Colloids and Surfaces
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Lecture-05
Characterisation of Colloidal Particles-I

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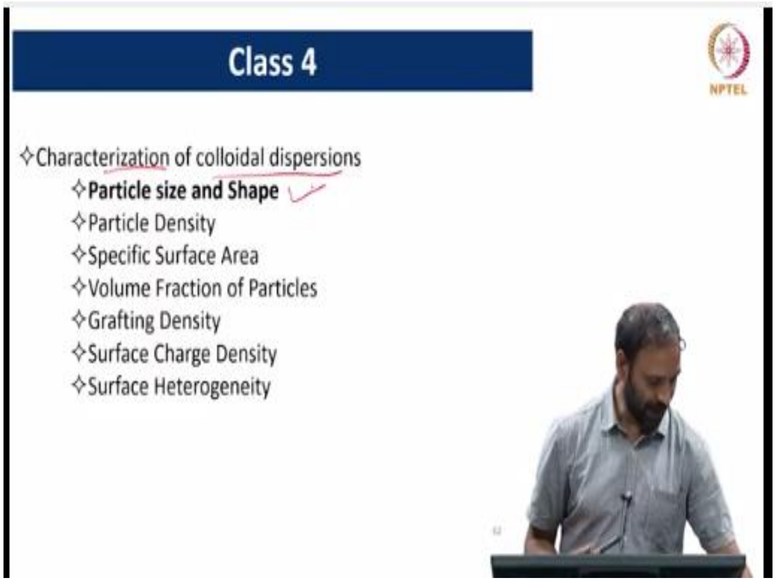

Ok, so, this is a class 4. So, we will continue with the characterization of colloidal dispersions. We briefly started looking at how to characterize particle size and shape.

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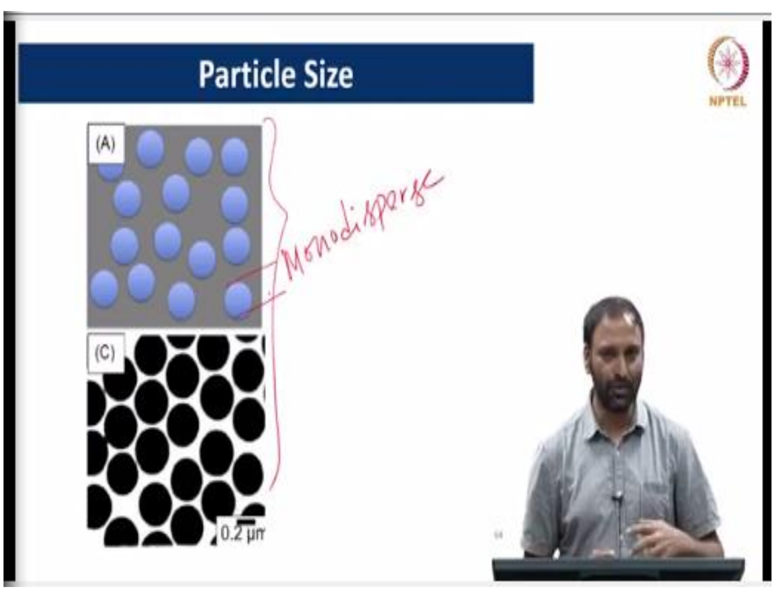

I had mentioned that you know there are several techniques available for characterizing particles, light scattering based and microscopy based in which we briefly discussed about, you know dynamic light scattering, static light scattering. And in terms of microscopy, there is optical microscopy, electron microscopy. So, all these techniques can be used. And what you are looking at the pictures here are cases where you have something called as a monodisperse particles.

That means particles are all of identical size, right. But that need not be the case always because whenever you do synthesis you will always end up with something like this.

