Interfacial Engineering

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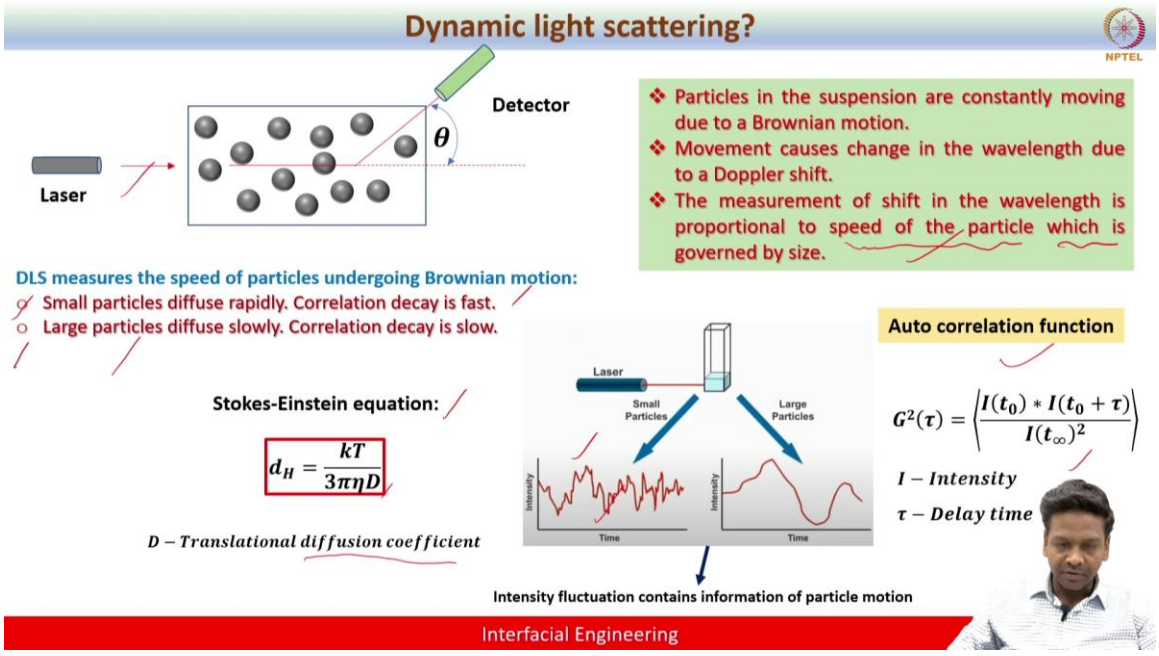
Lecture-40

Demonstration of zeta potential measurements

Dynamic light scattering basics to perform particle size distribution analysis, method of cumulants, Siegert equation;

Welcome back. So in this video lecture, we will look at the demonstration of zeta potential measurements using zeta sizer. With this lecture, we will come to an end of the module 4 as well as the course on interfacial engineering. So let us first look at some of the basic principles of dynamic light scattering and then we will move on to the demonstration part. Let's begin.

Time: 0.55mins



Right, so dynamic light scattering basically help us determine the speed of the particle, okay, which is again useful for us to calculate the diffusion coefficient, translational diffusion coefficient, which is again, you know, used to calculate what is known as

