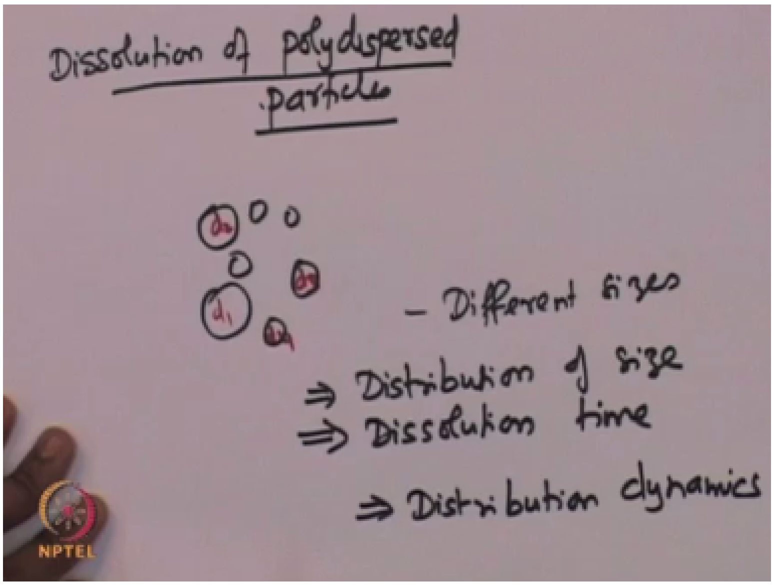
Chemical Reaction Engineering II
Prof. Ganesh. A. Viswanathan
Department of Chemical Engineering
Indian Institute of Technology– Bombay

Lecture - 48
Fluid-Solid Non-Catalytic Reactions VI

(Refer Slide Time: 00:32)



Dissolution of polydispersed particles

- Different sizes

⇒ Distribution of size

⇒ Dissolution time

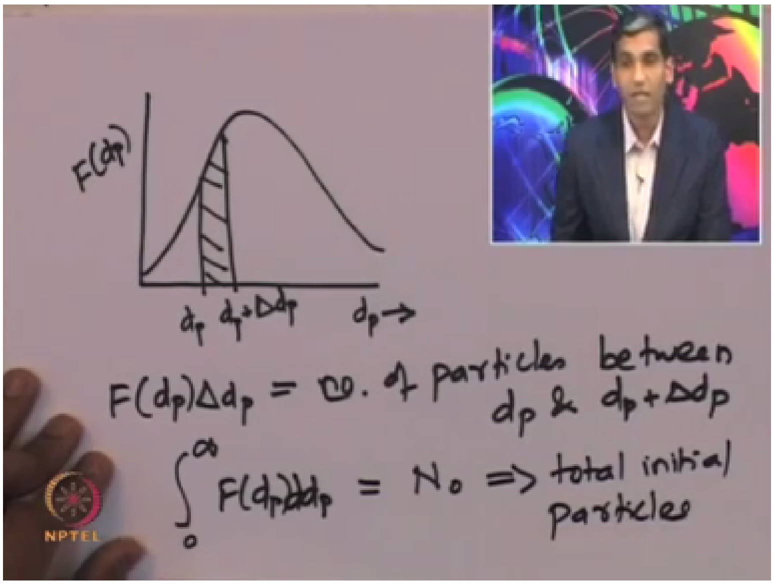
⇒ Distribution dynamics

So let us look at dissolution of; let us see how to capture this behavior dissolution of polydispersed particles. So what is polydispersed particles? Suppose you have collection of particles which are of different sizes for example this big one could be of size d1 it could be d2 or it could be d3 and this could be d4 and so on and so forth. So there will be collection of particles and each of these are different in size and so there are particles of different sizes.

Now not just that initial states the particles will be of different size there will be distribution of sizes of particles all through the time and the dissolution is actually occurring. So therefore clearly there is a distribution, there is a size distribution and the question is to find out what is the dissolution time. The objective is to find the dissolution time and in order to find the dissolution time for particles who are actually placed in the certain distribution one need to actually follow the distribution dynamics.

So the distribution dynamics have to be followed. So let us look at what is a distribution.

