Powder Metallurgy
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Lecture - 24
Dynamic Light Scattering - 1

Hello everyone, and welcome back to this lecture series on Powder Metallurgy. So, right now we are on this topic of particle size measurement. And, in the last couple of classes we have discussed about how the particle size data is collected and how it is represented. So, we have seen that when you collect the data and present it, there should be a basis on which the data has to be presented.

Now, the two techniques that we have chosen to demonstrate this basis are: the weight basis or the sieving method and the microscopy technique or the population based method. These two techniques have their own limitation, especially with regard to the particle size range. These techniques are mostly limited to narrow particle size range.

For example, if you talk about the sieving method, it is difficult to make smaller screens. And even if you make them it is difficult to use, because the smaller particles will tend to agglomerate and it will be difficult to make them pass through the smaller openings that you have in the finer sieves.

Similarly, in the microscopy technique, if you have smaller particles and if they form agglomerate it will be difficult to distinguish the individual particles and therefore, it will be difficult to measure their size. Therefore, the particle size range which can be measured by these techniques is limited.

So, therefore, we need to find out alternative techniques which are more capable and can overcome such limitations. In this class, we are going to talk about one such technique which is a widely accepted method for particle size analysis, due to its adaptability to a broad range of particle size and sample types.

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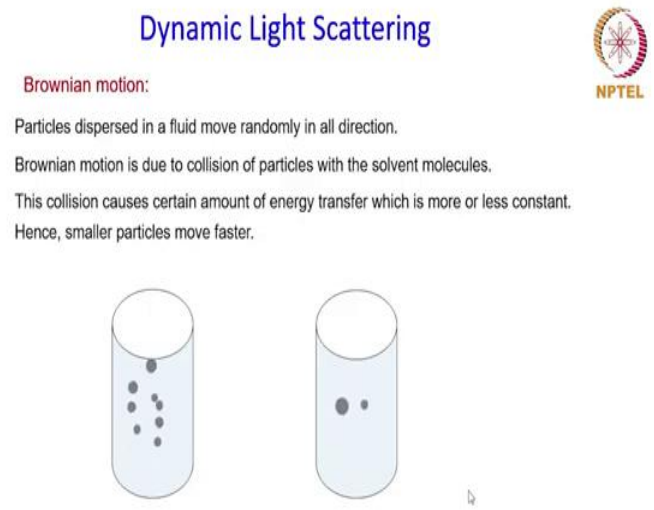

The technique is called dynamic light scattering or DLS in short. This technique uses the scattering of light by the particles to measure the particle size and the size distribution as well.

And it is a common practice to disperse the particles in an appropriate solvent and get a good suspension which is used to derive the particle size. Now, when the particles are suspended in a liquid they are not stationary and they move in random directions. Such motion of the particles in the solvent is known as the Brownian motion. This motion arises due to the collision of particles with the solvent molecules. The collision causes certain amount of energy transfer which is more or less constant and therefore, the smaller particles will move faster compared to the larger ones.

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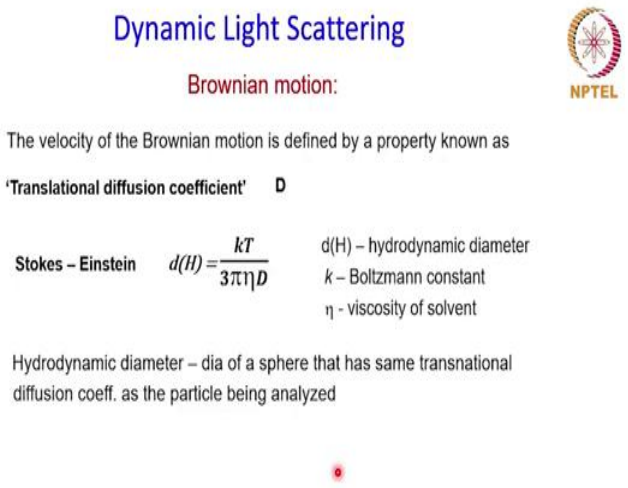

The velocity of the Brownian motion is defined by a property known as translational diffusion coefficient, written as D. And the D is related to the size of the particles by the Stokes-Einstein equation which is given as follows.

$$d(H) = \frac{kT}{3\pi\eta D}$$

Where, d(H) is the hydrodynamic diameter.

The particle size is defined by this hydrodynamic diameter; k is the Boltzmann constant and η is the viscosity of the solvent. The hydrodynamic diameter, d(H), is defined as the a diameter of a sphere that diffuses at the same rate as the particle being measured. So, that is how the size of the particle is defined. Wherein all the parameters such, as k, T (the absolute temperature) and η are known. So, if we can derive this translational diffusion coefficient D, then this particle size can be obtained from this equation.

