Crystal frame:

$J_A = -D_A \nabla c_A$

$J_B = -D_B \nabla c_B$

$$D_B = \left(\frac{L_{BB}}{x_B} - \frac{L_{AB}}{x_A}\right) x_B \frac{\partial \mu_B}{\partial x_B} \Omega$$

Laboratory frame

$$v = -V_m (J_A + J_B) = \frac{J_v}{c_0}$$

↳ velocity in the lab frame.

$$V_m = \frac{1}{c_0} = \frac{V}{N_A + N_B}$$

$$\tilde{J}_A = J_A + v c_A = -\tilde{D} \nabla c_A$$

$$\tilde{J}_B = J_B + v c_B = -\tilde{D} \nabla c_B$$

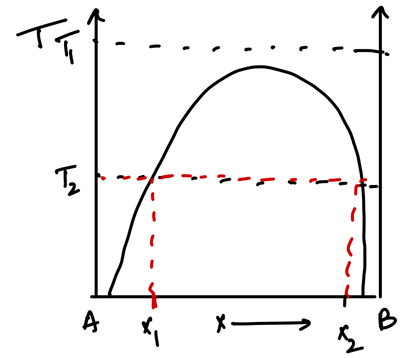
$$\tilde{D} = x_B D_A + x_A D_B$$

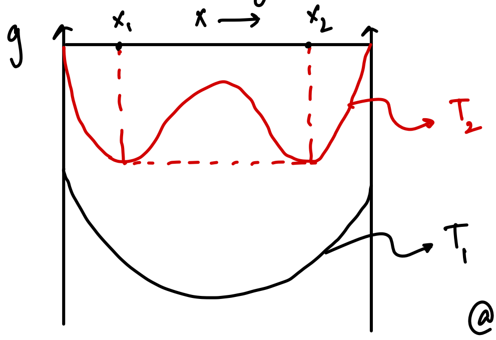
$$\boxed{\tilde{D} = \tilde{L}\, \Omega \frac{\partial^2 g}{\partial x^2}}$$

→ Similar to the diffusion coefficient in the crystal frame.

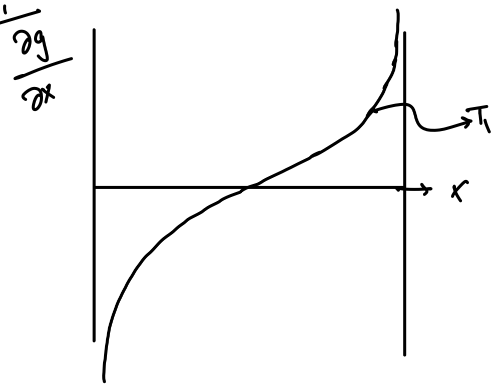
SPINODAL DECOMPOSITION:

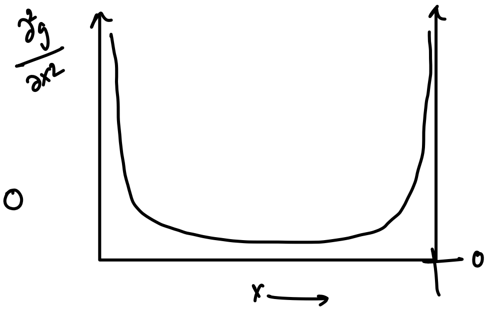
(Thermodynamics is described by the model in Question 2 in PSET III)



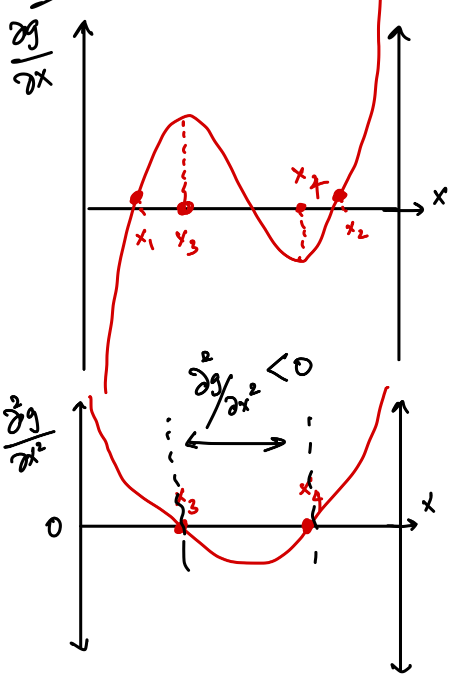


@ T_1





@ T_2



$$\frac{\partial^2 g}{\partial x^2} > 0 \Rightarrow \left(\tilde{D} \propto \partial^2 g / \partial x^2\right) > 0$$

