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

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Module No.4
Lecture No.20

Failure of classical Diffusion equation

Welcome so we are looking at the diffusion equation so time dependent diffusion equation which is.

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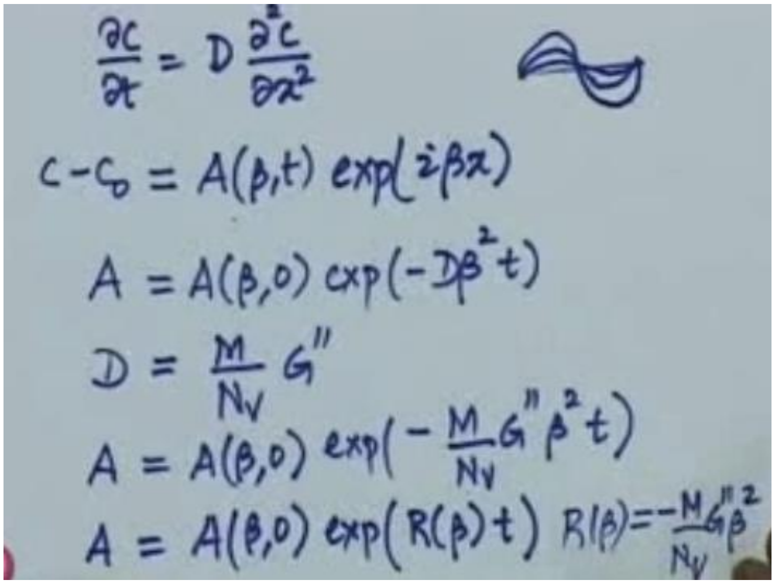

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

$$c - c_0 = A(\beta,t)\exp(i\beta x)$$

$$A = A(\beta,0)\exp(-D\beta^2 t)$$

$$D = \frac{M}{N_v}G''$$

$$A = A(\beta,0)\exp\left(-\frac{M}{N_v}G''\beta^2 t\right)$$

$$A = A(\beta,0)\exp(R(\beta)t) \quad R(\beta) = -\frac{M}{N_v}G''\beta^2$$

$\partial c/ \partial t = D \partial^2 c/ \partial x^2$ and you can substitute a solution to this equation of the type $C - C_0$ where C0 is a constant is equal to A which is some constant which depends on a the amplitude which depends on the wave number β and time T times exponential iβx okay this is solution of sinusoidal type and the amplitude is given by this A and this amplitude depends on what the wavelength that I am choosing as well as a function of time as a function of time.

What happens to this wavelength I mean this is going to amplitude this is going to grow or this is going to die down okay so that is what is prescribed as this one, so we can substitute it here and we end up with a ordinary differential equation. You can solve that ordinary differential equation and you get an expression which looks like this A = A(β, 0) so that is some constant times exponential $(-D \beta^2 t)$ okay this is where we introduce the expression $D = M/N_v G''$.

So you substitute it back here so you get amplitude $A = A(\beta, 0) \exp(/M/N_v G'' \beta^2 t)$ okay so let me call this quantity M/Nv G'' as β^2 as R(β) so A = A(β, 0) exp (R(β)t) where what is R(β)? R(β) = -M/Nv G'' okay. So this is what happens to the amplitude that this is what we derived in one of the earlier modules and now we are looking at what happens to this R(β), so because R(β) depends on M/Nv G'' β^2 and β is the wave number it is anyway squared okay, M is a constant its mobility it is positive and Nv is number of atoms where mole for example or there would be volume for example.

So that is a constant positive. So G'' sign is going to decide everything about R β now if G'' is positive so where does that happen, that happens in the meta stable region, when G'' is positive you can see that this is a positive quantity exponential minus so that is going to decay so the amplitude as a function of time is going to decay this is what we said is the homogenization solution, right.