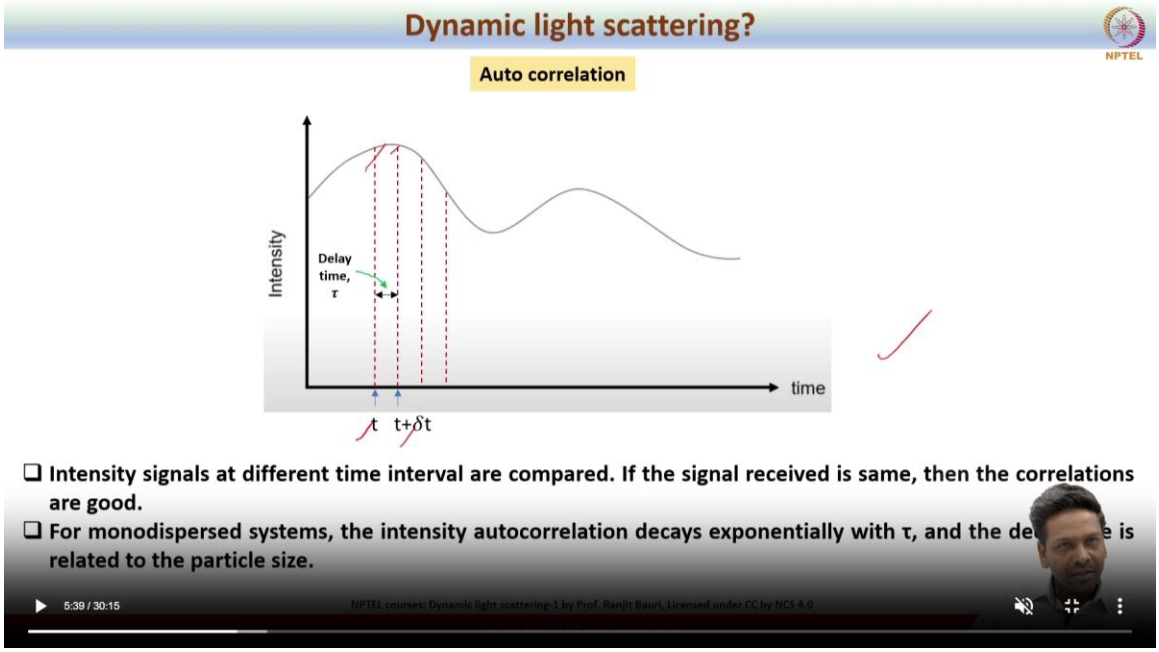
hydrodynamic diameter of the particle based on the Stokes-Einstein equation under certain assumptions, okay.

So basically, what it does is whenever you shine a laser light, it strikes the particle surface. So particles are, I mean, you know, responding to the Brownian motion, right? So there will be the particles will be constantly moving around and they will scatter this light. And the detector which captures this information and then by processing this data, we will be able to get the, what is known as diffusion coefficient. So basically when you shine the laser light, because the particles are constantly moving around, so more one or more particles will scatter the light okay because of which there will be change in the intensity okay so for example so as you know there is something called doppler shift okay so basically it will the wavelength it will there will be a shift in wavelength because of the doppler effect okay and that is proportional to the speed of the particle okay as the particles are moving around the wavelength of the light we you know continuously change so there is something called constructive interference and destructive interference okay whenever these particles scatter the light and if it is if the scattered light are in phase we call that as a constructive interference If the scattered light are not in phase, we call that as destructive interference.

In the case of constructive interference, the intensity change, I mean, there will be increase in intensity. In the case of destructive interference, there will be decrease in intensity. Okay, so because of these differences, variation, you will get the time dependent intensity data. There will be fluctuation in intensity. So you will be able to obtain intensity as a function of the time, right? So basically, the intensity versus time data will look like this.

For small particle, the fluctuation will be huge compared to the large particle. That is because small particles diffuse rapidly. okay and large particles diffuse slowly right and there is something called autocorrelation function this is very important you know one in the DLS so this autocorrelation function is nothing but a mathematical framework this help us get this process this data that is intensity time dependent intensity data to get what is known as the decay constant mean decay constant that is useful for us to calculate the diffusion coefficient which is which help us calculate the hydrodynamic diameter of the particle okay right.

