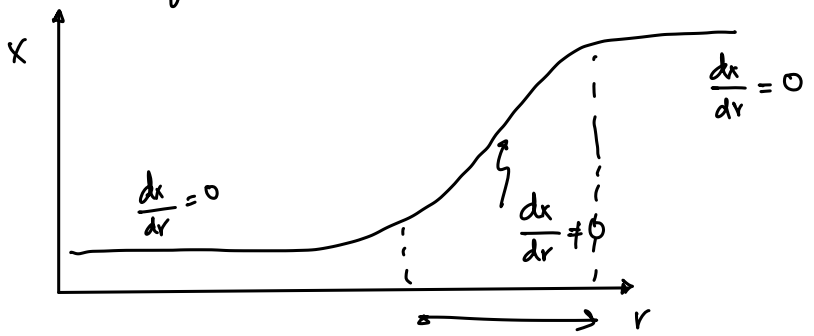
$$G = \int_V \left\{ g(x) + \frac{1}{2} \sum_{\alpha\beta} K_{\alpha\beta}(x) \frac{\partial x}{\partial r_\alpha} \frac{\partial x}{\partial r_\beta} \right\} \frac{d\vec{r}}{\Omega}$$

$$\boxed{K_{\alpha\beta}(x) = m_{\alpha,\beta}(x) - \bar{n}_{\alpha\beta}} \longrightarrow \text{Gradient energy coefficient.}$$

"Penalizes concentration profiles with large concentration gradients".



Transition region between two different compositions cost energy.

* GRADIENT ENERGY COEFFICIENT:

Gradient energy penalty:

$$\sum_{\alpha\beta} K_{\alpha\beta} \left(\frac{\partial x}{\partial r_\alpha}\right)\left(\frac{\partial x}{\partial r_\beta}\right) = \begin{bmatrix} \frac{\partial x}{\partial r_1} & \frac{\partial x}{\partial r_2} & \frac{\partial x}{\partial r_3} \end{bmatrix} \begin{pmatrix} K_{11} & K_{12} & K_{13} \\ K_{21} & K_{22} & K_{23} \\ K_{31} & K_{32} & K_{33} \end{pmatrix} \begin{bmatrix} \frac{\partial x}{\partial r_1} \\ \frac{\partial x}{\partial r_2} \\ \frac{\partial x}{\partial r_3} \end{bmatrix}$$

Some symmetries of the gradient energy coefficient:

$$\left.\begin{aligned} K_{12} \frac{\partial x}{\partial r_1} \frac{\partial x}{\partial r_2} &= K_{21} \frac{\partial x}{\partial r_2} \frac{\partial x}{\partial r_1} \end{aligned}\right] \Rightarrow K_{12} = K_{21} \Rightarrow \underline{K} \text{ is asymmetric matrix.}$$

The gradient energy term should be +ve $\longrightarrow$ (a) should be a penalty and should not "lower" the energy of the system.

$$\begin{bmatrix} \frac{\partial x}{\partial r_1} & \frac{\partial x}{\partial r_2} & \frac{\partial x}{\partial r_3} \end{bmatrix} \underline{K} \begin{bmatrix} \frac{\partial x}{\partial r_1} \\ \frac{\partial x}{\partial r_2} \\ \frac{\partial x}{\partial r_3} \end{bmatrix} \geq 0 \quad \forall \left(\vec{\nabla} x\right) \Rightarrow \underline{K} \text{ is positive definite}$$

$\Rightarrow$ all eigenvalues are positive.

If the material is isotropic:

$$\underline{K} = k \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

NEXT STEPS: - What is the eq^m concentration profile $x(\vec{r})$?
- What is the equivalent chemical potential μ?

At eq^m:

$G[x(\vec{r})]$ → total free energy that is a functional of the concentration profile will be minimized at eq^m

$G[x(\vec{r})]$ → but in a function $x(\vec{r})$ → get out a number

We want to minimize $G[x(\vec{r})]$ with respect to all possible concentration distributions.

subject to the constraint that $\int_V \frac{x(\vec{r})}{V} d\vec{r} = N_{tot}$ [the # of atoms in the system is fixed]

★ LAGRANGE MULTIPLIERS (QUICK REMINDER):

Say we want to minimize $f(x)$ under the constraint that $g(x) = 0$

Define: $\mathcal{L}(x, \lambda) = f(x) - \lambda \cdot g(x)$

Instead of minimizing $f(x)$ subject to a constraint, we can instead find the stationary points of $\mathcal{L}(x, \lambda)$. Which is equivalent to finding values of x and λ such that

$$\frac{\partial \mathcal{L}}{\partial x} = 0 \quad \text{and} \quad \frac{\partial \mathcal{L}}{\partial \lambda} = 0$$

