Introduction to Polymer Science
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Lecture – 29
Dilute Solution Viscometry, Light Scatting Techniques for MW

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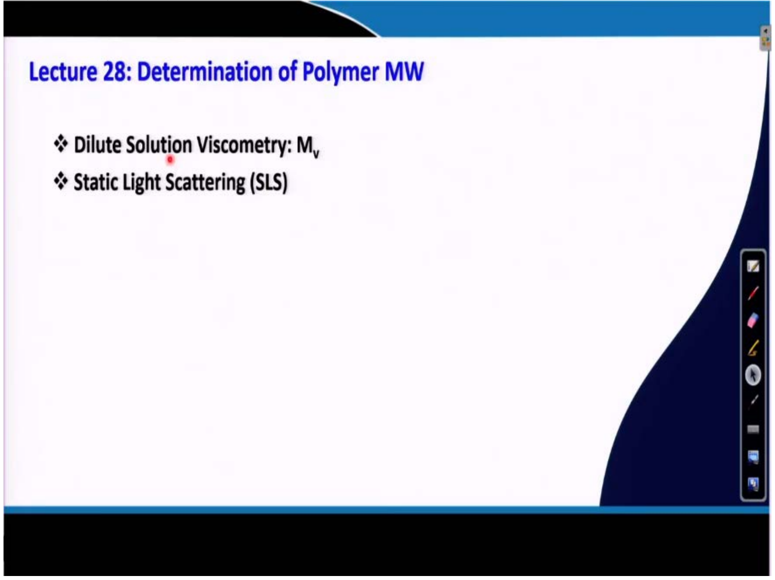

Lecture 28: Determination of Polymer MW

- ❖ Dilute Solution Viscometry: M_v
- ❖ Static Light Scattering (SLS)

Welcome back, we will continue our discussion on determination on polymer molecular weight. In this lecture I will talk about dilute solution viscometry which is utilized to determine viscosity average molecular weight and we will also talk about static light scattering.

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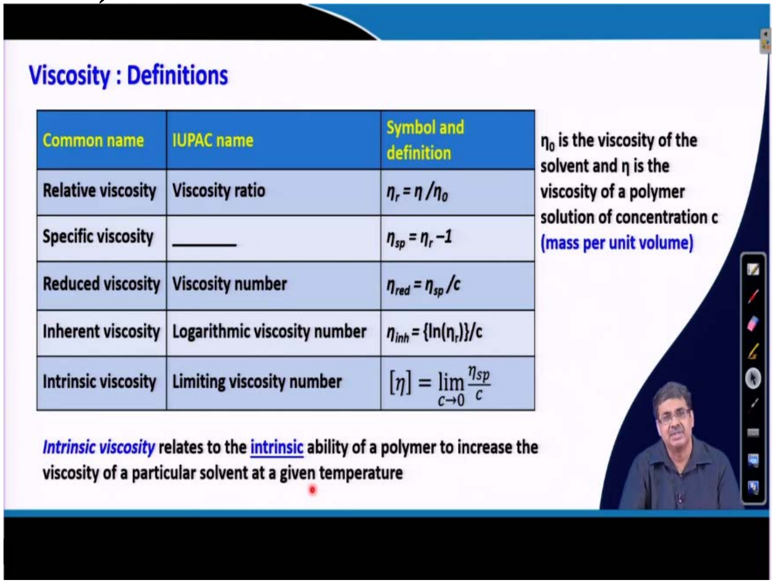

Viscosity : Definitions

Common name	IUPAC name	Symbol and definition
Relative viscosity	Viscosity ratio	$\eta_r = \eta / \eta_0$
Specific viscosity	______	$\eta_{sp} = \eta_r - 1$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp} / c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = \{\ln(\eta_r)\}/c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = \lim_{c\to 0} \frac{\eta_{sp}}{c}$

η_0 is the viscosity of the solvent and η is the viscosity of a polymer solution of concentration c (mass per unit volume)

Intrinsic viscosity relates to the intrinsic ability of a polymer to increase the viscosity of a particular solvent at a given temperature

When talking about viscometry, we are dealing with viscosity of a solution. There are some common terminologies which are very frequently used even now e.g. η_r is a ratio of η and η_0, $\eta_r = \eta/\eta_0$ where η_0 is the viscosity of the solvent and η is the viscosity of polymer solution of concentration c, again c is mass/unit volume. Now η_r is a ratio, so it is unit less as it is the ratio of 2 viscosities. Hence, instead of naming it as relative viscosity, IUPAC suggested to be more technically correct as viscosity ratio. Intrinsic viscosity is very important, it deals with the intrinsic ability of a polymer to increase the viscosity of a particular solvent at a given temperature.

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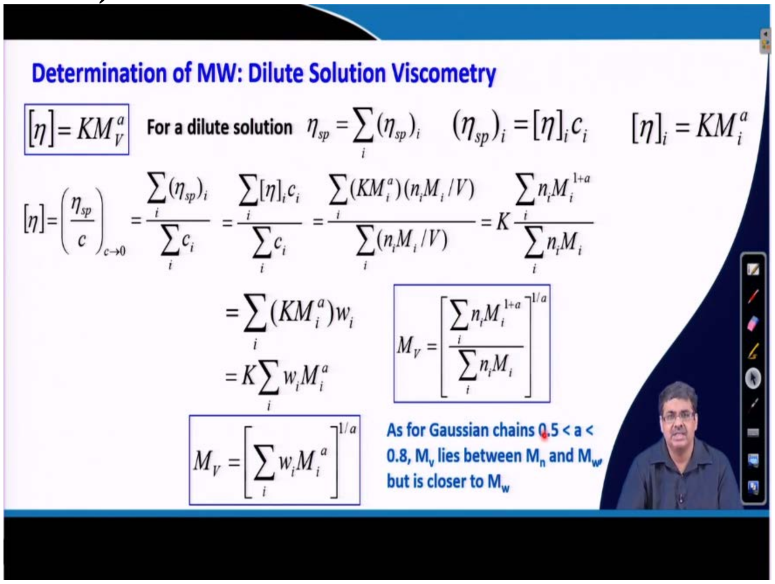

