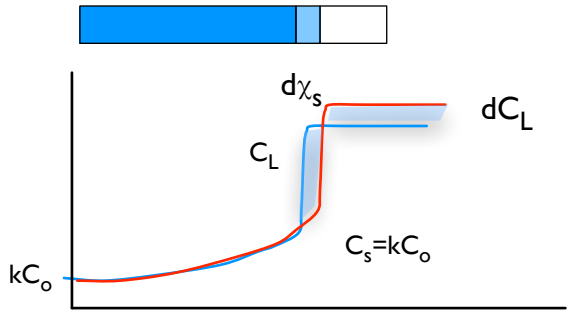


Solute Redistribution

Topic 6

M.S Darwish

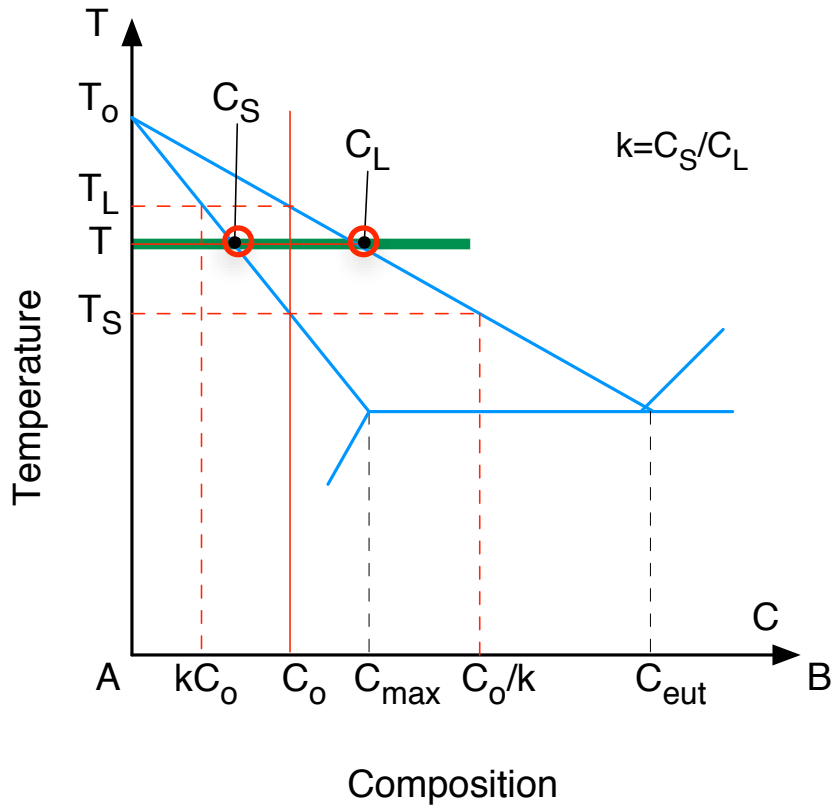
MECH 636: Solidification Modelling

Introduction

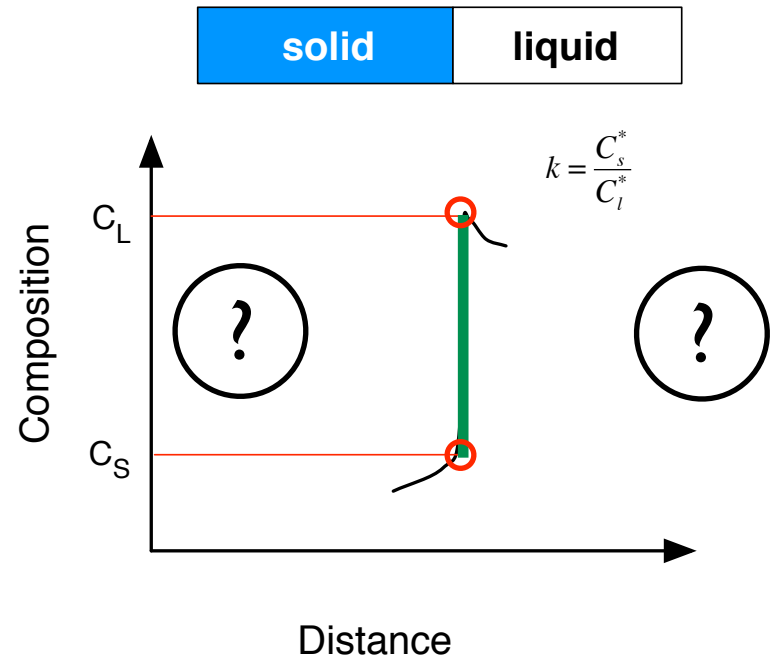
- Local Equilibrium
  - Solidus and liquidus curves
  - Equilibrium distribution coefficient, k_0
  - Tie–line "jump"
- Macrosegregation at Planar Interfaces
  - Gulliver–Scheil equations
    - » Assumptions
    - » Mass balance
    - » Limitations
  - Transport–limited segregation
    - » Initial Transient
    - » Steady–state solute distribution
    - » Terminal Transient
- Effects of Stirring & Convection
  - Burton–Prim–Slichter Theory, k_{BPS}

Lever Rule

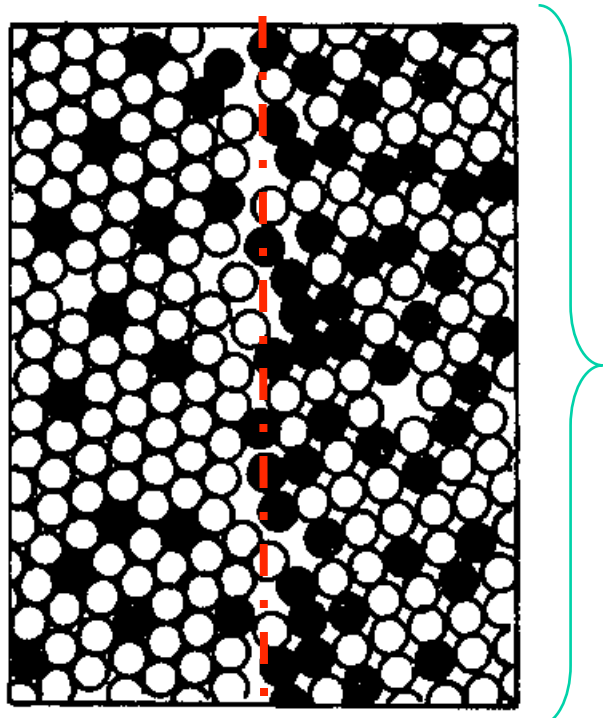
Introduction



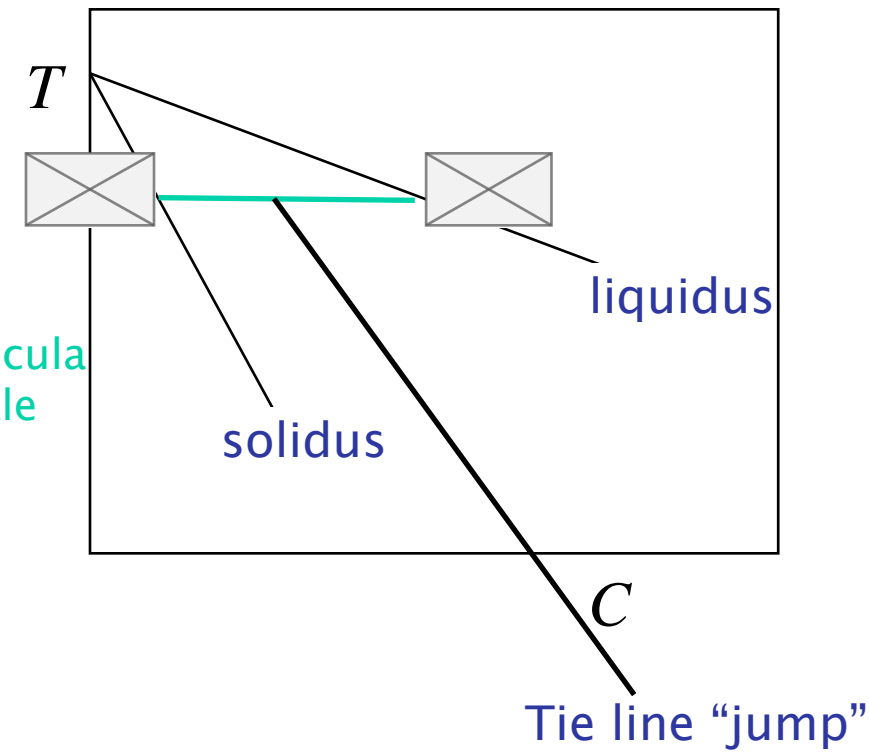
In practice equilibrium is maintained at the solid liquid interface where composition agrees with the phase diagram

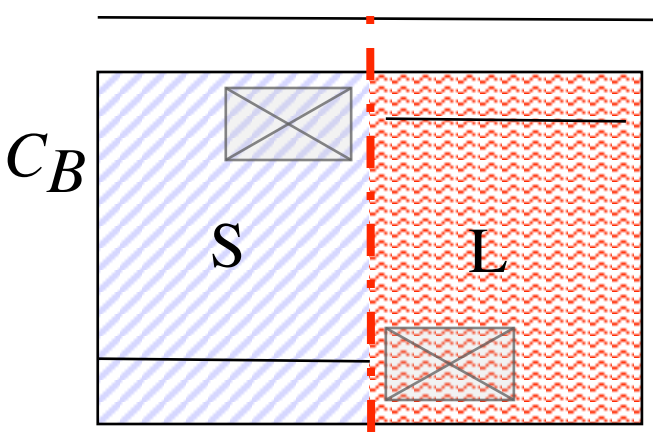


Equilibrium at S/L



Molecular scale

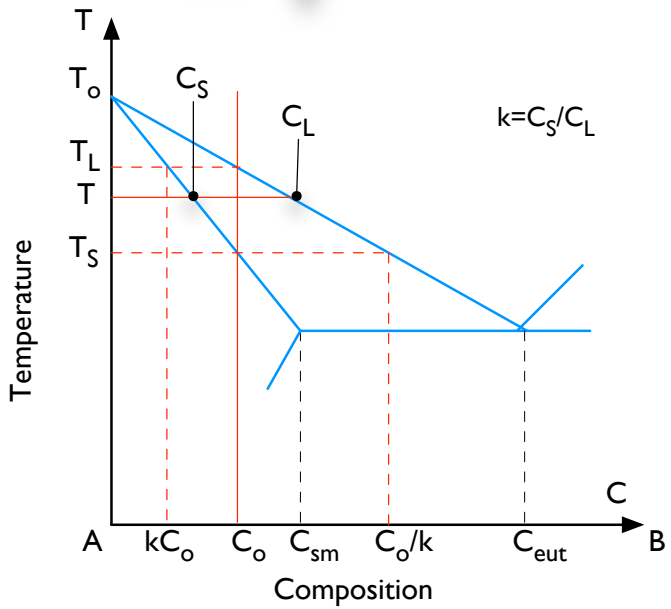




Continuum scale

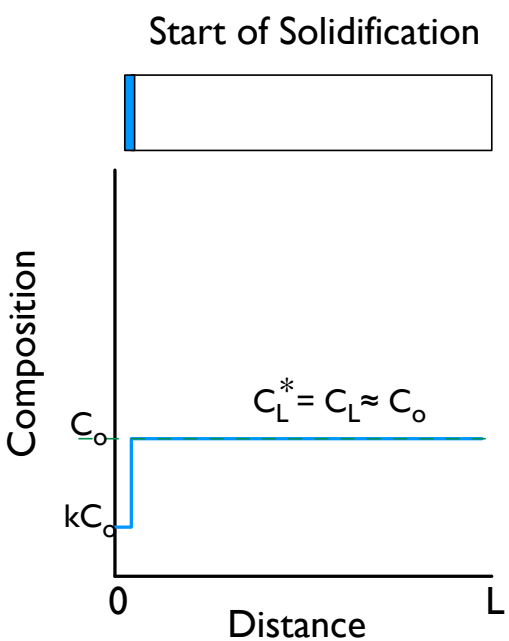
?

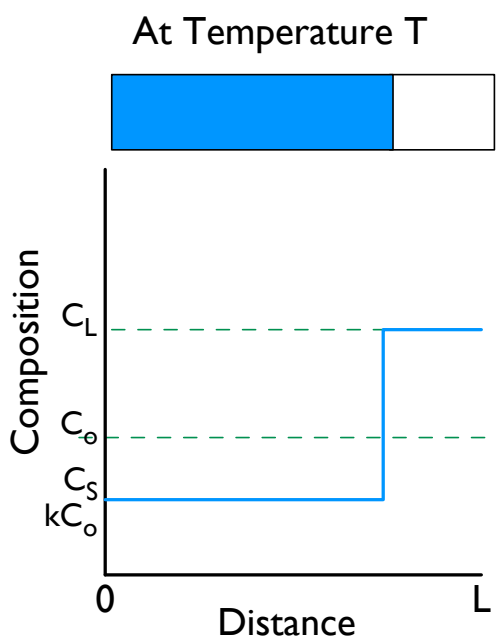
Equilibrium Solidification

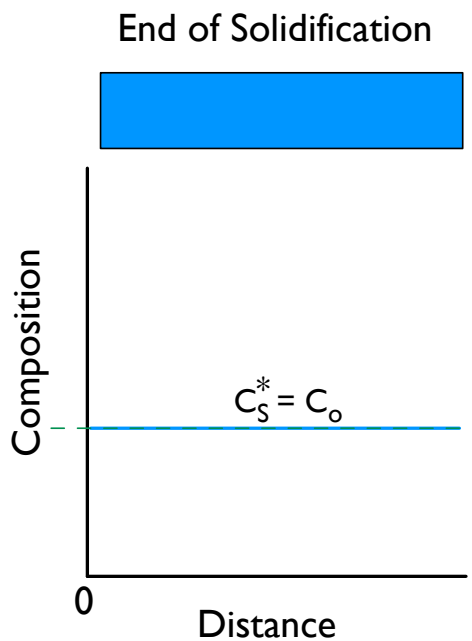


Complete Diffusion in Solid and Liquid Respectively

$$\chi_s C_s + \chi_l C_l = C_o$$ Lever Rule





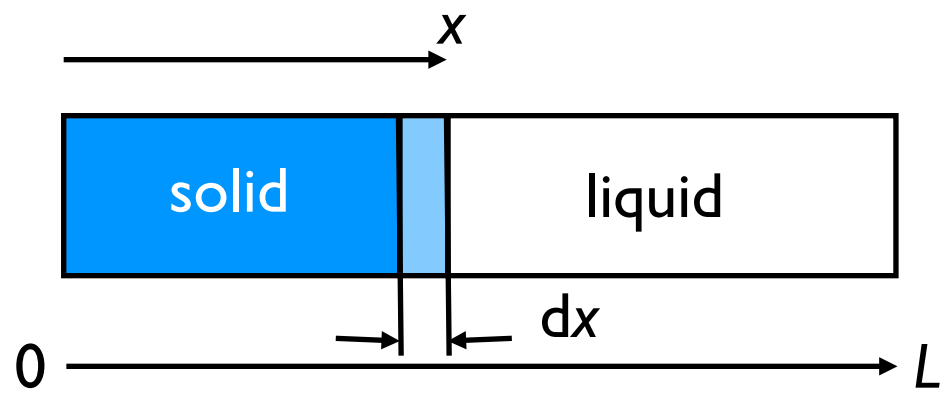


Schiel Rule

Gulliver-Scheil Differential Mass Balance

- Although local interfacial equilibrium generally holds during solidification, the system cannot remain in "global" equilibrium because diffusion rates in the solid are too slow.

- G. Gulliver (1921) and E. Scheil (1942) both assumed:
  - Perfect mixing in liquid $\left(C_l = C_l^*\right)$
  - No diffusion in solid
  - Local equilibrium at S/L interface



$$\left(C_s^* - C_l^*\right)\mathrm{d}\,x = \left(L - x\right)\mathrm{d}C_l$$

$$C_l^*\left(\frac{C_s^*}{C_l^*} - 1\right)\mathrm{d}\,x = \left(L - x\right)\mathrm{d}\,C_l$$

$$C_l^*\left(k - 1\right)\mathrm{d}x = \left(L - x\right)\mathrm{d}\,C_l$$

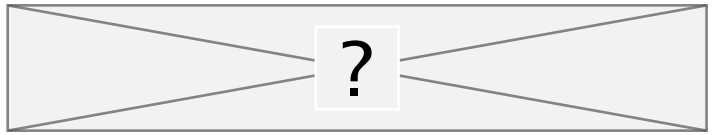
$$\left(k - 1\right)\int_0^x \frac{\mathrm{d}x'}{\left(L - x'\right)} = \int_{C_0}^{C_l} \frac{\mathrm{d}\,C_l'}{C_l'}$$

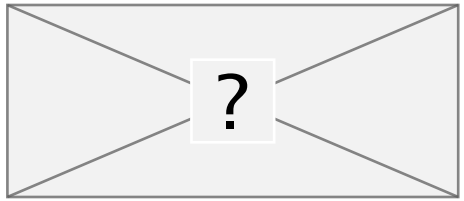
note that $\chi_s = \frac{x}{L}$

Gulliver-Scheil Segregation Equation

- The Gulliver–Scheil mass balance eventually leads to non–physical predictions as $\chi_s \rightarrow 1$.

