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Phase field modeling; the materials science, mathematics and computational aspects

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Module No.14
Lecture No.58
Derivation of Cahn-Hilliard (CH) equation I

Welcome in today's lecture we want to understand the phase field modeling, the first equation that we write for doing phase field modeling which is known as a Cahn-Hilliard equation. For doing that we are going to go back to the thermodynamics we are going to write the free energy functional and from there we will try to derive the Cahn-Hilliard equation. For doing that I would like to remind of some other things that we have discussed in the past.

Let us consider the two phase equilibrium for example, we have seen that using a simple regular solution kind of model one can see that when there is two phase co-existence the free energy versus composition curve looks like this.

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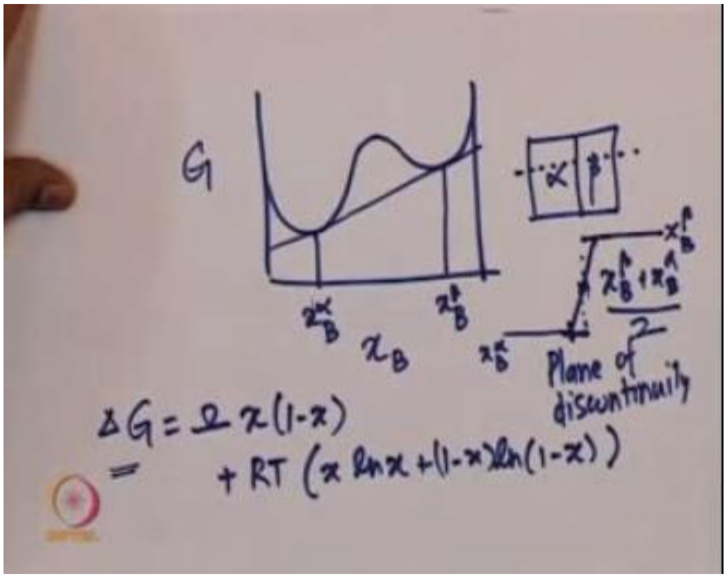

In a binary alloy right, so you have something like this and you have something like this. So we have a common tangent construction and the points, so this is free energy, this is composition and this is for example X_B^α this is for example X_B^β. So if you have some α and β phase the equilibrium compositions are the α and β phase are given by this, if this is the free energy versus composition diagram.

Now if you, for example, go across this line, and plot the composition, so in α phase it is going to be the X_B^α and wherever the interface and beyond that it is going to be X_B^β. Now what happens at the interface is the cohesion. So many of the classical models take this composition in α phase to be X_B^α to the interface and X_B^β to be X_B^β up to the interface and the interface is plain of discontinuity.

Now in this picture if you look at the free energy, so free energy is a minimum because this is the mechanical mixture free energy, so if you have these two N compositions of free energy will lie somewhere here. However there is a problem with this kind of assumption, because we see that there is a discontinuity in composition that means there is a sudden change in composition and that can actually contribute some energy.

To understand this better for example, if suppose I said that up to this plain it is X_B^β and there is an intermediate plain which has composition which is an average of these two compositions β+ $X_B^\alpha/2$ and from here it is X_B^β composition, so the interface is something like this. Then there is this X_B^β+ $X_B^\alpha/2$ region so that composition is going to lie somewhere here. So there is a cost associated with making the interface more diffuse instead of keeping it as very sharp, that comes from the free energy itself.

So this the classical free energy, but what the classical free energy misses is that if you assume that the β and also compositions are uniform toward the phase then at the interface there is a discontinuity that discontinuity will contribute to the free energy even if you have a continuous of a composition curve the gradient then will start contributing to the free energy, this gradient contribution has to be accounted far.

The way we are accounting far is that, for example this free energy is a regular solution free energy right, so you can get it by having the regular solution free energy as X(1-x)+RT(xlogx+(1-x) log (1-x)) okay, something like this +GA+GBX GA (1-x)GA+GB will actually give something like this. So in this we are only considering the composition and only composition is contributing to the free energy.

So this is the free energy function and you can take the derivative of the free energy function with respect to composition, you get what is known as the chemical potential. But a problem with this kind of model, especially when you have two phases is that we are assuming a constant α composition, constant β composition in the α and β phases and interfaces have discontinuity in composition.

And this is also not acceptable from a purely thermodynamic point of view, because once you have set down the thermodynamic parameters like temperature, pressure, number of atoms, composition etc… then there are no other information that one needs to specify, the system will choose for example, whatever interface with it wants to choose. It is wrong to arbitrarily assigned it to be a plane of zero weight or one atomic plane or several atomic planes and so on and so forth. So to avoid this is why we are looking at the modification to the free energy and the modification to the free energy comes from tailor expanding the free energy by assuming.

