Particle Characterization

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Module No. # 03

Lecture No. # 12

Morphological Characterization: Nano-particle size analysis

Good morning. Welcome to the twelfth lecture in our nano-particle character, particle characterization course. In the last lecture, we looked at how particle size distributions could be represented as continuous functions and how these continuous functions, could then be analyzed to find parameters like mean size and so on. We also looked at a technique, that is particularly useful for concentrated suspensions, which is based on acoustic attenuation spectroscopy. Again, keeping in mind that, light scattering techniques are predominantly useful for dilute suspensions, the acoustic method gives us a viable alternative, when we are looking at, a more concentrated fluids.

We also need to discuss a little bit about how, or methods of size characterization need to be adopted for nano-particles. So, we will do that in the first part of this lecture and then, we will spend some time reviewing the material that we have covered so far in this course. I will try to pose some questions, that you can use, to test your understanding of the material. So, when we apply particle characterization, particularly size characterization methods for nano-particles, the single biggest challenge, well, there are two. As we saw earlier, light scattering intensity ((falls)) of a particle diameter to the power 6. So, the signal that you would get from a nano-particle, would be very, very weak and in fact, if it is suspended in a fluid, the scattering you get from the molecules of the fluid will be comparable, to the scattering that you get from the particles. So, that noise level will be very high, compared to the signal. But the second challenge is that, nano-particles have an inherent tendency to agglomerate and, and because of that, when you measure the size of so called nano-particles in a fluid, you can never be sure, whether you are looking at the size of an individual particle or a cluster of particles.

And so, the data that you get, the purely quantitative data, must always be questioned, in terms of, whether it really represents the sizes of individual particles in the system or collections of particles. And, some techniques have evolved to be able to do this, but ultimately, the best way for verification is actually, to capture the particles on a slide, look at the slide under microscope and really characterize visually, whether, what the particle size analyzer is measuring as a size of a particle, it is truly the size of an individual particle or whether it is a, due to again, an agglomerate of particles. So, you have to kind of, fall back on s e m, t e m type of techniques, to ultimately validate the results that you get, from a quantitative instruments, such as a particle size analyzer or a particle counter.

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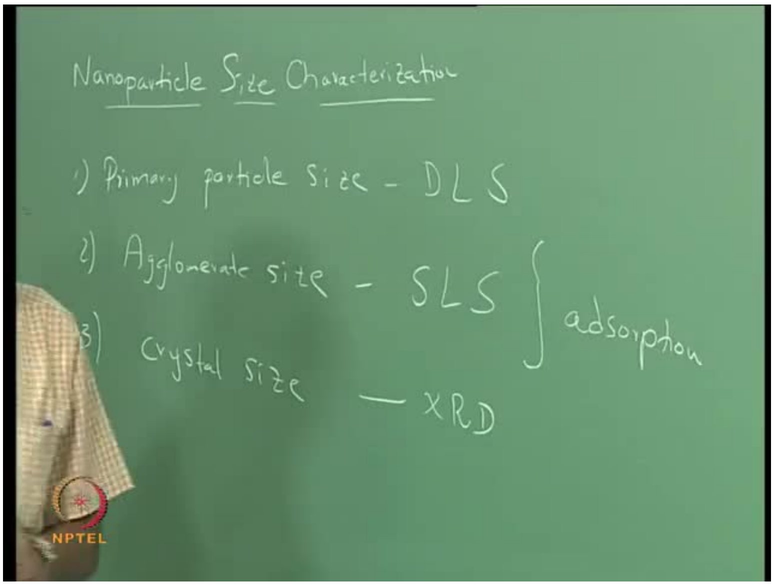

Nanoparticle Size Characterization

1) Primary particle size - DLS

2) Agglomerate size - SLS } adsorption

3) Crystal size — XRD

Now, when we look at nano-particles, such as suspended in fluids, there are really three characteristic sizes that we can talk about. The first is, what we call a primary particle size; the second is an agglomerate size; the third is crystal size. And, corresponding to each of these sizes, there are instruments that are particularly suitable for measuring these various sizes. Crystal size is typically measured using an XRD, X-ray Diffraction Analyzer. Agglomerate size is measured using a technique called Static Light Scattering and the primary particle size is characterized by a technique known as Dynamic Light Scattering.

Now, there are other techniques as well, which are mostly, again, applicable to the agglomerate. For example, methods based on adsorption. So, we will talk about these techniques a little bit. Now, when we look at the difference between an agglomerate and a single particle, the most obvious difference is visual. When you, when you actually look at a, look at a an agglomerate of particles under high magnification, you can see the discrete particles that are included in that agglomerate.

But, you can also tell, by looking at the transport properties of the particle. For example, as fine particles start to agglomerate and become larger clusters, they actually slow down, because, the primary transport mechanism in that size range, is diffusion, Brownian diffusion. And, Brownian diffusion essentially, goes, the rate goes as the inverse of particle size. So, simply by looking at the Brownian diffusion characteristics of whatever it is that you are seeing in the, in the fluid, you can actually assess, whether it is a single particle or an agglomerate of particles. Static light scattering is a, is a technique, where you essentially examine the particle fixed in place.

