Introduction to Polymer Science
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Lecture – 30
Light Scattering Techniques for MW and Size Measurement (Contd.,)

Welcome back. In this lecture, light scattering technique for molecular weight measurements will be discussed. Other techniques related to size measurements for polymer molecules will also be discussed.

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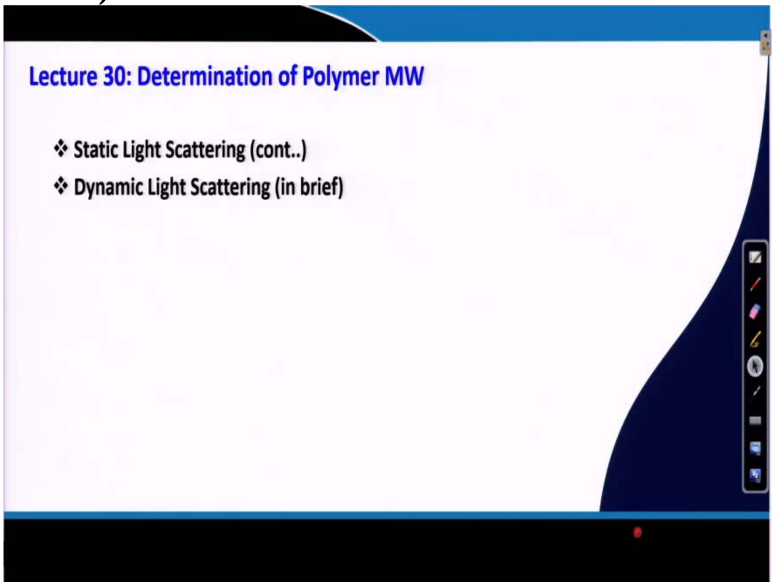

Lecture 30: Determination of Polymer MW

- Static Light Scattering (cont..)
- Dynamic Light Scattering (in brief)

So basically, I will continue with the discussion on static light scattering. And I will briefly talk about dynamic light scattering techniques.

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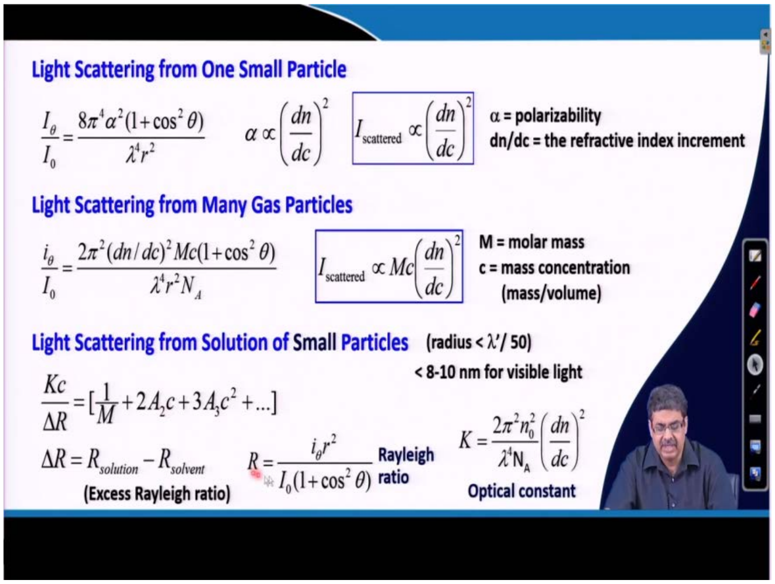

Light Scattering from One Small Particle

$$\frac{I_\theta}{I_0} = \frac{8\pi^4\alpha^2(1+\cos^2\theta)}{\lambda^4 r^2} \qquad \alpha \propto \left(\frac{dn}{dc}\right)^2 \qquad \boxed{I_{scattered} \propto \left(\frac{dn}{dc}\right)^2}$$

α = polarizability
dn/dc = the refractive index increment

Light Scattering from Many Gas Particles

$$\frac{i_\theta}{I_0} = \frac{2\pi^2(dn/dc)^2 Mc(1+\cos^2\theta)}{\lambda^4 r^2 N_A} \qquad \boxed{I_{scattered} \propto Mc\left(\frac{dn}{dc}\right)^2}$$

M = molar mass
c = mass concentration (mass/volume)

Light Scattering from Solution of Small Particles (radius < λ′/ 50)
< 8-10 nm for visible light

$$\frac{Kc}{\Delta R} = [\frac{1}{M} + 2A_2c + 3A_3c^2 + ...]$$

$$\Delta R = R_{solution} - R_{solvent}$$

(Excess Rayleigh ratio)

$$R = \frac{i_\theta r^2}{I_0(1+\cos^2\theta)}$$

Rayleigh ratio

$$K = \frac{2\pi^2 n_0^2}{\lambda^4 N_A}\left(\frac{dn}{dc}\right)^2$$

Optical constant

As discussed in the last lecture for light scattering from one small particle, the expression as given below shows that the polarizability α, is related to $\left(\frac{dn}{dc}\right)^2$ where $\frac{dn}{dc}$ is the refractive index increment. For a collection of small particles like gaseous particles and for light scattering from many gas particles, we got the expression where M is the molar mass or molecular weight c the mass concentration in terms of mass/volume. Next, we discussed light scattering from a solution of small particles, i.e. which have radius < λ′/50, where λ′ is the wavelength of the incident light in the medium. This is not a very hard and fast rule that this radius has to be less than λ′/50, could be λ′/40 or λ′/30, depending upon the particles.

Light scattering from one small particle;

$$\frac{I_\theta}{I_0} = \frac{8\pi^4\alpha^2(1+cos^2\theta)}{\lambda^4 r^2}$$

$$\alpha \propto \left(\frac{dn}{dc}\right)^2$$

$$I_{scattered} \propto \left(\frac{dn}{dc}\right)^2$$

Light scattering from many gas particles;

$$\frac{i_\theta}{I_0} = \frac{2\pi^2 (dn/dc)^2 Mc(1 + cos^2\theta)}{\lambda^4 r^2 N_A}$$

$$I_{scattered} \propto Mc\left(\frac{dn}{dc}\right)^2$$

Light scattering from solution of small particles;

$$\frac{Kc}{\Delta R} = \left[\frac{1}{M} + 2A_2c + 3A_3c^2 + \cdots\right]$$

$$\Delta R = R_{solution} - R_{solvent}$$

$$R = \frac{i_\theta r^2}{I_0(1 + cos^2\theta)}$$

$$K = \frac{2\pi^2 n_0^2}{\lambda^4 N_A}\left(\frac{dn}{dc}\right)^2$$

In case of visible light this small particle will have radius around 8-10 nm. So the particles which have radius less than 10 nm, we would have this light scattering expression applicable to them. Light scattering for solution also depend on the light scattering due to concentration fluctuation of the solvent molecules as well as the solute molecules, in this case polymer molecule.

