Transport Phenomena in Biological Systems

Prof. G.K. Suraishkumar
Department of Biotechnology
Indian Institute of Technology-Madras

Lecture - 15
Unsteady-state Diffusion

Welcome back to the next lecture. Today we will look at some different aspect. But that small difference makes a very large difference in the processing of the equations and so on so forth, okay. The aspect that we are going to look at today is of course, we are still at mass flux. However, so far, we looked at steady state diffusion. Today we are going to look at unsteady state diffusion.

Recall what steady state is? The properties of interest at a particular point in the system do not vary with time that is steady state. If it varies with time, then it is unsteady state, okay? Because the properties do not vary with time, we could put the time derivatives to zero earlier, we cannot do that here.

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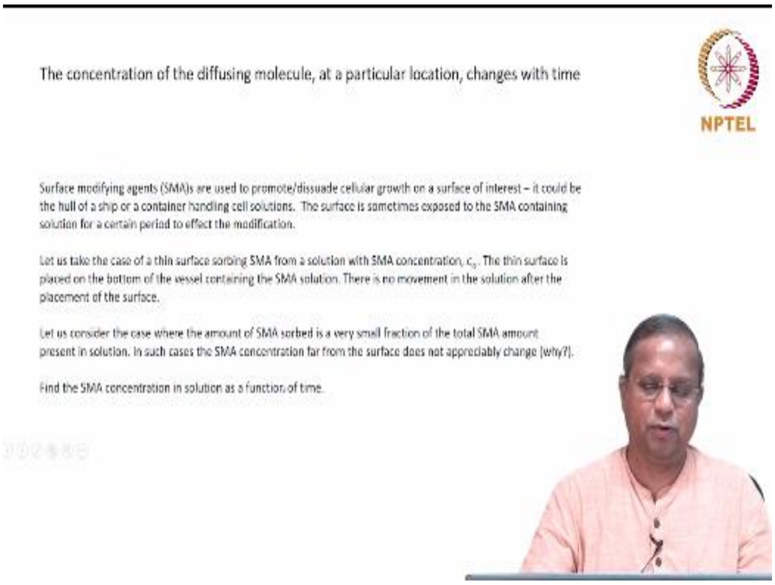

To understand this, yeah it is worthwhile repeating, the concentration of the diffusing molecule at a particular location changes with time. If it is pure diffusion, or diffusion in a membrane, and so on so forth. This is what is actually happening. To understand this a little better, let us again look at it from the framework of a problem, the context of a problem. And that problem is something like this.

Surface modifying agents, SMAs for short, are used to promote or dissuade cellular growth on the surface of interest. Sometimes it is used to promote and other times it is used to dissuade. It is used to dissuade for example, growth on the hull of a ship or a container handling cell solution, you do not want cell growth there.

Therefore, you could use a surface modifying agent to modify the surface of the hull of the ship or the container handling cell solutions. The surface is sometimes exposed to the SMA containing solution for a certain period to affect the modification. You just contact the surface to a liquid that contains SMA and there will be transfer of the SMA onto the surface and that is what treats the surface with SMA which attributes desirable properties to the surface.

Let us take the case of a thin surface sorbing SMA from a solution with SMA concentration c_0, okay. The solution has an SMA concentration of c_0 and the thin surface is sorbing that. The thin surface is placed at the bottom of the vessel containing the SMA solution. There is no movement in the solution after the placement of the surface. Let us consider the case when the amount of SMAs sorbed is a very small fraction of the total SMA amount present in solution.

In such cases, the SMA concentration far from the surface does not appreciably change. I have asked you to think about it. While you think about it if you cannot get it write to me and I will tell you why it is. Find the SMA concentration in solution as a function of time, okay. This is the problem here.

