Crystal frame:

$$J_A = -D_A \nabla C_A$$

$$J_B = -D_B \nabla C_B$$

$$D_B = \left(\frac{L_{BB}}{x_B} - \frac{L_{AB}}{x_A}\right) x_B \frac{\partial \mu_B}{\partial x_B} \Omega$$

Laboratory frame

$$v = -V_m (J_A + J_B) = \frac{J_v}{C_0}$$

v → velocity in the lab frame.

$$V_m = \frac{1}{C_0} = \frac{V}{N_A + N_B}$$

$$\tilde{J}_A = J_A + v C_A = -\tilde{D} \nabla C_A$$

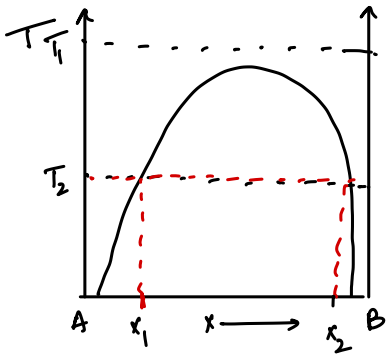
$$\tilde{J}_B = J_B + v C_B = -\tilde{D} \nabla C_B$$

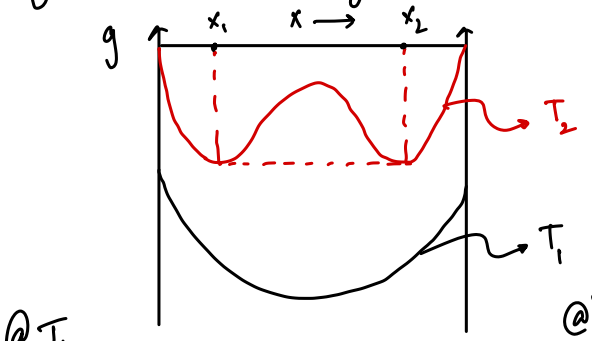
$$\tilde{D} = x_B D_A + x_A D_B$$

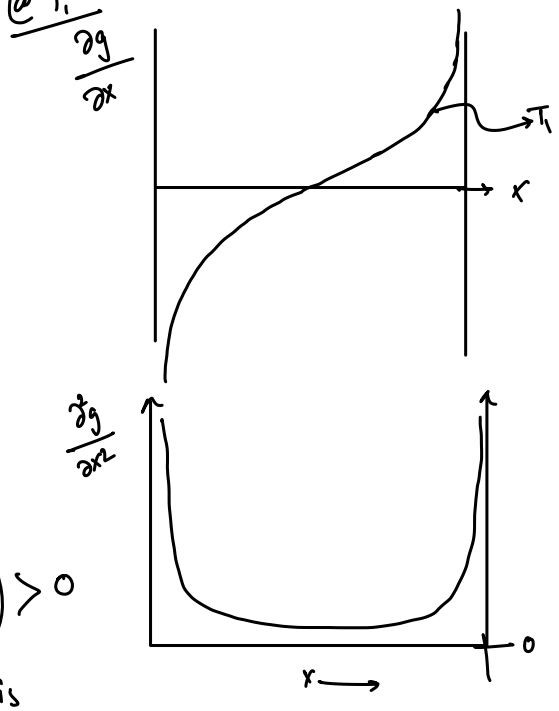
$$\boxed{\tilde{D} = \tilde{L} \Omega \, \partial^2 g / \partial x^2}$$

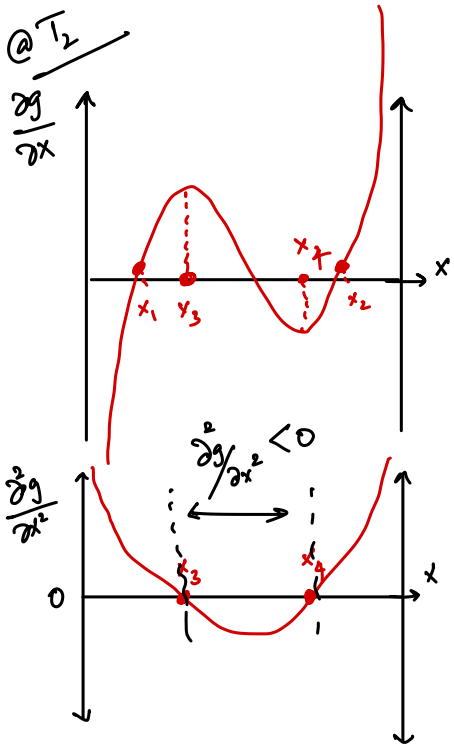
→ Similar to the diffusion coefficient in the crystal frame.

