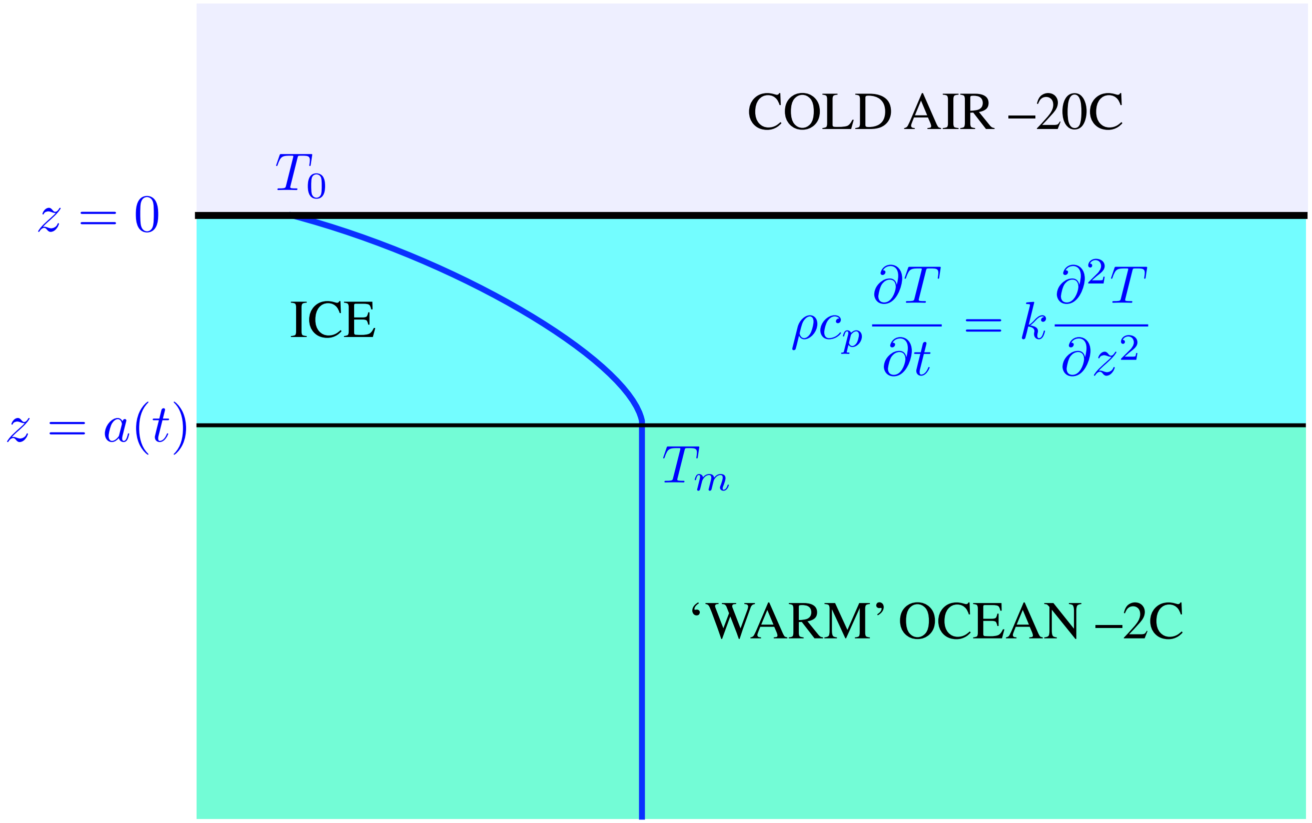
Measurements of Sea-Ice Thickness

http://icestories.exploratorium.edu

Dutch ship Varna stuck in pack ice during first International Polar Year 1882–83

Calculating the Thickness of Sea Ice

Stefan's Problem



The location of the interface between ice and ocean is determined by the

Stefan condition $$\rho L \frac{da}{dt} = k \frac{\partial T}{\partial z}\bigg|_{z=a-}$$

Similarity Solution to Stefan's Problem

(Neumann 1860's)

Diffusion equation

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

Boundary conditions

$$T = T_0 \quad (z = 0)$$

$$T = T_m \quad (z = a(t))$$

Stefan condition

$$\rho L \frac{da}{dt} = k \frac{\partial T}{\partial z}\bigg|_{z=a-}$$

Scale temperature differences with $\Delta T = T_m - T_0$, lengths with H, times with τ

Scaling relationships

$$\frac{\Delta T}{\tau} \sim \kappa \frac{\Delta T}{H^2} \quad \Rightarrow \quad H \sim (\kappa\tau)^{1/2}$$

$$\rho L \frac{H}{\tau} \sim k \frac{\Delta T}{H} \quad \Rightarrow \quad H \sim \left(\frac{\kappa\tau}{\mathcal{S}}\right)^{1/2}$$

No intrinsic timescale. Only extrinsic timescale is elapsed time t so choose $\tau \sim t$.