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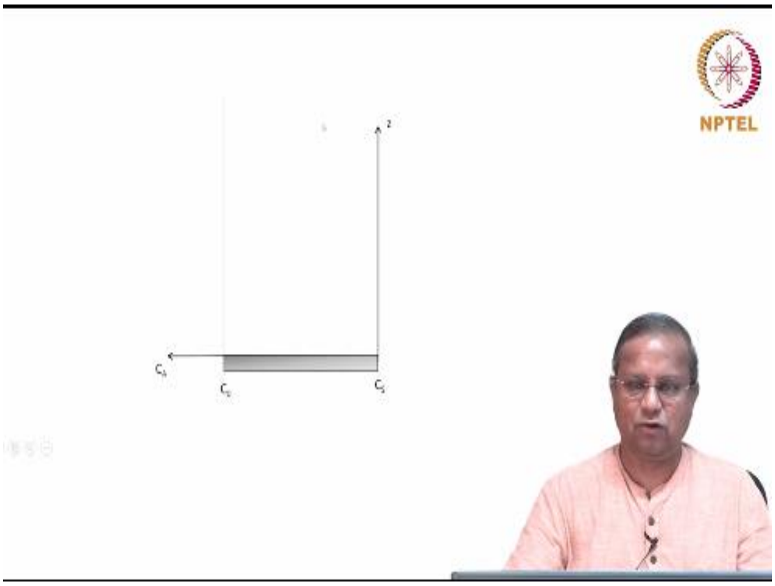

If you represent it as this, this is the surface that needs to be treated, this shaded rectangle that is shown here. This is the z axis which is the distance from the surface. We said that it is placed at the bottom of the vessel and the liquid here contains SMA. The SMA moves from here to the surface to treat the surface.

I have converted this to a concentration axis c_i, c_i is the concentration of the SMA in this space, in the solution space, okay. That is what we are looking at.

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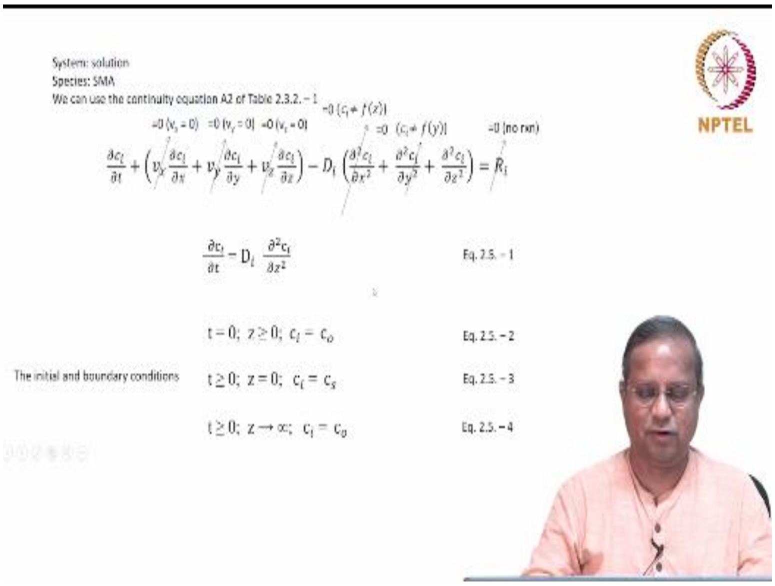

So let us take the system as the solution that is the space. We are going to focus on the space here. We are going to leave out the surface from our concentration because we want to know the concentration profiles, the variation of the concentration profiles here with time. That is what is given here, right. Yeah, find the SMA concentration in solution as a function of time and space.

So we are going to consider the solution as a system. The species of course, is the surface modifying agent, SMA. We can use the continuity equation because this is again motion of SMA right. So we can use an appropriate coordinate system. In this case, you can see that the motion is only in one dimension. So rectangular Cartesian coordinate system is the easiest to use and also D_{AB} are constants.

ρ, c, D_{AB} are constants. Therefore, we could directly use equation A2 from table 2.3.2-1. Please make a copy of this table either hard or soft that you can access the equations from. So if you write the equation A2, it will be this. We have already seen this earlier, $\frac{\partial c_i}{\partial t}$ plus this is the convective term convective motion of the liquid. This is the diffusive term and this is the reaction term.

