Phase Transformations in Materials
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Lecture – 28
Atomic Mechanism of Growth

So, let us continue our discussion on the atomic mechanism of the growth. As we have seen in the last lecture, we can actually use flux balance across the solid interface to get growth rate.

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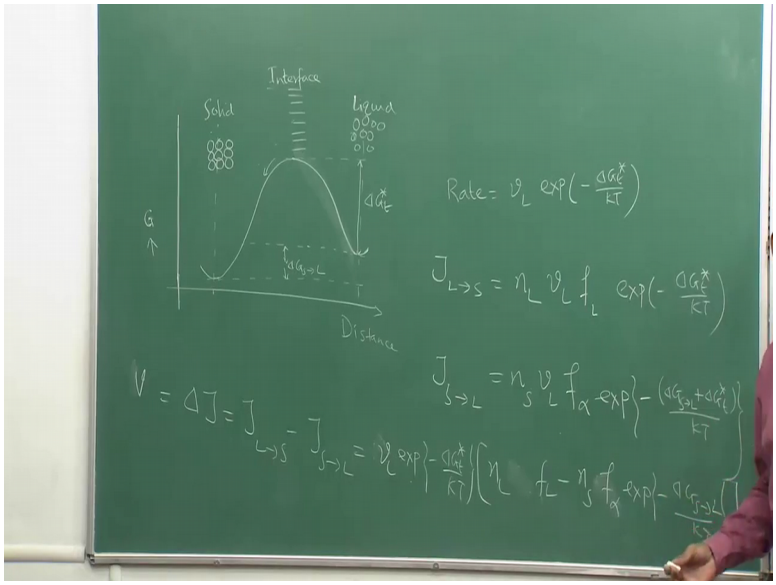

So, let us now simplify the equation as you know the; we can always assume basically assume means we can always consider that.

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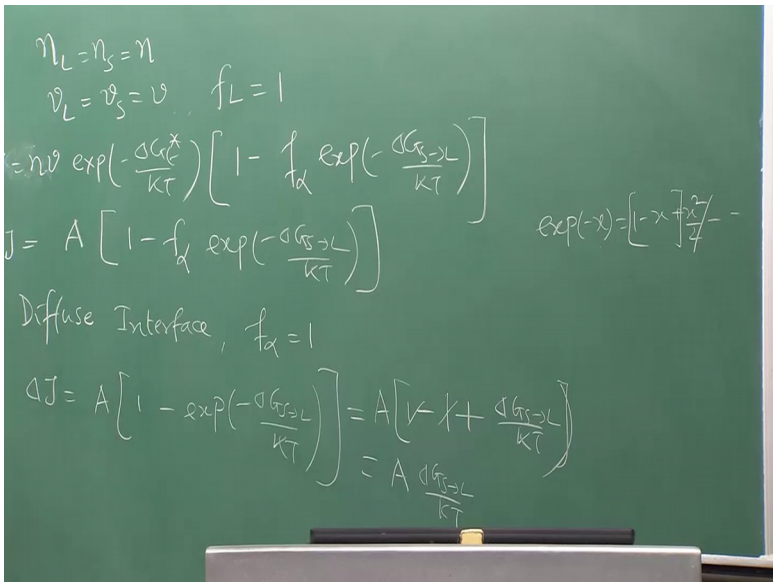

The number of atoms in the liquid can be equal to number of atoms in solid at any time; it is possible, but it is an assumption. So, let us assume this is equal to n; again we can also think that as soon we have done already mu L is equal to mu S is equal to mu I have already done that basically I have already taken this as a mu S mu L equal. So, we have we can do that if we do not do it; it will become like that, but this is this assumption is correct because frequencies of the atomic formation will not very much.

Second; now question is that if I have a diffuse interface the one which just now discussed diffuse interface will have large number of sites in which atoms can easily grow go and sit. So, therefore, in a diffuse interface the f alpha will be quite large and here what you can also assume that f L; f L is nothing, but fraction of the atoms which I want to successful jump is in the liquid can be one because it has higher energy temperature is the liquid is higher vibration frequency is also you know there are number of times they are able to make jumps is also higher.