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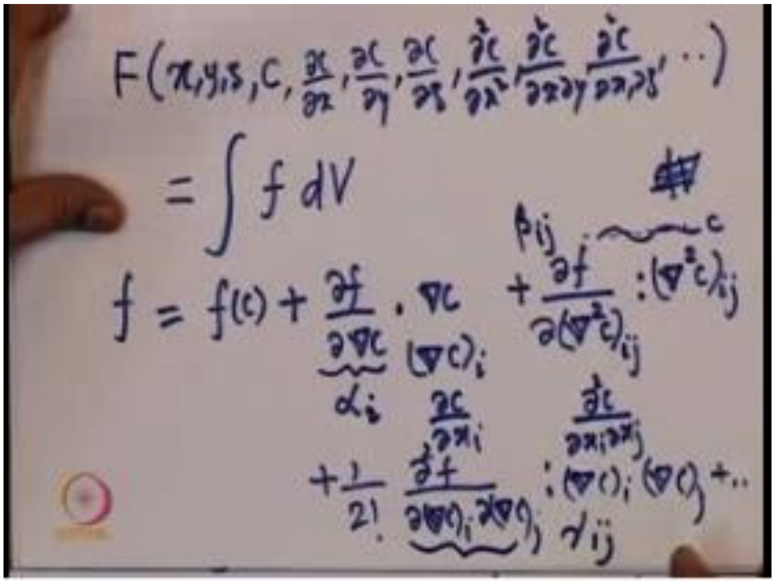

$$F\left(x,y,z,c,\frac{\partial c}{\partial x},\frac{\partial c}{\partial y},\frac{\partial c}{\partial z},\frac{\partial^2 c}{\partial x^2},\frac{\partial^2 c}{\partial x\partial y},\frac{\partial^2 c}{\partial x\partial z},\cdots\right)$$

$$= \int f \, dV$$

$$f = f(c) + \underbrace{\frac{\partial f}{\partial \nabla c}}_{\alpha_i} \cdot \underset{\substack{(\nabla c)_i \\ \frac{\partial c}{\partial x_i}}}{\nabla c} + \overbrace{\frac{\partial f}{\partial (\nabla^2 c)_{ij}}}^{\beta_{ij}} : (\nabla^2 c)_{ij}$$

$$+ \frac{1}{2!} \underbrace{\frac{\partial^2 f}{\partial (\nabla c)_i \, \partial (\nabla c)_j}}_{\gamma_{ij}} : \overset{\frac{\partial^2 c}{\partial x_i \partial x_j}}{(\nabla c)_i (\nabla c)_j} + \cdots$$

Tthat the free energy is function of x, y, z positions because we are assuming that the free energy is going to be not homogeneous and constant everywhere. So it is composition and we are going to assume that it is also, and the second derivative $\partial C/ \partial x^2$, $\partial^2 C/ \partial x \, \partial y$ and so on that is a free energy functional, because now the free energy is not just a functional composition, but also its gradients and curvature and so on.

And that is written as an integration over volume, and so we have this free energy F and this F, Fdv that we have so this F I am going to write as a taylor series expansion by expanding so I am going to consider a compositions some nominal composition of c about which there are some changes so I am going to write the free energy for such a system so f of f for this such a system is f(c) where c is the nominal composition.

So if there were no composition variations positionally if you have uniform c composition what is the free energy that is the first term and then I have the Taylor expansion terms so the first term is $\partial f/\ \partial\nabla c$. with ∇c and this is I rank tensor. So let me call it as α I so to indicate that. So because this is now vectorial notation I will also call this as $(\nabla c)_I$ meaning that this is $\partial c/\ \partial x_i$ in a similar fashion I have the second term which is $\nabla f/\partial\nabla^2 c$ and again ij then it is 2 inner products with $\nabla^2 c_{ij}$ the notation again meaning $\nabla^2 c_{ij}$ means $\partial^2 c/\ \partial x_{ij}$ that is what this means + ½! $\partial^2 f/\partial\nabla c_i\ \partial\nabla c_j$ again two products with ∂c_{ij} and so on okay.

So this is the free energy functional that we are going to put. So this is a first rank tensor I am going to call α this is a second rank tensor that I am going to call β_{ij} this is another second rank tensor I am going to call this as γ_{ij} so in this fashion we can now write the free energy functional as follows.

