

* How Do WE INTERPRET THE SOLUTION?

Define $A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Delta C_0(r,0) \cos(kr) dr$ $B(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Delta C_0(r,0) \sin(kr) dr$

$\Delta \tilde{C}_0(k,0) = A(k) + iB(k)$

$$\Delta C(r,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp(-k^2Dt) \exp(-ikr) \overbrace{\Delta \tilde{C}_0(k,0)}^{A(k)+iB(k)} dk$$

$\left[\cos(kr) - i \sin(kr) \right]$
Euler's formula

$$\Delta C(r,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp(-k^2Dt) \left[A(k) \cos(kr) + B(k) \sin(kr) + i(B(k) \cos(kr) - A(k) \sin(kr)) \right] dk$$

$$\Delta C(r,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp(-k^2Dt) \left[A(k) \cos(kr) + B(k) \sin(kr) \right] dk$$

+ i $\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp(-k^2Dt) \left[B(k) \cos(kr) - A(k) \sin(kr) \right] dk$

odd function of $k \Rightarrow$ integral is zero.

$$\Delta C(r,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp(-k^2Dt) \left[A(k) \cos(kr) + B(k) \sin(kr) \right] dk$$

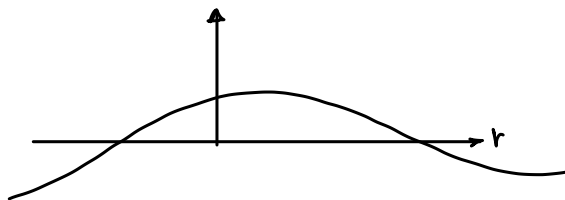
time

Superposition of sines and cosines. each having wavelength $\lambda = 2\pi/k$

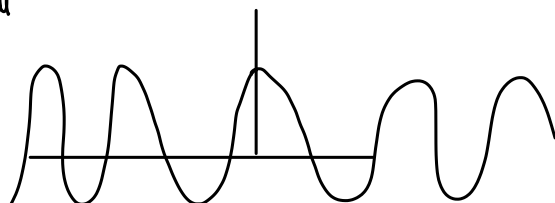
— each modulation of wavelength λ has a DECAY (OR AMPLIFICATION) factor of $\boxed{\exp(-k^2Dt)}$

— Behavior of different wavelengths:

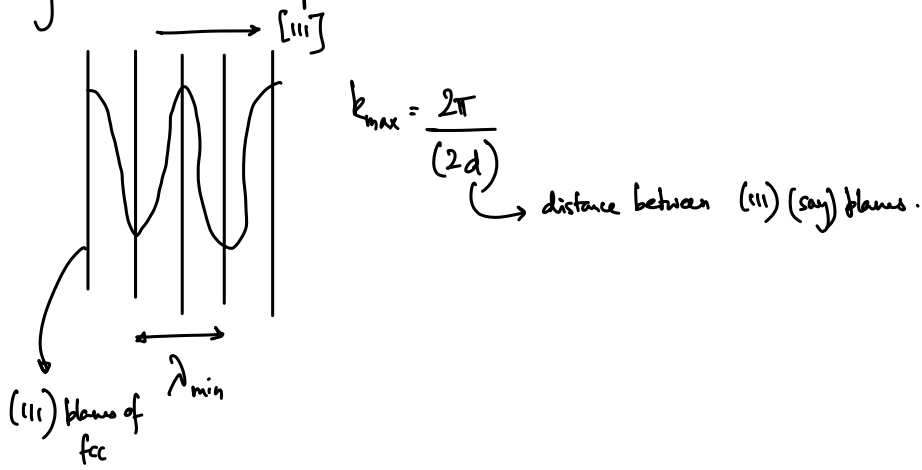
① $k = \text{small} \quad \lambda = \frac{2\pi}{k} \rightarrow \text{large}$



② $k = \text{large} \quad \lambda = \frac{2\pi}{k} \rightarrow \text{small}$



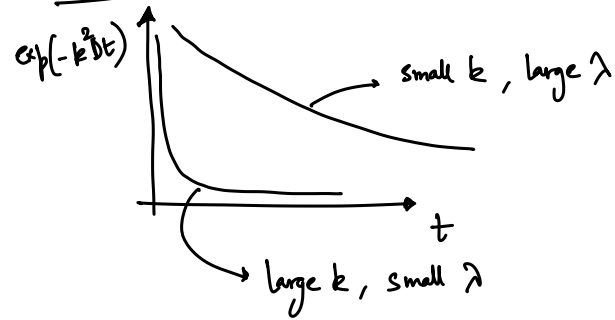
— Physically fluctuations in composition smaller than the distance between atoms would not make sense.



