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.

* How do we interpret the solution?

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

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

$$\Delta C(r,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp(-k^2 Dt) \exp(-ikr) \Delta C_0(k,0)\, dk$$

($\exp(-ikr)$ → Cos(kr) − i Sin(kr) (Euler's formula); $\Delta C_0(k,0)$ → A(k) + iB(k))

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

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

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

odd function of k ⇒ integral is Zero.

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

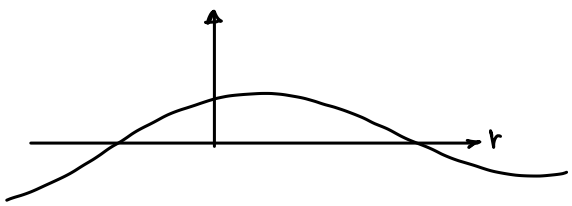
$\exp(-k^2 Dt)$ → time

$A(k)\cos(kr) + B(k)\sin(kr)$ → Superposition of sines and cosines. each having wavelength $\lambda = 2\pi/k$

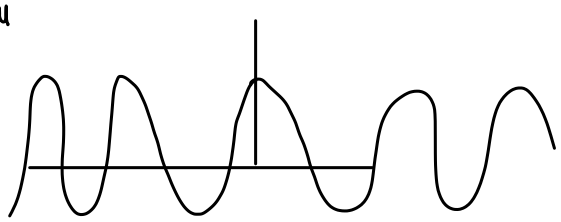
— each modulation of wavelength λ has a DECAY (OR AMPLIFICATION) factor of $\exp(-k^2 Dt)$

— Behavior of different wavelengths:

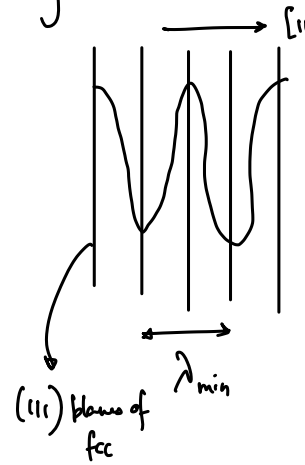
① k = small $\quad \lambda = \frac{2\pi}{k} \longrightarrow$ large



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



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



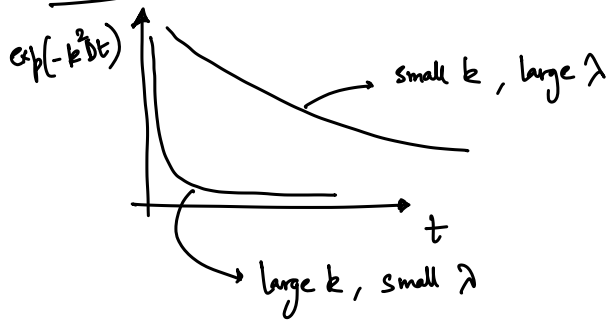
$k_{max} = \frac{2\pi}{(2d)}$

↳ distance between (111) (say) planes.

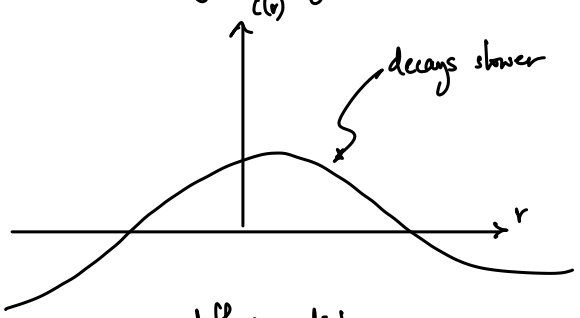
— What is the decay (or amplification) rate for different waves?

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

CASE I: $D > 0$

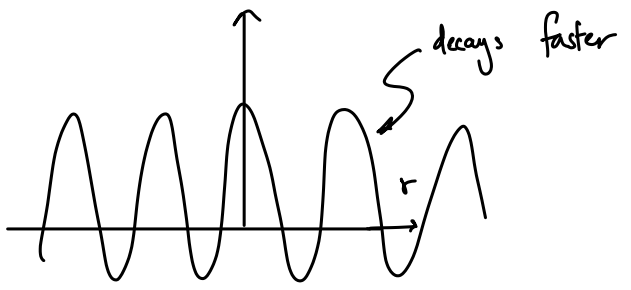


→ time decay of long wavelengths is slower than short wavelengths.



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: $D < 0$

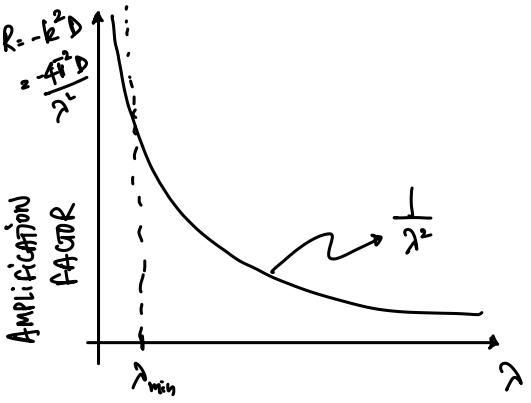
$$\exp(-k^2 D t) = \exp(k^2 |D| t) = \exp\left(\frac{|D| 4\pi^2 t}{\lambda^2}\right) \Longrightarrow \text{Concentration fluctuations get amplified.}$$

$k \rightarrow$ large $\Rightarrow \lambda \rightarrow$ small $\Rightarrow$ amplification factor is large

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

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

$\Rightarrow$ Atoms want to phase separate !!

