

**NPTEL
NATIONAL PROGRAMME ON
TECHNOLOGY ENHANCED LEARNING**

IIT BOMBAY

**CDEEP
IIT BOMBAY**

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

**Prof. M P Gururajan
Department of Metallurgical Engineering
And materials Science, IIT Bombay**

**Module No.13
Lecture No.57
Free energy functional**

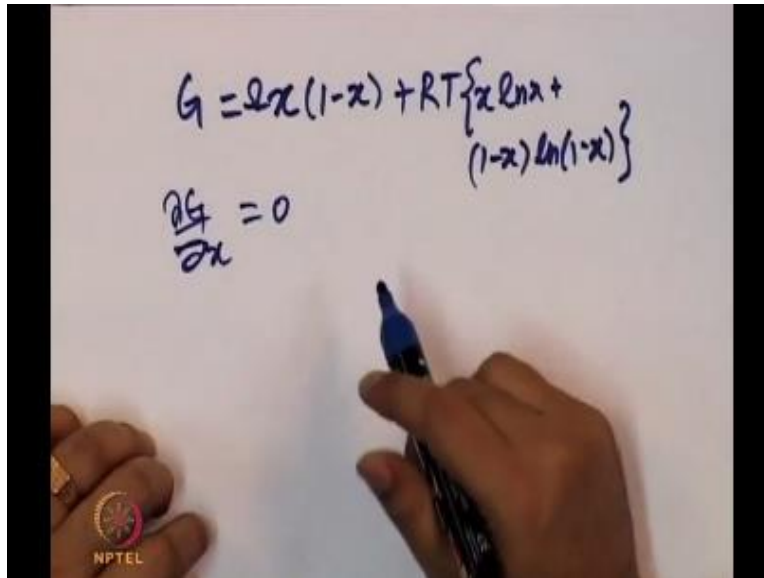
Welcome we are looking at a variational calculus and we want to understand why variations are important when we are trying to do phase field models so one of the things that we did earlier was to look at the diffusion equation and we tried to motivate the diffusion equation and, we said that spontaneous processes or processes in which the free energy is always getting minimized so, when you have this free energy versus composition curve, when you look at its minimization the which is what should automatically lead to diffusion.

We find that whenever this free energy composition curve has a concave region in those regions it looks as if the diffusivity has become negative we have found an explanation for this, we realized that the fick's law as it is written has to be modified, we have to say that the flux is proportional to chemical potential gradient instead of staying concentration gradients if you do that you can explain the negative sign that the diffusivity fields.

Basically it comes from the curvature of the free energy versus composition curve the sign of curvature actually matters so, if it becomes negative then it looks as if the diffusivity becomes negative, if that is all there is to it then you can go with so we wrote a free energy which was the

classical regular solution free energy which was something like this so we wrote it as $\Omega x(1-x) + RT\{x \ln x + (1-x) \ln(1-x)\}$, so this is basically a polynomial in x , so the minimization meant that $\delta G / \delta x = 0$, and we did all this and we found out the miscibility gap and all that.

(Refer Slide Time: 02:14)


$$G = \Omega x(1-x) + RT \left\{ x \ln x + (1-x) \ln(1-x) \right\}$$
$$\frac{\partial G}{\partial x} = 0$$

The curvature of this will have a negative sign in when Ω is positive you can find regions where that would become positive, that would become negative and that would then lead to what is known as spinodal decomposition. We solve that, but there is a problem because if the diffusivity becomes negative and if you solve the classical diffusion equation, that is the what you derive from the fick's law that is modified fick's law even, so you assume that flux is proportional to conserve chemical potential gradients and use mass conservation you end up with the same equation $\delta C / \delta T$ is some modified whatever diffusivity times $\delta^2 c / \delta x^2$.

So in this case you find that because diffusivity is negative any fluctuation that you put any noise that you put is going to grow and then the even very small noise, the noise with very small wavelength will grow in fact smaller the wavelength the faster would be the growth rate and this leads to a case where you might have very small wavelengths, composition fluctuations of growing.