So, therefore, f L can be one. So, if I then write down delta j can be equal to exponential minus delta G T star by k T multiplied by these factors will come out. So, as you know n L is equal to n then. So, I can write down here n mu L become mu and then what I got back n L mu L goes out. So, f L; I have already consider 1; it can be, then it is become f alpha exponential minus delta G solid to liquid this equation becomes very simple we can always consider these as a constant A because number of atoms frequency; they are

constant a fixed temperature; this very high, it is also fixed temperature it will be constant only; we can create A suppose; this is the constant term, then it becomes one minus f alpha exponential minus delta G solid to liquid divided by k T.

Now, let us apply like this equation for different types of interfaces; first interface will confess; diffuse the one I told you diffuse means in a case of a diffuse interface, you know the large number of sites available for the atoms to go and sit. So, therefore, in those cases, we can always assume f alpha to be equal to one in this cases if you see here why its f alpha is one because we have basically it is not doing one, but it will be very high fraction will be close to you know close to one because you have large number of sites available to the point to go and sit there. So, you can make these assumptions. So, for diffuse interface f alpha can be one. So, therefore, for the diffuse interface the flux balance which is equal to go through; it is equal to a one minus exponential minus delta G solid to liquid by k T that is what it is and this is an exponential function.

So, therefore, we can clearly see the growth on a diffuse interface will be exponential increases function of temperature or as a function of undercooling as you increase the undercooling here basically decrease the temperature so; that means, where the main diving force for these growth or whatever nucleation growth everything is coming from the undercooling that we discuss in the last lecture. So, therefore, I more I increase the undercooling more it is my growth rate this is one minus exponential. So, therefore, this factor will become smaller as you see here the T will increase the factors become smaller. So, one minus of these will increase and the A is a constant term. Therefore, growth will increase. So, as you can clearly see that for diffuse interface such a simplified expression people are using all throughout if an one can actually use much simplified expression I can actually expand this term and get a better term what the mechanical engineers use.

So, you know exponential minus x is nothing, but 1 minus x plus x square by 2 goes on. So, if I truncate here; if I truncate there if I say higher terms are not up an importance to us, then I can write down 1 plus this term delta G solid to liquid by k T and then it has become A because 1 gets cancel; multiplied by delta G solid to liquid k T and as you knows therefore, I will get back here; I will move it here because you cannot see it and now what actually you get; let us see what actually.

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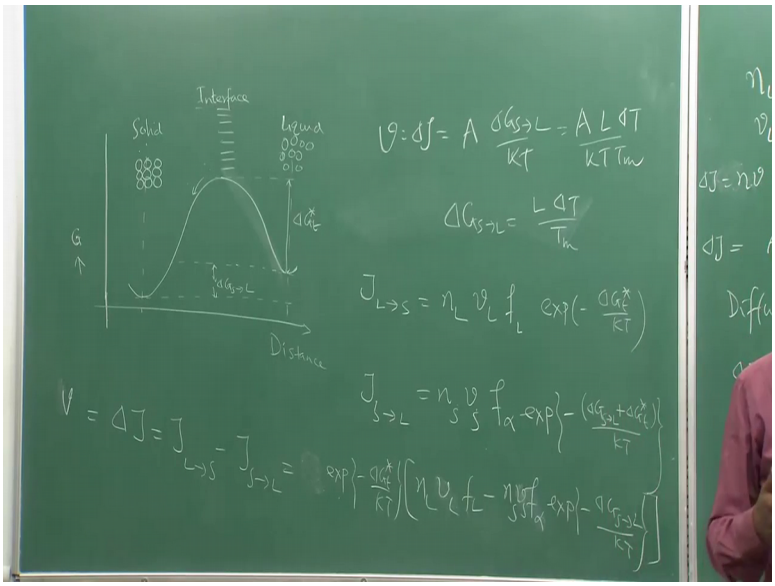

You get there. So, you get the growth rate is equal to the flux difference is equal to a delta G solid to liquid by k T and what is delta G solid to liquid we know that delta G solid to liquid transformation can be converted to latent heat delta T by T m. So, therefore, I can write down this is physically proportional to latent heat delta T k T t m so; that means, what the growth rate is directly proportional to the undercooling and this kind of growth is known as continuous growth in the literature where atoms will keep on jumping and attaching to these solid surface from the liquid they will jump attached direct to the solid and they their higher the undercooling higher is the velocity.

