Colloids and Surfaces
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Lecture-11
Relation Used to Study Colloidal Systems

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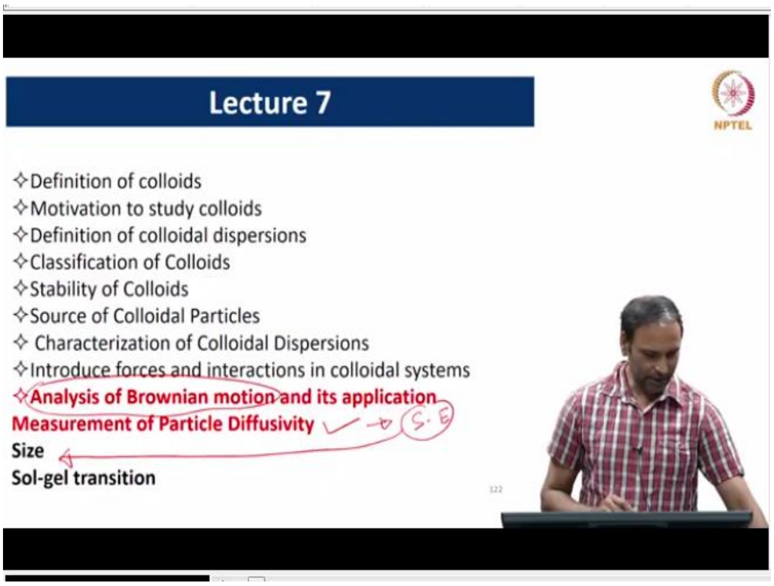

Lecture 7

✧Definition of colloids
✧Motivation to study colloids
✧Definition of colloidal dispersions
✧Classification of Colloids
✧Stability of Colloids
✧Source of Colloidal Particles
✧ Characterization of Colloidal Dispersions
✧Introduce forces and interactions in colloidal systems
✧Analysis of Brownian motion and its application
Measurement of Particle Diffusivity
Size
Sol-gel transition

Okay, so we will continue with analysis of Brownian motion, yesterday we looked at measurement of particle diffusivity and then we also derived an expression or an equation which is what is called as a Stokes Einstein relation, that will help you to calculate what is the dimension of the particle if you know the diffusivity right, that is what we had done.

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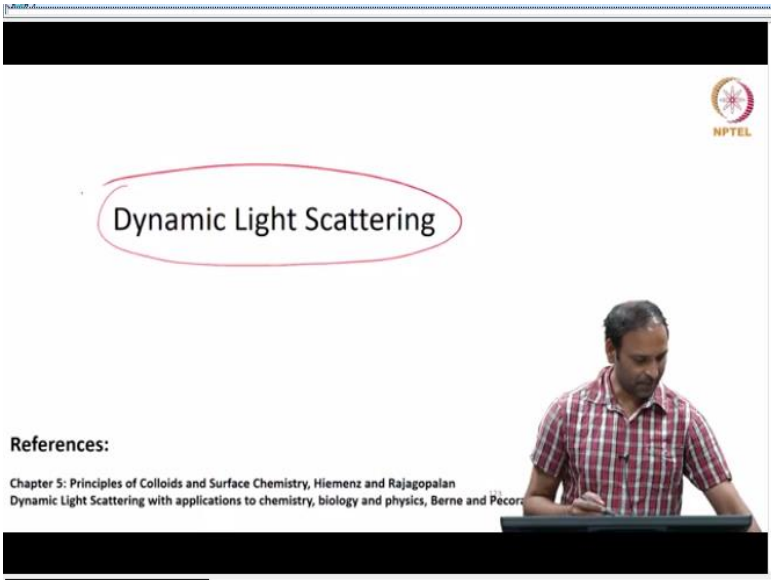

Dynamic Light Scattering

References:

Chapter 5: Principles of Colloids and Surface Chemistry, Hiemenz and Rajagopalan
Dynamic Light Scattering with applications to chemistry, biology and physics, Berne and Pecor

And in that connection we had just started with what is called as a dynamic light scattering. So, I just want to clarify a few things.

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Introduction

https://go.activecalendar.com/fablab/event/new-laser-light-show-the-how--wow/

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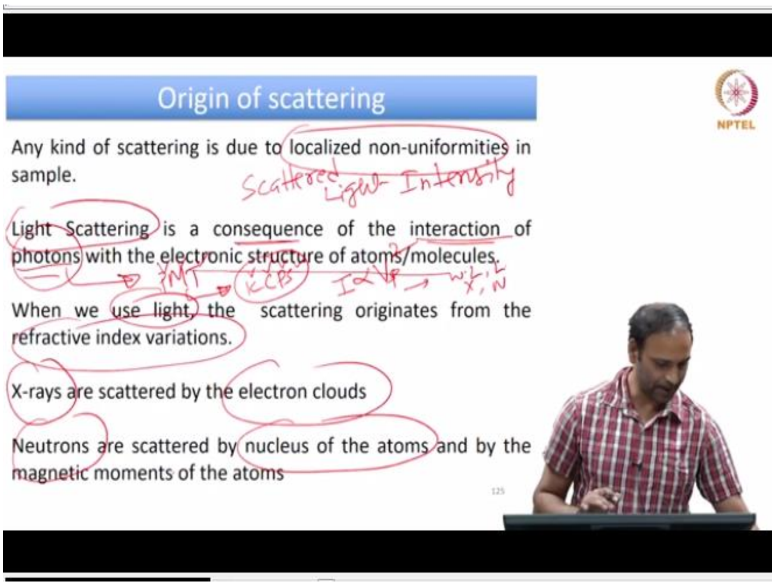

Origin of scattering

Any kind of scattering is due to localized non-uniformities in sample.

Scattered Light Intensity

Light Scattering is a consequence of the interaction of photons with the electronic structure of atoms/molecules.

MT → KCBS $I \propto V_p^2 \rightarrow$ w, t, x, N

When we use light, the scattering originates from the refractive index variations.

X-rays are scattered by the electron clouds

Neutrons are scattered by nucleus of the atoms and by the magnetic moments of the atoms

So, I had mentioned that you know the scattering of light typically comes about if you have any localized non uniformities or heterogeneities in the sample okay and light scattering is a consequence okay of interaction of photons right, because you know whenever you take any light source you know it is made up of photons right and interaction of the photons that make up the light with the electronic structure of the atoms or the molecules that make up the particle okay or the dispersed phase is what gives rise to what is called as light scattering okay.

And whenever people do light scattering measurements what they do is they measure what is called as scattered light intensity okay and the way it is measured is they will have a instrument which can measure radiation right and typically photons okay and this photons again it depends on the kind of radiation measurement device that you are using , typically people use a PMT you know what is called a photo multiplier tube okay in which what is done is you basically collect the number of photons that fall onto the device that you are using.

And typically the measurement of photon or the intensity is expressed in something called the KCPS kilo cycles per second okay and depending upon the kind of a scattering unit that you have okay this the photon count that you measure it varies okay, in general one thing that you should know is that any scattered intensity okay I that is detected by any device that one is using, it is actually proportional to volume of the particle that you have in the dispersion to the power 2.

If Vp is the volume of the particle that you have in the dispersion, the scattered intensity goes as volume of the particle to the power 2 that means larger particles will have will scatter more light okay or the intensity of the light that is scattered by a larger particle is higher compared to the intensity of the light that is scattered by a smaller particle okay, then as I mentioned people can use a white light , laser light, laser source or x-rays or neutrons for scattering right as a light source.

And as I mentioned when one uses white light okay what is exploited is the difference in the refractive index between the particle and the medium is what is exploited, if x-rays are used okay the scattering actually comes because of the interaction of x-rays with the electron clouds you know that the atoms and the molecules will have and if you have neutrons as a source of the radiation.

Then the scattering occurs because of the interaction of the neutrons with the nucleus of the atoms or the magnetic moments of the atoms of the molecules that constitute the particles right. So, that is a difference, but except for the origin of scattering the way the data is analyzed okay, the way the scattered intensity is analyzed from any of these experiments where you use light x-ray or neutron the analysis is very similar okay. But only thing is the scattering originates from different, different reasons okay.