⇒ Diffusion flux is down the composition gradient

(ie) diffusion is from high concentration to low concentration.

x_3 & x_4 are often called the SPINODES

$\frac{\partial^2 g}{\partial x^2} < 0$ b/w x_3 & x_4

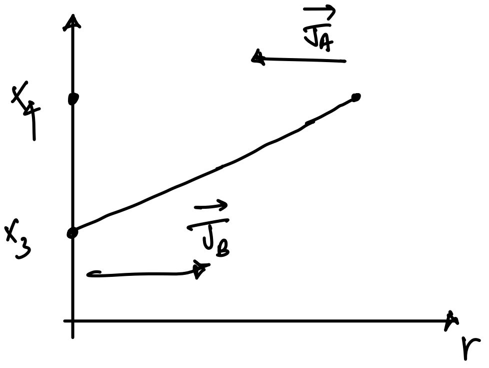
$$J_A = -\tilde{D} \frac{\partial c}{\partial r}$$

$$\left(\tilde{D} \propto \frac{\partial^2 g}{\partial x^2}\right) < 0$$

⇒ UPHILL DIFFUSION

* UPHILL DIFFUSION & SPINODAL DECOMPOSITION:

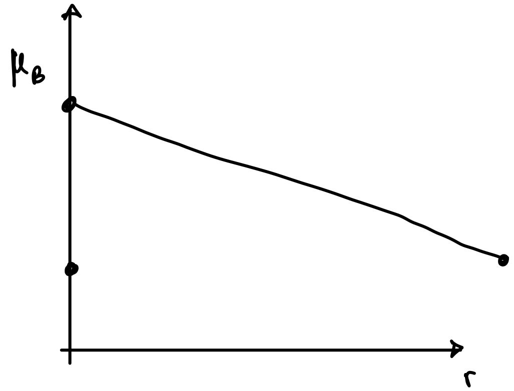
$$J_A = -\tilde{D}\frac{\partial c}{\partial r} \Rightarrow @\, T = T_2 \;\&\; x_3 < x < x_4 \Rightarrow \tilde{J}_A = \underbrace{|\tilde{D}|}_{\text{absolute value.}}\frac{\partial c}{\partial r}$$



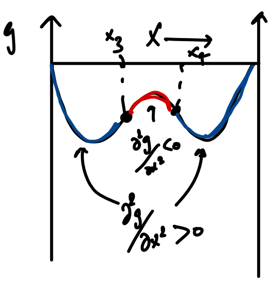
A-rich regions will get richer in A, & B-rich regions will get richer in B

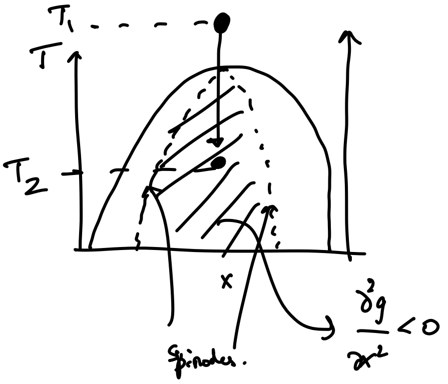
..... DOES THIS MAKE SENSE?? ..

⟺



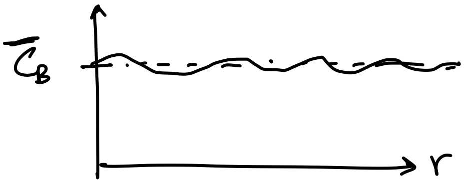
B (and A) are still diffusing down a chemical potential gradient despite moving up a composition gradient.





– What happens to an alloy annealed @ T_1 that is then quenched to T_2?

