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

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

these are equal and will cancel.

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

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

neglect concentration dependence.

$\mathcal{L}$ is extremized when:

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

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

$$\frac{\partial}{\partial\epsilon}\left(\frac{\partial x_0}{\partial r}\right) + \frac{\partial}{\partial\epsilon}\left[\epsilon\frac{\partial\xi}{\partial r}\right] = \left(\frac{\partial\xi}{\partial r}\right)$$

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

Integration by parts to turn $\frac{\partial\xi}{\partial r}$ into ξ

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

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 <u>interstitial solid solution</u>:

$$\left.\mu = \frac{\partial g}{\partial x}\right] \text{ usually}$$

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

EVOLUTION EQUATION:

$J = -L\nabla\mu.$

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

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

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

Compare with

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 anlysis only valid for small concentration fluctuations.

② K → Constant.

③ L → Constant.

④ Ω independent of concentration.

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

$$\frac{\partial c}{\partial t} = \underbrace{L\Omega\frac{\partial^2 g}{\partial x^2}}_{D}\frac{\partial^2 c}{\partial r^2} - \underbrace{2LK\Omega}_{M}\frac{\partial^4 c}{\partial r^4}$$

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

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

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

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

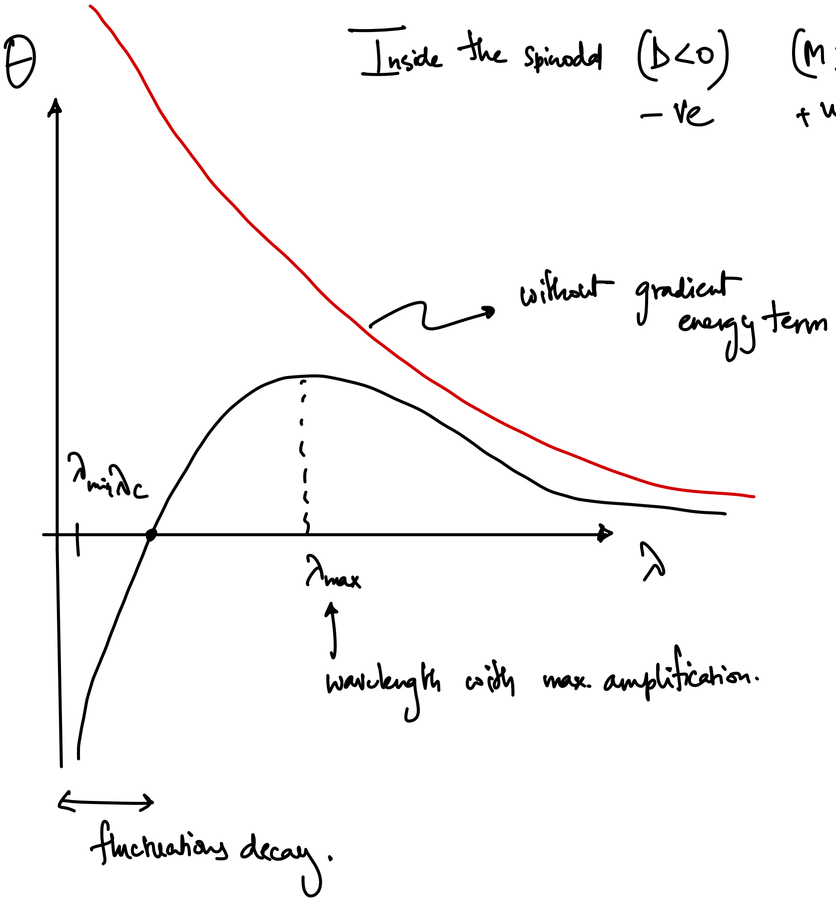
or equivalently:

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

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	$(D<0)$ −ve	$(M>0)$ +ve.

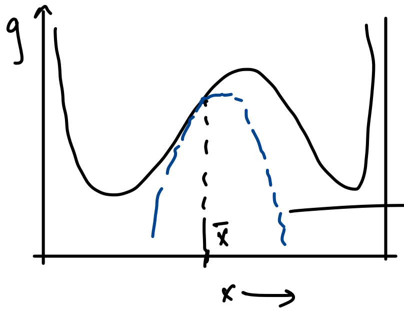


- λ_{max}: fastest growing wavelength ⟶ results in a characteristic periodicity within the microstructure. ~ 100 Å
- $\lambda < \lambda_c$: very short wave lengths decay.
  gradients are too large for short λ ⟹ high free energy penalty.
- Analysis only valid for early stages of spinodal decomposition:

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

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

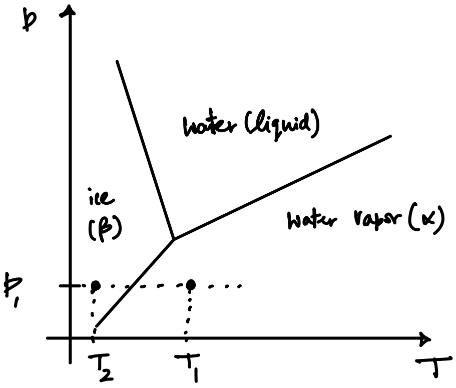
only Valid when (Δx) is within the range where this approximation holds.

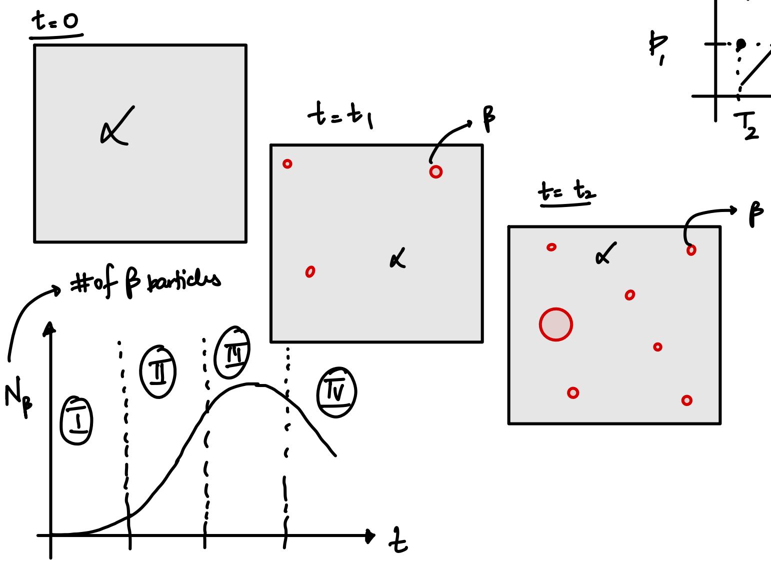
NON-LINEAR CAHN-HILLIARD EQUATION IS TYPICALLY SOLVED NUMERICALLY:

⟶ mobility coefficients : $L \sim x(1-x) f(x)$
$g(x)$ & $K(x)$

HOMOGENEOUS NUCLEATION

Consider a single component material, say water. Say we cool down the water vapor from a temperature of $T_1 \rightarrow T_2$ @ a pressure p_1





4-stages of the phase transformation

(I) → Incubation; α is metastable, small clusters of the β phase are formed and decomposed.

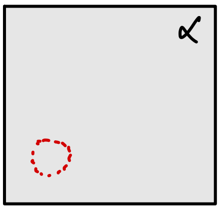
(II) → Quasi steady state nucleation; stable nuclei are continuously produced.

(III) → Decreased rate of nucleation; typically due to a decrease in supersaturation.

(IV) → late stages; Nucleation of new particles is negligible; Existing nuclei grow

We will primarily focus on (I) & (II)

CLASSICAL THEORY OF NUCLEATION



Say there are N particles of α

$\alpha \rightarrow \beta$ will result in a free energy change.

STEPS TO COMPUTE THE FREE ENERGY CHANGE

① Pick n particles that form a cluster and remove them ⇒ forms a void in α

② rearrange the n particles to form β

③ Insert the β phase back into α

$$\Delta G_{cluster} = \Delta G_{bulk} + \Delta G_{interfacial} + \Delta G_{strain}$$

bulk free energy change due to transition from $\alpha \rightarrow \beta$

energy penalty due to interface between α & β

neglect for now

ASSUME:

① Spherical cluster with radius r

② Isotropic interfacial energy

③ No strain energy

$$\Delta G_{bulk} = V_{cluster}\, \Delta g^{\alpha\to\beta}$$

free energy change / unit volume.