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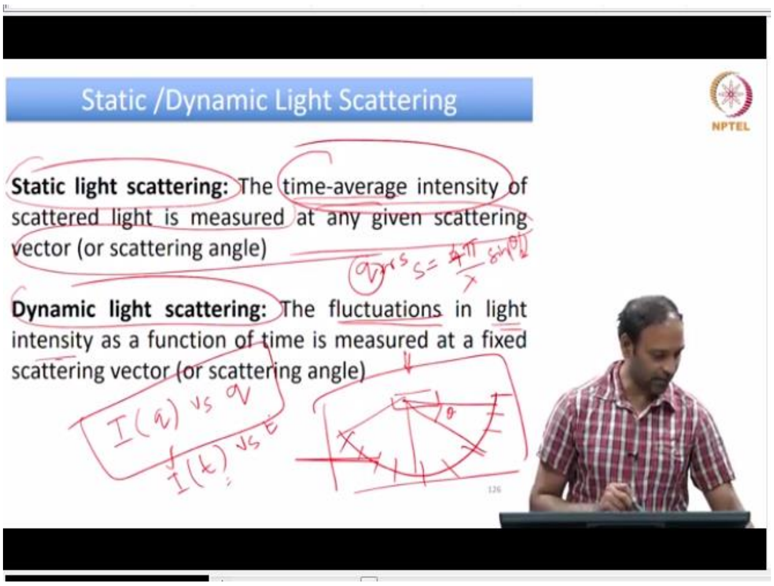

Static /Dynamic Light Scattering

Static light scattering: The time-average intensity of scattered light is measured at any given scattering vector (or scattering angle)

Dynamic light scattering: The fluctuations in light intensity as a function of time is measured at a fixed scattering vector (or scattering angle)

I mentioned this so we typically people do 2 kinds of scattering experiments what is called as a static light scattering okay in which what is basically measured is you have a sample, you have a detector and then you go on accumulating intensity as a function of time and then what you know what you get out of the measurement is a time average intensity okay, time average scattered intensity okay. There is a term here is called a scattering vector okay.

So, that scattering vector actually is defined something like this is typically people use either q or s it goes as 4 pi okay divided by lambda, where lambda is the wavelength of the radiation source that you are using multiplied by sin theta by 2, where theta is the angle at which you are collecting the radiation you know the scattered intensity okay**.** So, in static light scattering what is measure the time average intensity is what is measured.

In dynamic light scattering what are measured are the fluctuations okay in the light intensity as a function of time okay that is what is measured and typically whenever people do static light scattering there is a radiation source, there is a sample okay and you collect scattered intensity across many detectors okay, that means I am basically collecting scattering intensity at different theta right okay.

That is what is typically so what you get from the static is it is I of q okay, that is q here okay as a function of q is what you get from static light scattering experiments, you are measuring the scatter intensity as a function of you know this scattering vector okay, that is a data that you get and you analyze that data to get any meaningful quantity that you want to get out of your experiment okay.

And in the dynamic like scattering measurements what is measured is a fluctuations in the light intensity, what you are measuring is your I of t okay, that is your measuring scattering intensity as a function of time okay, that is the difference between the static light scattering and the dynamic light scattering okay.

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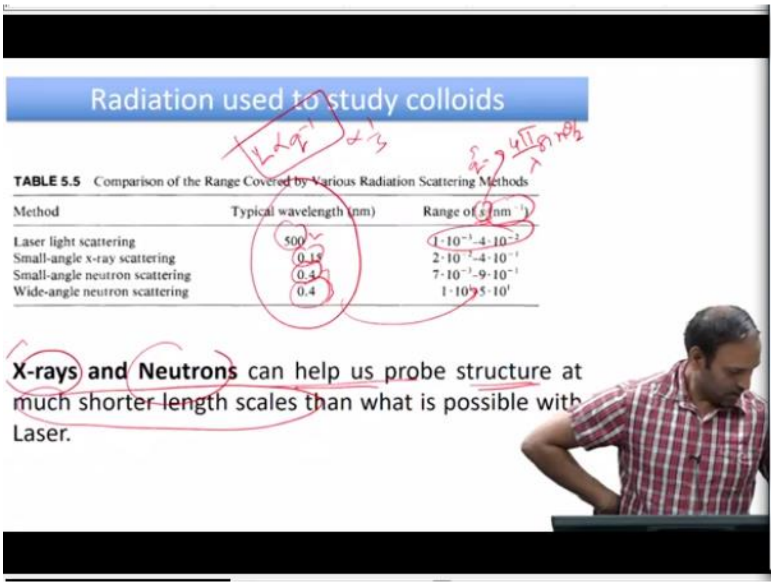

Radiation used to study colloids

TABLE 5.5 Comparison of the Range Covered by Various Radiation Scattering Methods

Method	Typical wavelength (nm)	Range of s (nm^{-1})
Laser light scattering	500	$1\cdot10^{-3}$–$4\cdot10^{-2}$
Small-angle x-ray scattering	0.15	$2\cdot10^{-2}$–$4\cdot10^{-1}$
Small-angle neutron scattering	0.4	$7\cdot10^{-3}$–$9\cdot10^{-1}$
Wide-angle neutron scattering	0.4	$1\cdot10^{1}$–$5\cdot10^{1}$

X-rays and **Neutrons** can help us probe structure at much shorter length scales than what is possible with Laser.

So, this s I have already defined that right it goes as 4 pi by lambda into sin theta by 2 okay. So, now depending upon the wavelength of the light source okay, depending upon the wavelength of the light source you know the range of s that I have access to will vary okay, if lambda is more okay your q right or s is going to be smaller right, if the lambda is small your q is going to be larger okay.

You should think about q okay, so inverse of q okay you see the q will have a unit of nanometer inverse, therefore inverse of q will have units of some length scale. So, therefore what you are changing okay what you are doing by changing the wavelength is that I am basically able to access different length scale by using different radiation length source and that length scale that you have access to okay if you call it as you know some length scale L is proportional to 1 over q inverse okay or 1 over s right.

Now therefore if you use x-rays and neutrons okay which have a lower wavelength then they can help us probe structures at much shorter length scale okay, I am able to go to much smaller and smaller length scale and I am able to access micro structural information at a very small length scale compared to what you would do if you use laser or visible light okay.

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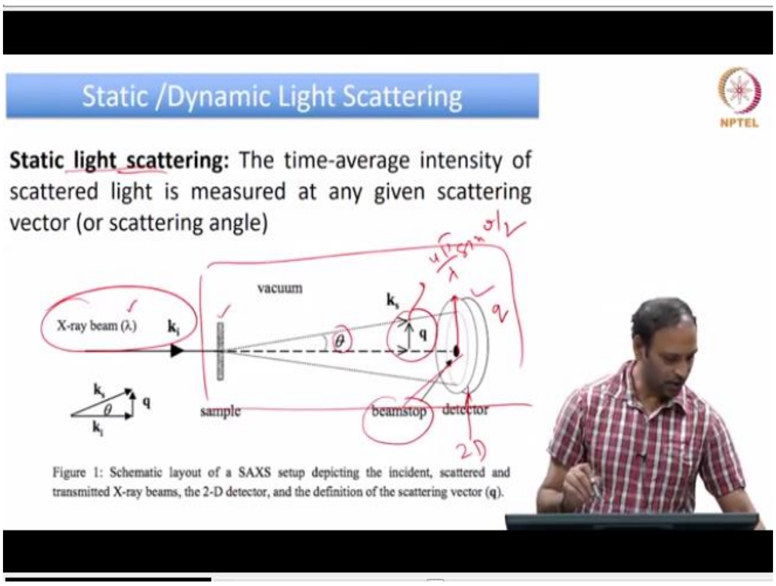

Static /Dynamic Light Scattering

Static light scattering: The time-average intensity of scattered light is measured at any given scattering vector (or scattering angle)

Figure 1: Schematic layout of a SAXS setup depicting the incident, scattered and transmitted X-ray beams, the 2-D detector, and the definition of the scattering vector (**q**).

Yeah so typical light scattering experiments, so this is for the case of static light scattering as I mentioned earlier. So, there is a beam of light in this case x-ray wavelength lambda okay and there is a sample and I had mentioned that typically you know these the sample and the detector are actually kept in a vacuum environment you do not want you know light to scatter off from you know whatever medium in which it is typically as I said you can get okay.

So, in this case the detector is what is called a 2 dimensional detector okay because it is a basically a screen okay, you should think about there is a sample, there is a x-ray beam and something is scattered and it falls onto a beam okay and then this q is again 4 pi by lambda into sin theta by 2 okay, that is au know scattering vector.

And typically what is done is there is actually something with a beam stop the role of the beam stop is the intensity that is in the center will be very, very high okay, if you do not have beam stop it could damage your screen itself, therefore typically you put some you know carbon source or some stuff which really absorbs you know it does not cause some kind of damage to the and it also acts as a reference right.

