

**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.18
Lecture No.72
Gibbs-Thompson effect**

Welcome we are looking at a phase field modeling in the last lecture we looked at two-dimensional solution to the Cahn Hilliard and Allen Cahn equations we started with the noisy profile and we allowed the system to evolve in the process we found that Cahn Hilliard equation represents the micro structural evolution when there is phase separation and the Allen Cahn equation shows what happens in the case of order disorder transformation.

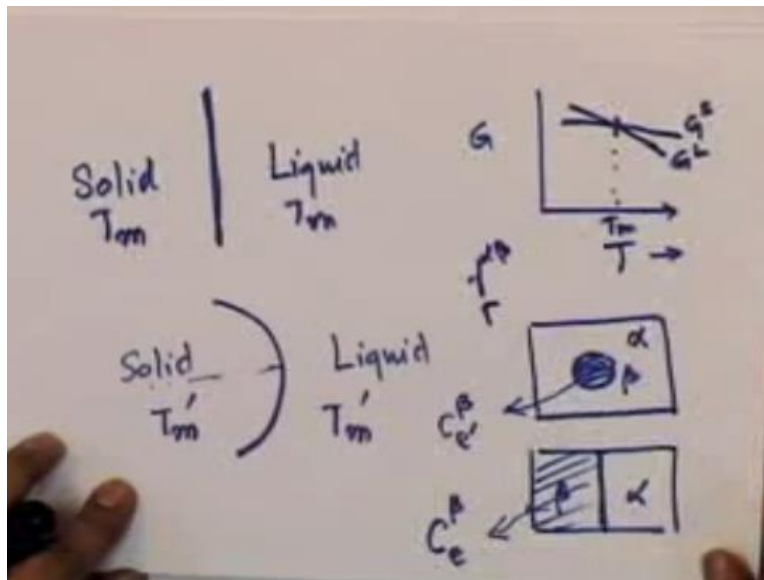
How the domain structure evolves, so in this lecture we are going to modify those scripts a little bit to study two problems that are of interest, the first one is the problem of Kiff's Thompson effect the second one is the problem of grain growth, so before we go and modify the scripts for these two problems let us discuss these problems a little bit and that will also help us formulate the equations and the way I am going to formulate it is that.

They are the same as the Cahn Hilliard and Allen Cahn equations that we solved for last time except for the initial profile so that is how we are going to formulate these problems, to do that first let us start with what is known as the Kiff Thompson effect, a Kiff Thompson effect is a curvature

effect or sometimes it is called the capillary effect it is the effect on equilibrium in systems because of interfacial energy so what happens to the equilibrium in systems because of interfacial energy is what is given by these so-called Kiff Thomas effect, for example if you have a solid and liquid in contact with each other at their melting temperature this temperature at which they will be at equilibrium.

So thermodynamically we define the melting temperature as that temperature in which the solid and liquid are in equilibrium that is at that temperature if you keep the solid and it is melt in contact with each other neither the solid will grow nor it will shrink, if it is above that temperature then the solid will melt if it is below that temperature then the solid will grow, so that is how we define the melting temperature. Now this melting temperature is for a solid liquid interface that is separated by a planar boundary so it is something like this.

(Refer Slide Time: 02:42)



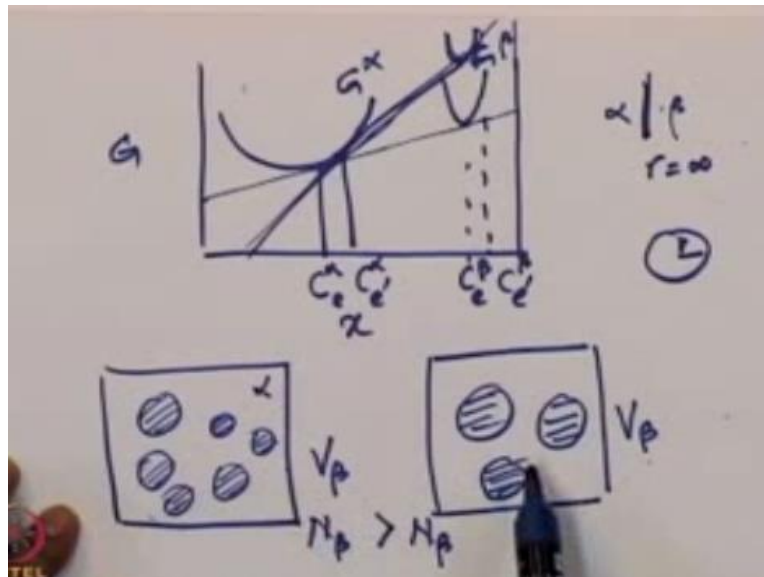
So if I have a boundary between solid and liquid thermodynamically we say if you plot the free energies as a function of temperature so you have the, so this is the free energy suppose temperature is increasing this way then this is the lower temperature at lower temperature you want the solid to be preferred so this should be the solid free energy this should be the liquid free