So, the assumption here is that, the clusters or the agglomerates are large enough, that they are not going to have significant transport rates, or movement rates in the fluid in which they are suspended. So, static light scattering technique is really, only good, for looking at the total agglomerate size. It assumes that, the particles stay in place, which is a good assumption, only, when you start approaching particle sizes of at least 10 nanometers and above. The dynamic light scattering method on the other hand, is one, that actually uses this property of fine particles, to move about in a fairly rapid and random manner.

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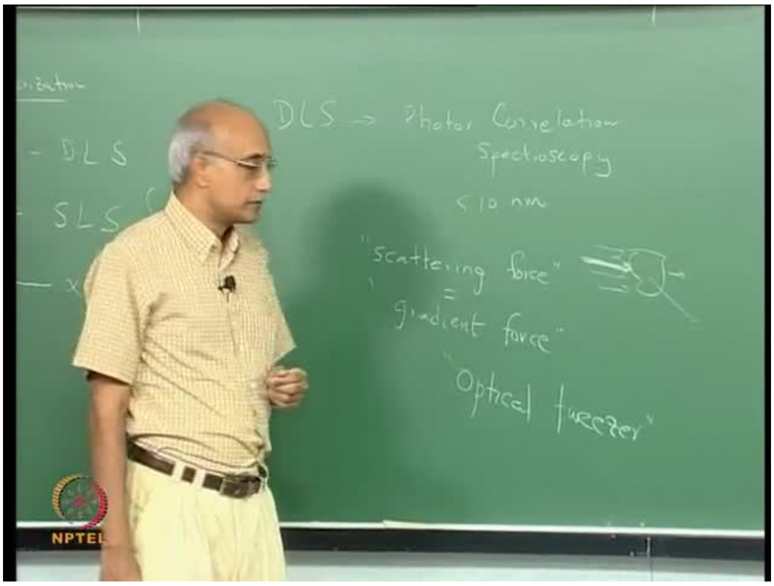

So, what the, the D L S does is, actually, take two successive images and it correlates the images. Actually, another name for this technique is, Photon Correlation Spectroscopy. So, by considering two images that are taken at successive time intervals, and correlating the images, a D L S can actually estimate the size of the instrument. Because you can predict, how far, particles of different sizes will move, within a certain period of time, based on their diffusion characteristics. So, the D L S, indirectly uses the rate at which fine particles move, as a way of characterizing their size. And, this technique is, is very useful for particles, that are less than 10 nanometers.

In fact, if you try to measure particles that are less than 10 nanometers with S L S, or static light scattering techniques, you will make mistakes, because of the fact that, the, the sample you are looking at, is not stationary; it is moving. And, in fact, another problem, in both the D L S range, but particularly in the S L S range is that, when you take a very, very fine particle and you irradiate it with light, what is going to happen to it. Just based on conservation of momentum principles, when a particle is that fine, the momentum exchange is sufficient, to actually cause it to move. So, simply by irradiating a particle with light, you can make it move and this motion, is due to what is known as a scattering force.

So, as, as particles experience incident light and therefore, they scatter the light, they are simultaneously, also dissipating momentum; and therefore, they have a tendency to move in the direction of the incident light. So, if you have a particle sitting here and light is hitting here, yes, it will get scattered, and the measurement of the scattered intensity will give you an idea about the size. But at the same time, there is a very, very small displacement of the particle, in the direction in which the light is being radiated. So, what do you do? What this means is that, your assumption of a particles that is being held static, for you to analyze, it is being violated.

So, the way you handle this, is actually, by providing an equal and opposing force, that will position the particle, where it is. The way you do that is essentially, by providing what is known as a gradient force. Now, gradient force, essentially, is based on the principle that, if the light that you are radiating the particle with, is uniform in its intensity throughout the cross section of the particle, then, there is really no force that you can develop, to counteract this scattering force. However, if you get a very, very sharp focus, so that, the light is actually concentrated in one area of the particle, and then, there is a gradient of the force, away from this one plane, where there is high intensity, then, that itself creates a force.

The existing gradient in the intensity of the incident light, is sufficient to cause a force to develop. So, the idea is, to actually use this gradient force, that is associated with non-uniform transmission of light to the particle, to counteract the scattering force and hold to the particle in place, for analysis. Now, this technique is called the optical tweezer; in fact, as you can imagine, it almost acts like a tweezer. You have equal and opposing forces in two directions, that are holding the particle in place.

