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

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Module No.4
Lecture No.19
Diffusion & mobility II

Okay, so we derived an expression for the flux with respect to Matano interface.

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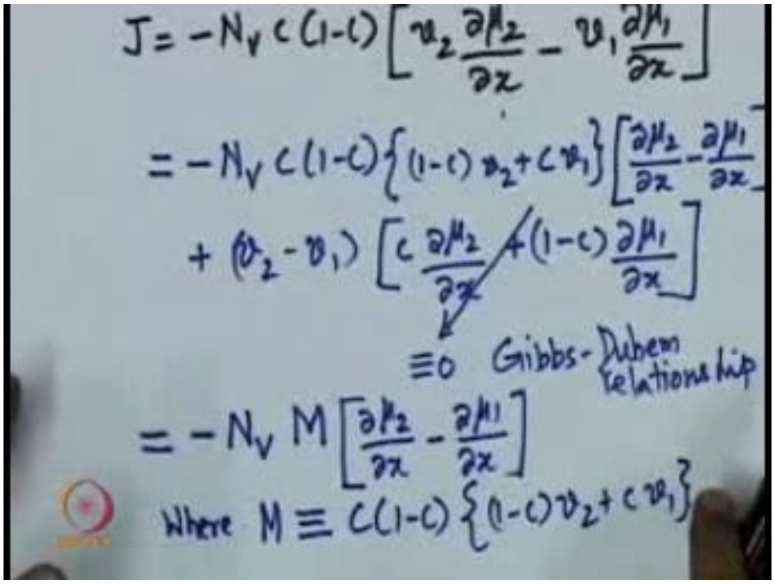

$$J = -N_v c(1-c)\left[v_2 \frac{\partial \mu_2}{\partial x} - v_1 \frac{\partial \mu_1}{\partial x}\right]$$

$$= -N_v c(1-c)\left\{(1-c)v_2 + c v_1\right\}\left[\frac{\partial \mu_2}{\partial x} - \frac{\partial \mu_1}{\partial x}\right]$$

$$+ (v_2 - v_1)\underbrace{\left[c\frac{\partial \mu_2}{\partial x} + (1-c)\frac{\partial \mu_1}{\partial x}\right]}_{\equiv 0 \text{ Gibbs-Duhem relationship}}$$

$$= -N_v M\left[\frac{\partial \mu_2}{\partial x} - \frac{\partial \mu_1}{\partial x}\right]$$

Where $M \equiv c(1-c)\left\{(1-c)v_2 + c v_1\right\}$

And that expression is given by this NvC(1-C)[v2 ∂μ2/ ∂x-v1 ∂μ1/ ∂x]. I am going to write it by doing a little bit of algebraic manipulation and the expression that I am going to write is like this. So NvC(1-c) so that is what I am going to keep, then I am going to write this (1-C)V2+Cv1 this entire thing is multiplied by [∂μ2/ ∂x- ∂μ1/ ∂x] +V2-V1 [C ∂μ2/ ∂x+(1-C) ∂μ1/ ∂x] okay. So this is a simple algebraic manipulation you can do the algebra and show that it comes back to this expression you can check it for yourself.

The reason why I am doing that is that as you might have studied in your materials thermodynamics course C times ∂μ+1-C ∂μ1=0 by what is known as the Gibbs-Duhem relationship okay. The reason why we modified this expression and wrote it in this form is to make sure that this part goes away, because by Gibbs-Duhem relationship we know that any term that has C ∂μ2+1-C ∂μ1 is going to be 0 right.

So what are we left with, we are left with only the first line of this modified expression. So let me write that expression and I am going to make a simple modification. So I am going to say, that Nv times the C times (1-C){(1-C)V2+CV1} I am going to call that as, so let me keep the NV, so let me call C(1-C) times (1-C)V2+CV1 as the mobility and this quantity ∂μ2/ ∂x- ∂μ1/ ∂x, this is the diffusion potential.

And this is the mobility times Nv okay. So where okay, obviously I have written all this as M, so M is nothing but C times 1-C times (1-C)V2+CV1 okay. So this is how we have defined and so let us proceed further okay. So we have obtained an expression for J in terms of mobility and gradient on what is known as the diffusion potential okay. So what is the diffusion potential.