- The phase diagram provides limits to how high the concentrations, C_l or C_s can rise due to segregation. Second phase formation (generally from eutectic reaction) then occurs.



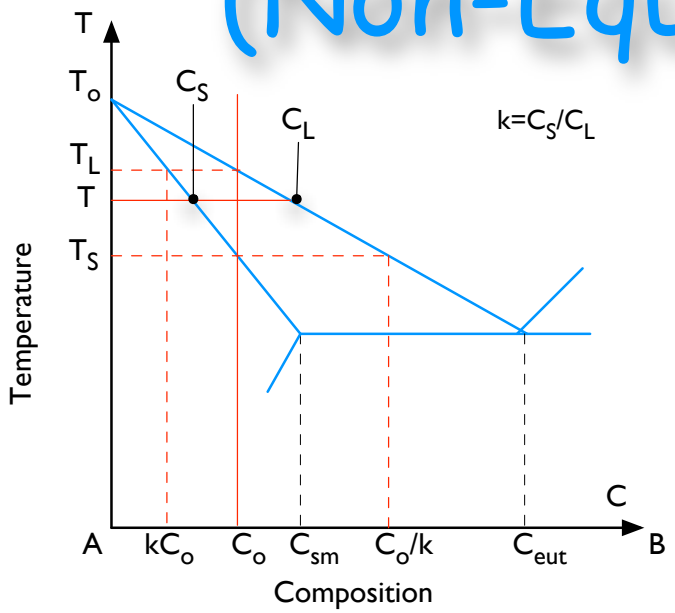


$$(1-\chi_s)^{(k_0-1)} = \frac{C_l}{C_0}$$

Where $\chi_s = \frac{x}{L}$

Gulliver–Scheil is *independent* of the shape of the S/L interface!

No Solid Diffusion (Non-Equilibrium Lever Rule)



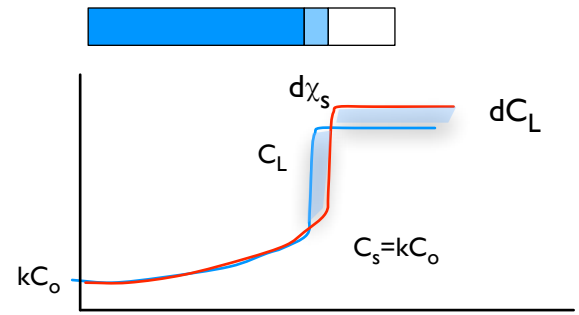
solidification of $d\chi_s$

$$\left(C_l - C_s^*\right)d\chi_s = \left(1-\chi_s\right)dC_l$$

rejected solute from solid

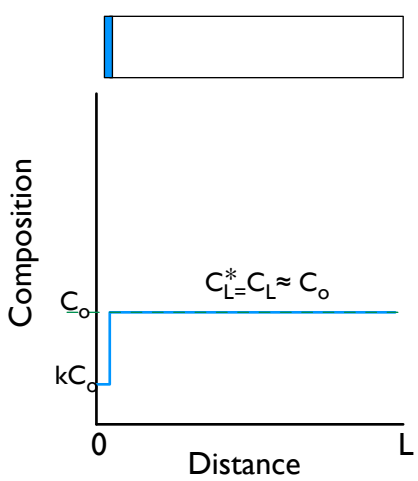
solute increase in liquid

$$\int_0^{\chi} \frac{d\chi}{1-\chi} = \int_{C_o}^{C_l} \frac{dC_l}{C_l(1-k)}$$

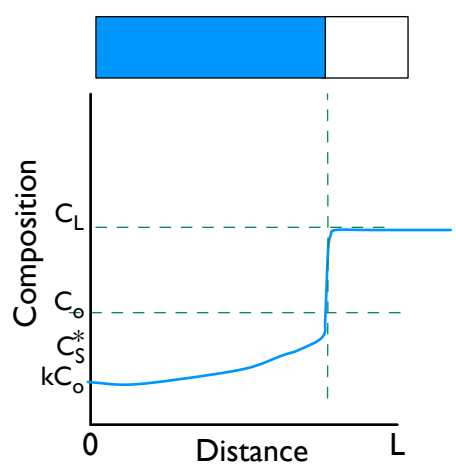


$$C_l = C_o\left(1-\chi_s\right)^{k-1} \quad C_s^* = kC_o\left(1-\chi_s\right)^{k-1}$$ Scheil relation