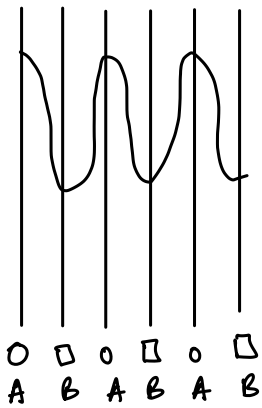


Asymptotic Microstructure: in the long time limit

λ with the largest amplification factor will dominate

$$\Rightarrow \Delta C(r,t) \approx \left[A(k_{max}) \cos(k_{max} r) + B(k_{max}) \sin(k_{max} r)\right] \exp(-k_{max}^2 D t)$$

(approximate)



$\Rightarrow$ 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 ⇒ This is @ odds with the eqm 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:

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

  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: ⟶ large gradients.
- Our model does not penalize interfaces! ⇒ We end up forming atomically thin layers.

SOLUTION:

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

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

In 3-dimensions:

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

($\frac{\partial x}{\partial r_\alpha}$: 3 of these; $\frac{\partial^2 x}{\partial r_\alpha \partial r_\beta}$: 6 of these)

Total free energy:

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

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

($m_{\alpha\beta}$: 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:

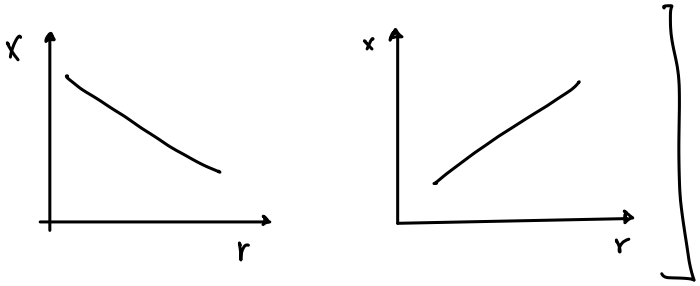
Assume: $g\left(x, \frac{dx}{dr}\right) = g(x,0) + \left.\frac{\partial g}{\partial\left(\frac{dx}{dr}\right)}\right|_{(x,0)}\cdot\left(\frac{dx}{dr}\right) + \frac{1}{2}\left.\frac{\partial^2 g}{\partial\left(\frac{dx}{dr}\right)^2}\right|_{(x,0)}\cdot\left(\frac{dx}{dr}\right)^2 + \dots$

($g\left(x, \frac{dx}{dr}\right)$: only a function of x and gradient of x ⟶ not $d^2x/dr^2, \dots$)

$\left.\frac{\partial g}{\partial\left(\frac{dx}{dr}\right)}\right|_{(x,0)} = H(x)$

$\frac{1}{2}\left.\frac{\partial^2 g}{\partial\left(\frac{dx}{dr}\right)^2}\right|_{(x,0)} = k(x)$

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



Consider the following composition profiles.

If a crystal has inversion symmetry.

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

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

$\Rightarrow$ CANT DEPEND ON THE DIRECTION OF THE GRADIENT

$\Rightarrow H(x) = 0$

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

* Going back to 3D:

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

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

Approximate the free energy upto 2nd order:

$$G = \int_V \left\{ g(x) + \frac{1}{2}\sum_{\alpha\beta}\eta_{\alpha\beta}(x)\frac{\partial x}{\partial r_\alpha}\frac{\partial x}{\partial r_\beta} + \underbrace{\frac{1}{2}\sum_{\alpha\beta}\eta_{\alpha\beta}(x)\frac{\partial^2 x}{\partial r_\alpha \partial r_\beta}}_{\text{Consider one } \alpha,\beta \text{ pair}} \right\}\frac{d\vec{r}}{\Omega}$$

$$\int_V \eta_{\alpha\beta}(x)\frac{\partial^2 x}{\partial r_\alpha \partial r_\beta}\,dV = \int_V \frac{\partial}{\partial r_\alpha}\left(\eta_{\alpha\beta}(x)\frac{\partial x}{\partial r_\beta}\right)dV - \int_V \frac{\partial \eta_{\alpha\beta}(x)}{\partial r_\alpha}\frac{\partial x}{\partial r_\beta}\,dV$$

Integrate by parts.

$$= \underbrace{\oint_S \left(\eta_{\alpha\beta}(x)\frac{\partial x}{\partial r_\beta}\right)dS}_{\text{Scales with the surface} \ll V \text{ So we will neglect this term}} - \int_V \underbrace{\frac{\partial \eta_{\alpha\beta}(x)}{\partial x}}_{\bar{\eta}_{\alpha\beta}(x)}\frac{\partial x}{\partial r_\alpha}\cdot\frac{\partial x}{\partial r_\beta}\,dV$$