SPINODAL DECOMPOSITION: (Thermodynamics is described by the model in Question 2 in PSET III)









$$\frac{\partial^2 g}{\partial x^2} > 0 \Rightarrow \left(\tilde{D} \propto \partial^2 g / \partial x^2\right) > 0$$

$\Rightarrow$ Diffusion flux is down the composition gradient

(i.e.) diffusion is from high concentration to low concentration.

$$\frac{\partial^2 g}{\partial x^2} < 0 \text{ b/w } x_3 \text{ \& } x_4$$

$$J_A = -\tilde{D} \frac{\partial c}{\partial x}$$

$$\left(\tilde{D} \propto \frac{\partial^2 g}{\partial x^2}\right) < 0$$

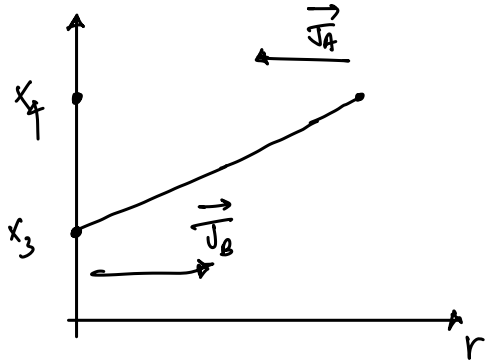
$\Rightarrow$ UPHILL DIFFUSION

x_3 & x_4 are often called the SPINODES

✱ UPHILL DIFFUSION & SPINODAL DECOMPOSITION:

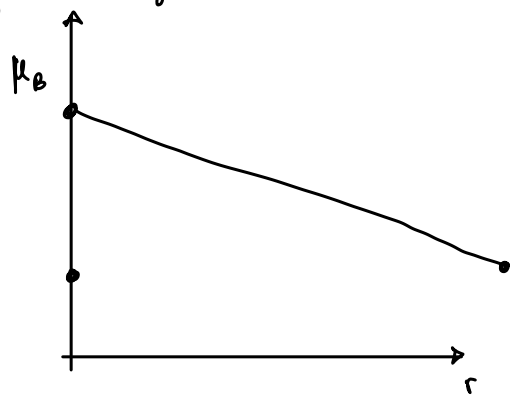
$$\tilde{J}_A = -\tilde{D}\frac{\partial C}{\partial r} \Rightarrow @\, T = T_2 \;\&\; x_3 < x < x_4 \Rightarrow \tilde{J}_A = |\tilde{D}|\frac{\partial C}{\partial r}$$

(absolute value.)

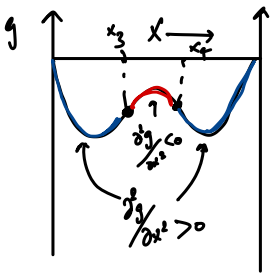


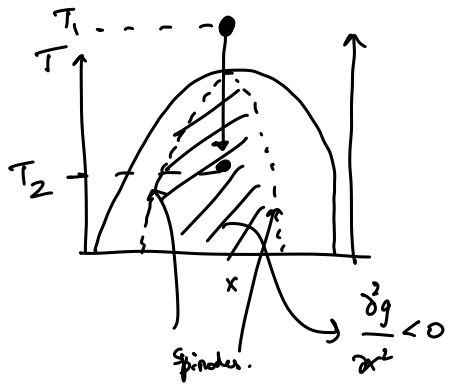
A-rich regions will get richer in A, & B-rich regions will get richer in B

.... DOES THIS MAKE SENSE??



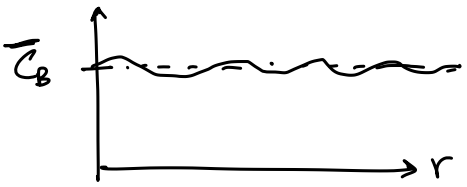
B (and A) are still diffusing down a chemical potential gradient despite moving up a composition gradient.





— What happens to an alloy annealed @ T_1 that is then quenched to T_2 ?

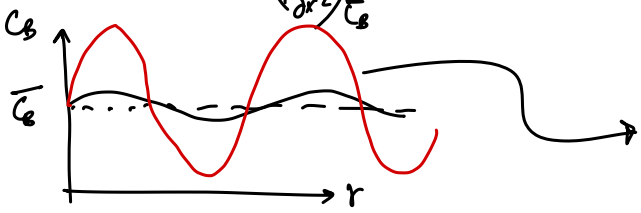
1) @ T_1



$\frac{\partial^2 g}{\partial x^2} > 0$ everywhere $\Rightarrow D > 0$

there will always be spontaneous fluctuations in concentration around $\bar{C}_B$, however they will decay and not grow

2) Quench to T_2; $\left(\frac{\partial^2 g}{\partial x^2}\right)_{\bar{C}_B} < 0 \Rightarrow D < 0 \Rightarrow J = |D|\nabla C$



concentration fluctuations are amplified. B diffuses from low C_B to high C_B

★ ATTEMPT 1 @ ANALYZING THE MICROSTRUCTURE EVOLUTION DURING SPINODAL DECOMPOSITION:

- Understand the behavior of small fluctuations around an otherwise uniform concentration profile.
- ASSUME:
  1. Infinite domain (sample size)
  2. 1 dimensional model ONLY
  3. Kinetic parameters independent of alloy concentration

- To predict time evolution:

FICKS II LAW: $\frac{\partial c}{\partial t} = -\nabla J$

$\longrightarrow$ FICKS I LAW

$$\frac{\partial c}{\partial t} = -\nabla\left(-D\nabla c\right)$$

D is a constant $\longrightarrow$ ASSUME

$$\boxed{\frac{\partial c}{\partial t} = D\nabla^2 c}$$

$\hookrightarrow$ Integrate to compute $c(\vec{r}, t)$

in 1D: $\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial r^2}$

★ FOURIER TRANSFORMS TO SOLVE PDE:

$c(\vec{r}, t)$

$$\hat{c}(\vec{k}, t) = \mathcal{F}\{c(\vec{r}, t)\} = \frac{1}{(2\pi)^{3/2}} \iiint c(\vec{r}, t)\exp\left(+i\vec{k}\cdot\vec{r}\right) d\vec{r}$$

Inverse fourier transform:

$$c(\vec{r}, t) = \frac{1}{(2\pi)^{3/2}} \iiint \hat{c}(\vec{k}, t)\exp\left(-i\vec{k}\cdot\vec{r}\right) d\vec{k} = \mathcal{F}^{-1}\{\hat{c}(\vec{k}, t)\}$$

In 1D: $k = \frac{2\pi}{\lambda}$; $k \to 0$ $\lambda \to \infty$ $\Rightarrow$ "long wavelengths"

$k \to \infty$ $\Rightarrow$ "short wavelengths"

$$\hat{c}(k, t) = \mathcal{F}\{c(r, t)\} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(r, t)\exp(ikr)\, dr$$

$$c(r, t) = \mathcal{F}^{-1}\{\hat{c}(k, t)\} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(k, t)\exp(-ikr)\, dk$$

★ FOURIER TRANSFORM THE DIFFUSION EQUATION:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial r^2} \longrightarrow \mathcal{F}\left\{\frac{\partial c}{\partial t}\right\} = D\mathcal{F}\left\{\frac{\partial^2 c}{\partial r^2}\right\}$$

$$\mathcal{F}\left\{\frac{\partial c}{\partial t}\right\} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\partial c}{\partial t}\exp(ik\cdot r)\, dr = \frac{\partial}{\partial t}\underbrace{\left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(r, t)\exp(ikr)\, dr\right]}_{\hat{c}(k, t)} = \frac{\partial \hat{c}(k, t)}{\partial t}$$

$$\mathcal{F}\left\{\frac{\partial^2 c}{\partial r^2}\right\} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\partial^2 c}{\partial r^2}\exp(ikr)\, dr$$

$$= -k^2 \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(r, t)\exp(ikr)\, dr$$

↑ Integrate by parts

In general: $\mathcal{F}\left\{\frac{d^n c}{dr^n}\right\} = (-ik)^n \mathcal{F}\{c(r,t)\} = (-ik)^n \hat{c}(k,t)$

Diffusion equation: $\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial r^2} \longrightarrow \boxed{\frac{\partial \hat{c}(k,t)}{\partial t} = -Dk^2 \hat{c}(k,t)}$ ODE!

$\hat{c}(k,t) = \hat{c}(k,0)\exp(-Dk^2 t)$

— Lets make a few variable transforms:

Instead of solving for $c(r,t)$ → we will solve for $\Delta c(r,t) = c(r,t) - \bar{c}$

$\bar{c}$ → average concentration.

$\frac{\partial \Delta c}{\partial t} = D\frac{\partial^2 \Delta c}{\partial r^2} \Rightarrow \frac{\partial (c-\bar{c})}{\partial t} = D\frac{\partial^2 (c-\bar{c})}{\partial r^2} \Rightarrow \frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial r^2}$

These are equivalent.

$\mathcal{F}\left\{\frac{\partial \Delta c}{\partial t}\right\} = \mathcal{F}\left\{D\frac{\partial^2 \Delta c}{\partial r^2}\right\} \Rightarrow \boxed{\frac{\partial \Delta \hat{c}}{\partial t} = -k^2 \Delta \hat{c}(k,t)}$

Say the initial composition profile is $\Delta c_0(r,0)$

$$\Delta \hat{c}_0(k,0) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \Delta c_0(r,t)\exp(ikr)\,dr$$

Solution to the eqn:

$$\boxed{\Delta \hat{c}(k,t) = \Delta c_0(k,0)\exp(-k^2 Dt)}$$

To evaluate $\Delta c(r,t)$ → Inverse Fourier transform.

$$\Delta c(r,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \Delta \hat{c}(k,t)\exp(-ikr)\,dk =$$

$$\boxed{\Delta c(r,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \Delta c_0(k,0)\exp(-k^2 Dt)\exp(-ikr)\,dk}$$

→ k is integrated out!

time dependence

position dependence.