Because when you are changing theta okay, theta in the center is going to be 0 right okay, you are because you know your incident beam and the scattered beam the angle between them at that particular location would be 0, you can you know and therefore if you go outward okay what is changing is theta and in turn what is changing is your q okay.

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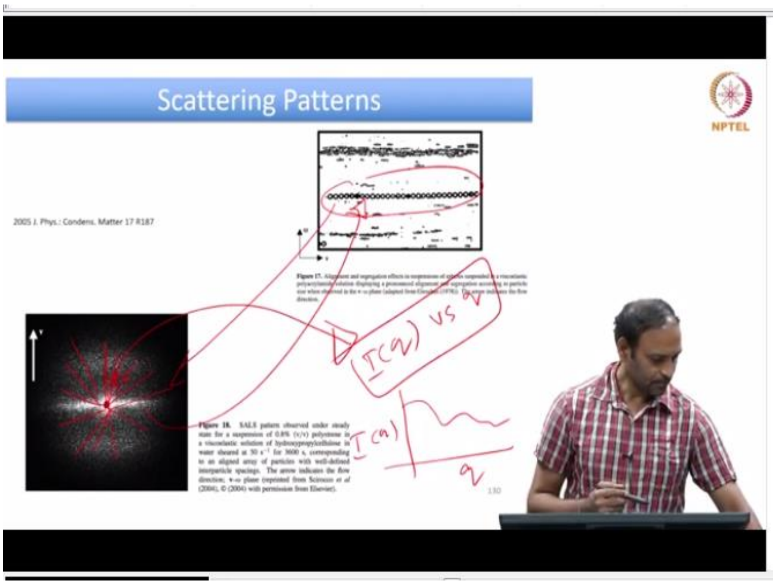

Scattering Patterns

2005 J. Phys.: Condens. Matter 17 R187

So, typically you know one gets patterns like this and these patterns will have information about you know the structure okay that is you know inherent to the sample that you are working with okay. In this case there is a chain of particles and if you have a chain okay you will typically get a pattern which looks something like this okay and what people do is you can go back and read up a little bit about it.

So, what people do is they do what is called a radial averaging okay, what I can do is I can of course this pattern is not very symmetric right, but if you have a pattern which is very symmetric what I can do is I can do what is called a radial averaging. So, if I do, if I go from here to this direction and what I do is I rotate that basically I am taking a particular line where I am basically changing the radius right okay from the center which in turn I am basically changing q right.

And if I average it across many lines like that like you know the many, many lines okay or all the lines that I could draw then I get a average intensity as a function of q okay. This is so basically from the 2D patterns you do radial averaging to get 1 dimensional you know scattering intensity patterns. So, therefore your data would look something okay, I have q may as a function of q you know may look something like that it depends on your sample again okay maybe at some point I will show you some data you know from a particular sample which has some well-defined particles of some sizes.

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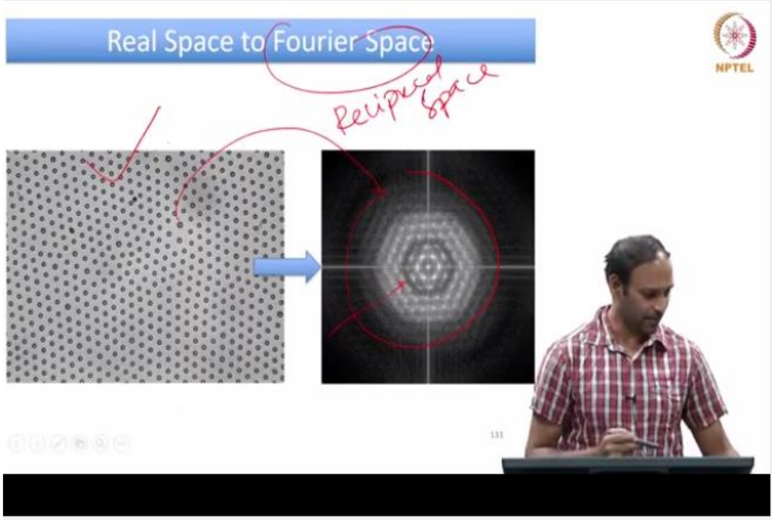

Real Space to Fourier Space

And I had mentioned that you know what you are doing you can think about scattering as imaging in a Fourier space okay or what is called as a reciprocal space okay, this is an example so that is a microscope image, if I to do Fourier transform your patterns would look like this, that means if I have any sample which has you know arrangement like this like what is shown here. Then if you do experiment your scatting pattern would look something like this okay.

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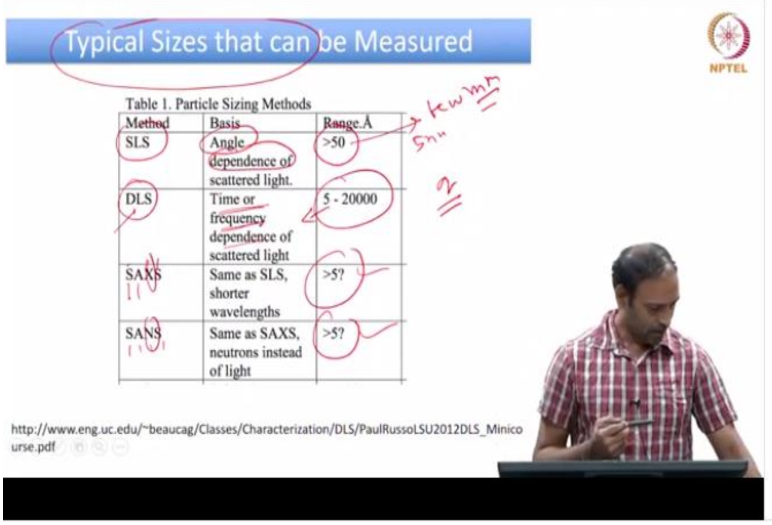

Typical Sizes that can be Measured

Table 1. Particle Sizing Methods

Method	Basis	Range Å
SLS	Angle dependence of scattered light.	>50
DLS	Time or frequency dependence of scattered light	5 - 20000
SAXS	Same as SLS, shorter wavelengths	>5?
SANS	Same as SAXS, neutrons instead of light	>5?

http://www.eng.uc.edu/~beaucag/Classes/Characterization/DLS/PaulRussoLSU2012DLS_Minicourse.pdf

So, before we move on further , so this is again will tell you something about the typical sizes that one can measure by using scattering experiments. So, if you look at SLS the static light scattering what is measured is the angle dependence of the scattered light okay and typically you can measure anything of size larger than about 50 angstrom that means about 5 nanometer and above okay is what you can measure with SLS okay.

And there are instruments where I can measure you know by using SLS principles you can measure things up to a few millimeters as well okay, it really gives you a very large you know size window that you can measure with this technique. DLS what is measured is time or frequency dependence of the scattered light and typical size range one could measure uh there are instruments where you can go to you know as low as you know a nanometer okay.

And typically yeah, so I will come back when I talk about DLS I will mention this point. So, his question is in DLS is the wave vector constant okay. So, we will come back to that okay and of course there is something called as s stands for small a small angle x-ray scattering okay and small angle neutron scattering okay, these experiments are similar to SLS but you are using you know x-ray and neutron as a source.

And typical length scale that I can have access to is you know about 0.5 nanometers or depends on the wavelength of the x-ray one could generate but you can you know look at sizes of this order okay.

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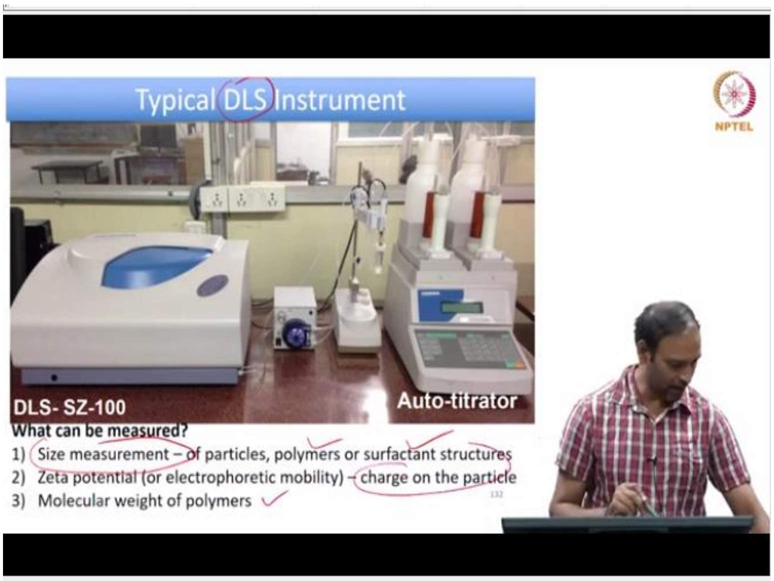

Typical DLS Instrument

What can be measured?

