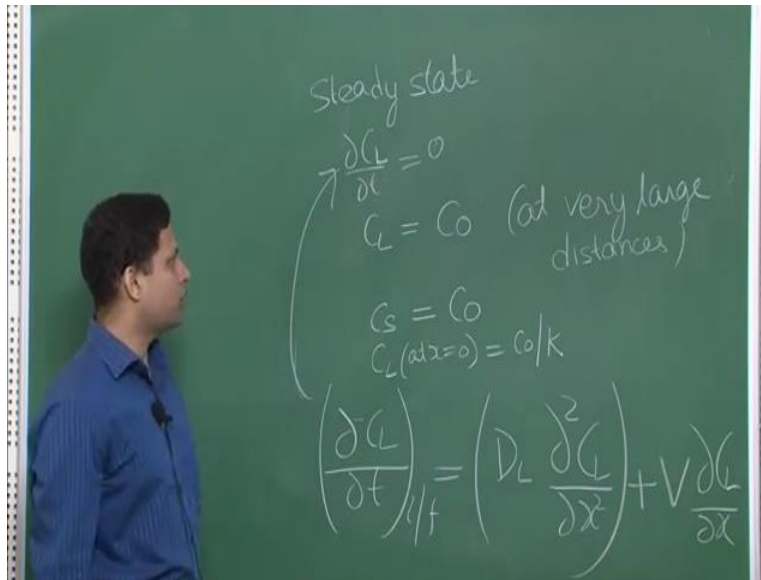


Fundamentals of Materials Processing (Part-1)
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Lecture Number 17
Mixed Mode Solidification

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So we will continue with solving our equation for the steady state. So you remember this is the equation that we came to, which is if we, if we now write it in terms of liquid, so this becomes $\frac{\partial C_L}{\partial t}$ with respect to interface reference frame is equal to D_L , which is the diffusivity in the liquid by times $\frac{\partial^2 C_L}{\partial x^2}$ plus $V \frac{\partial C_L}{\partial x}$. And, there were two conditions where there is steady state and when there is transient, depending on whether this is 0 or not. So we are assuming that this is 0 for the first case where it is steady state; so for the steady state, we are not assuming, steady state implies that this is equal to 0, and therefore we are left with this equation, which is.

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No solid diffusion, limited liquid diffusion

$$DL \frac{d^2 C_L}{dx^2} + V \frac{dC_L}{dx} = 0$$

soln

$$C_L = \alpha \exp(\beta x) + \gamma$$
$$\frac{dC_L}{dx} = \beta \alpha \exp(\beta x)$$
$$\frac{d^2 C_L}{dx^2} = \beta^2 \alpha \exp(\beta x)$$
$$DL \beta^2 \alpha \exp(\beta x) + V \beta \alpha \exp(\beta x) = 0$$
$$\left(\beta = -\frac{V}{DL} \right)$$

Now this is a very standard equation in differential equation, and there is a very standard solution for this. So, we will write what is the standard solution for this. Standard solution is of the form C_L . So the equation the solution for this will be C_L as a function of x ; so C_L is equal to alpha times exp, which is exponential, beta x plus gamma. So this is a standard solution for equations of this form, where alpha, beta and gamma are some constant values. We can find out those values by putting in the boundary conditions. We know already some of the boundary conditions, we have seen that C_L is equal to C_0 at very large distances, which means at x equal to infinity.

So at x equal to infinity, C_L is equal to C_0 ; at x equal to 0, C_L is equal to C_0 by K . Now let us take double differential differential of this; differentiate this with respect to x , and then double differentiate it with respect to x , and put it back into that equation. So we will be able to get something out of it. Let us see what do we get. So first differentiating with respect to x , we get, beta will come out, beta times alpha times exp beta x ; gamma is not a function of x , so it when you differentiate it, it becomes 0.