Time: 4.41mins

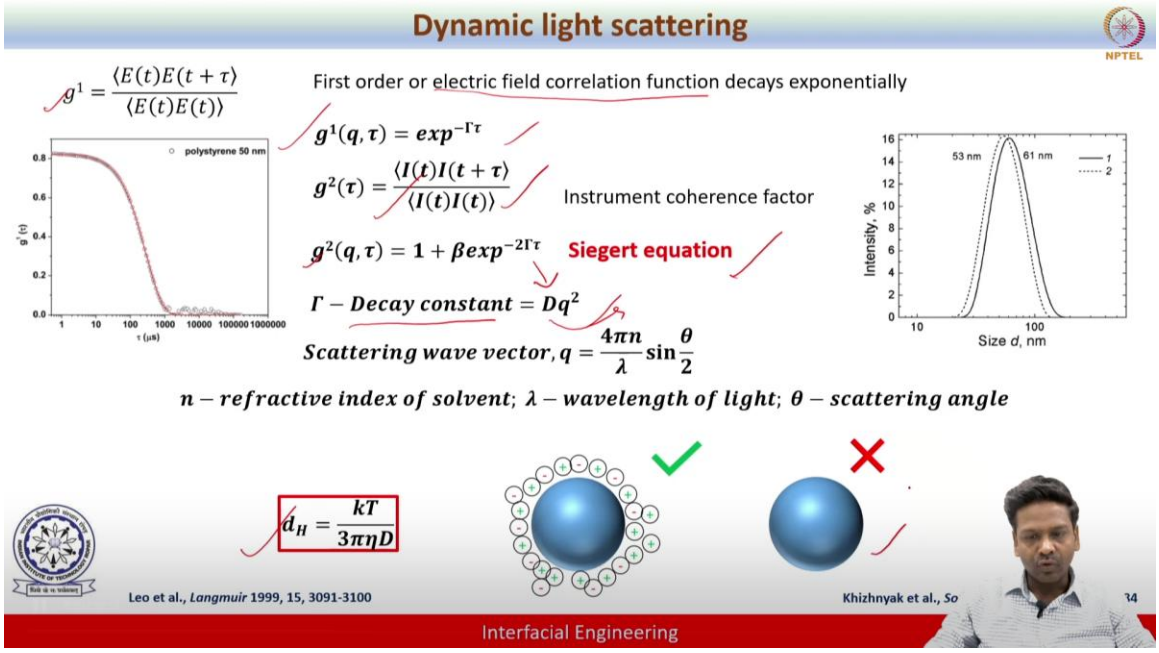


So this autocorrelation, so how this autocorrelation function works is basically, you know, when intensity signals at different time interval, you can see t and t plus delta t, when they are compared, okay, if the signal received is same, then we say that the correlation is good. Okay, in this case, the correlation is good because the signal received are same.

Whereas if you compare this time t with other any other time t plus delta t you see that the correlation the signal is not same so the correlations are lost or poor okay. So basically what you will do is that the system will do is it will try to give you a mean decay constant by you know processing these data. Okay. For example, if you deal with a mono dispersed system, basically the autocorrelation decay will be exponential in nature and you can easily, you know, find out the decay constant and that can be used to calculate the particle size.

Right. Right.

Time : 5.49mins



So the important part of the dynamic light scattering is how we basically calculate the decay constant. So once you know how it is determined, then it is easy to understand the principle. So basically, there is something called g^1. This is nothing but electric field correlation function.

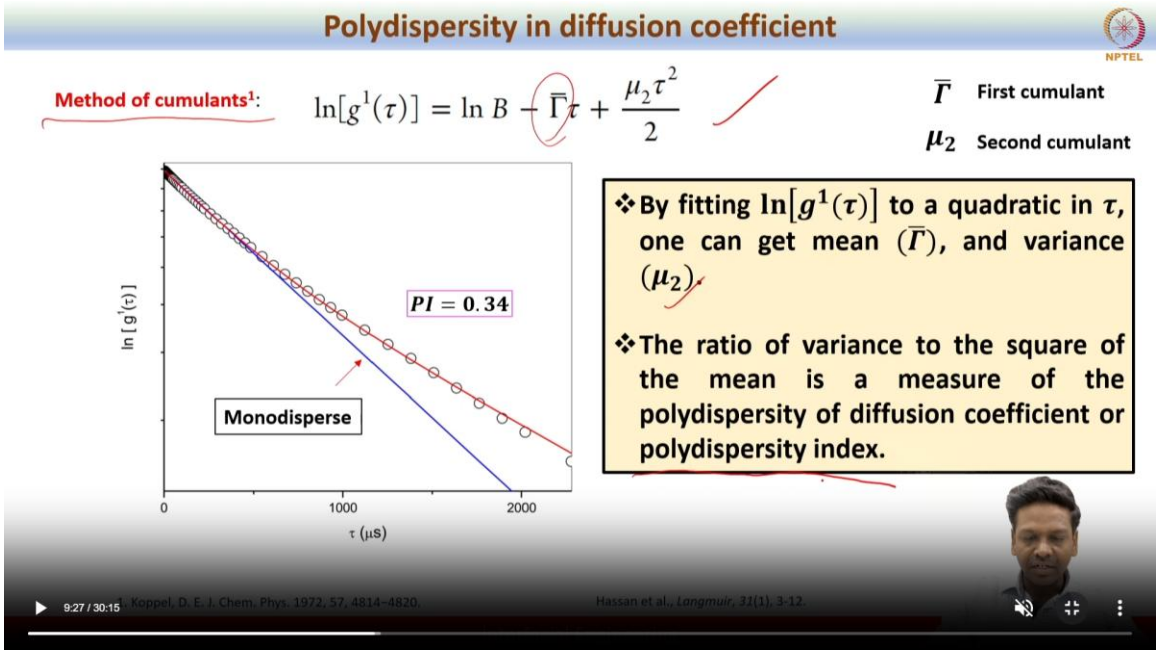
And that is given here. There is something called g^2. This is intensity correlation function. So basically, this autocorrelation function that we saw is nothing but the intensity correlation function. But fortunately, we have the function, I mean electric field correlation function relate the decay constant.