1) Size measurement – of particles, polymers or surfactant structures
2) Zeta potential (or electrophoretic mobility) – charge on the particle
3) Molecular weight of polymers

So, now you know we will move on to DLS okay. I said this is a commercially available you know example of a commercially available instrument I would mentioned you know you can use it for measuring size of the particles polymer surfactant structures people also use you know this for measuring charge in the particle also it gives you a way of measuring molecular weight as well.

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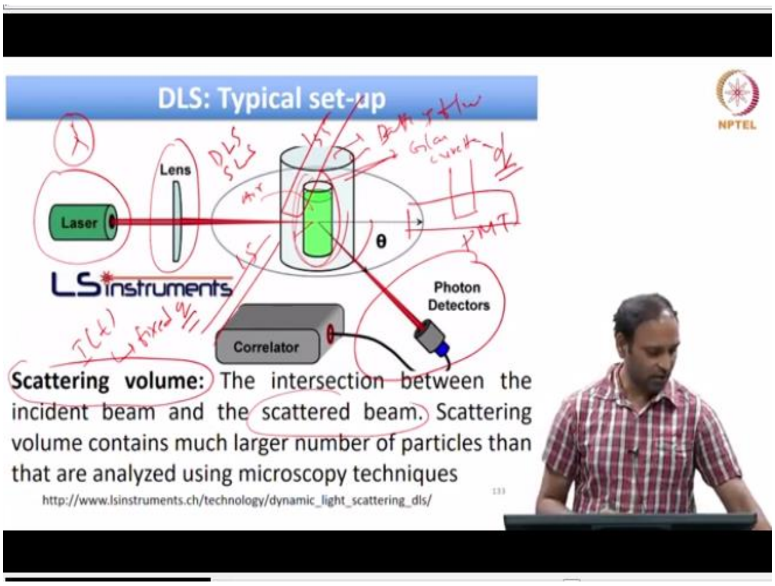

DLS: Typical set-up

Scattering volume: The intersection between the incident beam and the scattered beam. Scattering volume contains much larger number of particles than that are analyzed using microscopy techniques

http://www.lsinstruments.ch/technology/dynamic_light_scattering_dls/

Typical if you open the instrument right so typically this is what it will have essential components would be laser okay which basically will give you, you know radiation of a particular monochromatic light of a particular wavelength and there is set of lenses basically to get a collimated beam and there is a sample okay. So, this what is shown here are 2 beakers right.

There is 1 beaker here and there is a small beaker there okay and the reason why not every instrument will have this kind of a setup, the reason why it is done is that when you have a beam coming in it is coming typically in air right and then it is going to go into your sample okay. Now when that happens there is going to be a change in the refractive index right, you do not want any of that happening.

So, what is done is you let you take your sample and you put this sample say that this sample is in a glass cuvette okay and you immerse that sample in a container which has a fluid whose refractive index is same as that of the glass okay. Therefore it will essentially you know avoid you know some scattering effects that may come from the cuvette itself okay change the refractive index.

So, but you know but if you do not use glass cuvette these days you know you have you know a plastic cuvette which you know can be used without this path of fluid okay and typically you will have a PMT or some kind of a device where you can measure the photons that are that are scattered from the sample.

And this theta right and as you can see here right, so these photons are corrected at a fixed location okay, typically if you go back and look up instruments there are instruments where this theta you know you can collect it at 90 degree okay, you can collect at something like 135 degree somewhere here or you can also collect at some 15 degrees. So, it depends on the instrument specifications of course there are instruments where I have access to changing the length as well okay.

In such a case I can vary it across a large range of theta and I can do both DLS and SLS with the same instrument, because you know basically if I can do DLS measurements at every theta that is as good as doing a SLS measurements right, they are instrument like that but a lot of table top instruments typically work at fixed theta, that means your q is fixed ok.

Therefore your scattered intensity that you are collecting is always done at a fixed q yeah and I mentioned something with scattering volume the interaction of the light beam and the incident beam and the scattered beam will give you what is called as a scattering volume and unlike microscopy based technique this scattering volume will have a large number of samples.

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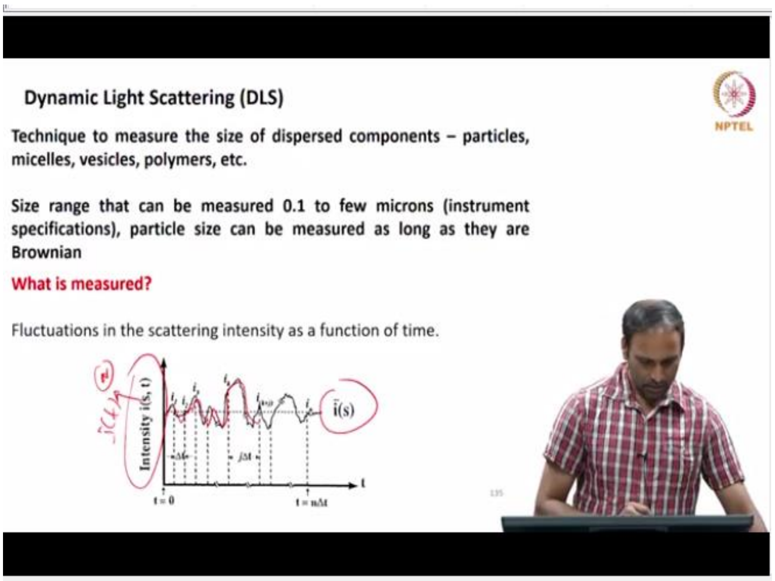

Dynamic Light Scattering (DLS)

Technique to measure the size of dispersed components – particles, micelles, vesicles, polymers, etc.

Size range that can be measured 0.1 to few microns (instrument specifications), particle size can be measured as long as they are Brownian

What is measured?

Fluctuations in the scattering intensity as a function of time.

Therefore you get a better average okay of the size of the particle that you have. I have mentioned this already, it can be measured you can measure the size of the particles micelles, vesicles, polymers you name it okay. The only thing is there should be a enough refractive index difference okay between the dispersed phase and the continuous phase right. Again size range I had mentioned that you can measure sizes as long as particles exhibit Brownian motion okay.

And what is measured is a fluctuations in the scattering as a function of time, it looks something like this okay, here this is your intensity okay, s is same as q okay, but of course q is fixed here. So, either I can call it as IFT itself because you know your q is fixed for in the case of DLS measurements and that is measured as a function of time okay. These are the fluctuations that you have okay. That is how it varies, it varies around a mean value okay.

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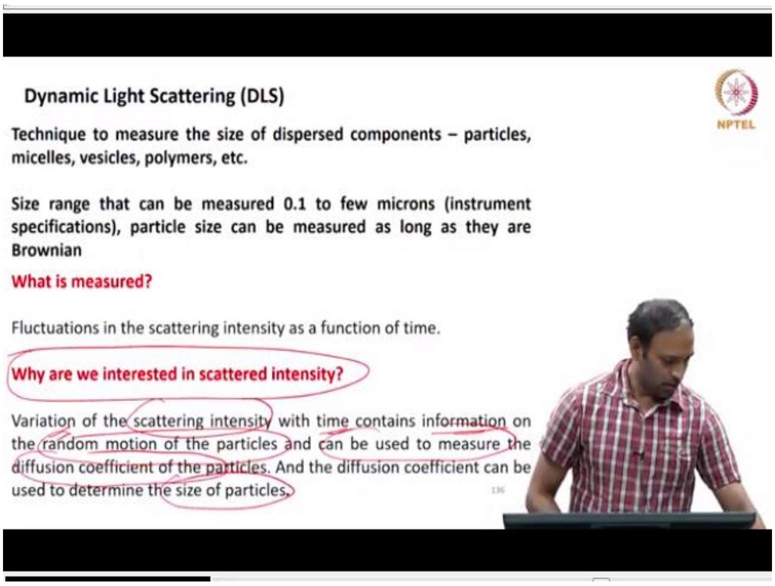

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Size range that can be measured 0.1 to few microns (instrument specifications), particle size can be measured as long as they are Brownian

What is measured?