In the dynamic light scattering technique, we will essentially try and measure this diffusion coefficient, so that we can use it in the Stokes-Einstein equation to derive the size of the particles. So in order to understand how that is done, you need to first understand the effect of the Brownian motion on the scattering of light by the particles.

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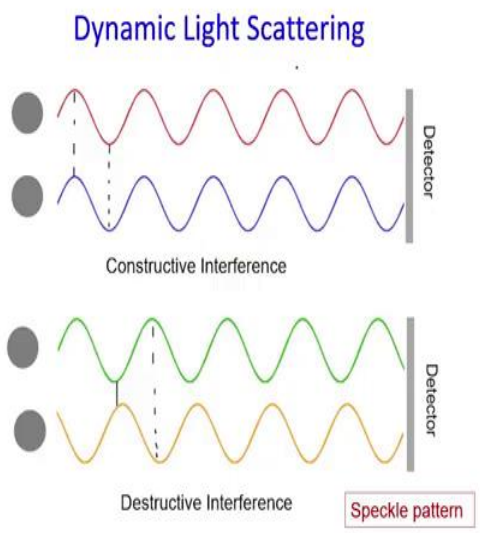

Let us consider two scattered beams of light (slide above). So, in this case (upper image) you can see that these two beams of light are in phase in the sense that positive to positive and negative to negative matches exactly. This kind of waves are known to be in phase and their intensity at any given point of time will be added to each other. And as a result of that, if you have the detector over here (slide above), the intensity which is received at the detector will be enhanced. And therefore, this kind of interaction between waves is known as constructive interference.

On the other hand, you can have two waves one like this and the other one like this (bottom image), wherein we can see that the negative is coinciding with the positive for these two beams. So, in this case, these two waves will cancel out each other since the negative is coinciding with the positive and therefore, the intensity which is received at the detector will be 0. And this kind of interference is therefore known as, destructive interference.

So therefore, the intensity which is received at the detector from the particles will form a pattern; where the constructive interference will give rise to the bright spots in that pattern and the destructive interference will give rise to the darker spots. And this kind of pattern is known as a speckle pattern.

Now, if these particles are static then the intensity of this speckle pattern will also be static or constant. The intensity will not be a function of time; it is going to remain constant because, the conditions are static.

But when the particles are dispersed in a fluid, which is often the case for the particle size measurement by the DLS technique, the condition is dynamic because these particles are in Brownian motion and as a result of that their positions with respect to the detector are continuously changing. So, the conditions here are dynamic and hence the name dynamic light scattering.

So the intensity which is being received at the detector will fluctuate, as opposed to the static condition where the intensity remains constant. So this intensity fluctuation is recorded by this technique in order to obtain the particle size by deriving the translational diffusion coefficient.

So in order to derive the translational diffusion coefficient from this intensity data, we need to see how this intensity varies and what its relation is with the particle size.

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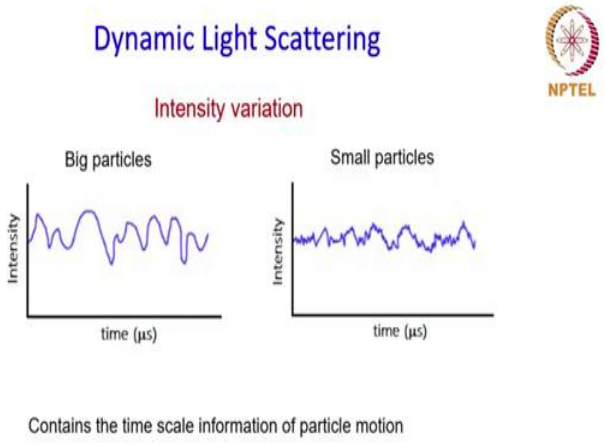

The intensity variation for the big particles (slide above) is slower or the frequency of the intensity fluctuation is lower. And on the other hand, for smaller particles, the intensity fluctuation is quicker or the frequency of this fluctuation is higher. That is how the particle size is related to the intensity fluctuation.

And the intensity fluctuations contain the time scale information of the particle motion. And from this information we can actually derive the translational diffusion coefficient and then use it in the Stokes-Einstein equation to derive the particle size.

So that is the idea behind this technique, to capture this intensity variation and use it to derive the particle size. However, in order to derive these intensity fluctuations certain method has to be used to derive the useful information out of this that can be finally used to derive the particle size.