Similarity Solution to Stefan's Problem

Dimensionless variables $$T - T_0 = \Delta T\, \theta\left(\frac{z}{H}, \frac{t}{\tau}\right) = \Delta T\, \theta\left(\frac{z}{\sqrt{\kappa t}}, 1\right) = \Delta T\, \theta(\eta)$$

Similarity variable $$\eta = \frac{z}{2\sqrt{\kappa t}}$$

Equation and boundary conditions become

$$\theta'' + 2\eta\theta' = 0$$

$$\theta(0) = 0$$

$$\theta(\lambda) = 1$$

$$\mathcal{S}\lambda = \frac{1}{2}\theta'(\lambda) \qquad \mathcal{S} = \frac{L}{c_p \Delta T}$$

where $a = 2\lambda\sqrt{\kappa t}$

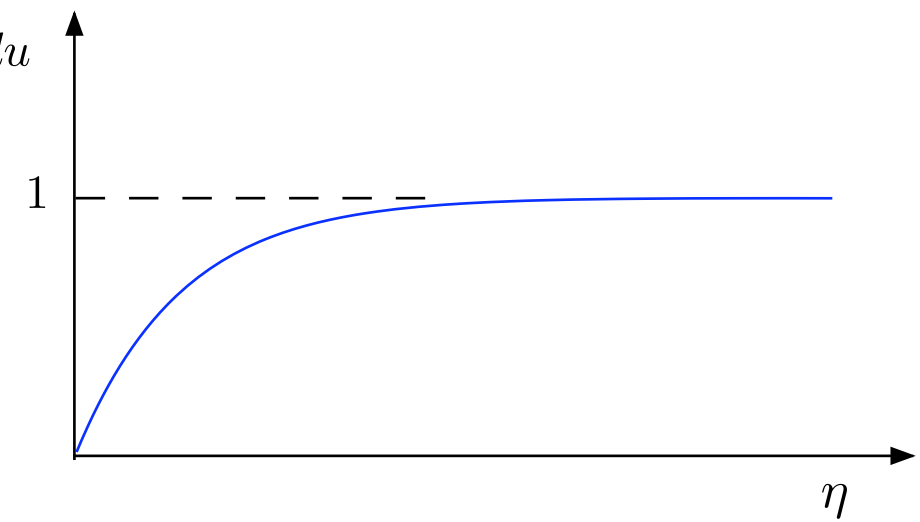
Similarity Solution to Stefan's Problem

Temperature in the ice is $$T = T_0 + (T_m - T_0)\frac{\operatorname{erf}\eta}{\operatorname{erf}\lambda}$$

where $$\eta = \frac{z}{2\sqrt{\kappa t}}$$

with $$a = 2\lambda\sqrt{\kappa t} \qquad \sqrt{\pi}\lambda \mathrm{e}^{\lambda^2} \operatorname{erf}\lambda = \mathcal{S}^{-1}$$

$$\operatorname{erf}\eta = \frac{2}{\sqrt{\pi}}\int_0^\eta \mathrm{e}^{-u^2}\,du$$

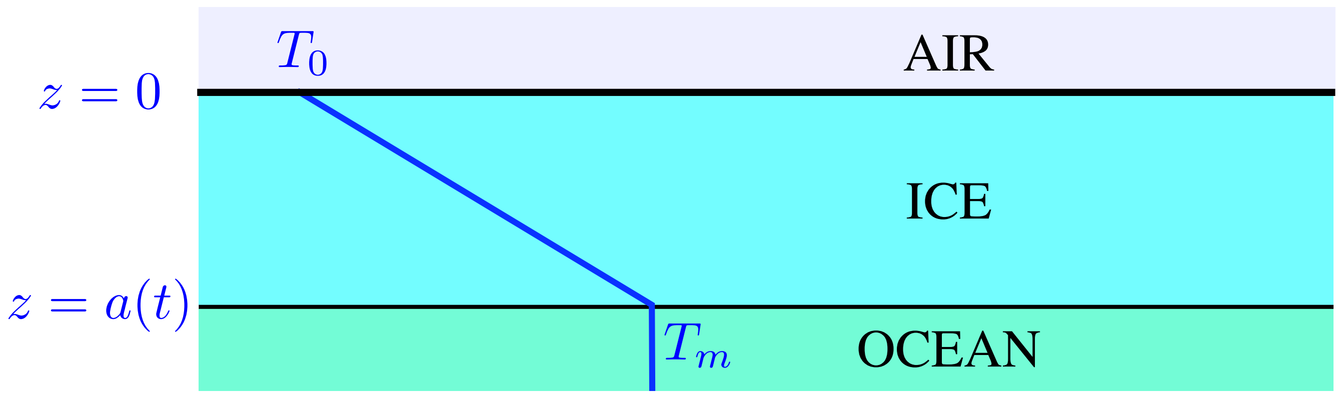


Quasi-Steady Approximation

valid for large Stefan number

Scale temperature differences with $\Delta T = T_m - T_0$, times with τ, lengths with $H \sim \left(\frac{\kappa\tau}{\mathcal{S}}\right)^{1/2}$