energy so this temperature is the melting temperature. So above melting temperature liquid has lower free energy below melting temperature solid has lower free energy so these will be the states that would be preferred so this temperature is defined as the melting temperature and that at that temperature if you keep the solid and liquid suppose both of them are at T_M then this interface will neither move to the right or not to the left however the temperature at which this happens is different if the interface is for example curved.

Suppose this solid and this liquid now the temperature at which they will be at equilibrium is not the same temperature as this let us call this as some T_M' if you do not want this interface to move that the temperature at which the solid and liquid will be equilibrium is basically determined by the curvature of this interface, now and this can be extended to other systems also suppose if you are looking at an α phase matrix in which you have a β precipitate if suppose you have an α phase in which you have another β phase now in these two cases the equilibrium composition of β will be different.

So suppose If this is the case where the equilibrium composition of β is $C_e \beta$ in this case $C_e \beta$ will be different so it will be $C_e' \beta$ so the $C_e' \beta$ and $C_e \beta$ how they are related can be obtained using thermodynamic arguments we will do it as a tutorial this is $C_e \beta E'$ is related to A the curvature of this and B the interfacial energy of the $\alpha\beta$ interface so it depends both on $\gamma_{\alpha\beta}$ and r which is the radius of this precipitate. There is another way in which one can understand the Kiff Thompson effect that is by looking at the phase equilibrium.

(Refer Slide Time: 05:43)



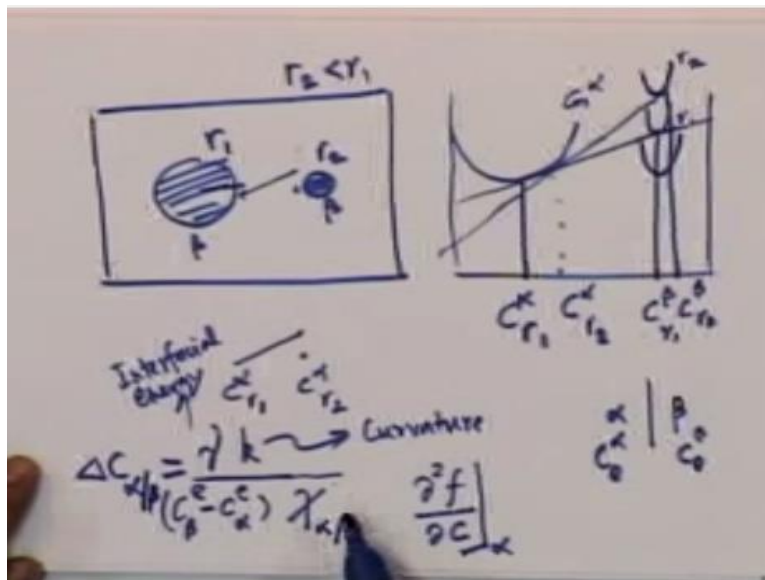
Let us take the case when I have the equilibrium between the α phase so these are the free energy versus composition diagrams let us say that this is the free energy of the α phase let us say that this is the free energy of the β phase, now the composition at which they are in equilibrium is obtained by drawing the common tangent, so this point will give C_e^α and this point will give me C_e^β .

This is this free energy is assuming that it is a flat α/β interface or the radius of curvature is 0 or r is equal to infinity suppose there is a β of given r then this curve is shifted upwards which means if you draw a common tangent between these two curves now then that common tangent cuts both these curves to the left, so this curve is now is $C_e'^\alpha$ now this is $C_e'^\beta$ so any precipitate which has a radius R or a radius of curvature $1/r$ will have a composition in both β and α .