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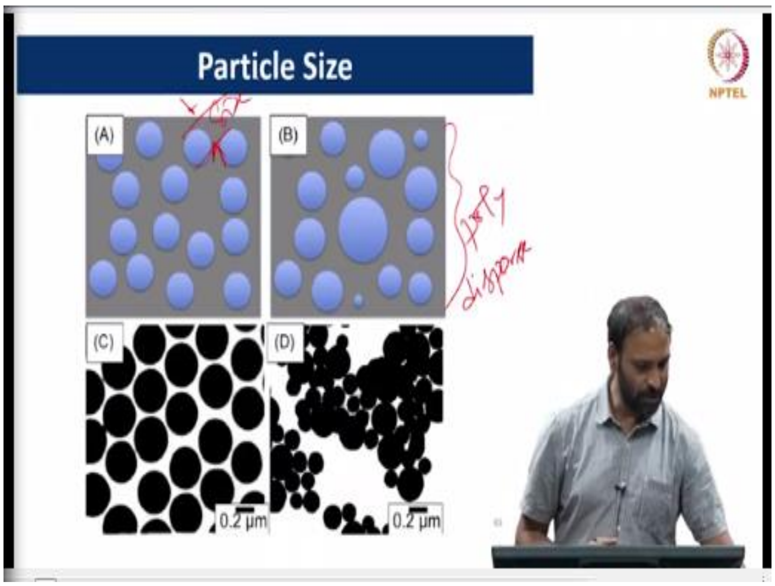

You may have a distribution of sizes, this is what is called us polydisperse, right ok. So, when you have monodisperse particles, the only parameter that you have to characterize the particles for is in terms of the physical dimension just the size, right. If it is a spherical particles, you just say diameter of the particle or the radius of the particle that is good enough ok.

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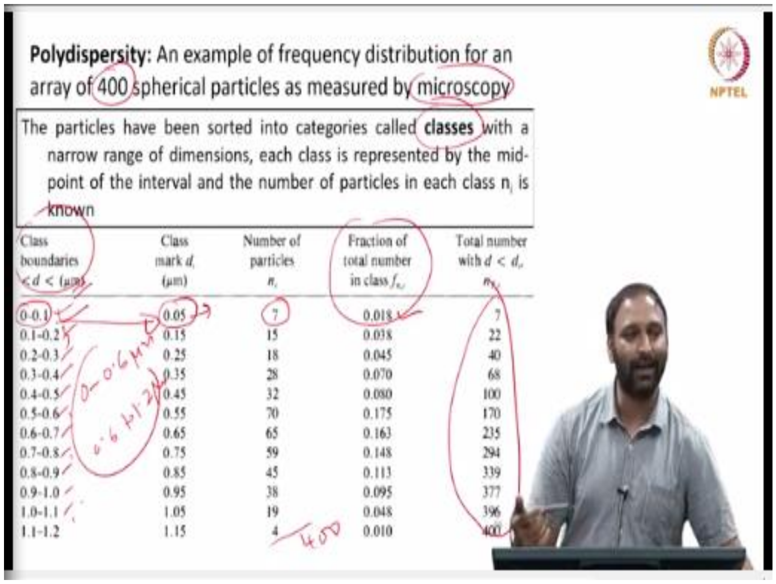

Class boundaries $< d <$ (μm)	Class mark d_i (μm)	Number of particles n_i	Fraction of total number in class $f_{n,i}$	Total number with $d < d_i$ n_c
0-0.1	0.05	7	0.018	7
0.1-0.2	0.15	15	0.038	22
0.2-0.3	0.25	18	0.045	40
0.3-0.4	0.35	28	0.070	68
0.4-0.5	0.45	32	0.080	100
0.5-0.6	0.55	70	0.175	170
0.6-0.7	0.65	65	0.163	235
0.7-0.8	0.75	59	0.148	294
0.8-0.9	0.85	45	0.113	339
0.9-1.0	0.95	38	0.095	377
1.0-1.1	1.05	19	0.048	396
1.1-1.2	1.15	4	0.010	400

However, when you have a polydisperse particle**,** so what you typically do is you kind of do something like this, ok. So, what you are seeing is an example where what is been done and so, they have considered 400 spherical particles. And then size has been measured by could be microscopy, right. So, you have pictures of particles in the picture which has particles of different sizes.

And then what you do is you categorize these particles into classes, ok, this class essentially means this is a, what is called the class boundary out of all the particle that I have. So, I am going to put them into classes of you know size ranging from in this case 0 to 0.1 micrometer ok and the second class is 0.1 to 0.2 like that, right. So, therefore, you out of all the sizes that you have measured, you classify them into different bins.

If you want to call them as all different classes of some size range, right. And corresponding to that class, or a bin you are going to have average size, right. So, therefore, if 0 and 0.1 is your bin, ok then your average size is going to be 0.05 micrometer right, so you do that and then of course you tabulate what is the number of particles that you have in each of these classes, ok. And I can actually get what is the fraction of total number of particles in each of these things, right.

If my total number is say 400, so 3 by 400 will give you this number, ok and of course, you can look at cumulative numbers and things like that, ok, So, now you will always have a question as to how many classes that I should divide the entire particle size distribution into, I think what you should do is, you should not go for 2 fewer classes you know. For example, I cannot have 2 classes.