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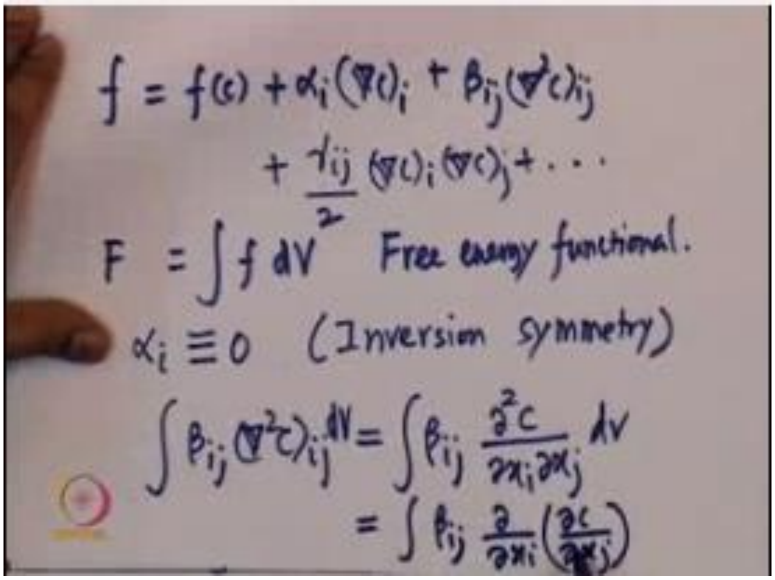

$$f = f(c) + \alpha_i(\nabla c)_i + \beta_{ij}(\nabla^2 c)_{ij} + \frac{\gamma_{ij}}{2}(\nabla c)_i(\nabla c)_j + \cdots$$

$F = \int f\,dV$ Free energy functional.

$\alpha_i \equiv 0$ (Inversion symmetry)

$$\int \beta_{ij}(\nabla^2 c)_{ij}\,dV = \int \beta_{ij}\frac{\partial^2 c}{\partial x_i \partial x_j}\,dV = \int \beta_{ij}\frac{\partial}{\partial x_i}\left(\frac{\partial c}{\partial x_j}\right)$$

This is f(c)+ αi $\nabla c_i + \beta_{ij}\ \nabla^2 c_{ij}$ where we are assuming the Einstein summation conversation + $\gamma_{ij}/2\nabla c_i\ \nabla c_j$ + so on so the total free energy is nothing but dv so this is the free energy functional now we are going to use some of the properties that we are learned about tenors properties and their representation in crystals first thing to assume is that we are in system in which there is a center of symmetry or inversion symmetry so all odd rank tensors in such systems is going to be 0.

So αi is going to be 0 because I am assuming inversion symmetry the other way to also say that this term is 0 is to say that we are going to look at free energies which are going to have a minimum at some c value and about the minim then the condition would be that you cannot have any such first rank terms because they will change sign if you go either way but the suppose if you take very small changes in compotation these terms are not important then this term will be positive in one case negative in one case.

So you will not get minimum if you add this term so you want to make that 0 another way or arguing about the odd rank tensor going to 0the vector term going to 0 now if you look at these two terms then it is possible to make them both in the same form as this so how do we do that to do that let us consider this $\beta_{ij}\ \nabla^2 c_{ij}$ that is nothing but $\beta_{ij}\ \nabla^2 c/\ \nabla_i \nabla_j$ that is dv so this is integral and so I am going to make this as $\beta_{ij}\ \partial/\ \partial$xi of 2c/ ∂x_j right so we know that this term is nothing but ∇c(j) so I am going to write this.

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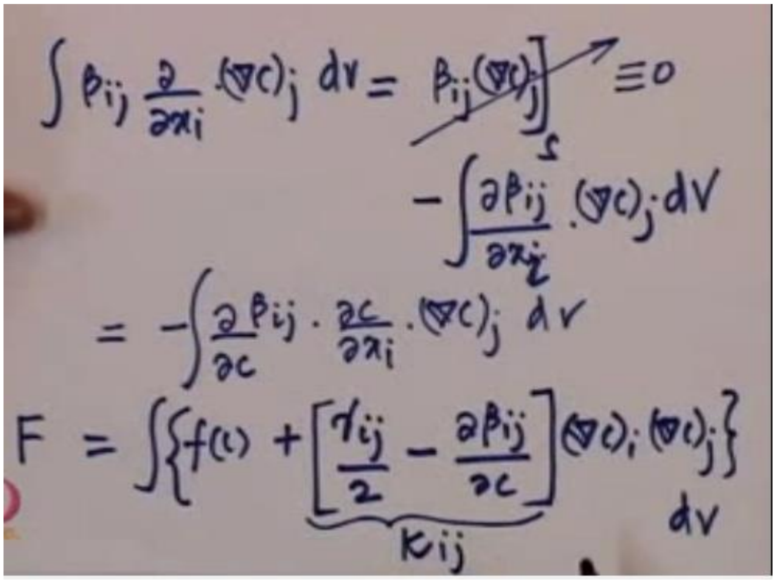