(Refer Slide Time: 02:16)



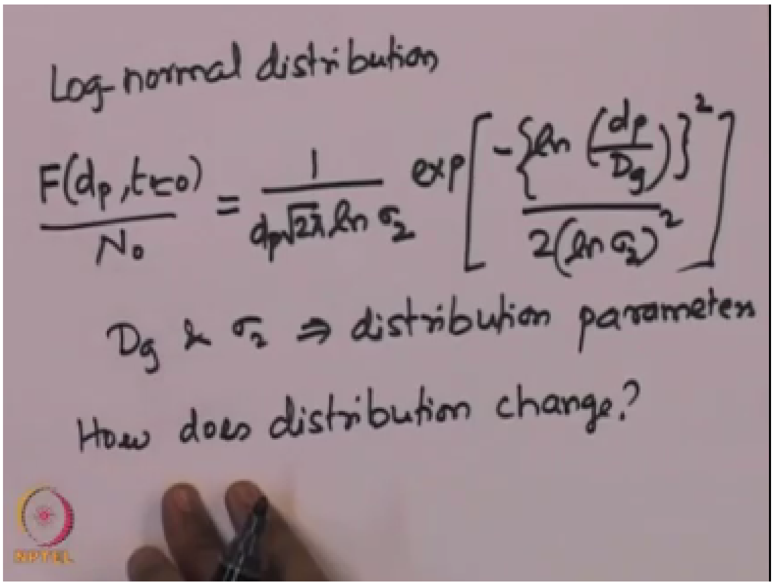
$F(d_p)\Delta d_p$ = no. of particles between d_p & $d_p + \Delta d_p$

$\int_0^\infty F(d_p)\Delta d_p = N_0 \Rightarrow$ total initial particles

So suppose if I look at the plane of number of particles versus the fraction of the number of particles that are actually of a particular size. So then we expect that it is a certain histogram where the location between let say dp and dp+ delta dp which is a small increase in the small difference in the particle size. So in that case the area under the curve in this location it signifies the number of particles which are actually present in the system whose diameter is between these 2 numbers.

So therefore F dp multiplied by delta dp that is basically the number of particles between dp and dp+ delta dp. So that is the number of particles and moreover if we integrate this expression from 0 to infinity F dp*dp*dp into the differential of diameter of particle that should be=N0 which is the total that is the total initial particles which are actually present. Now if we assume that it follows a log-normal distribution.

(Refer Slide Time: 03:51)



Log-normal distribution

$$\frac{F(d_p, t=0)}{N_0} = \frac{1}{d_p\sqrt{2\pi}\,\ln\sigma_2}\exp\left[\frac{-\left\{\ln\left(\frac{d_p}{D_g}\right)\right\}^2}{2(\ln\sigma_2)^2}\right]$$

D_g & σ_2 ⇒ distribution parameters

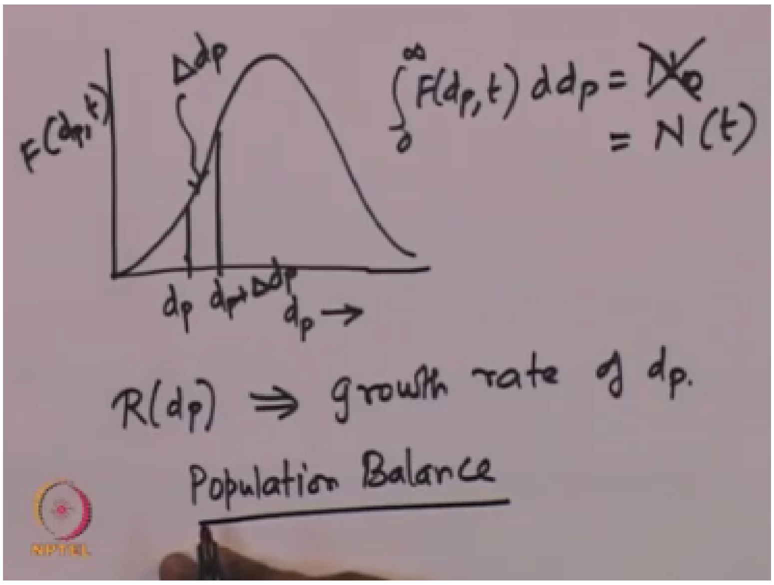
How does distribution change?

Let us assume that the initial distribution of the particles they follow a log-normal distribution let us assume that they follow a log-normal distribution. So now the fraction of the species where fraction of the particles whose size is dp at time t=0 and that normalize by N0 is actually given by 1/dp square root of 2 pi* ln of sigma 2 multiplied by exponential of –ln of dp/Dg and square of that/2 times ln sigma 2 square.

So that is the expression for the log normal distribution where Dg and sigma 2 are essentially the distribution parameters these are the distribution parameters. So now the question is in order to find out what is the dissolution time of the particles which are actually in this polydispersed system is to actually find out what is the how the distribution itself changes instead of monitoring every drug particle it is better to monitor simply the population itself.