Determination of MW: Dilute Solution Viscometry

$$\boxed{[\eta] = KM_V^a}$$

For a dilute solution $\eta_{sp} = \sum_i (\eta_{sp})_i \qquad (\eta_{sp})_i = [\eta]_i c_i \qquad [\eta]_i = KM_i^a$

$$[\eta] = \left(\frac{\eta_{sp}}{c}\right)_{c\to 0} = \frac{\sum_i (\eta_{sp})_i}{\sum_i c_i} = \frac{\sum_i [\eta]_i c_i}{\sum_i c_i} = \frac{\sum_i (KM_i^a)(n_i M_i / V)}{\sum_i (n_i M_i / V)} = K \frac{\sum_i n_i M_i^{1+a}}{\sum_i n_i M_i}$$

$$= \sum_i (KM_i^a) w_i$$

$$= K \sum_i w_i M_i^a$$

$$\boxed{M_V = \left[\frac{\sum_i n_i M_i^{1+a}}{\sum_i n_i M_i}\right]^{1/a}}$$

$$\boxed{M_V = \left[\sum_i w_i M_i^a\right]^{1/a}}$$

As for Gaussian chains $0.5 < a < 0.8$, M_v lies between M_n and M_w, but is closer to M_w

We have seen this expression earlier, *a* and K are the two constant terms which are constant for a particular polymer, temperature and solvent combination. If we change one of these three, then K and a value changes. This is intrinsic viscosity and this is defined as specific viscosity divide by c as c tends to 0. For a dilute solution, we can assume that the specific viscosity of the solution can be obtained by adding up the specific viscosities of the individual polymer molecule in polydisperse polymer sample.

$$[\eta] = KM_V^a$$

$$For\ a\ dilute\ \ solution, \qquad \eta_{sp} = \sum_i (\eta_{sp})_i ; \quad (\eta_{sp})_i = [\eta]_i c_i \ ; [\eta]_i = KM_i^a$$

$$[\eta] = \left(\frac{\eta_{sp}}{c}\right)_{c\to 0} = \frac{\sum_i (\eta_{sp})_i}{\sum_i c_i} = \frac{\sum_i [\eta]_i c_i}{\sum_i c_i} = \frac{\sum_i (KM_i^a)(n_i M_i / V)}{\sum_i (n_i M_i / V)} = K \frac{\sum_i n_i M_i^{1+a}}{\sum_i n_i M_i}$$

$$= \sum_i (KM_i^a) w_i$$

$$= K \sum_i w_i M_i^a$$

For a dilute solution, the specific viscosity can be written as the intrinsic viscosity for the particular chain multiplied by concentration using this expression. We can also write that intrinsic viscosity of a particular chain is given by this expression where we are basically using the molecular weight of that particular chain. Hence, we can write intrinsic viscosity as summation of the intrinsic viscosities of individual molecules and total concentration as summation of the concentration of individual molecules and this term $c_i / \sum c_i$ is the weight fraction for individual chains. Hence, this is a constant and we can take this out the summation.

$$M_V = \left[\frac{\sum_i n_i M_i^{1+a}}{\sum_i n_i M_i}\right]^{1/a}$$

$$M_V = \left[\sum_i w_i M_i^a\right]^{1/a}$$

We can also write this way where concentration is expressed in terms of number of moles of that particular chain, V is the volume, M_i this is a molecular weight of individuals chains. These are two same expressions, basically we are expressing in terms of weight fraction because this is the easier way as we generally deal with polymer weight samples other than number of moles when we make a solution. For a Gaussian chain like random coils, this value of *a* is between 0.5 and 0.8.

Hence, the value of M_v, viscosity average molecular weight, lies between M_n and M_w but closer to M_w. If you have a very elongated cylindrical type polymer chains then *a* value even goes beyond 0.8, and is closer to 1. In that case, the M_v value would be very close to weight average molecular weight, but for normal random coil Gaussian chain, the M_v value is between M_n and M_w but closer to M_w.

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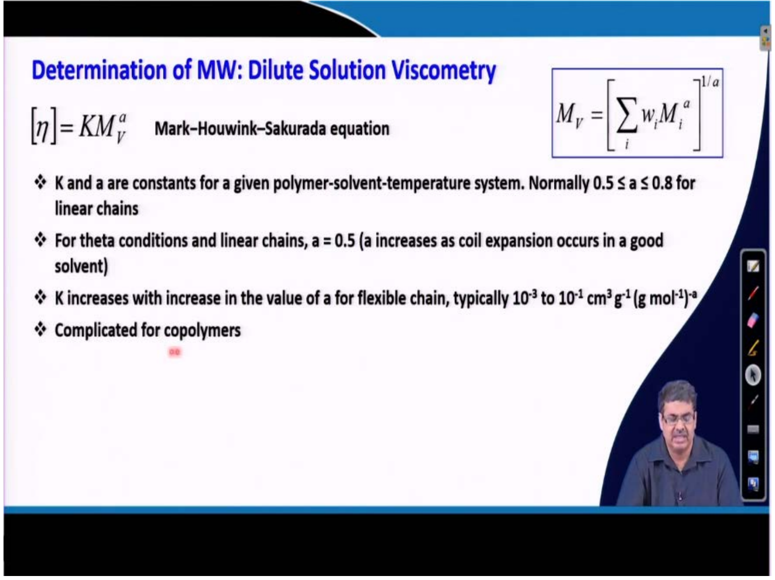

Determination of MW: Dilute Solution Viscometry

$[\eta] = KM_V^a$ Mark–Houwink–Sakurada equation

$$\boxed{M_V = \left[\sum_i w_i M_i^a\right]^{1/a}}$$

- K and a are constants for a given polymer-solvent-temperature system. Normally $0.5 \le a \le 0.8$ for linear chains
- For theta conditions and linear chains, a = 0.5 (a increases as coil expansion occurs in a good solvent)
- K increases with increase in the value of a for flexible chain, typically 10^{-3} to 10^{-1} $cm^3 g^{-1} (g\ mol^{-1})^{-a}$
- Complicated for copolymers

This expression we have used earlier, I have written this Mark Houwink equation earlier but sometimes, it is also called Mark Houwink Sakurada equation. K values are constant for a given polymer-solvent-temperature systems. Normally for linear chain under θ conditions, *a* is 0.5 and K increases with increase in the value of *a* for flexible chains and the type typical value is given and this is very difficult to calculate for copolymer.