$$\int \beta_{ij} \frac{\partial}{\partial x_i} (\nabla c)_j \, dv = \cancel{\beta_{ij} (\nabla c)_j \Big]_S} \equiv 0$$

$$- \int \frac{\partial \beta_{ij}}{\partial x_i} \cdot (\nabla c)_j \cdot dV$$

$$= - \int \frac{\partial \beta_{ij}}{\partial c} \cdot \frac{\partial c}{\partial x_i} \cdot (\nabla c)_j \, dv$$

$$F = \int \left\{ f(c) + \underbrace{\left[\frac{\gamma_{ij}}{2} - \frac{\partial \beta_{ij}}{\partial c} \right]}_{K_{ij}} (\nabla c)_i (\nabla c)_j \right\} dv$$

So this is the term we are look at $\partial\ \partial/\ \partial x_i$ of 2c/ ∂xj dv so that is nothing but so you can write this β_{ij} ∇c(j) which is evaluated at this phase – ∫∂∂/ ∂x_j ∇c ∂xi ∇c(j) dv and suppose if you are interested in infinite system or you're not interste4d in what is happening at the surface are you will choose the surface for your volume in such a way that the opposite surfaces will give equal contribution so there are several different ways in which you can make this term go to 0 we are going to assume that this is identically = 0.

So we consider this and this can further be written as $-\partial / \partial$ c of β_{ij} and $\partial c/ \partial$ xi and $\nabla c(j)$ dv so if you substitute this back into the free energy so we see that my $F= \int f(c)$ the first αc the first α is term is 0 that we already argued so then I have this γ term + $\gamma_{ij} / 2$ – this term $[\partial\beta_{ij}/\partial c](\nabla c_i)(\nabla c_j)$ the total deviate, this is the free energy functional, we have and I am going to replace this quantity by some Kappa $K_{ij,}$ okay and this other higher order terms also I have neglected.

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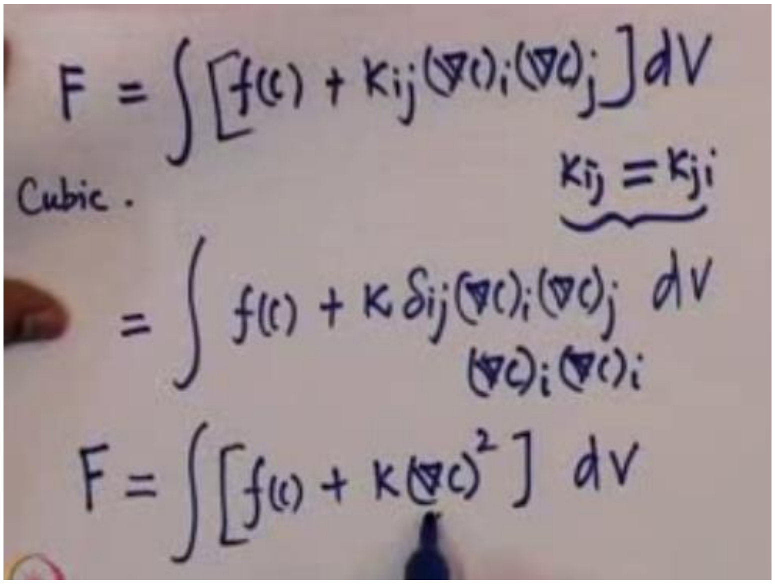

$$F = \int \left[f(c) + K_{ij} (\nabla c)_i (\nabla c)_j\right] dV$$

Cubic.

$$\underbrace{K_{ij} = K_{ji}}$$

$$= \int f(c) + K \delta_{ij} (\nabla c)_i (\nabla c)_j \, dV$$

$$(\nabla c)_i (\nabla c)_i$$

$$F = \int \left[f(c) + K(\nabla c)^2\right] dV$$

So my free energy functional happens to be this $[f(c) + K_{ij} (\nabla c_i) (\nabla c_j)]$dv so this is the free energy functional I have and I am going to now assume cubic systems in which this is the symmetric second rank tensor because $K_{ij} = K_{ji}$ that is because it does not matter whether you take $\nabla c_i \nabla c_j$ or $\nabla c_i \nabla c_j$ so it is has its intrinsic symmetry, so such symmetric tensors is cubic systems. So second rank tensors they will also be isotropic so that's we have already seen so I can further reduce this to f(c) + $K\delta_{ij} \nabla c_i \nabla c_j$ dv so that is ∇ij acting on this is going to make it $(\nabla c_i)(\nabla c)_I$ and if you use

Einstein summation convention again that is nothing but $f(c) + K(\nabla c)^2$ dv this is the period metric function, so what we now has is a free energy functional and it is free energy functional.