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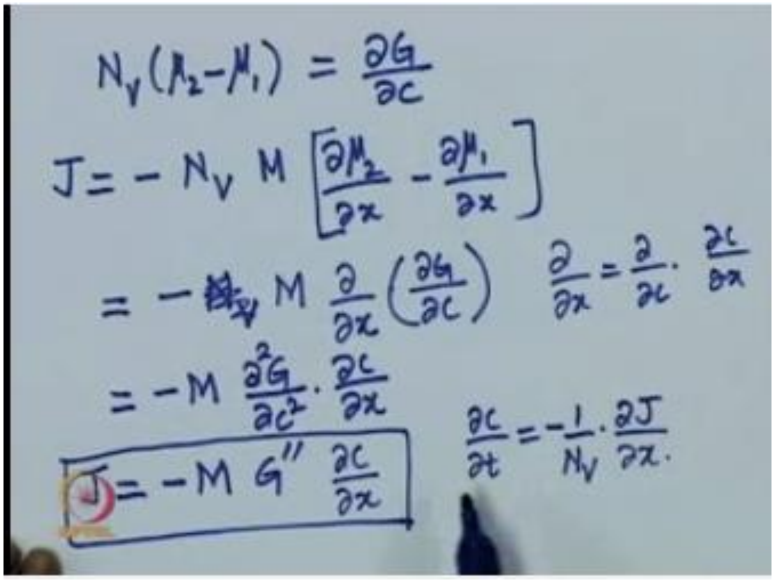

$$N_v(\mu_2-\mu_1) = \frac{\partial G}{\partial c}$$

$$J = -N_v M\left[\frac{\partial \mu_2}{\partial x} - \frac{\partial \mu_1}{\partial x}\right]$$

$$= -\cancel{N_v} M \frac{\partial}{\partial x}\left(\frac{\partial G}{\partial c}\right) \qquad \frac{\partial}{\partial x} = \frac{\partial}{\partial c}\cdot\frac{\partial c}{\partial x}$$

$$= -M \frac{\partial^2 G}{\partial c^2}\cdot\frac{\partial c}{\partial x}$$

$$\boxed{J = -M G'' \frac{\partial c}{\partial x}} \qquad \frac{\partial c}{\partial t} = -\frac{1}{N_v}\cdot\frac{\partial J}{\partial x}.$$

Because Nv times $(\mu2-\mu1)$ is nothing but $\partial G/\partial C$ okay. So we are going to use this expression because remember the expression that we derived said that $J = -Nv$ times M times $\partial\mu2/\partial x-\partial\mu1/\partial x$ okay. So $\mu2-\mu1$ is nothing but $1/Nv\ \partial G/\partial C$, so this Nv times $\mu2 - \mu1$ if I can take then I can see this is nothing but –Nv M, okay so Nv I am going to absorb, so that is nothing but M $\partial/\partial x$ of $\partial G/\partial C$ okay.

So I am going to do one more manipulation, so –M this is $\partial/\partial x\ (\partial G/\partial C)$ so I am going to write that as $\partial^2G/\partial C^2.\ \partial C/\partial x$ okay. So instead of acting $\partial/\partial x$ on this quantity I am going to say that $\partial/\partial x$ is nothing but $\partial/\partial C(\partial C/\partial x)$ so $\partial/\partial C$ acting on this is going to give me $\partial^2G/\partial C^2$ and so $\partial C/\partial x$ okay. So what did I do, I replaced this operator by $\partial/\partial C$ and $\partial C/\partial x$ I am writing by okay. So instead of $\partial/\partial x$ operating I made it $\partial/\partial C$ operating on this, because of that I had to multiply by $\partial C/\partial x$ so this is what I have done.

So let me give a short hand notation, so this is –M, let me call this as G'' which is what we have been calling, because this is nothing but the second derivative of the free energy with respect to composition right, free energy versus composition curve we should take the second derivative, this is G'' which is what defined in this spinodal point obviously right, that is the reason why we are interested in this, this becomes negative or this becomes positive or this becomes 0, wherever this becomes 0 is actually the spinodal line.

So we have ∂C/∂x that is J right. So this is the expression that we have for it. So now we are going to derive, so once you have the expression for J we know that ∂C/∂t=-1/Nv times ∂J/∂x where does this come from, this comes from the mass conservation right. Previously when we are talking about composition there were no Nv factors okay, so the, this number of atoms per unit volume or per mole quantity this Nv will always appear in these type of derivation, they do not appear in the usual Fick's law, the usual Fick's it said ∂C/∂t is - ∂J/∂x right.

But this Nv is there, because we are now discussing about chemical potential which was defined in the pair atom, so this Nv is going to keep appearing everywhere. Now let me put this J into this expression, so what do I get, I get an expression for the rate of change of composition in terms of the concentration gradient which is what that usual Fick's law is, so let us do that.