And so if you know the electric field correlation function, you can calculate the decay constant. Whereas what we get is the intensity correlation function, not the electric field correlation function. So how you can relate this so that you will get the decay constant? Thanks to Siegert equation, this help us relate the electric field correlation function with the intensity correlation function in this way. And this help us calculate what is known as the capital gamma this capital gamma symbol represents the decay constant okay so why we should know the decay constant is because if you know the decay constant you can calculate easily the diffusional coefficient from this equation rest everything is a constant so with this you will be able to get the hydrodynamic diameter of the particle by using the Stoke-Einstein relation. So that is the idea.

So thanks to Siegert equation, based on this relation only, we are able to get the decay constant, okay? So why we call it as a hydrodynamic diameter is because you are, so the size that we measure is not just the particle size, it is also the associated ions, right? You

know, that move along with the particle, okay? For example, the electrical double layer, right? So stern layer, shear layer, and diffuse layer, whatever the layer associated with the particle that moves, okay, that move along with the particle is also measured in this technique. That's why the size measured is always greater than the electron microscopy that we measure, right, that we use to calculate the size, right?

Time: 8.27mins

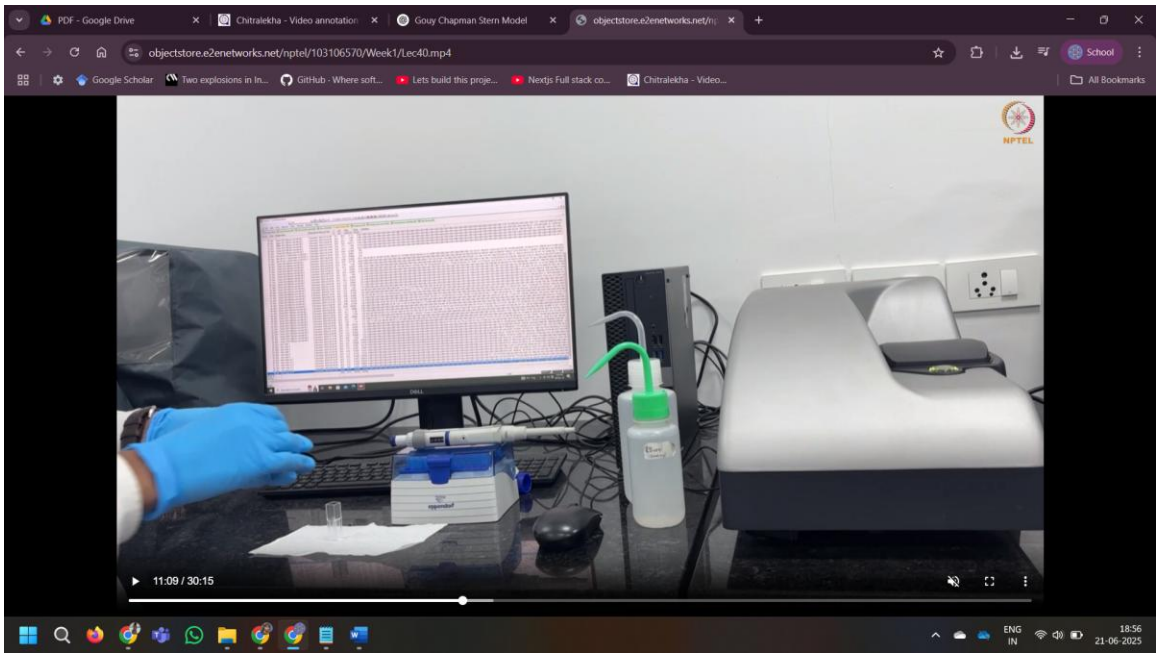


So this is nothing but method of cumulance. This is the mathematical framework that I was talking about. So what DLS gives you is the raw data between $g^1(\tau)$ to τ. So by plotting the logarithmic of $g^1(\tau)$ vs τ, you will get the mean of the decay constant.

If it is a more dispersed particle, you will only have this one term. But for polydispersed sample, you will have higher order terms as well in this equation. So by knowing the mean value, that is mean of the decay constant and the variance, that is μ_2, for polydispersed sample, you can also calculate what is known as the polydispersity index. So this method of cumulant is useful for us to calculate not just the average decay constant but also the variance that is again helpful for us to calculate the polydispersity index using the ratio of variance to the square of the mean. So I will stop here.