Now the natural end of this process or conclusion that you derive from this process is that if suppose you have a system in which you have A and B atoms and they are going to face separate in the spinodal then you will see that they are all A atoms on one and all B atoms on next plane all A atoms on next plane all B atoms on next plane in etc so, this is like the ordered structure so this happens only when $\Omega < 0$.

So we started with a case $\Omega > 0$, because that is what is related to spinodal and we write a diffusion equation and we solve it and we end up with a solution which corresponds to this case, which is the ordering case. So this was a problem and this was a problem because the one of the important pieces of physics was left out and that piece of physics is related to interfacial energy. right what is interfacial energy? It is the excess free energy associated with interface and when we wrote this free energy expression, we never considered the fact that if you have a two-phase system suppose all A rich and all B rich wherever there is an interface between the A region and B rich region that interface is also going to contribute to some free energy.

(Refer Slide Time: 05:11)

The image shows handwritten notes on a whiteboard. At the top, the free energy equation is written as $G = \Omega x(1-x) + RT \{ x \ln x + (1-x) \ln(1-x) \}$. Below this, the derivative equation $\frac{\partial G}{\partial x} = 0$ is written. In the center, there is a diagram of four vertical chains of atoms, represented by circles. The first chain has four open circles, the second has two open and two filled circles, the third has two filled and two open circles, and the fourth has four filled circles. To the right of the diagram, the conditions for ordering and spinodal regions are noted: $\Omega < 0$ Ordering and $\Omega > 0$ Spinodal. The 'Spinodal' text is enclosed in a hand-drawn box. An NPTEL logo is visible in the bottom left corner of the whiteboard.

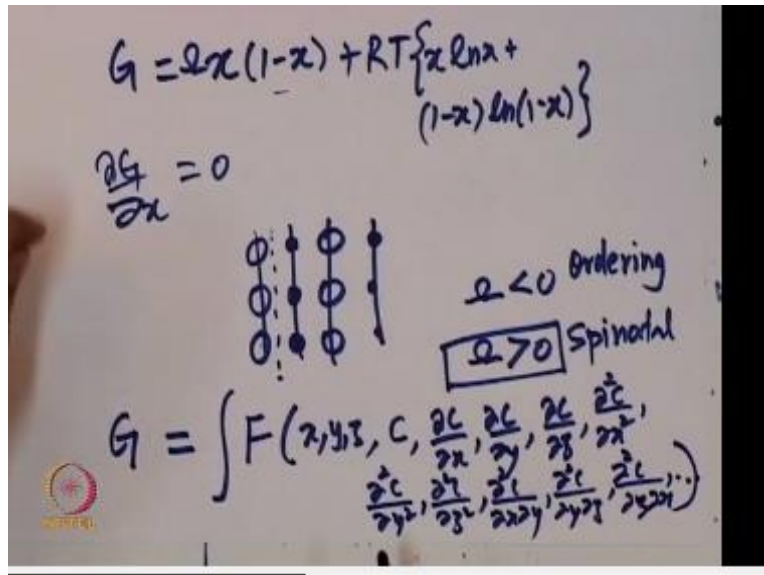
We neglected that part here completely and that is the reason why we ended up with this contradiction because now this in terms of pure A, pure B if, you think of it this is all pure A this all pure B so, this is basically AB interface and Ω was positive because the A B interface had higher energy and that is what happens in the interfaces and we have completely neglected that physics and that is why we ended up with this problem.

So there was an attempt to correct this as I have discussed earlier so Hilliard's work on a domestic calculations showed that this interfacial energy has to be incorporated and Hilliard basically did that. The way they did that was to say that you have to consider your free energy as a functional and so they wrote it in the class in a classical functional form by saying that this free energy functional, so let me call it as some F is a function of x, y, z okay.