For solute molecules, the light scattering from solvent molecules were nullified by taking excess Rayleigh ratio as represented here and the concentration fluctuation from solute molecules were accounted by this Rayleigh expression related to osmotic pressure.

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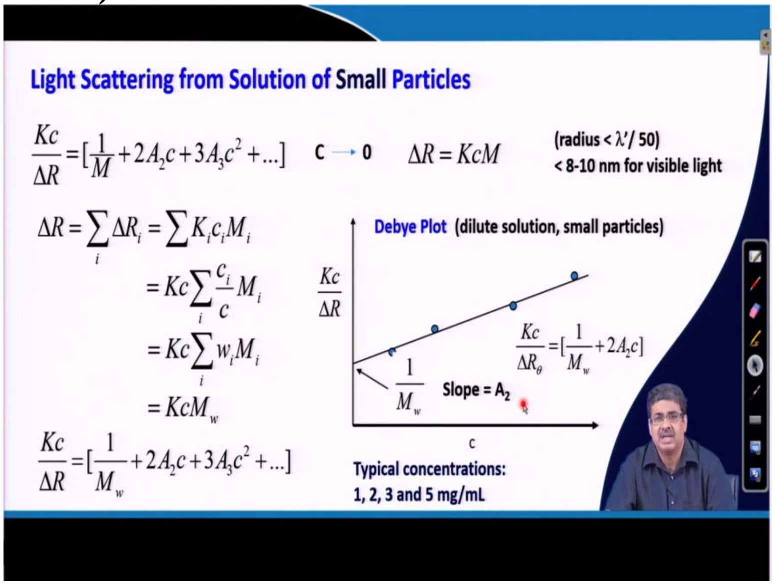

Light Scattering from Solution of Small Particles

$\frac{Kc}{\Delta R}=[\frac{1}{M}+2A_2c+3A_3c^2+...]$ c → 0 $\Delta R=KcM$ (radius < $\lambda'/50$) < 8-10 nm for visible light

$$\Delta R=\sum_i \Delta R_i=\sum K_i c_i M_i$$
$$=Kc\sum_i \frac{c_i}{c}M_i$$
$$=Kc\sum_i w_i M_i$$
$$=KcM_w$$
$$\frac{Kc}{\Delta R}=[\frac{1}{M_w}+2A_2c+3A_3c^2+...]$$

Debye Plot (dilute solution, small particles)

Typical concentrations:
1, 2, 3 and 5 mg/mL

When we talk about polymer molecules we actually have a mixture of molecular weights. So in this case which molecular weight, whether it is a number average molecular weight, weight average molecular weight is applicable, that we will see now. For that we will consider the solution having very low concentration, near to 0. Then that expression will turn out to be this.

$$\frac{Kc}{\Delta R}=\left[\frac{1}{M}+2A_2c+3A_3c^2+\cdots\right];\ c\to 0;$$
$$\Delta R = KcM$$
$$\Delta R=\sum_i \Delta R_i=\sum K_i c_i M_i=K_c\sum_i \frac{c_i}{c}M_i=K_c\sum_i w_i M_i=KcM_w$$
$$\frac{Kc}{\Delta R}=\left[\frac{1}{M_w}+2A_2c+3A_3c^2+\cdots\right]$$

We assume that this excess Rayleigh ratio for the number of polymer molecules in solution is given by summation of the excess Rayleigh ratio for individual polymer molecules. Hence, we can write the total excess Rayleigh ratio as the summation of Rayleigh ratios for individual molecules. Hence we can write this expression where M_i is the molecular weight of individual polymer molecules and c is the concentration for individual polymer molecules, remember this is in weight/volume.

So we divide both sides by c and multiply by c. The M which we are talking about is M_w. Hence we will write the expression for a polydisperse polymer molecule. Now for a small particle we can get the value of M_w by this expression itself if we make few solutions of that particular polymer having different concentrations in the range of dilute polymer solution and then plot $\frac{K_c}{\Delta R}$ against concentration. Then we will get the intercept as $\frac{1}{M_w}$ and the slope would be A_2 because if we deal with very low concentration solution, the higher terms will be neglected. This plot is known as Debye plot and it is applicable for dilute solution and small particle and by small particle we mean particle which has a radius about less than 10 nm for visible light experiment.

Now the typical concentration is about 1-5 mg/mL, generally used for this experiment. We can vary these concentrations depending upon our polymer solvent system, polymer molecular weight as well. So when the polymer size is small enough then we can calculate or we can determine the scattering intensity at any angle and by plotting this with concentration of solution from the intercept we can get the value of M_w using Debye plot. We can also get the value of A_2, which will give us the value of polymer solvent interaction parameter χ.

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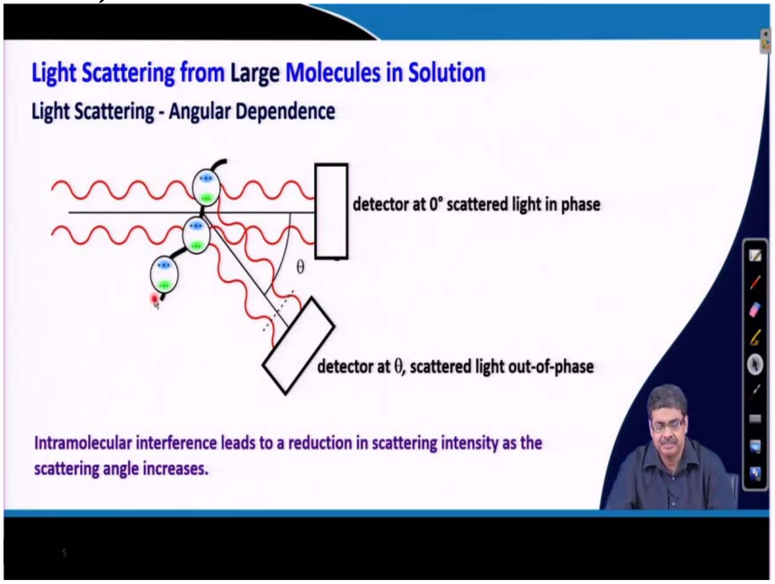

Light Scattering from Large Molecules in Solution

Light Scattering - Angular Dependence

Intramolecular interference leads to a reduction in scattering intensity as the scattering angle increases.

Next, let us move to light scattering from large molecules in solution. Now there are polymer samples which have very large molecules and we will now discuss light scattering for large particles to know the equations relevant for those systems. Large means as we discussed, the radius has to be greater than λ′/50. If we have a large particle, in that case the scattering intensity or the scattered light from different parts of these large molecule, like in case of a polymer molecule will have different path length to cover.