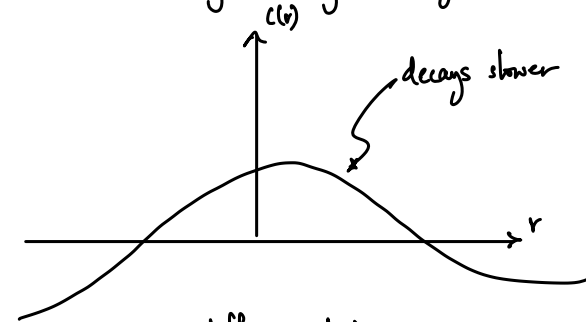
— What is the decay (or amplification) rate for different waves?

$$\exp(-k^2 Dt) = \exp\left(-\frac{4\pi^2}{\lambda^2} Dt\right)$$

CASE I: $D > 0$

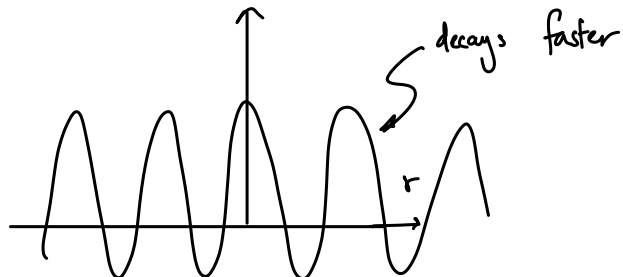


→ time decay of long wavelengths is slower than short wavelengths.



diffusion distances to even out composition fluctuations are longer

⇒ Takes more time to redistribute matter



shorter diffusion distances to even out composition fluctuations.

CASE II: $D < 0$

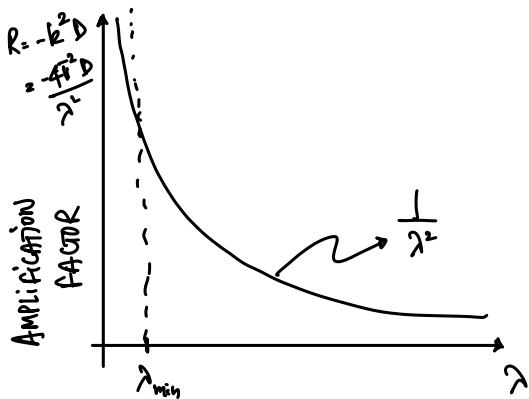
$$\exp(-k^2 D t) = \exp(k^2 |D| t) = \exp\left(\frac{|D| 4\pi^2 t}{\lambda^2}\right) \Rightarrow \text{Concentration fluctuations get amplified.}$$

$k \rightarrow \text{large} \Rightarrow \lambda \rightarrow \text{small} \Rightarrow \text{amplification factor is large}$

$k \rightarrow \text{small} \Rightarrow \lambda \rightarrow \text{large} \Rightarrow \text{amplification factor is small.}$

- time amplification of short wavelengths is much faster than that of long wavelengths

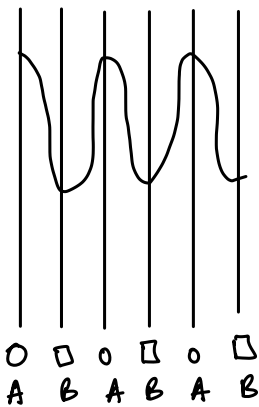
\Rightarrow Atoms want to phase separate !!



Asymptotic Microstructure: in the long time limit

λ with the largest amplification factor will dominate

$$\Rightarrow \Delta c(r, t) \approx \underset{\text{approximate}}{\uparrow} [A(k_{\max}) \cos(k_{\max} r) + B(k_{\max}) \sin(k_{\max} r)] \exp(-k_{\max}^2 D t)$$



\Rightarrow A & B separate and occupy alternate atomic planes.

..... DO WE HAVE A PROBLEM?

PROBLEMS/ISSUES:

- ① We expected phase separation, but we got a particular ordering of A & B atoms \Rightarrow This is @ odds with the eq^m phase diagram.
- ② Experimentally spinodal decomposition is found to have a "characteristic" length scale.