Fluctuations in the scattering intensity as a function of time.

Why are we interested in scattered intensity?

Variation of the scattering intensity with time contains information on the random motion of the particles and can be used to measure the diffusion coefficient of the particles. And the diffusion coefficient can be used to determine the size of particles.

Now okay why are we interested in the scattered intensity as a function of time because the variation of scattered intensity with time contains information on the random motion of the particles okay. Let us get the intensity fluctuation that you saw here that arises because the particles are not fixed in space if you somehow fix them in space okay. Then what will happen is your intensity is going to be a constant.

But the fact that the particles are continuously moving around is what gives rise to this fluctuation the intensity okay and this can be used for measuring the diffusion coefficient and once the diffusion coefficient is known I can actually get what is the size of the particle right.

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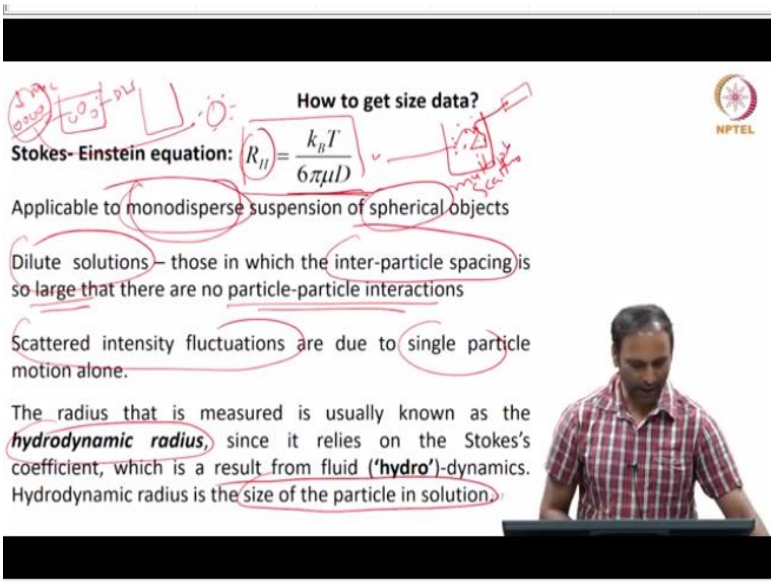

How to get size data?

Stokes- Einstein equation: $R_H = \frac{k_B T}{6\pi\mu D}$

Applicable to monodisperse suspension of spherical objects

Dilute solutions – those in which the inter-particle spacing is so large that there are no particle-particle interactions

Scattered intensity fluctuations are due to single particle motion alone.

The radius that is measured is usually known as the ***hydrodynamic radius***, since it relies on the Stokes's coefficient, which is a result from fluid (**'hydro'**)-dynamics. Hydrodynamic radius is the size of the particle in solution.

And typically size of the particles are measured by something called as Stokes Einstein relation, this is applicable if you have monodisperse particles, this particular expression right because the particles are of same size okay and of course it is the particles are spherical and one has to ensure that you work with dilute solutions okay. This is one of the important requirements whenever you do DLS measurements okay.

So, what do I mean by dilute solutions is where the inter particles spacing okay inter particle spacing is very large that means there are no particle, particle interactions okay. That is one reason why you should be working with dilute dispersion, the second reason why you should be working with dilute dispersions is also because if you have too many particles okay. If you have too many particles what will happen is your incident beam it is diffracted or it is deviated when it hits a particular particle.

And before it comes to the detector it may hit many other and come out okay, there could be what is called as multiple scattering events okay, when you have multiple scattering events okay you cannot apply the analysis that we are going to do you know for such you know the typical analysis that is applicable for monodisperse you know dilute dispersions okay. That is because as I said the scattered intensity we are assuming that whatever is scattered is because of the a single particle motion alone okay.

And if you have too many particles close by you know the other particles could also influence this fluctuation okay and what is typically measured in DLS is what is called a hydrodynamic radius okay which is the size of the particle in the solution okay, what I mean by that is that so if I were to take some particle dispersed in a fluid okay and say that I have taken a same particles okay a small drop of it and I have dried these particles.

Now the particles are on a substrate okay, now I do some microscopy okay. So, in this case I get the size of the particles you know in the dry form and in the second case if I do DLS measurements I get the size of the particles in solution, it turns out that typically the size that you measure with the DLS measurements is always slightly larger than the size of the particle that you measure in the dry form okay.

And the reason is because you know you could have a particle that could have some charges on the surface, the effective size of the particle may be slightly larger because you know you have charges okay you know depending upon you know like say the surface charge density depending upon the arrangement of water molecules around the particle surface typically you may measure sizes that is slightly larger than what you would measure with a dry technique okay. So, the sizes that you measure with DLS is what is called as a you know hydrodynamic size.

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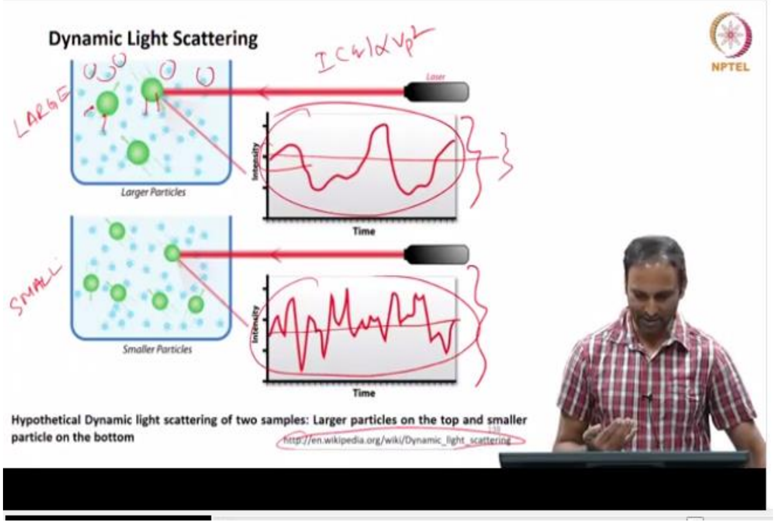

Dynamic Light Scattering

Hypothetical Dynamic light scattering of two samples: Larger particles on the top and smaller particle on the bottom

http://en.wikipedia.org/wiki/Dynamic_light_scattering

Again I have taken this example from you know the source what you are looking at is a schematic of cases where you have you know these are all water molecules right, these are all water molecules okay and they are essentially bombarding the particle right, this is a large particle, this is a small particle what can you say about these two small particle has more Brownian motion okay which is reflected by the fluctuations are too many right okay.

And that is a little here of course what is not apparent in this is that I said that your scatter intensity goes as volume of the particle square right. Therefore if I were to look at you know the average value of the intensity this will be much larger for this compared to what you would see for this right. So, these are some, so when you do your experiments you can you know you can look for all these things. So, then you will get an idea as to whether you know what I am measuring is something reasonable or not yeah okay.

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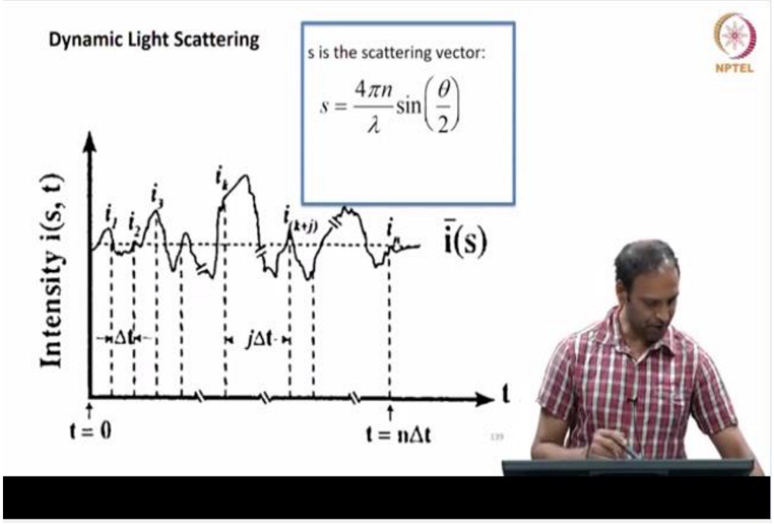

Dynamic Light Scattering

s is the scattering vector:

$$s = \frac{4\pi n}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

So, now okay that is what you measure.