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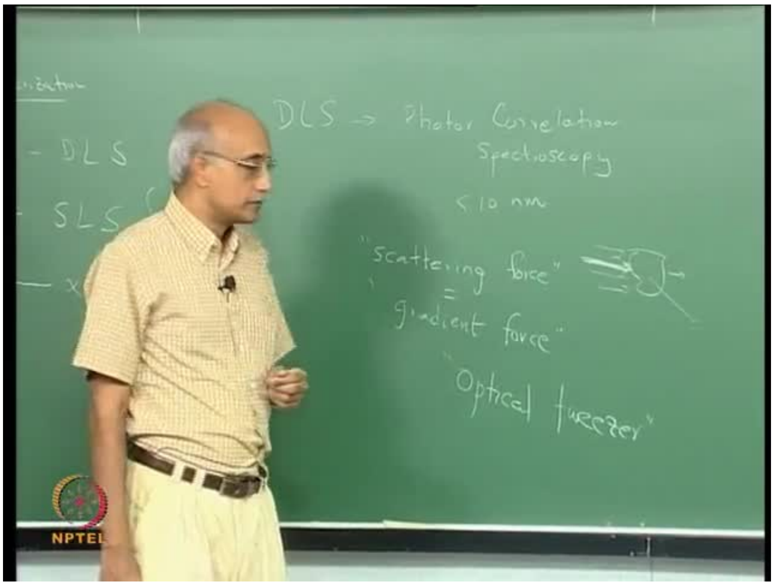

So, once you use this and you hold the particle in place, then, you can apply your static methods of analysis. Again, what this requires, is a well directed and highly focused light beam, whose width has to be smaller than that of the particle dimension, in order for us, to be able to use this gradient force, to balance the scattering force. So, when we are looking at agglomerates, the ability or the requirement that it must be held in place is very high; however, when we are looking at a dynamic light scattering device, which is actually what most of our scattering based instruments are based upon, the instrument automatically allows for a certain movement of the particle by diffusion.

Now, the diffusion force is, obviously, going to be greater than either of these forces. Scattering force and the gradient force, really only come in to play for larger agglomerates; because, for individual particles, if you really have a nano, or sub nano-particle, its diffusional rate of movement is much greater; the diffusional force is much greater than either the scattering force or the gradient force. So, you do not really have to worry too much about these. It is only when the particles get finer and finer, and you actually start getting in to the single particle regime, that you have to worry about these fine adjustments, to hold the particle in place for analysis.

Other techniques that have evolved for looking at particles in this very fine size range are based upon, essentially, exposing the particle or astro-particles to a gas, which gets adsorbed on the surface, either as a monolayer or as several monolayers. For example, you can expose the particle to Nitrogen gas and you allow a monolayer of Nitrogen to be adsorbed on the surface. And then, you desorb the nitrogen, which can be done simply, by heating the, the particle for example. And, you look at the volume of nitrogen that has been adsorbed, which is then desorbed, when you reverse the process. The total volume of the gas that has been adsorbed on the surface, gives you an indication of total surface area of the particle and by assuming sphericity, you can then obtain an equivalent diameter.

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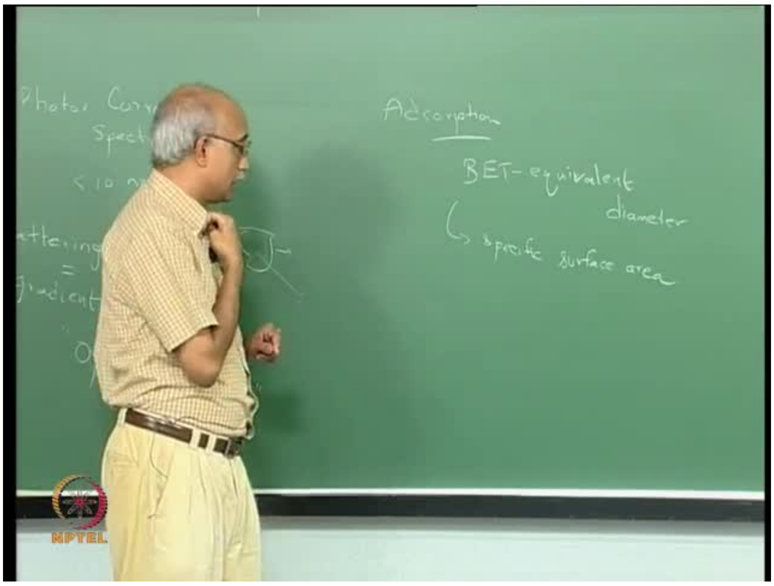

So, this diameter, that you obtained by using adsorption as your technique, it is called the B E T equivalent diameter, where this is named after Brunauer, Emmett and Teller, who were the scientists, that really developed the theory of multi-layer adsorption, extending the previous work by Langmuir, on the Langmuir adsorption isotherm, which assumes monolayer adsorption. Again, we will discuss these aspects in more detail, in a, in a later lecture. But the point is, the B E T equivalent diameter, is a representation of specific surface area of the particle; that is, surface area per unit volume. And, in the case, where we are trying to estimate the size of the primary particle, this technique would really not work very well, because, the diffusion or the adsorption, always occurs along the outer envelope of the agglomerate.

And, but, when you will, when you use the B E T technique, there is the possibility of subsurface adsorption as well. So, instead of, for example, with the Langmuir adsorption, you are only looking at adsorption on the outer surface; because, it is a single, monolayer adsorption. In B E T technique, the gas is essentially, allowed to diffuse into the bulk of the particle or the subsurface of the particle. So, multilayer adsorption becomes possible. So, the B E T technique, can once again, indirectly, predict, or characterize the nature of the surface region, as well as the subsurface region. By looking at the adsorption characteristics, we can actually tell, whether there is, how porous the outer surface is, how much relative surface area there is, in the subsurface region compared to the surface region.