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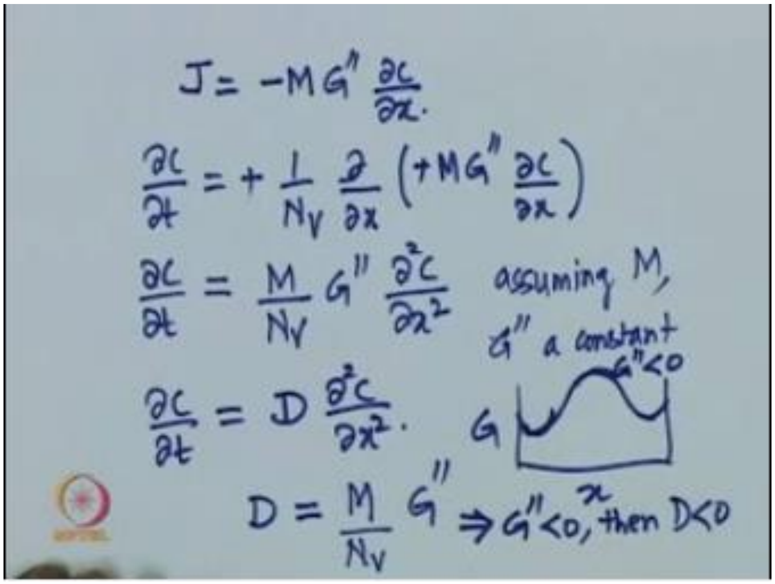

$$J = -MG'' \frac{\partial c}{\partial x}.$$

$$\frac{\partial c}{\partial t} = +\frac{1}{N_V}\frac{\partial}{\partial x}\left(+MG''\frac{\partial c}{\partial x}\right)$$

$$\frac{\partial c}{\partial t} = \frac{M}{N_V} G'' \frac{\partial^2 c}{\partial x^2}$$ assuming M, G'' a constant

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}.$$

$$D = \frac{M}{N_V} G'' \Rightarrow G'' < 0, \text{ then } D < 0$$

So J which is equal to –MG''∂C/∂x we add this expression and ∂C/∂t is equal to -1/Nv ∂/∂x of J, so I am going to put this quantity here –MG''∂C/∂x. So – and – is going to become +, I am going to assume that M and G ‘’ are constant, because I am going to take this $\partial/\partial x$ here. If I assume that they are constant, then I get M/NvG’’ $\partial^2 C/\partial x^2$ okay, assuming this is very important, the mobility m and the G’’ are constant.

What is G’’, this is the curvature of the free energy versus concentration diagram okay. So this is $\partial C/\partial t$, now let us compare with the usual diffusion equation, what that say, let me say that, that is some D times $\partial^2 C/\partial x^2$. If you compare these two expression you see that diffusivity is connected to the mobility some number of atoms information is there, through the second derivative of the free energy curve with respect to composition.

Now spinodal region right we had the free energy versus composition curve which was like that, spinodal is the region where G’’ is less than 0, so because G’’ is less than 0 mobility is positive, Nv is just a number which is positive, so diffusivity becomes negative right. So this implies that if G’’ is less than 0, then D is less than 0 right. So in the other case where G’’ is positive, you can see that the diffusivity is positive.

So Fick’s law happens to be a special case right, when we are writing in terms of diffusivity we are really not worried about the sign of G’’, because that works in regions where G’’ is actually positive, when G’’ becomes negative then the diffusivity has to become negative right. So we discuss this in one of the earlier modules we said that, the diffusivity becomes negative whenever there is an optical diffusion right.

Now this is the derivation that we have done, identifying the diffusivity in terms of the mobility shows that diffusivity and mobility are connected through this second derivative of the free energy with respect to composition. So obviously the sign of G’’ is going to define the sign of diffusivity, so from this derivation you can understand why suddenly diffusivity will become negative under certain circumstances.

It depends on what kind of free energy versus composition curve you have in your system right. So this is what the relationship that I used in one of the previous modules when I was deriving the relation between the amplitude of a sinusoidal composition which was put as a solution to the diffusion equation to this, the same equation and we said what happens to such sinusoidal composition fluctuations.

There I introduced this relationship between diffusivity and mobility and this is how this relationship is derived okay. So we were trying to look at a solution of this equation by putting A times exponential $i\beta x$ kinds of solutions, and were A was dependent on the β on time. So there I introduced this expression, this is the origin of this expression. So we have derived how this D and M are related to G'' which automatically explains as to why in this spinodal region you expect the diffusivity to be negative okay.

So in the next part we will go back to the expression that we derived for the amplitude are rate of change of amplitude and see what happens to it as a function of β which is a wave number or the λ the wavelength which is the inverse of β and discuss what happens in this spinodal diffusion. Thank you.

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