Previously we had one independent variable time or x like that but, now you have x, y, z because in 3d, so composition is a variable which is what we are looking at which is the parameter and which is what is called x here let me call it C here and the gradients and composition so composition wherever it is constant, that will be either A rich phase or B rich phase and wherever composition has a gradient, wherever it is changing from A rich to B rich is basically the interface between A rich phase and B rich phase.

So we can then have so $\delta C/\delta x, \delta C/\delta y, \delta C/\delta z$ and we do not have to stop here, you can of course have higher order terms so you can have $\delta^2 C/\delta x^2, \delta^2 C/\delta y^2, \delta^2 C/\delta z^2, \delta^2 C/\delta x \delta y, \delta^2 C/\delta y \delta z, \delta^2 C/\delta z \delta x$ etc, okay now what we have is a functional so integrated over the dx, dy, dz right, so that is so this is some x point one point to some x_2 point okay so, the integral over the entire domain because this is a volume integral is what is going to be the free energy.

(Refer Slide Time: 07:37)



$$G = 2x(1-x) + RT \left\{ x \ln x + (1-x) \ln(1-x) \right\}$$

$$\frac{\partial G}{\partial x} = 0$$

$Q < 0$ Ordering
 $Q > 0$ Spinal

$$G = \int F(x, y, z, C, \frac{\partial C}{\partial x}, \frac{\partial C}{\partial y}, \frac{\partial C}{\partial z}, \frac{\partial^2 C}{\partial x^2}, \frac{\partial^2 C}{\partial y^2}, \frac{\partial^2 C}{\partial z^2}, \frac{\partial^2 C}{\partial x \partial y}, \frac{\partial^2 C}{\partial x \partial z}, \frac{\partial^2 C}{\partial y \partial z}, \dots)$$

So instead of a function the free energy has now become a functional, it has become a functional because previously, it was just a function of composition but now it is a function of composition, its gradients, and its curvature and so on and so forth okay. Now how do we deal with this quantity for doing that we and let me also write it in a slightly different form, so I write this free energy functional as x, y, z, C and ΔC and $\Delta^2 C$ etcetera now ΔC is basically a vector, why is a vector because ΔC includes $\delta C / \delta x, \delta C / \delta y, \delta C / \delta z$ right, in other words if I write it as $\delta C / \delta x_i$ it is a quantity with one index so x, y, z I can write as x_i, C is a scalar composition and ΔC is $\delta C / \delta x_i$.

So that becomes a vector by the same token $\Delta^2 C$ is nothing but $\delta^2 C / \delta x_i \delta y_j$, it is a quantity with the two indices it is going to be a second rank tensor, so this is F and we have the free energy functional which is basically integral over the volume and remember this is a free energy, so which means this is a scalar quantity suppose, if I Taylor expand this what does the Taylor series expansion look like? So let me take F and let us assume that it is not an explicit function of x, y, z , so it is a function of $C, \Delta C$, etcetera.

So what is what does this quantity look like so this quantity is some $f(c) + \delta f / \delta \Delta C * \Delta C + \delta^2 f / \delta \Delta^2 C * \Delta^2 C + \delta^2 f / \delta \Delta C \delta \Delta C * (\Delta C)^2$ and etc there are other higher order terms okay, so now if you take F which is a scalar and if you differentiate it with respect to ΔC which is a vector, you get a vector and that vector dotted with ΔC is going to give me a scalar, In this case because this is going to give me a second rank tensor, I have to do a contraction with respect to two indices to get because this is also a second rank tensor, so second rank tensor inner multiplied with another second rank tensor is going to become scalar and this is another second rank tensor multiplying another second rank tensor etcetera.