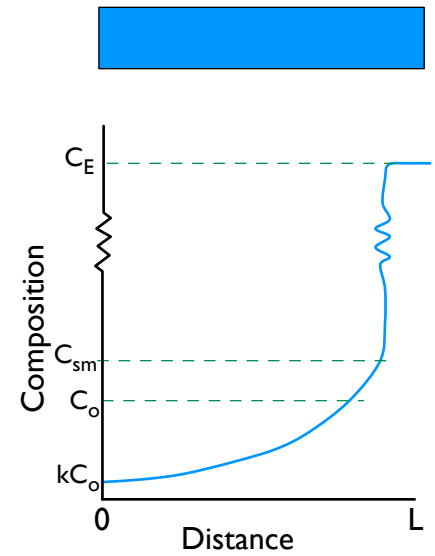
Start of Solidification



At Temperature T

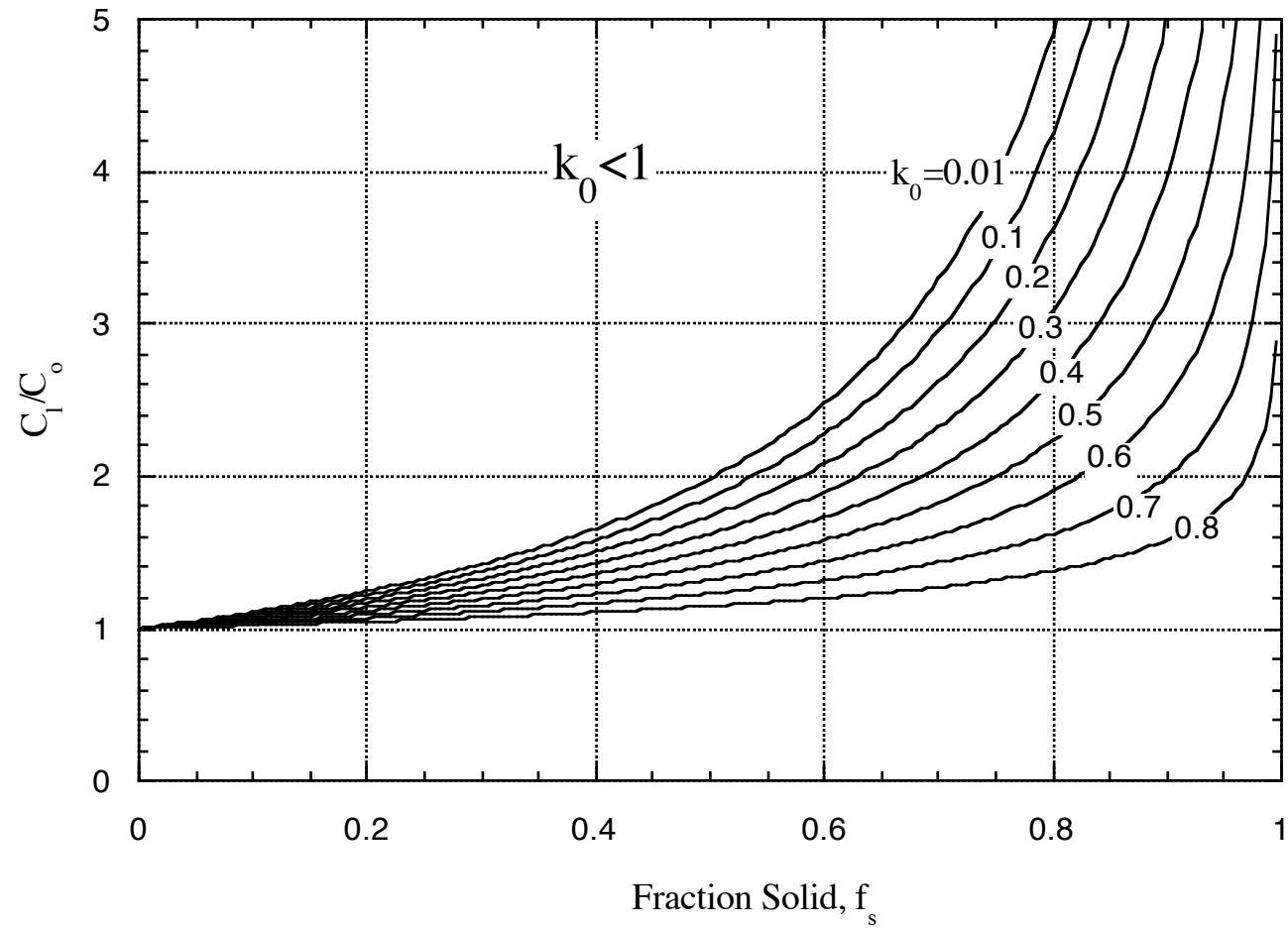


End of Solidification



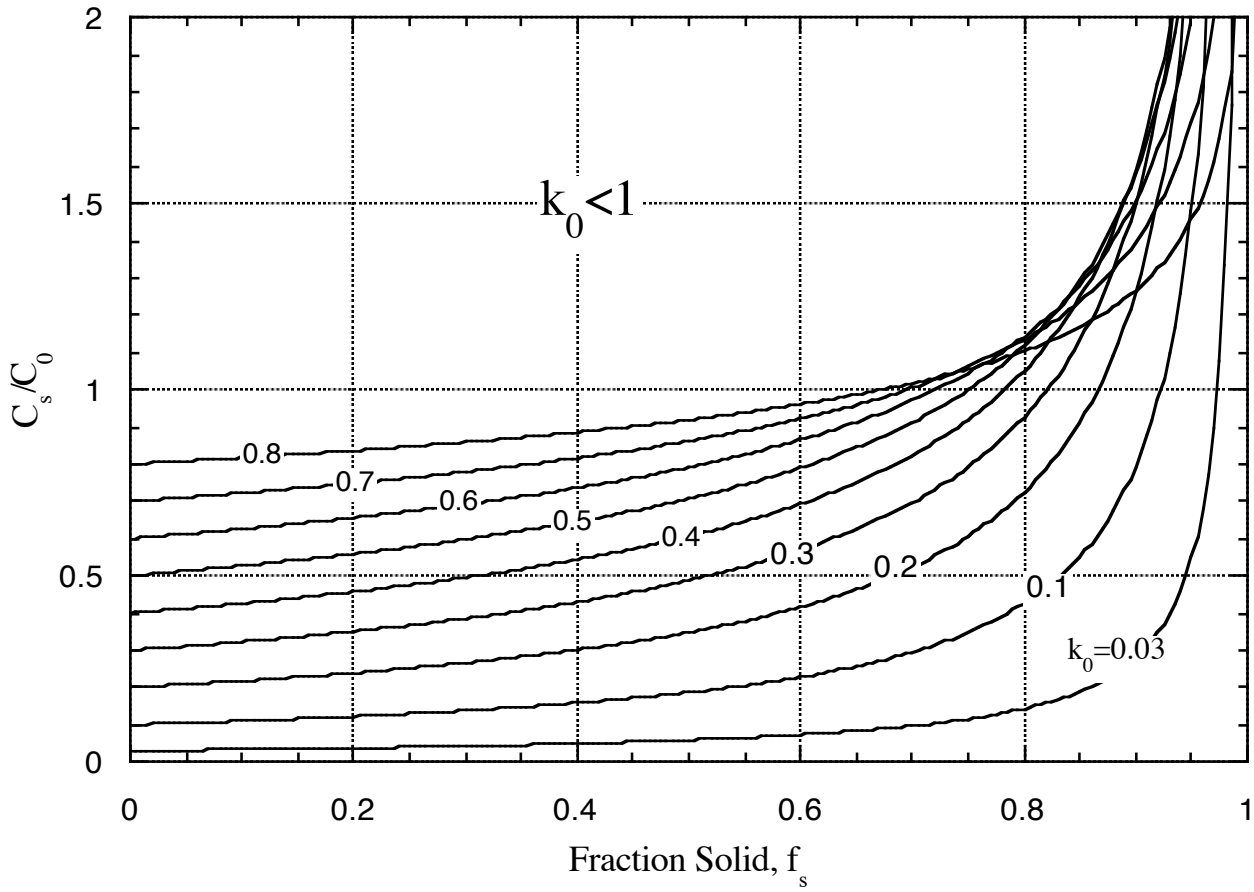
Gulliver-Scheil Segregation Equation

$$(1-\chi_s)^{(k_0-1)} = \frac{C_l}{C_0}$$



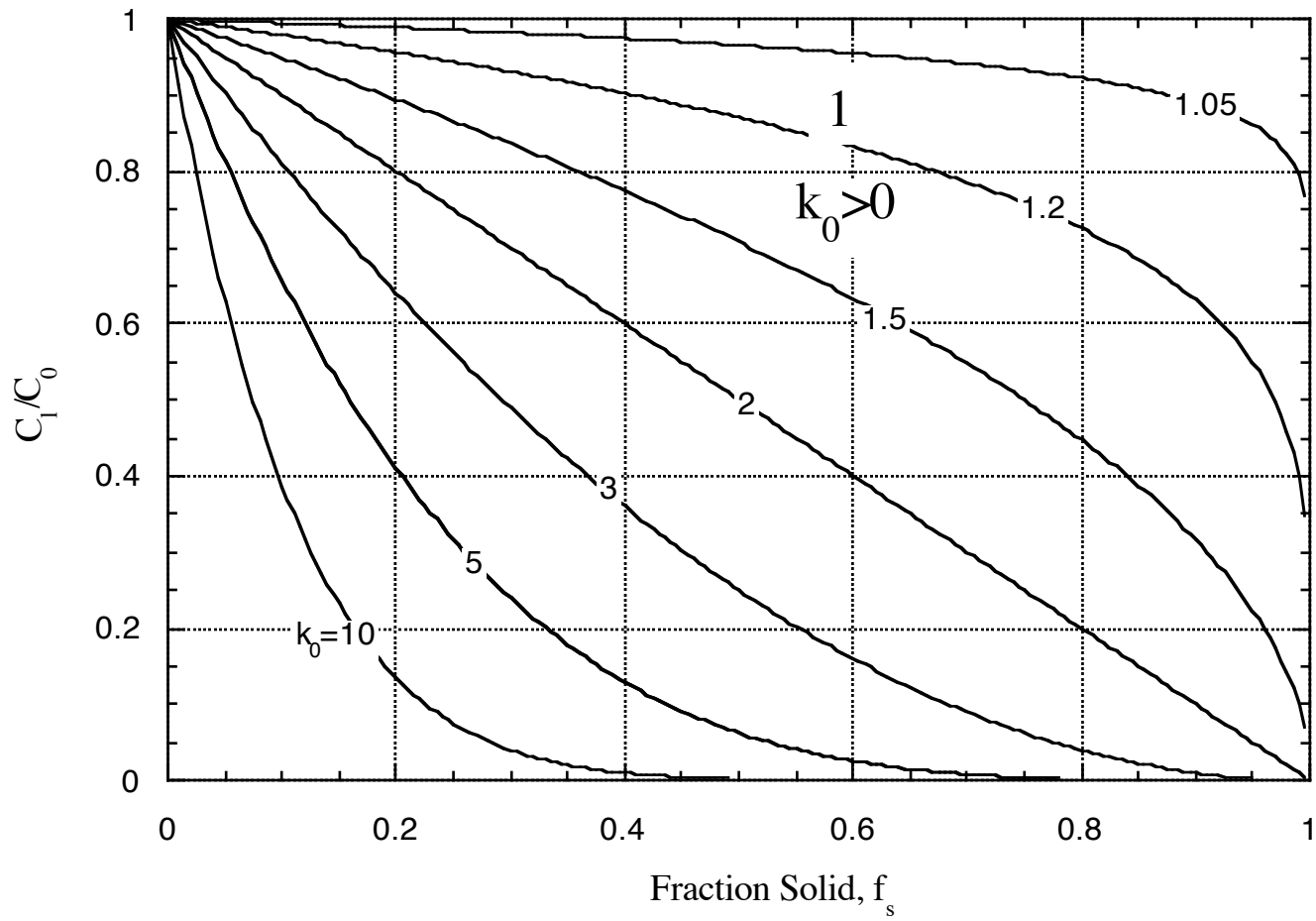
Gulliver-Scheil Segregation Equation

$$k_0(1-\chi_s)^{(k_0-1)} = \frac{C_s}{C_0}$$



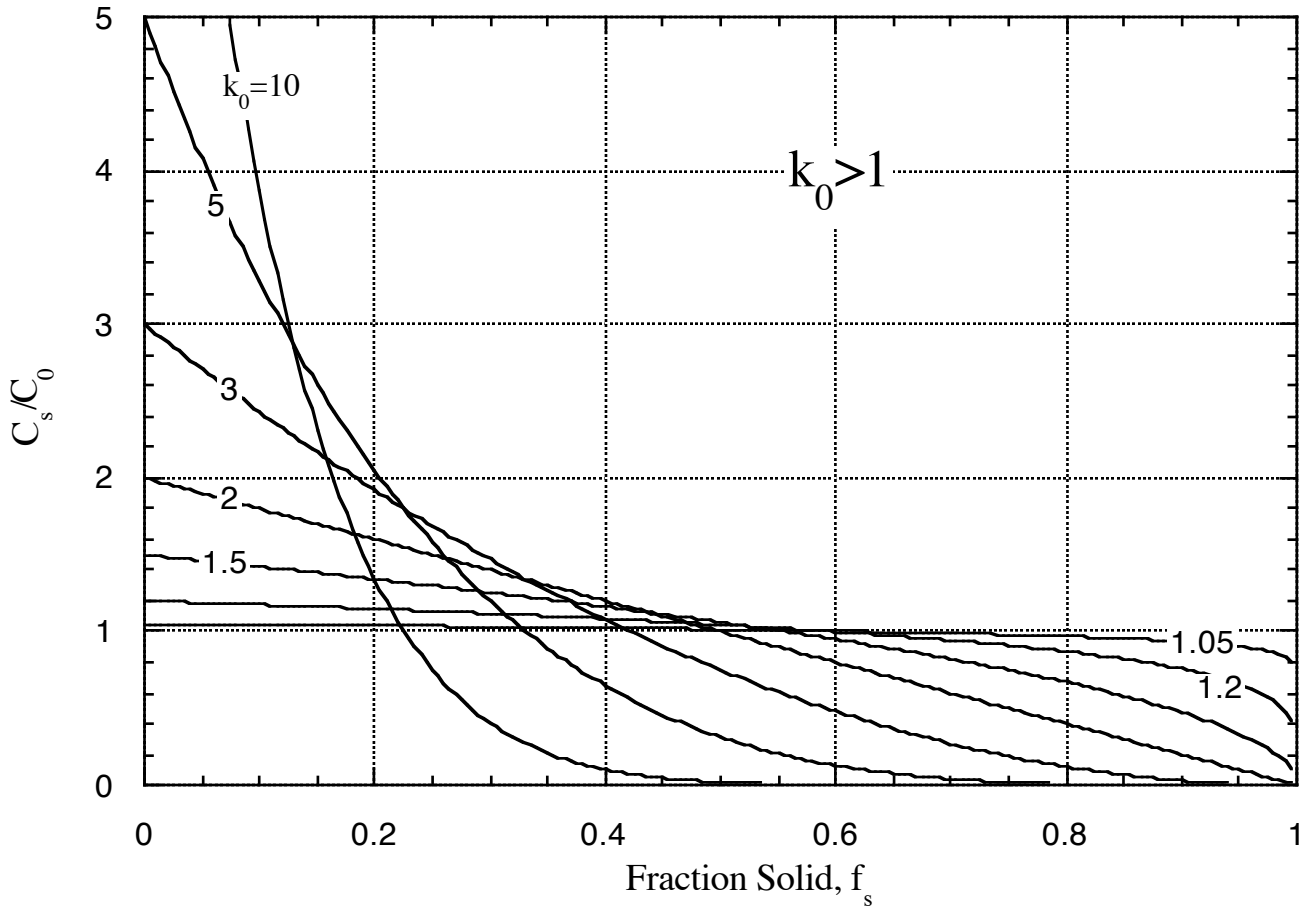
Gulliver-Scheil Segregation Equation

$$(1-\chi_s)^{(k_0-1)} = \frac{C_l}{C_0}$$

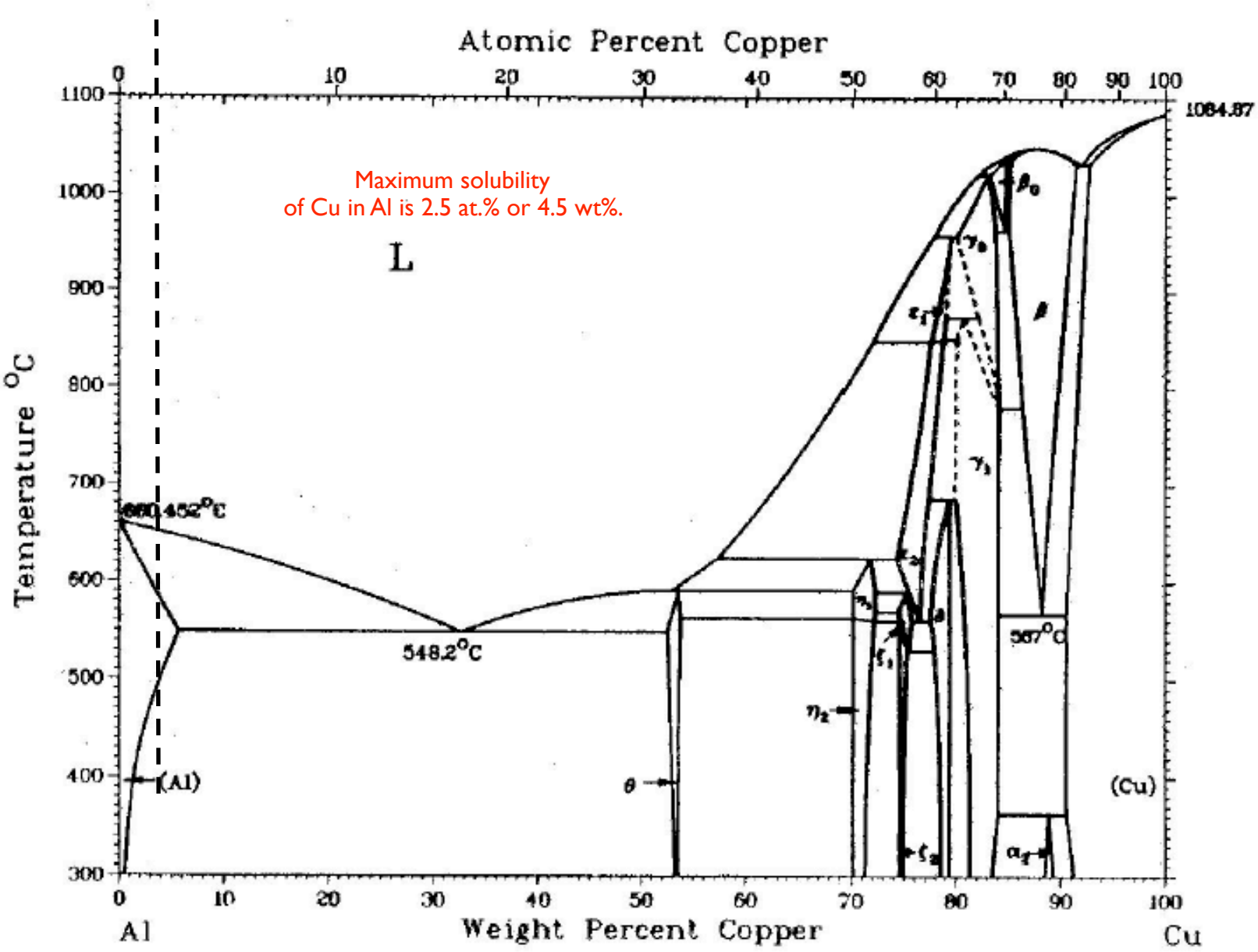


Gulliver-Scheil Segregation Equation

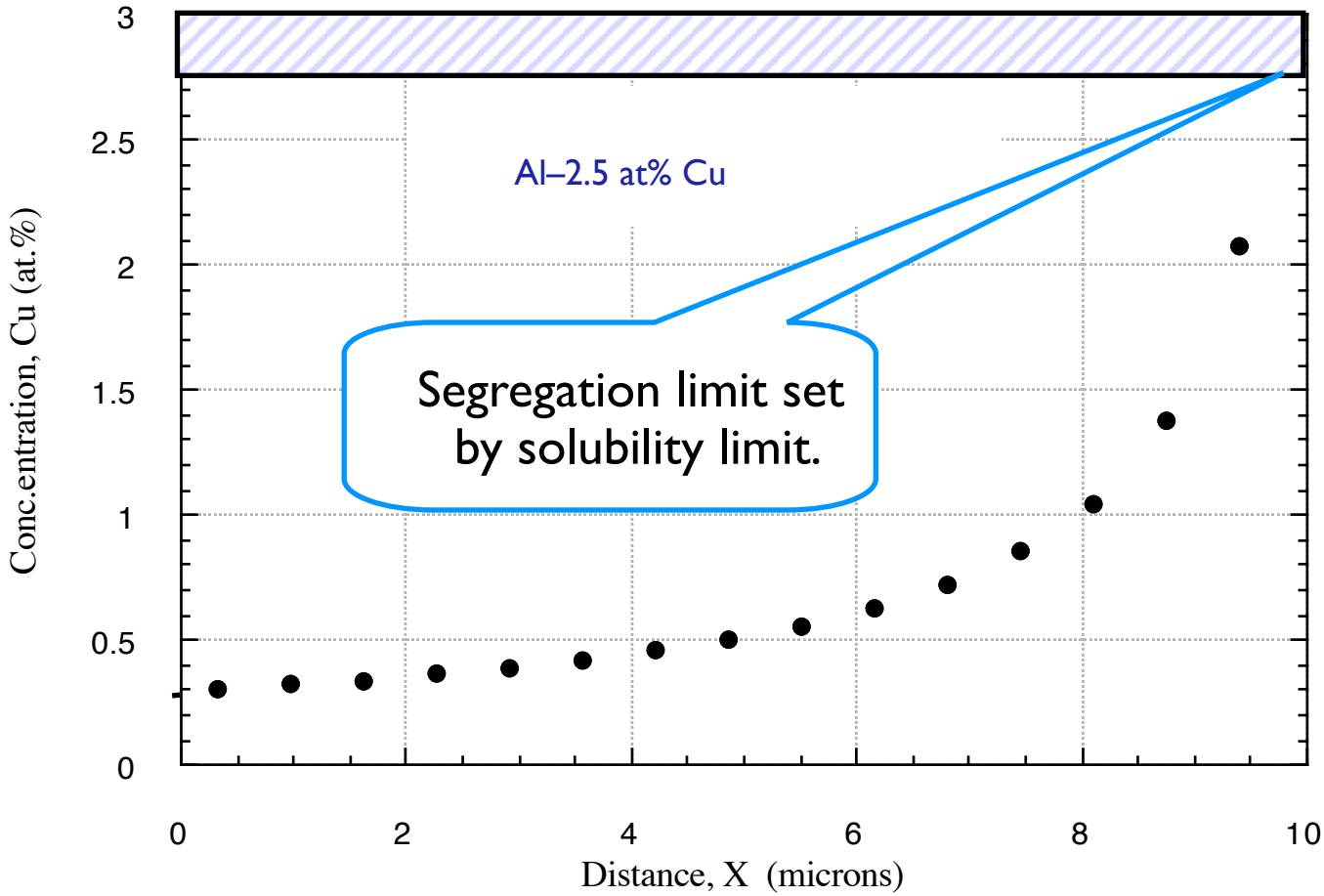
$$k_0(1-\chi_s)^{(k_0-1)} = \frac{C_s}{C_0}$$



Al-Cu Phase Diagram

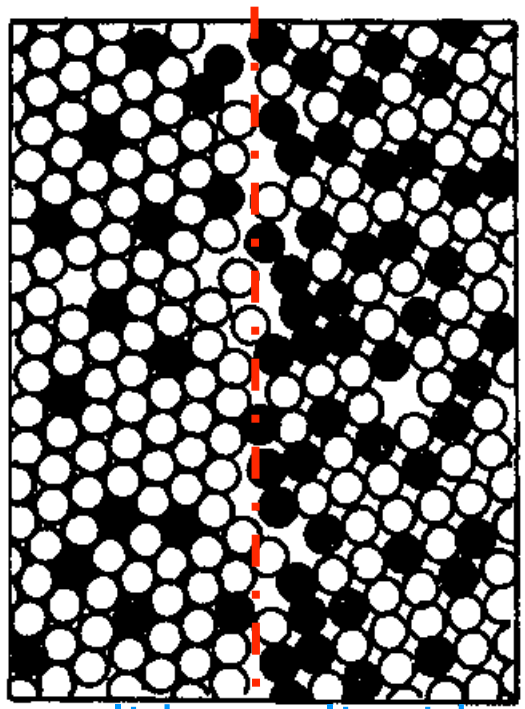


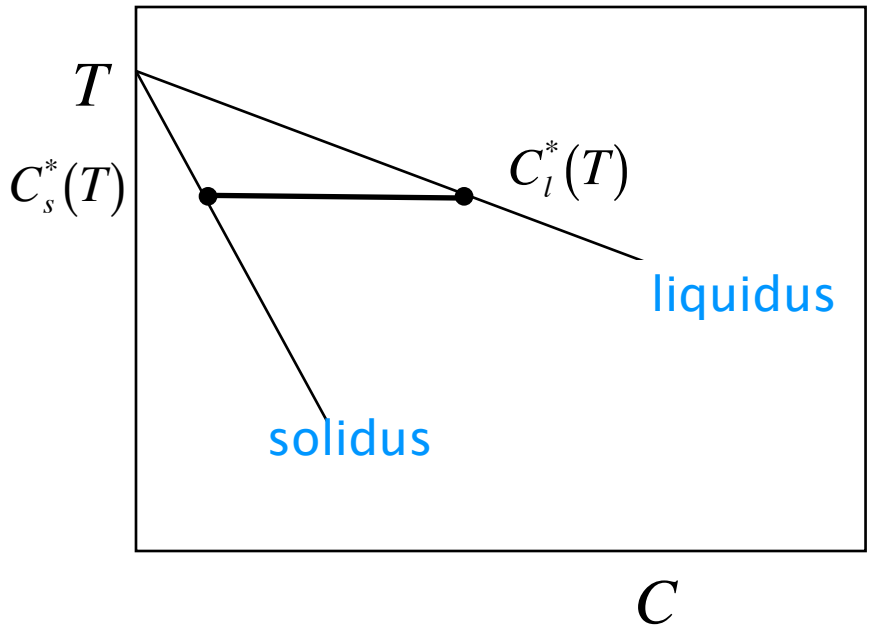
Application of Gulliver-Scheil Segregation