So the independent variable x, y ,z are not explicitly appearing c is a function of xyz and also time T and ∇c is the gradient on c, so we have a functional which depends on a variable C and its gradients. So we can write Euler Lagrange equation so the minimization of free energy means that you can take the variation derivative.

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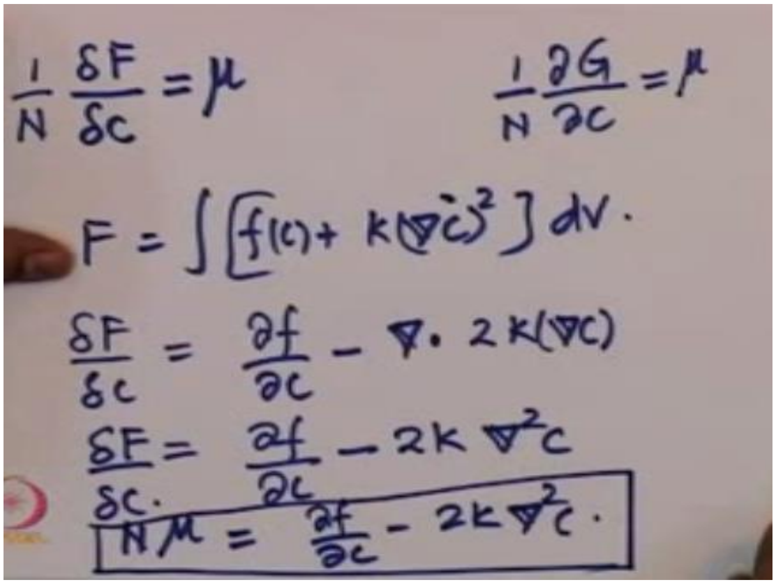

$$\frac{1}{N}\frac{\delta F}{\delta c} = \mu \qquad \frac{1}{N}\frac{\partial G}{\partial c} = \mu$$

$$F = \int \left[f(c) + K(\nabla c)^2 \right] dv.$$

$$\frac{\delta F}{\delta c} = \frac{\partial f}{\partial c} - \nabla \cdot 2K(\nabla c)$$

$$\frac{\delta F}{\delta c.} = \frac{\partial f}{\partial c} - 2k\nabla^2 c$$

$$\boxed{N\mu = \frac{\partial f}{\partial c} - 2k\nabla^2 c.}$$

Of F with respect to C this quantity is nothing but the chemical potential because remember in the case if G is a function then ∂G/ ∂C is nothing but μ 1/N right, 1/N because ∂G/ ∂N be is μ and so the by N if you put and multiply by N so that becomes C so that is the reason so we are going to use a same thing so 1/N δF/ δC is the chemical potential so what is δF/ δC that is obtained by the Euler Lagrange equation.

What does it say, so if you have a functional which is like because F = [f(c) + K(∇C)^2] dv so when we take δF/ δC that is going to be ∂F/ ∂c - ∇ acting on this quantity so differentiated with respect to ∇C so when you differentiate this the only term that has ∇C so 2 K(∇C) this is what you get, if you assumed that K is a constant you can pull it out so you get $\partial F/ \partial c - 2K(\nabla^2 c)$ this is $\delta F/ \delta C$.

So if you the μ, N μ is nothing but this quantity $\delta F/ \delta C$ so that is $\partial F/ \partial C - 2K(\nabla^2 c)$ so this is the first term so we have obtained the chemical potential in the case of a functional so we went from a function for free energy to a functional for free energy that is because free energy was initially only a functional composition now it is also a function of the concentration gradient its composition gradients that is because we want to incorporate the contribution from the interfaces, interfaces are regions where composition changes from one value to other value bulk system bulk phases are phases where the composition is uniform.

So interface contribution is then incorporated by incorporating the gradients and any higher derivatives so to get the free energy for such a system which has compositional heterogeneous the Taylor expanded and produced a free energy functional and by taking the variation derivative of the free energy function with respect to composition we get the chemical potential, once we have the chemical potential of course we know how to get the diffusion equations.