⊛ $\boxed{\frac{\partial f}{\partial x} - \lambda \frac{\partial g}{\partial x} = 0 \quad \text{and} \quad g = 0}$ ⇒ 2 equations in 2 unknowns can be solved for x_0 & λ_0

Often constraints of interest are of the form:

$g(x) = c \Rightarrow \boxed{g(x) - c = 0}$

$$\mathcal{L} = f(x) - \lambda(g(x) - c) \Rightarrow \frac{\partial \mathcal{L}}{\partial x} = \frac{\partial f(x)}{\partial x} - \lambda \frac{\partial g}{\partial x} = 0 \quad \text{and} \quad g(x) - c = 0$$

Let the value of x that minimizes $\mathcal{L}$ subject to the constraint $g(x) - c = 0$ be denoted x^*

In general $x^*(c)$ as the optimal value will change with the precise value of the constant c

$$\boxed{\mathcal{L}(x, \lambda, c) = f(x) - \lambda(g(x) - c)}$$

@ $x = x^*(c)$, $\lambda = \lambda^*(c)$

$$g(x^*(c)) = c \Rightarrow \boxed{\mathcal{L}(x^*(c), \lambda^*(c), c) = f(x^*(c))}$$

$$\frac{df(x^*(c))}{dc} = \frac{d}{dc}\left(\mathcal{L}(x^*(c), \lambda^*(c), c)\right) = \cancel{\frac{\partial \mathcal{L}}{\partial x}}^{\,0}\Big|_{x^*, \lambda^*} \frac{dx^*}{dc} + \cancel{\frac{\partial \mathcal{L}}{\partial \lambda}}^{\,0}\Big|_{x^*, \lambda^*} \frac{d\lambda^*}{dc} + \frac{\partial \mathcal{L}}{\partial c}\Big|_{x^*, \lambda^*} \cancel{\frac{dc}{dc}}^{\,1}$$

Since we evaluate @ the minimum.

$$\frac{df}{dc} = \frac{\partial \mathcal{L}}{\partial c} = \frac{\partial}{\partial c}\left[f - \lambda(g-c)\right] = \lambda$$

$$\boxed{\frac{df}{dc} = \lambda}$$

* Circling Back To Our Minimization Problem:

minimize $G[x(\vec{r})] = \int_V \left\{ g(x) + \frac{1}{2}\sum_\alpha \sum_\beta K_{\alpha\beta}(x) \frac{\partial x}{\partial r_\alpha}\frac{\partial x}{\partial r_\beta} \right\} \frac{d\vec{r}}{\Omega}$ subject to the constraint $\int_V \frac{x(\vec{r})}{\Omega} d\vec{r} = N_{tot}$

define the Lagrangian:

$$\mathcal{L} = G - \lambda\left(\int_V \frac{x(\vec{r})}{\Omega} d\vec{r} - N\right)$$

$$\lambda = \frac{\partial G}{\partial N} = \mu$$

↑ chemical potential!!

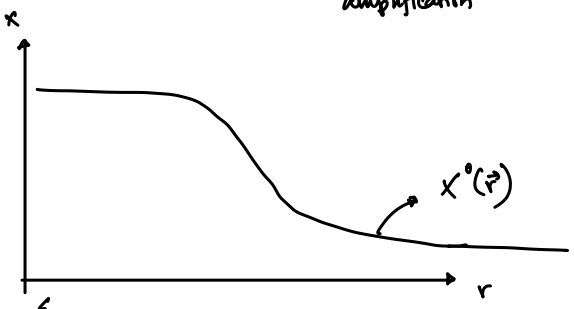
We will variationally minimize $\mathcal{L}$:

Let $x^\circ(\vec{r})$ be the concentration profile that minimizes $\mathcal{L}$

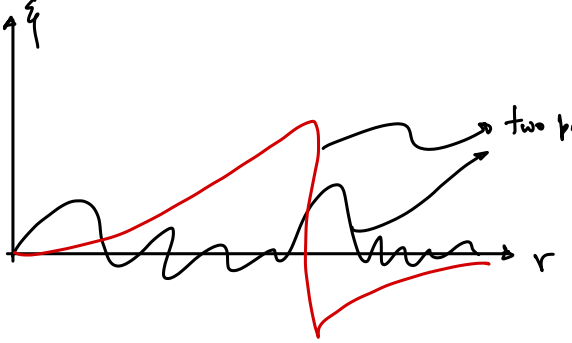
$$x(\vec{r}) = x^\circ(\vec{r}) + \epsilon \xi(\vec{r})$$