Scaled equations
$$\frac{da}{dt} = \left.\frac{\partial T}{\partial z}\right|_{z=a-} \qquad \frac{\partial^2 T}{\partial z^2} = \frac{1}{\mathcal{S}}\frac{\partial T}{\partial t}$$

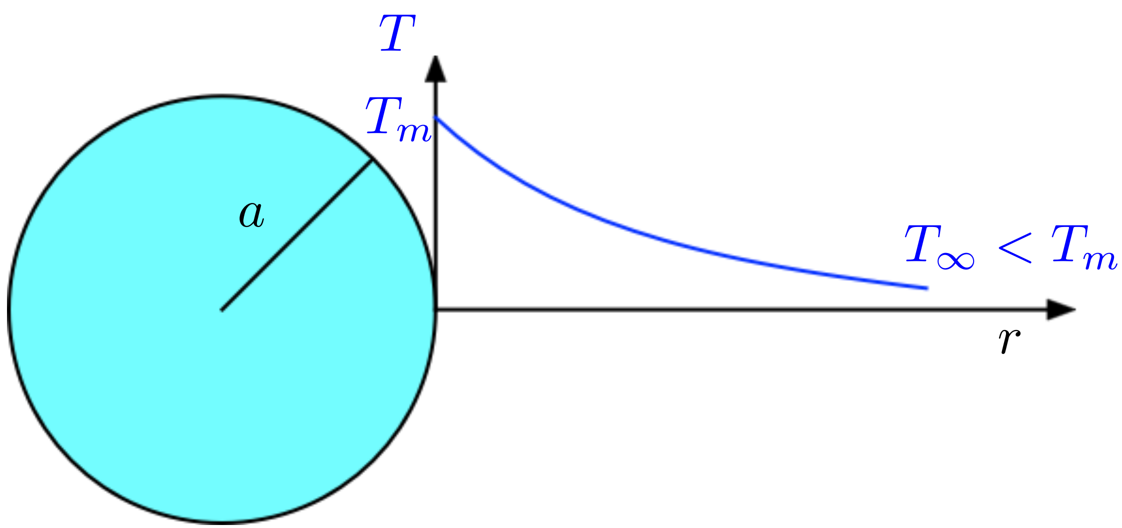


Stefan condition
$$\rho L \frac{da}{dt} = k\frac{T_m - T_0}{a}$$

$$a = \sqrt{\frac{2\kappa}{\mathcal{S}}t}$$

Agrees with full similarity solution when $\mathcal{S} \gg 1$

Sphere Growing into a Supercooled Melt

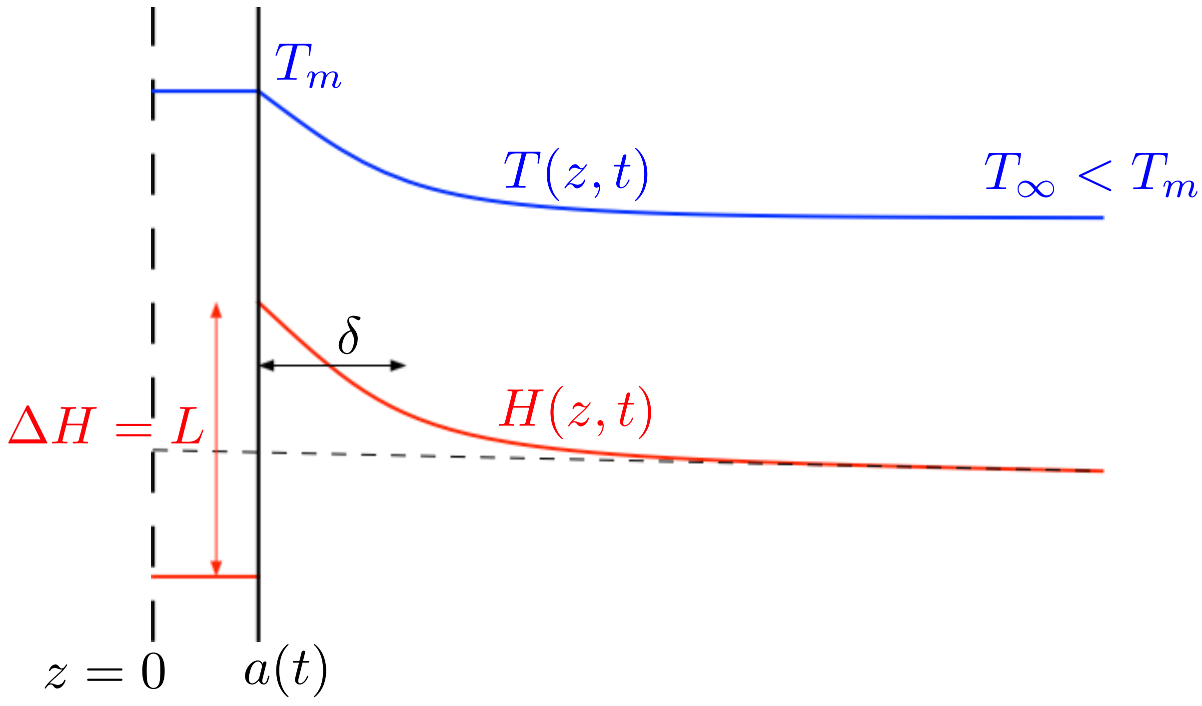


Using quasi-steady approximation $\nabla^2 T = 0 \quad \Rightarrow \quad T = T_\infty + (T_m - T_\infty)\frac{a}{r}$

Stefan condition $\rho L \frac{da}{dt} = -k \frac{\partial T}{\partial r}\bigg|_{r=a+} = k\frac{T_m - T_\infty}{a}$

$$a = \sqrt{\frac{2\kappa}{\mathcal{S}} t}$$

Planar Growth into a Supercooled Melt

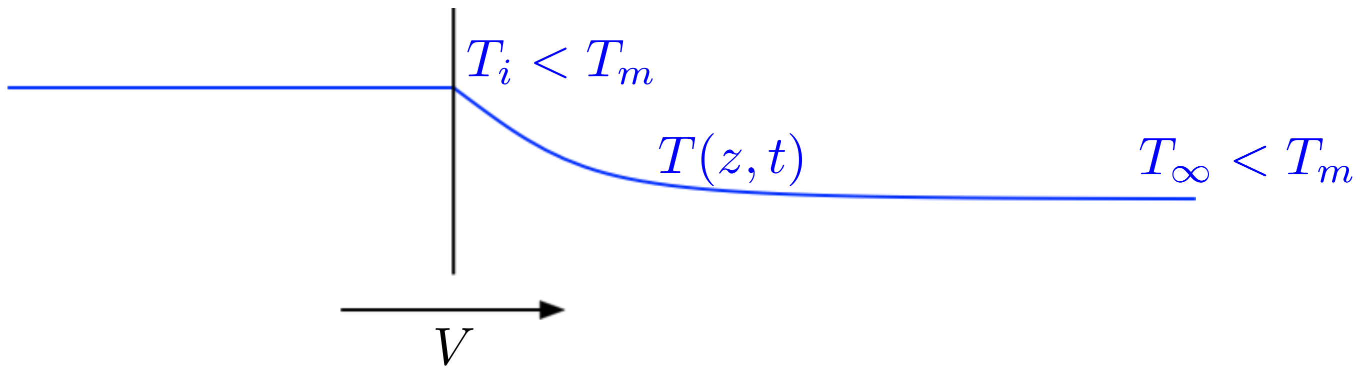