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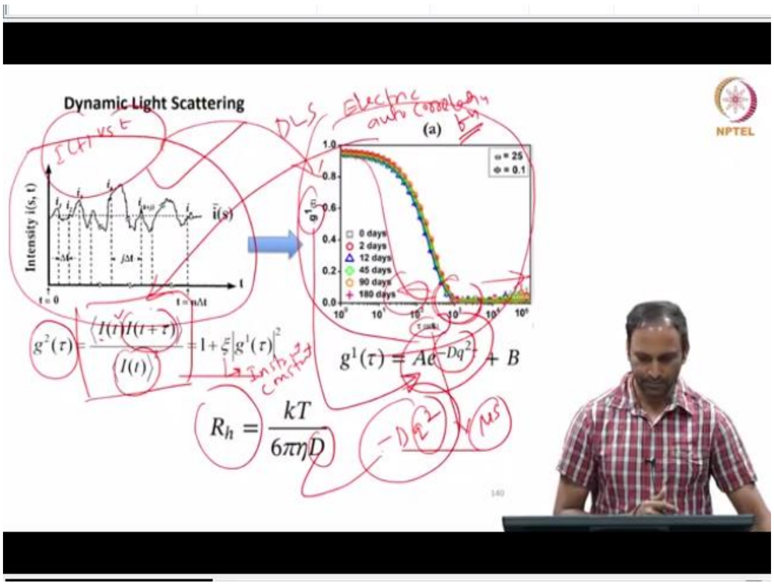

Dynamic Light Scattering

$$g^2(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle} = 1+\xi\left|g^1(\tau)\right|^2$$

$$g^1(\tau) = Ae^{-Dq^2} + B$$

$$R_h = \frac{kT}{6\pi\eta D}$$

So, there are instruments where you can actually access this information okay, if you take a commercially available instrument a DLS instrument there are instruments where they display this scattered intensity as a function of time, but many instruments do not okay, but what they show when you use any particular instrument is looks something like this okay. This is actually obtained from you know that scattered intensity measures a function of time okay.

That is g1 of tau ok because I know how I of t varies as a function of time I can guess this quantity right, this is intensity at a particular time, intensity at a particular time plus some delay okay and intensity at a particular time right. I have access to all these information, I can calculate g2 of tau and this is what is called the instrument constant. So, what I am trying to say is that the scattered intensity as a function of time is reported as what is called as a electric field auto correlation function okay which is derived from the fluctuation in the intensity that you measure okay.

Now this function okay you can fit that to a exponential function okay and from that exponential function I can get - D times q square right you have g1 of tau as a function of tau is what you measure and you should look for this number okay, this is tau is in microsecond depending upon the length scale of the particles that you have as a dispersed phase you know your this unit would vary okay.

If you have very large particles you know then you will see that you know this decay right it happens somewhere you know towards a larger tau, if you have very small particles you know it will have it will happen to a u know in the decay right, it will decay at a lower tau okay, therefore one could actually look at you know where does it decay to 0 and then already kind of infer about what is the size of the particle that you have in the dispersed phase okay.

So, now from the exponential fit I can actually get what is - D times q square I know q square because I am doing experiments at a fixed q and I get this and from that I can actually get what is the size of the particle okay, that is what you know is typically done.

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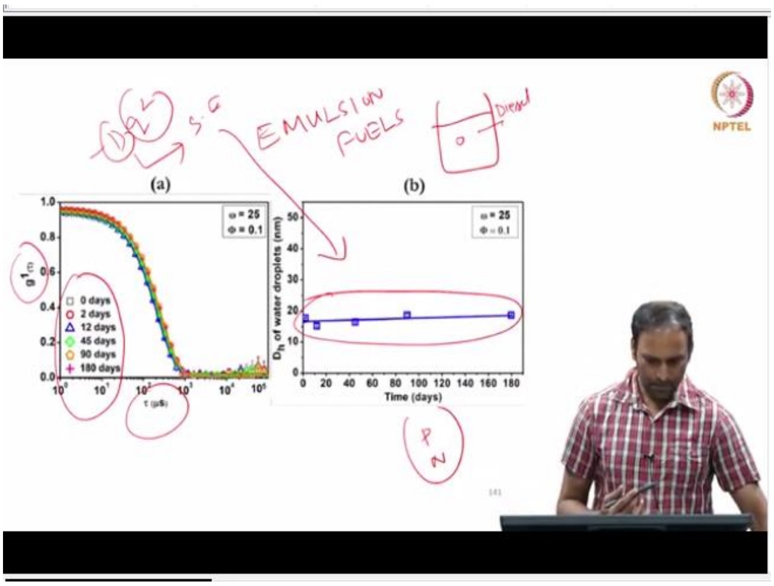

So, this is some data where you know we were trying to look at these are example of what is called the emulsion fuels ok, these have very tiny water droplets in diesel okay, the work done in our lab with Preetika and Niket okay and what is being measured is whenever you have an emulsion fuel right, you would want the fuels to be stable right for a long period of time. So, we were trying to look at what happens to the fuel if you store them for a long period 6 months right.

And this is the autocorrelation function measured as a function of decay time and one thing to notice is I know all of them you know overlap right almost lie on top of each other that means if I were to extract size of the particles from this experiment I would expect the size to remain the same right. And that is what you actually see okay which is done by a simple exponential fit okay I get D times q square okay I know what is q and from that I get D okay and then use Stokes Einstein and get the size okay. So, you can do analysis like this okay.

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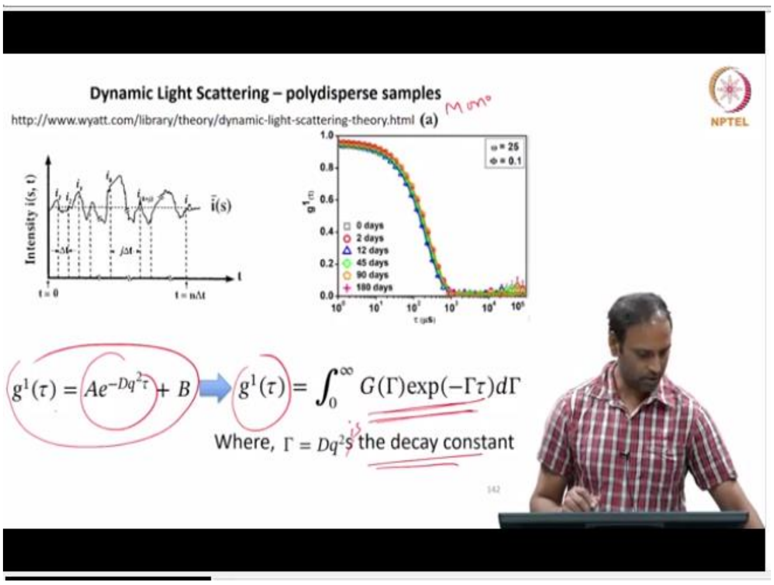

Dynamic Light Scattering – polydisperse samples

http://www.wyatt.com/library/theory/dynamic-light-scattering-theory.html (a)

Mono

$g^1(\tau) = Ae^{-Dq^2\tau} + B \Rightarrow g^1(\tau) = \int_0^\infty G(\Gamma)\exp(-\Gamma\tau)d\Gamma$

Where, $\Gamma = Dq^2$ is the decay constant

But it is not necessary then you should always have you will have monodispersed particles right. So, if you do not have monodisperse particles what you do is instead of expressing g1 of tau as a single exponent you basically express that as a sum of exponents okay**.** So, you can express them as depending upon if you have bi-dispersed particles then I can say that you know it will be sum of 2 exponential functions.

If you have tri-disperse you know I could use you know 3 exponential functions therefore in general if you have a size distribution then I can express g1 of tau as summation of many, many exponential functions.