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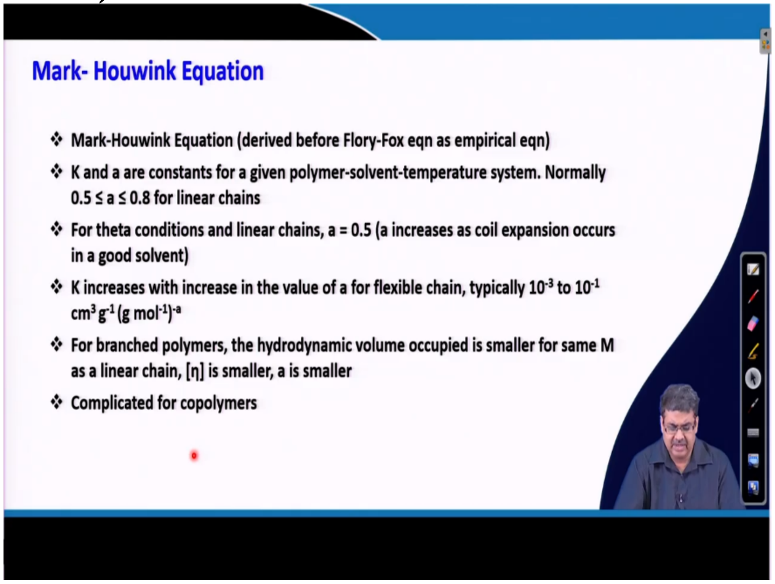

Mark- Houwink Equation

- Mark-Houwink Equation (derived before Flory-Fox eqn as empirical eqn)
- K and a are constants for a given polymer-solvent-temperature system. Normally $0.5 \leq a \leq 0.8$ for linear chains
- For theta conditions and linear chains, a = 0.5 (a increases as coil expansion occurs in a good solvent)
- K increases with increase in the value of a for flexible chain, typically 10^{-3} to 10^{-1} $cm^3 g^{-1} (g\ mol^{-1})^{-a}$
- For branched polymers, the hydrodynamic volume occupied is smaller for same M as a linear chain, [η] is smaller, a is smaller
- Complicated for copolymers

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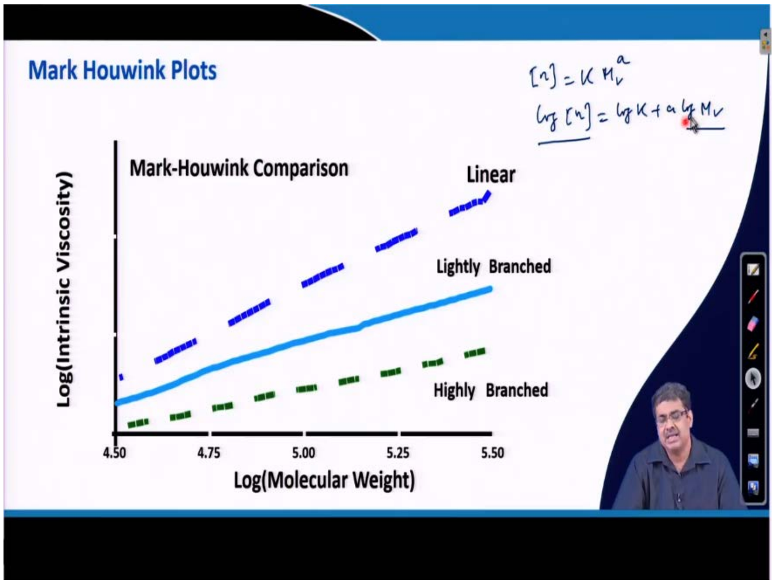

Mark Houwink Plots

$[\eta] = K M_v^a$

$\underline{\log [\eta]} = \log K + a \underline{\log M_v}$

This is the Mark Houwink equation we had talked about this. To find out the viscosity average molecular weight we can plot log of intrinsic viscosity as given by, $[\eta] = KM_v^a$. If we take logarithm of both sides we get $\log [\eta] = \log K + a \log M_v$. So if we plot this in the y axis and this in the x axis, from the slope we can get the value of *a* and from the intercept we can get the value of log K. This value intrinsic viscosity depends on the density of a polymer coil. For a given molecular weight if we have more branches, then the coil density goes up, hydrodynamic volume comes down, intrinsic viscosity also comes down. So depending on the polymer architecture this intrinsic viscosity can be changed, hence this K and *a* value also change. For lightly branched polymers we get lower intrinsic viscosity value. This plot has a lower slope, a value is lower, similarly for very highly branched, a value is even lower and if you have a very elongated polymer then we can have an even steeper slope because that a value will go up. Now the question comes if you have synthesized a new polymer molecule then how can we get the molecular weight? What is the way we can get the molecular weight for unknown polymer molecule?

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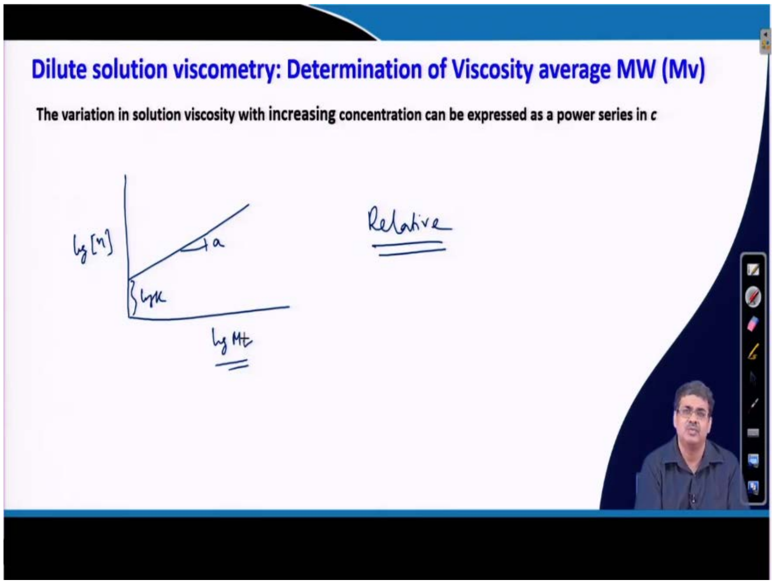

Dilute solution viscometry: Determination of Viscosity average MW (Mv)