Which is higher than the equilibrium composition it would have if the interface is planar, now this is what also explains what is known as a coarsening, coarsening is when for example if you have an α matrix and in which you have lots of precipitates lots of β precipitates, right so the volume fraction of the β precipitate suppose the volume of β is V_β then as time proceeds the smaller precipitates disappear the bigger ones grow at the cost of smaller precipitate.

And you get few big precipitates so V_β remains the same here also the volume fraction is β the N_β in this case is higher than the N_β in this case, so the number of precipitates decrease they hence the overall size increases the overall volume fraction of the β phase remains same. This is known as coarsening or Oswald ripening and the way this happens can be explained using this Thompson effect. So how do we explain that so let us take a look at the case.

(Refer Slide Time: 08:57)



Where I have say one big β precipitate and one small β precipitate, okay now I want to find out the composition of the α phase outside of this precipitate so we will go by the same common tangent construction so I have the g_α so I have 1 β which is for r equal to infinity then I have let us say this is r_1 let us say this is r_2 and $r_2 < r_1$ so which means the curve corresponding to r_2 will be higher than the curve corresponding to r_1 .

So if you now draw the common tangent between the two phases, okay so this is C_α for r_1 and this is $C_\alpha R_2$, similarly so this is $C_\beta R_1$ and this is C_β sorry β are too so if you look at the composition outside so at these points you have $C_\alpha R_1$ and here you have $C_\alpha R_2$, $C_\alpha R_2$ is higher

value than r_1 so there is a concentration gradient the concentration in α is like this which means more atoms from here are going to move towards this.

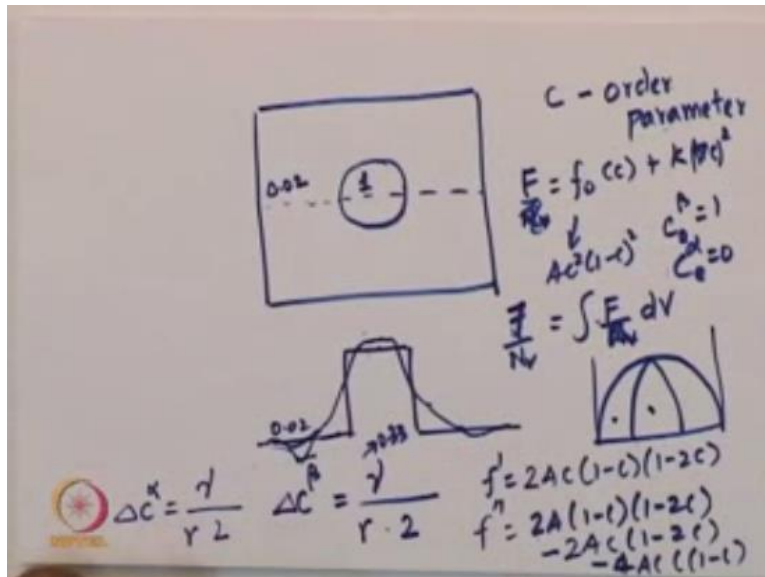
Which means this then is going to shrink because it has to maintain this composition outside and as it shrinks the equilibrium α is still going to be higher so as it shrinks this is going to be a self-reinforcing so this precipitate will become smaller and smaller and eventually disappear and the diffusion will make this grow, so this is the diffusion limited coarsening and as you can see the driving force for coarsening comes from what is known as the Kiff Thompson effect.

It can be shown that the change in composition suppose for the α or β phase I want to know the change in composition then that change in composition let us say is for the α phase is given by an expression which is γ which is the interfacial energy okay so this is the α β interfacial energy and the curvature of the interface in 2d it is nothing but $1/r$ and then C_β equilibrium minus C_α equilibrium.

So that is the when the interface is planar between α and β what is the composition of α and what is the composition of β , so this is basically what the phase diagram gives because phase diagram generally does not include the interfacial energy contribution, so this times a quantity called χ which is nothing but second derivative of free energy with respect to the composition at α in this case and if you want for β then you have to calculate at β okay.

So now let us consider a case let us go back to the problem that we were looking at so we were trying to solve the Conn Hilliard equation and we took a profile in which we have put noise about 0.5.

(Refer Slide Time: 13:09)



Instead let us consider a composition so if you go across a line like this you will see the composition let us say that the α composition is some 0.02 and the β composition is 1, so my initial profile is such that it is 0.02 and then at this point it is going to go to one is going to remain as one and then it is going to come down, so in such a case what happens because this precipitate now has a curvature.