So here again we said there is no motion of the liquid after the surface is placed at the bottom. Therefore, certainly there are no v_x, v_y, v_z which are the components of the convective motion or the bulk motion of the liquid. This cannot be put to zero because there is variation of concentration with time in the system, right, so that cannot be put to zero. And that complicates things a lot as you would see.

So here, as I said v_x equals 0, v_y equals 0, v_z equals 0, no convective or bulk motion. Here, dy equals 0. It is not a function of y, it is weighing only in one dimension, and dx equals 0 because it is not a function of x. And of course, there is no reaction in the solution. The reaction if happens at the surface of the at the surface that is being modified and that we have very nicely had it removed from the system, okay. Our system does not contain that and therefore, there is no reaction that is occurring in the system.

So, we have this expression

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial z^2} \qquad 2.5\text{-}1$$

To repeat, there is no convective motion therefore v_x equals 0, v_y equals 0, v_z equals 0. And there is no variation in the x and y directions of the concentration. The variation is only in the z direction. Let us call this equation 2.5-1. This is a partial differential equation. There is a variation with time and a variation with space. This is second order variation with respect to space and there is a variation with time.

So you need an initial condition to take care of the time variation. You need two boundary conditions to take care of the second order nature of this to solve this differential equation. This you know from your math course. So the initial condition is something like this.

At t = 0, that is the initial condition, and z much greater than 0, far away from the surface c_i, the concentration of the SMA distribution equals a certain standard c_0, which is the bulk concentration in the liquid. 2.5-2. Now to the boundary conditions. At all times greater than 0, right from apart from the initial time point. At z = 0 at the surface, $c_i = c_s$. Although surface is not a part of the system, the layer of liquid that is immediately above the surface is what is z= 0 is. So there $c_i = c_s$, which is the surface concentration at that liquid layer 2.5-3. And t greater than 0 at z equals ∞ , far off $c_i = c_0$, 2.5-4. So this is what we have here. Now be prepared for a good amount of math.

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial z^2} \qquad (2.5\text{-}1)$$

The initial and boundary conditions are

$$t = 0;\ z \geq 0;\ c_i = c_o \qquad (2.5\text{-}2)$$

$$t \geq 0;\ z = 0;\ c_i = c_s \qquad (2.5\text{-}3)$$

$$t \geq 0;\ z \to \infty;\ c_i = c_o \qquad (2.5\text{-}4)$$

The only difference between this equation and the very first equation that we got for steady state for rectangular coordinate system is this term. This term did not exist earlier, this was 0. And that made the solution a lot simpler compared to this. Just one more derivative here completely complicates the solution part of it. But that is okay. The analytical solution has a lot of insights that it can offer.

It has a lot of benefits and that is the reason why we are looking at the analytical solution here. Also numerical solution, you need another set of skills to be good at numerical solutions. We will not get into too much of numerical simulations in this course. So anyway, the situation now is you have is given in 2.5-1. Just mentally prepare yourself for some concentrated time, the time that requires concentration.

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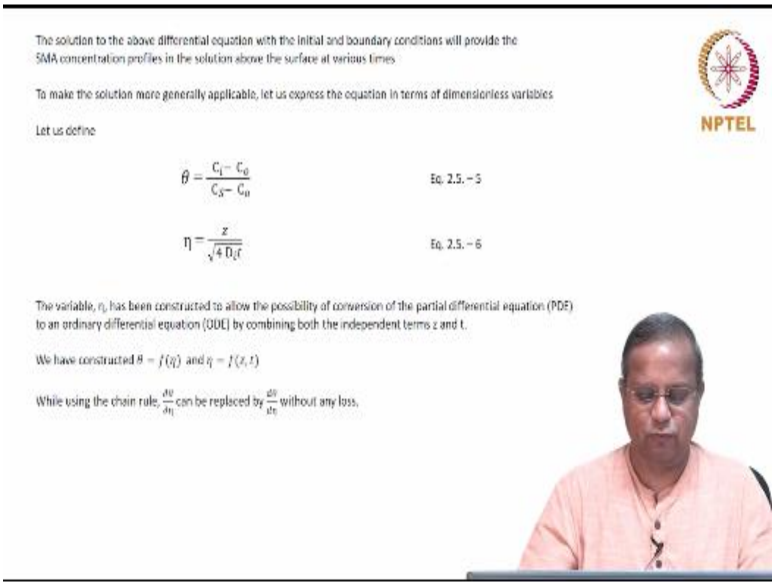