The variation in solution viscosity with increasing concentration can be expressed as a power series in *c*

We can make several concentration of polymer solutions and find out [η] for those solutions and then if we know the value for K and a for that particular polymer-solvent-temperature combination then from the intrinsic viscosity we can find out the value of M_v. If we do not know the value of K and a, then what can we do? In that case we need a calibration. We need to find out log [η] and log M_v and we need to find a calibration from which we can get log K and a value. So for generating this straight line, we need to have same polymer with different molecular weights, then only we can find out this log M_v. If we do not know the molecular weight itself how can we plot this? That is a very difficult thing to do or it is not possible. For that what do we need to do? We need to get same polymer sample with different molecular weight of narrow dispersity and measure the molecular weight of those different polymer samples using some other absolute techniques like light scattering, which will be discussed a little later, or osmometry where we can get absolute M_n value. As we have very narrow disperse polymer sample, we can consider that those M_n value or

M_w value which we measured using that absolute technique as equal to M_v. Hence we can use those values and generate a calibration curve from which we can get the value of K and a. Hence, this technique of determining molecular weight depends on a calibration curve, which need to be constructed by determining the molecular weight of a set of polymer samples using other techniques which means this is a relative technique, not an absolute technique because it depends on a calibration curve which need to be constructed using a set of polymer of known molecular weights which need to be determined by some other techniques. Hence, this is a relative technique.

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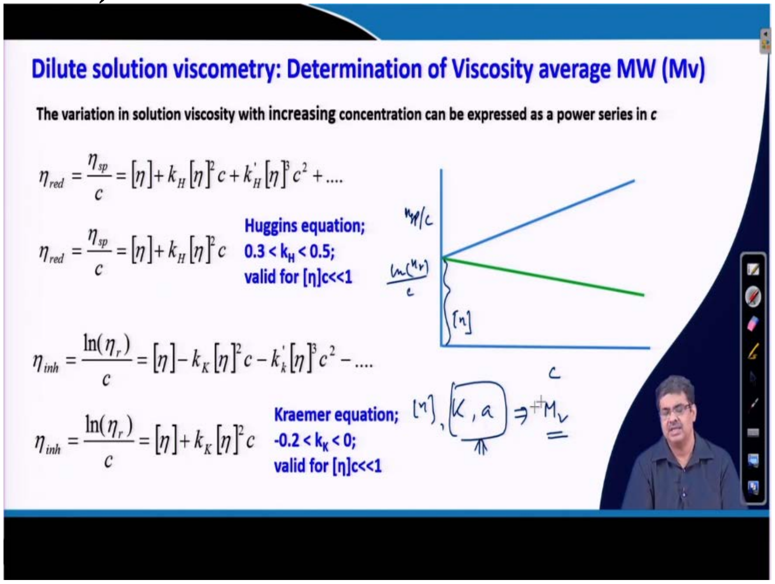

Dilute solution viscometry: Determination of Viscosity average MW (Mv)

The variation in solution viscosity with increasing concentration can be expressed as a power series in *c*

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c + k_H' [\eta]^3 c^2 + ...$$

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c$$

Huggins equation;
$0.3 < k_H < 0.5$;
valid for $[\eta]c<<1$

$$\eta_{inh} = \frac{\ln(\eta_r)}{c} = [\eta] - k_K [\eta]^2 c - k_k' [\eta]^3 c^2 - ....$$

$$\eta_{inh} = \frac{\ln(\eta_r)}{c} = [\eta] + k_K [\eta]^2 c$$

Kraemer equation;
$-0.2 < k_K < 0$;
valid for $[\eta]c<<1$

$[\eta], \boxed{K, a} \Rightarrow M_v$

How to get the value of intrinsic viscosity, now this variation of solution viscosity with increasing concentration can be expressed as a power series and these are the two expressions can be possible. This is Huggins equation and this is valid for dilute solution and for dilute solution elucidation we can basically plot η_{sp} / c with concentration and get this. So from this intercept we can get the value of eta or there is another expression.

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c + k_H'[\eta]^3 c^2 + \cdots$$

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c; \qquad 0.3<k_H<0.5$$

Kraemer equation which plots this term with concentration. So for that we can plot ln $[\eta]_r / c$ with concentration and we will get ideally same intercept. So using either of these expressions or using both expressions to be sure we can get the value of intrinsic viscosity. So for that we need to calculate either η_{sp} or this for a number of solutions having different concentration and η_{sp} is nothing but viscosity.

$$\eta_{inh} = \frac{ln(\eta_r)}{c} = [\eta] - k_k[\eta]^2 c - k'_k[\eta]^3 c^2 - \cdots$$

$$\eta_{inh} = \frac{ln(\eta_r)}{c} = [\eta] + k_k[\eta]^2 c; \quad -0.2<k_k<0$$

You need for that you need to find out the viscosity of the solvent as well as viscosity of the different solutions. You can use any standard technique in our standard teaching labs we have this ostwald viscometer, Ubbelohde viscometer which can be used to measure the viscosity of volume of solution or there are now very sophisticated techniques which can give directly the viscosity of the solution very quickly.

So we can use one of those viscometers to find out the viscosity value for different solutions having different concentration of polymer and the solvent, and for which we can calculate these η_{sp} / c and plot as a function of concentration of solution and from which we can get the intrinsic viscosity value. If we know the intrinsic viscosity value with knowledge from K and a we can find out the molecular weight. So [η], K and a which gives us the value of M_v. For a lot of polymers-solvent-temperature combination these values are available in the literature. So we can take advantage of these values available in the literature we can measure the intrinsic viscosity to find out M_v. So most of the common polymers we can use this technique to find out the M_v for the newly synthesized polymer also.