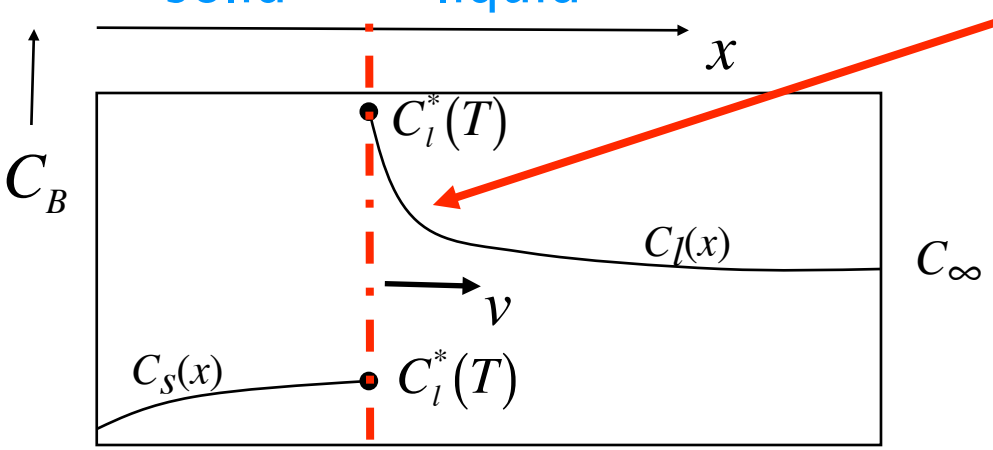


Plane Front Solidification

Moving S/L

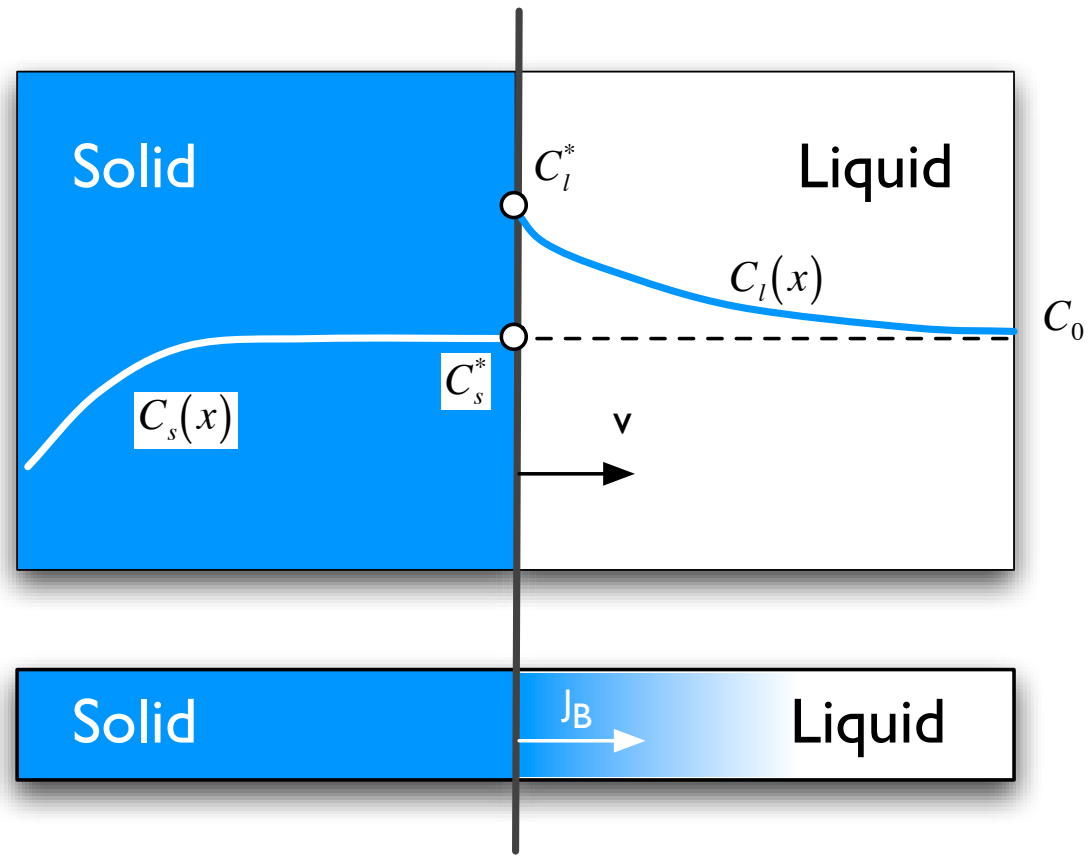




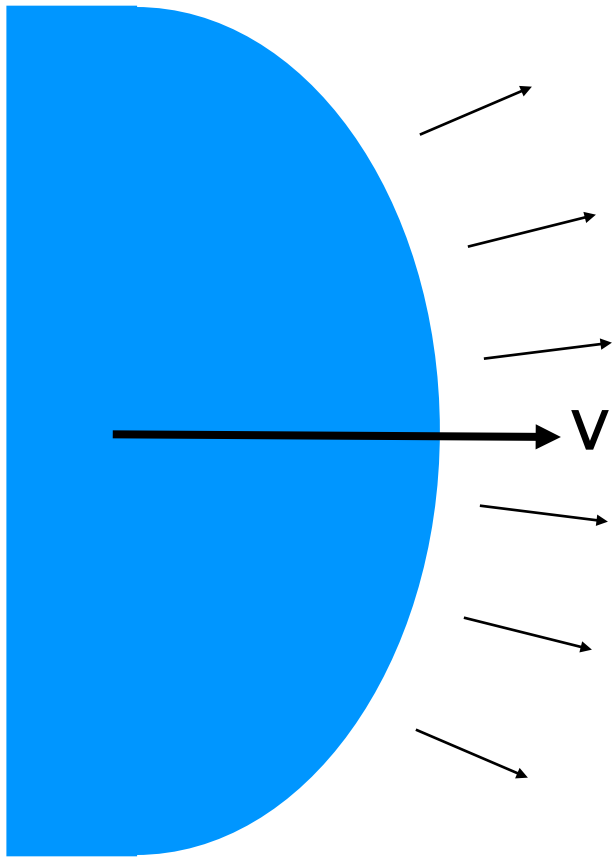


Solute boundary layer develops ahead of the advancing S/L interface.

Steady State Solute Boundary Layer

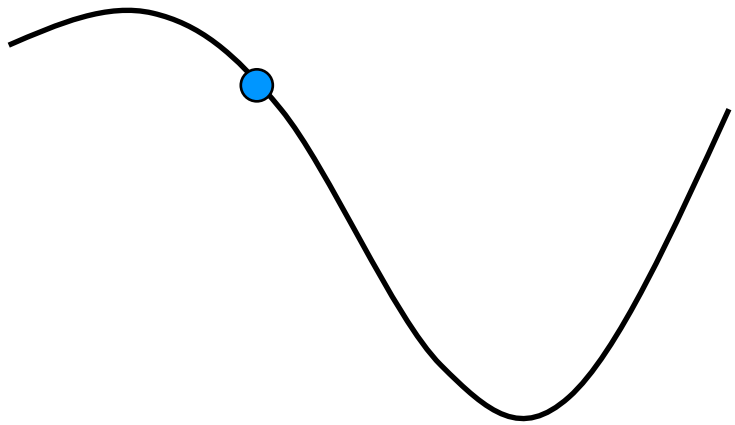


Computing the Steady-State Solute Profile



- Consider Geometry
- Apply Fick's second law
- Find the general SS solution
- Apply boundary conditions
- Find solute gradient at the interface

Apply Fick's Law and SS Condition

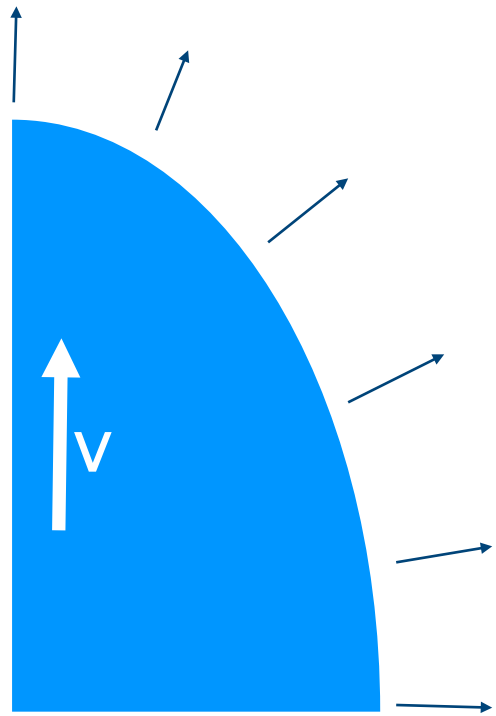


$$\frac{dC}{dt} = \nabla \cdot D\nabla C \approx D\nabla^2 C$$

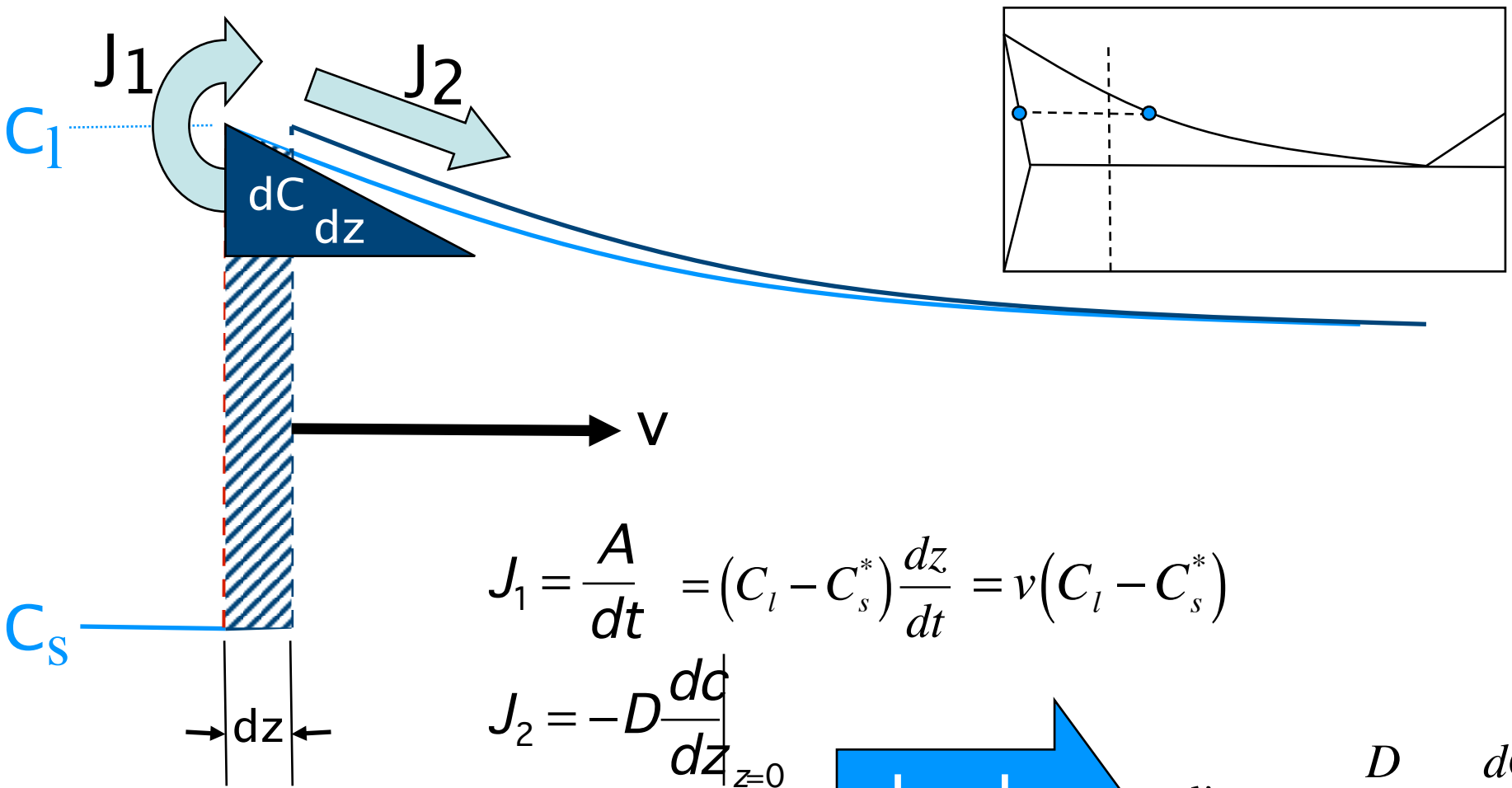
In 1-D

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

$$\frac{dC}{dt} = D\frac{\partial^2 C}{\partial z} = 0$$



Apply a Flux balance at Interface



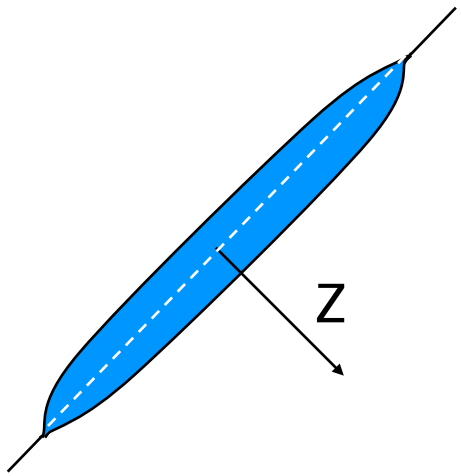
$$J_1 = \frac{A}{dt} = (C_l - C_s^*)\frac{dz}{dt} = v(C_l - C_s^*)$$

$$J_2 = -D\frac{dc}{dz}\Big|_{z=0}$$

J1=J2

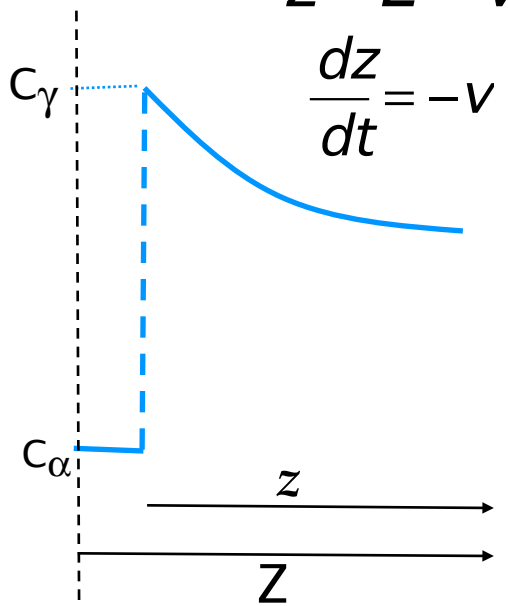
$$v = -\frac{D}{(C_l - C_s^*)}\frac{dC}{dz}\Big|_{z=0}$$

Example 1



$$z = Z - vt$$

$$\frac{dz}{dt} = -v$$



$$c = c(Z,t) = c(z(t))$$

$$dc = \frac{\partial c}{\partial z}dZ + \frac{\partial c}{\partial t}dt$$

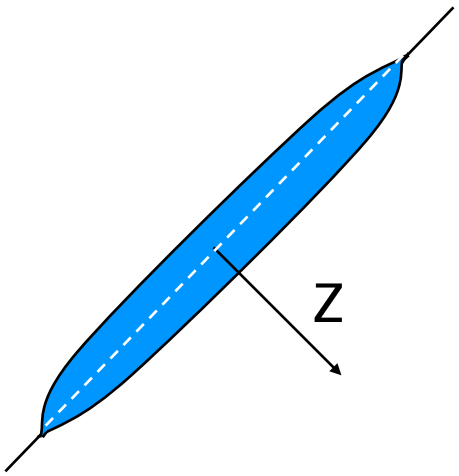
$$\frac{dc}{dt} = \frac{\partial c}{\partial z}\frac{dZ}{dt} + \frac{\partial c}{\partial t}$$

$$D\frac{\partial^2 c}{dz^2} = -\frac{\partial c}{\partial z}v + \frac{\partial c}{\partial t}$$

$$\frac{1}{D}\frac{\partial c}{\partial t} = \frac{\partial^2 c}{dz^2} + \frac{v}{D}\frac{\partial c}{\partial z}$$

$$\frac{\partial^2 c}{dz^2} + \frac{v}{D}\frac{\partial c}{\partial z} = 0$$

$$c(z) = a_0 + a_1 \exp\left(-\frac{v}{D}z\right)$$



$$c(z) = a_0 + a_1 \exp\left(-\frac{v}{D} z\right)$$

Apply Boundary conditions to evaluate the constants:

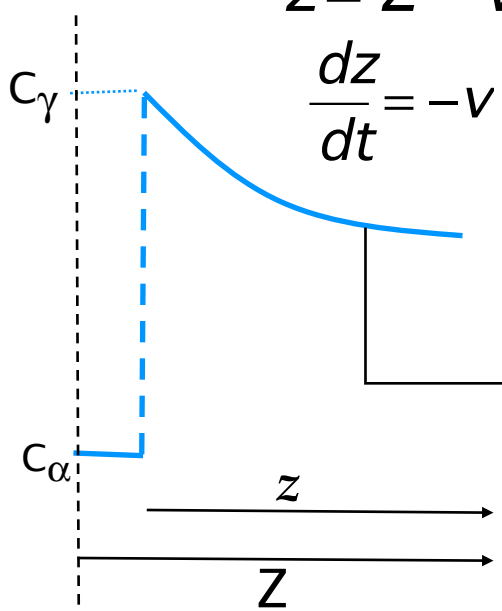
$$c(z=\infty) = C_0 \qquad c(z=0) = C_\gamma$$

$$a_0 = C_0 \qquad a_1 = C_\gamma - C_0$$

$$\boxed{c(z) = C_0 + (C_\gamma - C_0)\exp\left(-\frac{v}{D} z\right)}$$

$$z = Z - vt$$

$$\frac{dz}{dt} = -v$$



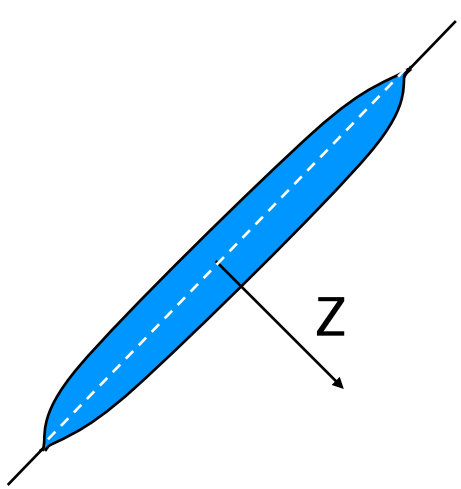
Flux Balance at SS: $v(C_\gamma - C_\alpha) = -D\left(\frac{\partial c}{\partial z}\right)_{z=0}$