Now when you take second differential $d^2 C_L$ by dx^2 , this becomes beta square alpha exp beta x . So this is the second differentiation. Now, let us put this back into that equation. So DL times this plus V times this, is equal to 0. So we will get DL beta square exp beta x plus V beta alpha exp beta x equal to 0. Now assuming that exp of beta x is not 0, we can cancel that out and what will be left with is this. So we have obtained one constant, value of one constant for

this equation. Now let us try to find the other constants, and for that, we will, although I am erasing this, but remember what are the boundary conditions, because we will need these boundary conditions to solve or to obtain the other constants.

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$C_L = C_0$ at $x \rightarrow \infty$
 $C_L = C_0/k$ at $x=0$

$$C_L = \alpha \exp\left[\frac{-x}{D_L/V}\right] + \gamma$$

$$C_L = \alpha + \gamma = \frac{C_0}{k}$$

$$\alpha = \frac{C_0}{k} - \gamma$$

$$C_0 = \gamma \Rightarrow \alpha = \frac{C_0}{k} - C_0$$

$$C_L = C_0 + \frac{C_0(1-k)}{k} \exp\left[\frac{-x}{D_L/V}\right]$$

$\frac{D_L}{V} \rightarrow$ characteristic length
 At every $\frac{D_L}{V}$ distance $\ln(C_L - C_0)$ falls by $1/e$

So our CL now becomes; we have not yet obtained gamma, so gamma is still there, alpha is still there, and we have obtained beta, so we have put that beta into over here. Now, like we said, we will put the boundary conditions; boundary conditions, just let me write it in a small note over here, CL equal to C0 at x equal to infinity and CL equal to C0 by K at x equal to 0. So, you put this x equal to 0, and what you get is CL equal to alpha plus gamma; because when you put x equal to 0, this whole thing becomes 1; so this is alpha plus gamma, and this is equal to C0; sorry this is equal to C0 by K. And therefore you can say that alpha is equal to C0 by K minus. Okay, I missed one step over here, which is when you put x equal to infinity over here, if you put this one, what you will get is C0 equal to gamma.

Now when you put x equal to infinity, this term goes to 0, this term becomes C0; so C0 is equal to gamma in the second one, which is this one, when you put x equal to 0, you get CL equal to alpha plus gamma equal to C0 by K, and therefore alpha is equal to C0 by K minus gamma. But from here, we know that gamma is equal to C0. Therefore we can say alpha is equal to C0 by K minus C0. So now we have obtained alpha, beta, gamma, all the three constant values. Now we

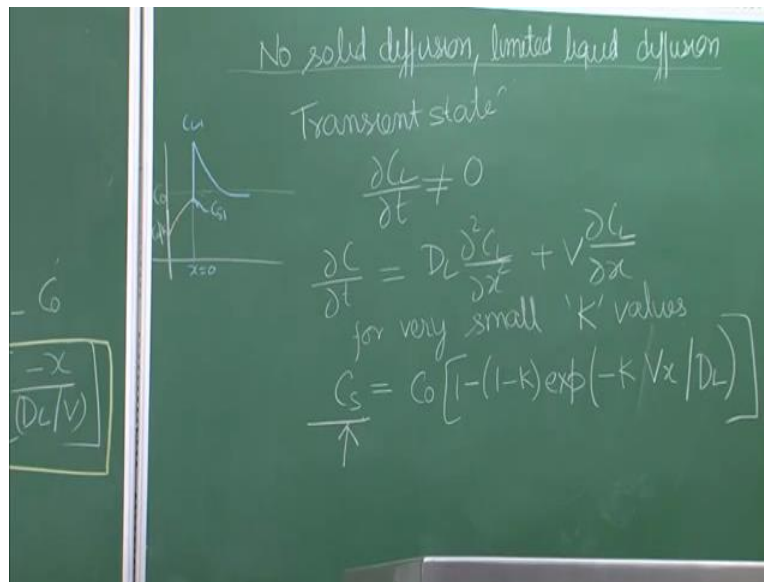
are in a position to write the equation CL in terms of the known parameters, and you would see that it comes out to something like this.

So for the condition of no solid diffusion with limited liquid diffusion, and if the steady state, we have obtained the concentration profile of the liquid. So if you were to look at what we are talking about, let us again draw this plot. We had this C_0 , and somewhere the solid is forming, and since the solid is, it is in the steady state where we said that the crystal is so long that the solid concentration is also equal to C_0 ; so this is the concentration of solid over here. From over here we do not know, it is a transient state. So somewhere over here, it has reached steady state; and at this point, this is the concentration of liquid.