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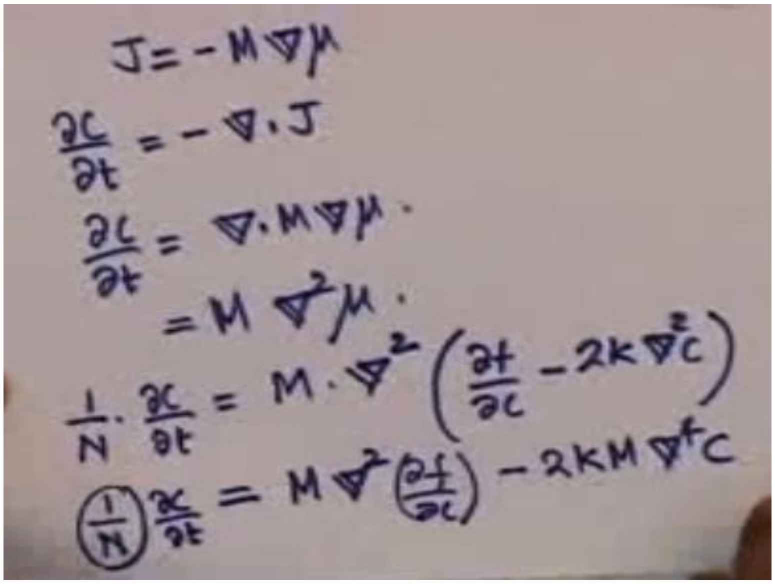

$$J = -M\nabla\mu$$

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

$$\frac{\partial c}{\partial t} = \nabla \cdot M\nabla\mu \cdot$$

$$= M\nabla^2\mu \cdot$$

$$\frac{1}{N} \cdot \frac{\partial c}{\partial t} = M \cdot \nabla^2\left(\frac{\partial f}{\partial c} - 2K\nabla^2 c\right)$$

$$\boxed{\frac{1}{N}}\frac{\partial c}{\partial t} = M\nabla^2\left(\frac{\partial f}{\partial c}\right) - 2KM\nabla^4 c$$

So we will go back and do it so initially we said that the flux is $-M \nabla \mu$ where μ is the chemical potential and now and $\partial C/ \partial t = -\nabla . J$ and so putting together $\partial C/ \partial t$ is nothing but $-\nabla .M \nabla \mu$ let me further assume that M is a constant so $M \nabla^2 \mu$ and we know the μ value okay, so M μ value so I am going to have this N pulls out so we will have $1/N\ \partial C/ \partial t = M\nabla^2$ acting on $\partial F/ \partial C - 2k\nabla^2 c$ and so that you can write it as $M\nabla^2 (\partial F/ \partial C) - 2KM(\nabla^2 c)$ assuming that K again is a constant.

So we get an equation which is the modified diffusion equation, okay. Suppose if we incorporate this the free energy that we wrote in term is per atom then one can get rate of this n term, so we will get something that looks like that, okay. So assuming that the free energy that I wrote is for the entire volume I divide by the number of atoms sp I per atom free energy.

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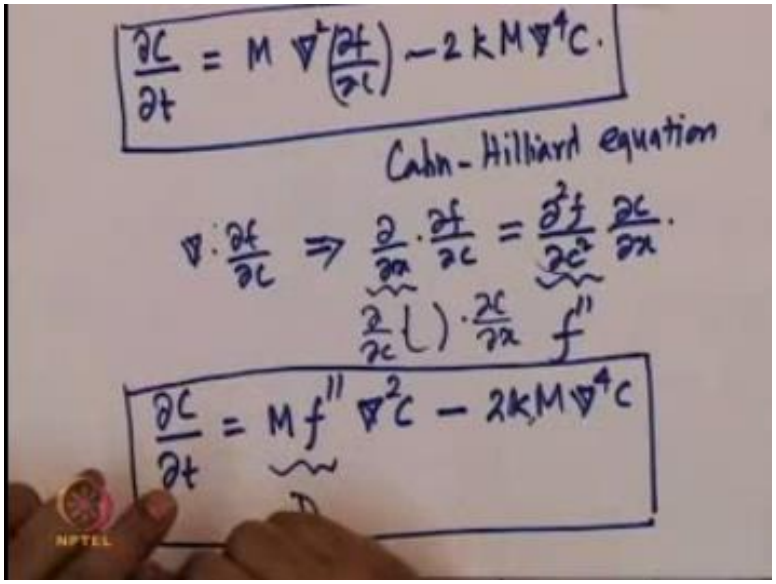

$$\boxed{\frac{\partial c}{\partial t} = M \nabla^2\left(\frac{\partial f}{\partial c}\right) - 2kM\nabla^4 c.}$$