So the question is how does the how does distribution change so that is what we are going to look at.

(Refer Slide Time: 05:36)



Now suppose if we look at the distribution at any time and if it is some general curve like this. Now we can write a simple balance on the population of these drug particles and suppose if we take a small element between dp and dp+ delta dp. So therefore the thickness of this element is delta dp if we assume that thickness is delta dp and by this definition of the histogram the integral of 0 to infinity F of dp, t * d dp should be=N0 that should be the total number of particles that were actually initially present.

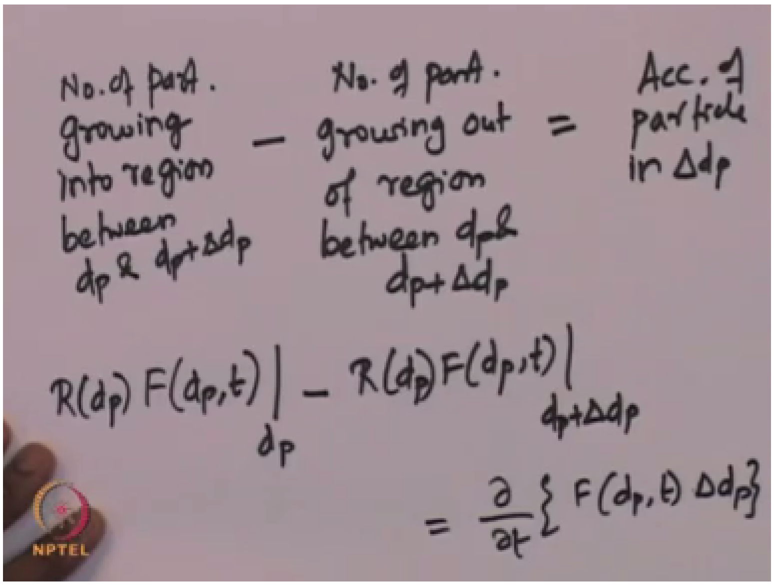
And because there were no new particles are added it is only the particles actually dissolve and disappear. So therefore the integral under the curve up to infinity if we assume that the particles are actually are of some finite sizes at all time then that should be= total number of particles itself. Now if that is not the case then this should be a function of time. So the number of particles will change because some of these particles will dissolve and disappear and when that happens then this integral between 0 to infinity should actually be a function of time.

Now one other quantity which is required in order to model this system is the growth rate suppose Rdp is the growth rate of every particles and of course it depends upon the size of the particle itself. So that is the growth rate of particle whose diameter is dp then one can actually write a population balance equations in order to capture the dynamics of the whole distribution itself as the reaction actually proceeds.

So the population balance equation can be written as the balance between the number of particles which are actually growing and reaching the diameter whose size is between dp and delta dp and also we need to account for the particles which are already present in this small element dp and delta dp and they grow and they actually become bigger than dp+ delta dp so which mean they leave the small element delta dp.

And there is no addition of new particles because once the drug is being fed it is just being dissolved and so there is no other mechanism by which the particles are actually being added into that small element that delta dp and then the other term is the accumulation term. So therefore putting them all together.

(Refer Slide Time: 08:44)



No. of part. growing into region between dp & dp+Δdp − No. of part. growing out of region between dp & dp+Δdp = Acc. of particle in Δdp

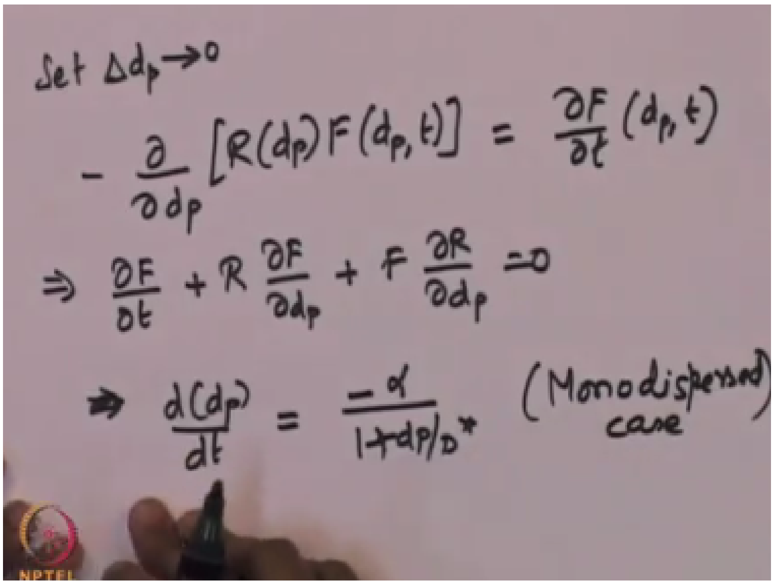
$$R(d_p)\,F(d_p,t)\Big|_{d_p} - R(d_p)\,F(d_p,t)\Big|_{d_p+\Delta d_p} = \frac{\partial}{\partial t}\left\{F(d_p,t)\,\Delta d_p\right\}$$