So this, beyond this, this is the liquid concentration like this; and what is the maximum, what is this concentration of the liquid? Here, which is our x equal to 0; this is what we said is C_0 by K, this is C_0 , and at x equal to infinity, you can see. So, if I want to draw it in a way, let us draw liquid in blue. So this is the liquid part, and let us draw the solid in the red part. And here, I have left it open, because this is the transient state for which we have not yet talked about. So somewhere, it reached a steady state, from whereon, the solid has a concentration C_0 , and at the point where the solidification is taking place, just at that point, the liquid concentration is C_0 by K to begin with; that is at x equal to 0; and at very far distances, it is again C_0 .

So we are describing this equation is describing the concentration profile of this liquid. So this is what we have obtained here so far. So this is the steady state condition. Now what is the non steady state condition, and what do we obtain over there? Let us look at it.

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So non steady state or transient state. How is it different from the steady state? Simply because $\frac{\partial C_L}{\partial t}$ is not equal to 0. So this value is still finite, and it exists in the equation. So this becomes $\frac{\partial C}{\partial t}$ your diffusion equation becomes $\frac{\partial C}{\partial t} \times D_L$; that is the whole, all the terms are there in this particular equation, we cannot cancel out any of these terms. Now the again, if you want to solve this, it is very difficult condition, because if were to draw it, then this is how it would look like. This is C_0 , and somewhere over here, this liquid the solid that forms, it starts with C_0 by K .

But beyond that, we do not know, just because I know, I will just draw it like this, it will somewhere like this; so this is upto this, it is a transient condition somewhere here. And at this point, let us say, there is a liquid; it will have a concentration. So if the concentration of the solid is C_{S1} , this will be corresponding C_{L1} , which you can obtain from the phase diagram; and again the liquid concentration would be something like this.

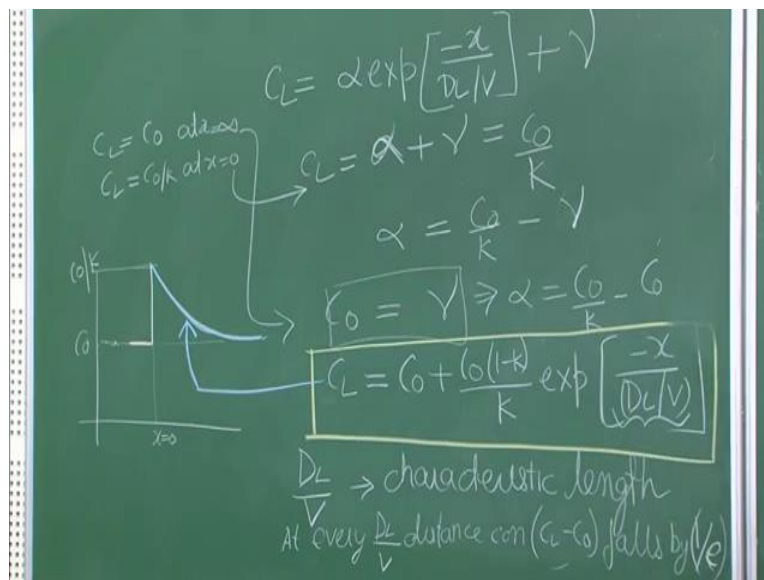
Now you see, this whole thing, what will happen to the solid concentration? Solid concentration will slowly reach C_0 ; and therefore this whole profile, this concentration of liquid at x equal to 0, all of those will change. And that is why we say it is a transient state. And since, what is the concentration of the liquid is not so important; we have we were looking at liquid concentration because that is the only thing that is changing. Here, what we are more interested in is how the

solid concentration is changing, and for that, people have found solution for very small values of K .