ϵ: amplification

ξ: some function that is zero at the boundaries and acts as a "perturbation" on top of $x^\circ(\vec{r})$

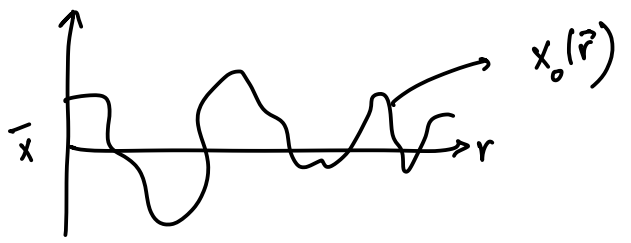


OPTIMAL CONCENTRATION PROFILE



two possible realizations of $\xi(\vec{r})$

RECALL:



we seek a solution $x(\vec{r},t)$ to describe microstructure evolution as

Total free energy of the system:

$$G[x(\vec{r})] = \int_V \left\{ g(x(\vec{r})) + \sum_{\alpha\beta} K_{\alpha\beta}(x(\vec{r})) \frac{\partial x}{\partial r_\alpha} \frac{\partial x}{\partial r_\beta} \right\} \frac{d\vec{r}}{\Omega}$$

Constraint: $\int_V \frac{x(\vec{r})}{\Omega} d\vec{r} = N$

$$\mathcal{L} = G[x(\vec{r})] - \mu \left(\int_V \frac{x(\vec{r})}{\Omega} d\vec{r} - N \right)$$

we will variationally minimize $\mathcal{L}$

To keep the math simple we will variationally minimize $\mathcal{L}$ in Δ:

$$\mathcal{L} = G\left[x^0(r) + \epsilon\,\xi(r)\right] - \mu\int_V \left(x^0(r) + \epsilon\,\xi(r)\right)\frac{dr}{\Omega} + \mu N$$

$$\mathcal{L} = \int_V \left[g\left(x^0 + \epsilon\xi\right) + K\left(\frac{\partial(x_0 + \epsilon\xi)}{\partial r}\right)^2 - \mu(\epsilon\xi)\right]\frac{dr}{\Omega} + \underbrace{\mu N - \mu\int_V x^0\frac{dr}{\Omega}}_{N}$$

these are equal and will cancel.

$$\mathcal{L} = \int_V \left[g\left(x^0 + \epsilon\xi\right) + K\left(\frac{\partial(x_0 + \epsilon\xi)}{\partial r}\right)^2 - \mu(\epsilon\xi)\right]\frac{dr}{\Omega}$$

neglect concentration dependence.

$\mathcal{L}$ is extremized when:

$$\left.\frac{\partial\mathcal{L}}{\partial\epsilon}\right|_{\epsilon=0} = 0$$

$$\frac{\partial\mathcal{L}}{\partial\epsilon} = \int_V \left[\frac{\partial g}{\partial x}\xi + 2K\,\frac{\partial(x_0+\epsilon\xi)}{\partial r}\cdot\underbrace{\frac{\partial\left(\frac{\partial(x_0+\epsilon\xi)}{\partial r}\right)}{\partial\epsilon}}_{\frac{\partial}{\partial\epsilon}\left(\frac{\partial x_0}{\partial r}\right) + \frac{\partial}{\partial\epsilon}\left[\epsilon\frac{\partial\xi}{\partial r}\right]} - \mu\xi\right]\frac{dr}{\Omega}$$

$$= \left(\frac{\partial\xi}{\partial r}\right)$$

$$\left.\frac{\partial\mathcal{L}}{\partial\epsilon}\right|_{\epsilon=0} = \int_V \left[\left(\frac{\partial g}{\partial x}\right)\xi + \underbrace{2K\,\frac{\partial x_0}{\partial r}\,\frac{\partial\xi}{\partial r}}_{\text{Integration by parts to turn } \frac{\partial\xi}{\partial r} \text{ into } \xi} - \mu\xi\right]\frac{dr}{\Omega} = 0$$

$$\int_V 2k \frac{\partial x_0}{\partial r} \frac{\partial \xi}{\partial r} \frac{dr}{\Omega} = \left[2\xi \left(\frac{\partial x_0}{\partial r} \right) k \right]_{r_1}^{r_2} - \int_V 2k\xi \frac{\partial^2 x_0}{\partial r^2} dr$$