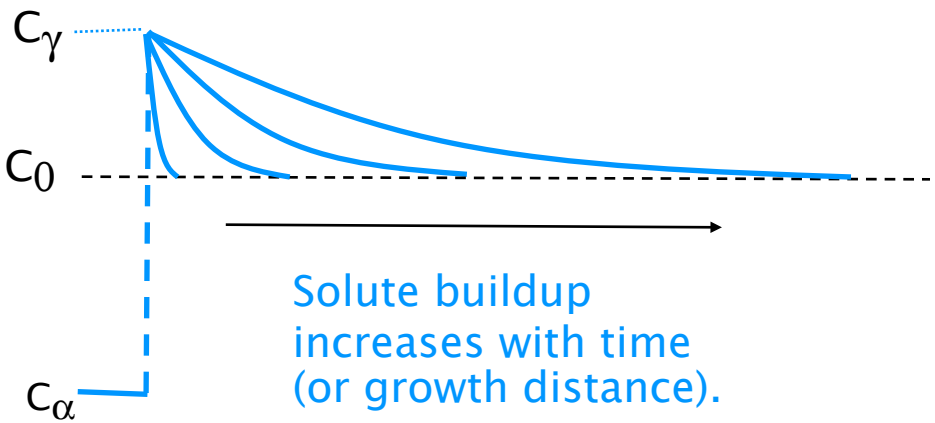
Evaluate dc/dz: $\left.\frac{\partial c}{\partial z}\right|_{z=0} = -\frac{v}{D}(C_\gamma - C_0)$

$$v(C_\gamma - C_\alpha) = -D\left[-\frac{v}{D}(C_\gamma - C_0)\right]$$

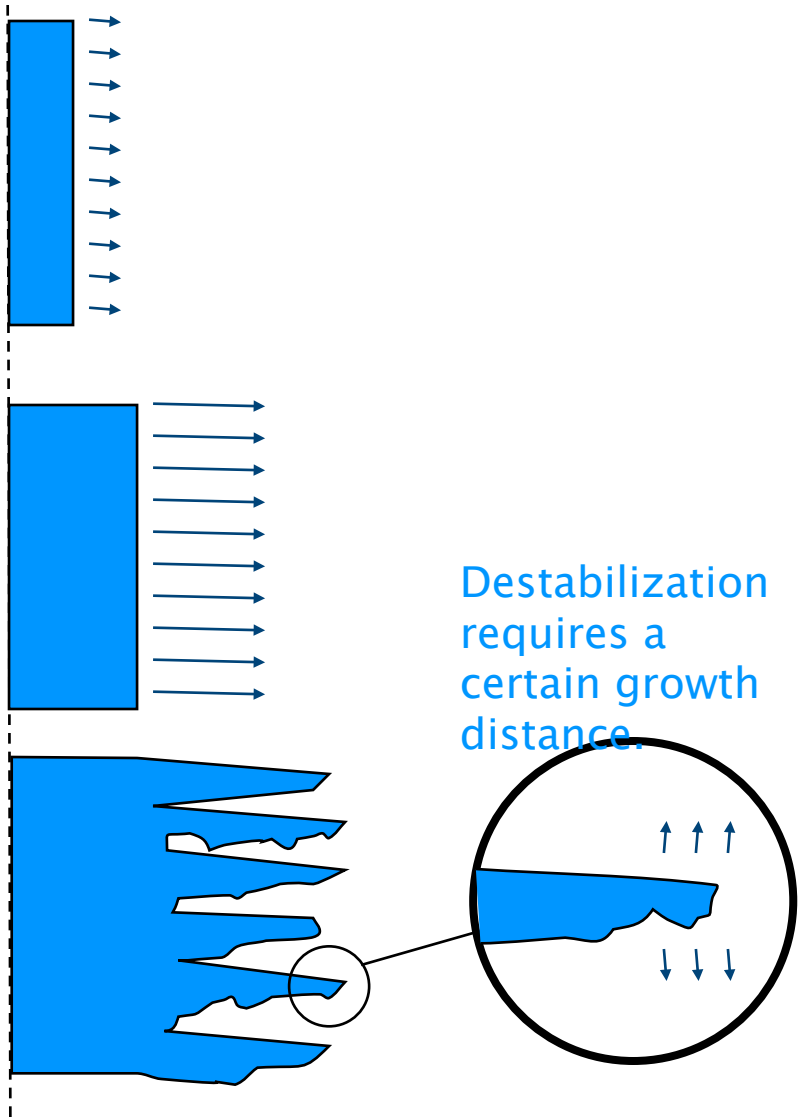
$$\frac{(C_\gamma - C_0)}{(C_\gamma - C_\alpha)} = 1 \quad = \Omega$$ (Supersaturation)

Must equal 1 for SS!





Solute buildup increases with time (or growth distance).

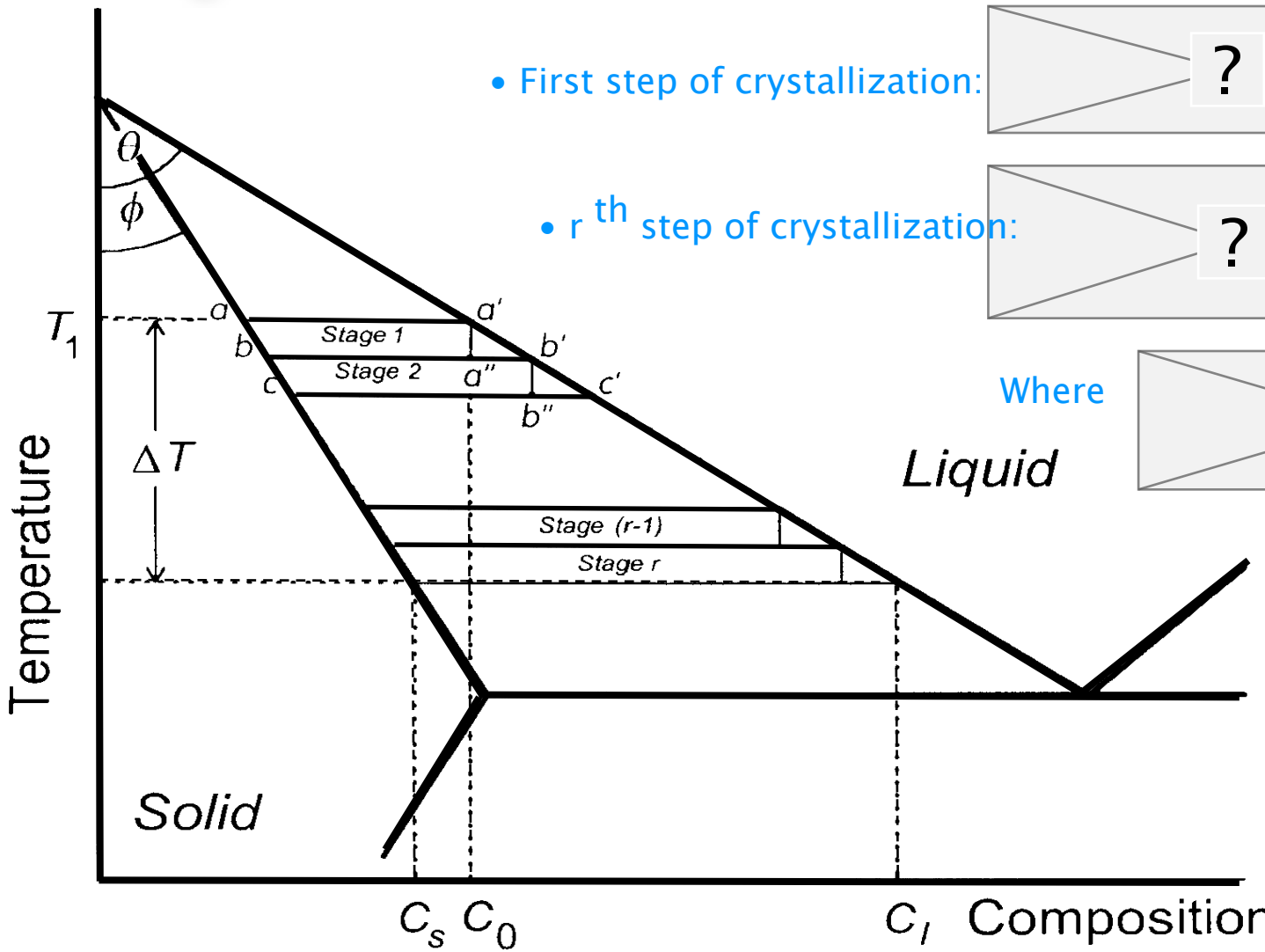


Destabilization requires a certain growth distance.

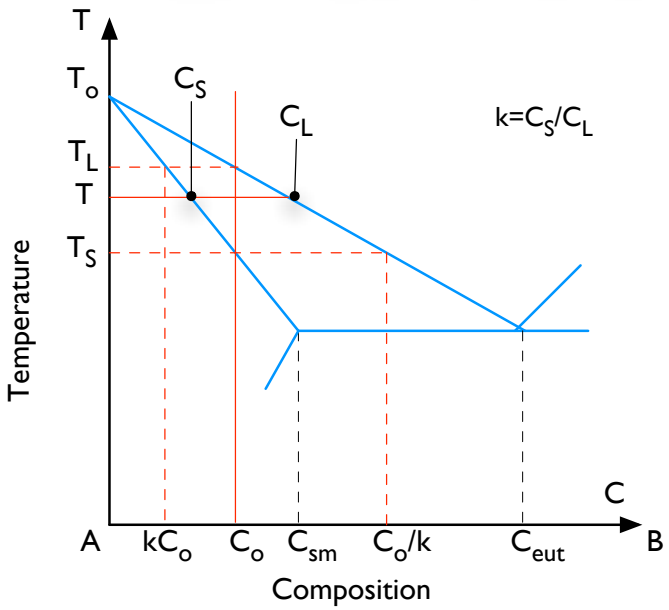
Sequential Crystallization Concepts

- First step of crystallization: ?
- r th step of crystallization: ?

Where ?



Limited Liquid Diffusion



At the interface

$$C_l = C_o / k$$

$$-D\left(\frac{dC}{dx}\right)^* = v\left(C_l^* - C_s^*\right)$$

$$\left(\frac{dC}{dx}\right)^* = -\frac{v}{D} C_l^* (1-k)$$

far from the interface

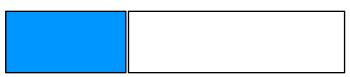
$$C_l = C_o$$

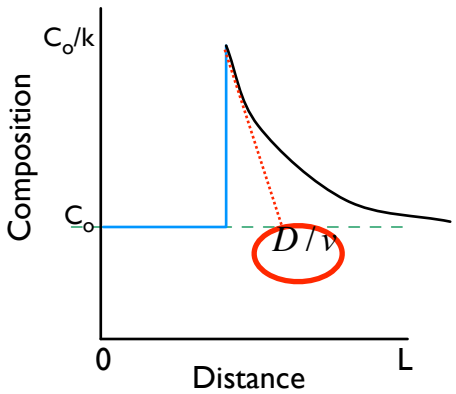
$$\frac{dC}{dt} = D\frac{d^2C}{dx^2} \qquad \frac{dC}{dx}\frac{dx}{dt} = v\frac{dC}{dx}$$

$$v\frac{dC}{dt} = D\frac{d^2C}{dx^2} \qquad C_l = C_o\left(1 + \frac{1-k}{k} e^{-\frac{x}{D/v}}\right)$$

