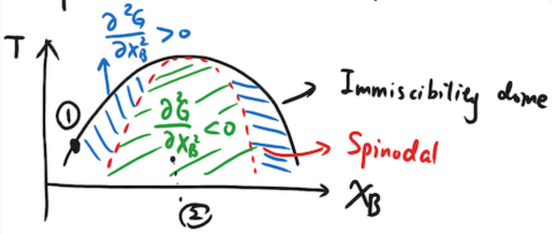
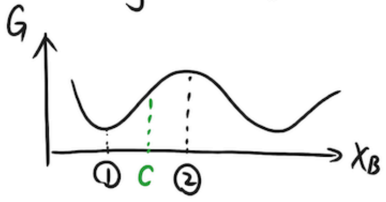
MATE664 L16

Spontaneous Phase Transformation — Spinodal Decomposition



Stability statement



At each extremum, we have

$$G(X_B^0 + \delta X_B) = G(X_B^0) + \overset{\Uparrow\, 0}{\underline{\frac{\partial G}{\partial X_B}\Big|_{X_B^0}}} \cdot \delta X_B$$

$$+ \frac{1}{2} \frac{\partial^2 G}{\partial X_B^2}\Big|_{X_B^0} (\delta X_B)^2$$

$$= G(X_B^0) + \frac{1}{2} \frac{\partial^2 G}{\partial X_B^2}\Big|_{X_B^0} (\delta X_B)^2$$

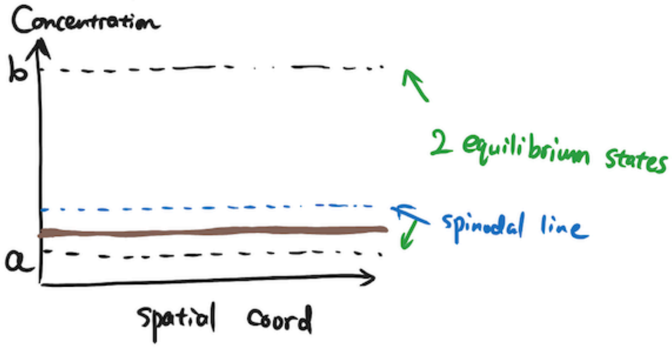
① point: stable because any $\delta X_B \rightarrow$ higher G

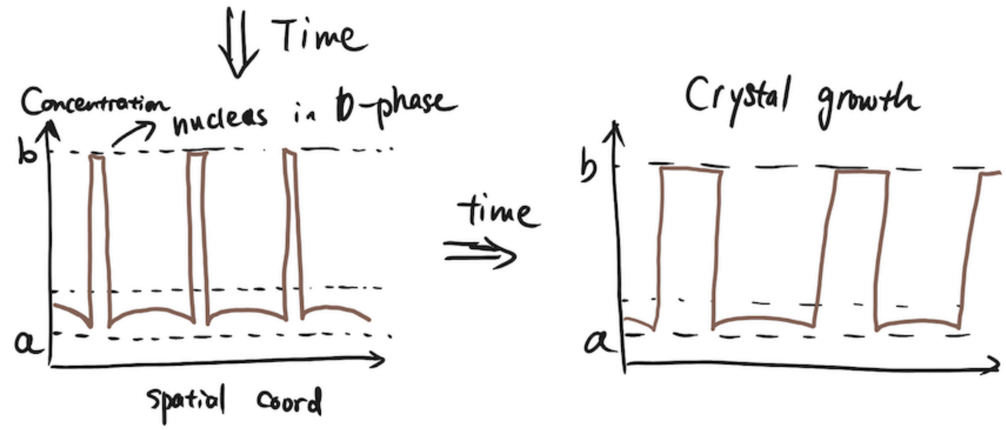
① → C points: metastable → $\frac{\partial^2 G}{\partial X_B^2} > 0$

C → ② points: unstable → $\frac{\partial^2 G}{\partial X_B^2} < 0$ Any small change will drop!