And, all of these data, are actually very useful in terms of deriving some qualitative, as well as quantitative information, about the shape as well as the surface area of the particle. So, again, we will discuss the, the multi-layer versus monolayer adsorption in a little more detail, in one of the future lectures. The use of X R D for crystal size characterization is essentially based on the fact that, when you irradiate the single crystal with X-rays, they interact with the electrons in the, in the crystallite structure and the wavelength, the X-rays get diffracted.

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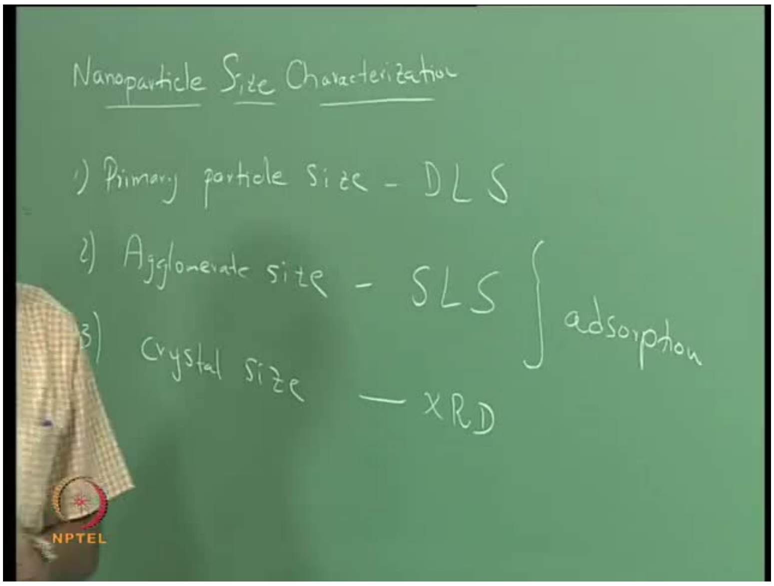

So, by looking at the diffraction pattern, you can actually get an idea, about the crystal structure. And, by using Bragg's law, you can basically, estimate the crystal lattice dimensions. So, the X R D technique is very widely used, particularly by metallurgists, material scientists, to characterize the crystalline structure of a material. But, it can also be used in a very quantitative way, to estimate the size of this crystalline structure.

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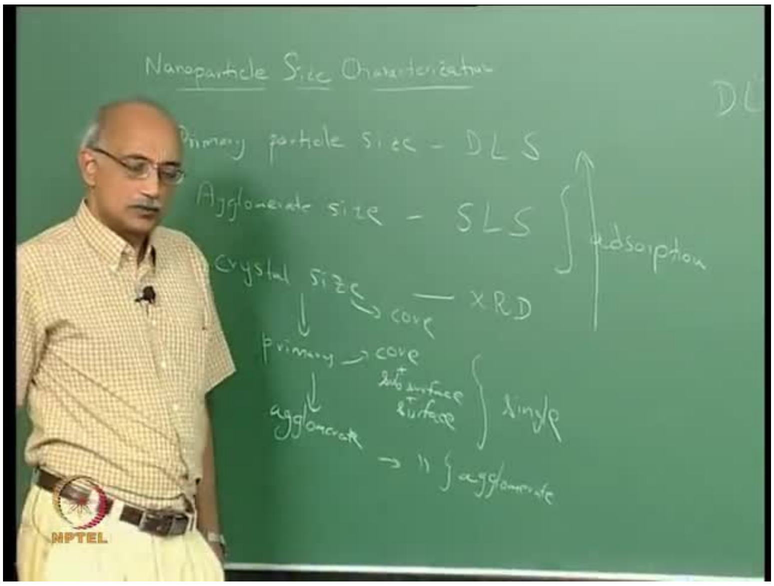

And, if you look at, in a actual magnitudes, the, the size that you estimate, will increase, as you go up this way. In other words, the crystal size will be the smallest, I am sorry;

the crystal size will be the smallest, followed by the primary particle size, followed by the agglomerate size. The crystal, the crystalline structure, is basically, the core of the single particle; the primary size, that you…So, this represents the core; this represents the core, plus the subsurface, plus the surface of a single particle. And finally, the agglomerate size will include all three components, of all particles in an agglomerate of particles. So, depending on your application, you would use, one, two, or all of these techniques, to get the data that you are looking for.

If your primary interest is in the crystal size, you are probably better off using X R D; because, this technique is particularly applicable, to looking at the crystalline structure of the material. Of course, if you have an amorphous particle, then, the use of X R D becomes somewhat questionable; because, X R D is a technique, that is very, very sensitive, to analysis of crystalline materials. But, when we have more amorphous material, the signals that you get from the X R D, tend to be little more diffused, and it becomes more difficult, particularly, to analyze the data in a quantitative fashion, and extract, you know, dimensions and other types of information.