So, like I said, this problem is not so very tractable, we will not try to solve it; but I will give you solution which has been obtained for certain condition which is for very small K values; that is when you are talking about slopes which are very very large over there. The slopes of the liquidus and the solidus are very large, or in fact, what we have is the solidus has very large slope, and liquidus has very small slope, then you will have very small K values. And for this, it has been shown that the concentration is CS.

So note that we are here talking in terms of concentration of the solid, because the liquid concentration is not constant, it is varying with time. Overall, we do not know the liquid (conce), we cannot, at least from now, for now on, at this point, we are not in a position to define the concentration of liquid. But, if you know the concentration of solid of course, you know that at this particular interface, because of the equilibrium interface, what should have been the liquid concentration. So, although we are not talking in terms of liquid concentration; you can still obtain liquid concentration from over here.

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On the other hand, here we are talking only about the liquid concentration, because the solid concentration in the steady state is equal to C_0 throughout, in the steady state only in the steady state region. So these are the two different conditions, steady state and the transient state, for the

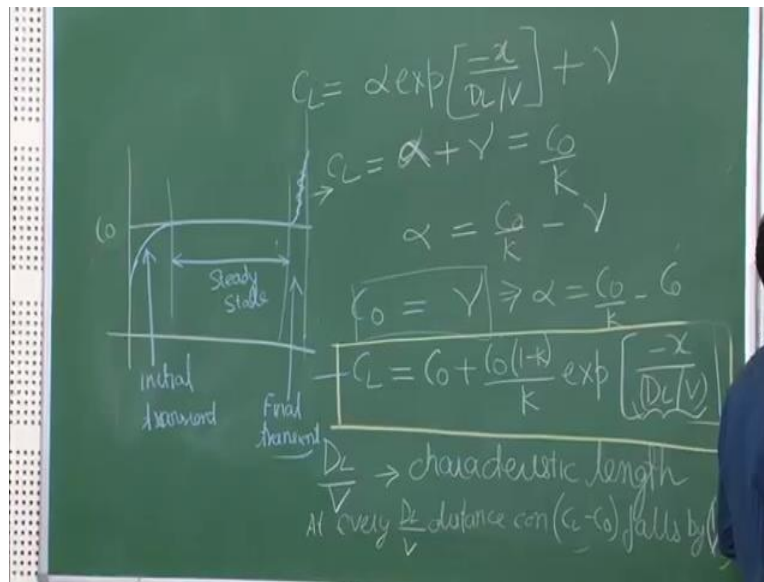
condition of no solid diffusion and limited liquid diffusion. Now you will see that over here there is this term DL over V . Okay. This DL over V , and over here we have x which is also, which is a unit length. So it means that DL over V must also be, must also have unit of length; and whenever you have something like this, you know that it has some significance. So what is the significance of DL over V ?

So DL over V can be described as 'characteristic length'. What is 'characteristic length'? It says that when you move by this distance, at every DL over V distance, the concentration falls, this concentration C_L minus C_0 falls by '1 by e ', where ' e ' is the exponent, e to the power 1. So as you move in the liquid by this distance DL over V , the concentration C_L minus C_0 falls by a factor '1 over V '. So that is the significance of this value DL over V . And, as I have already mentioned, its unit would be equal to that of length, because we are dividing x by this quantity DL over V .

So now we have covered three different conditions for solidification; one was the equilibrium, next was the solid, no solid diffusion but complete homogenization in liquid, and this third one was no solid diffusion and limited liquid diffusion. So now we will move onto a even, you can say more stringent condition or again, you can say in other words that it is more realistic, and that realistic condition is that we will have some amount of convection in the liquid. So now there is not only diffusion; in diffusion what we are saying is that, the liquid is not being stirred, or it is not being moved by any other means, and the liquid is standing still. Whatever concentration variation is taking place, it is taking place because of concentration gradient and because of diffusion.