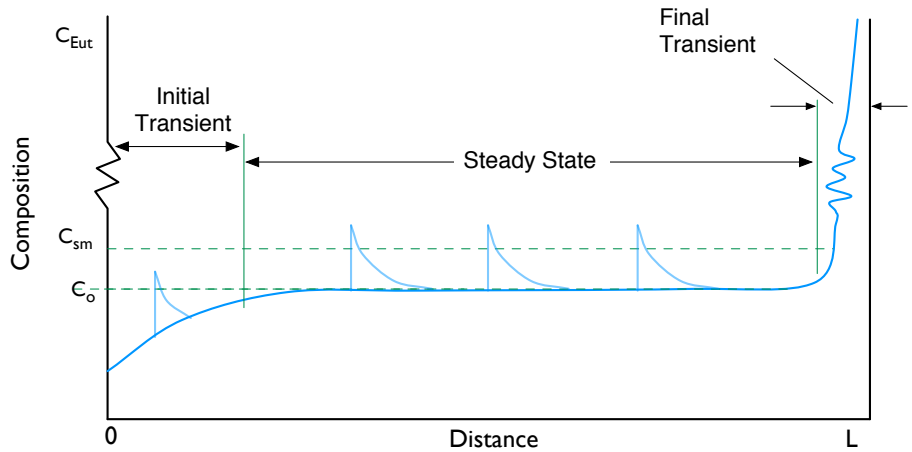
Characteristic Distance

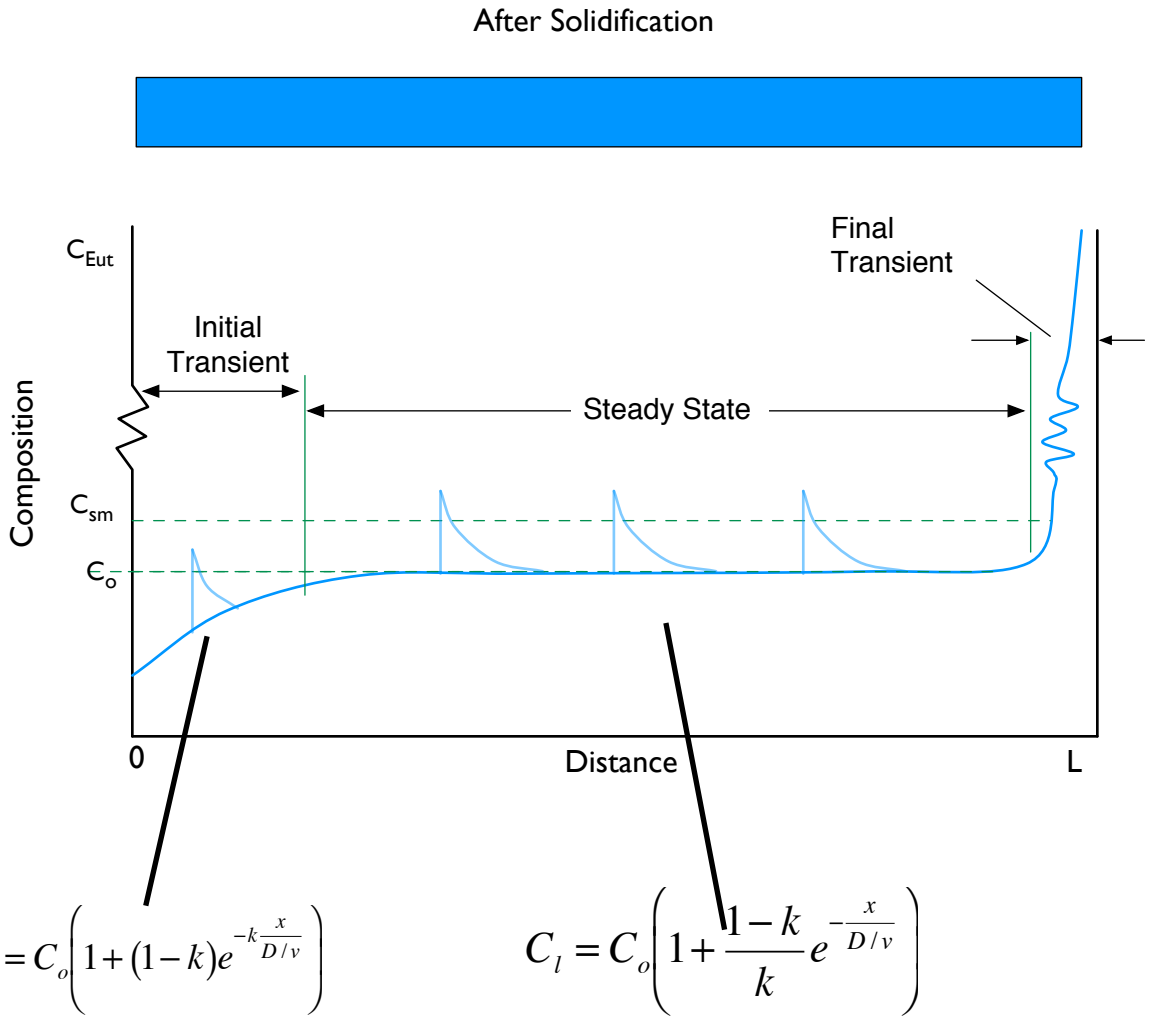
Start of Solidification





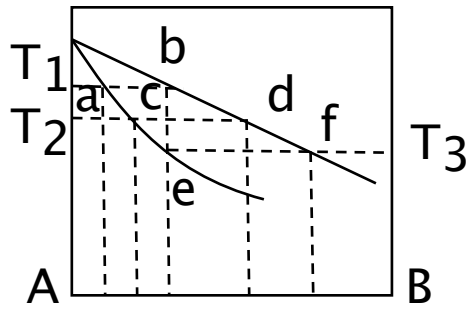
After Solidification

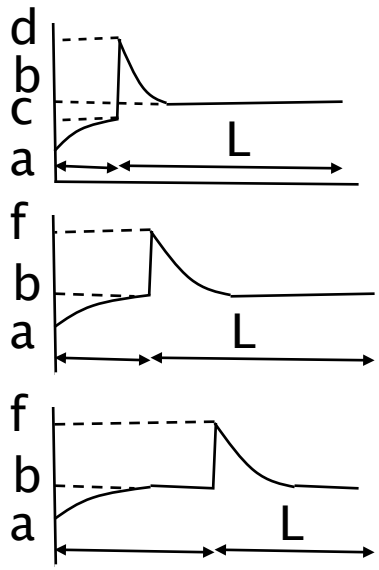




$$C_s^* = C_o\left(1+(1-k)e^{-k\frac{x}{D/v}}\right)$$

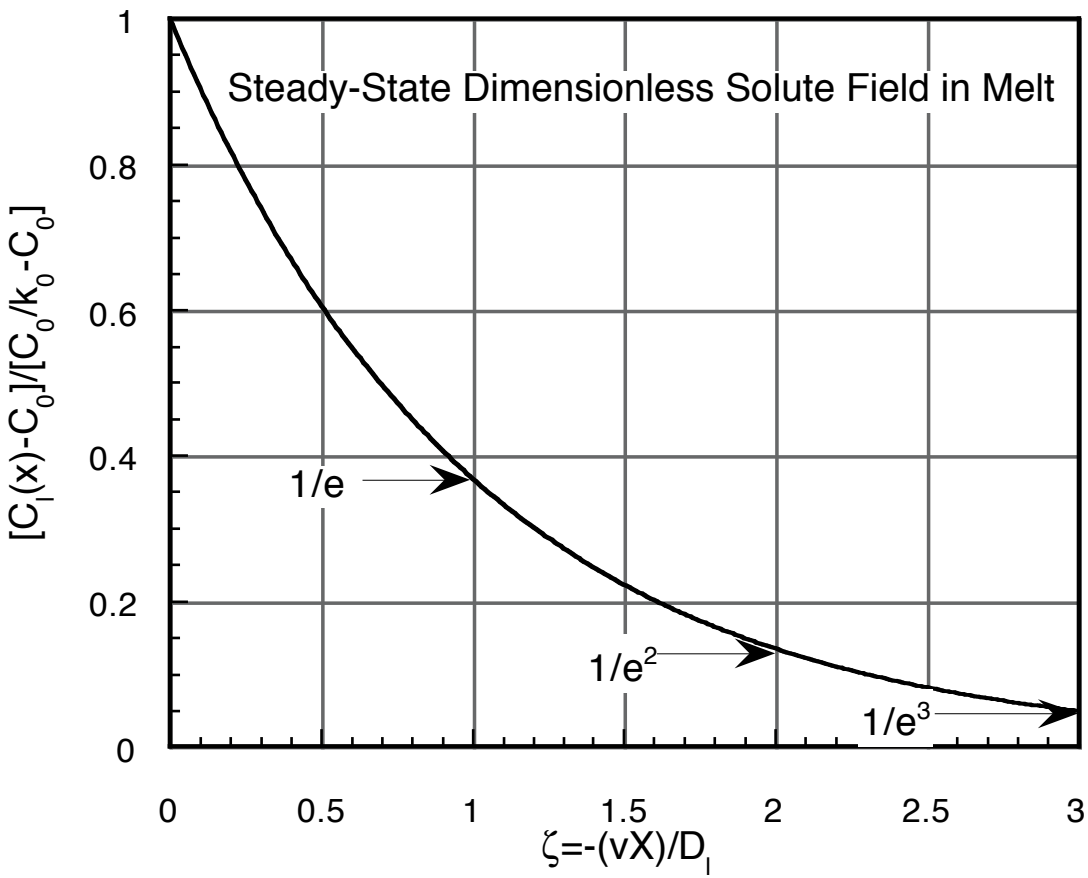
$$C_l = C_o\left(1+\frac{1-k}{k}e^{-\frac{x}{D/v}}\right)$$





Solute Boundary Layer

?

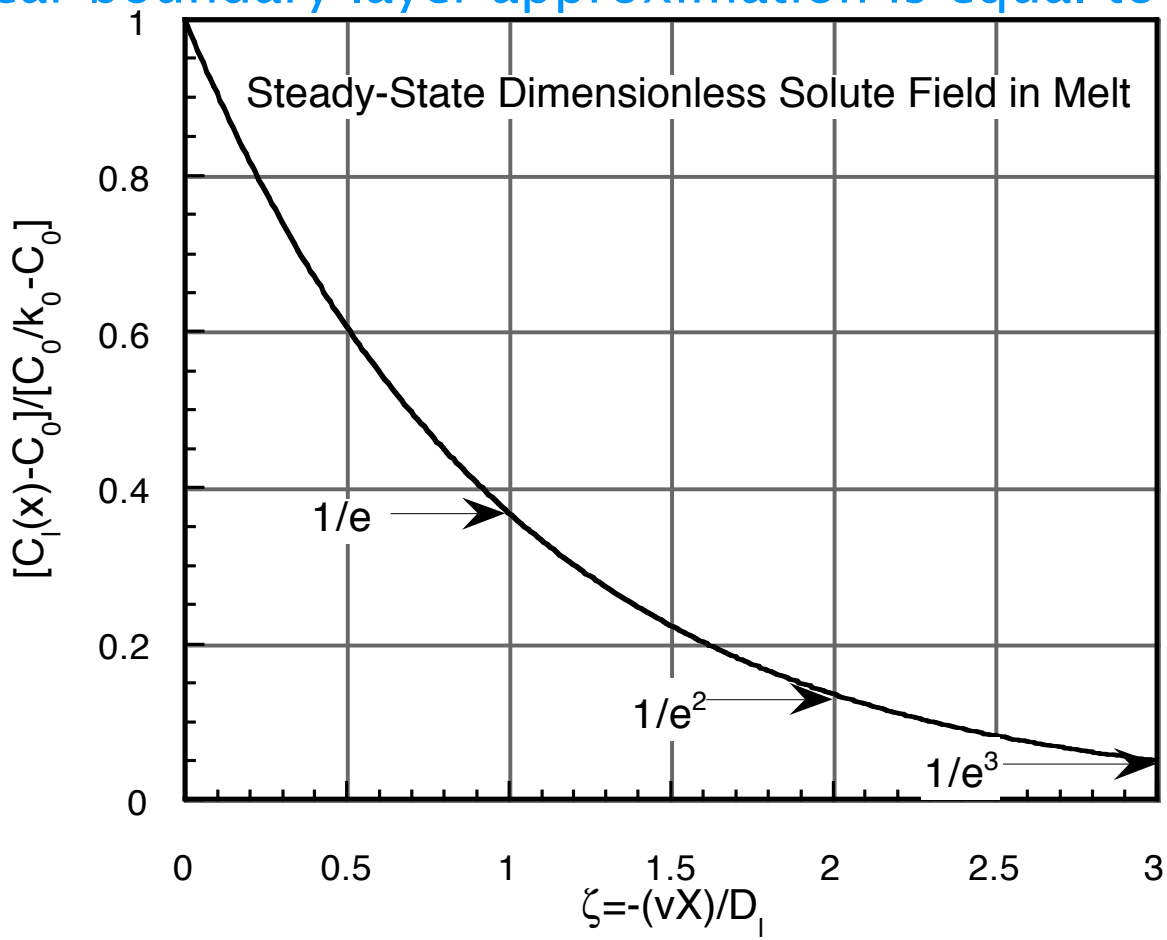


Note the characteristic diffusion length, ζ,

?

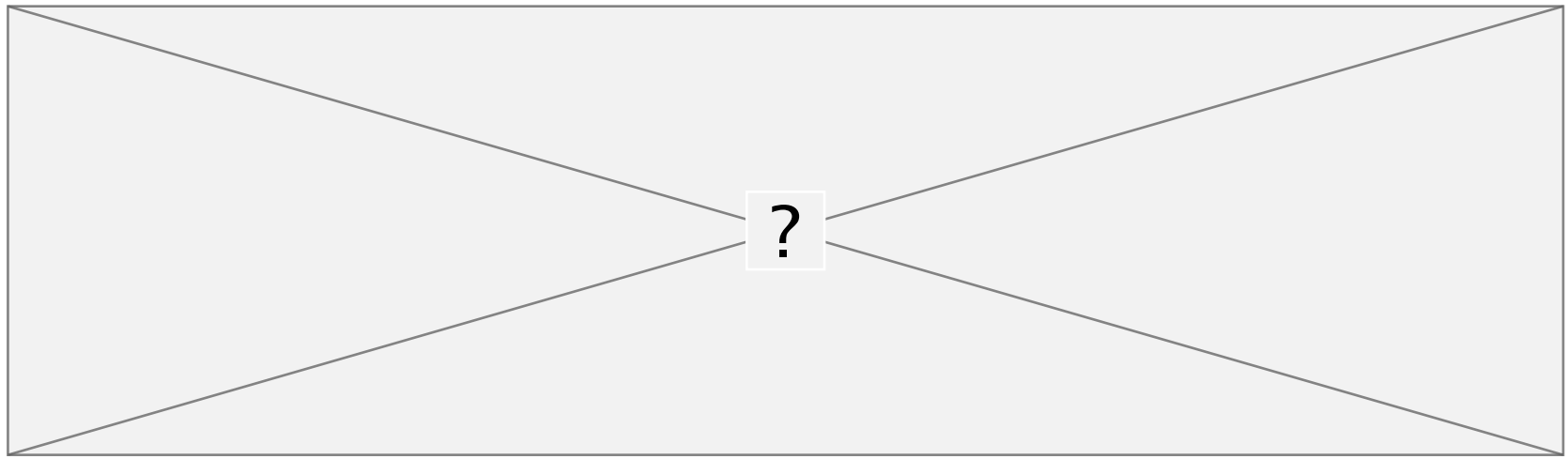
Diffusion Limited Steady State Segregation

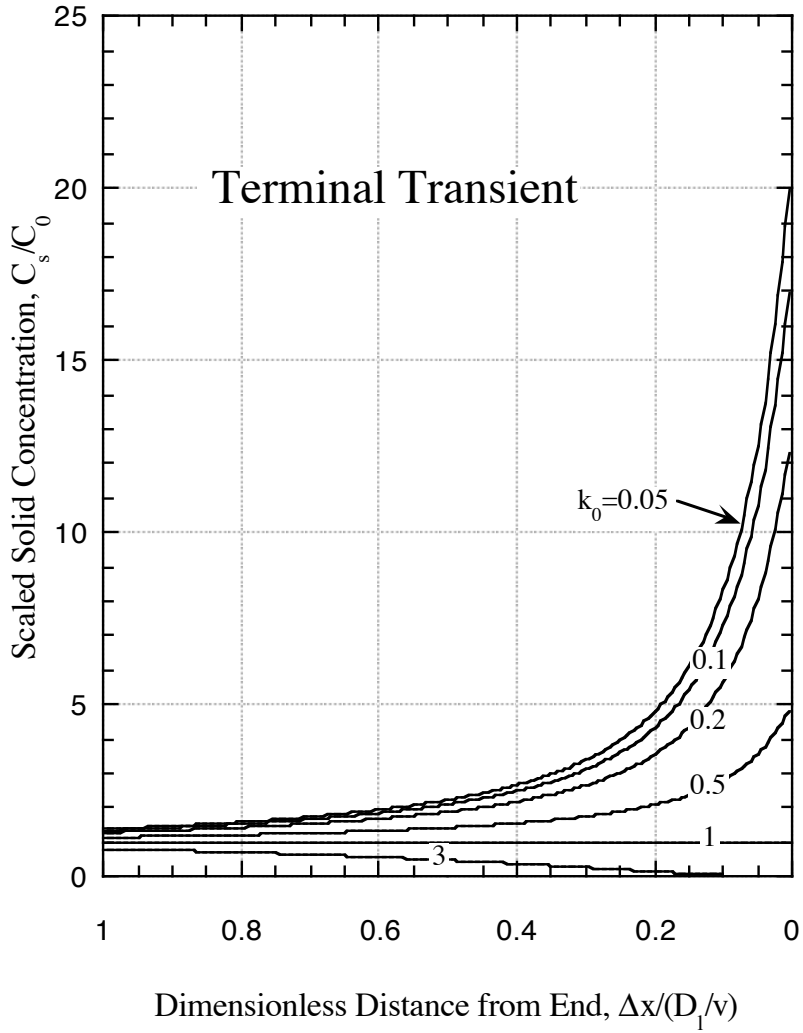
- Diffusion is negligible beyond 3 e-folding lengths from the S/L interface.
- The linear boundary layer approximation is equal to 1 e-folding, $\zeta=1$.



Terminal Solidification Transient

Terminal freezing was studied by V.G. Smith, W.A. Tiller, and J.W. Rutter, *Canadian Journal of Physics*, **33**, p. 723, (1955). They obtained the following infinite series solution. Here Δx is the distance to the end of the ingot:

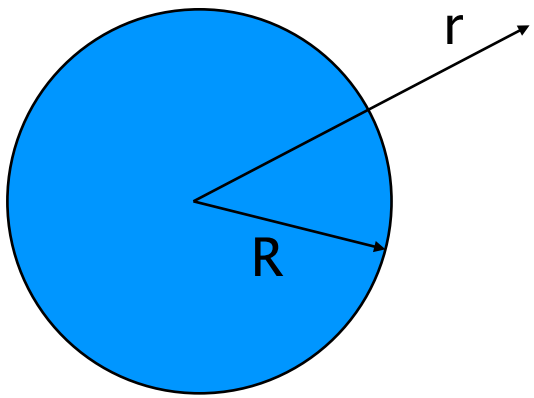




- As a practical note, terminal transients are seldom of interest in real crystal growth processes. The growth process is usually halted before this transient begins.

- Note, little if any interaction occurs when the S/L interface is more than a distance D_l/v from the end of the crucible.

Example 2: SS Spherical Growth



Fick's 2nd law: $\frac{dc}{dt} = \nabla \bullet D\nabla c \approx D\nabla^2 c$

In spherical coordinates:

$$\nabla^2 c = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) + \frac{1}{\sin\phi}\frac{\partial}{\partial \phi}\left(\sin\phi\frac{\partial c}{\partial \phi}\right) + \frac{1}{\sin^2\phi}\left(\frac{\partial^2 c}{\partial \theta^2}\right)\right]$$

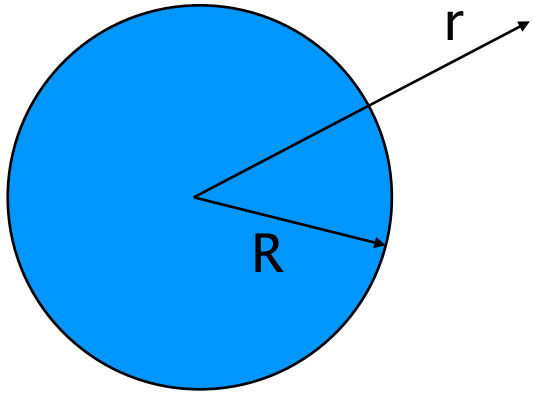
For spherical symmetry: $\frac{\partial c}{\partial \phi} = \frac{\partial c}{\partial \theta} = \frac{\partial^2 c}{\partial \theta^2} = 0$

$$\frac{dc}{dt} = \nabla^2 c = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right)\right]$$

For steady-state: $\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) = 0$ thus $r^2\frac{\partial c}{\partial r} = -a$

and $c(r) = \frac{a}{r} + b$

where a and b are constants.