If you are primarily interested in how particles in a suspension look, when they are presented to the next stage in the process, then, the agglomerate diameter is the one, that is most relevant to you; because, that is, in reality, that is how the particles exist. So, in terms of looking at storage, in terms of looking at flowability, dissolution, chemical reactivity, all these product functional characteristics, the agglomerate diameter is the one, that is most relevant. The primary particle size is of interest to you because, if you want to avoid agglomeration, if you want to keep the particles well dispersed in solution, then, this gives you the target size, to aim at. If you have perfect dispersion, and if you have zero agglomeration, then, this is the size, that you should be obtaining, for each isolated particle. So, it is gives you something to shoot at, basically. So, all of these diameters are relevant in different applications, and which of these you choose to measure, really depends, on what you are trying to accomplish with your measurements.

So, particle size measurement, that we have discussed in the last few lectures, preceded by our discussion of shape, is, is the most critical aspect of particle characterization, from a physical viewpoint or a morphological viewpoint. Size and shape are the two most important physical properties of the particle and any discussion of particle characterization has to start with, first, characterizing shape and size. So, that is basically, what we have covered in our lecture so far, and next, we will be discussing, actually, the structure of the particle and also, the way in which particles interact with their surroundings.

But, before we do that, let us take a few minutes, to review what we have covered in this course so far. If you recollect, we started our discussion in the first lecture by examining the why part of it; why should we care about particle characterization; and in particular, we discussed a few applications, where particles play a beneficial role and a few, where they are actually very undesirable in your system and you need to come up with ways, to avoid particles in your, in your process. So, if I were to ask questions of someone who has taken this course, one of the first questions I would ask would be, why? Why should we study particle characteristics? Give me some examples of processes, that are affected by particle characteristics.

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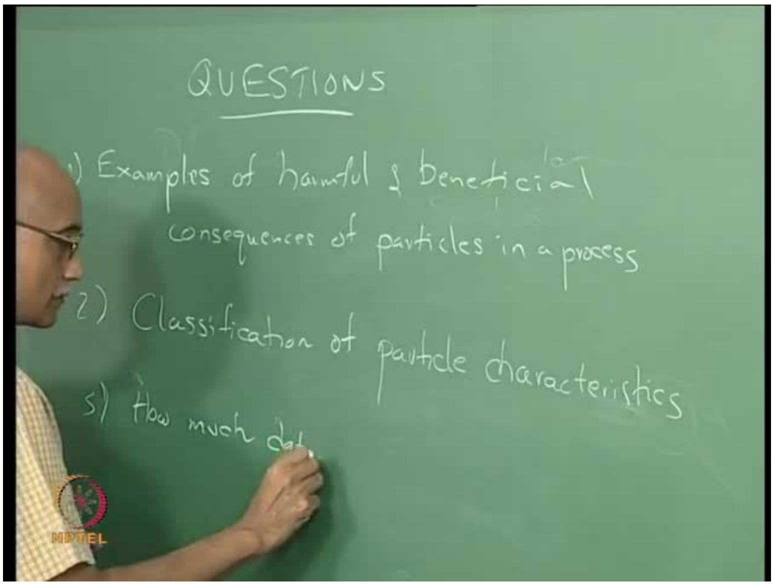

QUESTIONS

1) Examples of harmful & beneficial consequences of particles in a process
2) Classification of particle characteristics
3) How much dat

Examples of harmful and beneficial consequences of particles, in a process. So, if were to ask you for three examples of each, you know, it is, things just pop in to your head, you know, what are some harmful consequences. We talked, a lot about high precision semiconductor manufacturing applications, where particles can actually be a source of defect in your product; hard drives, where particles can get trapped between the head and the disk; or, even human health and hygiene aspects, where ingestion of particles can lead to problems such as toxicity and so on. And of course, beneficial consequences -

nano-technology, the various applications of nano-technology, catalysis, pharma; these would all be illustrations, of where particles do play a very significant, enhancing role in our everyday life. And again, the understanding of the characteristics of such particles, will enable us to design better systems, better products and so on.

Later, we started discussing the various aspects of particle characterization. And, one of the things you should also be aware of is, how do you classify particle characteristics. And, in terms of classification, we said that, the morphological characterization is where it begins and that is, basically, what we have studied so far, in this course. The second aspect is, structural characterization, chemical characterization, interfacial characterization, which is really a representation, of how particles behave, with respect to their environment. And, in fact, the next two classifications that we are going to talk about are, structural and interfacial. Then, we will talk about the, the chemical characterization of particles, and then, the transport aspects. Again, as chemical engineers, there is a lot of interest in looking at, how the transport properties of particles affect both their harmful, as well as beneficial consequences in a process.

And then, we will talk about functional characteristics of particles, looking at some real world applications, of where critical characteristics of particles, actually influence their functional behavior. Then, when we discussed, we started our discussion of shape characterization in a little more detail. And, when we talk about shape characterization, I think, one of the first things you should have clearly in your mind is, when is the information that you have collected sufficient, for shape analysis? How much is the data are enough for shape analysis?