So as we did last time we are going to describe a phase field model so composition is my order parameter so I have decided that I am going to describe my stress system using composition order parameter it is a conserved order parameter so we are going to write content equation later and I am going to assume a free energy functional which is nothing but $f_0(c)$ and $F_0(c)$ as usual I am going to assume that it is $A c^2(1-c)^2 + K \nabla C^2$ okay so integral F so this is f/Nv .

So this is per atom so $f/Nv dv$ is basically going to be the energy free energy functional item okay, so this is per atom so let me not put NV here so by NV is basically given by this integral $f DV$ which means we are basically looking at the same free energy functional last time we used for getting this P nodal decomposition.

Except that I am going to choose the overall alloy composition in such a way that it is away from the sphenoid a line but still it is within the two phase regime in other words if this is the miscibility gap and if this is the sphenoid regime previously I had started with a composition which was smack in the middle 0.5 about which I had some fluctuations but now I am going to choose some composition which is on this side, okay.

Very low B so the composition is going to be very small, now if you consider such a scenario then there is no sphenoid decomposition but because there is some excess saturation super saturation in the matrix, matrix would like to be 0.0 but it is 0.02 so this excess C atoms the excess B atoms are going to come and grow this precipitate, so after sometimes the precipitate is going to have a composition profile that looks like that.

The reason this is going above one is that if you calculate so ∇C^β if I calculate then it will be γ, γ in this case we know is $0.33 / k$ is $1/r$ so $1/r$ and in this case the equilibrium α and β compositions are c_β is 1 and C equilibrium α is 0, so $\beta - \alpha$ is basically one and if you take the second derivative of this free energy with respect to composition and if you put $c = 1$ in this case so let us do that so $2AC(1-C)(1-2C)$ is basically f'' .

So f'' will be $2A(1-C)(1-2C) - 2A$ so $C(1-2C) - 2$ so that is $-4AC(1-C)$ now if I put the composition at to be $C = 1$ so this goes to 0 this goes to 0 this is the only case so I will get minus, minus so plus $2AC$ which is 1 so it is $2A$ we have assumed a to be 1 so it gives me a value of two, when a $\nabla C \alpha$ is also going to be the same because γ and the same radius and the same and you can also see f'' when $c = 0$ in these two are going to go to zero.

So when $c = 0$ again this is going to be 1 this is going to be 1 so you get $2A$, $A = 1$ so you get the same thing in other words how much is this composition is increasing on the α side that the composition is going to dip by the same amount so that is the composition that will be in equilibrium for this given size as the size becomes bigger this comes towards one and that this composition goes towards zero so that will be the equilibrium composition that you will achieve okay.

So this is what we want to see so as you can see because I use the same order parameter because I am using the same free energy functional in the implementation if I just make the initial profile not a noisy one but with a specific radius then that problem will give me this solution okay, so which is what we want to do now so let us go back to the code that I wrote last time it was called 2d-conn Hilliard FFT, 2D CHFFT.

So we will take the code I have copied in it into a script called the Kiff Thompson .oct so we are going to modify the initial profile and in this case we do not want to look at the micro structure because we want to see the compositional variation so I am going to plot the composition across this line okay these are the only two differences i am going to change the initial profile initial profile now is going to be a circular precipitate embedded in a matrix which has a small amount of super saturation.

And the plotting is going to be at the beginning of the simulation i am going to plot it across the line at the end of the simulation again i am going to plot it at the central line and we will look at the composition differences and we will go look at how much is the composition change in β it should increase in α also it should increase from zero so it should of each this value corresponding to the r value that we will use so that is the modification we will do try to run the code.

(Refer Slide Time: 20:01)

```
k4 = k2*k2;

chat(i,j) = (chat(i,j) - M*dt*k2*ghat(i,
j))/(1.+2*M*kappa*k4*dt);

endfor
endfor

c = real(iff2(chat));

endfor
endfor
Cprofile(:,halfNx);
plot(Cprofile,'b;Final Profile;');
PTEL 58,9 Bot
```

So as usual so I login to the machine go to the relevant directory and I have this code which is the copy of the code that we wrote last time for sphenoid decomposition so I am going to change only the initial profile before doing that let me take this half Nx, half Ny and put them here, okay because it is useful for me, so I am going to define R which is the radius of the precipitate that I am going to introduce.