We said that the diffusion equation has this physical meaning namely that the rate of change of concentration at any point is given by the curvature of the concentration that is concentration with respect to position how does that curve look like and if it has negative curvature in those regions the concentration is going to go down if it has positive curvature in those regions the concentration is going to go up in effect if you have a.

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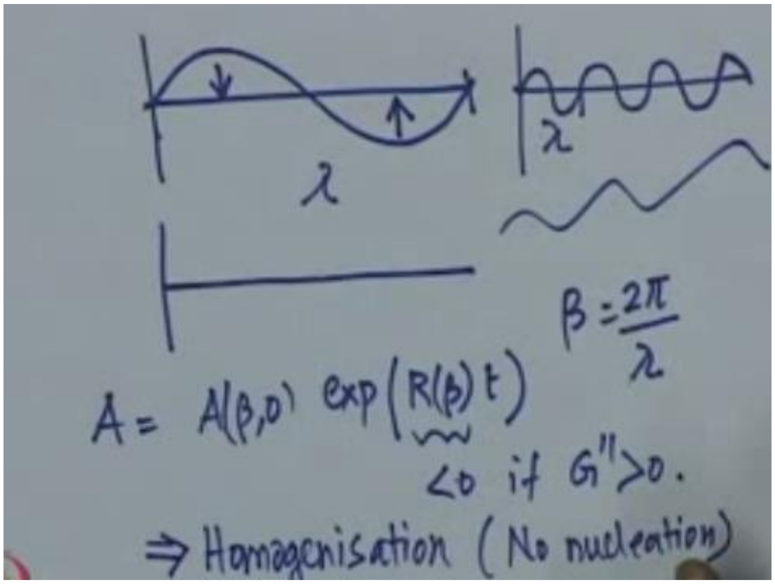

Concentration profile which looks like that then it is going to come down here it is going to go up here so after sometime you end up with the concentration profile which looks like that, the same information is what is being given by this derivation also, so A = A(β, 0) so this is some constant exp(R(β)t) now this R(β) is negative right this quantity is less than 0 if G’’ > 0 in that case then this quantity is going to decrease which means the amplitude of the wave whatever be the wavelength or the wave number of the wave that you are introducing right, β is nothing but 2Π/ λ. Where λ is the wavelength so what is that mean.

So in this how many ways you are having that is the wave right, I can have more than one wave in the same distance for example I can have a wave like that, right. So the wavelength in this case will be this so 2Π/ λ is β so whatever be the β because this quantity is going to be negative then exponentially that is going to decay, so that means the amplitude of these waves.

As times goes by is going to decrease so which means all wavelength you know any generic composition profile that you have can be thought of to be made up of a combinations of these different wavelengths they are all going to decay so everything is going to become movement, so the classical diffusion equation solution which we said indicates that the equation itself right we said that the Fix second law equation itself indicates that the solution is going to be a homogenous solution, okay.

Which is what is being reiterated by this derivation also, most important point to note here is that this equation also tells you that there can be no nuclear because nucleation means heterogeneous there has to be some reasons where the composition becomes some particular value so nucleation typically happens because of compositional punctuations which are result of thermal punctuation.

That physics is not incorporated in this analysis, so this derivation shows you that the solution is going towards homogenization, so obviously the solution also rules out nucleation, okay. So of you want to develop a theory for nucleation that has to be done by incorporating thermal punctuations and then that will lead to nucleation and after that nucleation there will be grown but as such this is indicating that there is going to be homogenization. On the other hand if G’’ becomes negative right R(β).