It will be number of particles growing into region between dp and dp+ delta dp- the number of particles growing out of the region between dp and dp+ delta dp that should be=the accumulation of particles in delta dp in that small element. Now suppose if R is the growth rate which is what we have defined a short while ago then the number of particles growing into the regions between dp and dp+ delta dp is actually given by R*dp.

So that is the growth rate when the particle is right whose size is exactly dp and then that multiplied by the corresponding fraction will tell; will provide a clue as to what is the number of particles that are actually growing into the region in this small interval of diameter. And that evaluates the dp- delta dp and that should be=d/dt so that is the accumulation of particles in delta dp=F of dp, t multiplied by delta dp.

So that is the rate of change that is the rate at which the particles are actually being accumulated in that small element. So now rearranging this equation and setting delta dp=0.

(Refer Slide Time: 10:44)



Set $\Delta d_p \to 0$

$$-\frac{\partial}{\partial d_p}\left[R(d_p)F(d_p,t)\right] = \frac{\partial F}{\partial t}(d_p,t)$$

$$\Rightarrow \frac{\partial F}{\partial t} + R\frac{\partial F}{\partial d_p} + F\frac{\partial R}{\partial d_p} = 0$$

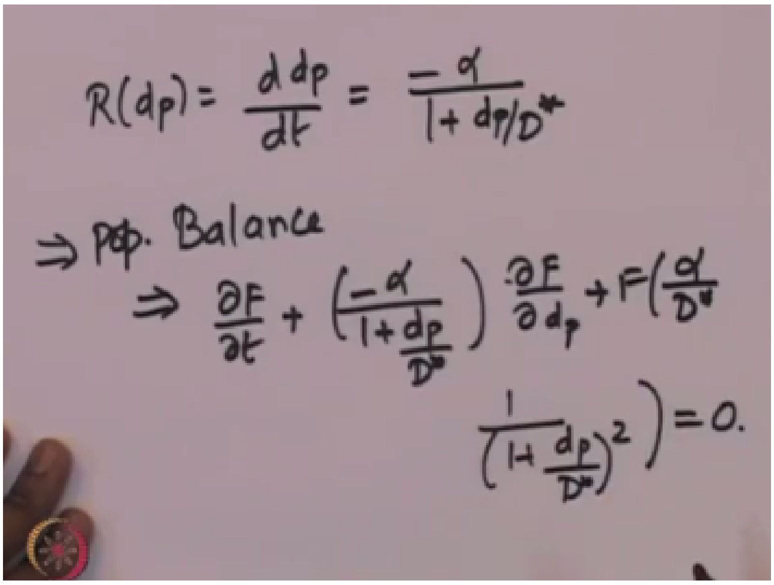
$$\Rightarrow \frac{d(d_p)}{dt} = \frac{-\alpha}{1+d_p/D^*}$$ (Monodispersed case)

So set delta dp to be 0 then it can be written as –d/d of the particle diameter into F of dp, t that should be= dou F/dou, t so that is the expression for that is the population balance. So now what do we do with this population balance. So we can solve this equation in order to find the radius of the particle in order to find the how the distribution the radius distribution actually changes.

So now this can actually be rewritten as dF/dt+R* dF/ddp+F * dR/d dp that is=0. So now where Rdp is essentially the growth rate of the particle of size dp and if suppose in the earlier case if the particles were monodispersed we actually found out what is the growth rate. So therefore for every particle of a certain size that expression can be used as a growth rate of the particle of that particular size.

So therefore from here it will be d dp/dt that should be=-alpha/1+dp/D star so that is the rate at which the monodispersed particles are actually growing. So plugging that into the expression plugging that into the population balance we will find that so that is for the monodispersed case.