$$= \left(\frac{4}{3}\pi r^3\right) \Delta g^{\alpha\to\beta}$$

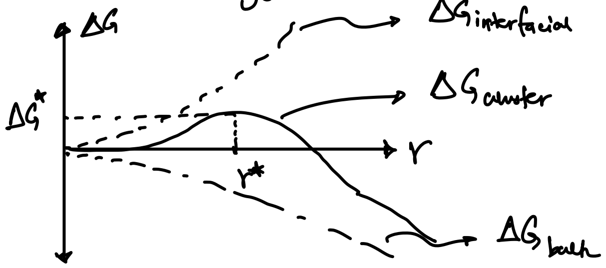
$$\Delta G_{interfacial} = \left(4\pi r^2\right)\gamma$$

surface energy per unit area

$$\Delta G_{cluster} = \frac{4}{3}\pi r^3 \Delta g^{\alpha\to\beta} + 4\pi r^2 \gamma$$

when $T < T^{\alpha\to\beta}$; α is metastable and $\Delta g^{\alpha\to\beta} < 0$

surface energy is positive



$\Delta G^*(r^*, T)$ is the free energy @ the critical radius (r^*) beyond which the free energy decreases with increasing size.

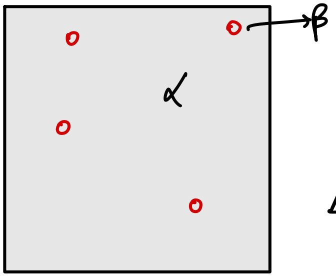
$$\left.\frac{\partial \Delta G_{cluster}}{\partial r}\right|_{r=r^*} = 0 = 4\pi r^* \left[\Delta g^{\alpha\to\beta} r^* + 2\gamma\right]$$

$$r^* = \begin{cases} 0, \\ -\dfrac{2\gamma}{\Delta g^{\alpha\to\beta}} \end{cases}$$

$r^* \downarrow$ as $\gamma \downarrow$ or $\Delta g^{\alpha\to\beta}$ becomes more negative

$$\boxed{\Delta G^*(r^*, T) = \frac{16\pi\gamma^3}{3(\Delta g^{\alpha\to\beta})^2}}$$

* In a real system at a temperature $T > T^{\alpha\to\beta}$



clusters of β will stochastically appear and disappear

Let a cluster have c atoms

surface area of the cluster $A \propto \eta c^{2/3}$ → shape factor

$$\Delta G(c) = \underset{\substack{\text{bulk free energy} \\ \text{per atom}}}{c\,\Delta g^{\alpha\to\beta}} + \eta c^{2/3}\gamma$$

surface energy.

Let there be N_c clusters of size c and $\mathcal{N}$ total atoms

\# of atoms in the β phase $= \sum_c N_c c = N_\beta$

\# of atoms in the α phase $= \mathcal{N} - N_\beta = \mathcal{N} - \sum_c N_c c = N_\alpha$

Free energy of the system:

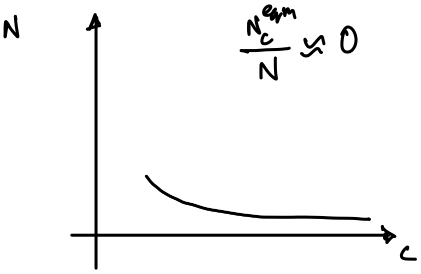
$$\Delta G = \underbrace{\sum_c N_c \Delta G(c)}_{\substack{\text{free energy change} \\ \text{to form } \beta}} + \underbrace{k_B T\left[N_\alpha \log\left(\frac{N_\alpha}{N_\alpha + \sum_c N_c}\right) + \sum_c N_c \log\left(\frac{N_c}{N_\alpha + \sum N_c}\right)\right]}_{\substack{\text{Configurational entropy of arranging } N_c\ \beta \text{ clusters} \\ \text{and } N_\alpha\ \alpha \text{ atoms.}}}$$

Notice $\Delta G(\{N_c\}) \longrightarrow$ # of clusters of size c

@ eq^m:

$$\frac{\partial \Delta G}{\partial N_c} = 0 \Rightarrow \boxed{\frac{N_c^{eqm}}{N} \approx \exp\left(-\frac{\Delta G(c)}{k_B T}\right)}$$

when $T > T^{\alpha \to \beta}$; $\Delta G(c) > 0$



$$\frac{N_c^{eqm}}{N} \approx 0$$

* Consider now a scenario where α is metastable $\Rightarrow T < T^{\alpha \to \beta}$

$J_c(t)$ = rate of growth or depletion of a cluster of size c to a cluster of size c+1