I cannot say that, hey, look, I want to go from 0 to 0.6 micrometer is one class and then 0.6 to 1.2 micrometer you know what you have is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 classes. But you know, I cannot say I will only take 2 classes, right. Because if you do that, then you know, you are going to end up with not a good representation of the size distribution that you have, ok. On the other hand, you should also not have too many classes because you know what it will do is it will increase the calculation that you are going to do, right.

You know is it really worth dividing them into 10 classes or maybe 20 classes, 30 classes, ok. Then we would end up spending a lot of time for not so much improvement in the accuracy with which you can get the size data, ok. So, therefore there is an optimum number that one has to worry about, ok, that you should think a little bit you know when you are going to do these things, ok.

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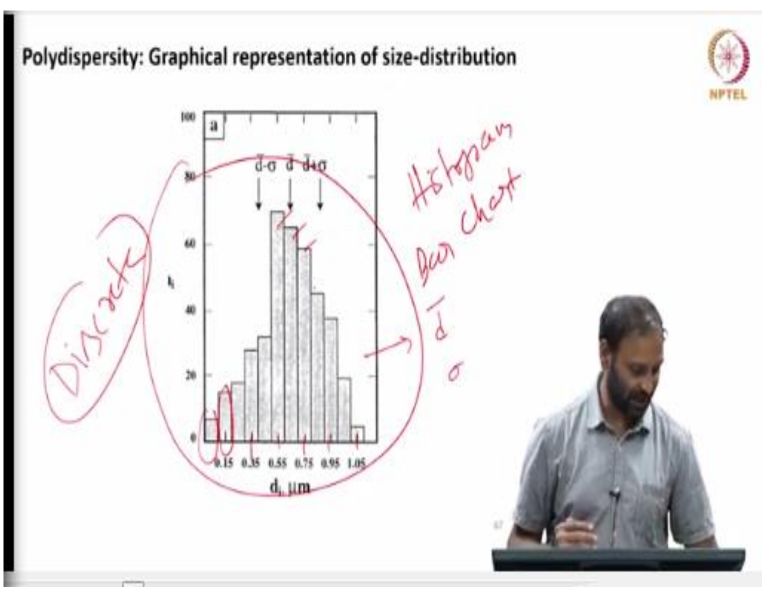

And typically when you get data like this, you represent the size distribution in a what is called is a histogram, ok or a bar chart, right. And that is your first class, second class, ok all these vertical lines that you see these are the average size that corresponds to each of these classes therefore you get a distribution like this ok. And once you have a distribution like this, so from this what you can do is I can get what is the average size.

And I can also get what is the standard deviation ok, that is the best way to represent your data when you have polydisperse sample. And once you have this is what is called as a discrete distribution, right. Because you are depending upon the number of class I am going to have, ok, I can have a few of these bars or a large number of them, ok, that still is a discrete representation of the data that you have obtained from your image analysis for example.

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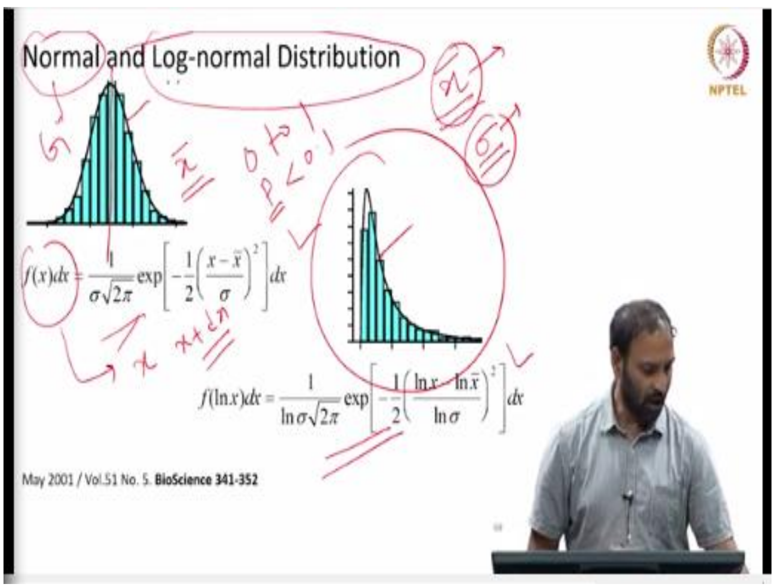

So, what people do is, you can actually use some continuous distribution function something called as a normal distribution function, it is also called as a Gaussian distribution function or what is called as a log normal distribution function which are actually represented respectively by these 3 expressions. And then I can fit these known distribution function to the discrete data that you have obtained.