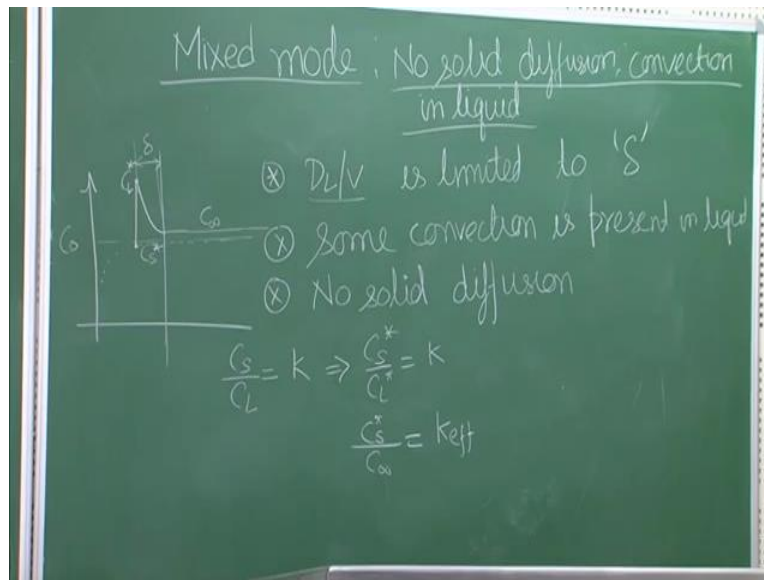
But now we will talk about a more realistic condition, which is mixed mode; usually called as mixed mode. What it means is no solid diffusion, like always. And there is some amount of convection in liquid. So that is why it is mixed, because it is in between complete homogenization and only liquid diffusion dominated concentration gradient. So there is, you are saying that it is not completely mixed, but it is not even being left alone. So this is no solid diffusion and convection in liquid. And before I move on, there is one thing that I forgot to mention regarding the previous condition. So let me just, that is just one plot that we that you should be aware of when we are talking about this particular case.

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So if you look at the overall view, just looked at the concentration changes piece-wise. But if you are looking at the concentration as a whole, this is how it will look like. So this is, this was the region that we were calling as steady state; so without spending too much time on this part which we have already discussed, I will just draw something that you must be aware of. This is initial transient for which we have given the solution not derived it; and this is final transient; we have not discussed it, but this is it is not of much consequence, because there is very small length of this final transient. Okay so I will leave it at that, I will not get into more, that is all you have to know about that plot.

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So we will get back to our 'mixed mode'; we were talking about no solid diffusion and convection in liquid. What it does is basically what whenever we say mixed mode, what we are saying is that the distance D_L/V that we had over over there, that, that distance is now being limited to another value or a fixed value because of convection to something as delta. So now that that there is a small distance delta at which your concentration falls back to the infinity value. So whatever is at at x equal to delta, that is the concentration that will remain constant beyond that.

So if you were to draw this particular condition; again, we are talking overall concentration is C_0 , remember. And somewhere over here, there is a transient and again we need to talk in terms of the steady state. So over here, let us say we are talking here; this is the concentration C_s , corresponding to this there is a C_L . And, because of convection, there is only a small distance delta, at which it reaches the infinity value. So beyond this, say let us call this infinity concentration as C_∞ ; it may be C_0 for some examples, but usually it will be larger than C_0 .

So this is the concentration in the liquid that will be maintained beyond this point. So now you see, when you are studying the liquid, there is some kind of mixing, then what you have done is reduced this zone where there was a lot of diffusion and the diffusion layer was falling was extending to a very good extent; you have reduced that to a very small distance delta. So that is

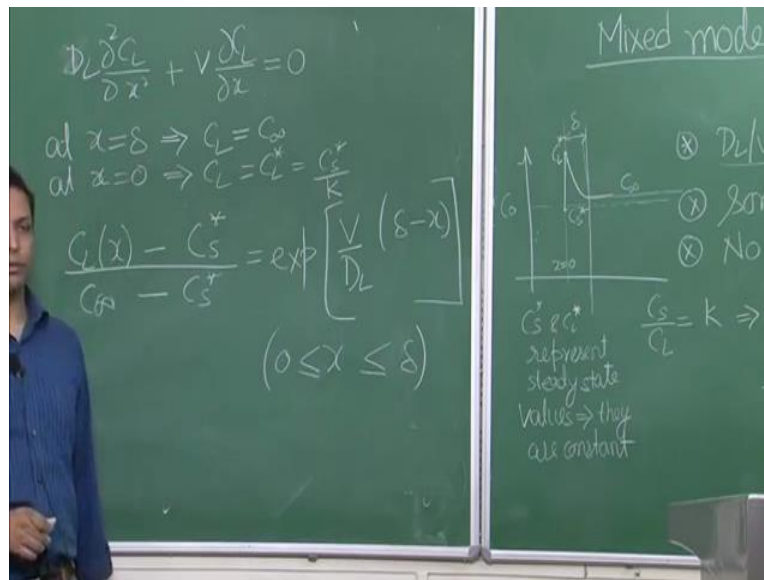
what you have done. And this is the steady state concentration of solid, so it will remain like this throughout. And this is how the plot the concentration plot will look like in this condition. So this is what I mean when I say DL over V has been limited to δ .

