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

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Module No.2

Lecture No.9

Failure of classical Diffusion equation

Welcome, this is the last segment of this module we are trying to understand diffusion as described by Fick's law and cases where Fick's law seems to fail in the usual way it is formulated so let us take a look at two cases.

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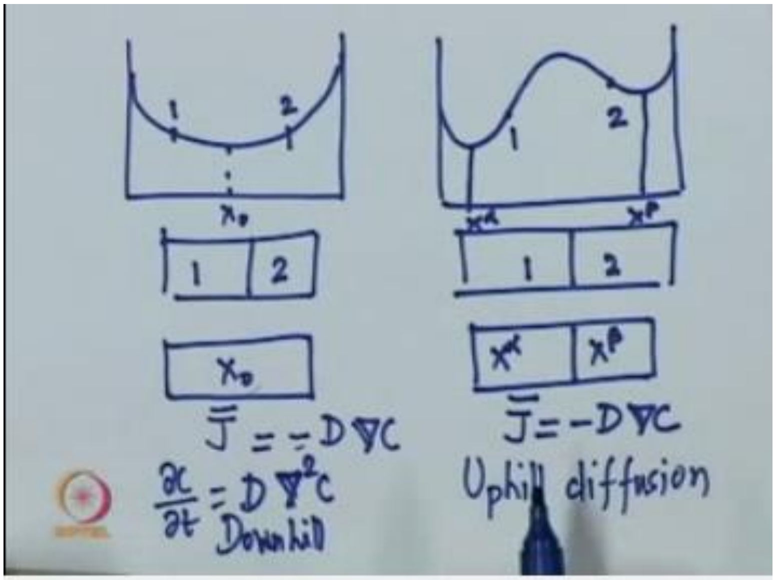

We are discussing a case where the free energy is like this and then I am talking about a weld which consists of compositions 1and 2 and in this case the overall alloy composition is somewhere here and the system goes to that overall alloy composition and there is another case in which I have a double well potential and again I pick some a rich and some be rich alloy and I put them together they weld them together and then they get to some mechanical mixture which consists of two end compositions one goes to X α 2 goes to X β.

Now the classical diffusion equation which said that the flux is proportional to concentration gradient would explain this behavior because there is a concentration gradient A atoms are more here they are less here and this negative sign said that they should move in such a way that the concentration gradient become zero so if you have more A here less A here if A atoms move from here to here a concentration gradient will go away.

Similarly when you have more B and less B here B Adam should move in that way so the concentration gradient will even out so this is what is happening here which is described very well by this equation and of course you can add law of conservation of mass which is a universal law to this that also gave you the same information namely the rate of change of composition at any point in time in such a system is given by the gradient of the composition profile the curvature of the composition profile and the curvature basically tells you whether the composition at a point will increase or decrease or remain constant and if you take a sinusoidal profile you can show that this equation shows that composition will become a homogeneous.

On the other hand if we want to explain the same phenomena here we have a problem because if you use the same $j = -D \nabla C$ you find that unless your diffusivity is negative in which case this sign will go away then it will be such that if you have concentration gradient that the flux will be in such a way as to accentuate those concentration gradients that is region rich in A will become richer and richer in A regions poorer B will become poorer and poorer would B.

So this can happen if the diffusivity becomes a negative in a system it is not clear why suddenly diffusivity should change sign okay so the initial explanations that came for the behavior that you see here were assuming that the diffusivity is negative so it was called up hill diffusion okay as opposed to downhill diffusion okay you can see in the words itself that this was sort of problematic for people to understand because down will hill we understand okay you pour water it will go downhill.

but rarely you will see water going up right so similarly most of the times you will see that diffusion will take place to even out concentration gradients but there seem to be some cases suddenly where diffusion is taking place against the concentration okay so it is accentuating the concentration gradients instead of getting rid of them and making everything is homogeneous. So this was known as up Hill diffusion or sometimes this is known as the classical diffusion and this is non classical equation there is nothing non-classical about it.

Except for that for the way in which we are trying to describe there is a problem okay so initial explanations we're in terms of D suddenly becoming negative and it was not clear why suddenly D becomes negative and I am going to give you a hint as to how one might explain as to why suddenly diffusivity gets a negative sign okay so that is to think of the Fick’s law but modify the Fick’s law so how do we modify we know that fixed law says.