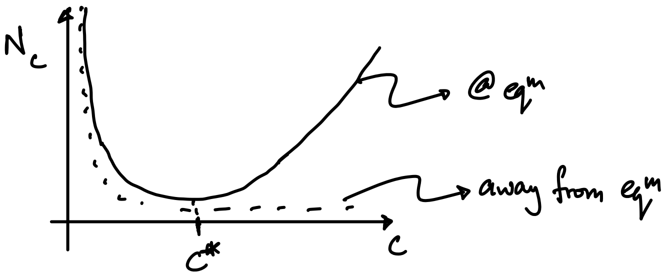
$$J_c(t) = \underbrace{\beta_c N_c(t)}_{\text{rate @ which single atoms attach to the clusters of size c from } \alpha} - \overbrace{\alpha_{c+1} N_{c+1}(t)}^{\text{rate @ which an atom detachs from the cluster to } \alpha}$$

ASSUME: no clusters beyond a size C_{max} are allowed to grow. $c_{max} \gg c^*$ $\longrightarrow$ critical cluster size

At eq^m: $$\frac{N_c^{eq}}{N} = \exp\left(-\frac{\Delta G(c)}{k_B T}\right)$$

During Stage I: after eq^m is reached $\Rightarrow J_c(t) = 0 \longrightarrow$ the distribution should be stationary.

$$\beta_c N_c^{eq} - \alpha_{c+1} N_{c+1}^{eq} = 0 \Rightarrow \alpha_{c+1} = \beta_c \left(\frac{N_c^{eq}}{N_{c+1}^{eq}}\right)$$



$$J_c(t) = \beta_c N_c^{eq} \left[\frac{N_c(t)}{N_c^{eq}} - \frac{N_{c+1}(t)}{N_{c+1}^{ea}}\right]$$

$$\frac{d}{dc}\left(\frac{N_c(t)}{N_c^{eq}}\right) \approx \frac{N_{c+1}(t)}{N_{c+1}^{eq}} - \frac{N_c(t)}{N_c^{eq}}$$

$$\boxed{J_c(t) = -\beta_c N_c^{eq} \frac{d}{dc}\left(\frac{N_c(t)}{N_c^{eq}}\right)}$$

During stage II: under quasi-steady state $\Rightarrow J_c(t) = J \longrightarrow$ constant rate that is indeendent of time & cluster size

$$J = -\beta_c N \exp\left(-\frac{\Delta G(c)}{k_B T}\right) \frac{d}{dc}\left(\frac{N_c(t)}{N_c^{eq}}\right)$$

$$\Rightarrow \quad -\frac{1}{J}\int_1^0 d\left(\frac{N_c}{N_c^{eq}}\right) = \frac{1}{N}\int_1^\infty \frac{1}{\beta_c} \exp\left(\frac{\Delta G(c)}{k_B T}\right) dc$$

(i) when c is small; $\frac{N_c}{N_c^{eq}} \approx 1 \longrightarrow$ small clusters are easy to form and inderendent of time, should be close to eq^m

(ii) when c is large; $N_c/N_c^{eq} \to 0 \longrightarrow$ only a few clusters will grow past critical cluster size

__APPROXIMATE:__ $\beta_c \simeq \beta_{c^*}$ = Constant = β

$$\Delta G(c) \simeq \Delta G(c^*) + \frac{(c-c^*)^2}{2} \left.\frac{\partial^2 \Delta G(c)}{\partial c^2}\right|_{c=c^*} + \text{higher order terms.}$$

$$\left.\frac{\partial^2 \Delta G(c)}{\partial c^2}\right|_{c=c^*} = -\frac{2}{3}\frac{\Delta G(c^*)}{(c^*)^2}$$

$$-\frac{1}{J}\int_1^0 d\left(\frac{N_c}{N_c^{eq}}\right) = \frac{1}{N\beta \exp\left(-\frac{\Delta G(c^*)}{k_BT}\right)} \int_1^\infty \exp\left(-\frac{(c-c^*)^2}{(c^*)^2}\frac{\Delta G(c^*)}{3k_BT}\right) dc$$

↳ replace with $-\infty$ (has negligible impact on the integral)

RHS is a Gaussian integral

$$\Rightarrow J = \underbrace{\left(\frac{\Delta G(c^*)}{3\pi c^{*2} k_BT}\right)^{1/2}}_{\text{Zeldovich factor } (Z)} \beta N \exp\left(-\frac{\Delta G(c^*)}{k_BT}\right)$$

$$\boxed{J = Z\beta N \exp\left(-\frac{\Delta G(c^*)}{k_BT}\right)}$$

$Z \sim 0.1$

$J \rightarrow$ the rate of formation of clusters of size c^* is smaller than the value we would anticipate if clusters CANNOT decrease in size.