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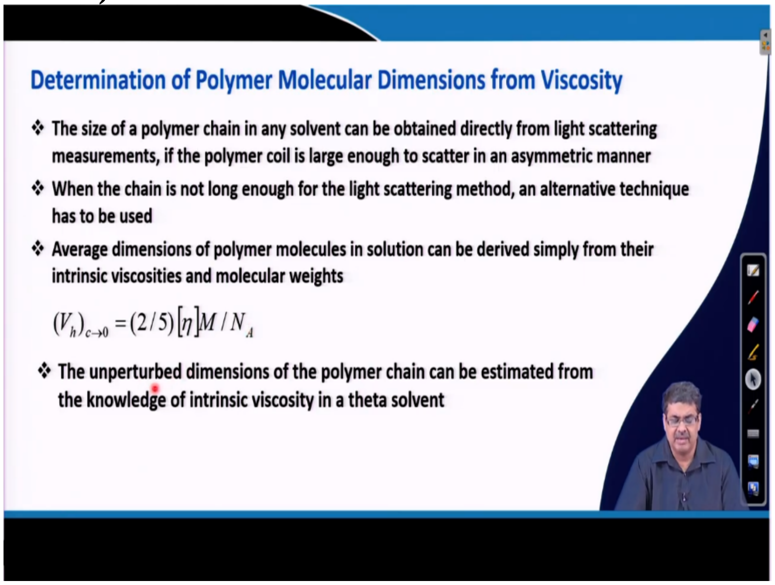

Determination of Polymer Molecular Dimensions from Viscosity

- The size of a polymer chain in any solvent can be obtained directly from light scattering measurements, if the polymer coil is large enough to scatter in an asymmetric manner
- When the chain is not long enough for the light scattering method, an alternative technique has to be used
- Average dimensions of polymer molecules in solution can be derived simply from their intrinsic viscosities and molecular weights

$$(V_h)_{c\to 0} = (2/5)[\eta]M/N_A$$

- The unperturbed dimensions of the polymer chain can be estimated from the knowledge of intrinsic viscosity in a theta solvent

The sizes of the polymer chains in any solvent can be obtained directly from light scattering measurement. If the polymer coil is large enough to scatter in an asymmetric manner then we can use light scattering technique to find out directly the size of the molecule. If the chain is not long enough then light scattering technique is not sufficient then we can use viscometry to find out the size indirectly. An average dimension of polymer molecule in solution can be derived simply from the intrinsic viscosity and molecular weight.

$$(V_h)_{c\to 0} = (2/5)[\eta]M/N_A$$

We have seen this expression that hydrodynamic volume at very dilute solution is given by this expression where M is the molecular weight, $[\eta]$ intrinsic viscosity and N_A Avogadro number. The unperturbed dimension of the polymer chain can be estimated from the knowledge of intrinsic viscosity in θ solvent.

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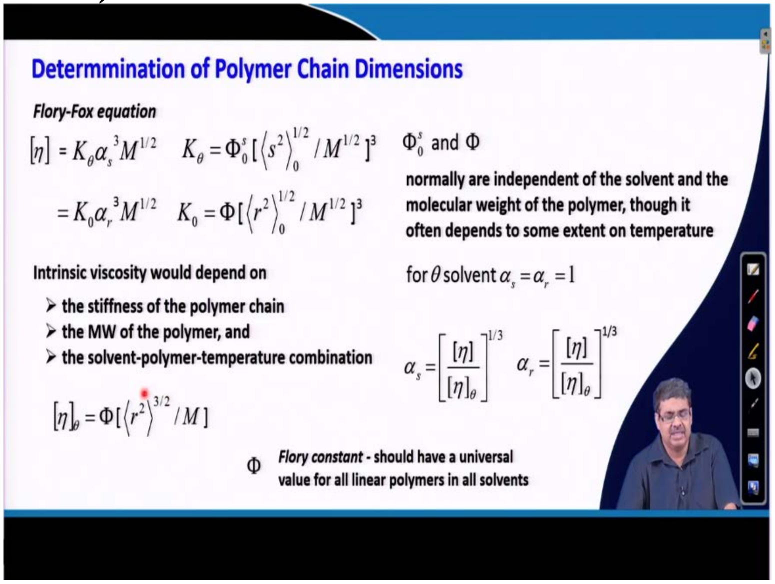

Determmination of Polymer Chain Dimensions

Flory-Fox equation

$[\eta] = K_\theta \alpha_s^{3} M^{1/2} \quad K_\theta = \Phi_0^s [\langle s^2 \rangle_0^{1/2} / M^{1/2}]^3$

$= K_0 \alpha_r^{3} M^{1/2} \quad K_0 = \Phi [\langle r^2 \rangle_0^{1/2} / M^{1/2}]^3$

Φ_0^s and Φ

normally are independent of the solvent and the molecular weight of the polymer, though it often depends to some extent on temperature

Intrinsic viscosity would depend on

- the stiffness of the polymer chain
- the MW of the polymer, and
- the solvent-polymer-temperature combination

for θ solvent $\alpha_s = \alpha_r = 1$

$\alpha_s = \left[\frac{[\eta]}{[\eta]_\theta}\right]^{1/3} \quad \alpha_r = \left[\frac{[\eta]}{[\eta]_\theta}\right]^{1/3}$

$[\eta]_\theta = \Phi [\langle r^2 \rangle^{3/2} / M]$

Φ *Flory constant* - should have a universal value for all linear polymers in all solvents

So we have seen the Flory-Fox equation where intrinsic viscosity is given by this expression

$$[\eta] = K_\theta a_s^3 M^{1/2}$$
$$= K_0 a_r^3 M^{1/2}$$

where K_θ is given by this and we can also express,

$$K_\theta = \phi_0^s \left[\frac{\langle s^2 \rangle_0^{1/2}}{M^{1/2}}\right]^3 ; K_0 = \phi \left[\frac{\langle r^2 \rangle_0^{1/2}}{M^{1/2}}\right]^3$$

this is the expansion factor. In this case, we are talking about radius of gyration; in this case, we are talking about RMS end-to-end distance. Now these two constants are normally independent of solvent and the molecule weight of the polymer, though it often depends on some extent on temperature. These expressions are same, one is expressed in terms of radius of gyration and the other is expressed in terms of average end to end distance. So from this expression we know how we can basically estimate that the intrinsic viscosity depends on the stiffness of the polymer chain. This ratio gives us the stiffness of polymer chain. Intrinsic viscosity relates to the stiffness of the polymer chain, also on the molecular weight of the polymer and the polymer-solvent-temperature combination which gives the value of this expansion factor. For θ solvent, the value of expansion factor is 1 as we have already discussed. Hence, this expansion factor can be obtained by measuring the intrinsic viscosity in any particular solvent and intrinsic viscosity in θ solvent.

$$a_s = \left[\frac{[\eta]}{[\eta]_\theta}\right]^{1/3}$$

$$a_s = \left[\frac{[\eta]}{[\eta]_\theta}\right]^{1/3}$$

Remember I have just given an example that acetonitrile is a θ solvent for PMMA at 30℃. So osmotic pressure π/c does not change with concentration. So we can use the intrinsic viscosity in theta solvent and in another solvent to get the value of this expansion factor in terms of radius of gyration or end to end distance. So if you know the intrinsic viscosity in θ solvent then this expression can be written like this.

$$[\eta]_\theta = \phi\left[\langle r^2\rangle^{3/2}/M\right]$$

Where ϕ is the Flory constant and this should have a universal value for all linear polymers in all solvents. We can find out the intrinsic viscosity in θ solvent and if we know the molecular weight for that particular sample, then we can determine or we can get the value of the chain dimension, the average end to end distance or average radius of gyration for the chains which are even not long enough to get analyzed by light scattering technique.