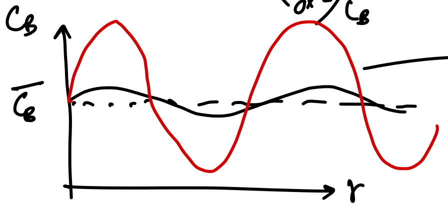
1) @ T_1



$\frac{\partial^2 g}{\partial x^2} > 0$ everywhere $\Rightarrow D > 0$

there will always be spontaneous fluctuations in concentration around $\bar{C}_B$, however they will decay and not grow

2) Quench to T_2; $\left(\frac{\partial^2 g}{\partial x^2}\right)_{\bar{C}_B} < 0 \Rightarrow D < 0 \Rightarrow J = |D|\nabla C$



concentration fluctuations are amplified.
B diffuses from low C_B to high C_B

★ ATTEMPT 1 @ ANALYZING THE MICROSTRUCTURE EVOLUTION DURING SPINODAL DECOMPOSITION:

- Understand the behavior of small fluctuations around an otherwise uniform concentration profile.
- ASSUME:
  - ① Infinite domain (sample size)
  - ② 1 dimensional model ONLY
  - ③ Kinetic parameters independent of alloy concentration

- To predict time evolution:

Ficks II LAW: $\frac{\partial c}{\partial t} = -\nabla J$

$$\frac{\partial c}{\partial t} = -\nabla\left(-D\nabla c\right) \longrightarrow \text{Ficks I LAW} \qquad \boxed{D \text{ is a constant}} \longrightarrow \text{ASSUME}$$

$$\boxed{\frac{\partial c}{\partial t} = D\nabla^2 c} \longrightarrow \text{Integrate to compute } c(\vec{r},t)$$

in 1D: $\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial r^2}$

★ FOURIER TRANSFORMS TO SOLVE PDE:

$c(\vec{r},t)$

$$\check{c}(\vec{k},t) = \mathcal{F}\{c(\vec{r},t)\} = \frac{1}{(2\pi)^{3/2}}\iiint c(\vec{r},t)\exp(+i\vec{k}\cdot\vec{r})\,d\vec{r}$$

Inverse fourier transform:

$$c(\vec{r},t) = \frac{1}{(2\pi)^{3/2}}\iiint \check{c}(\vec{k},t)\exp(-i\vec{k}\cdot\vec{r})\,d\vec{k} = \mathcal{F}^{-1}\{\check{c}(\vec{k},t)\}$$

In 1D: $k = \frac{2\pi}{\lambda}$; $k \to 0$ $\lambda \to \infty$ ⇒ "long wavelengths"
$k \to \infty$ ⇒ "short wavelengths"

$$\check{c}(k,t) = \mathcal{F}\{c(r,t)\} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} c(r,t)\exp(ikr)\,dr$$

$$c(r,t) = \mathcal{F}^{-1}\{\check{c}(k,t)\} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \check{c}(k,t)\exp(-ikr)\,dk$$

★ FOURIER TRANSFORM THE DIFFUSION EQUATION:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial r^2} \longrightarrow \mathcal{F}\left\{\frac{\partial c}{\partial t}\right\} = D\,\mathcal{F}\left\{\frac{\partial^2 c}{\partial r^2}\right\}$$

$$\mathcal{F}\left\{\frac{\partial c}{\partial t}\right\} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\frac{\partial c}{\partial t}\exp(ik\cdot r)\,dr = \frac{\partial}{\partial t}\underbrace{\left[\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} c(r,t)\exp(ikr)\,dr\right]}_{\check{c}(k,t)} = \frac{\partial \check{c}(k,t)}{\partial t}$$

$$\mathcal{F}\left\{\frac{\partial^2 c}{\partial r^2}\right\} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\frac{\partial^2 c}{\partial r^2}\exp(ikr)\,dr \underset{\substack{\uparrow \\ \text{Integrate by parts}}}{=} -k^2\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} c(r,t)\exp(ikr)\,dr$$

In general: $\mathcal{F}\left\{\frac{d^n c}{dr^n}\right\} = (-ik)^n \mathcal{F}\{c(r,t)\} = (-ik)^n \check{c}(k,t)$

Diffusion equation: $\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial r^2} \rightsquigarrow \boxed{\frac{\partial \check{c}(k,t)}{\partial t} = -Dk^2 \check{c}(k,t)}$ ODE!

$$\check{c}(k,t) = \check{c}(k,0)\exp(-Dk^2 t)$$

— Lets make a few variable transforms:

Instead of solving for $c(r,t) \longrightarrow$ we will save for $\Delta c(r,t) = c(r,t) - \underbrace{\bar{c}}_{\longrightarrow \text{ average concentration.}}$

$$\underbrace{\frac{\partial \Delta c}{\partial t} = D\frac{\partial^2 \Delta c}{\partial r^2}}_{\uparrow} \Rightarrow \frac{\partial (c-\bar{c})}{\partial t} = D\frac{\partial^2 (c-\bar{c})}{\partial r^2} \Rightarrow \underbrace{\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial r^2}}_{\uparrow}$$