So one of my students will be showing you the demonstration of the zeta sizer in this lecture. So thank you. Let's stop here. Thank you.

Time: 9.44mins



Hello everyone and welcome to this NPTEL lecture where we will be exploring the use of dynamic-like scattering or you can say DLS instrument.

DLS is widely used in research to determine the size distribution of small particles including nanoparticles, proteins, and polymers suspended in the solution. In addition to particle sizing, DLS can also measure data potential which gives us insight into the surface size of articles. Influencing the stability in suspension. Today we will explore the entire process starting from sample preparation to running the measurement and analyzing the results. Let me first introduce you to the instrument.

This is our DLS system. We are using the Zeta Sizer Nano ZS manufactured by Malvern. Here, I am using a five hundred nm standard polystyrene particle, which I have already prepared at a concentration of 0.01%. Remember, if you are going to measure the size of the particle or system, the concentration must be as low as possible, ideally around 0.01%, which is suitable level for DLS. Here, we are using two different types of cuvettes for the measurement.

One cuvette, as you can see here, has a volume of around near about 5 to 6 ml. And another cuvette, which is called microcuvette, which has a volume of around 700 microliter. Now, let's see how to prepare the sample for the measurement in DLS. Whenever we are going to measure the size of the particle, the cuvette must be properly cleaned. Here I am using a microcuvette.

for the small volume for this demonstration purpose So if you have to treat your cuvette

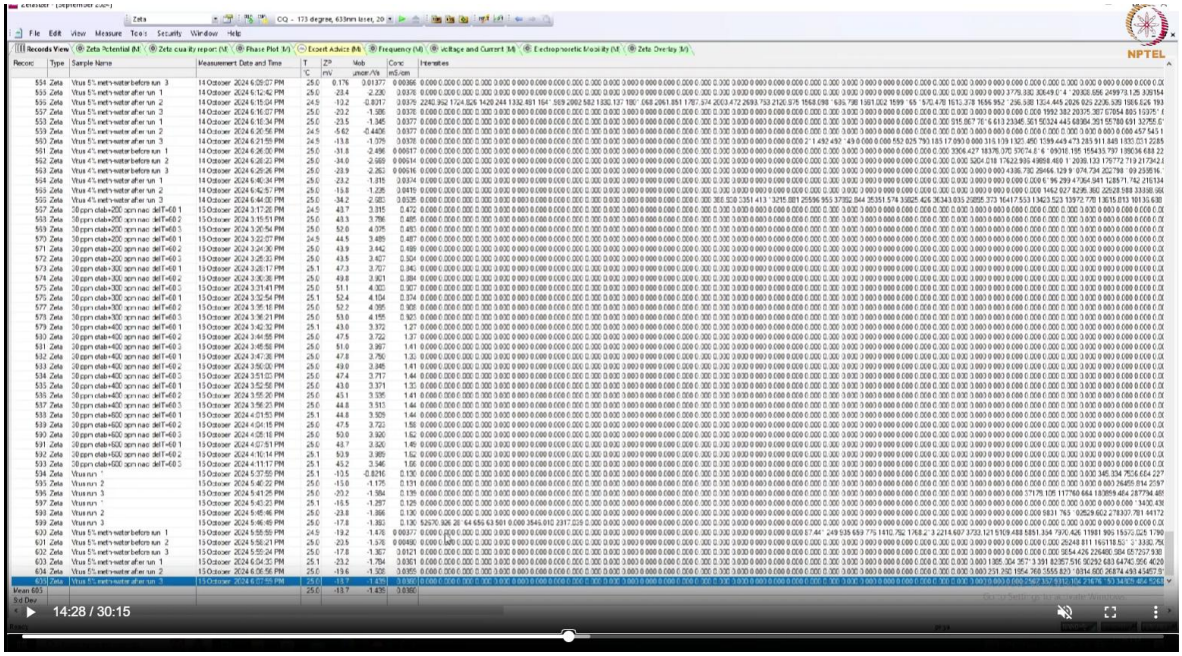
first using deionized water After cleaning with the deionized water you can use the ethanol After cleaning with the deionized water you should clean it with some solvent to ensure proper cleaning I am using ethanol which is good solvent for this purpose. Make sure you thoroughly clean the cuvette so that all the traces of the previous sample are removed. You can also use the pipette for this configuration. Now you can fill the sample that you have prepared. Remember when you are going to measure the size of your sample, this cuvette must be hundred percent free from any external contaminants.