(Refer Slide Time: 12:43)



$$R(d_p) = \frac{d\,d_p}{dt} = \frac{-\alpha}{1+d_p/D^*}$$

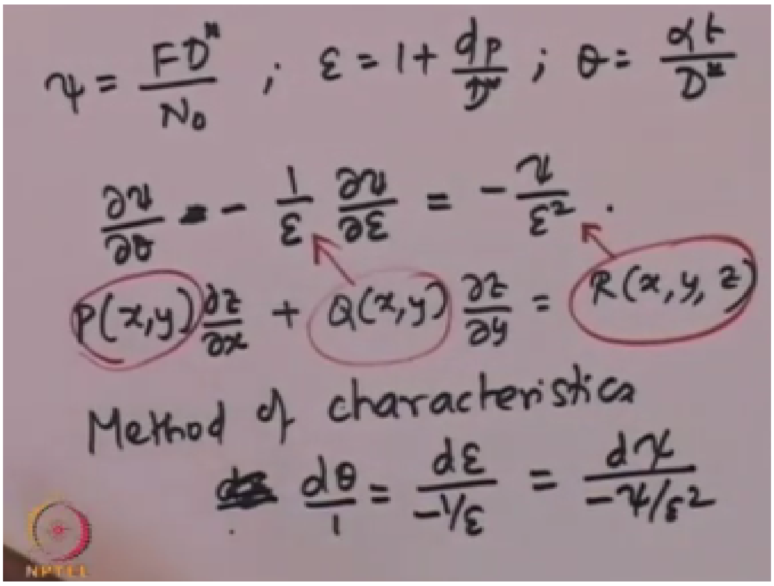
⇒ Pop. Balance

$$\Rightarrow \frac{\partial F}{\partial t} + \left(\frac{-\alpha}{1+\frac{d_p}{D^*}}\right)\frac{\partial F}{\partial d_p} + F\left(\frac{\alpha}{D^*}\frac{1}{\left(1+\frac{d_p}{D^*}\right)^2}\right) = 0.$$

So plugging that into expression we will find that the rate of Rdp that is=-alpha 1+dp/D star and so the population balance will be dF/dt+-alpha/1+ dp/D star*dF/d dp+ F* alpha/D star *1/1+dp/ D star the whole square that is=0. So that is the expression so that is the population balance that actually captures how the dynamics of this distribution actually changes with time how the distribution changes with time.

So now if we introduce a few dimensionless quantities which is actually useful in solving this problem.

(Refer Slide Time: 13:58)



$$\psi = \frac{FD^*}{N_0}\ ;\ \varepsilon = 1+\frac{d_p}{D^*}\ ;\ \theta = \frac{\alpha t}{D^*}$$

$$\frac{\partial\psi}{\partial\theta} - \frac{1}{\varepsilon}\frac{\partial\psi}{\partial\varepsilon} = -\frac{\psi}{\varepsilon^2}.$$

$$P(x,y)\frac{\partial z}{\partial x} + Q(x,y)\frac{\partial z}{\partial y} = R(x,y,z)$$

Method of characteristics

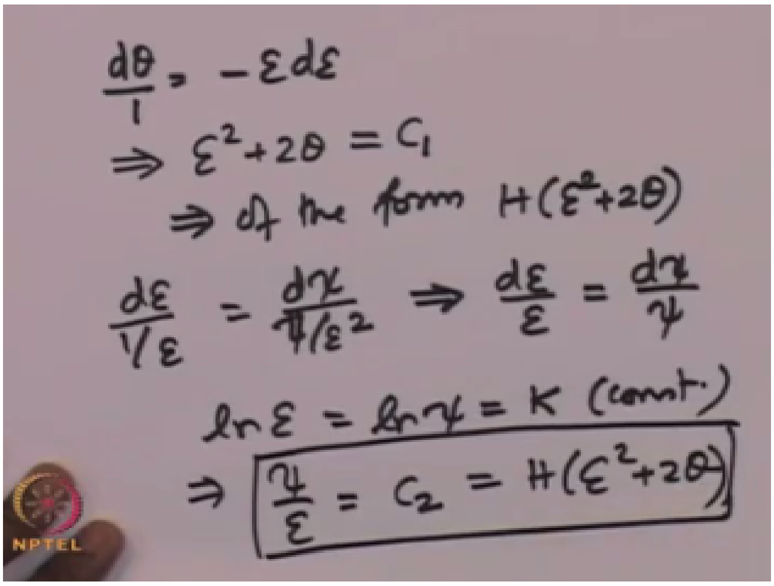
$$\frac{d\theta}{1} = \frac{d\varepsilon}{-1/\varepsilon} = \frac{d\psi}{-\psi/\varepsilon^2}$$

So Psi= F* D star/N0 where F is the distribution of the particles based on the size and D star is the ratio of the is the diameter when the mass transport rate and the reaction rate are= each other and N0 is the initial total number of particles then epsilon is defined as 1+dp/D star and theta is defined as alpha * t/D star. So now if we introduce these dimensionless quantities we can rewrite the population balance as d Psi/d theta that is -1/epsilon * d Psi/d epsilon that is=-Psi/epsilon square so that is the expression.