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So, in this context, you should be able to recall, the rate of diminishing returns curve that we drew, where, if you plot number of data points versus precision, in our shape characterization, typically, you will see a curve like this. So, initially, for the amount of data points that you gather, there is a rapid increase in the amount of information that you can gather about the shape of a particle. But then, as you cause, start, keep collecting more and more data, the relative usefulness of the new data will rapidly diminish. So, when you have a behavior like this, as a shape analyst, you have to make a decision on, where do you stop. Do you stop as soon as you have reached here, or do you stop here? Or, do you keep collecting data, until you have reached the finest refinement in the shape that you can obtain? So, that is one of the judgment calls, that as a particle scientist, you may need to make in your shape characterization.

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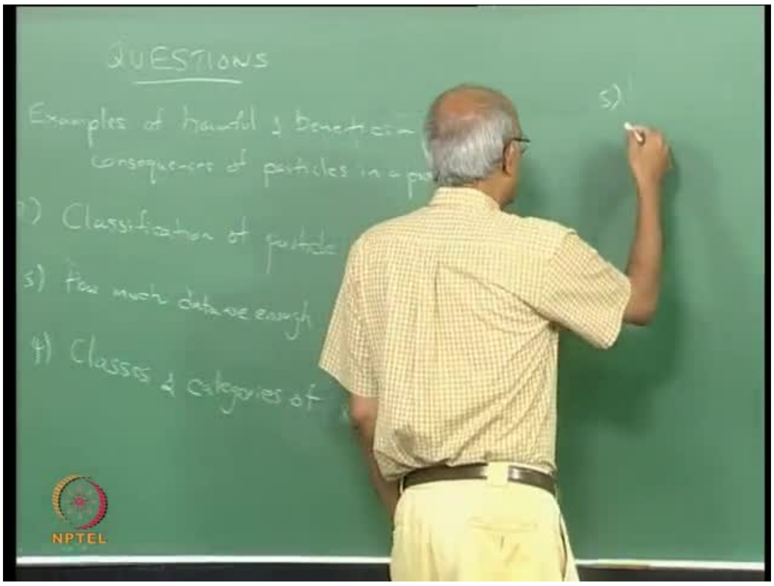

Of course, the, the, the different classes and categories of shape characterization is important for you to know. So, we talked about, essentially, four classes of methods, right. Methods based on single particle analysis, methods based on bulk powder characterization, methods based on mathematical representation of data and methods based on syntactic techniques or verbal descriptors. And, within each of those classes, we had defined further, sub-categories of analyses. So, single particle analysis, we have three methods; one is based on distance between tangents, that are parallel to the contour of the particle. Then, we have the shape comparators method, and the third was, the lengths of specific intercepts of the particles.

Under bulk powder characterization, we talked about the, the Beddow method or the tap test, where we looked at the apparent density to tap density ratio. But we also said that, other parameters such as flowability, compactability, porosity can also be used, as indirect measures of shape, in, in shape distribution, in a population of particles. And then, the third class of methods, which is the mathematical methods. Again, three major classifications; one is simply, the, the digital characterization, and representing the shape of the particle, essentially, as a three dimensional matrix map, which can be compared against other similar maps. The second is, polynomial fits; taking the data and fitting a continuous function, through the discrete data points, in order to obtain a functional representation of the profile of the particle. Then, the third method was, Fourier analysis, where you obtain certain distinctive or characteristic peaks, corresponding to a particular shape and compare it with spectra in your library, or, or, in your reference, and then, assign a shape to the particle that, that matches best from your reference spectra.

And finally, again, the, the verbal descriptors are usually not used as an independent method, but, as a supplement to the previous three methods. Once you have obtained a shape, in order to communicate it easily to other people, you start to call it something. So, you may want to say things like disc like, or rod like, or spherical, or so on. So, these are essentially, establishing a grammar of describing the shape of a particle in words, which will facilitate communication of this information with other researchers in this area. So, these were some of the questions. And then, of course, in terms of shape analysis, given that you have such a wide variety of methods available to you, it is very important to develop essentially, a systematic method for doing shape analysis, which is also basically, based upon pattern recognition.

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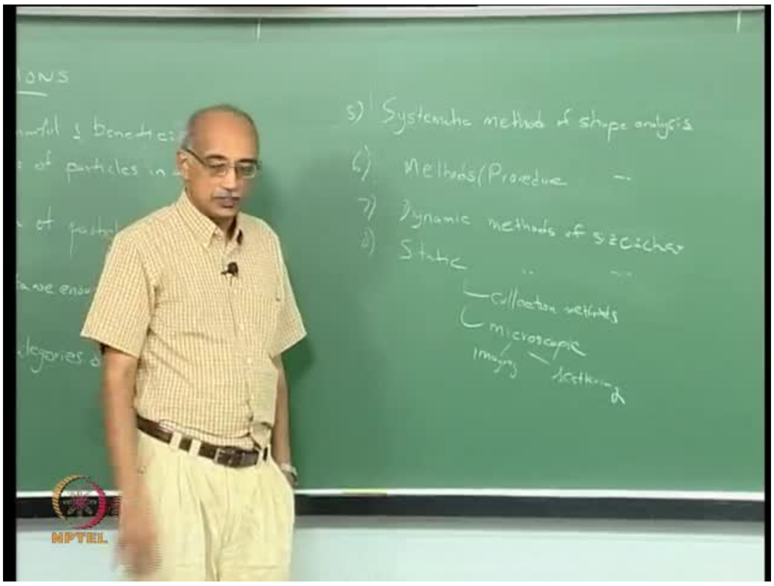