So this solution of the differential equation will provide the concentration profiles of the surface modifying agent in the solution. That is how we have set up the problem. And that would be at various times. For example, at a certain time there would be a certain profile. At a different time there would be a different profile. At an even different time there would be a third profile and so on so forth. Now again, to make the solution more generally applicable, we are going to express the equation in terms of dimensionless variables, non-dimensional variables.

If we solve Eq. 2.5-1 with the above initial and boundary conditions, we can get SMA concentration profiles in the solution above the surface at various times, as shown in Fig. 2.5-1. This particular partial differential equation (PDE) can be solved by converting it into an ODE. To do that, and also to make the solution independent of the actual dimensions of each system, let us define the following dimensionless variables:

$$\theta = \frac{c_A - c_o}{c_s - c_o} \qquad (2.5\text{-}5)$$

This calls for a lot of insight, in order to define it this way, it calls for a lot of insight. This has already been done. This is a very standard way of solving this. I am not doing this here. This I picked from a certain textbook. So do not worry about how I would be able to do this without any practice. No, we are not expecting you to do that. However, this is the way to solve this problem.

And by repeated seeing of solutions, and if you have insights, you can do this on your own for other things. And that level of manipulation may not be expected in this course. However, so do not worry about how do you come up with this. This calls for a lot of insight by the way, okay. This variable especially calls for a lot of insight. This is to give you a preview.

This has been defined to convert the partial differential equation into an ordinary differential equation. As you know, ordinary differential equations are far easier to solve than partial differential equation. So with a lot of insight as to how this solution will progress has come up by the first person who came up with this, we are just following it okay.

$$\eta = \frac{z}{\sqrt{4 D_i \ t}} \qquad (2.5\text{-}6)$$

Note that we have constructed $\theta = f(\eta)$ and $\eta = f(z, t)$. While using the chain rule, $\frac{\partial \theta}{\partial \eta}$ can be replaced by $\frac{d\theta}{d\eta}$ without any loss in accuracy. The variable, η, has been constructed to allow the possibility of conversion of the partial differential equation (PDE) to an ordinary differential equation (ODE) by combining both the independent terms z and t.

As I mentioned, this variable η has been constructed to allow the possibility of conversion of the PDE into ODE by combining both the independent terms z as well as the time, okay. The space variable as well as the time variable has been combined very cleverly into this variable and this formulation is going to help us convert the PDE into a ODE. So we have constructed θ to be a function of η because c_i is a function of η, a function of space and time. Whereas η again is explicitly a function of z and t. That is how we are starting out.

Here, θ is only a function of η and therefore, this partial can be replaced with the total and that is a part of the requirement here to convert. So that is one of the reasons why we have done this in equation 2.5-6. I am just explaining why it is. Do not stop thinking about how I am going to do it. Do not worry about it for now. Or how you are going to do it? Do not worry about it for now.