So more appropriate would be that the total diffusion length has been limited to δ . But, in the effect, we can also say that DL over V has been limited to δ . And that is because, some convection is present in liquid. So these are two important facts that you need to know. Of course other than that, you must not forget that there is no solid diffusion like always. See the more realistic we are talking about, we have to be strict about the solid diffusion because solid diffusion is a very very slow phenomena; and for any casting of significant size, the solid diffusion would be slow so slow that it cannot homogenize. So no solid diffusion is a much better condition to assume.

So these are some of the facts that will be related or that are associated with this particular condition. Now when we are talking about C_S over C_L , this C_S over C_L , if we call, let us call this C_S as a star, because these are the steady state values; so what we will do is represent these by star values. And anyhow all the C_S by C_L is equal to K , which implies C_S star by C_L star is also equal to K . Now when we are talking about the mixed mode, there is another term which becomes very useful, and that is called K effective, and that is given by C_S star by C infinity; meaning what is the partition, or what is the partition of solute in the solid with respect to liquid at infinity?

Now in most cases this will become your C_0 , but let us not assume that, and let us say this is some concentration at infinity; so this is say, whatever is the solid that is formed, average amount of solid that is being formed, what is its partition with respect to the liquid at infinity, or the overall alloy composition? And this is termed as K effective. Now we will use this to get to; first we will try to get equation for the concentration change in the liquid part for this, and then we will use it to define or relate K effective with K for this kind of condition, and then we will even extend it to other conditions as you will see very soon.

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Again, our equation remains same, which is $D_L \frac{d^2 C_L}{dx^2} + v \frac{d C_L}{dx} = 0$. So this is starting equation and again we said that we are talking about steady state; you remember C_S^* and C_L^* star, so let me write it somewhere that these two C_S^* and C_L^* star represent steady state values; meaning they are constant. So C_S^* and C_L^* star we are using as, as values which remain constant. Now with that, let us move on. What is the boundary condition that we have over here? We know that at x equal to δ , what should be the value? This is your x equal to 0, remember; so this is x equal to δ . At x equal to δ , what is the concentration of C_L ? It is C_L equal to C_∞ . At x equal to 0, what is the value of concentration of liquid? It is equal to C_L^* , equal to C_S^* by K .

So this is the (con) the boundary condition that we have, and if you look at the boundary condition, then C_L as a function of x using these boundary conditions, again you can find a very straight forward solution for this kind of thesis, and it will come out to. Here you can clearly see that if you put x equal to δ , this will become 0, and then e to the power 0 is equal to 1; therefore C_L is equal to C_∞ . So at x equal to δ , meaning at this particular point, the concentration of liquid comes out equal to C_∞ , which is what we said.

So this equation, you must also realize, is only valid for a distance between x equal to 0 to δ ; you cannot use it beyond x equal to δ because beyond that, the variation is constant, so we are not trying to derive the equation for this. So, keep that in mind that this is valid for x

greater than equal to 0 to less than equal to delta. Which implies that our equation is in the right form. Next what we will do is for the 'x equal to 0' condition, when we put the 'x equal to 0' condition, we will be able to put CL equal to CL star; and hence we will be able to obtain a relation you would see between K and K effective for this kind of situation. So I will get back to this in the next lecture. Thank you.