And if you recall, we based, we broke this down into two aspects; the first is, in order to obtain the shape of a particle, you have to first define a class of particle shapes, to which this particle could be compared against. And, secondly, you have to develop decision criteria; you have to establish certain rules that say that, when I compare this particle to one of my reference particles, I will ease, I will use these rules to say, whether this particle is closest in shape to this or this, or this, from your reference library. And, once you have developed these criteria, and a set of reference documents, or reference shapes, the next aspect is, how do you actually go about your shape assessment procedure? What are the steps? So, the first step is, a general inspection, low magnitude magnification and so on.

And then, at each stage, the inspector makes a decision, on whether there is sufficient analysis done; can I stop here, or should I keep going? So, the second step, is to separate the data into relevant and irrelevant data, analyze the relevant data, and decide, again, sequentially, how far you want to go. And, so, this gives you the basics of a system for a particle shape analysis. And then, we talked about various methods of shape analysis, which are used; methods, or procedures for shape characterization. And here, we talked about methods, such as the, the membership roster concept was one; the common property approach, the property clustering approach, were three of the methods that were commonly used for shape assessment.

And, we also talked about the various iterative schemes that are used, right. The distance function, the maximum likelihood function, we talked about trainable classifiers in a deterministic sense, and trainable classifiers in a statistical sense. So, these are the iterative algorithms that are used, to essentially converge to a shape and the, the set theory based analysis, then allow you to home in on a particular shape, that you can assign to the particular particle. So, the combination of all these, gives you a way, of finally deciding, what is the shape of the particle. That is the very important first step, because, you really cannot determine its size, unless you determine shape, and vice versa.

In fact, when we talked about size analysis, the first point I made is, many of the properties of particles that you measure for shape analysis, also yield size. So, shape is essentially, taking ratios of, for example, dimensions in two directions. You take the ratio, it gives the shape. If you take the actual, absolute numbers, it gives you the size, right. So, many measurement methods are common for shape and size analysis; however, size analysis, in particular, is done in two modes; static mode and dynamic mode, right. And, so, we, what are the, some of the dynamic methods of size characterization? We talked about, methods such as sieving, sedimentation, centrifugation as methods, that essentially set particles in motion, and by looking at their characteristic, their dynamics, you assess the shape of a…These methods are typically used, to obtain, not single particle sizes, but rather, the size characteristics of a population of particles.

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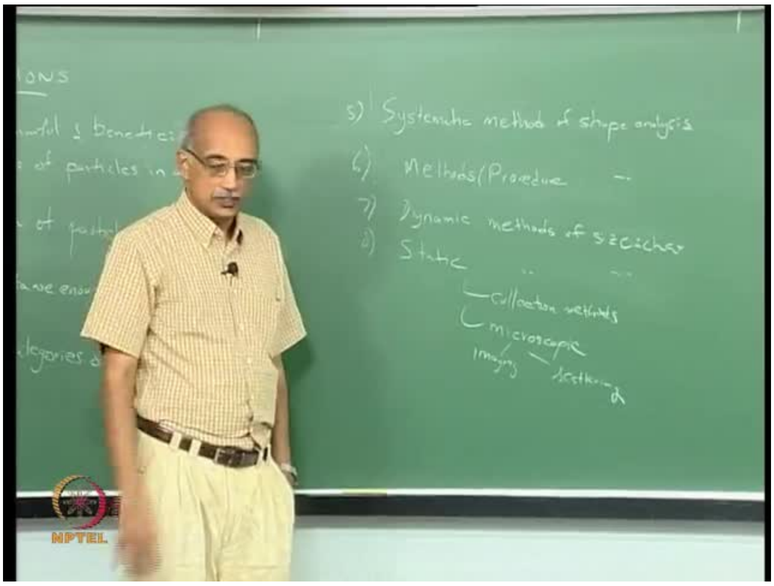

And then, we have static methods of size characterization, which begins by collection methods, right. In order to analyze particles in static mode, you first have to collect them. And, we talked about various methods, in which particles could be collected for size analysis. So, methods such as, impactors, settlers, impingement devices, filters, isokinetic samplers, thermal devices, which use thermophoresis, electro static devices, that use electro static forces; of course, you can use magnetic force fields for collecting particles. Of course, this optical tweezer method that we talked about today, is another example of a collection method, which provides, which makes available, a sample of particles for you to analyze.

So, again, it is important to understand the role that, these methods of collecting particles plays. Without that, you really cannot proceed to the next step, which is the actual methods of analysis. And here, we said that, microscopic methods are really the most fundamental way of characterizing particle size. You look at the particle, either with naked eye, or with a magnifying glass, or with an optical microscope, or an electron microscope, and, as we go through this sequence, you keep increasing your magnification, at which you are analyzing the data.