When our scattering angle is not zero then you can see that the two scattered radiation are not in phase and hence the scattering intensity will get reduced as we increase the scattering angle. At scattering angle zero there will be no destructive interference. So the scattered light will be in phase and will have the highest intensity of scattered light. Unfortunately, we cannot determine the intensity of scattered light at zero angle because there is a transmitted light, which is the major portion of the light that will come into this detector, and it is impossible for any equipment to determine the scattered light intensity by detector, which is placed at 0º. So intramolecular interference leads to a reduction in scattering intensity as the scattering angle increases. Higher is the scattering angle higher would be this interference. As a result, the scattering intensity will come down and that happens for a large particle.

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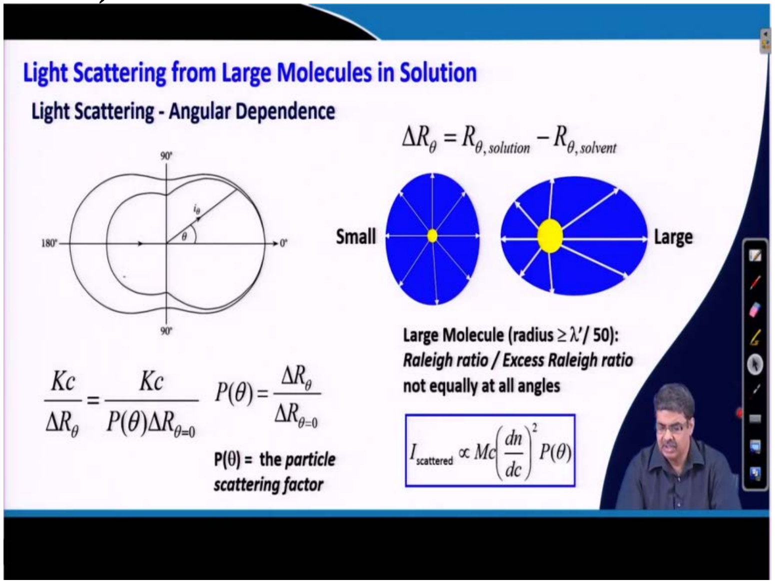

Light Scattering from Large Molecules in Solution

Light Scattering - Angular Dependence

$$\Delta R_\theta = R_{\theta,solution} - R_{\theta,solvent}$$

Large Molecule (radius ≥ λ′/ 50):
Raleigh ratio / Excess Raleigh ratio
not equally at all angles

$$\frac{Kc}{\Delta R_\theta} = \frac{Kc}{P(\theta)\Delta R_{\theta=0}} \qquad P(\theta) = \frac{\Delta R_\theta}{\Delta R_{\theta=0}}$$

P(θ) = the *particle scattering factor*

$$\boxed{I_{scattered} \propto Mc\left(\frac{dn}{dc}\right)^2 P(\theta)}$$

If we see the scattering envelop, this outside one is symmetric which is for sample having particle of small size. So in this case, $i_\theta = 180^o - \theta$. Whereas for large particles where this symmetry is broken and as the θ increases, the intensity of scattered light actually decreases. So instead of i_θ if you plot the excess Rayleigh ratio, then for small particle we will get an angle independent scattering, as we discussed earlier.

Light scattering-Angular dependence

$$\frac{Kc}{\Delta R_\theta} = \frac{Kc}{P(\theta)\Delta R_{\theta=0}}$$

$$P(\theta) = \frac{\Delta R_\theta}{\Delta R_{\theta=0}}$$

$$\Delta R_\theta = R_{\theta,solution} - R_{\theta,solvent}$$

$$I_{scattered} \propto Mc\left(\frac{dn}{dc}\right)^2 P(\theta)$$

The value of excess Rayleigh scattering, excess Rayleigh ratio or Rayleigh ratio is independent of the angle for a small particle but it is dependent on the angle scattering angle for large particle. For a large particle the Rayleigh ratio or excess Rayleigh ratio is not equal at all angles. So we will have to add an another term P(θ) for the expression which we deduced earlier where P(θ) is the ratio at the angle of measurements with the $\Delta R_{\theta=0}$. In this case we are putting a subscript θ that means this term is for a particular angle θ, since for larger particle this value will depend on the value of θ whereas for small particle we did not put this θ because the term is not dependent on the value of θ. P(θ) is particle scattering factor and as the size increases or the angle of measurements or scattering angle increases, the value of P(θ) actually comes down and the highest value of P(θ) when θ becomes zero is 1, so P(θ) either 1 or less than 1.

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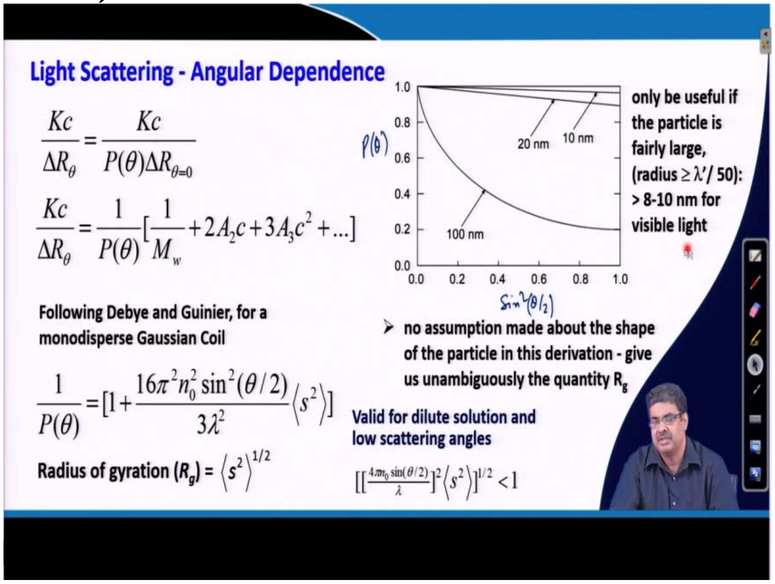

Light Scattering - Angular Dependence

$$\frac{Kc}{\Delta R_\theta} = \frac{Kc}{P(\theta)\Delta R_{\theta=0}}$$

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{P(\theta)}\left[\frac{1}{M_w} + 2A_2c + 3A_3c^2 + \ldots\right]$$

Following Debye and Guinier, for a monodisperse Gaussian Coil

$$\frac{1}{P(\theta)} = \left[1 + \frac{16\pi^2 n_0^2 \sin^2(\theta/2)}{3\lambda^2}\left\langle s^2\right\rangle\right]$$