Energy conservation $$H \equiv [\rho c_p(T_m - T_\infty) - L]\, a + \int_a^\infty \rho c_p (T - T_\infty)\, dz = 0$$

Approximate $$\int_a^\infty T(z,t)\, dz \approx (T_m - T_\infty)\delta$$ gives $$\delta \approx (\mathcal{S} - 1)a$$

Stefan condition $$\rho L \frac{da}{dt} = k \frac{T_m - T_\infty}{\delta}$$ gives $$a = \sqrt{\frac{2\kappa}{\mathcal{S}(\mathcal{S}-1)} t}$$

Kinetic Undercooling



Kinetic growth $$V = \mathcal{G}(T_m - T_i)$$

In frame of interface $$-V\frac{\partial T}{\partial z} = \kappa\frac{\partial^2 T}{\partial z^2}$$ gives $$T = T_\infty + (T_i - T_\infty)\mathrm{e}^{-Vz/\kappa}$$

Stefan condition $$\rho L V = \rho c_p \kappa (T_i - T_\infty)\frac{V}{\kappa}$$ gives $$(T_i - T_\infty) = \mathcal{S}(T_m - T_\infty)$$

Whence $$V = \mathcal{G}(1 - \mathcal{S})(T_m - T_\infty)$$

Gibbs-Thomson Undercooling

Clausius-Clapeyron equation (equilibrium)