This is only possible in pure metals normally let me tell you pure metals are pure pour ceramic metal solids where each in ceramic solid each molecule can easily jump as a object as basically entity and attach to the solid. So, once you can see here after making. So, much assumption the theory actually falls downs to very simplified equations where you can do that, but you know the moment we think of this kind of interfaces diffuse interfaces such kind of continuous growth mechanism is possible, but if I change the interface if I change the interface from this diffuse or you know smooth interface to the jigger one which are shown you in the last slides like silicon and in case of germanium this assumption will not be true many of these assumptions. So, what will happen there let us see what are things happens atomistically, then we will go back to the mathematical equations the solvency.

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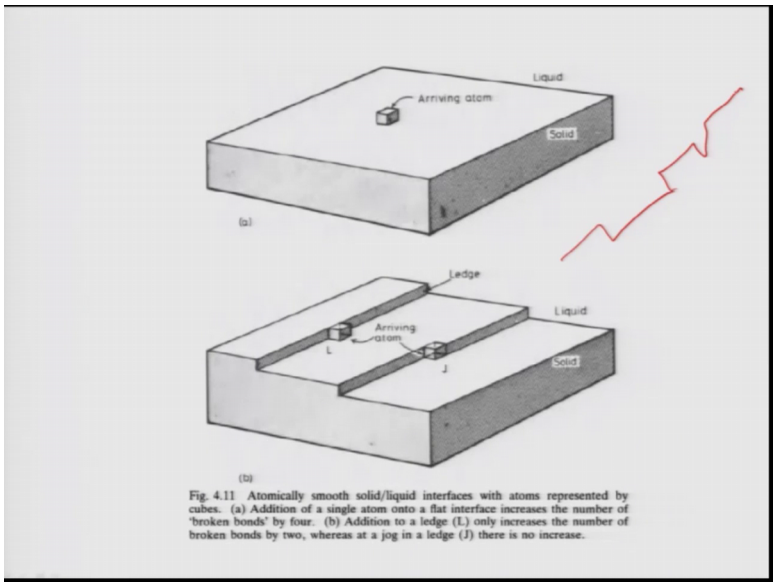

Fig. 4.11 Atomically smooth solid/liquid interfaces with atoms represented by cubes. (a) Addition of a single atom onto a flat interface increases the number of 'broken bonds' by four. (b) Addition to a ledge (L) only increases the number of broken bonds by two, whereas at a jog in a ledge (J) there is no increase.

Well let us suppose this is again taken from protonystelling if I have a solid and a liquid I interface very very very very kind of a flat. So, if as the interface is flat. So, therefore, if the atom from the liquid jump and sits on the surface of the solid it will only satisfy one bond suppose this q is basically considered to be as atom and if is all bonds we satisfied then all the 6 sides must be attaching with some other things right only here you see here this only getting attached with this one surface the bottom one and rest all surfaces are basically hanging.

So, therefore, the atom even it comes from liquid it will not feel completely comfortable because in the liquid it might have all the bonds are not satisfied in the solid; when it comes only one bond is satisfied. So, that is not my difference between these 2 situation as per energetic is concerned it will rather try because solid is considered to be order atomic element it has. So, it will try to atom will try to satisfy as many as bond possible. So, in such situation how the solid will grow solid grows what is known as by ledge mechanism what is a ledge this solid surface all liquid interface create a ledge is ledge is nothing, but a step and this steps are basically, I will come back to it how these steps are created steps are basically created by nucleation.