Cahn-Hilliard equation

$$\nabla \cdot \frac{\partial f}{\partial c} \Rightarrow \frac{\partial}{\partial x} \cdot \frac{\partial f}{\partial c} = \frac{\partial^2 f}{\partial c^2} \frac{\partial c}{\partial x}.$$

$$\frac{\partial}{\partial c}(\ ) \cdot \frac{\partial c}{\partial x} \quad f''$$

$$\boxed{\frac{\partial c}{\partial t} = M \underset{D}{f''} \nabla^2 c - 2kM\nabla^4 c}$$

Then my diffusion equation the modified diffusion equation that I derived becomes $M \nabla^2(\delta f/\delta c)- 2\kappa M \nabla^4 C$, so this equation is known as the Cahn-Hilliard equation, this is a modified diffusion equation that is not very difficult to see to see that it is a modified diffusion equation let us consider this $\nabla^2(\delta f/\delta c)$ term where it comes from the first one is in $\delta\mu$, okay so μ had this $\delta f/\delta c$ term and when we acted on this so there is a way to write this, so you can write so δ is nothing but for example, if it is 1d $\delta/\delta x$ suppose if you have $\delta f/\delta c$ then that is the same as some $\delta^2 f/\delta c^2$ $\delta c/\delta x$.

So how do we do that, so when I take $\delta/\delta x$ I can write it as $\delta/\delta c$ acting on this times $\delta c/\delta x$, okay so that is what this term, so $\delta f/\delta c$ which is the curvature of the free energy verses composition curve so that I can call this as f''. Remember, when we define spinodal where this quantity became negative is where the spinodal regime was, so this is the curvature of the free energy curve so I am going to assume that this is a constant, if you do that then when you put it back here so you have f'' $\delta c/\delta x$ and another ∇ acting on it so you will get $\delta c/\delta t$ as $Mf'' \nabla^2 C - 2\kappa M \nabla^4 C$.

Now Mf'' is the diffusivity that is why when f'' became negative diffusivity became negative and it was positive Mf'' was positive so it can explain both the cases and namely our downhill diffusion and uphill diffusion, so if you look at this part $\delta c/\delta t$ is the $\nabla^2 C$ is nothing but a classical diffusion equation, and what we have here is a modification to the classical diffusion equation. In fact it is a modification which incorporates a high order derivatives in composition.

So you can think of Cahn-Hilliard equation as a modified diffusion equation the modification being in addition to $\nabla^2 C$ you have a $\nabla^4 C$ term. Now what is the effect of this and what happens is something that we will discuss but at least from here it is very clear that this term as with this negative sign is the term and the κ came from concentration gradients and concentration gradients are represented into phases so this is term that is related to the interface.

And so the interfacial energy related effects will be incorporated through this term that means the contradiction that we saw when we were solving the classical diffusion equation that you start with spinodal system phase separating system but if you solve the classical diffusion equation you get the solution that it orders, that will be taken care of by this higher order term because this now sets limit to the lower wavelengths so beyond some system size if you try to increase these composition fluctuations that is if you make A rich regions A rich and b rich regions B rich.

If the regions that you are trying to enrich are smaller than some length scale then the interfacial contribution namely that AB bonds are not preferred and their energy is going to come into place so they are going the regions of A rich and B rich regions that would grow or the wavelength of any such disturbance that you have that will grow there is a lower wavelength limit, so that is basically setup by the interfacial energy. In this system now we can also understand the interfacial energy as follows or the interfacial width as follows.

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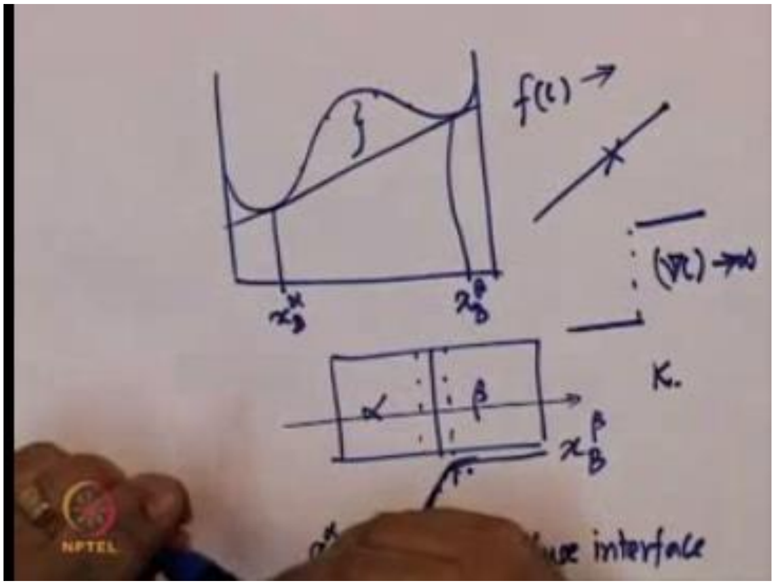

So we have this, so the f(c) could be a curve which is of this type, okay so it has these common tangent points so if you have a system which has α and β so there is a region over which the composition changes over and so if you go across a line like this and if you look at the composition the solution to the diffusion equation that we have written is going to be like this, okay. So this is x_B^β this is x_B^α where this is x_B^α and this is x_B^β and this region where you have this composition this thing is the diffuse interface, okay.