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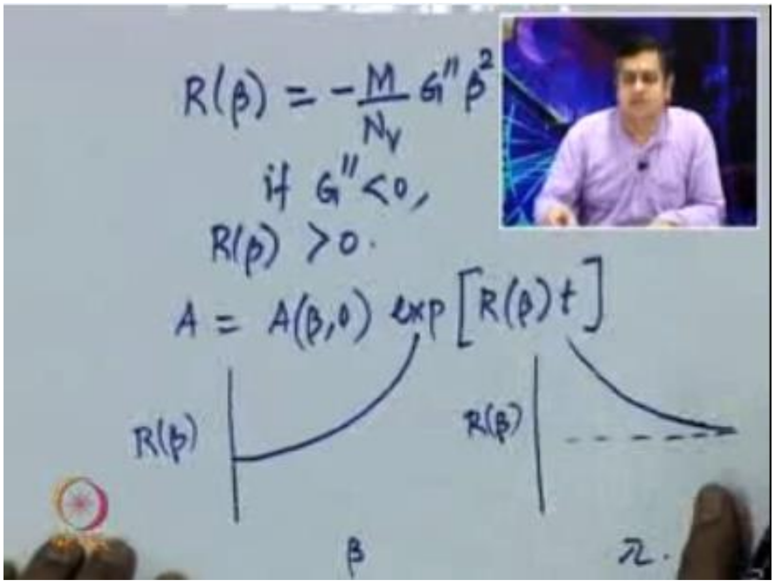

$$R(\beta) = -\frac{M}{N_v} G'' \beta^2$$

if $G'' < 0$,

$R(\beta) > 0$.

$$A = A(\beta, 0) \exp[R(\beta)t]$$

Right that is related to G’’ how this set related –M/Nv G’’ β^2 so if G’’<0 R(β) > 0 that means what is going to happen any concentration punctuation is going to grow right, for all B so you have this solution A = A(β, 0) exp [R(β) t] so as a function of time because R β is positive this quantity is going to grow, so in other words if you say take a look at a dA/dt right so that is going to give R β time A itself so in other words the solution is going to look something like this.

So you can plot in two different ways so you can plot it as a function of β what happens to R(β) right B0 means that wave length is infinite okay so that means so β is 0 so that is going to be 0 so at any non 0 β it is going to grow it is going exponential you can also plot it in terms of wave length λ and R(β) so that is inverse so what will happen is it will go like that infinite wave length will be the only one which will have 0 growth rate everything else will grow and as you are coming to smaller and smaller wave lengths it will grow much faster.

Now what does this mean this means that if I have some composition fluctuation right that is going to grow whatever be the wave length of that composition fluctuation it is going to grow okay so let us try to understand what it means in terms of the spinodal decomposition okay so we are saying that in the case of spindoal G´´ is negative which means R(β) is positive which means any wave length that you are going to introduced is going to grow so if you have suppose more or less homogenous solution and if yo introduce a small fluctuation that fluctuation is going to grow so if you have.

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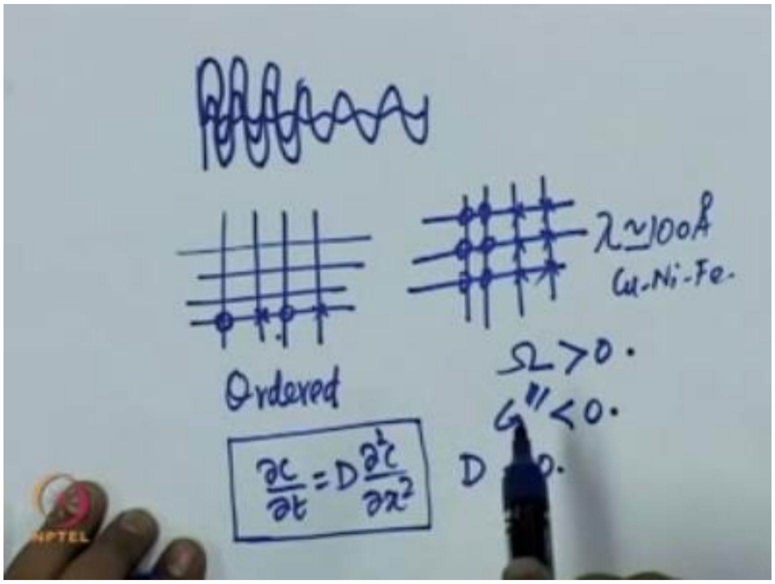

A small fluctuation like this then that fluctuation is going to grow right as a function of time is going to grow and it will grow still further because right so this is what this solution is saying in addition it is saying that this growth is irrespective what the β value is okay and as β becomes some larger and larger are the λ becomes smaller and smaller as the wave length becomes smaller the growth is really fast because it is exponentially growing right what is that mean that means suppose the λ cannot be arbitrarily small because we are looking at crystal line structures right.