So, let us first assume that a step is present then we will come back with how the step can be made. So, if I am a step created like on the surface which is shown as a ledge here this step actually now consider the situation here and there here actually the atom sits it

can satisfy at least 2 bonds if not if not more, but in the first situation here atom can satisfy only one bond that is because it is in touch with the bottom surface with the solid, but here it is in touch with bottom in a one of the sides correct now better situation will be to create a kink.

So, as you see here kink; kink is nothing, but this we can create a kink and this kink it can allow this is shown as a z can allow actually the atom to satisfy its three bonds. So, if I create many such kinks and I can actually allow many atoms to come and jump and attach to the surface of the solid this is exactly what happens in the silicon or in germanium as jog or kink is more easy to have places where the atoms in the liquid at can jump and join.

So; that means, what in this cases all the surface is not available for this liquid atoms to come and sit like in a diffuse interface in the diffuse interface, we assume a false factor be equal to f; f solid f alpha whatever its will be alpha is a solid face is one that is no longer valid here f alpha you will be a fraction and it will be very low fraction let me tell you. So, how this ledges or this kind of things can be created there are many ways one is known as surface nucleation.

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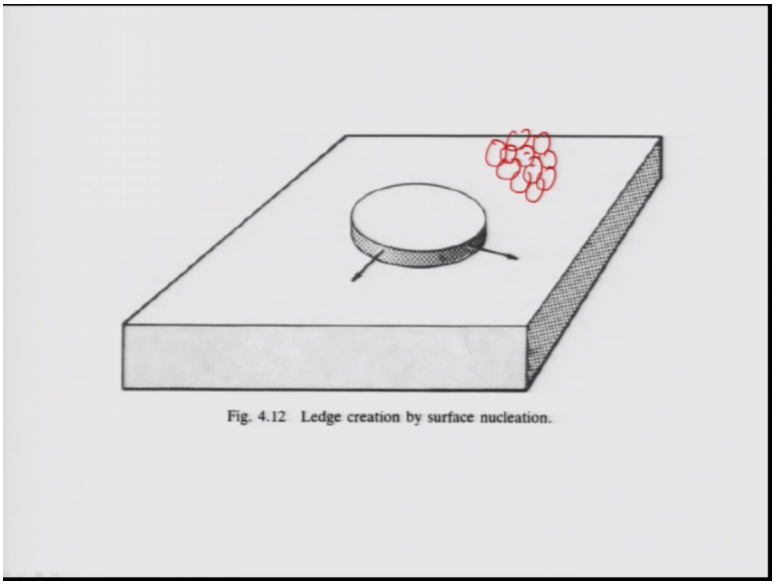

Fig. 4.12 Ledge creation by surface nucleation.

This is what I shown here what can do atom can sit here as couple of atoms or may be not couple may be several atoms can sit here and create a nuclei, it can create a nucleus actually not nucleus on the surface; what it can do basically; instead of one atom coming

and sitting in the surface a bunch of atom can come and sit that is much easier right if one atom come and sit there this only satisfy in one bond at the bottom of the surface, but if I suppose say many atoms are coming cluster of atoms are coming you can clearly see this atoms are satisfied many bonds similarly this atoms can satisfy many bonds which is energetically more favorable. So, therefore, this tude nucleation basically is more energetically favorable initially to create a step or create basically ledge that is what happens it creates this kind of ledges are created by surface nucleation.

So, what does it means; that means, what; that means, for such a kind of situations the growth rate is not likes step like function like which I shown you growth rate is basically depends on surface nucleation plus the attachment of the atoms on these ledges it is more more complex than we can think about it this happens actually in reality other is one way of doing that otherwise; we can do one more thing we can actually create a screw this location on the surface we can create a screw surface that is also possible because many of these solid surfaces.