Let me say that that is 10 now we are going to define if okay less than $R * R$ so what is less than $R * R$ so I am going to put a precipitate with the center at the middle that is why I need half Nx, so how do I do that, $I - \text{half } Nx$ right into $I - \text{half } NX$, okay so plus $J - \text{half } NY$ into $j - \text{half } NY$ so if that is less than R^2 okay then I am going to make the C_{IJ} to be 1.0 else if $c(I, j) = 0.0$ end for, end for, okay. So this basically makes sure that the composition profile I have is circular and now we want to only plot the profile so let me define a variable called C profile that is half Nx, okay.

So then I am going to plot C profile with a red line and it will say initial profile, okay so this is what I am going to do there is no need for a pause but instead I have to say hold on I think there is a hold on somewhere up there so let me let me put the hold on here and so I am going to

remove this I am going to copy paste the plot here, okay. So the final line I want to plot with blue and I wanted to call this as final profile, okay.

So now the rest of the evolution is the same as earlier so let us look at the code once more so I clear the variables I do not need more off and I define a 64 x 64 system and a half Nx is $NX/2$ half NY is $NY/2$ so I define the radius of the precipitate and I calculate from the center a distance which is of the radius R and whatever points within that Get the composition of one the rest of them get a composition of 0.02, right.

So we wanted to put a small for fuel composition ok, so after that we plot the initial profile we say hold on and this is time increment and these are the reciprocal space points A, M kappa they are all one so and then we are going to run for some about 200 steps I think i will make it 100 steps ok and we calculate GV Fourier transform and c and then we evolve this is periodic boundary condition implementation.

And we evolve using the Cornelia equation which is semi implicit for your spectral technique and take the composition back to real space and these two for are basically the time loops and at the end we come out and we plot the final profile.

(Refer Slide Time: 24:44)

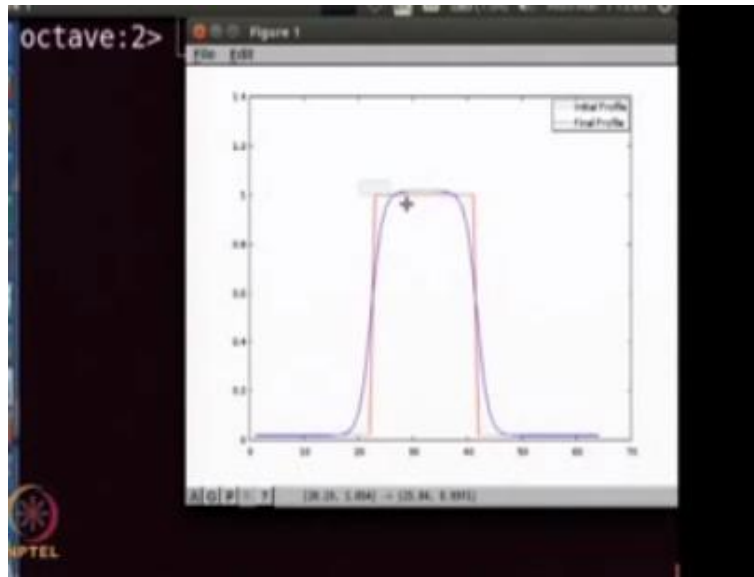
```
u octave:1> source "GibbsThomson.oct"
parse error near line 13 of file /home/gu
ru/Desktop/Teaching/PhaseFieldMOOC/GibbsT
homson.oct

syntax error

>>> elseif c(i,j) = 0.02;
           ^
error: source: error sourcing file '/home
/guru/Desktop/Teaching/PhaseFieldMOOC/Gib
bsThomson.oct'
octave:1> [guru@BharadwajAngiras$: ]
```

So let us now run this code okay.