This is the indirect way by measuring the intrinsic viscosity of a polymer sample in θ solvent and also from the knowledge of molecular weight of that particular sample, we can use this expression to find out or to guess or to estimate the size in terms of RMS end to end distance or radius of gyration by this expression.

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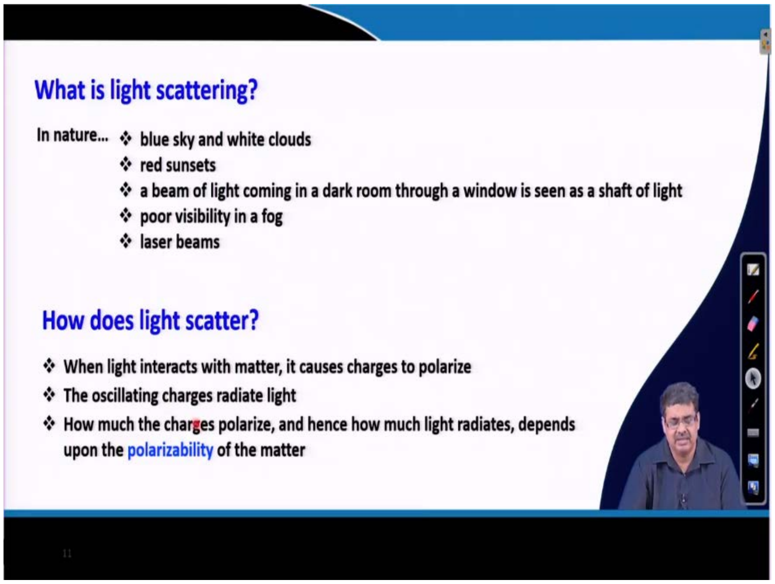

What is light scattering?

In nature...
- blue sky and white clouds
- red sunsets
- a beam of light coming in a dark room through a window is seen as a shaft of light
- poor visibility in a fog
- laser beams

How does light scatter?

- When light interacts with matter, it causes charges to polarize
- The oscillating charges radiate light
- How much the charges polarize, and hence how much light radiates, depends upon the polarizability of the matter

Next I will move to light scattering technique for determination of molecular weight. We have seen light scattering phenomena in nature and the reason for the blue sky or white clouds are basically due to light scattering of the gaseous molecules present in atmosphere. Similarly a red sunset or a beam of light seen coming through a narrow slit into a dark room are all due to the light scattered by the atmospheric particles. Similarly, poor visibility of fog is due to this light scattering of the tiny water droplets present in the air. We have seen this in several lasers shows where we can basically visualize the beam because of the scattering caused by the particles in the atmosphere. How does light scatter? When a light, which is electromagnetic radiation, interacts with the matter it causes the charges in a molecule or matter to polarize. Basically it induces some dipole that oscillates in sync with the electric field of the incident light. We know that oscillating charges actually radiate light and those are the scattered light. Light get scattered in all direction from the sample and how much light will scatter or the intensity of scattered light will depend upon the extent of polarization induced by the incident light. That depends on the polarizability of matter. Hence, the intensity of light scattered will depend on the value of polarizability of the matter.

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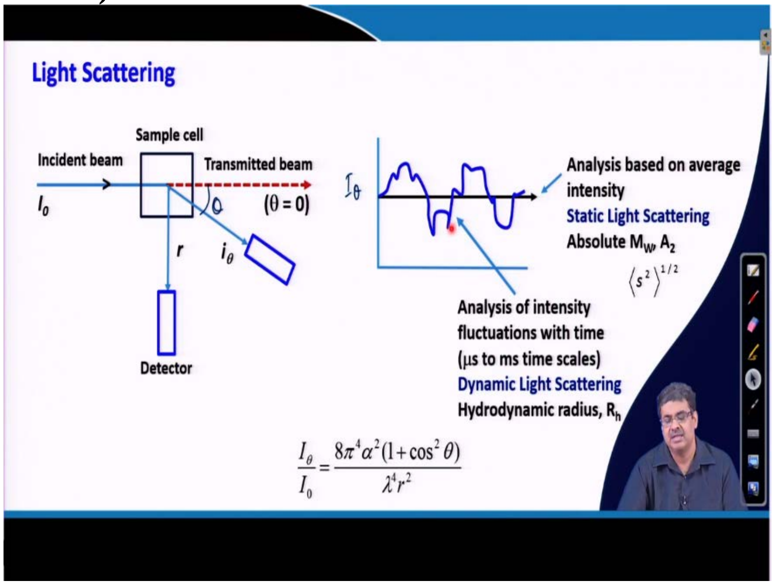

Light Scattering

Analysis based on average intensity

Static Light Scattering

Absolute M_W, A_2

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

Analysis of intensity fluctuations with time (µs to ms time scales)

Dynamic Light Scattering

Hydrodynamic radius, R_h

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

Now this is a simplified diagram showing how a light scattering measurement is done where the incident beam is applied to a sample and light get scattered in all directions. We can place these detectors in different angles to find out the amount of light scattered in that particular angle. The scattering angle is θ and this is the transmitted beam at θ = 0 and this distance is between the detector and the sample is *r*. As the light gets scattered, we can have two types of measurements. We can plot the intensity of light with time and we can see that there are fluctuating intensities with time and in this case the timescale in microseconds to milliseconds. If we measure the intensity of the scattered light in microseconds then we will see that the intensity signal is fluctuating with time. If we can consider it for longer time then we can consider it as the average intensity of light. So we can call this as average scattered intensity of light. Now we can use both information - the average light scattered intensity and also the fluctuation in the scattered light in a smaller time-frame. So this fluctuation in the intensity can be used to analyze to find out the hydrodynamic radius, which is a principle of dynamic light scattering technique. This average value can be used to determine this molecular weight and second virial coefficient, size of the molecule, and the technique is called static light scattering. So in this static light scattering we are considering the average scattered light and in case of dynamic light scattering we will basically we will consider the fluctuations in the light intensity.