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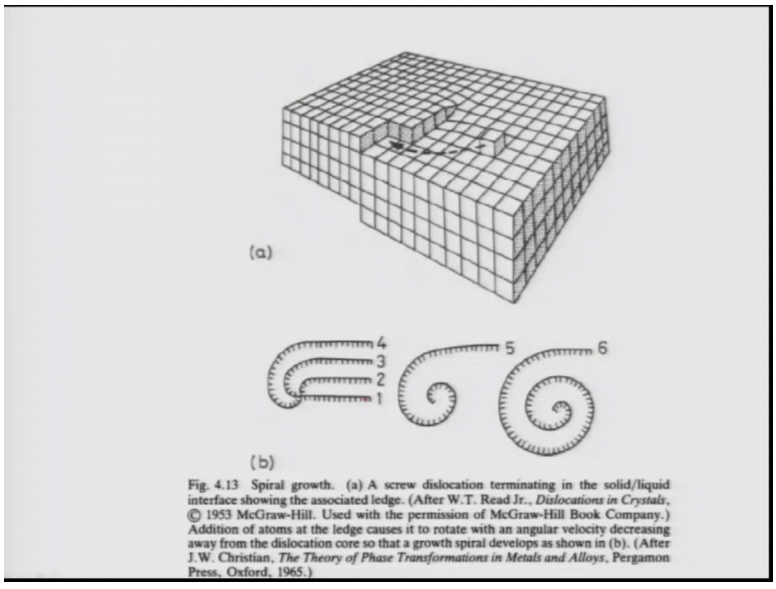

Fig. 4.13 Spiral growth. (a) A screw dislocation terminating in the solid/liquid interface showing the associated ledge. (After W.T. Read Jr., *Dislocations in Crystals*, © 1953 McGraw-Hill. Used with the permission of McGraw-Hill Book Company.) Addition of atoms at the ledge causes it to rotate with an angular velocity decreasing away from the dislocation core so that a growth spiral develops as shown in (b). (After J.W. Christian, *The Theory of Phase Transformations in Metals and Alloys*, Pergamon Press, Oxford, 1965.)

Can have a extra plane coming out just like a sleep happening in a in a crystal and better to have a screw dislocation then if you create a screw dislocations you see; there is a screw dislocations here at present and in this screw dislocations an extra atom coming from the liquid can easily sit there and satisfy many bonds correct, but when you do that the screw dislocation will be the screw dislocations terminating a solid liquid interfaces

shown there you can see this is taken from W T read; read is basically book in dislocation crystals read is one of the finest in dislocations.

So, addition of the atoms at the ledge causes it to rotate what will happen is that very interesting happen it can actually as the atom comes and joins this screw dislocation is rotate why it will rotate because if the atom comes it cannot no longer create no longer hit any screw natural it will as a more and more atoms come it will slowly lose its screw nature. So, to retain its screw nature it will try to rotate itself that is what you see here it is getting rotated as the more atoms comes this was there then its rotated comes like this; this was there quoted comes like this. So, screw dislocation is another way of creating a ledge a creating an surface structure where this atoms can actually attach. So, one is tude nucleation other one is screw dislocations.

Well these are the 2 basic things which people see here; Now I will simply today's whatever time I have four five minutes I am going to tell you what actually can happens when I have a surface nucleation let us discuss that part. So, you know as you see that what you need to modify we need to modify the expression this will remain same this; this kind of construction will remain in case of that only thing is going to change is that this now this is basically the total energy difference between the solid and liquid of the atoms; this one is going to change, here it was only simply migration or transport because of that the barrier, but in this type of situations it is not only that it all you need to have also nucleation barrier because you need to create either it would nucleation zone on which a ledge can be made or you need to create a dislocation structure either of these things will lead to energy because this not dislocation is lead to increase the standardization of a system or tude nucleation will increase the energy of these system also.

So, let us just consider tude nucleation case what will happen if I consider tude nucleation. So, let me rise this part we will use the nucleation theory again.