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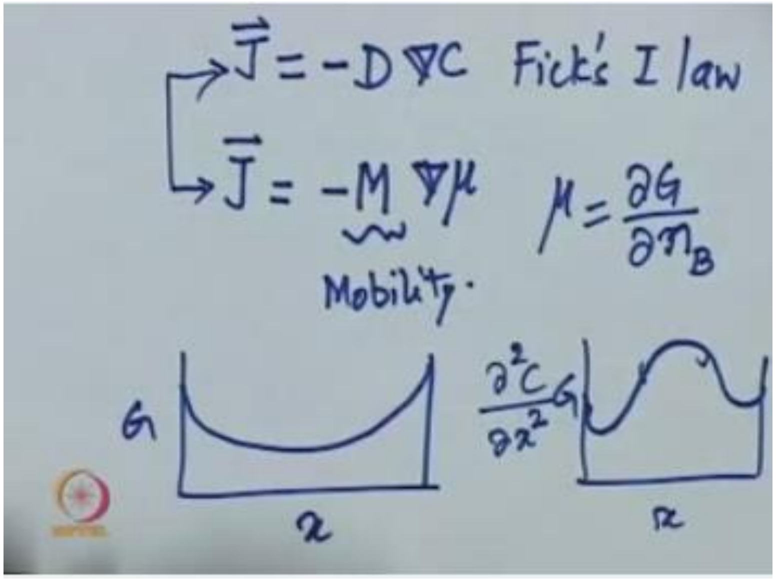

$\vec{J} = -D\nabla C$ Fick's I law

$\vec{J} = -\underbrace{M}_{\text{Mobility}}\nabla\mu$

$\mu = \frac{\partial G}{\partial n_B}$

$\frac{\partial^2 C}{\partial x^2}$

The concentration the atomic flux is in such a way that it is proportional to concentration gradient and the proportionality constant is diffusivity and there is a negative sign to indicate that concentration gradients are getting evened out but we know from our thermodynamic analysis that this is not how we should describe the system to be consistent with thermodynamics because we know that systems evolve in such a way that the free energies are getting minimized.

And you have also shown that free energy minimization is the same thing as chemical potential becoming equal free energy minimization and chemical potential becoming equal at in two systems where atomic fluxes allowed is the same thing which means we need to modify the so-called Fick’s law right this is Fick’s first law and we need to modify the Fick’s first law how do we modify we say that the atomic flux is proportional to chemical potential gradient.

And remember chemical potential gradient is in such a way that regions the higher in chemical potential A with respect to lower in chemical potential A the atomic flux will be in such a way as to even out this chemical potential difference so there is a negative sign what is the proportionality constant the proportionality constant is called M, M is called mobility okay so the way we define diffusivity is that it is the ratio of the atomic flux that is set up by unit concentration gradient okay similarly the atomic flux that is set up by unit chemical potential gradient is nothing but the mobility.

But remember μ itself what is μ, μ itself depending on so let us say that we are writing everything for the diffusivity of B so it is 2g / ∂ nb so μ itself is the partial derivative of free energy with respect to the B atoms which means the free energy versus a composition curve so that free energy change how it changes with B atoms is going to be part of this information and you can show that that tells that this diffusivity is nothing but this mobility times the curvature of the free energy versus composition curve okay.

This is this is something that for you to think about we will do it in greater detail we will do the algebra so what I am indicating is that if you have a free energy versus composition curve which has positive curvature then only the sign of the concentration profile matters only its sign matters as far as atomic clock systems and because that is but the moment you have a G versus X curve which has some negative curvature then the sign of that has to be incorporated because the diffusivity is nothing but the mobility times the curvature of the free energy versus composition.

Now that the curvature if it becomes negative then you can see that that will bring its own sign so then you can see that it is consistent with Fick's law so in other words this understanding the diffusivity suddenly becomes negative so why did it become negative so the answer seems to be that the sign of diffusivity depends not only on mobility which is a more basic parameter and it is mobility times the curvature of the G versus X curve so if it is positive then diffusivity is positive if it is negative then there is a negative sign that diffusivity picks up.

Mobility on the other hand is always positive for unit chemical potential gradient there will always be some atomic flux and that is a positive quantity so this is the first explanation in trying to understand the free and reversal composition curves of this type and the behavior of the system if you are in this region okay of course this is not the complete story this is also not satisfactory for several reasons so we will do this part in greater and greater detail in fact that will be the next part.

So whatever we have been discussing is part of standard phase transformation scores or a physical metallurgy course good textbook to look at is Poulter and D sterling which contains all this information that I have been discussing in greater detail and so we will also do some tutorials and problems to understand this better, but what we are going to do now is to try to understand going beyond whatever is there in these textbooks in terms of understanding the mathematical aspects and the computational aspects and the material size aspects of what is happening in systems.

Which have a concave region like this in their free energy versus compulsion diagrams so that is what is going to take us to be so called the phase field models, okay I will leave you with this thought, so you can go back and write the flux as to be proportional to chemical potential gradient and you know the chemical potential gradient is $\partial G/\partial$ nb you know the regular solution free energy take a case when $\omega > 0$ and ω is the dominant term and take a case when you have an ideal solution and find out what happens to this term.

If you compare then by taking this partial derivation and putting it here and then comparing these two terms okay so that will give us what is known as the thermo dynamic factor and the thermodynamic factor is how they are connected to each other. So I am going to stop it here in the next module we will continue further along these lines to understand the phase free modules. Thank you.

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