These are equivalent.

$$\mathcal{F}\left\{\frac{\partial \Delta c}{\partial t}\right\} = \mathcal{F}\left\{D\frac{\partial^2 \Delta c}{\partial r^2}\right\} \Rightarrow \boxed{\frac{\partial \Delta\check{c}}{\partial t} = -k^2 \Delta\check{c}(k,t)}$$

Say the initial composition profile is $\Delta c_0(r,0)$

$$\Delta\check{c}_0(k,0) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \Delta c_0(r,t)\exp(ikr)\,dr$$

Solution to the eqn:

$$\boxed{\Delta\check{c}(k,t) = \Delta\check{c}_0(k,0)\exp(-k^2 Dt)}$$

To evaluate $\Delta c(r,t) \longrightarrow$ Inverse Fourier transform.

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

$$\boxed{\Delta c(r,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \Delta\check{c}_0(k,0)\underbrace{\exp(-k^2 Dt)}_{\uparrow\ \text{time dependence}}\underbrace{\exp(-ikr)}_{\uparrow\ \text{position dependence.}}\,dk} \longrightarrow k \text{ is integrated out!}$$

* HOW DO WE INTERPRET THE SOLUTION?

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

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

$$\Delta C(r,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \exp(-k^2Dt)\underbrace{\exp(-ikr)}_{\substack{\boxed{\cos(kr) - i\sin(kr)} \\ \text{Euler's formula}}}\overbrace{\Delta\check{C}_0(k,0)}^{A(k)+iB(k)}\,dk$$

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

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

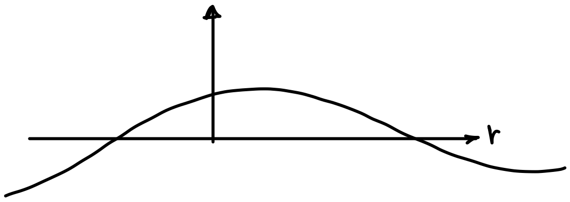
$$+\, i\,\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\underbrace{\exp(-k^2Dt)\Big[B(k)\cos(kr) - A(k)\sin(kr)\Big]}_{\text{odd function of } k \Rightarrow \text{ integral is zero.}}\,dk$$

$$\boxed{\Delta C(r,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \underbrace{\exp(-k^2Dt)}_{\text{time}}\underbrace{\Big[A(k)\cos(kr) + B(k)\sin(kr)\Big]}_{\substack{\text{Superposition of sines and cosines. each having} \\ \text{wavelength } \lambda = 2\pi/k}}\,dk}$$

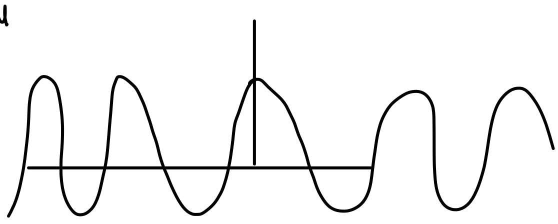
— each modulation of wavelength λ has a DECAY (OR AMPLIFICATION) factor of $\boxed{\exp(-k^2Dt)}$

— Behavior of different wavelengths:

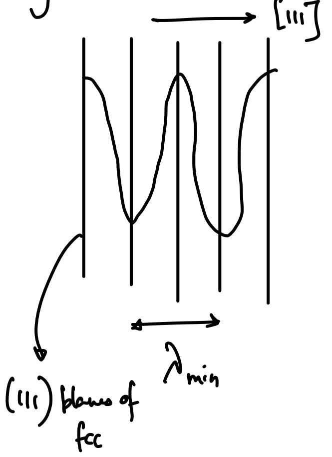
① k = small $\quad \lambda = \frac{2\pi}{k} \longrightarrow$ large



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.



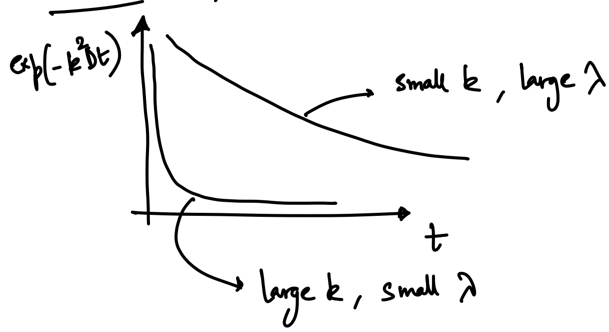
$$k_{max} = \frac{2\pi}{(2d)}$$

(2d) → distance between (111) (say) planes.