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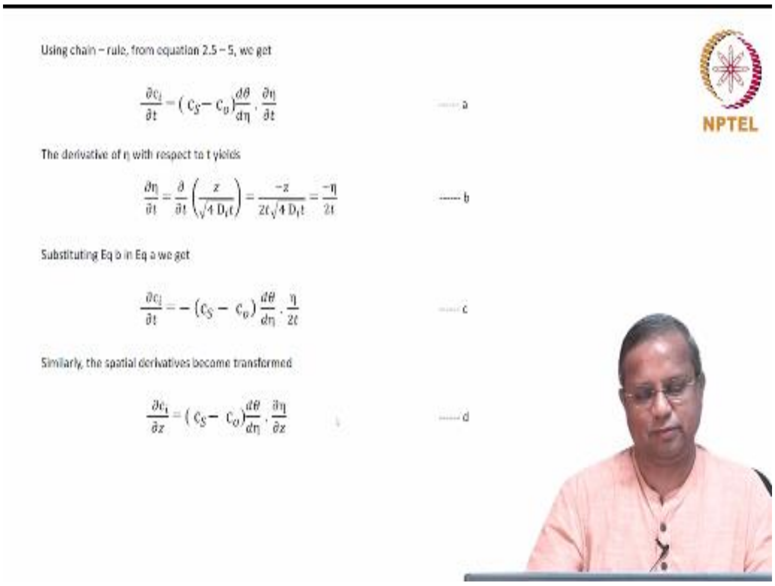

Thus, using the chain rule, from Eq. 2.5-5, we get

$$\frac{\partial c_i}{\partial t} = (c_s - c_o)\frac{d\theta}{d\eta}\cdot\frac{\partial \eta}{\partial t} \tag{a}$$

Now the derivative of η with respect to t yields

$$\frac{\partial \eta}{\partial t} = \frac{\partial}{\partial t}\left(\frac{z}{\sqrt{4D_i\ t}}\right) = \frac{-z}{2t\sqrt{4D_i\ t}} = \frac{-\eta}{2t} \tag{b}$$

Substituting Eq. (b) in Eq. (a) we get

$$\frac{\partial c_i}{\partial t} = -(c_s - c_o)\frac{d\theta}{d\eta}\cdot\frac{\eta}{2t} \tag{c}$$

Similarly, the spatial derivatives are transformed into

$$\frac{\partial c_i}{\partial z} = (c_s - c_o)\frac{d\theta}{d\eta}\cdot\frac{\partial \eta}{\partial z} \tag{d}$$

Okay, this you will have to do and confirm yourself. I have shown you how to do this here. Please stop the video here. Go back and see whether you actually get this and call this d. Pause, go back and then you can come back.

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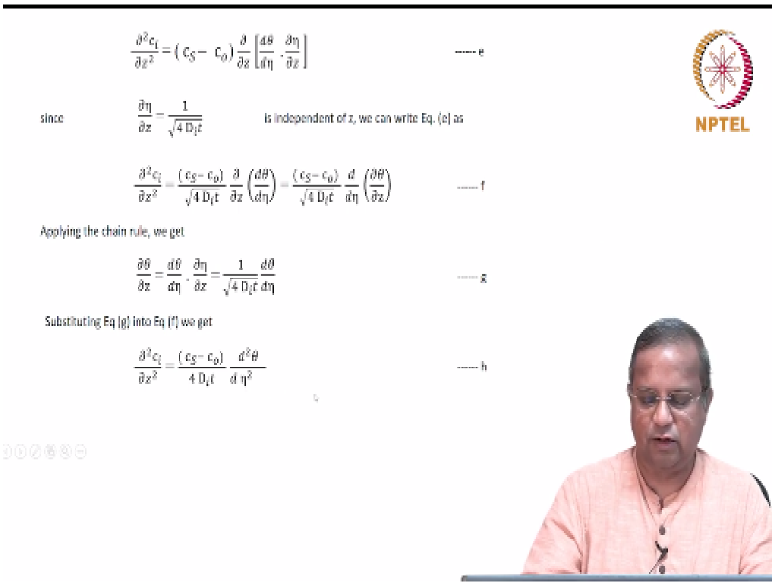

$$\frac{\partial^2 c_i}{\partial z^2} = (c_s - c_o)\frac{\partial}{\partial z}\left[\frac{d\theta}{d\eta}\cdot\frac{\partial\eta}{\partial z}\right] \tag{e}$$