And the more class that you are going to have, the more closer would be your discrete representation to the continuous you know representation that is represented by these lines, ok.

And if you have a log you know a normal distribution, so this f of x into dx will tell you something about what is the fraction of the particles that you have in the size range from x to x + dx you know in a particular the fraction of particles in that size range, ok.

And of course you are going to have a maxima right and that base response to x bar, which is the average size of your distribution. And if it looks like a bell shaped curve, that means around the mean is very symmetric, then you typically use this normal distribution a Gaussian distribution. And if you have cases like this ok where your size data is skewed, either towards the smaller size or a larger size then you go for what is called as a log normal distribution function, ok.

And the objective of fitting these functions to the size distribution data as I said is to get the average size x bar and your standard deviation, ok. So, once you have done that you have been able to characterize your particles for the average size and the standard deviation. And there are ways by which I can calculate what is called as a polydispersity index from such you know x bar and sigma.

And this polydispersity index typically varies from 0 to 1 more closest to 0 it is, that means it is mono disperse a sample are, and if the values are larger, then it is poly dispersed. Typically for all practical purposes if your polydispersity index is less than about 0.1 you can practically consider them to be monodisperse you know samples, ok. That is about the characterization the particle size.

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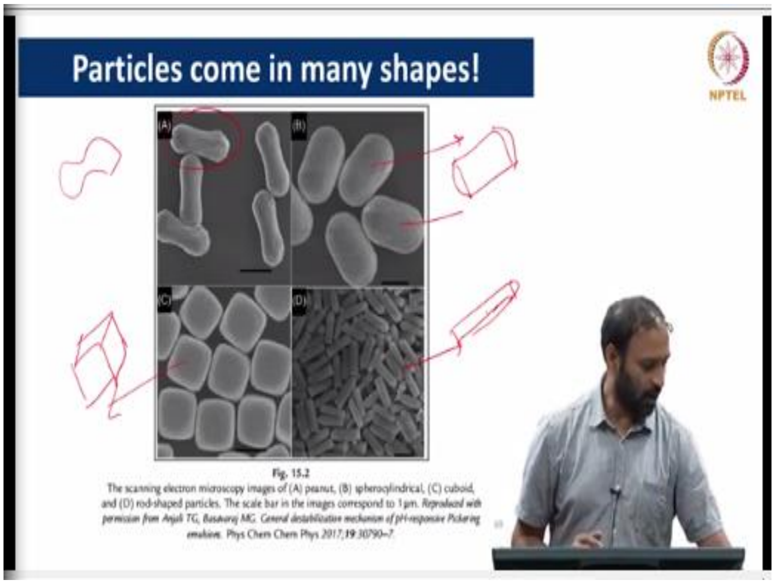

Of course, you can have particles of different shapes, right. So, what you are looking at is a cases where I have some particles which looks like a peanut right like a dumbbell kind of a shape or you could have something called as a spherocylinder which is basically a cylinder with 2 caps, right, something called as a spherocylinder. You could have cube like particles right perfect cubes ok or you can have rod like particles which are in this case this rod with a small kind of it is like a bullet shaped particle ok.

So, of course you can have particles of different shapes you know and we kind of make them in our lab. But there are definitely procedures available for you to make it what you can do in such cases is you know.

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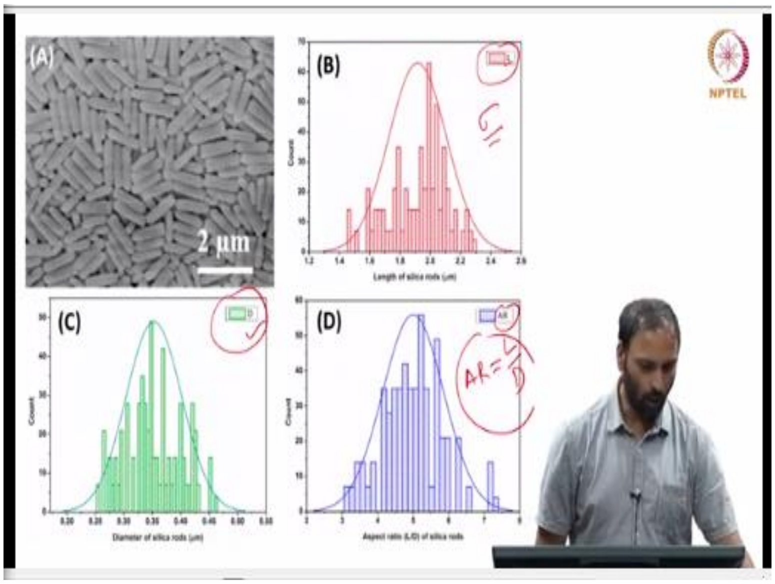