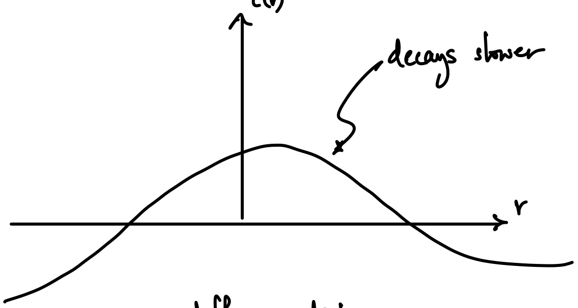
— What is the decay (or amplification) rate for different waves?

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

CASE I : D > 0

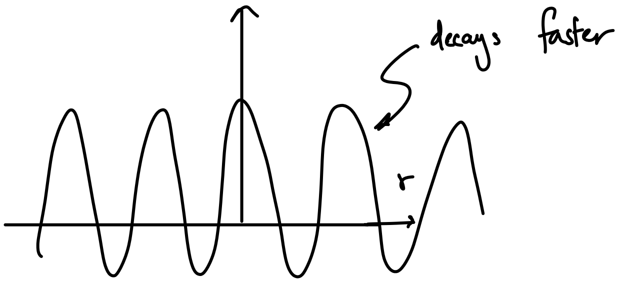


→ time decay of Long wavelengths is slower than short wavelengths.



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

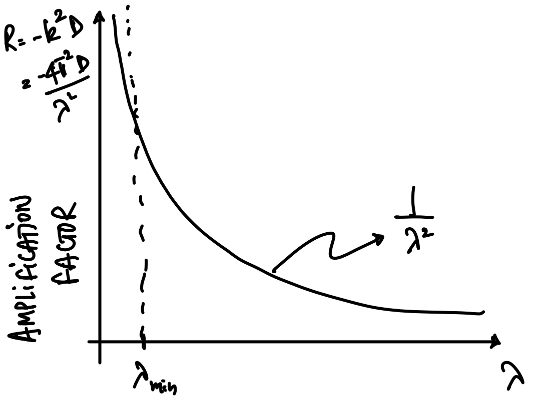
$$\exp(-k^2 D t) = \exp(k^2 |D| t) = \exp\left(\frac{|D| 4\pi^2 t}{\lambda^2}\right) \Longrightarrow$$ Concentration fluctuations get amplified.

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

$k \to$ small $\Rightarrow$ $\lambda \to$ 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 !!

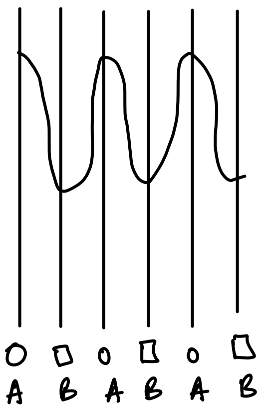


Asymptotic Microstructure: in the long time limit

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 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:

(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:

$$g\Big(x(\vec{r}),\ \underset{\text{3 of these}}{\frac{\partial x}{\partial r_\alpha}},\ \underset{\text{6 of these}}{\frac{\partial^2 x}{\partial r_\alpha \partial r_\beta}},\ \dots\Big)$$

Total free energy:

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

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

Lets Simplify the Taylor expansion in 1D:

Assume: $$\underbrace{g\left(x, \frac{dx}{dr}\right)}_{\substack{\text{Only a function of}\\ x \text{ and gradient}\\ \text{of } x \,\longrightarrow\, \text{not } d^2x/dr^2 \dots}} = g(x,0) + \underbrace{\frac{\partial g}{\partial\left(\frac{dx}{dr}\right)}\bigg|_{(x,0)}}_{H(x)}\cdot\left(\frac{dx}{dr}\right) + \underbrace{\frac{1}{2}\frac{\partial^2 g}{\partial\left(\frac{dx}{dr}\right)^2}\bigg|_{(x,0)}}_{K(x)}\cdot\left(\frac{dx}{dr}\right)^2 + \dots$$