Make sure to clean the cuvette from the outside. Additionally, ensure there is no air bubble in your sample inside the cuvette. As you can see, your sample is ready for the size measurement. Also, make sure to place the cuvette carefully without any fingerprint on it. Always wear gloves to avoid contaminating the cuvette.

As you can see, I am cleaning the cuvette. Do not rough the cuvette harshly to avoid scratches. As there are scratches on the cuvette, it will affect the measurement by changing the position of the phasor light. Now we will place the sample inside the instrument. There is an arrow on the cuvette and this arrow should face you when you inserting the cuvette into the system.

Place the cuvette firmly inside the instrument. Now we will go to the software interface. Now let's look at the software of the system. You can see this is the software that we already installed with the system.

Time: 14.19mins



The name of the software is ZetaSizer Software.

I have already opened it. You can see here that just after opening the software a window appears. In the system you can perform different type of measurement depending on the availability. am selecting size measurement within the software so that it will show as the interface for size measurement now this window is for size measurement as you can see here after this we need to go to the measure tab We will enter the details manually. After clicking on the manual entry, a pop-up window will appear. In this window, you need to provide the name of your sample.

I will name PS. If you want to include any notes, you can add them here as well. Next, we need to select the material. So we are using a polystyrene here. As polystyrene is already included in the database, and choosing it by selecting it from the directory, the software automatically shows the refractive index and absorption coefficient. If you are using an unknown sample that is not listed in the system directory, you must add that component here by providing its name, refractive index and absorption coefficient.

After selecting polystyrene, I am now moving on the dispersant. You should specify the medium in which your particle is suspended. You can choose from the available directory. I am using the water here as the dispersant as it automatically takes the properties of the water. If you want to modify or add any specific parameter, you can do so accordingly.

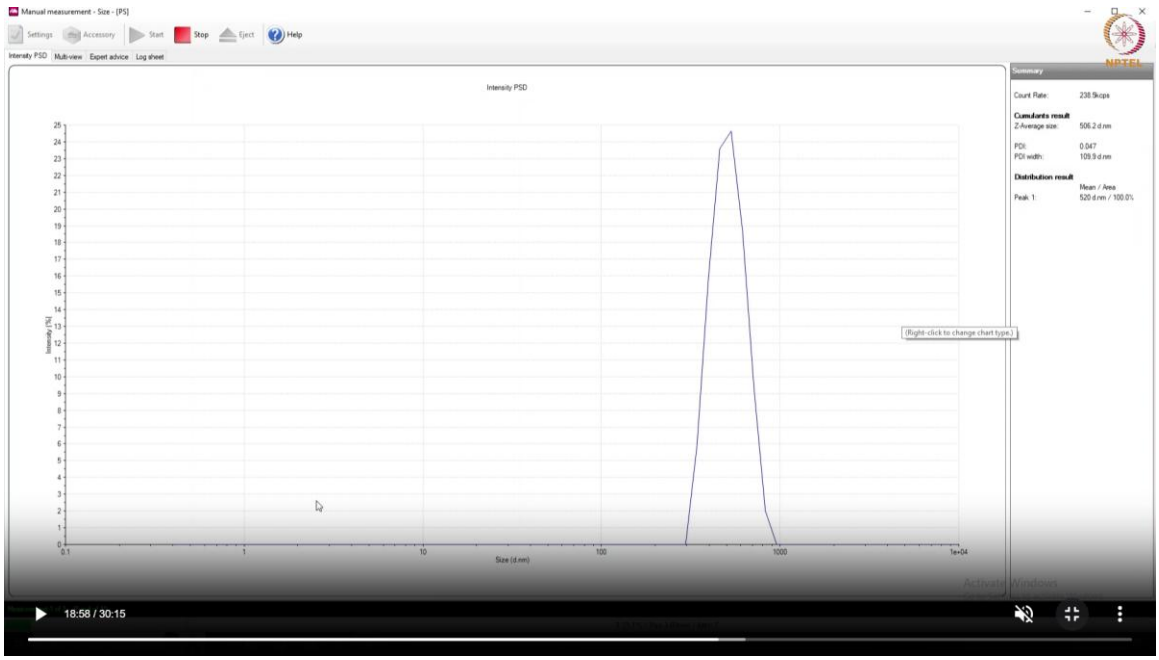
You also need to enter the temperature at which you want to measure. For size measurement, we usually use 25C. You can see here that the equilibrium time is defined. The equilibrium time corresponds to the time needed for the temperature to stabilize. Now, go to the next parameter that is cell.