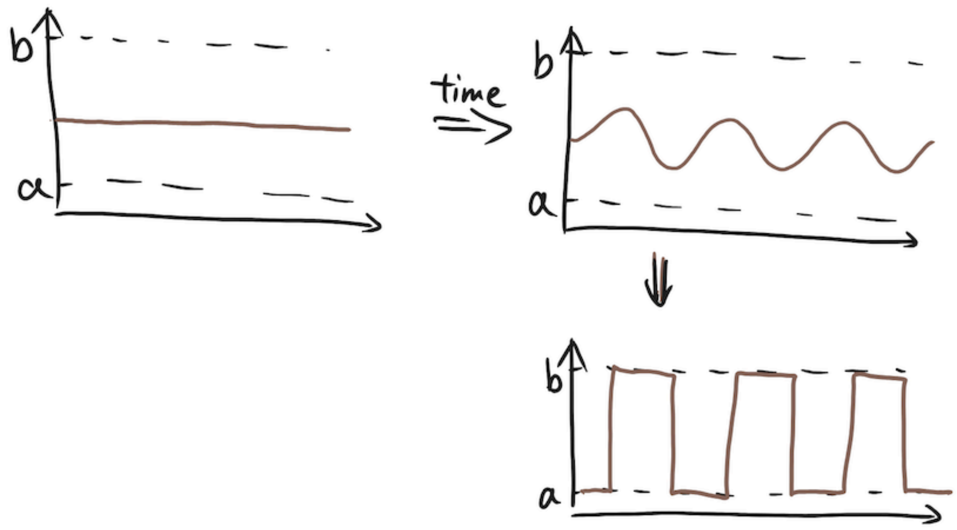
View of kinetics difference in nucleation & spinodal

Nucleation





Spinodal Decomposition



Formal description for spinodal decomposition

- Key questions we may discuss
  ① why is there a dependency on $\frac{\partial^2 G}{\partial X^2}$?
  ② description of the "uphill" behaviour

Treatment 1: diffusion equation of binary alloy

$$J_A^c = -L_A \nabla\mu_A \qquad J_B^c = -\underline{L_B}\nabla\mu_B$$

$$= -(L_{AA} - \frac{c_A}{c_B}L_{AB})\nabla\mu_A \qquad = -(L_{BB} - \frac{c_B}{c_A}L_{BA})\nabla\mu_B$$

We want to find $\tilde{D}$ interdiffusivity
should look in V-frame

$$J_A^V = J_A^C + v_o^V \cdot C_A \qquad J_B^V = J_B^C + v_C^V \cdot C_B$$

↖ relative frame velociy

From previous lecture $\Omega_A J_A^V + \Omega_B J_B^V = 0$

Simplify $\Omega_1 = \Omega_2 \Rightarrow J_A^V + J_B^V = 0$

$$-L_A\nabla\mu_A + v_c^v c_A \quad -L_B\nabla\mu_B + v_c^v c_B = 0$$

$$v_c^V = \frac{L_A\nabla\mu_A + L_B\nabla\mu_B}{C_A + C_B}$$

$$(C_A + C_B)\Omega = 1$$

$$= \Omega(L_A\nabla\mu_A + L_B\nabla\mu_B)$$

We're interested in J_B

$$J_B = J_B^c + c_B v_c^c$$

$$= -L_B \nabla\mu_B + c_B(\Omega)(L_A \nabla\mu_A + L_B\nabla\mu_B)$$

$$= -(c_A + c_B)\Omega L_B \nabla\mu_B + \cdots\cdots$$

$$= \Omega(c_A L_B \nabla\mu_B - c_B L_A \nabla\mu_A)$$

$$\underline{= X_A L_B \nabla\mu_B - X_B L_A \nabla\mu_A}$$

$$= X_A \cdot -J_B^c + X_B \cdot J_A^c$$

$\nabla\mu_A$ $\nabla\mu_B$ follows further simplificating

$$\begin{cases} (c_A + c_B)\Omega = 1 \\ c_A\Omega\nabla\mu_A + c_B\Omega\nabla\mu_B = 1 \end{cases}$$