I can of course get what is the length distribution, what is a distribution in the, the length of the particles or I can get the distribution in the diameter of the particle or you can define what is called as a aspect ratio AR which is defined as the length of the particle divided by the diameter ok. So, therefore, I can either characterize the particles for the length and the diameter or for a complete characterization, I would have to look at length, diameter as well as your aspect ratio, ok.

So, therefore I can use a similar principle that I used for analyzing spherical particles like you know getting the size distribution and fitting the distribution to a known function like Gaussian distribution or log normal distribution and an extract the average size and the sigma ok. I can do a similar thing also for each of the physical dimensions for non spherical particles ok, that is what you typically do.

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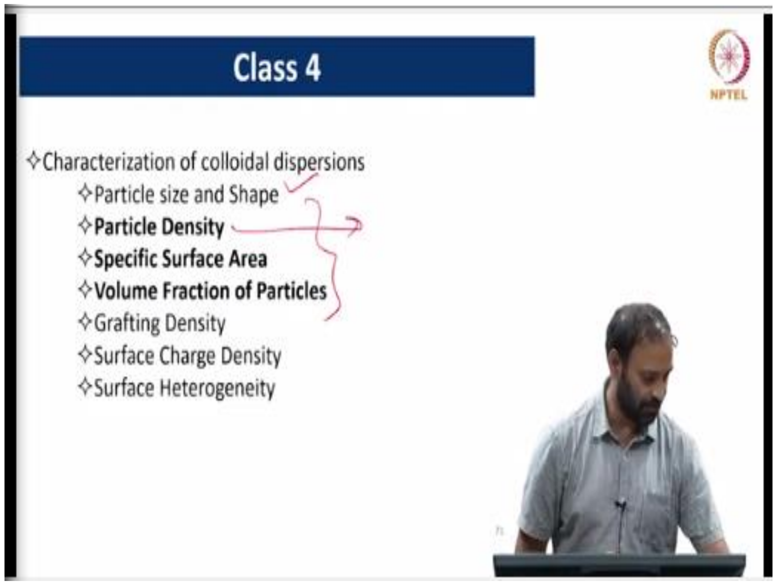

So, now that we have characterized the particles for you know the size and the shape. Let us look at some other parameters that you can use for characterizing the particle. So, I am going to start with particle density.

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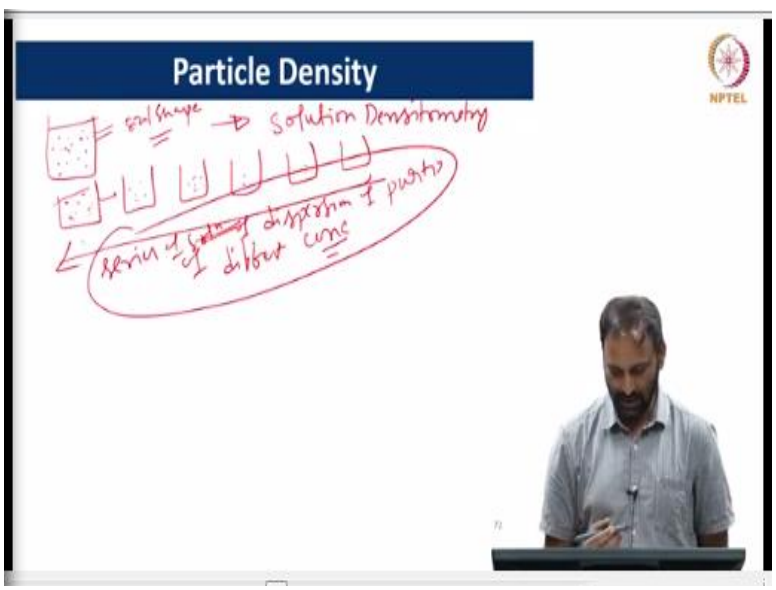

So, question again, so how do you characterize particles for the density, can you think of any method. So, I will give you a sample of colloidal dispersion and I will tell you go and tell me what is the density of the particle, how do you do it. Let us say that I have a container and it has particles, ok and I have characterize these particles for size and shape is done. Now let us look at how do we get the density ok.