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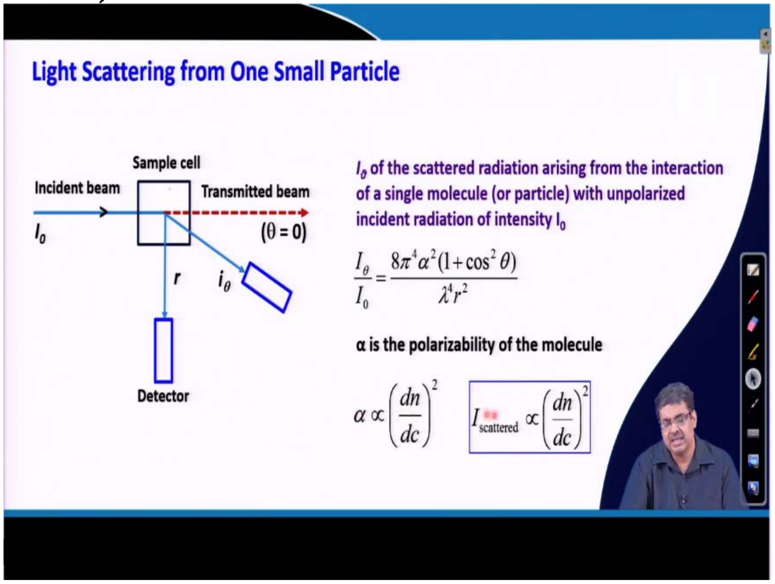

Light Scattering from One Small Particle

Sample cell

Incident beam

Transmitted beam

I_0

$(\theta = 0)$

r

i_θ

Detector

I_θ of the scattered radiation arising from the interaction of a single molecule (or particle) with unpolarized incident radiation of intensity I_0

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

α is the polarizability of the molecule

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

Now we will go one after one, first thing that will consider light scattering from one single particle or one single small particle. In that case the expression for I_θ / I_0,

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

I_0 is the intensity of the incident beam and I_θ is the intensity at a particular angle of the scattered light at a particular angle from a single particle which is given by this expression. So this expression is for the scattered radiation arising from interaction of a single molecule or single particle with unpolarized incident beam having intensity I_0. α is the polarizability, λ is the incident light wavelength, r is the distance as shown here and θ is the scattering angle. Now α is a polarizability the molecule which relates to this term dn / dc square, dn / dc is the refractive index increment.

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

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

If you plot refractive index of a solution with concentration then slope will be refractive index increment and which is related to α. Hence, the scattered light intensity for a small single particle is proportional to dn / dc square.

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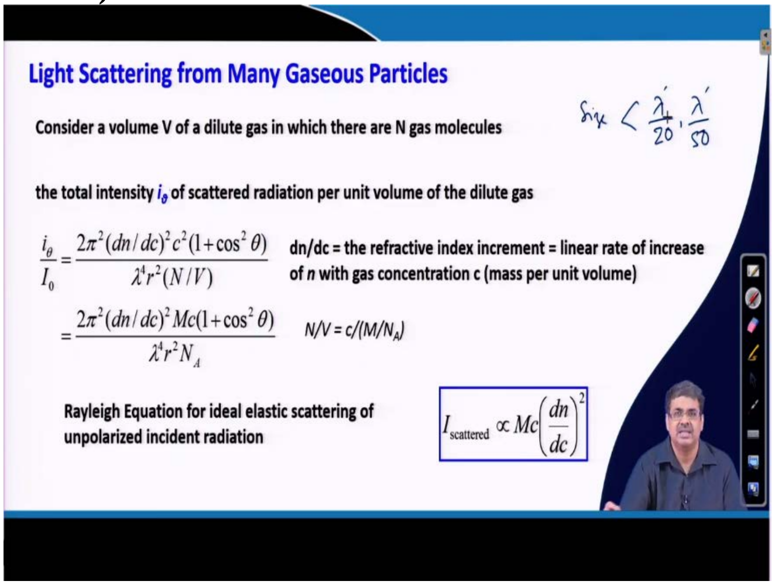

Light Scattering from Many Gaseous Particles

Consider a volume V of a dilute gas in which there are N gas molecules

Size $< \frac{\lambda'}{20}, \frac{\lambda'}{50}$

the total intensity i_θ of scattered radiation per unit volume of the dilute gas

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

dn/dc = the refractive index increment = linear rate of increase of *n* with gas concentration c (mass per unit volume)

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

$N/V = c/(M/N_A)$

Rayleigh Equation for ideal elastic scattering of unpolarized incident radiation

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

Now we will move from one particle to many gaseous particles together. Consider a volume V for dilute gas having n gas molecules. I mean in this, the case total intensity of the scattered radiation per unit volume of dilute gas is given by this expression where dn / dc we have discussed the refractive index increment, is the linear rate of increase of refractive index with gas concentration, c, again c is the mass per unit volume.

$$\frac{I_\theta}{I_0} = \frac{2\pi^2 \left({}^{dn}/_{dc}\right)^2 c^2 (1 + cos^2\theta)}{\lambda^4 r^2 \left({}^{N}/_{V}\right)}$$

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

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

This expression is the Rayleigh equation for ideal elastic scattering of unpolarized incident beam. I mean in this case we are talking about the size of the particle being small, less than approximately λ/ 20 or sometimes we call λ/ 50 depending on the samples, where λ' is the wavelength of the light in that solution.