Radius of gyration (R_g) = $\left\langle s^2\right\rangle^{1/2}$

only be useful if the particle is fairly large, (radius ≥ λ′/ 50): > 8-10 nm for visible light

- no assumption made about the shape of the particle in this derivation - give us unambiguously the quantity R_g

Valid for dilute solution and low scattering angles

$$\left[\left[\frac{4\pi n_0 \sin(\theta/2)}{\lambda}\right]^2\left\langle s^2\right\rangle\right]^{1/2} < 1$$

So we have now included in the expression for this value where we now included with term P(θ). Now following Debye and Guinier for a monodisperse gaussian coil we are not going to derivation of this expression, we can just write the expression for P(θ) which is given by this where this term is radius of gyration and this is valid for dilute solution and low scattering angles. Now if you look at the angle dependence of this P(θ), P(θ) is plotted with $\sin^2(\theta/2)$. In this case as you can see when the radius increases, the size of the particle increases, the angle dependence increases. So there is a sharp decrease in P(θ) value when the size increases but when the size becomes lower and lower the angle dependence actually comes down and when it is 10 nm this is very small. So in this case this was reduced there is no assumption was made for about this shape of the particle.

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{P(\theta)}\left[\frac{1}{M_w} + 2A_2c + 3A_3c^2 + \cdots\right]$$

$$\frac{1}{P(\theta)} = \left[1 + \frac{16\pi^2 n_0^2 sin^2(\theta/2)}{3\lambda^2}\langle S^2\rangle\right]$$

Radius of gyration, $(R_g) = \langle S^2\rangle^{1/2}$

$$\left[\left[\frac{4\pi n_0 sin(\theta/2)}{\lambda}\right]^2 \langle S^2\rangle\right]^{1/2} < 1$$

Hence these gives us unambiguously the quantity radius of gyration, of course looking at this curve we can see that this angle dependent experiment be only useful for the particle which has largest size which has angle dependence of this term but if the particle is size is low then there is no angular dependency on this term and this will not be useful. So this angular dependence experiment is only useful for particles having larger than this value which is nearly more than 10 nm for visible light.

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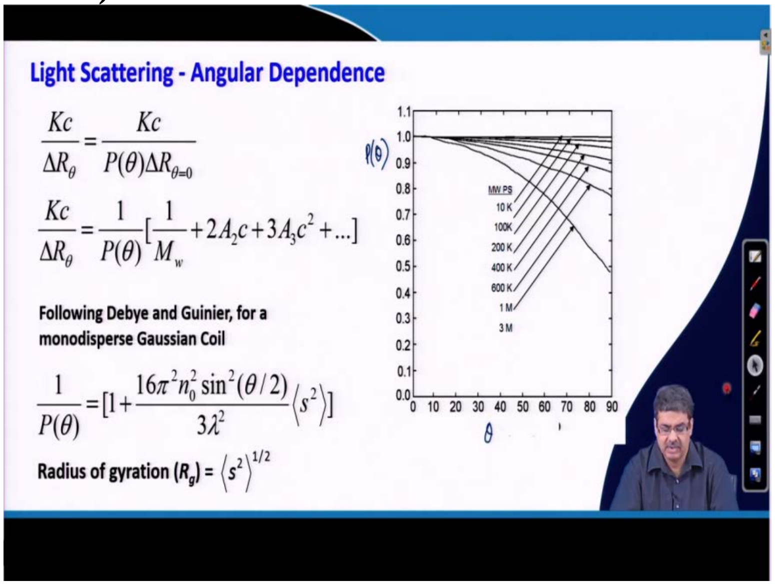

Light Scattering - Angular Dependence

$$\frac{Kc}{\Delta R_\theta} = \frac{Kc}{P(\theta)\Delta R_{\theta=0}}$$

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{P(\theta)}[\frac{1}{M_w} + 2A_2c + 3A_3c^2 + ...]$$

Following Debye and Guinier, for a monodisperse Gaussian Coil

$$\frac{1}{P(\theta)} = [1 + \frac{16\pi^2 n_0^2 \sin^2(\theta/2)}{3\lambda^2}\langle s^2 \rangle]$$

Radius of gyration (R_g) = $\langle s^2 \rangle^{1/2}$

So in last slide we showed about the size how does it translates to actual polymer molecule. So in this case again we plot P(θ) versus θ, the angle of measurement, and it is found that when this is polystyrene molecular weight is below about 100 K or below 1 lakh then the angle dependency of P(θ) is very negligible when the molecular weight increases then the angle dependency comes becomes significant.

So if we deal with polystyrene molecule which is less then approximately 1 lakh molecular weight then we do not need an angle dependent study. We can actually get the molecular weight information to a fairly accurate value by only using Debye plot where we can just consider the scattering intensity at any angle but if the sample or if the polymer which we are dealing with is higher than say about 1 lakh then we need to do an angle dependent light scattering study to get accurate information.

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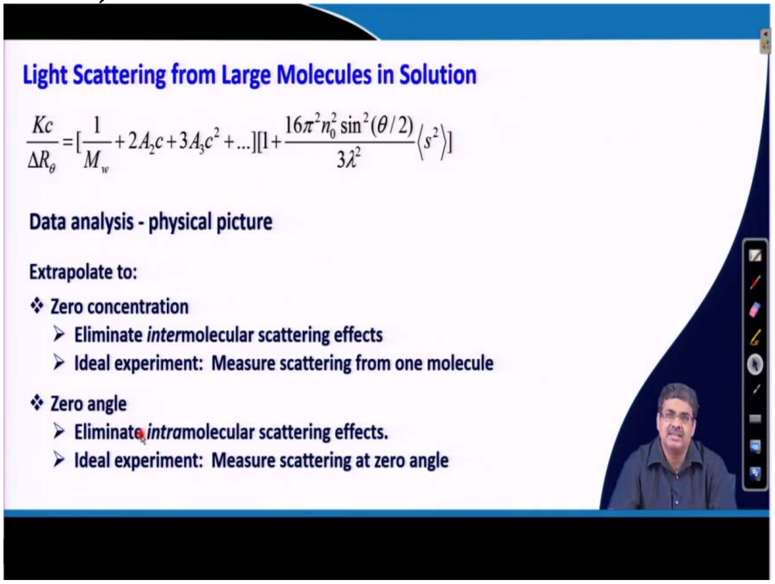

Light Scattering from Large Molecules in Solution

$$\frac{Kc}{\Delta R_\theta}=[\frac{1}{M_w}+2A_2c+3A_3c^2+...][1+\frac{16\pi^2 n_0^2\sin^2(\theta/2)}{3\lambda^2}\langle s^2\rangle]$$

Data analysis - physical picture

Extrapolate to:

- ❖ Zero concentration
  - ➢ Eliminate *inter*molecular scattering effects
  - ➢ Ideal experiment: Measure scattering from one molecule
- ❖ Zero angle
  - ➢ Eliminate *intra*molecular scattering effects.
  - ➢ Ideal experiment: Measure scattering at zero angle

Now so this is the final expression and we have seen that the light scattering intensity or the excess Rayleigh scattering, depends on both concentration of the polymer solution as well as the θ, which is scattering angle, and of course on the radius of gyration value and molecular weight value of the polymer molecule. For analyzing the data if we extrapolate to zero concentration then that will eliminate intermolecular scattering effect. So ideally we should do an experiment with 1 molecule but which is not possible for us.