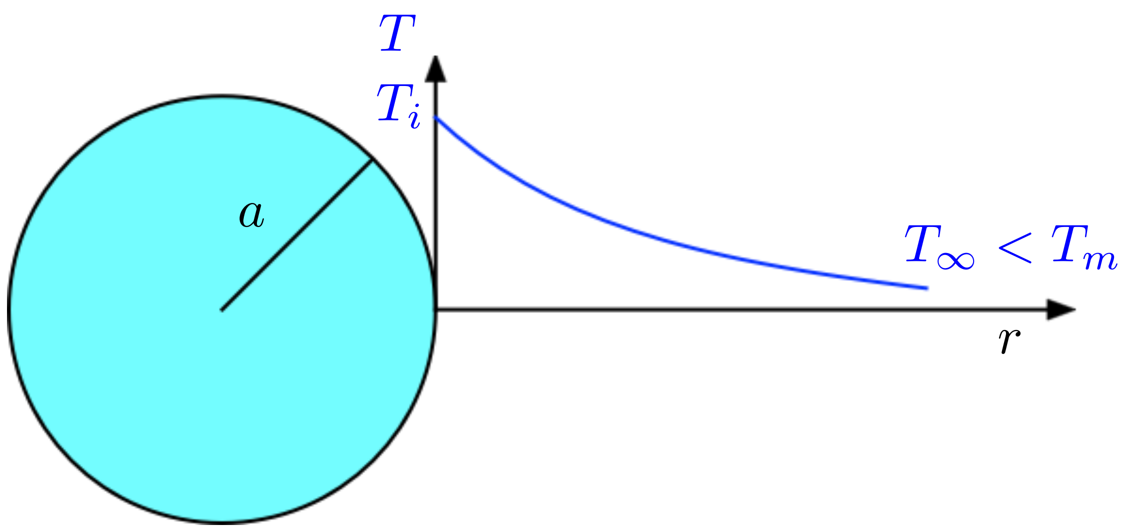
$$\rho_s L \frac{T_m - T_i}{T_m} = p_s - p_l + (p_l - p_m)\left[1 - \frac{\rho_s}{\rho_l}\right]$$

At a curved interface $\quad p_s - p_l = \gamma \mathcal{K} \quad$ where

Curvature $\quad \mathcal{K} \equiv \nabla \cdot \mathbf{n} = \frac{2}{a} \quad$ for a sphere of radius a

Interface temperature $\quad T_i = T_m - \frac{T_m}{\rho_s L}\gamma \mathcal{K} \equiv T_m - \Gamma \mathcal{K}$

Critical Nucleation Radius



Stefan condition

$$\rho L \frac{da}{dt} = k \frac{T_i - T_\infty}{a}$$

$$= k\left[(T_m - T_\infty)\frac{1}{a} - \frac{2\gamma T_m}{\rho_s L}\frac{1}{a^2} \right]$$