You can irradiate the sample using various sources of light. You can use visible light, or, you can use u v light, or, of course, you can use electrons. And, each one will show up particles with different features and characteristics. We also said that, this type of analysis of particles on a surface could be done, either in imaging mode, or in scattering mode. So, image analysis, you will irradiate the surface with an energy source and essentially, capture the image of the surface, with particles on it, in some device, and then, do your analysis offline; whereas, surface scattering techniques are based upon scanning the surface with, for example, a laser beam and looking at, how the laser beam is scattered at various locations on the surface and thereby estimating the particle coverage on the, on that surface.

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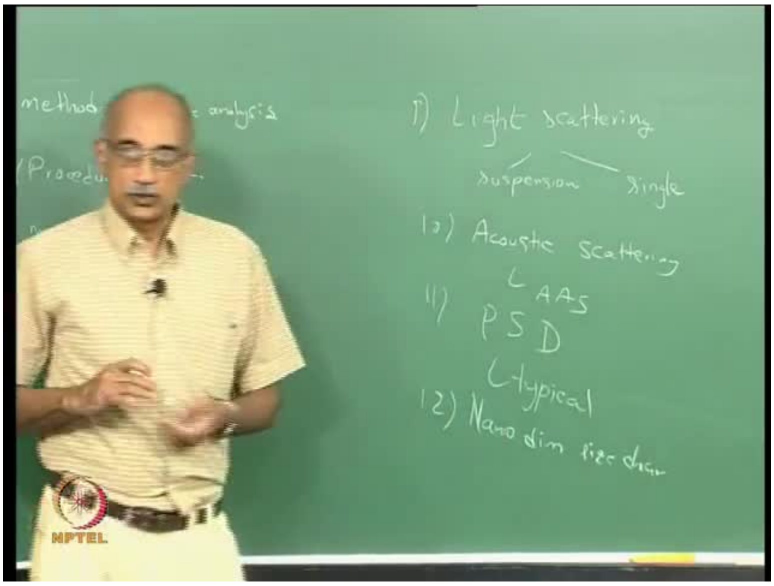

Then, again, under static methods, we started to discuss light scattering based techniques in more detail, and here, we actually covered two cases. You can look at light scattering or attenuation in a suspension using the Beer-Lambert law, which looks, which, which describes, how a light signal is attenuated, as it passes through a suspension of particles. And, we also looked at it, for single particles, where the scattering of light from single particles was divided into the Rayleigh regime and Mie regime and scattering laws were established, in each of these regimes.

Now, it is not necessary that, you have to remember the actual equations that describe scattering intensity in these various regions; however, I mean, that kind of information, you can always look up, you know, on the internet, if you want; but, what, what you should be able to recollect of offhand, is the size dependence or the wavelength dependence or the distance between the observer and the particle; what are the actual parametric dependencies? For example, in the, in the Rayleigh scattering regime, the scattered light intensity is proportional to, the incident light intensity, it is proportional to particle diameter to the power 6; it is inversely proportional to the square of the distance between the observer and the particle; and, it is inversely proportional to the fourth power of wavelength. So, these, you should be able to recollect and it has, a reasonably complex dependence on the refractive index.

Whereas, in the Mie scattering regime, it is still proportional to incident light, but the dependence on size, is not so obvious; and the dependence on wavelength, it is actually, it is now in the numerator, right, goes as r square, I mean, lambda square. And then, r squared is still the same. So, the, whether you are on the Mie regime or the Rayleigh regime, the scattered light intensity does drop off, as a square of the distance between the collecting device and, and the location, where the scattering happens, which actually, gives you some important clues, about how close the optics have to be, to where the scattering is taking place.

And then, we looked at acoustic scattering methods; in particular, the acoustic attenuation spectroscopy technique. Again, the key difference is, this is suitable for dilute suspensions and this is suitable for concentrated suspensions. And, of course, we looked at particle size distributions, how to represent them as a histogram, using tabulated data; how to represent particle size distributions as continuous functions. And, we also looked at some typical particle size distributions, such as, the normal, log-normal and power log distribution and so on. And finally, today, we concluded, by looking at nano-dimensional size characterization, which requires certain special techniques to be used. So, this in net, is a summary of the various topics that we have covered, in this course so far.

Now, the sample questions I have given, are all qualitative in nature, discussion oriented; but, each can also be stated in a, in a quantitative way. For example, you could be given a size distribution of a, you know, various size channels and the corresponding counts of particles, and we can be asked to plot the data and verify, whether it follows one of these standard distributions. You can be asked to do statistical analysis of the data. So, all of these, we should be able to handle again, after you have covered the, the materials in this course.

And, of course, even, in aspect, such as, for example, dynamic methods of size analysis, I expect that, you, students, who take this course, have a background from, from their undergraduate courses, and their laboratory training, on how sieve analysis works, for example, or how sedimentation works. So, you should be able to recollect those details. So, let us stop this discussion at this point, and again, we will begin the, the second part of this course, by talking about structural characteristics and interfacial characteristics of particles. Any questions? See you at the next lecture.