As I mentioned earlier, we have two different type of cells. One is 0040 and another one is 0012 is a micro cuvette cell and this one is a large volume cell and since i am using here 0040 cuvette i will select this option now go to the measurement tab the system operates at a one seventy three degree back scattering angle which is standard for most of the measurements you can change this to thirteen degree forward scattering angle if needed for the measurement duration you have two options one is automatic and another is manual if you choose automatic the system will take measurements automatically between ten to fifteen runs depending on the condition in manual mode you can specify how many runs you want and the duration of each run i am entering here ten runs for a single measurement and which will take around ten seconds per measurements. And I will conduct three measurements for consistency and to minimize instrumental error. Now go to the advanced settings. If you want to change advanced setting, you can do so here, or you can leave them as default.

Additionally, if you want to generate a report, you can select the analysis method and export your data in various formats, including PDF and Excel. Now, after confirming all the settings, I will start the measurements. As I have already placed the sample in the instrument, now I will click the start button. You can see we are measuring the PS, polystyrene sample. Now, we need to wait for one twenty seconds to reach a stable temperature of 25Cs.

After that, the measurement will begin. As you can see, our measurement has started. It will run for ten iterations. This is continuously running and our measurement is in process.

Time : 18.58mins



After the measurement is complete, you will see the results in tabulated form or you can view the graph directly. now our measurement is done and the instrument returned to its initial position you can close this window and here you can see the tabulated results you can see here all the measurements all the three measurements are recorded and the average value is displayed here is five zero eight nanometer and with the standard deviation of nine point four Select the tabulated data showing the size value.

Right click on the selected data. Choose copy. You can then paste this data into the Excel sheet. By pressing control V. This can be used for further analysis. If you want the intensity versus particle size distribution diagram, you can obtain that as well. You can also export the graphs that were donated during the measurement.

To do this, left click on the edit and choose copy size graph and then you can paste the graph into the excel. If you want to copy the size values, you can copy it from here and paste those values in the Excel sheet as well. After that, you can use those values to plot in different softwares you know like origin further if you want particle size distribution with respect to volume you can save here with the similar way copy size graph and copy size values and also the report as well after exporting The data in graphs, you can use Excel or other software to create customized plot, perform statistical analysis, or combine the measurement results with other datasets. This concludes the size measurement of particle using the DLS system. Next, we move forward to the measurement of zeta potential of the particle.

So, you can see here, this is our zeta potential cell. This cuvette is having a U-type shape from the inside and is equipped with the anode and the cathode, both of which are made of same material. Initially, we need to fill the sample in this cuvette. The volume that we have to use in this cuvette is seven huundred microliter.

So, now we will fill the sample in this cuvette. So initially, we will clean this cuvette as we did in the DLS system when we were measuring the size. So we need to remove any residue from previous uses by washing the cuvette thoroughly. So we can use an injection or pipette for the washing process depending on your choice. The cuvette need to be properly cleaned by continuous flowing water through the capillary as this is a capillary type cuvette. After rinse with water, you should use the solvent for proper cleaning if available after cleaning here I am using the ethanol for cleaning purpose after cleaning with the solvent wash it again with the water now I will Now I will fill the sample inside the detector potential cell.

Here we are using the 0.01% particle suspension for this measurement. One thing to remember is that particle concentration should not be too low or too high for the zeta potential measurement. Do not fill the cuvette completely. The particle suspension should be enough to ensure that the particles make contact with the electrodes. Also make sure to place the cuvette carefully without any fingerprint on it.

Always wear gloves to avoid any contamination. As you can see, now I will be filming the cuvette. Avoid harshly to avoid any scratches. If there are scratches on the cuvette, it will affect the measurement by changing the position of the laser light. Now we will place the sample inside the instrument.

There is an arrow. There is an arrow on the cuvette and this arrow should be face when you are inserting the keyword into the system. Place the keyword inside the system. After placing the keyword, we will go to the software interface. You can see that the software is

in initial state. We need to change the setting to the zeta potential measurement.