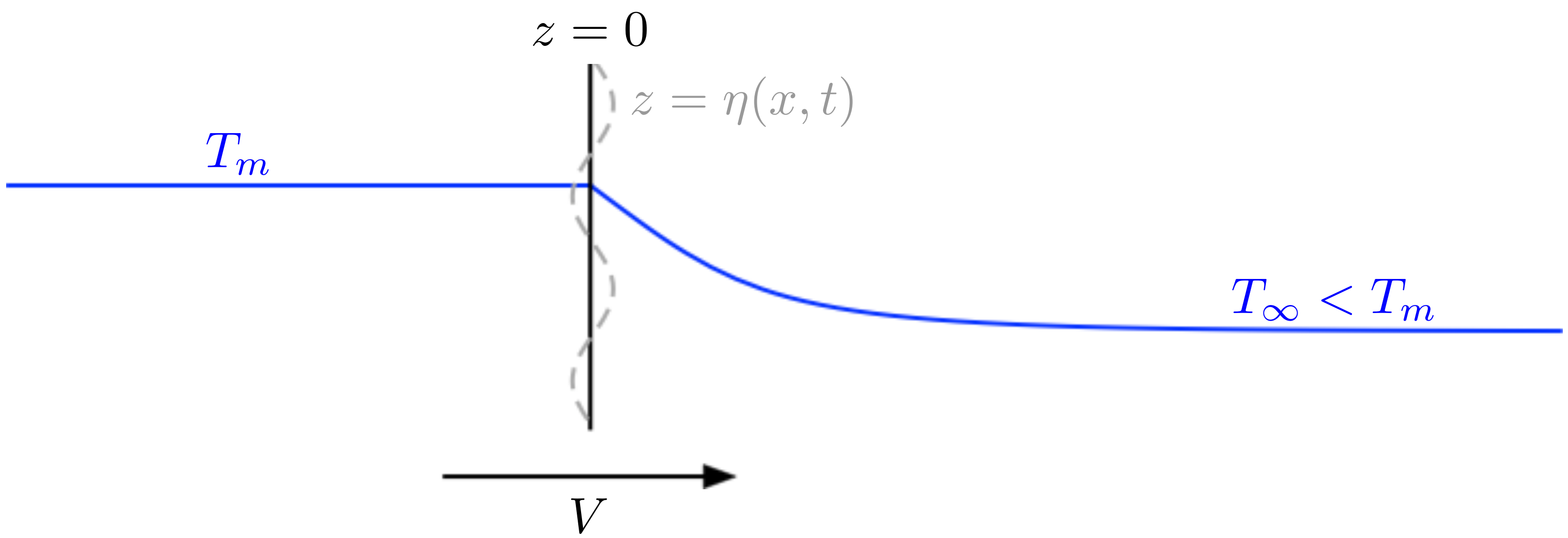
Sphere melts if

$$a < a_c \equiv \frac{2\gamma T_m}{\rho_s L (T_m - T_\infty)} \qquad \approx 6 \text{ nm} \quad \text{for} \quad \Delta T \approx 10^\circ\text{C}$$

Note

$$\Gamma = a_c \Delta T$$

Morphological Stability



Perturb interface $$z = \eta = \eta_0 e^{i\alpha x + \sigma t}$$

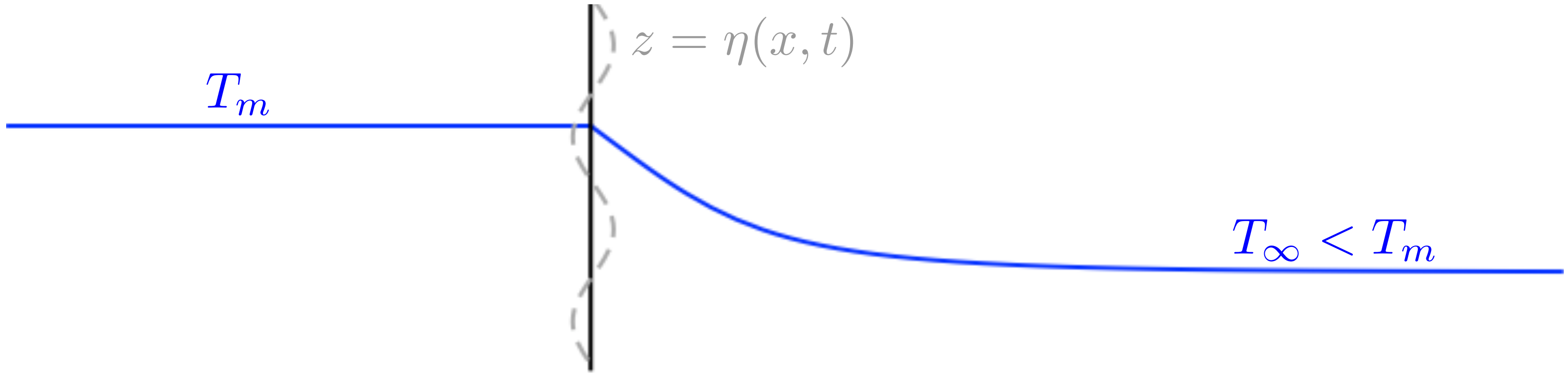
Perturbed temperature field $$T = T_\infty + (T_m - T_\infty)e^{-Vz/\kappa} + \theta(z,x,t)$$

Quasi-stationary perturbation
Large wavenumber

$$\nabla^2\theta = 0$$

$$\theta = \theta_0 e^{-\alpha z} e^{i\alpha x + \sigma t}$$

Morphological Stability



$$\eta = \eta_0 \mathrm{e}^{i\alpha x + \sigma t}$$

$$T = T_\infty + (T_m - T_\infty)\mathrm{e}^{-Vz/\kappa} + \theta_0 \mathrm{e}^{-\alpha z}\mathrm{e}^{i\alpha x + \sigma t}$$

Interfacial temperature
$$T_m - \Gamma\alpha^2\eta = T(\eta) = T_m - \Delta T\frac{V}{\kappa}\eta + \theta(0)$$

Stefan
$$\rho L(V + \sigma\eta) = -\rho c_p \kappa\left[-\Delta T\frac{V}{\kappa} + \Delta T\frac{V^2}{\kappa^2}\eta - \alpha\theta(0)\right]$$