(Refer Slide Time: 11:09)

$$G = \int F(x, y, z, c, \nabla c, \nabla^2 c, \dots) dV$$

$x_i, c, \nabla c$ (Vector)

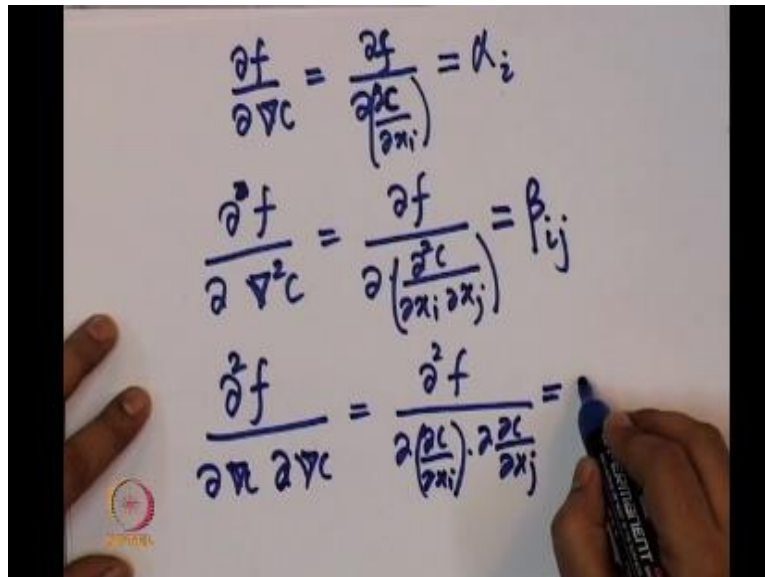
$$\nabla^2 c = \frac{\partial^2 c}{\partial x_i \partial x_j}$$

II rank tensor

$$F(x, y, z, c, \nabla c, \nabla^2 c, \dots) = f(c) + \frac{\partial f}{\partial x} \cdot \nabla c + \frac{\partial^2 f}{\partial^2 c} \nabla^2 c + \dots$$

Now we are going to use all the properties that we had derived so what is $\delta f / \delta \Delta C$, you can see that it is a first rank tensor okay, so what is this first rank tensor so $\delta f / \delta \Delta C$ which I am going to write as $\delta f / \delta(x/x_i)$ so, I am going to call this quantity as some α_i , it is a quantity with one index so it is a vector. Now let me consider this quantity $\delta^2 f / \delta \Delta^2 C$, I am going to consider this quantity sorry $\delta f / \delta \Delta^2 C$ so this is $\delta f / \delta (\delta^2 C / \delta x_i \delta y_j)$ so, this is a quantity with two indices and so this scalar when it is differentiated with respect to two indices is going to give me a second rank tensor let me call this β_j and then I have another second rank tensor $\delta^2 f / \delta \Delta C \delta \Delta C$ okay.

(Refer Slide Time: 12:59)



The image shows a whiteboard with three mathematical equations written in blue ink. The equations are:

$$\frac{\partial f}{\partial \nabla c} = \frac{\partial f}{\left(\frac{\partial c}{\partial x_i}\right)} = \alpha_i$$
$$\frac{\partial^2 f}{\partial \nabla^2 c} = \frac{\partial f}{\left(\frac{\partial^2 c}{\partial x_i \partial x_j}\right)} = \beta_{ij}$$
$$\frac{\partial^2 f}{\partial x_i \partial \nabla c} = \frac{\partial^2 f}{\left(\frac{\partial c}{\partial x_i}\right) \cdot \frac{\partial c}{\partial x_j}} =$$

A hand is visible on the right side of the whiteboard, holding a blue marker and pointing at the third equation.

Now I have made a mistake here in the earlier version so this should not be δ^2 it is $\delta f / \delta \Delta^2 C$ so, $\delta f / \delta \Delta C \delta \Delta C$ I am going to write it as $\delta f / \delta(\delta C / \delta x_i) * \delta(\delta C / \delta x_j)$ so let me call it as some γ_{ij} , so it is also a second rank tensor, so these quantities when this α_i is dotted with $\delta C / \delta x_i$ that will give me a constant and this is dotted with $\delta^2 C / \delta x_i \delta x_j$ that will give me a constant so that will give me a scalar and similarly this dotted with this will give me a scalar and this dotted with $\delta^2 C / \delta(\Delta C)^2$ that will give me a scalar.