(v, u')

edges of our 1D Domain

ξ @ edges $= 0$

$$\left. \frac{\partial \mathcal{L}}{\partial \epsilon} \right|_{\epsilon=0} = \int_V \xi \left[\frac{\partial g}{\partial x} - 2k \frac{\partial^2 x_0}{\partial r^2} - \mu \right] \frac{dr}{\Omega} = 0$$

Recall ξ can be ANY function

$\Rightarrow$ for the integrand to be zero

$$\boxed{\mu = \frac{\partial g}{\partial x} - 2k \frac{\partial^2 x_0}{\partial r^2}}$$

for an interstitial solid solution:

$$\mu = \frac{\partial g}{\partial x} \quad \text{usually}$$

we now have an EXTRA CONTRIBUTION due to the gradient energy term.

EVOLUTION EQUATION:

$$J = -L \nabla \mu$$

$$\mu = \frac{\partial g}{\partial x} - 2k \frac{\partial^2 x_0}{\partial r^2}$$

$$\Rightarrow J = -L \nabla \left(\frac{\partial g}{\partial x} - 2k \frac{\partial^2 x_0}{\partial r^2} \right) =$$

$$\boxed{J = -L \frac{\partial^2 g}{\partial x^2} \cdot \nabla x + 2Lk \nabla^3 x}$$

Compare with

$$\boxed{J = -L \frac{\partial^2 g}{\partial x^2} \nabla x}$$

Substitute J into fick's II Law:

$$\frac{\partial c}{\partial t} = -\nabla J$$

$$\boxed{\frac{\partial c}{\partial t} = L\frac{\partial^2 g}{\partial x^2}\nabla^2 x - 2Lk\nabla^4 x}$$

ASSUME:

① $\frac{\partial^2 g}{\partial x^2}$ = Constant ⟶ makes our analysis only valid for small concentration fluctuations.

② k ⟶ Constant.

③ L ⟶ Constant.

④ Ω independent of concentration.

$$c = \frac{x}{\Omega}$$

$$\frac{\partial c}{\partial t} = L\Omega\frac{\partial^2 g}{\partial x^2}\frac{\partial^2 c}{\partial r^2} - 2Lk\Omega\frac{\partial^4 c}{\partial r^4}$$

$L\Omega\frac{\partial^2 g}{\partial x^2} \rightarrow D$; $2Lk\Omega \rightarrow M$

$$\boxed{\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial r^2} - M\frac{\partial^4 c}{\partial r^4}}$$

⑤ defining $\Delta c = c(r,t) - \bar{c}$

$$\boxed{\frac{\partial \Delta c}{\partial t} = D\frac{\partial^2 \Delta c}{\partial r^2} - M\frac{\partial^4 \Delta c}{\partial r^4}}$$

Define the Fourier transform of $\Delta c \rightarrow \Delta\tilde{c}(k,t)$

fourier transform both sides of the equation.

$$\mathcal{F}\left\{\frac{\partial \Delta c}{\partial t}\right\} = \frac{\partial \Delta\tilde{c}(k,t)}{\partial t}$$

$$\mathcal{F}\left\{\frac{\partial^2 \Delta c}{\partial r^2}\right\} = (-ik)^2\Delta\tilde{c}(k,t) = -k^2\Delta\tilde{c}(k,t)$$

$$\mathcal{F}\left\{\frac{\partial^4 \Delta c}{\partial r^4}\right\} = (-ik)^4\Delta\tilde{c}(k,t) = k^4\Delta\tilde{c}(k,t)$$

$$\Rightarrow \boxed{\frac{\partial \Delta\tilde{c}}{\partial t} = (-k^2 D - k^4 M)\Delta\tilde{c}}$$

solution: $\Delta\tilde{c}(k,t) = \Delta\tilde{c}(k,t=0)\exp\left(-(k^2 D + k^4 M)t\right)$

$\Delta\tilde{c}(k,t=0)$ ⟶ fourier transform of the initial concentration profile.

$$\Delta c(r,t) = \mathcal{F}^{-1}\{\Delta\tilde{c}(k,t)\} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\Delta\tilde{c}(k,t=0)\exp\left((-k^2 D - k^4 M)t\right)\exp(-ikr)\,dk$$