WHAT WENT WRONG:

- We (implicitly) assumed that we could assign local thermodynamic properties to depend on only local concentration:

$$(c) \text{ @ } \vec{r} \Rightarrow g(x(\vec{r})), \mu(x(\vec{r}))$$

within this approximation:

$$J = -L \nabla \mu = -D \nabla c = -L \Omega \frac{\partial^2 g}{\partial x^2} \nabla c$$

- This approximation is OK as long as gradients in concentration are not too large.
- Should be applicable OUTSIDE the spinodal.
- Inside the spinodal: \rightarrow large gradients.
- Our model does not penalize interfaces! \Rightarrow We end up forming atomically thin layers.

SOLUTION:

The local free energy depends on the concentration and higher order derivatives of $x(\vec{r})$.

$$(c) \ g(x(\vec{r}), \frac{dx(\vec{r})}{dr}, \frac{d^2 x(\vec{r})}{dr^2}, \dots)$$

In 3-dimensions:

$$g(x(\vec{r}), \frac{\partial x}{\partial r_\alpha}, \frac{\partial^2 x}{\partial r_\alpha \partial r_\beta}, \dots)$$

\swarrow 3 of these \swarrow 6 of these

Total free energy:

$$G = \int_V g(x(\vec{r}), \frac{\partial x}{\partial r_\alpha}, \frac{\partial^2 x}{\partial r_\alpha \partial r_\beta}, \dots) \frac{d\vec{r}}{\Omega}$$

$$g(x(\vec{r}), \frac{\partial x}{\partial r_\alpha}, \frac{\partial^2 x}{\partial r_\alpha \partial r_\beta}, \dots) = g(x(\vec{r})) + \vec{A}(x(\vec{r})) \cdot \vec{\nabla} x + \frac{1}{2} \sum_{\alpha} \sum_{\beta} m_{\alpha\beta}(x(\vec{r})) \frac{\partial x}{\partial r_\alpha} \frac{\partial x}{\partial r_\beta} + \dots$$

\uparrow function of composition.

$$+ \sum_{\alpha} \sum_{\beta} n_{\alpha\beta} \frac{\partial^2 x}{\partial r_\alpha \partial r_\beta} + \dots$$

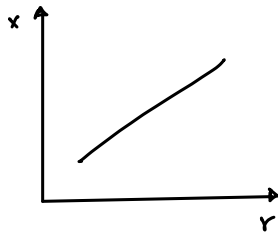
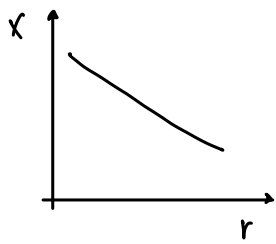
Lets simplify the Taylor expansion in 1D:

Assume:

$$g(x, \frac{dx}{dr}) = g(x, 0) + \underbrace{\frac{\partial g}{\partial (\frac{dx}{dr})} \Big|_{(x,0)}}_{H(x)} \cdot \left(\frac{dx}{dr}\right) + \frac{1}{2} \underbrace{\frac{\partial^2 g}{\partial (\frac{dx}{dr})^2} \Big|_{(x,0)}}_{K(x)} \cdot \left(\frac{dx}{dr}\right)^2 + \dots$$

\uparrow
 Only a function of x and gradient of $x \rightarrow$ not $d^2x/dr^2, \dots$

$$g(x, \frac{dx}{dr}) = g(x, 0) + H(x) \frac{dx}{dr} + k(x) \frac{dx}{dr}$$



Consider the following composition profiles.

If a crystal has inversion symmetry.

$$g(x, \frac{dx}{dr}) = g(x, -\frac{dx}{dr})$$



free energy should not change if we invert the coordinate system.

⇒ CAVS DEPEND ON THE DIRECTION OF THE GRADIENT

$$\Rightarrow H(x) = 0$$

$$g(x, \frac{dx}{dr}) = g(x, 0) + k \left(\frac{dx}{dr} \right)^2$$

* Going back to 3D:

$$g(x, \frac{\partial x}{\partial r_\alpha}, \frac{\partial^2 x}{\partial r_\alpha \partial r_\beta}, \dots) = g(x) + \vec{A}(x) \cdot \nabla x + \frac{1}{2} \sum_{\alpha} \sum_{\beta} m_{\alpha\beta}(x) \frac{\partial x}{\partial r_\alpha} \frac{\partial x}{\partial r_\beta} + \dots + \sum_{\alpha\beta} n_{\alpha\beta}(x) \frac{\partial^2 x}{\partial r_\alpha \partial r_\beta} + \dots$$

$\vec{A}(x) = 0$ for crystals with inversion symmetry.