So this expression is of a very familiar differential equation which is of the form P of x, y* dz/dx+ Q of x, y * dz/dy that is= R of x, y, z. So from here we can see that if a P of x, y is nothing but 1 and Q of x, y is like 1/epsilon and R of x, y is like Psi/-epsilon square. So the way to solve this equation is basically to use the method of characteristics is to use the method of characteristics where this problem is posed in a slightly different way.

So dx/p sorry d theta/1= d epsilon/-1/epsilon and that should be= d Psi/-Psi/epsilon square. So that is the way in which the population balance equation which is actually written here can actually be post in terms of the method of characteristics.

(Refer Slide Time: 16:14)



$$\frac{d\theta}{1} = -\varepsilon\, d\varepsilon$$

$$\Rightarrow \varepsilon^2 + 2\theta = C_1$$

$$\Rightarrow \text{of the form } H(\varepsilon^2 + 2\theta)$$

$$\frac{d\varepsilon}{1/\varepsilon} = \frac{d\psi}{\psi/\varepsilon^2} \Rightarrow \frac{d\varepsilon}{\varepsilon} = \frac{d\psi}{\psi}$$

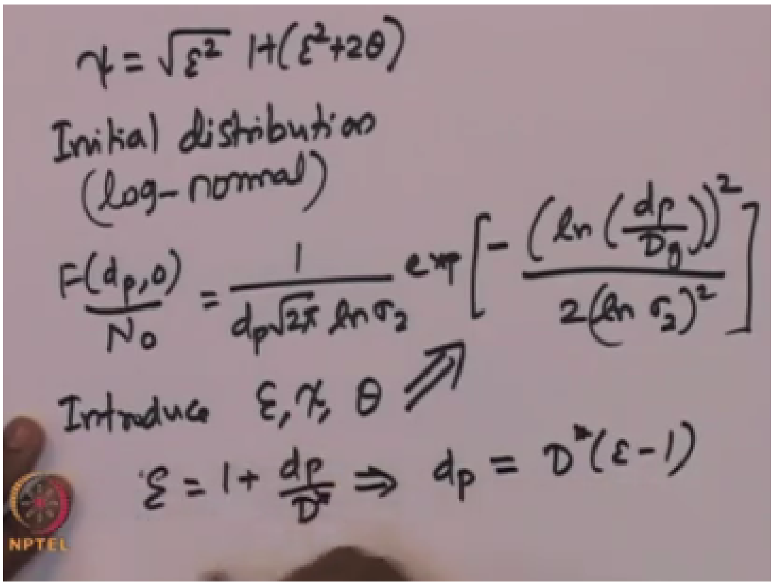
$$\ln\varepsilon = \ln\psi = K \text{ (const.)}$$

$$\Rightarrow \boxed{\frac{\psi}{\varepsilon} = C_2 = H(\varepsilon^2 + 2\theta)}$$

So now the first 2 terms in the repose problem basically it looks like d theta/1=-epsilon * d epsilon. So from here we can find out that epsilon square+2 theta= constant C1 and that should be of the form H of epsilon square+ 2 theta so that should be the functional form functional dependence of this particular expression. And then next let us look at the other case d epsilon/1/epsilon that should be= d Psi/ Psi/epsilon square.

So this can actually be rewritten as d epsilon/epsilon= d Psi/Psi which can be solved to obtain ln epsilon=ln Psi and that is= some constant K so that is a constant. So from here we can find that Psi/epsilon is nothing, but some constant C2 and that can be= H of epsilon square+ 2 theta. So that is the functional dependence so next we can actually see how to take this forward and find the distribution profile.

(Refer Slide Time: 17:39)



$$\psi = \sqrt{\varepsilon^2}\ H(\varepsilon^2+2\theta)$$

Initial distribution

(log-normal)

$$\frac{F(d_p,0)}{N_0} = \frac{1}{d_p\sqrt{2\pi}\,\ln\sigma_g}\exp\left[-\frac{\left(\ln\left(\frac{d_p}{D_g}\right)\right)^2}{2(\ln\sigma_g)^2}\right]$$