General solution:

$$c(r) = \frac{a}{r} + b$$

where a and b are constants.

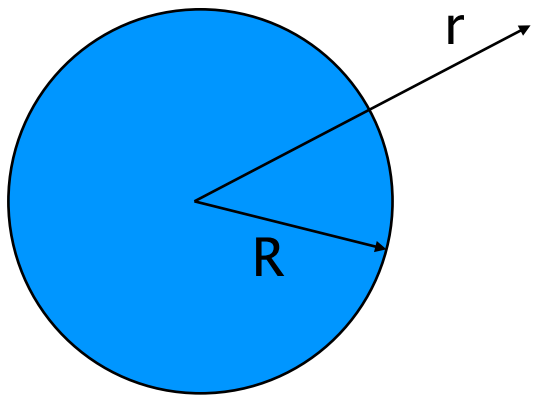
Boundary conditions:

$$C(r >> R) = C_0 = \frac{a}{r} + b \quad \Rightarrow \quad b = C_0$$

$$C(r = R) = C_l^* = \frac{a}{R} + b \quad \Rightarrow \quad a = R\left(C_l^* - C_0\right)$$

Particular solution:

$$C(r) = C_0 + \frac{R}{r}\left(C_l^* - C_0\right)$$



$$C(r) = C_0 + \frac{R}{r}\left(C_l^* - C_0\right)$$

Controlling solute gradient:

$$\frac{dC}{dr} = -\frac{R}{r^2}\left(C_l^* - C_0\right) \qquad \left.\frac{dC}{dr}\right|_{r=R} = -\frac{\left(C_l^* - C_0\right)}{R}$$

Flux balance: $J_1 = J_2$

$$v = -\frac{D}{\left(C_l - C_s^*\right)}\left.\frac{dC}{dz}\right|_{r=R}$$

Substituting yields:

$$\frac{Rv}{D} = \frac{\left(C_l - C_0\right)}{\left(C_l - C_s^*\right)} \quad \text{or} \quad v = D\left(\frac{1}{R}\right)\frac{\left(C_l - C_0\right)}{\left(C_l - C_s^*\right)}$$

NOTE:

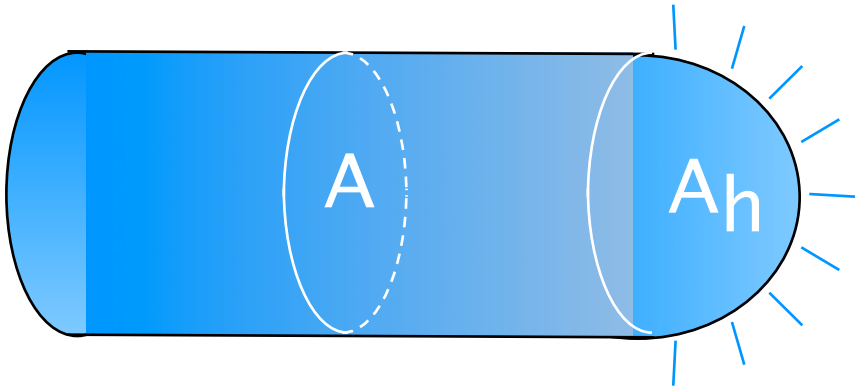
$$v = D\Psi\Omega$$

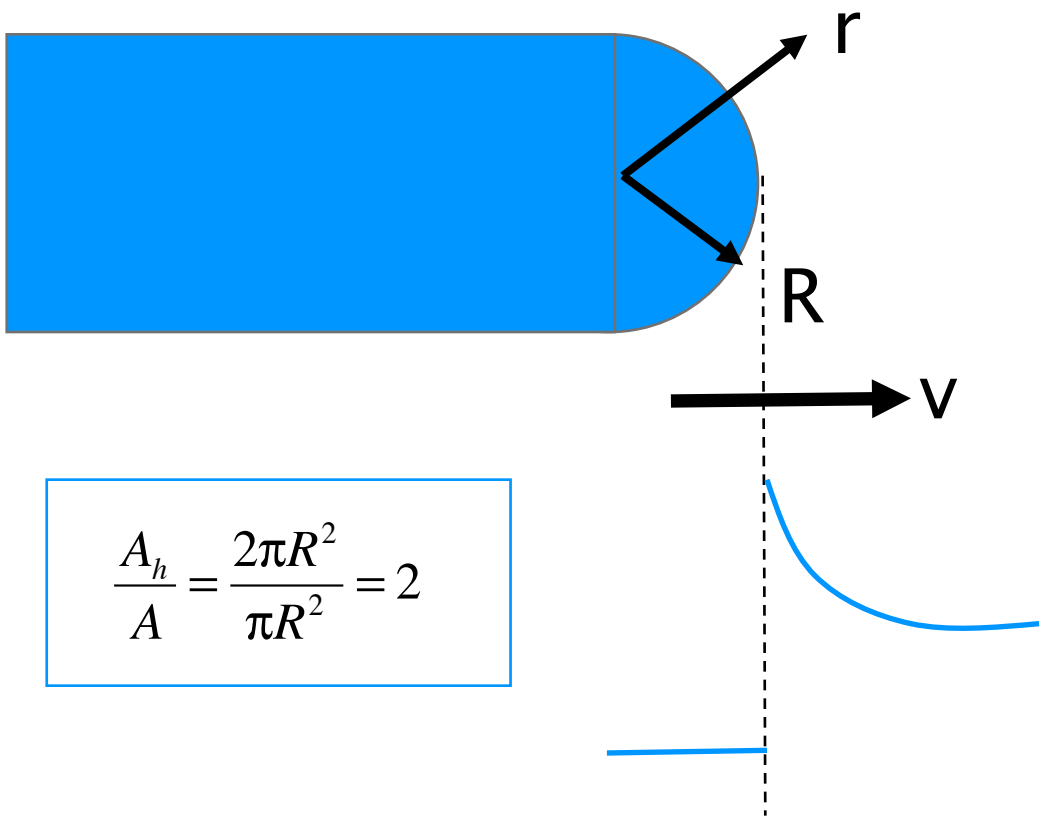
D = diffusivity

Ψ = shape factor

Ω = supersaturation

Example 3: SS Needle growth





Needle with hemispherical cap

$$\left.\frac{dC}{dr}\right|_{r=R} = -\frac{\left(C_l^* - C_0\right)}{R}$$

Flux balance

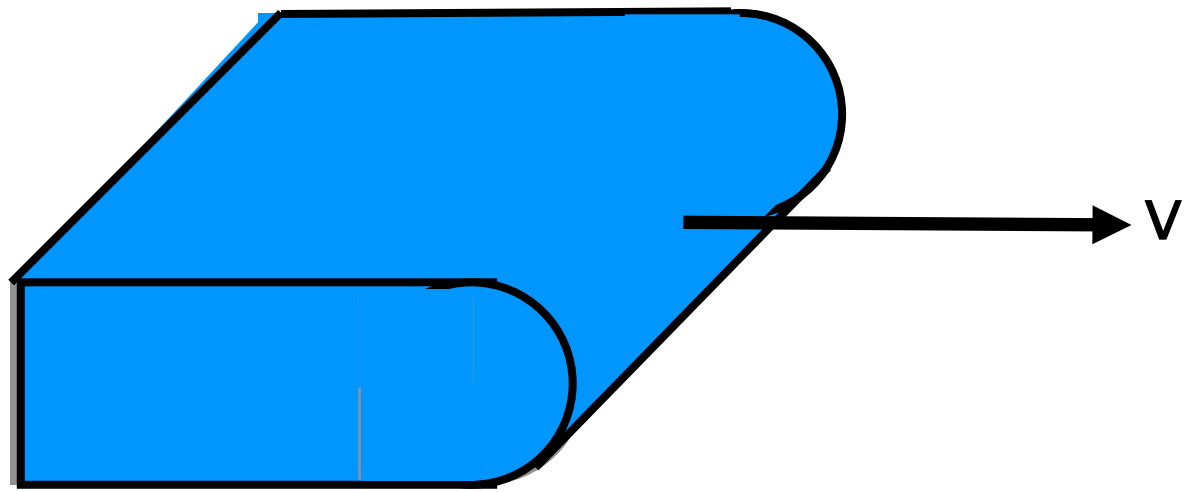
$$A\left(C_l^* - C_0\right)\frac{dz}{dt} = -A_h D\left.\frac{dC}{dr}\right|_{r=R}$$

$$v = D\left(\frac{A_h}{AR}\right)\frac{\left(C_l^* - C_0\right)}{\left(C_l^* - C_s^*\right)}$$

$$v = D\left(\frac{2}{R}\right)\frac{\left(C_l^* - C_0\right)}{\left(C_l^* - C_s^*\right)}$$

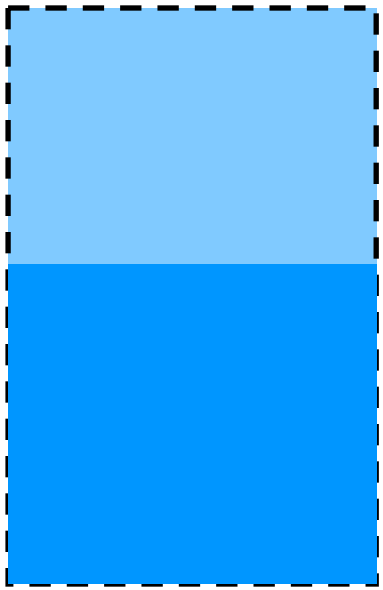
$$\frac{A_h}{A} = \frac{2\pi R^2}{\pi R^2} = 2$$

$$v = D\Psi\Omega$$



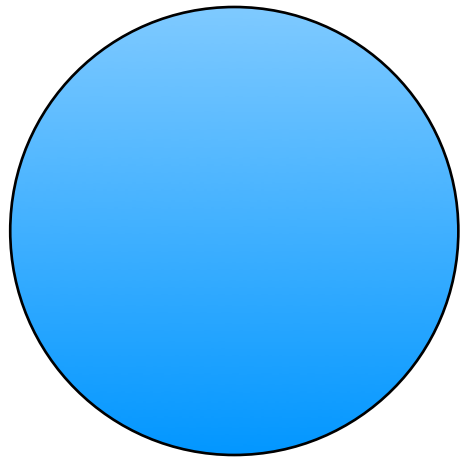
Left for homework…

The Shape Factor



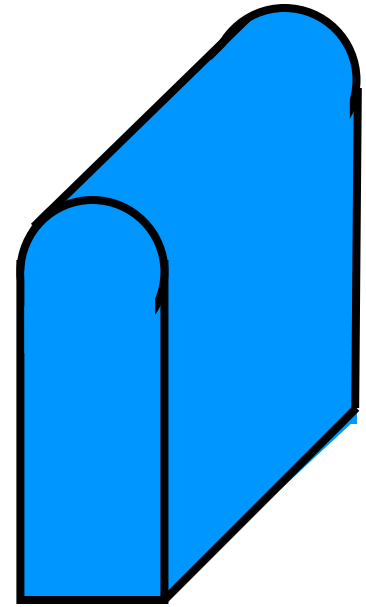
Plane

$$\Psi = \frac{1}{L} \propto \frac{1}{z}$$



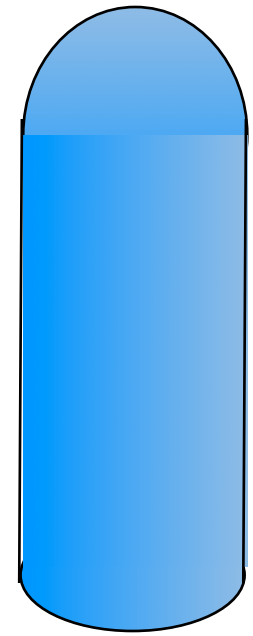
Sphere

$$\Psi = \frac{1}{R}$$



Plate

$$\Psi = ?$$

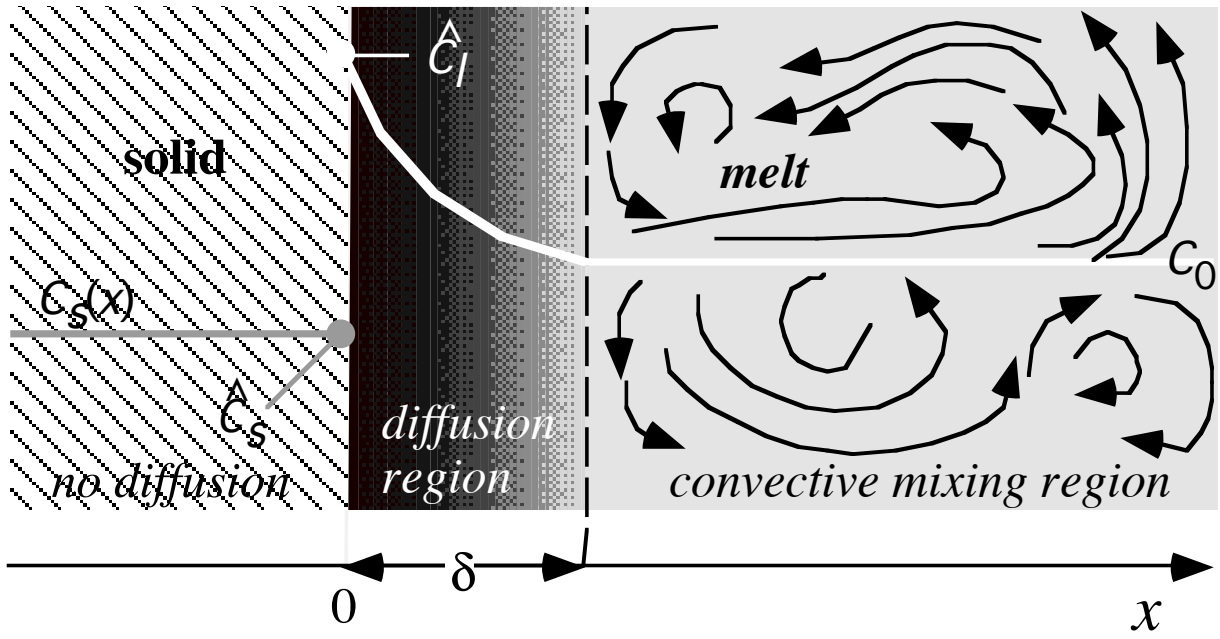


Needle

$$\Psi = \frac{2}{R}$$

Effect of Convection

Effect of Convection and Stirring



During crystal growth and plane–front solidification stirring occurs, which affects the segregation process. This was analyzed by Burton, Prim and Slichter (BPS Theory). They suggested three important zones:

- Solid zone (no diffusion)
- A "static" layer, δ, (diffusion transport)
- Liquid zone (complete mixing)

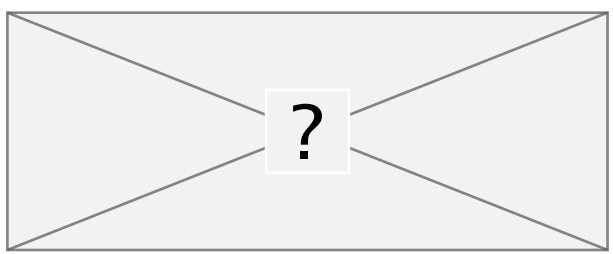
BPS Segregation Theory

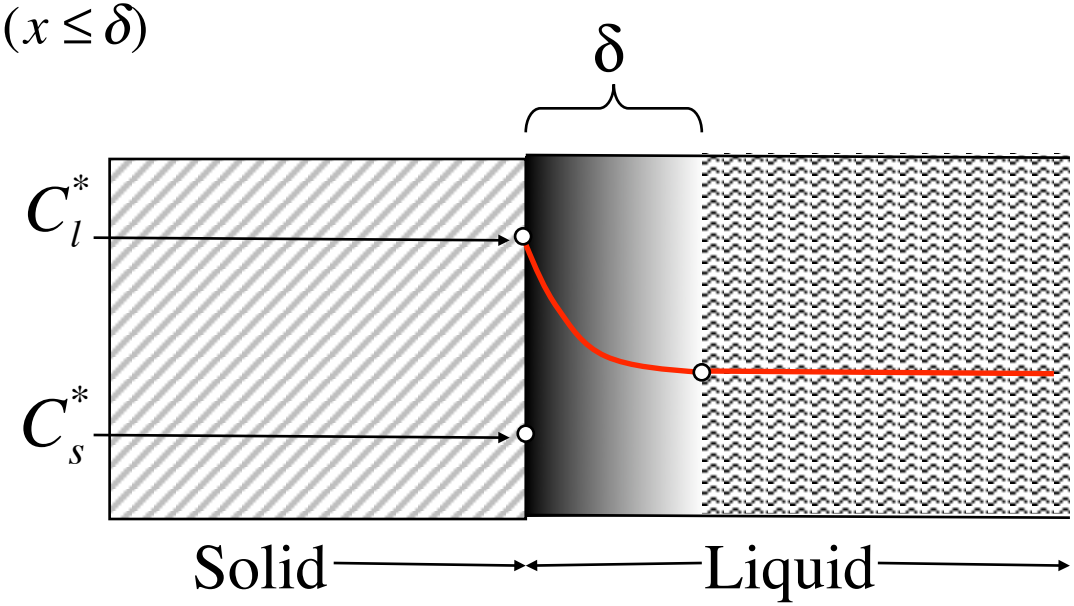
BPS approximated the fluid dynamic momentum boundary layer as a "static zone," and bulk liquid as fully mixed.
They derived segregation curves ("inner" & "outer") consistent with these approximations in the fluid mechanics.