So this is where the name diffuse interface approach or diffuse interface model comes from and what determines the thickness of this region it is determined by this barrier height and the κ. Why, because suppose if this barrier height is very high then if you try to setup a concentration gradient which is very, very shallow then the energy cause associated with having composition in between these two end points is going to raise very high so this is not preferred.

On the other hand if you make the concentration take a discontinuity here the ∇C which goes to infinity because there is a discontinuity that contribution to free energy is going to become very high so the system is actually going to chose an interface width in such a way that whatever is the κ the gradient energy co efficient whatever cost it has to pay for this and that so that means there are going to be compositions which are all over this points.

And they are going to increase the energy a little bit and it is going to gain some energy from this inter face part so the competition between the two the balance between the two it is going to determine what the inter face energy is going to be automatically from the system so once you have written the free energy functional once you know what this κ is and in the F(C) which is where this term comes the barrier is determine by f(c).

So once this is for instant 1κ is fix to the system will take an inter face width that is going to minimize the given free energy, so we have now derived the first face field equation or diffuse inter face equation this is known as Cahn Hilliard equation just to remind ourselves in terms of the derivation it is same as we derive the diffusion equation so you first assume that the flux is proportional to chemical potential gradient instant of concentration gradients.

So that a first difference and then you use continuity equation you get a diffusion equation so Cahn Hilliard or face willed equation is just a modified diffusion equation which is obviously because we are looking at concentration evaluation sop it will be a diffusion equation of some sort and the second difference is that the chemical potential is not derivative of the free energy with respect to composition that is classical thermo dynamics.

In this case we want to incorporate the in face effects so we have some non classical thermo dynamics in which the free energy is not just a function of composition but it is a functional so is ha composition and it is gradients and sometimes even the curvature terms and abrogation terms or any other higher order derivative of composition with respect to position as independent variables so you write a functional instead of a function so to get the chemical potential you have to take a variation derivative instead of just taking a classical derivative option derivative.

So this variation derivative gives the chemical potential and the chemical potential now pout back in to the constitutive law namely that flux is proportional to chemical potential gradient and the constant being the mobility and you put them back you get the equation of course we have made certain assumptions we have assumed that the material we are considering is having center of inversion, so that is the and that can also be motivated through other means you can also say that because I am looking for some mini mare to be there in my system.

The first derivative terns will not be there so there are several ways of motivating that the second most important assumption that we have made is that I am considering the cubic system so the second dragnets are became isotropy so isotropy system also it will hold but if suppose this was not a cubic system then there is no necessity that the co efficient the κ IJ has to be isotropic it can be isotropic Nyman principle does not roll out suppose it is tetragonal for example isotropy is much better symmetry or it is a larger symmetry so the minimum it should have is a tetragonal it can be better than that.

So it can be cubic or isotropic it cannot be worse than that so that is what is means so you can have a tetragonal system and in which case is need not be isotropic which means the c axis will have difference values from a and b the property along c direction will be different from the a and b in which case you will see that the κ IJ in such a system is that κ 11 κ22 might be equal but κ 33 is not equal so you will get a difference in terms of the constant that goes in the free energy function.

Otherwise the formulation is the same all that the cubit assumption got us was that it made the term that is multiplying the δ C as a isotropy terms it is not necessary and when you have this general free energy expression where δ CI or the independent components how to the write the variation derivative is described in the book that I refer to earlier in shames at then energy and finite element methods in structural mechanics, so one can write the most general expression and write the chemical potential by the taking the variation derivative use it to get the modified diffusion equation.

So that part is common the assumption or approximation we made that we will consider cubic system this is only to make the algebra little bit simpler but so without loss of generality the same procedure can be used for systems which are not cubic also, so we will stop it at this point and now that we have derived the equation the next step is to go ahead and the solve it so we have solved the diffusion equation using spectral techniques so we will use similar spectral techniques to solve this equation also and see how the solution look and how the solutions are different from that of the classical diffusion so that is what we will do in the next lecture. Thank you.

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