Of course there are different methods available in the literature, I am going to tell you a method which is based on what is called as a solution densitometry, ok. In which what you do is I take my dispersion, ok of particles, ok, I prepare a series of solutions where I have particles of different concentrations, maybe a little bit low and maybe without particles ok.

I basically have a series of solutions, ok or series of dispersions if you want to call them of dispersion of particles of different concentration, ok. This let us think a little bit how do we from that how do we get the particle density data. So, what we will do is, I am just goanna rub this off quickly ok. Let us think about.

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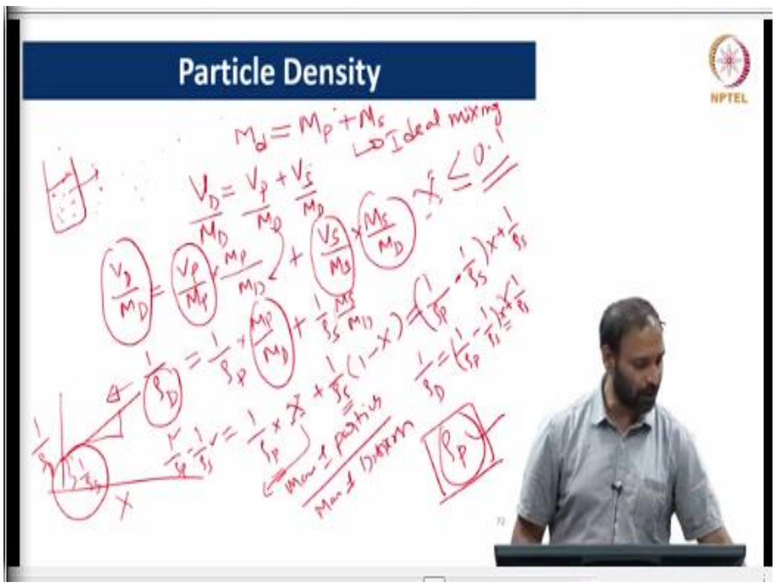

So, if I have a dispersion, ok, if M d is the mass of the dispersion that I have ok, I can write that as mass of the particles are have in the dispersion plus mass of the solvent is that ok right. And this is only true if I am considered what is called as a ideal mixing. Because you could have cases you know where I can mix 2 dispersions or you know 2 fluids and I could have you know change the volume as well, right ok or there could have change in the mass as well, right.

So, therefore you know what I will do is, I am going to say that volume of the dispersion is equal to volume of the particle that I have in the dispersion plus volume of the solvent, right, ideal mixing assumption, no change in the volume. So, what I will do is I will divide everything by mass of the dispersion, ok, I am dividing the entire equation by mass of the dispersion of on both the left hand side and the right hand side.

And V_d by M_D is equal to V_p I am going to divide this by mass of the particle in the dispersion multiply that by the mass of the particle divided by ok. I have M_D here plus volume of the solvent divided by again mass of the solvent multiplied by mass of the solvent again M_D, is that ok yeah a simple manipulation. So, this parameter, right, volume of the dispersion divided by mass of the dispersion that is same as 1 over rho of dispersion ok, that is the density of the dispersion right.

I have a solution ok, I have a dispersion of particles and I have you know if I have a way of measuring the density of the dispersion that is what is your 1 over rho D is equal to this is 1 over rho of particles, right multiplied by M_P by M_D I am just going to keep it the way it is plus this quantity is 1 over rho of solvent multiplied by again I am going to keep the M_S by M_D. This M_P by M_D, that is a mass of the particles in the dispersion divided by M_D mass of the dispersion.

$$M_D = M_p + M_s$$

$$V_D = V_p + V_s$$

$$\Rightarrow \frac{V_D}{M_D} = \frac{V_p}{M_D} + \frac{V_s}{M_D}$$

$$\Rightarrow \frac{V_D}{M_D} = \frac{V_p}{M_p} \times \frac{M_p}{M_D} + \frac{V_s}{M_s} \times \frac{M_s}{M_D}$$

$$\Rightarrow \frac{1}{\rho_D} = \frac{1}{\rho_p} \times \frac{M_p}{M_D} + \frac{1}{\rho_s} \times \frac{M_s}{M_D}$$

$$\Rightarrow \frac{1}{\rho_D} = \frac{1}{\rho_p} X + \frac{1}{\rho_s}(1 - X)$$

$$\Rightarrow \frac{1}{\rho_D} = \left(\frac{1}{\rho_p} - \frac{1}{\rho_s}\right) X + \frac{1}{\rho_s}$$