(Refer Slide Time: 14:04)

$$\frac{\partial f}{\partial \nabla c} = \frac{\partial f}{\partial \left(\frac{\partial c}{\partial x_i} \right)} = \alpha_i \left(\frac{\partial c}{\partial x_i} \right) \equiv \text{Scalar}$$

$$\frac{\partial^2 f}{\partial \nabla^2 c} = \frac{\partial f}{\partial \left(\frac{\partial^2 c}{\partial x_i \partial x_j} \right)} = \beta_{ij} \left(\frac{\partial^2 c}{\partial x_i \partial x_j} \right) \equiv \text{2nd rank}$$

$$\frac{\partial^3 f}{\partial \nabla^3 c} = \frac{\partial^2 f}{\partial \left(\frac{\partial c}{\partial x_i} \right) \cdot \frac{\partial^2 c}{\partial x_j}} = \gamma_{ij} \left(\frac{\partial^2 c}{\partial x_i \partial x_j} \right) \equiv \text{3rd rank}$$

So now these are now properties so this is a free energy the derivative with respect to the concentration gradient is first rank tensor suppose, if I assume that I am dealing with a material which is say cubic or isotropic with inversion symmetry then we know that all these odd rank tensors should be 0. Similarly if I assume that I am looking at an isotropic or cubic material then all these second-rank tensors should become isotropic so this is the reason why we were looking at the properties of materials tensile properties of materials and their representation in crystals.

So the underlying symmetry okay, this quantity for example you can already see has this intrinsic symmetry, it does not matter whether you call it ij or ji that is because when you take the derivative of composition with respect to x_i, x_j that is the same as $\delta^2 C / \delta x_i \delta x_j$ provided the composition field I has certain continuity properties, which we will assume because composition is a continuous field which is varying for all times for all positions and so it is smooth enough that you can take so many of these derivatives, so the continuity properties are there if you assume that β_{ij} and β_{ji} are basically the same and the same is true with γ_{ij} also whether it is $\delta f / \delta (\delta C / \delta x_i) * \delta (\delta C / \delta x_j)$ or you call it $\delta (\delta C / \delta x_i) * \delta (\delta C / \delta x_j)$ it does not matter.

So the γ_{ij} also has some intrinsic symmetry so this is intrinsic symmetry, symmetry which is already existing with respect to this property, so these are second-rank tensors because $i j$ is $j i$ these are symmetric second-rank tensors and then so this is the intrinsic symmetry, then by assuming something about the underlying crystal in which these are defined we can get some more of these properties of this materials the of these material properties in these systems which is what we will do in the next lecture so we will take it up from here.

One can already see that in the free energy functional the first term which gives rise to an odd rank tensor is going to be zero if we consider systems with inversion symmetry and if you consider cubic or isotropic systems the second rank tensors which are also symmetric or by definition isotropic so there is only one constant that is associated with them. So with this will be the starting point for our next lecture we where we will try to derive the modified diffusion equation which is known as the phase field equation or continuity equation. Thank you.

NPTEL

Principal Investigator

IIT Bombay

Prof. R.K Shevgaonkar

Head CDEEP

Prof. V.M Gadre

Producer

Arun Kalwankar

Digital Video Cameraman

&Graphics Designer

Amin B Shaikh

Online Editor

&Digital Video Editor

Tushar Deshpande

Jr. Technical Assistant

Vijay Kedare

Teaching Assistants

Arijit Roy

G Kamalakshi

Sr. Web Designer

Bharati Sakpal

Research Assistant

Riya Surange

Sr. Web Designer

Bharati M. Sarang

Web Designer

Nisha Thakur

Project Attendant

Ravi Paswan

Vinayak Raut

NATIONAL PROGRAMME ON TECHNOLOGY
ENHANCED LEARNING
(NPTEL)

Copyright NPTEL CDEEP IIT Bombay