$$C_l(x) = C_s^* + \left(C_l^* - C_s^*\right)e^{-\left(\frac{v}{D_l}x\right)}, \ (x \le \delta)$$

$$C_l(x) = C_0, \ (x > \delta)$$

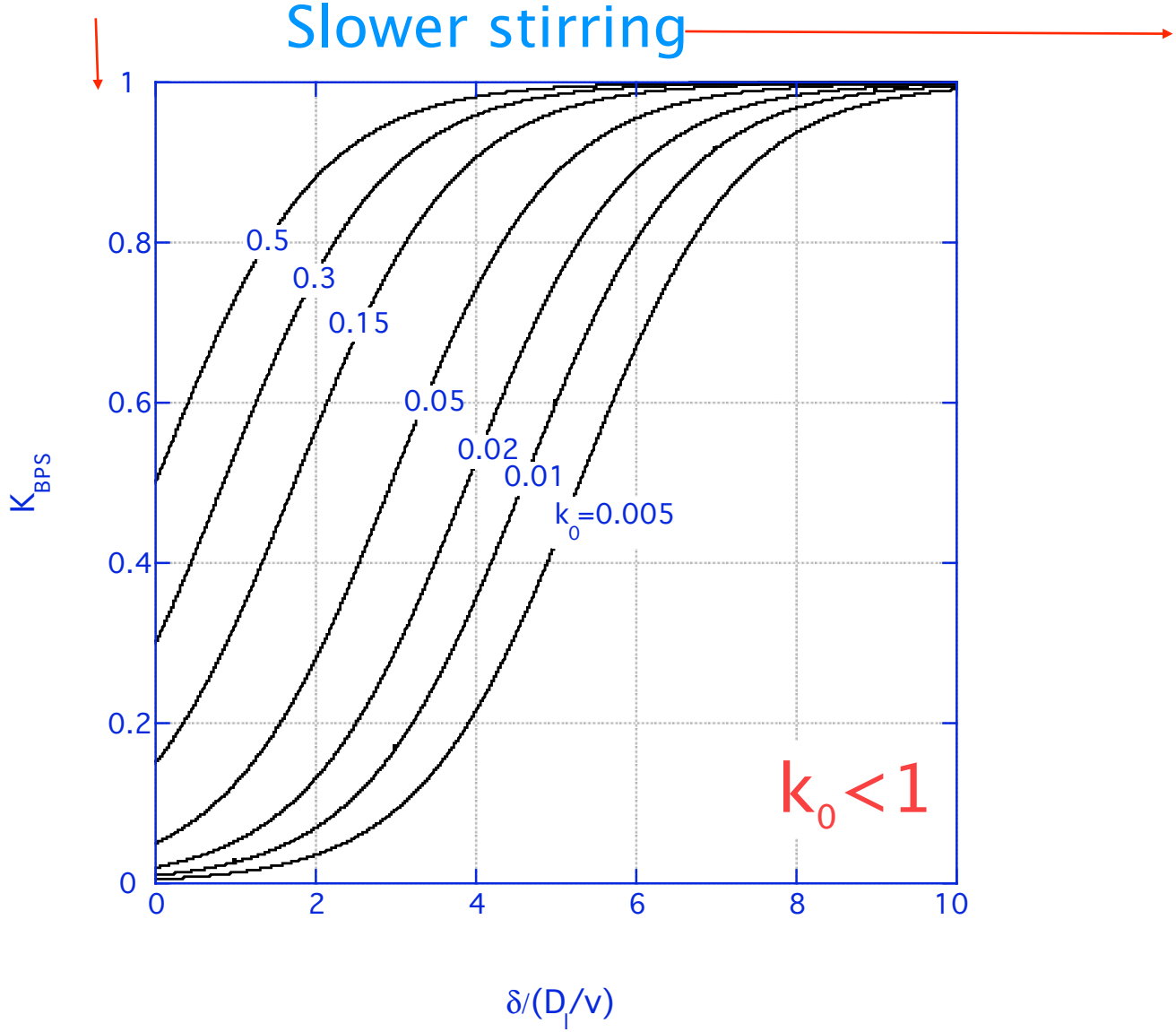
$$k_{BPS} \equiv \frac{C_s^*}{C_0}$$





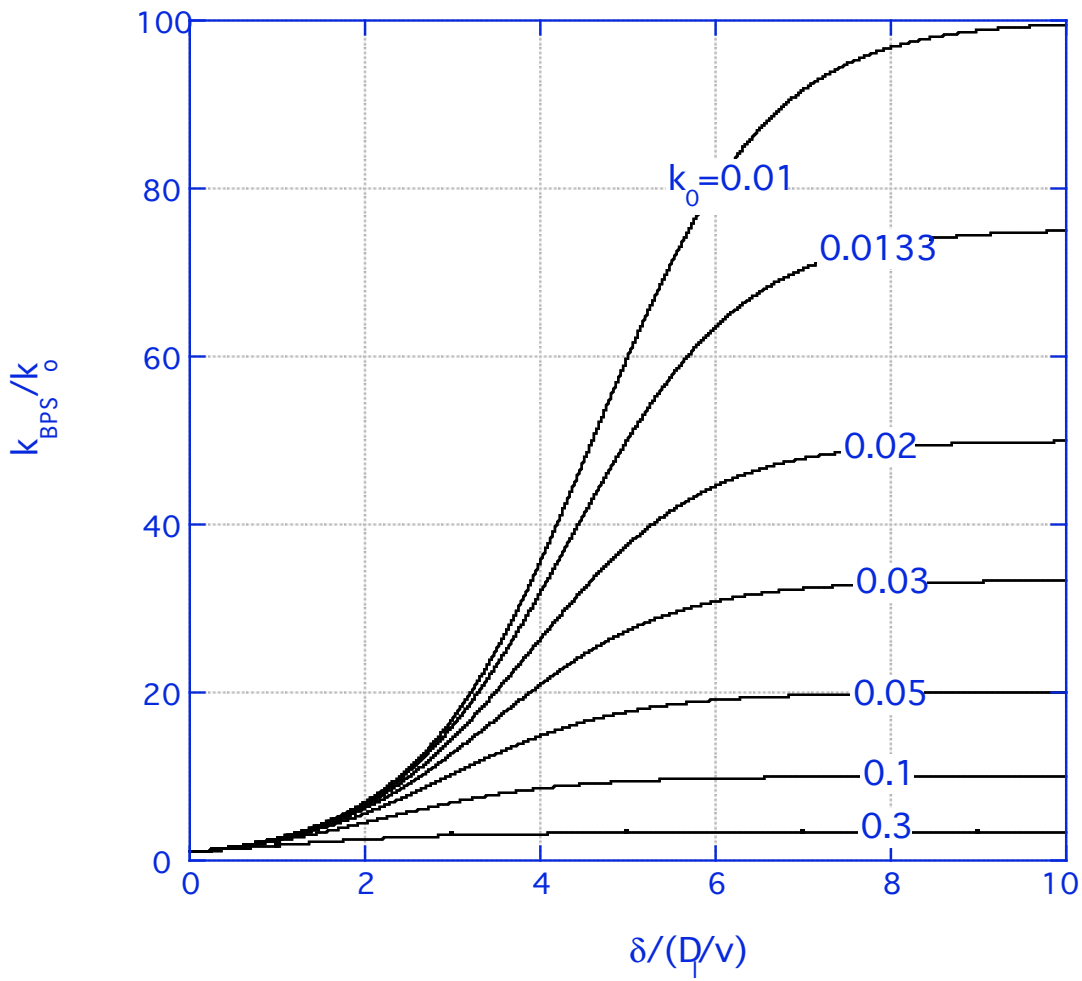
BPS results (ko<1)

Rapid stirring



Rapid stirring

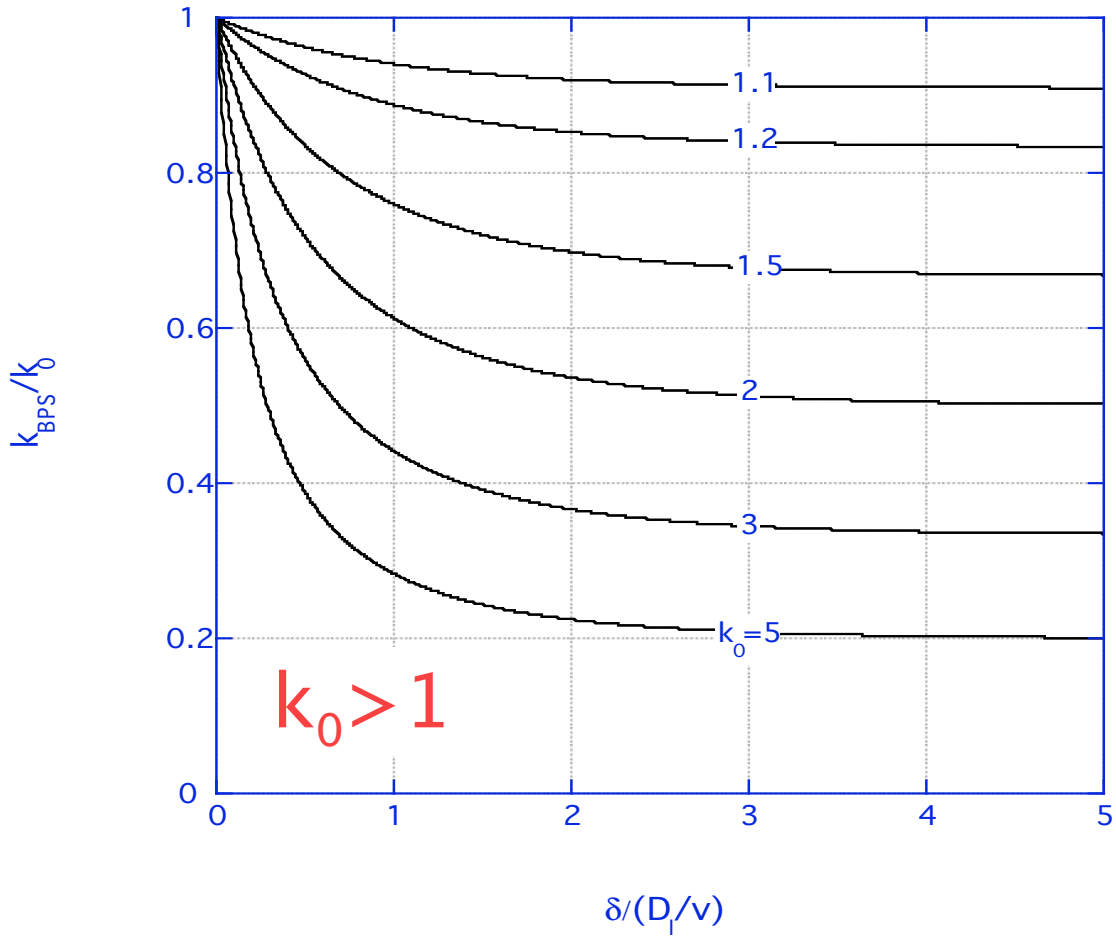
Slower stirring



BPS results (ko>1)

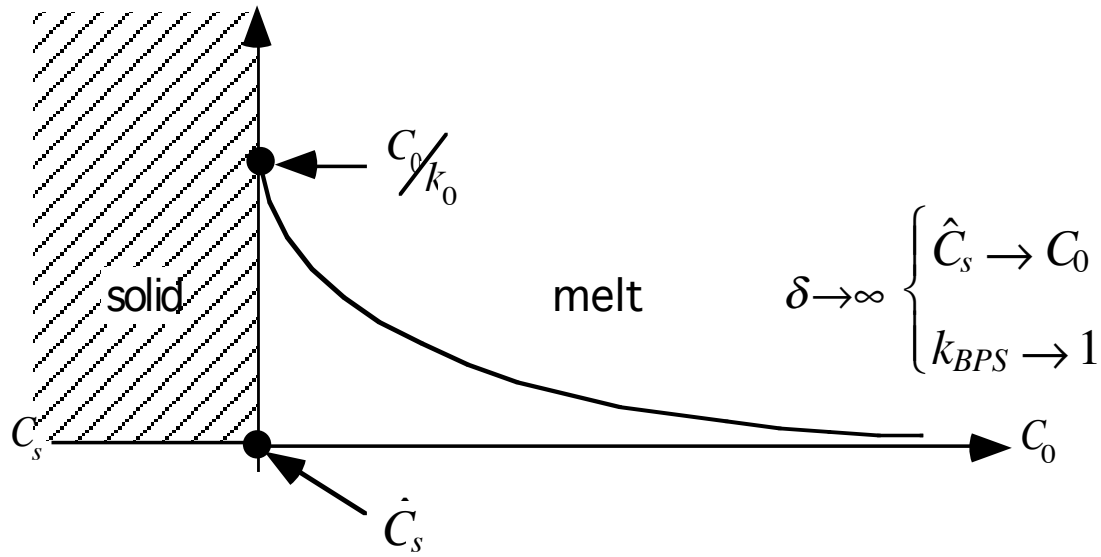
Rapid stirring

Slower stirring

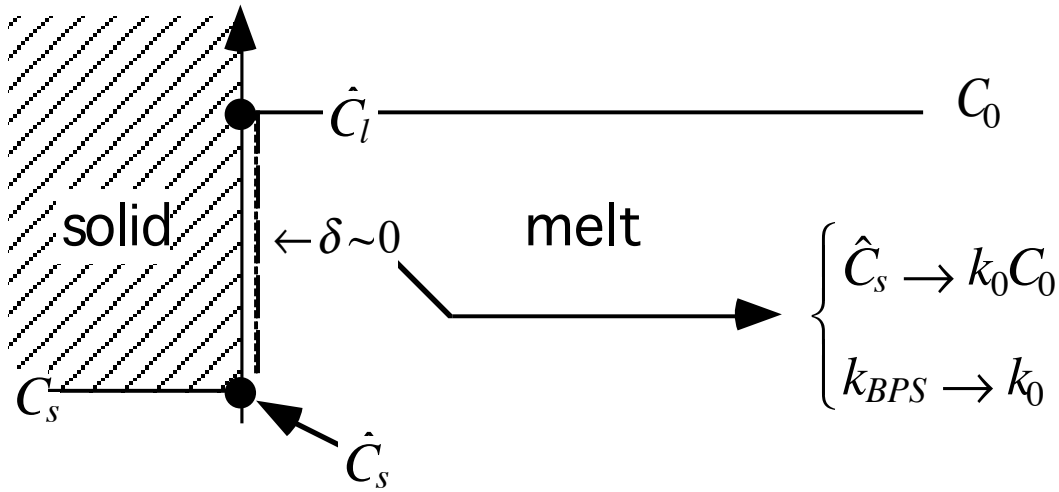


BPS Limits

i. no mixing: $\delta \to \infty$
No natural convection



ii. perfect mixing: $\delta \to 0$
Very rapid stirring



BPS Summary

As summarized below, stirring provides kinetic control on the amount of macrosegregation segregation during steady–state plane front growth.

Faster stirring

δ	k_{BPS}	C_s
0	k_0	$k_0 C_0$
$0<\delta<\infty$	$k_0< k_{BPS}<1$	$k_0 C_0<C_s<0$
∞	1	C_0

Key Points

- Equilibrium (lever-law) at S/L interfaces requires:
  - Tie-line "jumps"
  - Solidus & liquidus slopes (m_S & m_l)
  - Segregation coefficient, k_0
- Motion of the interface causes mass transport
  - Diffusion boundary layer
  - Solute rejection
- Gulliver-Scheil behavior leads to macrosegregation.
- Transients arise during solidification:
  - Initial
  - Steady-state
  - Terminal
- Bouyancy convection treated with Burton-Prim-Schlichter theory