Approximate the free energy upto 2nd order:

$$G = \int_V \left\{ g(x) + \frac{1}{2} \sum_{\alpha\beta} m_{\alpha\beta}(x) \frac{\partial x}{\partial r_\alpha} \frac{\partial x}{\partial r_\beta} + \frac{1}{2} \sum_{\alpha\beta} n_{\alpha\beta}(x) \frac{\partial^2 x}{\partial r_\alpha \partial r_\beta} \right\} dV$$

Consider one α, β pair

$$\int_V n_{\alpha\beta}(x) \frac{\partial^2 x}{\partial r_\alpha \partial r_\beta} dV = \int_V \frac{\partial}{\partial r_\alpha} \left(n_{\alpha\beta}(x) \frac{\partial x}{\partial r_\beta} \right) dV - \int_V \frac{\partial n_{\alpha\beta}(x)}{\partial r_\alpha} \frac{\partial x}{\partial r_\beta} dV \quad \left[\text{Integrate by parts.} \right]$$

$$= \oint_S \left(n_{\alpha\beta}(x) \frac{\partial x}{\partial r_\beta} \right) dS - \int_V \frac{\partial n_{\alpha\beta}(x)}{\partial r_\alpha} \frac{\partial x}{\partial r_\beta} dV$$

Scales with the surface

$\ll V$

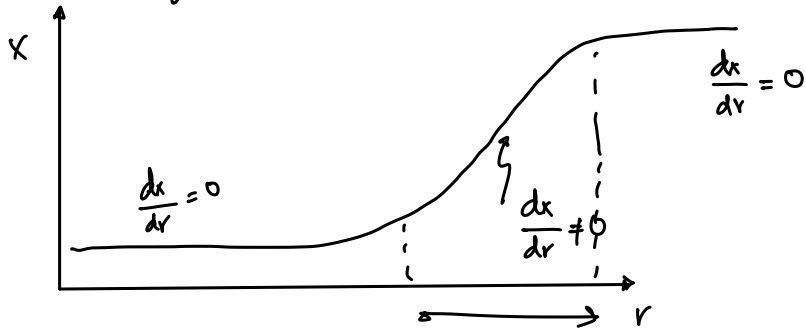
So we will neglect this term

$\bar{n}_{\alpha\beta}(x)$

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

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

"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:

$$K_{12} \frac{\partial x}{\partial r_1} \frac{\partial x}{\partial r_2} = K_{21} \frac{\partial x}{\partial r_2} \frac{\partial x}{\partial r_1} \Rightarrow K_{12} = K_{21} \Rightarrow K \text{ is symmetric matrix.}$$

The gradient energy term should be +ve \rightarrow (6) should be a penalty and should not "lower" the energy of the system.

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

If the material is isotropic:

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

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 $\int_V \frac{x(\vec{r})}{V} d\vec{r} = N_{\text{tot}}$ [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

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

$$\textcircled{1} \quad \left[\frac{\partial f}{\partial x} - \lambda \frac{\partial g}{\partial x} = 0 \quad \text{and} \quad g = 0 \right] \Rightarrow \text{2 equations in 2 unknowns can be solved for } x \text{ \& } \lambda.$$

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

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

$$\textcircled{2} \quad x = x^*(c), \quad \lambda = \lambda^*(c)$$

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

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

Since we evaluate @ the minimum.

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

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

* CIRCLING BACK TO OUR MINIMIZATION PROBLEM:

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

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!!

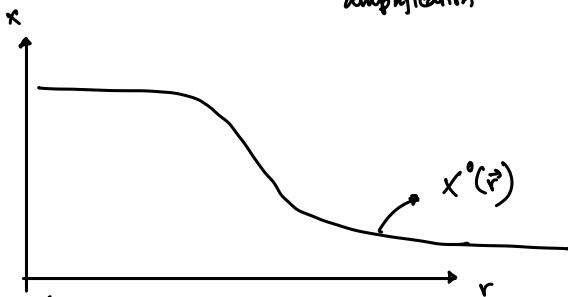
We will variationally minimize \mathcal{L} :

Let $x^0(\vec{r})$ be the concentration profile that minimizes \mathcal{L}

$$x(\vec{r}) = x^0(\vec{r}) + \epsilon \xi(\vec{r})$$

↑
amplification

some function that is zero at the boundaries and acts as a "perturbation" on top of $x^0(\vec{r})$



OPTIMAL CONCENTRATION PROFILE