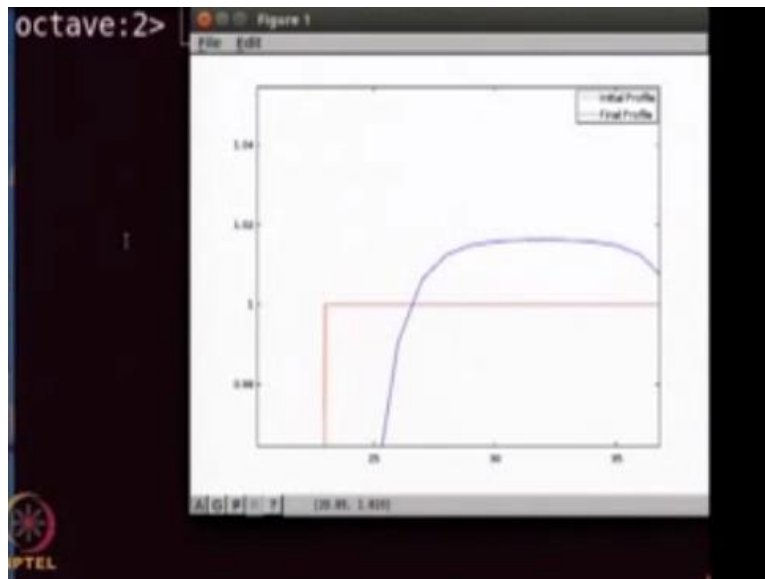
(Refer Slide Time: 24:57)



So there is a spelling mistake in else if corrected okay and if missing okay, so we have to take the composition profile and we have to take along a line and then call it as C profile okay so that is a mistake I made so let us now try to run it, okay so now the code is evolving the point behind this code is also to show that even though Conn Hilliard equation is meant for doing sphenoid decomposition if you are outside of the sphenoid regime.

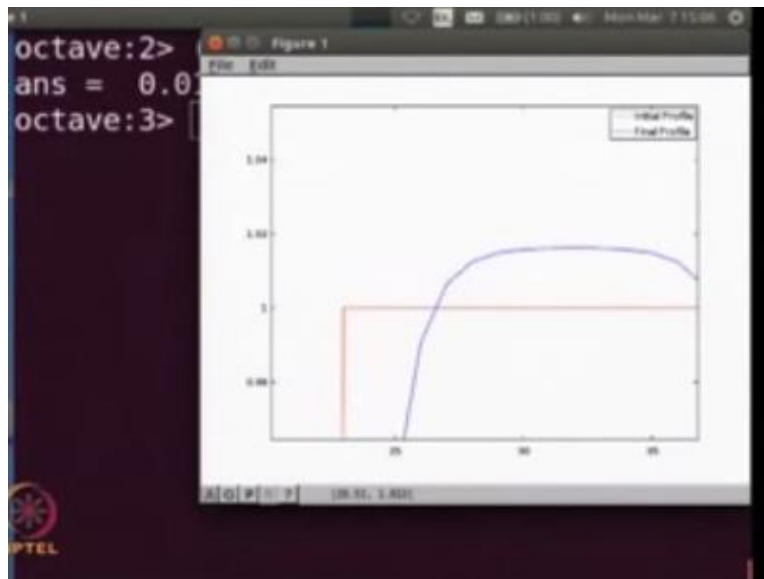
Which is like the growth regime then the same equation should also describe growth because we said that community equation is just generalized diffusion equation so in the special case where there is no negative diffusivity it should reduce to the usual diffusion equation okay so that is what we are seeing and as you can see the composition profile changes.

(Refer Slide Time: 26:34)



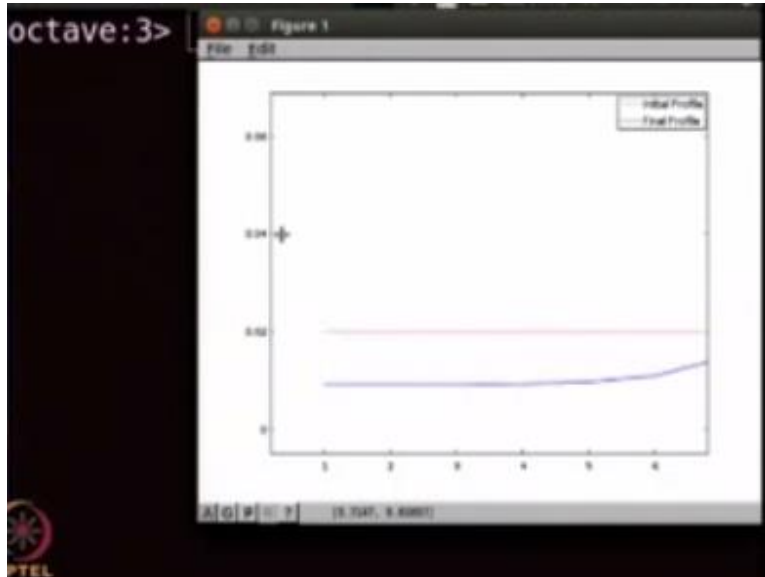
So if I go close to this and if I calculate so I see that the composition has changed by instead of one I get 1.016.