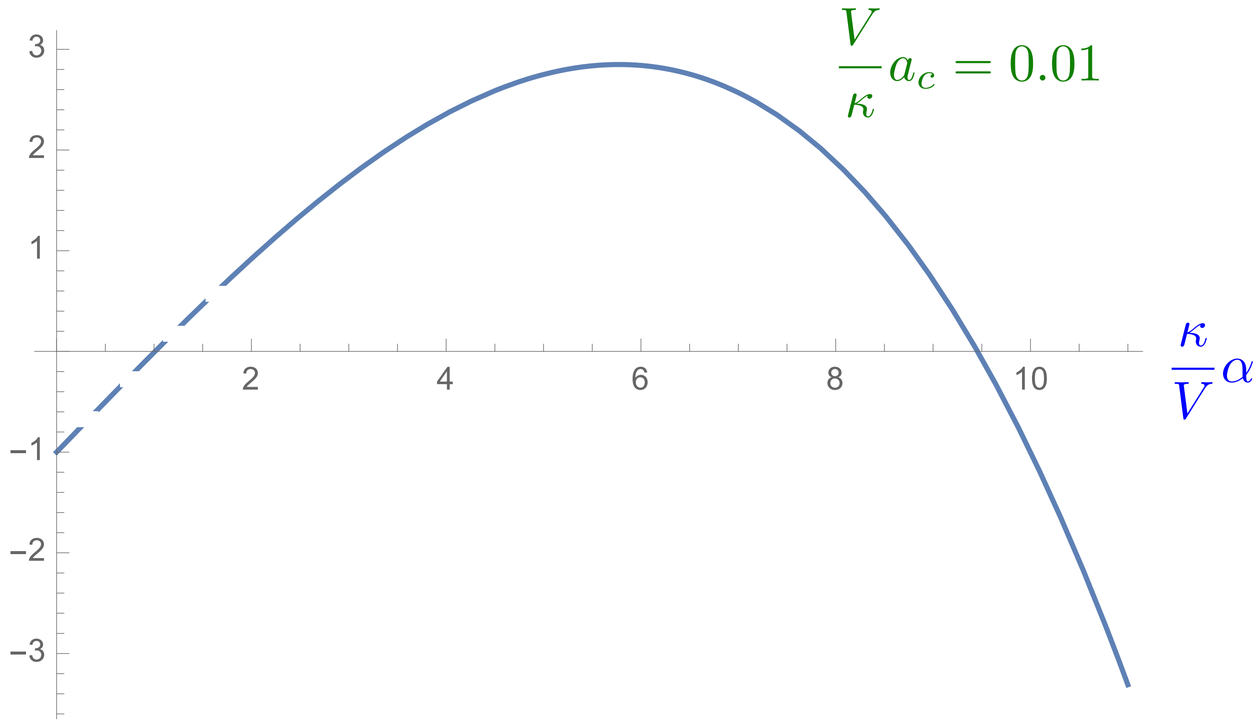
Linear terms
$$-a_c\alpha^2\eta_0 = -\frac{V}{\kappa}\eta_0 + \frac{\theta_0}{\Delta T}$$

$$\mathcal{S}\sigma\eta_0 = -\frac{V^2}{\kappa}\eta_0 + \kappa\alpha\frac{\theta_0}{\Delta T}$$

$$\mathcal{S}\sigma = -\frac{V^2}{\kappa} + \kappa\alpha\left(\frac{V}{\kappa} - a_c\alpha^2\right)$$

Dispersion Relation

$$\mathcal{S}\frac{\kappa}{V^2}\sigma = -1 + \frac{\kappa}{V}\alpha - \frac{\kappa^2}{V^2}a_c\alpha^3$$