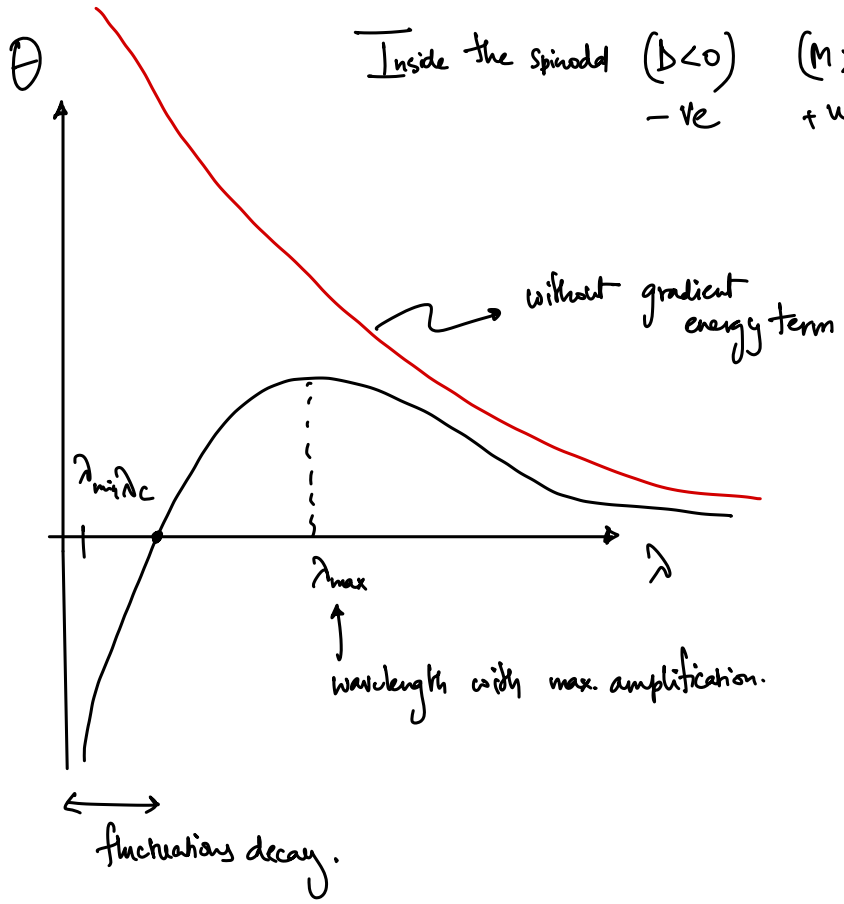
or equivalently:

$$\Delta c(r,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \underbrace{\left[A(k)\cos(kr) + B(k)\sin(kr)\right]}_{\text{Spatial dependence}} \underbrace{\exp\left(\left(-k^2 D - k^4 M\right)t\right)}_{\text{time dependence.}} dk$$

Amplification factor:

$$\theta = -\left(k^2 D + k^4 M\right) = -\left[\frac{4\pi^2 D}{\lambda^2} + \frac{16\pi^4 M}{\lambda^4}\right]$$

Outside the Spinodal	+ve	+ve
Inside the Spinodal	$(D<0)$	$(M>0)$
	−ve	+ve.

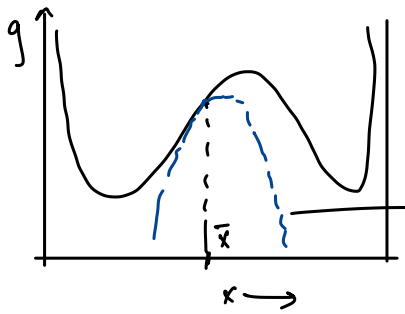


- λ_{max}: fastest growing wavelength ⟶ results in a characteristic periodicity within the microstructure. ~ 100 Å
- $\lambda < \lambda_c$: very short wavelengths decay.
  gradients are too large for short λ ⟹ high free energy penalty.
- Analysis only valid for early stages of Spinodal decomposition:

$$\boxed{\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - 2LK\Omega\frac{\partial^4 c}{\partial x^4}}$$

LINEARIZED CAHN-HILLIARD EQUATION.

We assumed $D, L, \frac{\partial^2 g}{\partial x^2}$, are all constant.



→ Approximation to $g(x)$ if we assum $\frac{\partial^2 g}{\partial x^2}$ = Constant

only valid when (Δx) is within the range where this approximation holds.

NON-LINEAR CAHN-HILLIARD EQUATION IS TYPICALLY SOLVED NUMERICALLY:

→ mobility coefficients: $L \sim x(1-x)f(x)$

$g(x)$ & $K(x)$