Expansion

$$c_A L_{\underset{(c_A+c_B)\Omega}{\wedge}B} \nabla\mu_B - c_B L_{\underset{(c_A+c_B)\Omega}{\wedge}A}\nabla\mu_A$$

$$\Downarrow$$

$$= \Omega[(c_A^2 L_B + c_B^2 L_A)(\nabla\mu_B - \nabla\mu_A)$$
$$+ (c_A L_B - c_B L_A)\underbrace{(c_A\nabla\mu_A + c_B\nabla\mu_B)}_{0}]$$

$$\Downarrow$$

Without any assumption

$$J_B^V = -\Omega^2(c_A^2 L_B + c_B^2 L_A)(\nabla\mu_B - \nabla\mu_A)$$

$$= -\Omega^2(c_A^2 L_B + c_B^2 L_A)\underbrace{\nabla(\mu_B - \mu_A)} \rightarrow \text{Driving force chem pot}$$

Without any assumption

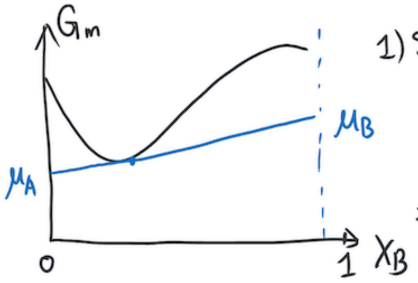
$$J_B^V = -\Omega^2 (c_A^2 L_B + c_B^2 L_A)(\nabla\mu_B - \nabla\mu_A)$$

$$= -\underbrace{\Omega^2 (c_A^2 L_B + c_B^2 L_A)}_{\text{V-frame mobility}} \underbrace{\nabla(\mu_B - \mu_A)}_{\to \text{Driving force chem pot}}$$

$$= -M \nabla(\mu_B - \mu_A)$$

① $M > 0$ (use $\dot{\sigma} > 0$ statement)

$\mu_B - \mu_A$, what does that mean?

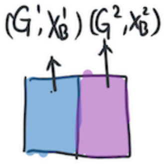


1) Slope of phase-diagram

$$\frac{\partial G}{\partial X} = \frac{\mu_B - \mu_A}{1}$$

2) What is $\nabla(\mu_B - \mu_A)$?

spatial gradient of $\mu_B - \mu_A$



③ $$J_B^V = -M \nabla(\mu_B - \mu_A)$$

$$= -\frac{M}{N_0} \underline{\underline{\nabla \frac{\partial G}{\partial X_B}}}$$

↑ chain rule $\left(\nabla\left(\frac{\partial Y}{\partial x}\right) = \frac{\partial^2 Y}{\partial x^2} \nabla c\right.$

$$= -\frac{M}{N_0 \Omega} \nabla \frac{\partial G}{\partial c_B} = -\frac{M}{N_0 \Omega} \frac{\partial^2 G}{\partial c_B^2} \nabla c_B$$

↑ $(c_B \Omega = X_B)$

$$= -\boxed{\frac{M\Omega}{N_0} \frac{\partial^2 G}{\partial X_B^2}} \nabla c_B$$

$$= -\tilde{D} \nabla c_B$$

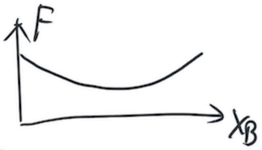
1) What have we done? We use the general chemical potential D.F.

$\Rightarrow$ interdiffusivity

2) $$\tilde{D} = \frac{M\Omega}{N_0}\frac{\partial^2 G}{\partial X_B^2} \quad (\text{In NPT})$$

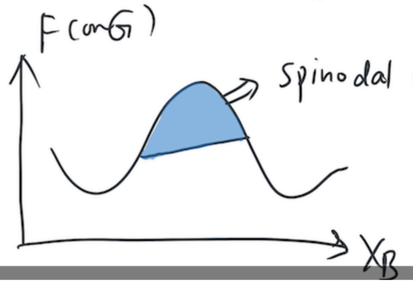
$$= \frac{\overset{>0}{M}\,\overset{>0}{\Omega}}{N_0}\underbrace{\frac{\partial^2 F}{\partial X_B^2}}_{\text{can change sign !}} \quad (\text{In NVT})$$