I can write it as 1 over rho p into multiplied by capital X, where X is the mass fraction of particles you have the dispersion ok. Mass fraction of particles that is mass of particles divided by mass of the dispersion ok plus 1 over rho s into M_S by M_D. It is going to be 1 minus capital X right, which is the mass of the solvent that you have in the dispersion. Because you know the total mass fraction is 1 therefore the mass of the solvent is going to be 1 over 1 - X.

Therefore I can simplify this as 1 divided by rho p into I have rho p here and rho s here - 1 over rho of solvent into X + 1 over rho s, is that ok what is that, now right it is fine, right. So, therefore what I have ended up is a equation which says 1 over rho of d is equal to 1 over rho of particle - 1 over rho of solvent multiplied by X + 1 over rho of solvent, ok. Now what you do is, we will go back to the you know the experiment that we are saying right

I am going to have a dispersion. I am going to prepare a series of dispersions in which I know what is the mass fraction of particles ok. And it is easy to find a mass fraction, right I take a dispersion and I evaporate all the fluid and I made I get the mass of the particles or dispersion right just by evaporating all the fluid and measuring the mass. Therefore the difference in the weights is going to give me what is the X, ok, therefore if I have a series of solutions, if I were to plot**.**

And if I have a way of measuring density of the dispersion that is 1 over rho d, I am able to measure that by using a densitometer. And then if I plot there is a function of X which is the mass fraction of particles in the dispersion, I would get a straight line where the intercept is going to be 1 over rho of s. And the slope is going to be 1 over rho P - 1 over rho s, ok, from the intercept I know what is 1 over rho s.

I can actually get 1 over rho p from that I can actually extract what is rho p which is the density of the particle, ok. This is a very simple way of preparing solutions of different concentrations and then measuring the density of the dispersion. And from that, I can extract out the density of the particle. Typically, the guideline is that if you are working with dispersions, you should consider dispersions of concentration X ok should be less than you know about 0.1 ok.

Anything more than 10% do not use it, therefore when you do densitometry measurements if you consider mass fraction of the particles should be less than about 10%. So, you prepare a series of variations within that range and then measure densitometry and get your particle density ok.

Now it is a simple parameter, right density of the particle is one of the most basic parameter it turns out there is a very useful quantity.

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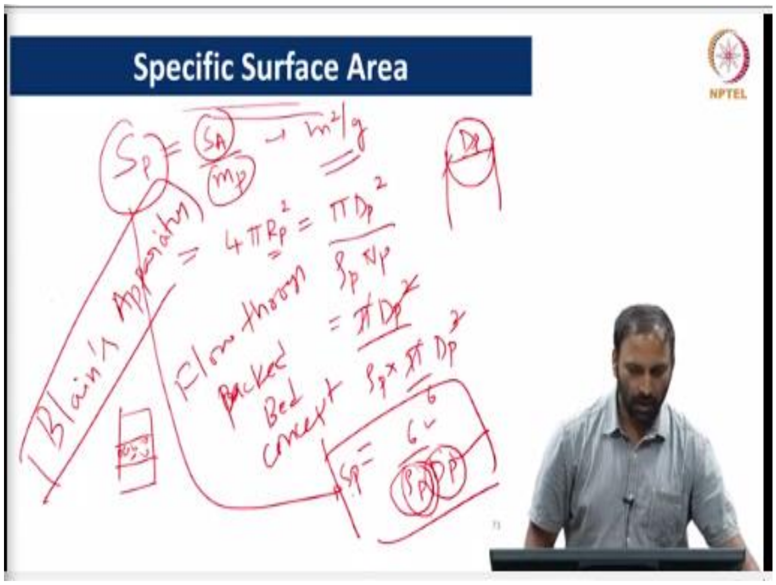

Because I can use that data also to get what is called as a specific surface area right, we define the specific surface area as the surface area of the particle divided by the mass of the particle, right. That is how we are defined and I said this has units of meter square per gram, right. So, therefore, if I have a spherical particle, ok, say that this spherical particle as a density sorry it has a size of Dp here that is your diameter of the particle that you have.