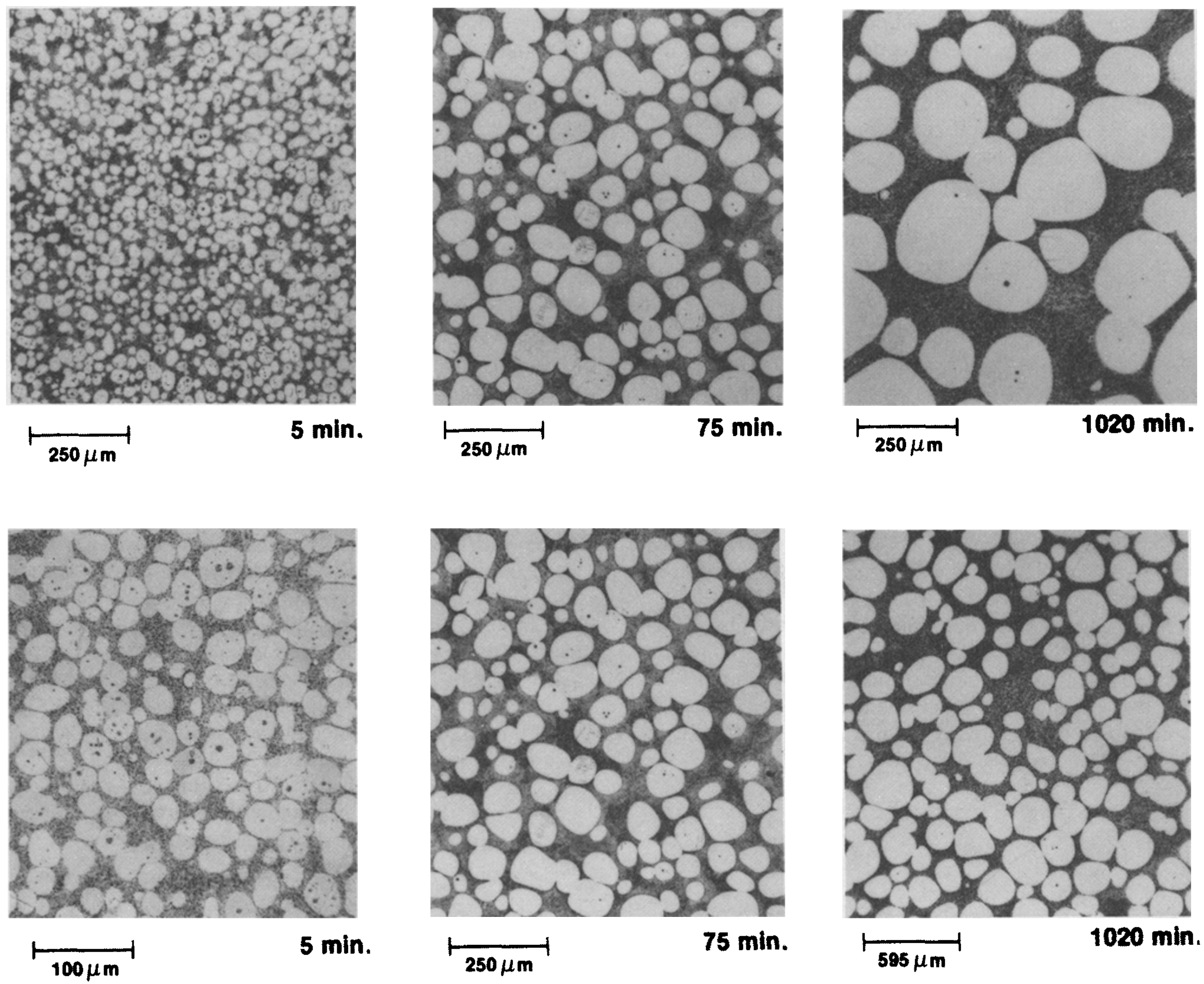


Maximum growth rate when $\frac{d\sigma}{d\alpha} = 0 \quad \Rightarrow \quad \alpha = \alpha_m \equiv \sqrt{\frac{3}{a_d a_c}}$

Wavelength $\lambda_m = \frac{2\pi}{\alpha_m} = \frac{2\pi}{\sqrt{3}}\sqrt{a_d a_c}$ where diffusion length $a_d = \frac{\kappa}{V}$

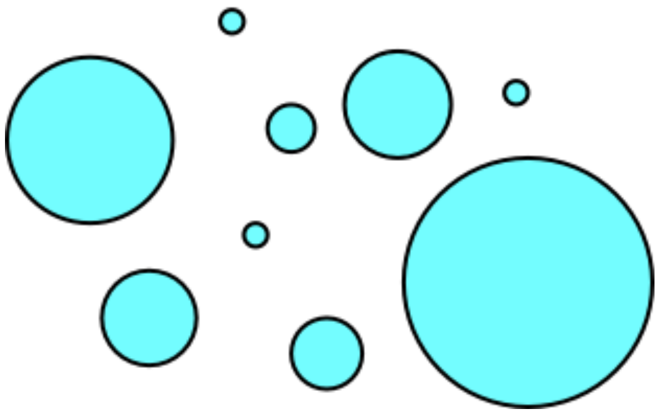
The Guardian. Photograph M. Scott Moon/AP

Ostwald Ripening



Hardy & Voorhees, Met. Trans. A 1988

Ostwald Ripening



Mean radius $a(t)$

Mean temperature $T(t)$

Stefan $$\rho L \dot{a} = k \left(\frac{T_m - \frac{2\Gamma}{a} - T}{a} \right) \qquad \rho \frac{L}{c_p} \dot{a} = k \frac{T_m - T}{a} - 2k \frac{\Gamma}{a^2}$$

Scaling $$\rho L \frac{a}{t} \sim k \frac{\Delta T}{a} \sim k \frac{\Gamma}{a^2}$$

Similarity solution $$a \sim \left(\frac{k\Gamma}{\rho L} t \right)^{1/3} \qquad \Delta T \sim \left(\frac{k\Gamma}{\rho L \Gamma^2} t \right)^{-1/3}$$

Summary

Diffusion-controlled solidification has thickness proportional to $\sqrt{\kappa t}$

At large Stefan number, thickness is proportional to $\sqrt{\dfrac{\kappa t}{\mathcal{S}}} \ll \sqrt{\kappa t}$

which allows use of the quasi-stationary approximation

Rapid solidification is limited by molecular kinetics, giving $T_i < T_m$

Solidification into a supercooled melt is morphologically unstable

Surface energy mitigates morphological instability and ultimately leads to coarsening

Morphological Stability