Now, since

$$\frac{\partial\eta}{\partial z} = \frac{1}{\sqrt{4D_i\ t}}$$

is independent of z, we can write Eq. (e) as

$$\frac{\partial^2 c_i}{\partial z^2} = \frac{(c_s - c_o)}{\sqrt{4D_i\ t}}\frac{\partial}{\partial z}\left(\frac{d\theta}{d\eta}\right) = \frac{(c_s - c_o)}{\sqrt{4D_i\ t}}\frac{d}{d\eta}\left(\frac{\partial\theta}{\partial z}\right) \tag{f}$$

Applying the chain rule, we get

$$\frac{\partial\theta}{\partial z} = \frac{d\theta}{d\eta}\cdot\frac{\partial\eta}{\partial z} = \frac{1}{\sqrt{4D_i\ t}}\frac{d\theta}{d\eta} \tag{g}$$

Substituting Eq. (g) into Eq. (f) we get

$$\frac{\partial^2 c_i}{\partial z^2} = \frac{(c_s - c_o)}{4D_i\ t}\frac{d^2\theta}{d\eta^2} \tag{h}$$

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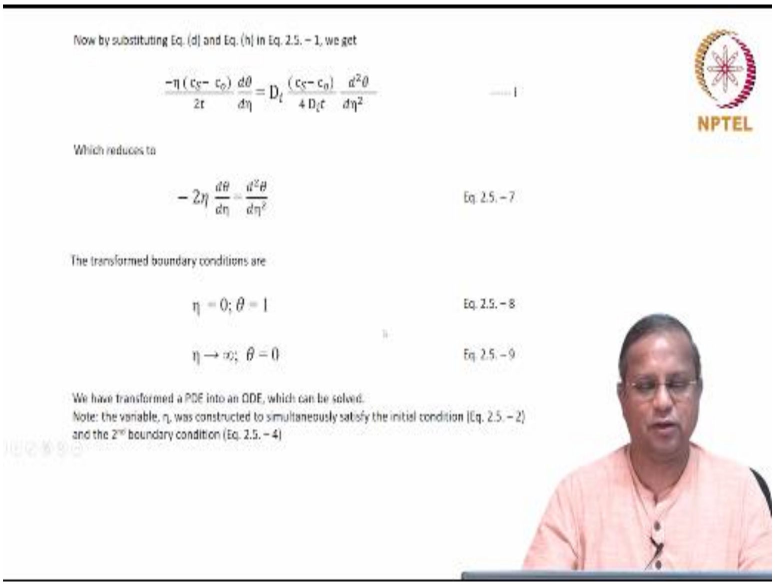

Now by substituting Eq. (d) and Eq. (h) in Eq. 2.5-1, we get

$$\frac{-\eta(c_s - c_o)}{2t}\frac{d\theta}{d\eta} = D_i \frac{(c_s - c_o)}{4D_i \ t}\frac{d^2\theta}{d\eta^2} \tag{i}$$

which reduces to

$$-2\eta\frac{d\theta}{d\eta} = \frac{d^2\theta}{d\eta^2} \tag{2.5-7}$$

The boundary conditions get transformed to

$$\eta = 0;\ \theta = 1 \tag{2.5-8}$$

$$\eta \to \infty;\ \theta = 0 \tag{2.5-9}$$

I think we have been at this intense mathematical manipulations for a while now. Let us let me see what the next thing is. Okay, before I do that, I need to tell you this.

The variable η was constructed simultaneously to satisfy both the initial condition as well as the boundary condition and kind of collapse that into simultaneously satisfy both these and that was also a part of the intuitive writing of η as the way it is written, okay. What else yeah, I think we need to take a break here. We have been at this for this intense working for some time.

It will get tiring and therefore let us take a break. When we come back in the next class, I will show you the solution of this. There are still many more steps to go for the solution. Just that one more derivate coming in there, instead of a zero has changed the solution from half a page to about five or six pages, right? That is what happens, especially when you have partial differential equation.

The solution is a lot more involved, but that is the nature of things. Okay. See you in the next class.