3) In solute of A&B



$$\frac{\partial^2 F}{\partial X_B^2} > 0 \Rightarrow \text{Darken's equation}$$

$$\tilde{D} = X_2 D_1 + X_1 D_2$$



spinodal region $\tilde{D} < 0$

Wavelength of fluctuations

Assume $\breve{D}$ is same everywhere

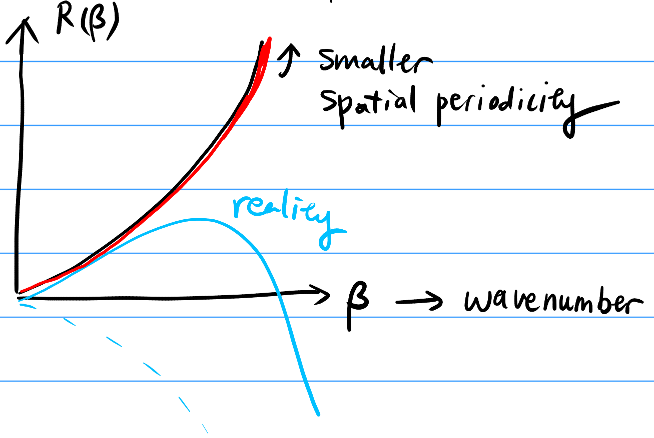
$$\frac{\partial c_B}{\partial t} = \breve{D}\,\nabla^2 c_B$$ in 1D, general solution

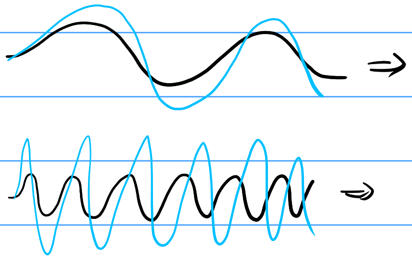
We assume c_B has spetial variation $C_B = A(t)\cdot\exp(i\beta x)$

$$\frac{\partial^2 C_B}{\partial x^2} = A(t)\,(-\beta^2)\exp(i\beta x) \Rightarrow \frac{dA(t)}{dt} = -\beta^2 A(t)\cdot\breve{D}$$

Solution for $A(t)$ is $A(t) = A(0)\cdot\exp(-\beta^2\breve{D})$

$\breve{D} < 0 \Rightarrow R(\beta) = -\beta^2\breve{D} > 0$! $A(t)$ exponentially grow



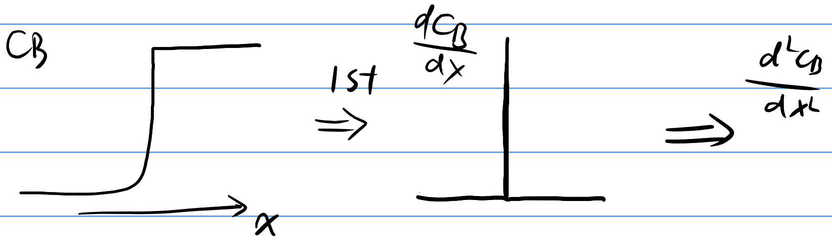


We can assume some term with higher power of β is counter balancing

⇓

surface energy ! (λ)

But how to define λ for diffuse interface?



What do you mean when $\breve{D} < 0$?

1) In spinodal decomposition, ∇C_B is <u>NO LONGER</u> a driving force!

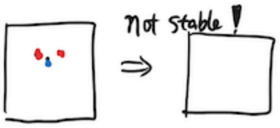
2) Uphill (against C_B gradient) diffusion can occur

3) From our analysis of diffusion equation (1D)

$$C(x,t) = \sum_{n=1}^{\infty} A_n \sin\left(\underset{\approx}{n}\pi \frac{x}{L}\right) e^{-\underset{\approx}{n}^2 \pi^2 \underline{\underline{D}} t / L^2}$$

$\breve{D} > 0 \Rightarrow$ smaller wavelength high n $\Rightarrow$ decay faster

$\breve{D} < 0 \Rightarrow$ smaller wavelength $\Rightarrow$ amplify!



---

1) In reality, surface areas <u>Regularize</u> the interface

2) Unlike nucleation, γ penalized larger particles!