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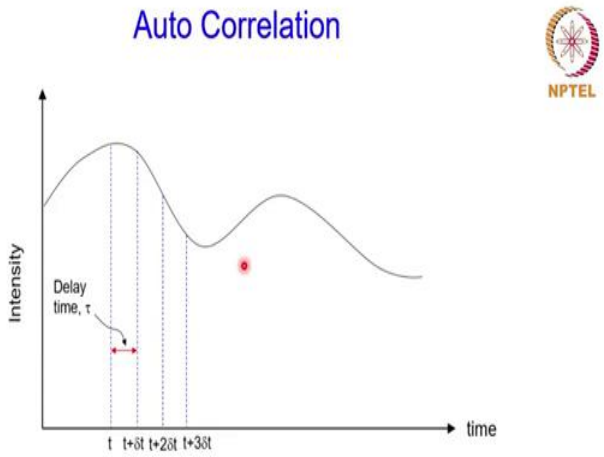

The method which is used to derive this is known as auto correlation. So, let us see about the autocorrelation function. Let us say, you have a signal like this (slide above), and there is some variation in the intensity (we are trying to capture the intensity variation with respect to time). Now, the auto correlation is derived on the basis of comparing this signal at a particular time t with the signal after a time interval δt.

So if you compare the signal intensity after a particular time interval δt with the original signal at time t, then you would be looking at how this signal at time (t + δt) compares with the original signal at t.

If it compares well then you can say that the correlation between the two signals is good. So that is how the correlation is derived when you compare the intensity of the signal after a particular time interval with that of the original signal at time t. So here, you can

see that the correlation of the original signal and the signal after a very small time interval δt is quite good (slide above).

And now if you increase this time interval let us say, to (t + 2δt), now you can still see some correlation, but as the time interval has increased the correlation has decreased. So if you keep on increasing this time interval, the correlation will keep on decreasing. And, the time interval across which the signal is compared with the original signal, the interval, is known as the delay time and it is written as τ.

So, if you continue to compare the signal at larger and larger time intervals, there will be a time when the correlation will be completely lost. That means, if you take time as a function and if you compare the signal from time at 0 to time at infinity, then you can see a decay in the correlation in this manner (slide below).

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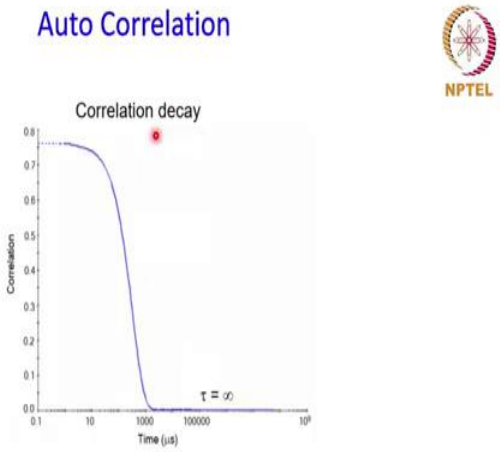

In the beginning, at time t = 0, the correlation is quite good. And as you increase the time interval, the correlation will decrease and at time infinity, when the time interval is large, the correlation is completely lost.

And one thing that you should note over here is that the time infinity is not really a very large time, because here we are talking about time intervals in microsecond or even nanoseconds. So a couple of seconds can be considered as the time infinity in this particular time scale that we use for doing DLS experiments.

The correlation function is the essence of the DLS analysis that will ultimately lead us to the particle size. So, to derive the decay in the correlation, there is an autocorrelation function which is first derived.

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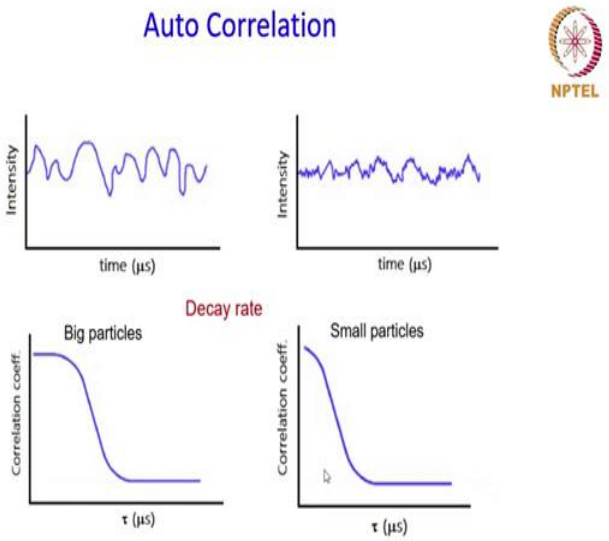

It is about the decay in the correlation or the decay rate that we are talking about. And we have already seen that the intensity fluctuations for the bigger particles are smaller, that is, the frequency of these fluctuations is smaller compared to that for the smaller particles. And therefore, the decay in the correlation will be slower in case of the bigger particles; that means, the decay rate will be smaller for bigger particles. On the other hand, for the smaller particles, because of the high rate of fluctuations, the decay rate will also be higher and the correlation will be quickly lost.