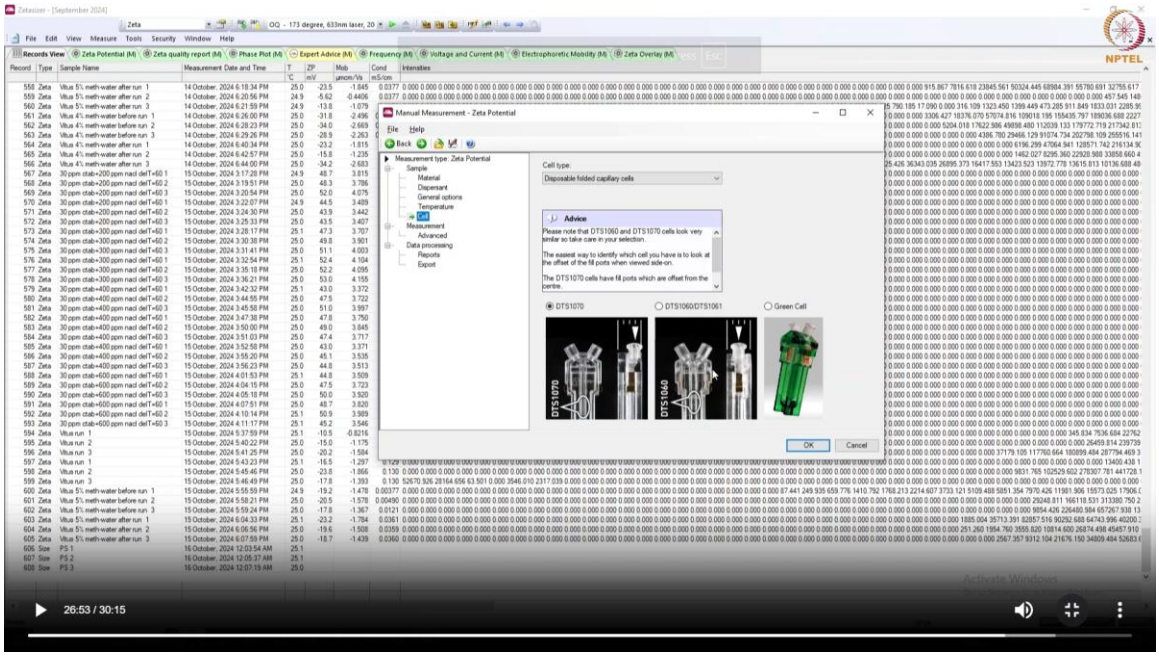
After switching to the zeta potential measurement window, We will set up the measurement condition manually. We will go to the measure tab. We will keep the same conditions as before. Set the sample name that is PS and select the material type such as the polystyrene latex and the dispersant that is water.

And we will go to the next one that is model. Here we are using the Smoluchowski model. You can use the Huckle model as well. And you can also customize the model. Going to the next parameter that is temperature.

We usually set the temperature to twenty five degrees Celsius. And the equilibrium time that is one twenty seconds for better accuracy. Now go to the cells. Here there are three types of cells, one is DTS one zero seven zero, another is DTS 1060and one is green cell. Basically DTS one zero seven zero keyword used for data potential measurement for general purpose samples. It has a folded capillary design that help in minimizing sample consumption and enhance the Sensitivity of the measurement.

The cuvette is suitable for non-corrosive active dispersion and work well with samples that does not degrade under laser light. And the another one that is DTS 1060is used for samples where minimal sample volume is needed. It is designed to hinder slightly more sensitive or low concentration sample.

Time: 26.52mins



The DTS 1060 cuvette allows for high precision in measurements of Zeta potential especially for smaller particles or more delicate suspensions. The green cell cuvette is designed specially for samples that are prone to decomposition or degradation when exposed to laser light. It has a special design to accommodate this type of sensitive sample, preventing laser-induced damage and ensuring more accurate results. Now go to the measurement. Here we are using the automatic mode, but you can adjust according to your convenience. Additionally, if you want to generate the report, you can select the analysis method and export your data in various formats, including PDF and Excel.

After confirming all the settings, I will start the measurement. I have already placed the sample in the instrument, and now I will click on the start button. You can see we are measuring the PS sample. Now we need to wait for one minute to reach a stable temperature of twenty-five degrees Celsius. After that, the measurement will begin.

As you can see, the measurement has started. The zeta potential is showing negative values as expected. The system will automatically perform a hundred runs in three measurements to reach a consistent value. The final result indicates that the zeta potential is -25.3 mV with a standard deviation of 1.33. You can export the result to Excel by copying the data and pasting it directly. Once the zeta potential measurement is complete, you will see the result displayed in the initial window to export the data.

Select the tabulated data. So in the Zeta potential values, right click on the selected data and choose copy. You can then paste it into an Excel sheet by pressing Ctrl V. Then you can use this for further analysis. You can also export the graphs that were generated during the measurement.

To do this, left-click on the edit. and choose copy data potential graph, then paste the graph into an Excel sheet by pressing control v, and you can use this for further analysis. After exporting the data and graphs, you can use Excel or other software to create a customized plot, perform statistical analysis, or combine the measurement results with other data sets