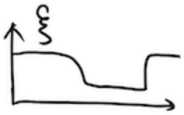
Let's look again at $\breve{D}$

$$\breve{D} = \frac{M\Omega}{N_0} \boxed{\frac{\partial^2 F}{\partial X_B^2}}$$

F as Helmholtz F.E.
is usually defined for homogeneous
systems

For inhomogeneous system, the "interface" may be ill-defined until clear boundary occur. Need formal way to describe by order parameter

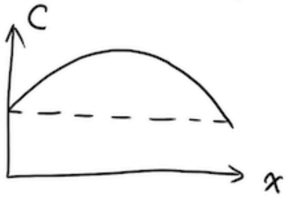
We need some functional to describe inhomogeneous F.E.



$\xrightarrow{F}$ Scalar free energy

Diffusion potential

$$\Phi(r) = \underbrace{\frac{\partial f^{homo}}{\partial \xi}}_{\Uparrow\ \text{Homogeneous}} - 2K\underline{\nabla^2 \xi} \Rightarrow \text{sec der. to order parameter?}$$



$\nabla^2\xi \Rightarrow$ local curvature of ordered parameter (like C)

penalty $K\cdot\nabla^2\xi \Rightarrow$ similar to penalty of local surface curvature

Cahn-Hilliard Equation

$$\begin{aligned}
J_B &= -L\,\nabla(\mu_B - \mu_A) \\
&= -L\,\nabla \frac{\partial F}{\partial c_B} \\
&= -L\,\nabla \left\{ \frac{\partial f^{hom}}{\partial c_B} - 2k_2 \nabla^2 c_B \right\} \\
&= -\frac{\breve{D}}{\left(\dfrac{\partial^2 f^{hom}}{\partial c_B^2}\right)} \nabla \left\{ \frac{\partial f^{hom}}{\partial c_B} - 2k_c \nabla^2 c_B \right\}
\end{aligned}$$

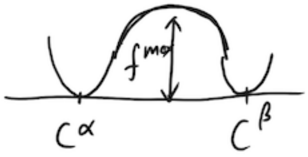
$\Leftarrow$ can be negative

$$\frac{\partial c_B}{\partial t} = -\nabla\cdot J_B = \nabla\cdot \left\{ \frac{\breve{D}}{\partial^2 f^{hom}/\partial c_B^2} \nabla \left[\frac{\partial f^{hom}}{\partial c_B} - 2k_c \nabla^2 c_B \right] \right\}$$

$$= \underbrace{M_0 \Big[\frac{\partial^2 f^{hom}}{\partial c_B^2}}_{\Downarrow \text{ like } D \text{ in Fick's second law}} \nabla^2 c_B - 2k_c \nabla^4 c_B \Big]$$

Cahn-Hilliard Eq Analysis

$$f^{homo} = \frac{16 f^{max}}{(c^{\beta} - c^{\alpha})^4} \left[(c_B - c^{\alpha})(c_B - c^{\beta}) \right]^2$$

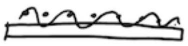


Let $C_B = \frac{c^{\alpha} + c^{\beta}}{2}$

$f(c_B = \frac{c^{\alpha} + c^{\beta}}{2}) = f^{max}$

Perturbation analysis

① Initial $C_B = C_0 = \frac{c^{\alpha} + c^{\beta}}{2}$



② perturb $C_B(z,t) = C_0 + \varepsilon(t) \sin \beta z$ wavelength $\lambda = \frac{2\pi}{\beta}$

The conc diff is wave-like

$$\frac{d\varepsilon(t)}{dt} = \underbrace{\frac{M_0 \beta^2}{(c^{\beta} - c^{\alpha})^2} \left[16 f^{hom}_{max} - 2k_c \beta^2 (c^{\beta} - c^{\alpha})^2 \right]}_{} \varepsilon(t)$$

This has a form $\frac{d\varepsilon}{dt} = A \varepsilon(t) \Rightarrow$ Solution has $e^{k(t)}$ format

$$\varepsilon(t) = \varepsilon(0) \cdot e^{R(\beta) t}$$

$R(\beta)$: amplification factor

① $\lambda > \lambda_{crit} = \frac{\pi}{2}(c^{\beta} - c^{\alpha}) \sqrt{\frac{2k_c}{f^{max}}} \Rightarrow R(\beta) > 0$ Grow

② Fastest growing wavelength?

$\lambda_{max} = \sqrt{2} \lambda_{crit}$