So, this is how first of all the small particles can be distinguished from the bigger particles. And this in fact, forms the basis for the particle size distribution that can be obtained from this particular technique.

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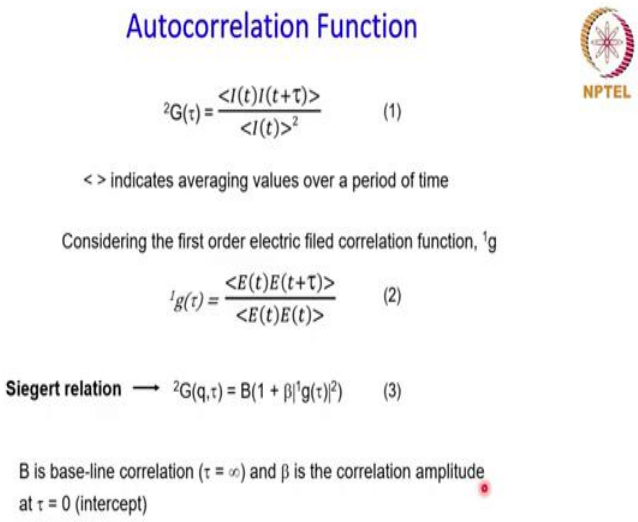

Now, as I said, we need this autocorrelation function to be derived first. So, this function is defined as a second order correlation function which is given here in equation below.

$$^2G(\tau) = \frac{< I(t)I(t+\tau) >}{< I(t) >^2}$$

Where I(t) is the intensity at time t and I (t+τ) is the intensity after a time delay τ. We are comparing the intensity at time t with that after a particular interval τ. The superscript 2 in the above equation indicates a second order correlation function. So, the second order auto correlation function is given by the above equation. And the pointed brackets indicate averaging values over a period of time. So, these values are actually averaged out over a period of time which is used during the experiments.

Now, if you consider the first order electric field correlation function ^{1}g in the equation below, the superscript one indicates first order.

$$^1g(\tau) = \frac{< E(t)E(t+\tau) >}{< E(t)E(t) >}$$

So, this electric field is the electric field of the scattered light beam and 'I' will be the intensity of that electric field.

Now, using this first order correlation function, the second order correlation function can be written as below:

$$^{2}G(q,\tau) = B(1 + \beta\left|\,^{1}g(\tau)\right|^{2})$$

Wherein, B is the baseline correlation; that is, the correlation at time infinity and beta is the correlation function amplitude at $\tau = 0$; that means, beta is the intercept.

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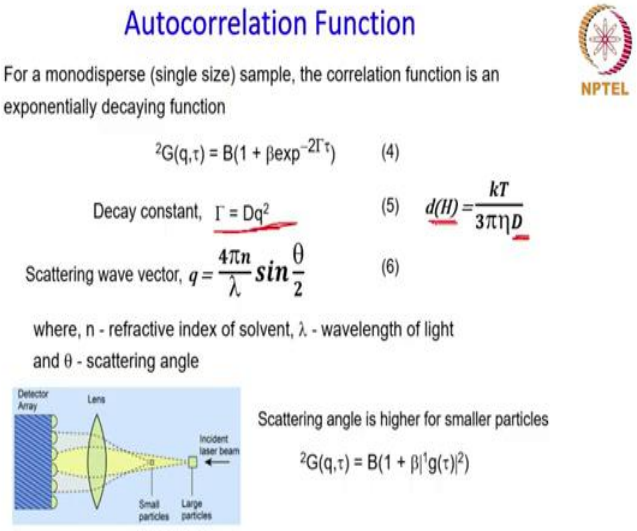

Now, if you have the mono dispersed sample; that means, a sample having a single size, the correlation function will be an exponentially decaying function which can be given as follows.

$$^{2}G(q,\tau) = B(1 + \beta exp^{-2\Gamma\tau})$$

$$\Gamma = Dq^{2}$$

So now this becomes exponential, as you can see from this exponential term, where Γ is known as the decay constant or the decay rate. And it is related to D the translational diffusion coefficient and another parameter q in this manner through the equation given above. q is known as the scattering wave vector which is given as follows.

$$q = \frac{4\pi n}{\lambda}\sin\frac{\theta}{2}$$

So, this contains the scattering angle θ, as well as the wavelength λ, of the light. And the other term that you see over here is n, which is the refractive index of the solvent which is being used to disperse the particles.