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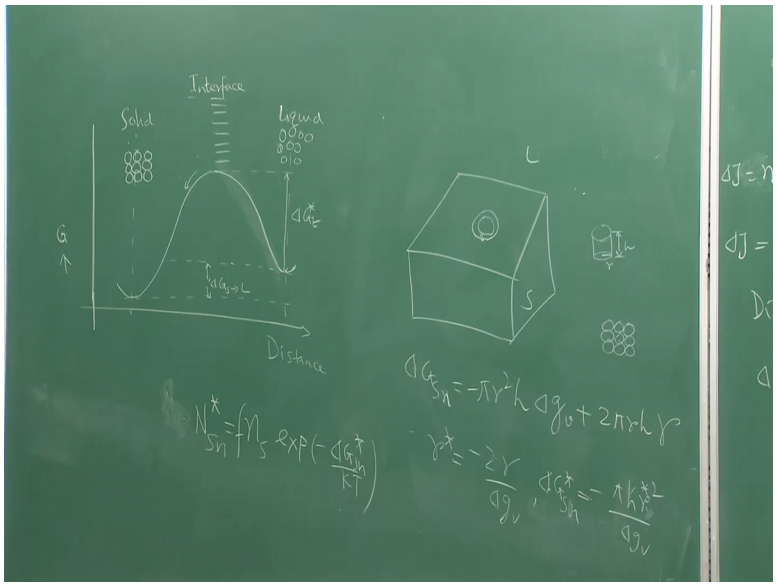

Let us suppose I have a tude nucleation I picture; I have shown you this is a surface like this; this is solid and liquid and you have created something like this; this is just like a cylinder it just like a cylinder; cylinder will have height h because this step will have height h and you can also have radius r because a couple of atom has come and then sit on the surface; they look like a cylinder they even though they will spread, but still it is better to have a cylinder why because if it is like this then many atoms many of this piece any of the atoms can satisfy bonds and then you can get another layer another layer another layer like that. So, I assume that is a cylinder of radius r and height G, then what is this you know energy this is nucleation surface nucleation surface nucleation because of that. So, this basically let us either volume; volume is phi r square h multiplies by free energy volume free energy per unit volume this is minus; obviously, for nucleation plus you creating a surface area twice pi r h surface area of that multiplied by the interface energy between the between this solid and that that is you what is basically is the very important factor.

So, that is what is basically the total energy of the surface nucleated force now you can do all mathematics on that you can actually find out what is critical size it will size a again 2 gamma by delta G v and delta G star you are creating a new delta G star that is surface nucleation that is what is important aspect for us that is what you want to know because you have to add this part this because this is already present migration things will be there always, but this is an extra term coming into picture in a calculation. So,

that is nothing, but if you do the proper calculation it will be pi h r square r square means r star square basically.

So, r star square divided by delta G v and. So, therefore, if I have that now I can write down the rate because we are calculating the growth rate. So, what is the nucleation rate nucleation rate equation if you go back nucleation rate n surface nucleation rate is equal to number of atoms present on the surface number of atoms be number of atoms coming there exponential you can also there will be frequency term coming to picture exponential minus delta G surface nucleation star by k T that is the rate.

So, we need to connect this rate into growth rate later on right then only you can get into such a kind of flux plus equations. So, what you need to do is that we can we leaves this nucleation rate and then bring into the growth rate equation. So, that will I will do it in the next lecture and show you how this will give you a interesting equations under which can alloy to explain the growth by dislocations or by surface nucleation in these materials. So, atomistically at the end; this 2 lectures today; this 2 lectures actually last one and this one atomic mechanisms of growth during solidification is very you know very interesting it actually not been discovered in one go basically took about 50 year research to understand; how this growth happens remember I have only talked about 2 different situation for the faceted interfaces one is this nucleation on this surface to create a ledge other one is a dislocation you can also have a twin situation.

You can also in case of silicon actually that happen you can have a twin reentrant angles you can actually have twins surface; surface twins based on the surface and this twins can actually allow that atoms to get attached and that is what happens in silicon mod and that is why an aluminum silicon allow as the twining silicon; silicon gets multiple twin and they have all kinds of features built it on the silicon fibers. So, that is all have a possibility so, but we will not have time to discuss each of this cases in detail manner this there in the books. So, we can actually have multiple situations of growth in case of faceted interfaces here you have steps on the; this kind of small steps on the interfaces. So, we will keep on discussing all this aspects in the next lecture also.