Introduce $\varepsilon, \psi, \theta$ $\Nearrow$

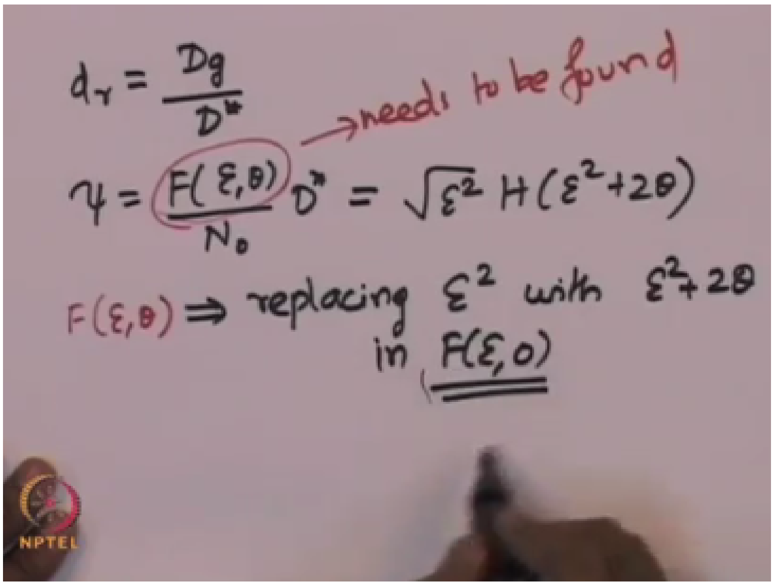
$$\varepsilon = 1+\frac{d_p}{D^*} \Rightarrow d_p = D^*(\varepsilon-1)$$

So suppose if we can rewrite the relationship between the phi and epsilon as phi= square root of epsilon square *H of epsilon square+2 theta. So in order to obtain the final distribution which is actually present in the definition of Psi. So Psi is almost like non dimensional distribution of the various size of the particles which are of different sizes. So if you look at the initial distribution which is actually given by log normal distribution.

So the log normal distribution as it goes here root 2 pi* ln sigma 2 * exponential of –ln dp/D star dp/Dg the whole square/2 ln sigma 2 and square of that. So that is the initial distribution. Now if you know the initial distributions then we can actually introduce the transformed variables so basically we introduce epsilon Psi and theta into this initial distribution and if you assume that so if you assume that epsilon=1+dp/D star so this comes from the non dimensional form of epsilon then from here we can get the dp=D star* epsilon-1.

Actually this is the non dimensional form of epsilon and from here we can find out the relationship between dp and the other parameters.

(Refer Slide Time: 19:38)



$d_r = \frac{D_g}{D^*}$

→ needs to be found

$$\psi = \frac{F(\varepsilon,\theta)}{N_0} D^* = \sqrt{\varepsilon^2}\, H(\varepsilon^2+2\theta)$$

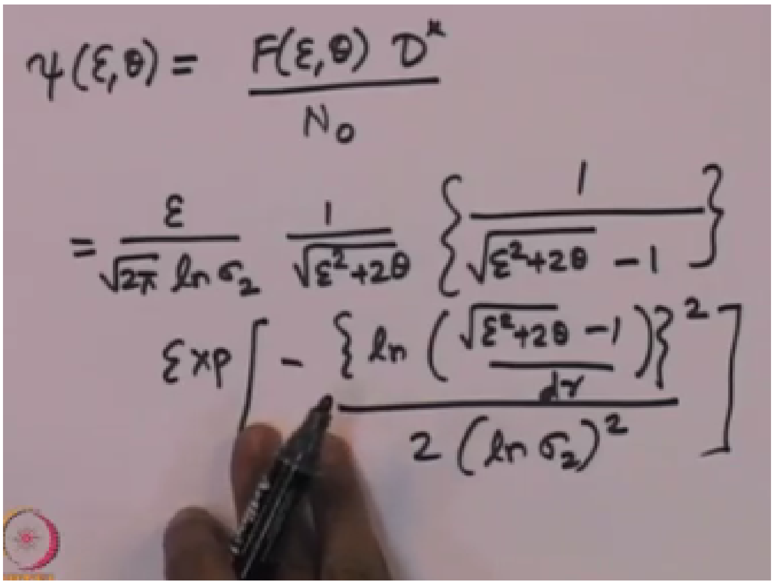
$F(\varepsilon,\theta) \Rightarrow$ replacing ε^2 with $\varepsilon^2+2\theta$ in $F(\varepsilon,0)$

So if we assume that dr if we assume a new variable dr=Dg/D star where Dg is some parameter of the distribution and D star is the diameter at which the mass transfer rate and the reaction rates are equal then we can find out that Psi= some F of epsilon, theta/ N0* D star that should be= square root of epsilon square* H of epsilon square+2 theta so that is the functional form of this variable Psi.