Light scattering from large molecules in solution,

$$\frac{Kc}{\Delta R_\theta}=\left[\frac{1}{M_w}+2A_2c+3A_3c^2+\cdots\right]\left[1+\frac{16\pi^2 n_0^2 sin^2(\theta/2)}{3\lambda^2}\langle S^2\rangle\right]$$

So we can actually extrapolate to zero concentration. In doing that we will be able to eliminate the intermolecular scattering effect. If we extrapolate to zero angle then we can eliminate the intramolecular scattering effect. And again ideally if we can do the experiment at zero angle then we can remove this intramolecular scattering effect as well. But as we cannot practically do a measurement at zero angle we need to extrapolate the scattering intensity at several angles to zero angle to remove the intramolecular scattering effect.

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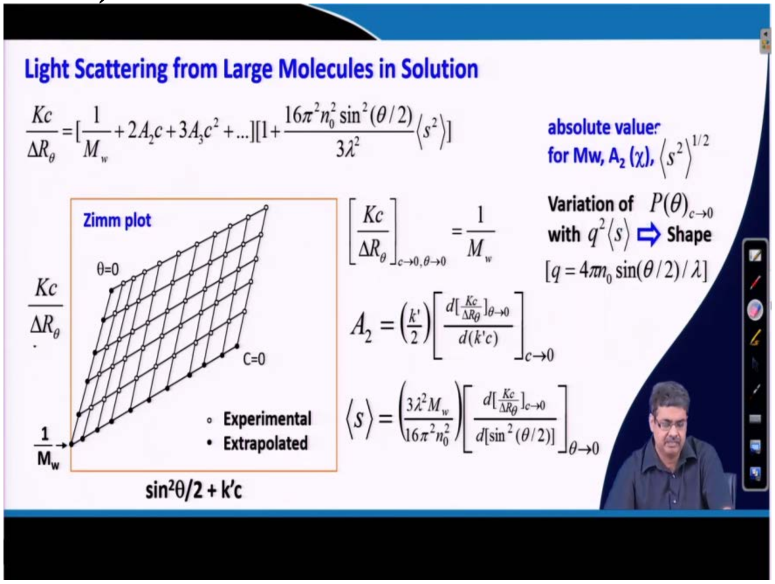

Light Scattering from Large Molecules in Solution

$$\frac{Kc}{\Delta R_\theta} = [\frac{1}{M_w} + 2A_2c + 3A_3c^2 + ...][1 + \frac{16\pi^2 n_0^2 \sin^2(\theta/2)}{3\lambda^2}\langle s^2 \rangle]$$

absolute values for Mw, A_2 (χ), $\langle s^2 \rangle^{1/2}$

Variation of $P(\theta)_{c\to 0}$ with $q^2\langle s \rangle$ ⇨ Shape

$[q = 4\pi n_0 \sin(\theta/2)/\lambda]$

$$\left[\frac{Kc}{\Delta R_\theta}\right]_{c\to 0,\theta\to 0} = \frac{1}{M_w}$$

$$A_2 = \left(\frac{k'}{2}\right)\left[\frac{d[\frac{Kc}{\Delta R_\theta}]_{\theta\to 0}}{d(k'c)}\right]_{c\to 0}$$

$$\langle s \rangle = \left(\frac{3\lambda^2 M_w}{16\pi^2 n_0^2}\right)\left[\frac{d[\frac{Kc}{\Delta R_\theta}]_{c\to 0}}{d[\sin^2(\theta/2)]}\right]_{\theta\to 0}$$

So this is what is done by scientist Bruno Zimm, and this plot is called Zimm plot. In this case a set of polymer solutions are made in different concentration in dilute region, say for example, c1, c 2, c 3, c 4, c 5 different concentration and measurements for each of these solutions are done at different scattering angle and these are the value of this is plotted the respect to $\sin^2(\theta/2) + k'c$, this k' is kind of arbitrarily choosing constant to make this data in a 2d matrix and c is the concentration.

$$\left[\frac{Kc}{\Delta R_\theta}\right]_{c\to 0,\theta\to 0} = \frac{1}{M_w}$$

$$A_2 = \left(\frac{k'}{2}\right)\left[\frac{d\left[\frac{Kc}{\Delta R_\theta}\right]_{\theta\to 0}}{d(k'c)}\right]_{c\to 0}$$

$$\langle S \rangle = \left(\frac{3\lambda^2 M_w}{16\pi^2 n_0^2}\right)\left[\frac{d\left[\frac{Kc}{\Delta R_\theta}\right]_{c\to 0}}{d[sin^2(\theta/2)]}\right]_{\theta\to 0}$$

$$q = 4\pi n_0 sin(\theta/2)/\lambda$$

These open circles are actually experimental data and these filled circle are extrapolated data. So we go through this line and then extrapolate this line to effectively zero concentration and at different scattering angles. Basically in this experiment we take a particular concentration of solution and measure scattering intensity at different angles, take another concentration and take a measurement at different angles and so on, and then we extrapolate each of these lines to zero angle and each of these concentration at a particular θ is extrapolated to zero concentration. Hence, this line would be for zero concentration and this line would be for zero angle. Now if you plot for concentration zero, in this case, then this line will give us the information about radius of gyration. And if we have θ = 0 then $1 + \frac{16\pi^2 n_0^2 sin^2(\theta/2)}{3\lambda^2}\langle S^2\rangle$ would be 1. Then this line will give an information about A_2 and intercept will give us the information about M_w. So from the intercept which ideally should be intersection of θ = 0 line and c = 0 line give us $\frac{1}{M_w}$ at c = 0 will give us information about radius of gyration and θ = 0 line give us information about the 2nd variant coefficient, hence the polymer solvent introduction parameter.

Now while doing the measurements we have not taken or we have not made any calibration curve. Hence these are absolute measurements. So in these experiments we get the absolute values of M_w, A_2, hence the polymer solid interaction parameter, and radius of gyration. We can also find out some idea about the shape if we plot the P(θ) value at $c \rightarrow 0$ and then plot with $q^2\langle S\rangle$, this should be this S where q is the scattering vector.