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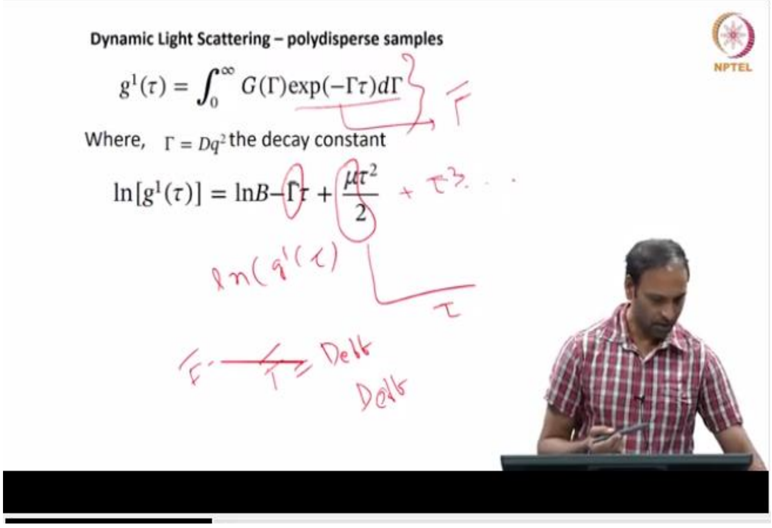

Dynamic Light Scattering – polydisperse samples

$g^1(\tau) = \int_0^\infty G(\Gamma)\exp(-\Gamma\tau)d\Gamma$ Γ

Where, $\Gamma = Dq^2$ the decay constant

$\ln[g^1(\tau)] = \ln B - \Gamma\tau + \frac{\mu\tau^2}{2} + \tau^3 \ldots$

ln(g'(τ))

τ

Γ ⟶ τ = Delt

Delt

And if you have something like that then what you do is you can expand exponential function around some average tau bar okay, this tau bar is what is called as a decay constant okay, it is what is called as a is s the decay constant and then if you know kind of leave out all the higher order terms okay so you what you do is if you plot ln of g1 of tau versus tau is what you have access to right.

Then I can fit a function and I can get what is tau bar and what is mu by 2 okay and from tau bar you know if it is tau bar I can get the effective, that is the effective diffusion coefficient not D anymore because you have particles of many different sizes and because I am interested to get what is the average size I will get what is D effective okay and this mu will have information about the polydispersity of the sample okay.

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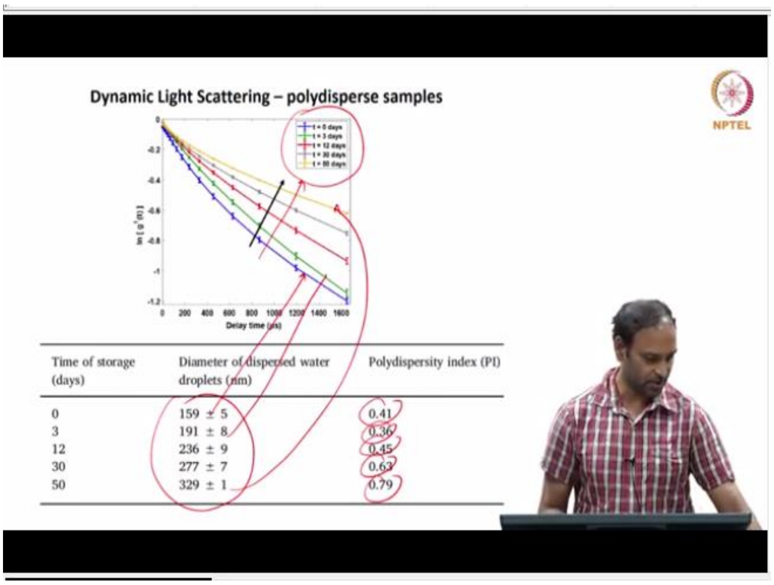

Dynamic Light Scattering – polydisperse samples

Time of storage (days)	Diameter of dispersed water droplets (nm)	Polydispersity index (PI)
0	159 ± 5	0.41
3	191 ± 8	0.36
12	236 ± 9	0.45
30	277 ± 7	0.63
50	329 ± 1	0.79

These are again some experiments where we were trying to measure again some size as a function of time for a different kind of emulsions where as a function of time you see that you know this is as a function of time okay, this variation already tells you that there is something changing right, there is a change in the size as you wait for many, many days okay and that is the data that you obtain okay.

For the first sample that is the size okay, second sample that is the size right and for the last sample that is the size and I can extract what is called a polydispersity index okay. So, therefore you can you know work with either monodisperse samples or polydisperse sample you can extract you know the size or the polydispersity index from such measurements.

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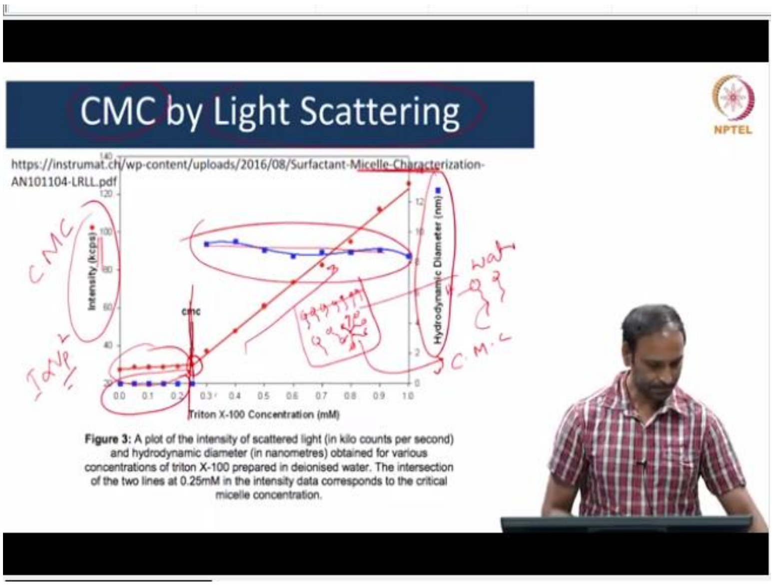

CMC by Light Scattering

https://instrumat.ch/wp-content/uploads/2016/08/Surfactant-Micelle-Characterization-AN101104-LRLL.pdf

Figure 3: A plot of the intensity of scattered light (in kilo counts per second) and hydrodynamic diameter (in nanometres) obtained for various concentrations of triton X-100 prepared in deionised water. The intersection of the two lines at 0.25mM in the intensity data corresponds to the critical micelle concentration.

I have couple of more example this is a using a light scattering to measure what is called a CMC right, critical micellar concentration right. So, typically what happens is if I have say for example water and I add surfactant molecules right which are represented something like this, that is the head group or the hydrophilic part and that is a tail group or the hydrophobic part, the moment I put them in water initially at low concentration you will have individual surfactant molecules.

And then some of them may go to the interface because of the surface active nature and then with increase in the concentration you will reach a case condition where the interface is completely populated with surfactant and when you add more surfactant that is when you get these micelles right and that concentration is what is called as a critical micellar concentration right, what you are measuring here is the intensity I mentioned right.

It is intensity is in KCPS and on the right side you have hydrodynamic size okay, I mentioned that if you look at because intensity I said intensity is proportional to volume square right initially you have only monomers right or small aggregates you know you do not have any scattering or very little scattering but at a particular location you see that the scattering basically increases right.

That you can think about this could be because of the change in the size from maybe a small aggregate to a micelle right. So, therefore that point you could think about as a CMC okay, the other way of looking at this would be that of course when you do use DLS measurements below a particular concentration again you have small species your sizes are going to be very small okay, maybe below the detection limit of the instrument itself.

But at a particular concentration you see that you know you get a size a significant size which can be measured with you know with reasonable accuracy with these instruments okay and that is where essentially, so you can see that you know the whatever I whether I look at the intensity at a particular concentration or the size both of them coincide right okay, that you can think about as a CMC.

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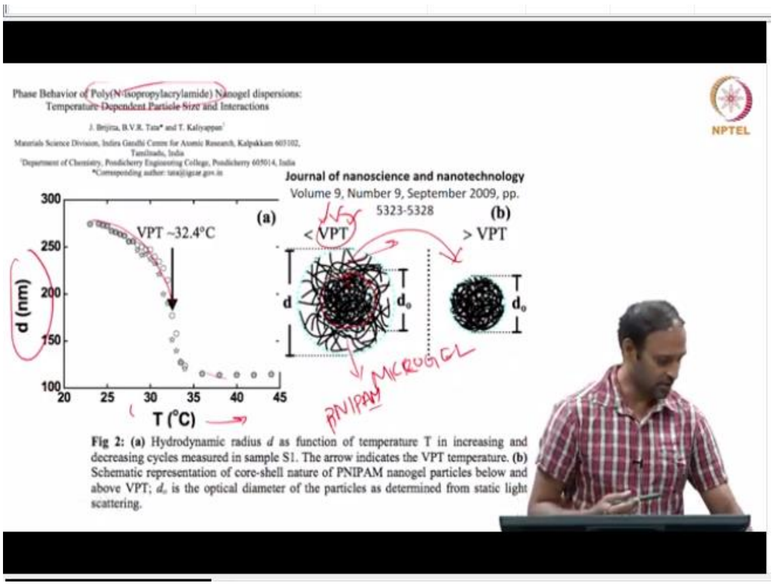

Phase Behavior of Poly(N-isopropylacrylamide) Nanogel dispersions:
Temperature Dependent Particle Size and Interactions

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Fig 2: (a) Hydrodynamic radius *d* as function of temperature T in increasing and decreasing cycles measured in sample S1. The arrow indicates the VPT temperature. (b) Schematic representation of core-shell nature of PNIPAM nanogel particles below and above VPT; d_o is the optical diameter of the particles as determined from static light scattering.