So now if you want to find out what is the final distribution we need to find this expression F of epsilon, theta. This expression need to be found in order to find out what is the instantaneous distribution of the sizes so how can we do this. So it can be done by actually using the distribution at the initial distribution at the initial state where the reaction has not started then F of epsilon, theta so this can be obtained by simply replacing epsilon square with +2 theta in F of epsilon, 0.

So note that this is the initial distribution and final distribution can simply be obtained by replacing epsilon square in this initial distribution with epsilon square+2 theta so that serves as the solution methodology.

(Refer Slide Time: 21:30)



$$\psi(\varepsilon,\theta) = \frac{F(\varepsilon,\theta)\, D^*}{N_0}$$

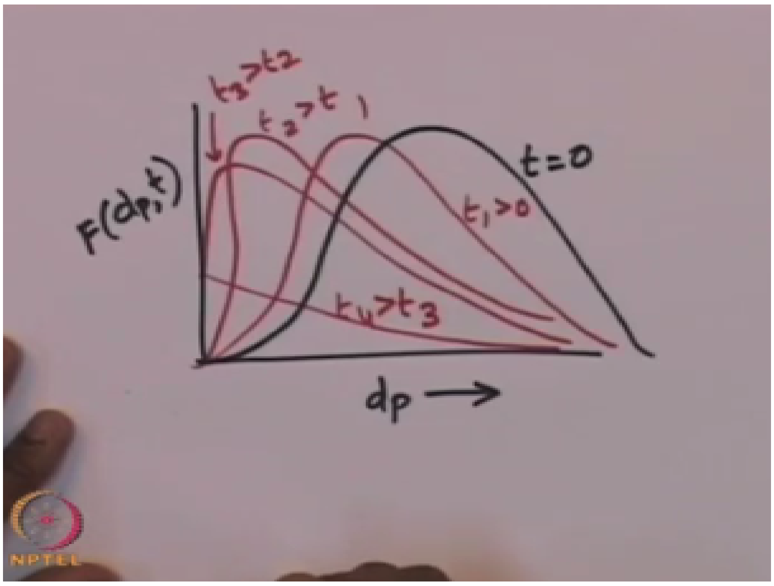
$$= \frac{\varepsilon}{\sqrt{2\pi}\,\ln\sigma_2}\,\frac{1}{\sqrt{\varepsilon^2+2\theta}}\left\{\frac{1}{\sqrt{\varepsilon^2+2\theta}-1}\right\}$$

$$\exp\left[-\frac{\left\{\ln\left(\frac{\sqrt{\varepsilon^2+2\theta}-1}{dr}\right)\right\}^2}{2(\ln\sigma_2)^2}\right]$$

So now we can rewrite this as Psi of epsilon, theta so that is= F of epsilon, theta so you can introduce we can now use the initial distribution in order to find out what is the value of Psi, what is the expression for Psi as a function of epsilon theta and that would be= epsilon/square root of 2 pi* ln sigma 2*1/square root of epsilon square+2 theta*1/square root of epsilon square+2 theta-1 multiplied by exponential of –ln of square root of epsilon squares+2 theta-1/dr.

And square of that/2* ln sigma 2 to the power of square of that. So that is the distribution at any time in the non-dimensional form so once we know this distribution we can look at the distribution profile as a function of time.

(Refer Slide Time: 22:45)



So suppose if this is dp the particle diameter and this is F of dp, time then if suppose if this is the initial distribution so that is time t=0 that is the initial distribution then as time progresses all the particles are actually undergoing the dissolution because of the heterogeneous reaction. And so as time goes by the distribution changes and so this is t1 which is > 0 then as time further goes by more dissolution will happen.

So this will be t2 which will be > t1 then further time elapses and then the distribution will be this will be t3 which is > t2 and then eventually when the conversion is going to be almost complete then the distribution will look like this where this is t4 which is > t3. So that is the kind of distribution that one can actually obtain as a function of time for this polydispersed particles which are undergoing dissolution.

So let us summarize what we have learnt in the last 3 lectures. So we have looked at the fluid solid non-catalytic heterogeneous reactions and this can occur through 2 modes one is where the particle size does not change and another one is the case where the particle size changes as the reaction progresses and there are 3 different possible resistances which are actually existing in this kind of a system.

One is the gas film resistance for diffusion resistance and the other one is the ash layer diffusion resistance and the third one is the reaction controlling resistance offered because of the surface reaction. So under these 3 regimes the time that is taken by the particles to reach a certain radius has been modeled and calculated and that is for different geometries have been looked into for both the shrinking or the changing size particle case.

And for the constant size particle case and then we looked at an example of dissolution of monodispersed particles and extended for a polydispersed system. Thank you.