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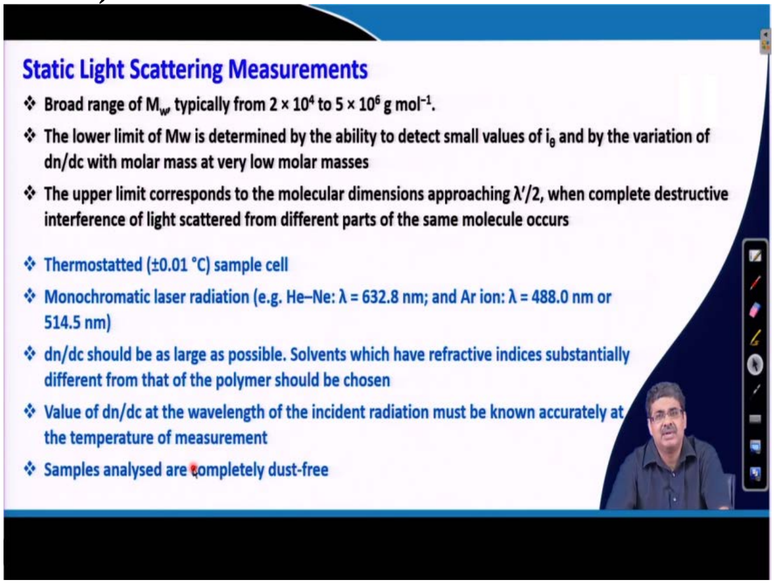

Static Light Scattering Measurements

- Broad range of M_w, typically from 2×10^4 to 5×10^6 g mol^{-1}.
- The lower limit of Mw is determined by the ability to detect small values of i_θ and by the variation of dn/dc with molar mass at very low molar masses
- The upper limit corresponds to the molecular dimensions approaching λ′/2, when complete destructive interference of light scattered from different parts of the same molecule occurs
- Thermostatted (±0.01 °C) sample cell
- Monochromatic laser radiation (e.g. He–Ne: λ = 632.8 nm; and Ar ion: λ = 488.0 nm or 514.5 nm)
- dn/dc should be as large as possible. Solvents which have refractive indices substantially different from that of the polymer should be chosen
- Value of dn/dc at the wavelength of the incident radiation must be known accurately at the temperature of measurement
- Samples analysed are completely dust-free

So in light scattering technique we can use to determine the molecular weight of a broad range. Measurement is determined by the ability to detect small value of scattering and also variation of

$\frac{dn}{dc}$ with molar mass at very low masses. Here, till now we have not considered that the $\frac{dn}{dc}$ was dependent on the molecular weight. We have considered these to be constant but at lower molecular weight range, this may become dependent on the molecule. Then that will limit the measurement as well as form the lower molecular weight polymer. The scattering intensity becomes low and low hence there is a limit to which we can go down in terms of measurements of lower molecular weight, the upper limit corresponds to the molecular weight dimension approaching $\lambda'/2$ when complete destructive interference of light scattered from different parts of the same molecule occurs.

If the particle size is too high then there will be complete destruction of scattered light due to interference from different parts. This experiment has to be done in varied temperature controlled system. It has to be thermostatted at ± 0.01℃. Otherwise there will lot of error and typically these are the lasers which are used for the measurements and because the scattering intensity is dependent on $\left(\frac{dn}{dc}\right)^2$, if you recall, α or the polarizability is dependent on $\left(\frac{dn}{dc}\right)^2$.

So $\frac{dn}{dc}$ should be as large as possible to make the measurements more sensitive and these solvents which have refractive index substantially different from that of the polymer should be chosen. And of course the value of $\frac{dn}{dc}$ at the wavelength of incident radiation must be known accurately at the temperature of measurement. This is another important parameter that samples must be dust free. If there are dust particles then they will actually scatter more light than the polymer sample and there will be lot of error in the measurement.

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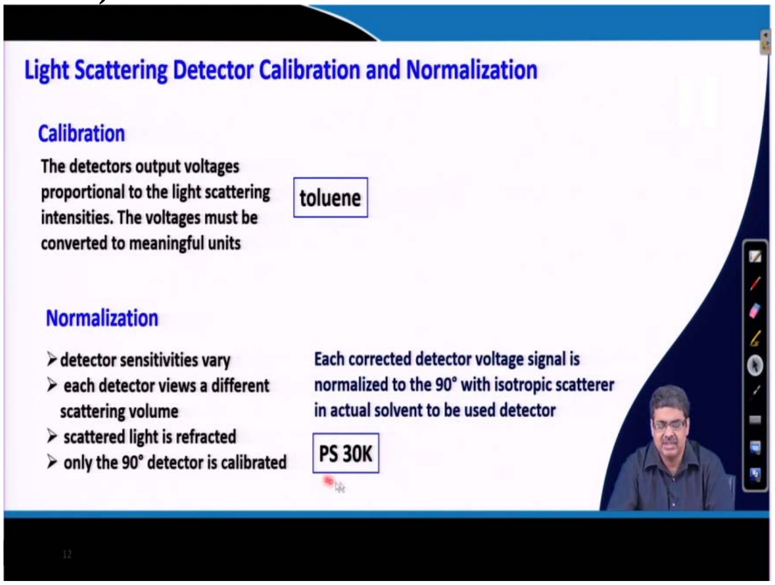

Light Scattering Detector Calibration and Normalization

Calibration

The detectors output voltages proportional to the light scattering intensities. The voltages must be converted to meaningful units

toluene

Normalization

- detector sensitivities vary
- each detector views a different scattering volume
- scattered light is refracted
- only the 90° detector is calibrated

Each corrected detector voltage signal is normalized to the 90° with isotropic scatterer in actual solvent to be used detector

PS 30K

Now the light scattering detector actually measures in terms of millivolts, hence the detector output has to be also calibrated. The signal in terms of millivolts has to be converted to light scattering intensity. For that, a solvent with known light scattering intensity is used to calibrate the detector and also the detector at different angles has to be normalized with respect to one particular detector and for that 90º detector is taken. One isotropic scatterer like polystyrene with 30000 molecular weight, which is known to scatter symmetrically, is taken. The signals from all other scattering angles are normalized with respect to 90º detector using polystyrene of 30K sample.