This is another experiment where they were looking at a dispersion which have what is called a VPT volume phase transition and that volume phase transition happens what do I mean by volume phase transition, you have a particle, it is an example what is called a micro gel particles okay and these micro gel particles you should think about them as there is a center where there is a high cross linking density.

These are polymeric particles, however with the center where the polymers are highly cross linked and a outer region where there is a the crossing density is less okay, such particles a particular class of such particles called pNIPAM polynipam okay which stands for something like this okay. These particles if you put them in water and if you heat them up okay if you subject them to temperature change they have a transition going from a expanded state to more like a collapsed state okay.

So, what is done here is measurement of size as a function of temperature okay and at some so this is you know as you decrease the size, so as you increase the temperature there is a decrease in the size right, you can do measurements like that to infer about volume phase transitions and in dispersions like this okay.

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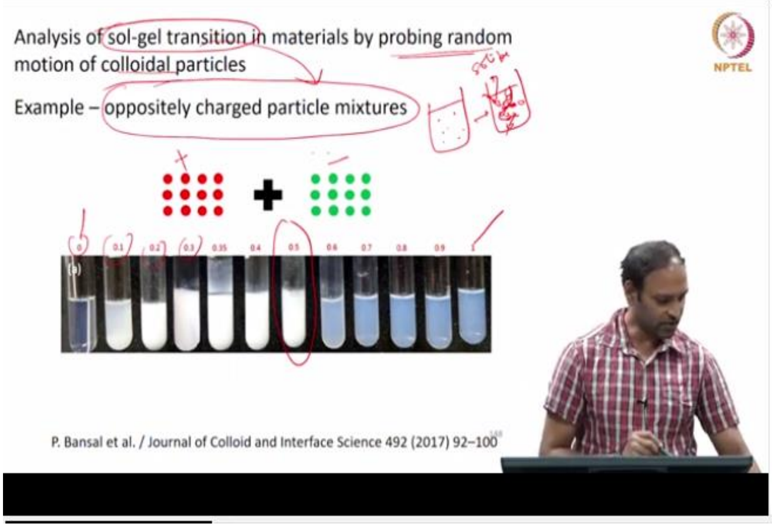

Analysis of sol-gel transition in materials by probing random motion of colloidal particles

Example – oppositely charged particle mixtures

P. Bansal et al. / Journal of Colloid and Interface Science 492 (2017) 92–100

So, now the last part that I wanted to look at is analysis of sol gel transition in materials by probing motion of colloidal particles okay. I have taken an example here just to give you what is sol gel transition, this is an example where you have oppositely charged particle mixtures you could think of this as positive recharge negatively charged particles you mix them okay.

And this number that you see here it tells you the mixing fraction okay. So, 0 means is completely one type of particle, 1 means is completely other type of particle 50 .5 means both of them are in equal proportion okay. Now I want to ask you a question as to of course they look very different right to visually they look very different, if I want to ask you is there a sol gel transition okay in these samples.

If I want to do that what will you do. So, we understand what is sol gel right, in sol you have particles in the gel the particles form a network right I had mentioned that you know is a solid like right, there is a space panning network of the particle right.

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Analysis of sol-gel transition in materials by probing random motion of colloidal particles

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One of the simplest way of doing this would be just invert the wires right, very simple you just invert the wires okay you see that liquid here it just flows there is in this case there is some you know a solid and some is fluid, but however at some concentration everything you know remains right, so right. Now if you want to infer sol gel transition in materials.

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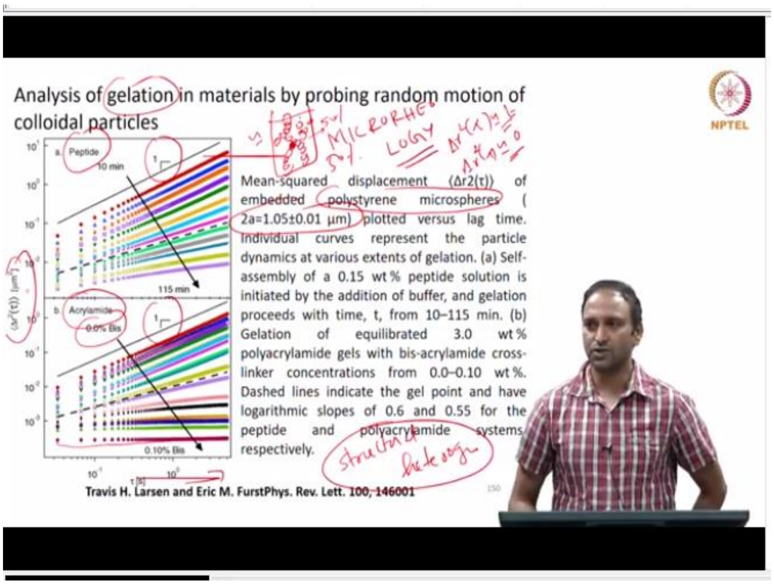

Analysis of gelation in materials by probing random motion of colloidal particles

Mean-squared displacement (Δr2(τ)) of embedded polystyrene microspheres (2a=1.05±0.01 μm) plotted versus lag time. Individual curves represent the particle dynamics at various extents of gelation. (a) Self-assembly of a 0.15 wt % peptide solution is initiated by the addition of buffer, and gelation proceeds with time, t, from 10–115 min. (b) Gelation of equilibrated 3.0 wt % polyacrylamide gels with bis-acrylamide cross-linker concentrations from 0.0–0.10 wt %. Dashed lines indicate the gel point and have logarithmic slopes of 0.6 and 0.55 for the peptide and polyacrylamide systems respectively.

structural heterog

Travis H. Larsen and Eric M. FurstPhys. Rev. Lett. 100, 146001

What people do is they use a technique called microrheology okay in which what you do is in the system that is undergoing gelation, you put in some probe particles okay. These probe particles if you are using microscopy typically you take particles which are you know micron size length scale. So, in this case they have taken polystyrene microspheres of you know 1.05 plus or minus 0.01 micrometer dimension.

You put these probe particles in a solution which is undergoing gelation okay and then the only thing that you should ensure is that the concentration of these particles is **is** very low and these particles in no way should influence the gelation process right and what you do is you look at these probe particles and you measure their Brownian motion I can get mean square displacement okay as a function of time okay.

We have discussed you know how to do that right and what you are looking at is 2 separate systems okay in one case it is a peptide in other cases it is a polymer okay and what is being measured is means displacement as a function of time and we learned that your mean square displacement okay will actually go as t that means your pre factor okay will have a slope of 1. If the particles are in a viscous fluid they are purely diffusive right they are in a viscous fluid.

However when the gelation happens your del square of r of tau should almost become 0 because the particles are stuck in a network okay and they do not exhibit any Brownian motion anymore okay. That is what you see here right, if you look at this case what they have done is that they have added a reagent which will induce gelation okay. When there is nothing here the slope of this you know mean square displacement as a function of time is 1.

But with increase in the concentration your it is almost flat okay. Therefore just by measuring mean square displacement as a function of time I can infer something about a sol gel transition okay, people also use these ah kind of probes to look at what is called as a structural heterogeneity okay. Again I am going to take this example of gels right. So, if I have a colloidal gel, now when I say colloidal gel.

So, this is say that you know this is a particle network okay. So, now if you look at a colloidal gel so it will have say that I have taken a dispersion which has say 50% particles by volume and I have made that to gel okay I have induced gelation. So, you will have 50% still water right or the fluid. The continuous phase okay whatever that you had it is still 50%. Now if I have a probe particle then depending upon the whether a probe particle is in that free space okay or whether it is embedded in the network okay.

It will either exhibit you know this random motion or it does not right depending upon okay whether it is in the part of the network or whether it is in the you know pores okay or the fluid between in the network okay. Therefore by doing some experiment like that I can actually look at what is a structural heterogeneity okay. So, therefore measurement of Brownian motion is a very powerful tool you could use it for you know studying particle size.

You can you know do experiment like this you know where I can infer something about gelation time or the dynamics leading to gelation and things like that okay. So, maybe with that I will stop here.