Therefore your surface area is going to be 4 pi R p square that is your radius or pi D p square, right that is your surface area ok divided by your mass of the particle. Mass of the particle is going to be density of the particle times volume of the particle, right. So, this is pi D p square, divided by rho p into volume of the particle is pi by 6 D p q right ok. So, that gets cancelled, I have that also gets cancelled therefore this is going to be 6 by rho p into D p.

$$S_p = \frac{S_A}{M_p} = \frac{\pi D_p^2}{\rho_p \times \frac{\pi}{6} D_p^3}$$

$$\Rightarrow S_p = \frac{6}{\rho_p D_p}$$

So, for a spherical particle your specific surface area is 6 divided by rho p into D p**.** If I have a way of measuring the size of the particle, if I have a way of measuring the density of particle I can actually directly get what is the specific surface area, ok. Of course there are other methods for measuring surface area you would have heard of a technique called Blain's apparatus, have you heard of this. In which what is typically done is you basically make a bed of particle.

So, if you have these particles you make them into a powder, you make a bed of particles and then you basically use the flow through pack bed, concept ok to measure the particle surface area So, we are not going to do that but I think this is one of the simplest way of measuring you know the specific surface area, you measure the size of the particle and your density and then size of particle then you get ok.

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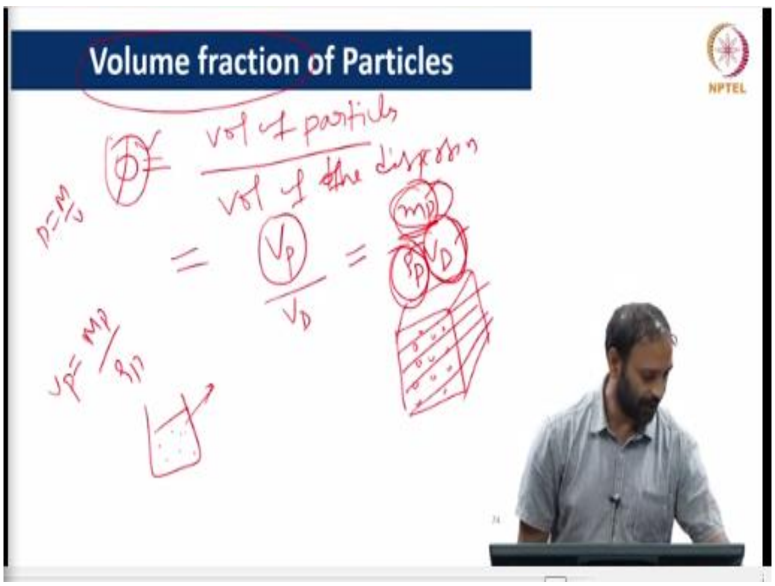

Now, the next parameter phi, ok we have defined this already, so phi is defined as the volume of particles divided by volume of the dispersion right ok. So, the volume of particle is going to be V p divided by the volume of the dispersion, right. And I can convert, so volume of the particle is going to be ok. So, therefore, your V p is going to be mass of the particle divided by density of the particle right.

$$\varphi = \frac{vol\ of\ particle}{vol\ of\ dispersion} = \frac{V_p}{V_D} = \frac{M_p}{\rho_p V_D}$$

So, Vp is going to be mass of the particle divided by density of the particle multiplied by V_D ok. Therefore if you have a dispersion of some concentration, you dry out all the fluid, I can measure, what is the mass of the particle in the dispersion. And I have measured what is the density of the particle again by solution densitometry. And if you know the volume is a dispersion that you are using for your experiment, I can actually plug in all these numbers, I can get the mass fraction, ok.

Again, there are other ways of measuring particle volume fraction you could think about you know if you have. Like for example, you say that you know I have a dispersion that contains particles right ok. So, if this is in a 3-dimensional volume what you can do is I can actually get the images of this container which has these particles and I can get immediate every location.

That means I take a slice I can get what is the basically for every slice I can actually get what is the area of fraction that the particle occupies ok. And I can basically put them together and I can construct a 3-D volume ok you can also do there are techniques like that where you know you can do a 3-D imaging of the entire dispersion. And from that you can calculate you know the volume fraction.

But this is one of the simplest ways of doing it, all that it requires is measurement of the mass of the particle and the density of the particle. And if you know the volume of dispersion that you are dealing with, I can get phi directly from these data, ok.