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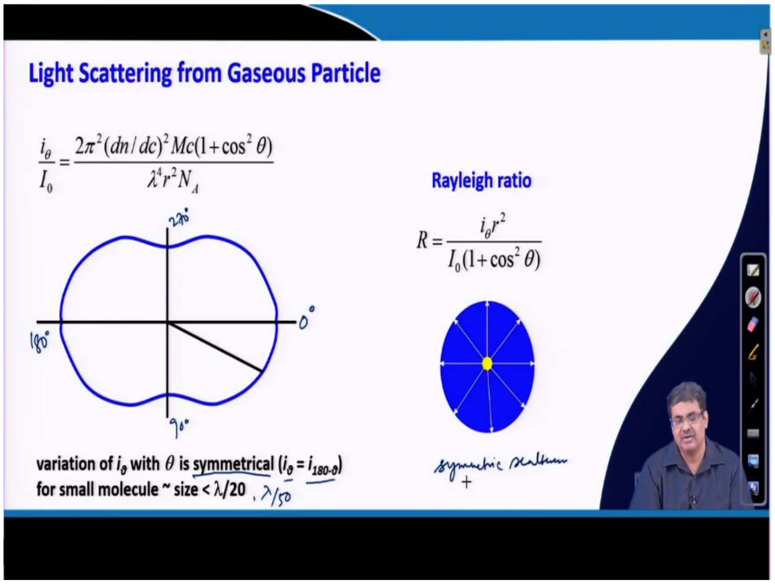

Light Scattering from Gaseous Particle

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

Rayleigh ratio

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

variation of i_θ with θ is symmetrical ($i_\theta = i_{180-\theta}$)
for small molecule ~ size < λ/20 , λ/50

symmetric scatterer

If you look at the scattering envelope, the scattering angle varies from 0° to 90° and to 180°. We write this is 270°. In this case, the scattering envelope or the variation of the scattering intensity at different angles are shown in 2D, you have to imagine in 3D term in real case.

When the scattering intensity is plotted against the scattering angle and the variation of this intensity from a sample is symmetrical in this particular case symmetrical means that I_θ is same as $I_{180-\theta}$. So basically we have a symmetrical shape and this happen for small molecule and as I said that this is not a fixed number we can sometimes we can write this as λ/ 50. For a small particle we have this type of scattering envelop. Now if we rearrange this expression and write R, which is Rayleigh ratio, then and then this variation of R with θ will now be spherical which means the value of R will not depends on this r or θ because the variation is taken care of in this term and we call these as a symmetric scatterer. So symmetric scatterer means the scattering happens in this way where I_θ is $I_{180-\theta}$ and the Rayleigh ratio is not dependent on the scattering angle or θ.

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

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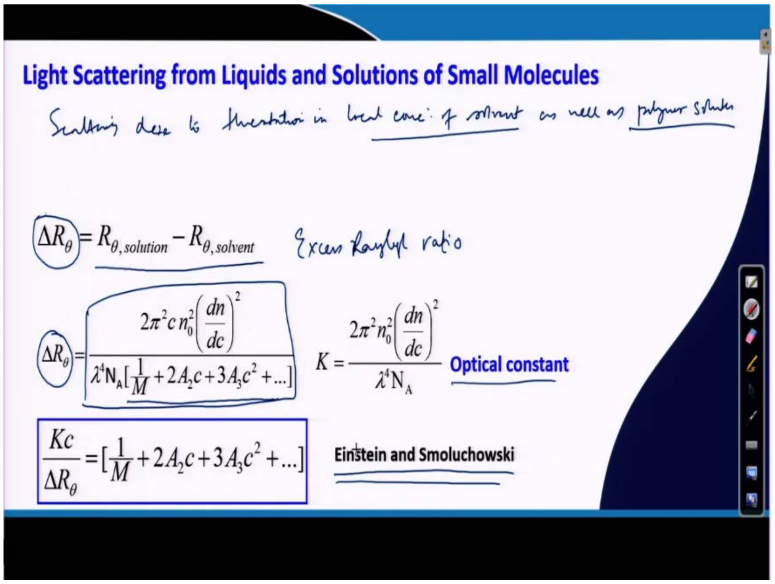

Light Scattering from Liquids and Solutions of Small Molecules

Scattering due to fluctuation in local conc. of solvent as well as polymer solutes

$$\boxed{\Delta R_\theta} = \underline{R_{\theta,solution} - R_{\theta,solvent}}$$ Excess Rayleigh ratio

$$\boxed{\Delta R_\theta} = \boxed{\frac{2\pi^2 c n_0^2\left(\frac{dn}{dc}\right)^2}{\lambda^4 N_A[\frac{1}{M} + 2A_2c + 3A_3c^2 + \ldots]}} \quad K = \frac{2\pi^2 n_0^2\left(\frac{dn}{dc}\right)^2}{\lambda^4 N_A}$$ Optical constant

$$\boxed{\frac{Kc}{\Delta R_\theta} = [\frac{1}{M} + 2A_2c + 3A_3c^2 + \ldots]}$$ Einstein and Smoluchowski

Now we will talk about liquids and solutions of small molecule. Light scattering does not only happen due to the interaction between the molecule and the light, but it also happens due to fluctuation in the concentration of solvent molecules as well as solute molecules. So there are light scattering due to fluctuation in local concentration of solvent as well as solute molecules, in this case polymer solutes. Now this fluctuation happens because of change in local temperature, very minuscule local temperature changes or pressure changes. As a result scattering happens, also due to fluctuation in the concentration. Now, we can take care of the solvent contribution by simply subtracting the scattering due to solvent from the solution. We are writing this as an excess Rayleigh ratio this is called excess Rayleigh ratio, which basically takes care of the or the removes the scattering due to solvent molecule from the solution.

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

$$\Delta R_\theta = \frac{2\pi^2 c n_0^2\left(\frac{dn}{dc}\right)^2}{\lambda^4 N_A\left[\frac{1}{M} + 2A_2c + 3A_3c^2 + \cdots\right]}$$

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

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

So we need to take care of the polymer solutes because of the local fluctuation in polymer concentration, there will be local osmotic pressure generation and we can actually use, as suggested by these two scientists, we can use the expression similar to osmotic pressure and using this excess Rayleigh scattering we can get an expression like this. Here we are taking care of both the fluctuations, scattering due to fluctuation of local concentration of solvent molecules and due to the fluctuation in the concentration of polymer molecules. We simplify this expression by writing K for the constant terms for the equipment and the solvent-polymer pair and this is called optical constant. In next lecture we will discuss asymmetric scattering which means when the solute size of the polymer size become large enough, so that the excess Rayleigh ratio is dependent on the θ value.