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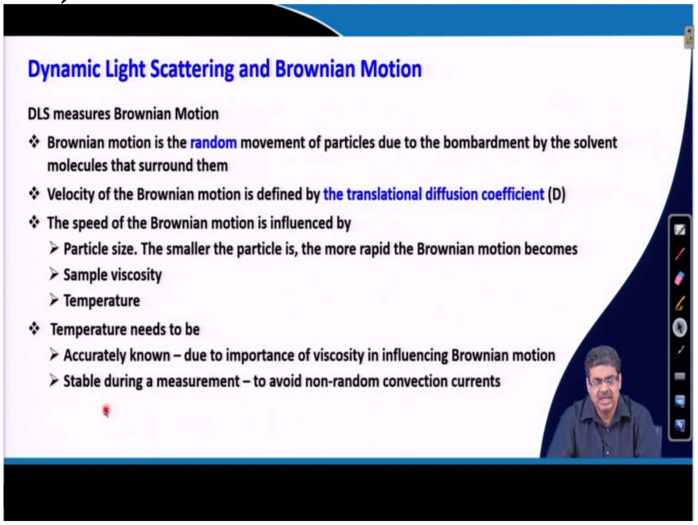

Dynamic Light Scattering and Brownian Motion

DLS measures Brownian Motion

- Brownian motion is the random movement of particles due to the bombardment by the solvent molecules that surround them
- Velocity of the Brownian motion is defined by the translational diffusion coefficient (D)
- The speed of the Brownian motion is influenced by
  - Particle size. The smaller the particle is, the more rapid the Brownian motion becomes
  - Sample viscosity
  - Temperature
- Temperature needs to be
  - Accurately known – due to importance of viscosity in influencing Brownian motion
  - Stable during a measurement – to avoid non-random convection currents

Now we will move to dynamic light scattering, which is used to measure the hydrodynamic size of a solute, in this case the polymer molecule. Dynamic light scattering measures Brownian motion, that is a random movement of particles due to bombardment by the solvent molecules which surround them. Velocity or the speed of Brownian motion is defined by translational diffusion coefficient, which is expressed as D. Speed of Brownian motion is influenced by particle size. Of course, the smaller is a particle, higher will be the Brownian motion; and the viscosity of the medium, higher the viscosity slower would be the Brownian motion; and temperature, temperature will affect the velocity of the sample as well as the speed of the particles present. Hence, temperature needs to be accurately known due as it can influence the viscosity, which can influence the Brownian motion. It must be stable during a measurement to avoid any non random convection currents.

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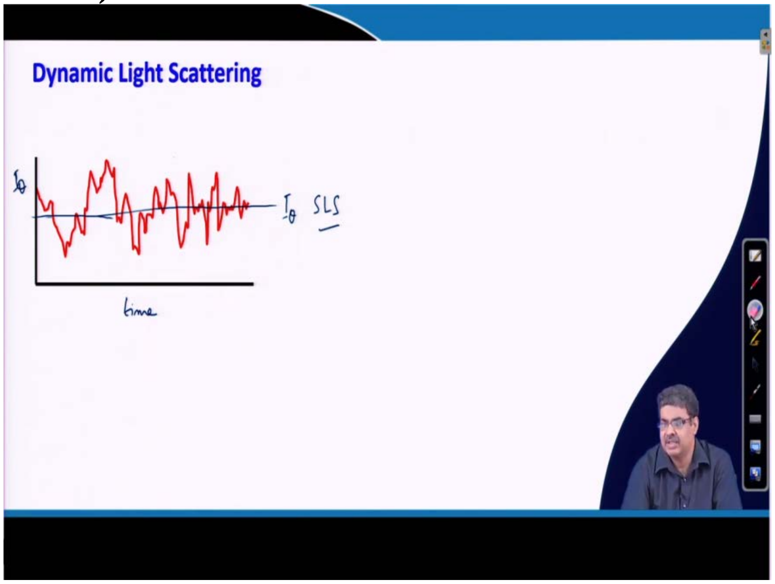

Dynamic Light Scattering

Now as we have seen earlier that in a light scattering experiment, the scattering intensity can be measured at different times and the average intensity is taken in case of static light scattering, but this fluctuation of intensity can be used to measure the translational and diffusion coefficient in dynamic light scattering technique. And that is what we will discuss now in brief.

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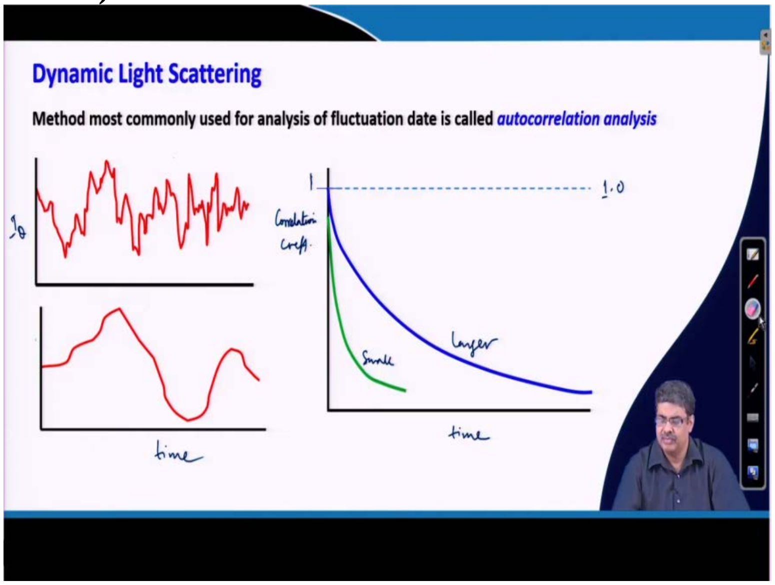

Dynamic Light Scattering

Method most commonly used for analysis of fluctuation date is called *autocorrelation analysis*

As you can understand that if we have a small particle then the fluctuation will be higher and if we have a large particle then the fluctuation will be lower. In this case y axis is i_θ and x axis is time. With time the fluctuation in the scattering intensity will be higher for a small particle because the Brownian motion speed is higher for smaller particle. Now we can use this information and find out the translational diffusion coefficient by a method called autocorrelation analysis.

In this case this signal is correlated at different times and in short, the correlation coefficient is plotted with time. So this smaller particle which will lose its correlation from initial signal; this correlation is one so the value of this is one. That means at the time there is no change in the signal but as more fluctuation happen which happens for small particle then the correlation is lost at the lower time, and when we have a larger particle then correlation is lost at a longer time.

This is like if we have a room with fixed dimensions. There are many people who are randomly moving around, and I have placed a camera on top and taking the photograph at different times. Now if there are small kids, they will run around faster. So the match between the photographs taken in different times will lose parity with the original photograph at much faster time. Whereas if the people were bulky nature or aged person then they will move slower. So the photographs at the beginning will have some similarity. So, it will take less time for the kids to lose the correlation with the initial photograph. With this information on correlation coefficient with time, we can get the information of a diffusion coefficient.