So A and B atoms are going to be sitting on lattices like this so there is a lower limit to the wave length that can be achieved right so it this can be A atom and this can B atom for example so there cannot be any wave length which is smaller than this but the smallest wave length will be of this order right that wave length is also going to grow so we started with spinodal decomposition and we said for spinodal decomposition G´´ is less than 0 we said G´´ is less than

0 because Ω is greater than 0 we said Ω is greater than o because AA BB bonds are preferred over AB bonds.

But if you put this solution that we have derived into the equation this solution is saying that all wave lengths are going to go they are going to grow irrespective of what the wave length is so even the smallest wave length is going to grow the smallest wave length that you can think of will be of two atomic plane distance if that wave length is also going to grow then that means that A rich plane B rich plane A rich plane B rich plane so that is going to be ordering at the atomic scale it is not going to phase separate so we have a contradiction okay so let me recap the arguments once more we started with the regular solution model.

We said that systems which are reverse spinodal decomposition have a Ω greater than 0 we said that Ω greater than 0 means that the system prefers AA BB bonds over AB bonds and we realized that the classical diffusion equation is not correct we have to deal with the diffusion in turns of the chemical potentials and if you write the appropriate diffusion equation then you have it in terms of the mobility and the section derivative of composition with respect second derivative of free energy with respective composition.

So the sing of that free energy with respective composition the second derivative is going to determine the sign of diffusivity and we found that the first spinodal systems that diffusivity becomes negative so if that is all there to it we could have made the diffusivity negative and we could have solved it we could have gotten the solutions so this is the difficulty that I was discussing when we discussed the historical progression of ideas in this field I said by current Dillinger’s theories had problems and this is the problem that they phase if the movement you assume that negative diffusivity is allowed then the system is going to phase separate and the phase separation is going to happen even at the very fine scale.

That is alternate planes you are going to have A and B atoms if that is going to happen then what you end up with an ordered system instead of a phase separated system how should a phase separated system look like phase separated system should like all A atoms like this and all B atoms like this so we started with the thermo dynamics corresponds to this we started with Ω greater than o which corresponded to a region where G’’ will be<0 and when we use G’’ < 0 we showed that this D will become negative and with this D < 0 we took this equation and try to solve it and we find that it goes to ordered so there is a contradiction here I start with thermodynamic which is constant with phase separation is solve the classical diffusion equation.

I end up with ordered structures which is not consistent which means this equation will not be able to explain phases separation even if you assume diffusivity to be negative see the first step is to say that no phase separation happens because chemical potential gradients are to be consider of course you can consider then that explains why diffusely looks as if it has become negative that is also right but diffusivity becoming negative alone is not sufficient to explain phase separation please remember the experiments of experiments for Daniel and Lipson should that there is wave length of the order of 100 Å. In copper nickel and insister right.

So this kind of wave length why do they developed that is you will have A rich regions and B rich regions and the size of this will be ordered of 100 Å. That is not what we are seeing if we use the classical diffusion equation there is a contradiction which mean we have misted some important piece of physics when we wrote this equation okay so what is that missing piece of physics is what was given by Hilliard initially using discrete latest model and by Cahn later.

So which is what we will discuss next why is there a discrepancy between the thermodynamic model which assume phase separation and they fixed law which say that for such systems under certain circumstances you will have ordering instead of having phase separation so where is the missing piece and what is that missing piece is what we will discuss in the next part of this lecture which will bring us to the so called Cahn Hilliard equation which is one of the phase field equations thank you

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