(Refer Slide Time: 26:46)



So we can calculate we know in this case that 0.33 is the γ and the curvature is calculated by 1 by 10 and the two is the second derivative of free energy into 10 (1 - 0) so that is the so if you calculate it is about 0.016 and that is what this composition profile is showing that the composition increases above one and it becomes 0.016 in the precipitate, so this is purely curvature driven effect.

(Refer Slide Time: 27:31)



For example if you make the composition the radius of the precipitate to be say 20 then we should expect the increase in composition to fall by a factor of two, so let us see whether it does that because now instead of 20 we should 20 then we have 20 so 0.008 is what it should be so if we run we will see that and in the similar you can also change A and Kappa using that you can change the interfacial energy again you can do it as an exercise.

If you change γ correspondingly the change in composition will also be there it will also scale accordingly so as you can see here so now I have precipitated composition so it comes to about 0.08 or something okay so and if you look at on the matrix side also here the precipitate is too big as compared to my but here also. You can see that it comes to about 0.09 so if you equilibrated after a while it will come to 0.008 and the other profile will also go to 0.008 but 64 is a small system on which I have taken a very large precipitate that is the reason why the diffusion fields are overlapping so it is not really equilibrated but in the case of 10 on the other side also.

You will see that on the matrix side also the composition shifts by the same amount, so what is it that we are showing we are showing that A it is possible to use the same Con Hilliard equation

and also study systems where there is growth it is very difficult to incorporate nucleation interface will models but in principle even that is possible so Cahn-Hilliard equation can study both nucleation and growth and spinodal decomposition so the same equation can do both but typically it is very difficult to get nucleation happen in the system so typically we throw in nuclei like I have put a small precipitate but the interfacial energy effect or that is associated with the curvature of the precipitate associated with the fact that the interface has an interfacial energy.

There is a change in the equilibrium composition across this curved interface the α and β faces will have a composition which is different from when you have the planar interface that is automatically captured I do not have to do anything the system automatically chooses the right composition however for the one-dimensional problem that we have looked at you can go back you can take that problem and there irrespective of what the precipitate size you put the composition of the precipitate will always remain at one.

The composition of the matrix will always remain at zero that is because in that case there is no curvature to define curvature you need to D, so in one dimension you do not see any curvature related effect so there you will see whatever is the phase diagram giving that is equivalent to taking a planar interface and going across the line so 1d problem can be thought of as a special case of this planar equilibrium case so that is why you always get the compositions that you would get from the phase diagram construction.

So this is an important point to remember and it is also very important if you are studying Nano materials for example, the melting temperature of Nano particles is different from bulk materials the composition across a Nano particle matrix the equilibrium composition of Nano particle and on the other side of the particle in the matrix the equilibrium composition are different than if they are bulk systems.

And you can prove as part of the tutorial to derive how much is the free energy shift this is available in Porter and Yost and we will do it as a tutorial you can calculate how much will be the shift and you can show that it is related to directly proportional to γ and inversely proportional to the radius of the precipitate are directly proportional to the radius of curvature of

the precipitate. And using typical values for interfacial energies for metallic systems you can show that the relevant radius of the precipitate where Gibbs free energy becomes important is of the order of nanometers so that is why nanometer sized particles will have a strong effect, so this is something that is unknown you can look up online for example gold Nano particles for example melt at a temperature which is very different from where bulk gold will melt for example.

So this excess energy associated with the interface shifts the equilibrium that equilibrium could be in terms of the melting temperature or would be the equilibrium composition and so on and so that is obtained in a phase field model automatically we do not have to do anything the system will automatically choose the right composition for the particular size, an effect of which we saw last time.

So we saw initially there was a spherulitic decomposition and then there were different sized particles and that microstructure started coarsening that coarsening like I explained it takes place through the change in composition on the matrix side on the α side so the diffusion profiles that are set up our set up because of the curvature related changes in composition in both the matrix phase and in the precipitate phase.

So which is what we saw last time but it was a very complex microstructure where it was difficult to see what was happening so if you change the initial profile a little bit and show a circular precipitate in super saturated matrix then we automatically obtain it, so this is the part about Kiff Thompson that is the other effect which is called grain growth, so in the next part of this lecture we will look at what grain growth is all about and then modify our Allen Cahn equation to look at the grain growth, 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