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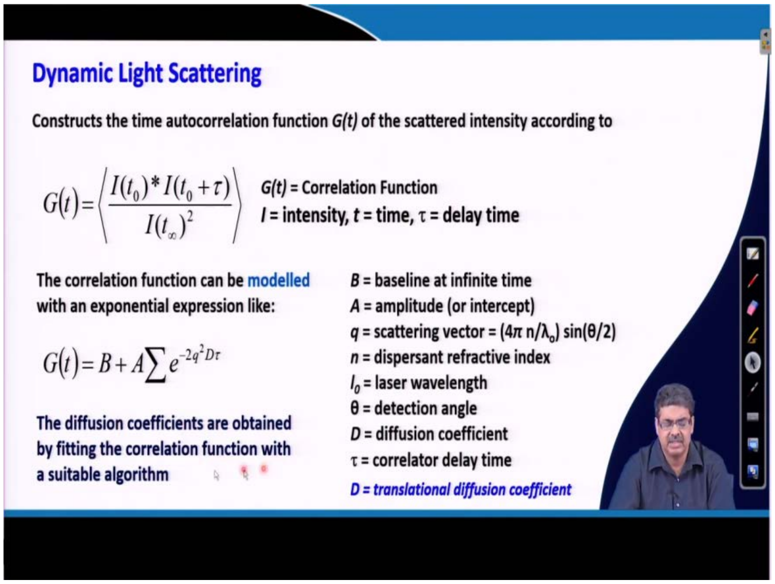

Dynamic Light Scattering

Constructs the time autocorrelation function *G(t)* of the scattered intensity according to

$$G(t)=\left\langle \frac{I(t_0)*I(t_0+\tau)}{I(t_\infty)^2}\right\rangle$$

***G(t)* = Correlation Function**

***I* = intensity, *t* = time, τ = delay time**

The correlation function can be modelled with an exponential expression like:

$$G(t)=B+A\sum e^{-2q^2D\tau}$$

The diffusion coefficients are obtained by fitting the correlation function with a suitable algorithm

***B* = baseline at infinite time**

***A* = amplitude (or intercept)**

***q* = scattering vector = $(4\pi n/\lambda_0)\sin(\theta/2)$**

***n* = dispersant refractive index**

l_0 = laser wavelength

θ = detection angle

***D* = diffusion coefficient**

τ = correlator delay time

D = translational diffusion coefficient

So this software can actually construct the time correlation function of the scattering intensity. According to this expression where I is the intensity, t is the time and this is the time difference of the delay time and this correlation function can be modeled like exponential function, where D is the translational diffusion coefficient. So using this correlation function we can get the value of D and the diffusion coefficients are obtained from this expression by fitting the correlation function with a suitable algorithm.

$$G(t) = \langle \frac{I(t_o)^{*} I(t_0+\tau)}{I(t_\infty)^2} \rangle$$

$$G(t) = B + A\sum e^{-2q^2Dr}$$

scattering vector, $(4\pi n/\lambda_0)sin(\theta/2)$;

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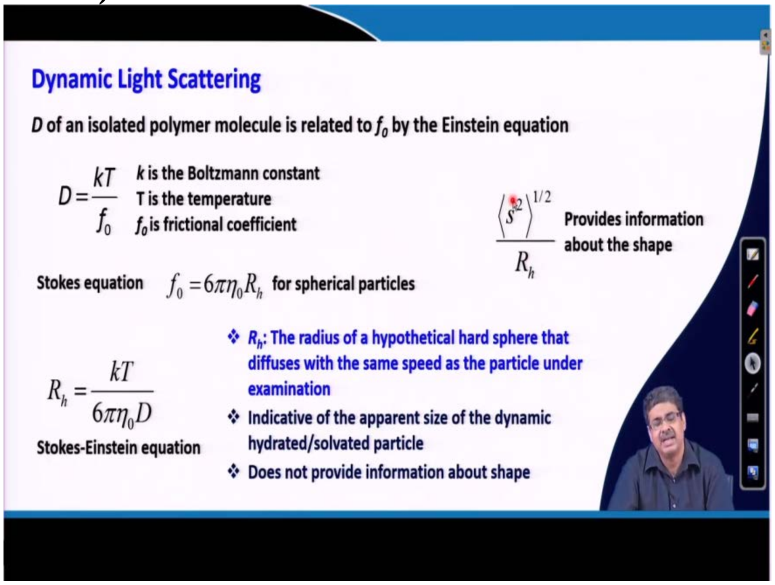

Dynamic Light Scattering

D of an isolated polymer molecule is related to f_0 by the Einstein equation

$$D = \frac{kT}{f_0}$$

k is the Boltzmann constant
T is the temperature
f_0 is frictional coefficient

$$\frac{\langle s^2 \rangle^{1/2}}{R_h}$$

Provides information about the shape

Stokes equation $f_0 = 6\pi\eta_0 R_h$ for spherical particles

$$R_h = \frac{kT}{6\pi\eta_0 D}$$

Stokes-Einstein equation

- R_h: The radius of a hypothetical hard sphere that diffuses with the same speed as the particle under examination
- Indicative of the apparent size of the dynamic hydrated/solvated particle
- Does not provide information about shape

Now D of isolated polymer molecule is related to frictional coefficient by Einstein equation and this friction coefficient of rigid spherical particle is given by Stokes equation where R_h is the radial hydrodynamic radius.

$$D = \frac{kT}{f_0}$$

Stokes equation for spherical particles,

$$f_0 = 6\pi\eta_0 R_h$$

Stokes-Einstein equation,

$$R_h = \frac{kT}{6\pi\eta_0 D}$$

So we combine these to get this expression for R_h and this expression is called Stokes Einstein equation. So we define R_h as the radius of a hypothetical hard sphere that diffuses at the same speed as the particle under examination. Now the particles for which we did measure the dynamic light scattering, that may not be exactly spherical. It could be a polymer random coil or an ellipsoid type or sometimes even like cylindrical type molecule.

But R_h means that we are assuming it to be a hard sphere which has the same translational diffusion coefficient like the particles which under examination. So please remember that this is the value of R_h which is obtained from dynamic light scattering. It is the radius for the equivalent or hypothetical hard sphere which has the same translational diffusion coefficient as the particles which we are examining. This is indicative of apparent size of dynamic hydrated or solvated particle. It does not provide any information about the shape. We can get information about this shape if we can accurately measure the radius of gyration from static light scattering technique. If we can get the value of hydrodynamic radius from dynamic light scattering by combining this static and dynamic light scattering technique which can get some idea about the shape of the polymer molecule or other molecules. With this we come to the end of this lecture. Gel permeation chromatography will be discussed in next lecture.