So, what it essentially means is that the order correlation function or the intensity variations are measured across a wide range of θ. And when you do that and use that intensity data in the auto correlation function, it will give you the intensity variation for particles of different sizes.

And, that is how the particle size information can be derived from this autocorrelation function, because it contains that size information and also the scattering angles. And, it is also known that the scattering angles for the smaller particles are higher compared to the larger particles. The smaller particles scatter light at larger angles compared to larger particles, as you can see from this particular diagram (slide above).

And for a poly-dispersed sample which contains particles of different sizes which is generally the case, the generic form of the auto correlation function can be used

$$^{2}G(q,\tau) = B(1 + \beta\left|\ ^{1}g(\tau)\right|^{2})$$

Where this term that you see over here ($\left|\ ^{1}g(\tau)\right|^{2}$), is the sum of all the exponential decays contained in the autocorrelation function.

So, to summarize we can say that the translational diffusion coefficient D which is obtained by the auto correlation analysis can be simply put into the Stokes-Einstein equation to derive the particle size.

And the streaming feature that this technique offers, that is, the suspension of the particles and the associated Brownian motion, will also allow us to derive the particle size distribution data from this apart from the particle size. So that is the beauty of the technique that you not only get the particle size, but you can also get the particle size distribution quite easily from the same data.

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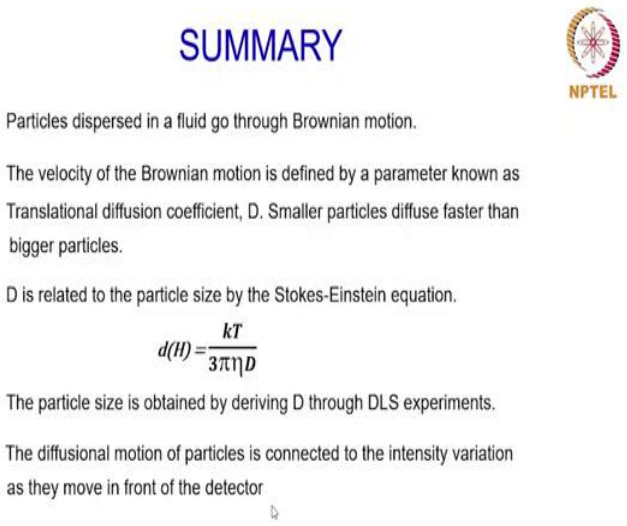

So, it is time for us to summarize today's lecture. So, today in this lecture we have learned about the basic principle of the dynamic light scattering technique; which is a well known method for measuring particle size and size distribution.

So today, we have learned that particles dispersed in a fluid go through the Brownian motion. And the Brownian motion of the particles plays a very important role in the DLS technique. The velocity of Brownian motion is defined by a parameter known as translational diffusion coefficient, and we have also seen that smaller particles diffuse faster than the bigger particles.

The translational diffusion coefficient D is related to the particle size by the Stokes-Einstein equation which is as follows;

$$d(H) = \frac{kT}{3\pi\eta D}$$

All the parameters except D is known. So, if we can derive D, the particle size d(H) can be obtained using this equation.

So, this is what is being measured by the DLS experiments. D is measured and as I said, using this equation the particle size is derived. Now, the diffusional motion of particles is connected to the intensity variation as the particles move in front of the detector. And

this intensity variation forms the basis of the derivation of this parameter D, from the intensity data which is recorded by the DLS instrument.

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The intensity varies because of the Brownian motion since the particles change their position with respect to the optical detector as a function of time. And as a result of that the intensity which is captured at the detector keeps on changing and this is recorded by the DLS instrument and is converted into the size data.

And the method which is used to convert the intensity information into size information is known as the auto correlation method; it basically uses a second order correlation function to define the intensity variation. And then from that autocorrelation function, the decay constant Γ, which is related to the scattering wave vector, q, is derived and from this, the diffusion coefficient is obtained, because the decay constant and the wave vector are related through the translational diffusion coefficient.

So, once D is derived with the help of the autocorrelation, it is used in the Stokes-Einstein equation and the particle size is obtained. Now we have seen that the intensity data can be collected across a wide range of scattering angles. So this allows the instrument to capture the intensity data for a wide range of particle size and we have also seen the smaller particles diffuse faster and scatter with larger angles compared to bigger particles. So therefore, the particle size distribution data can also be derived easily from the DLS data.

And with that, we come to the end of this class; but there is more to come on this topic. So I will see you again soon.

Thank you for watching.