Polymer Chemistry
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Lecture - 28
Polymer Solutions (Contd.) And Chain Dimensions

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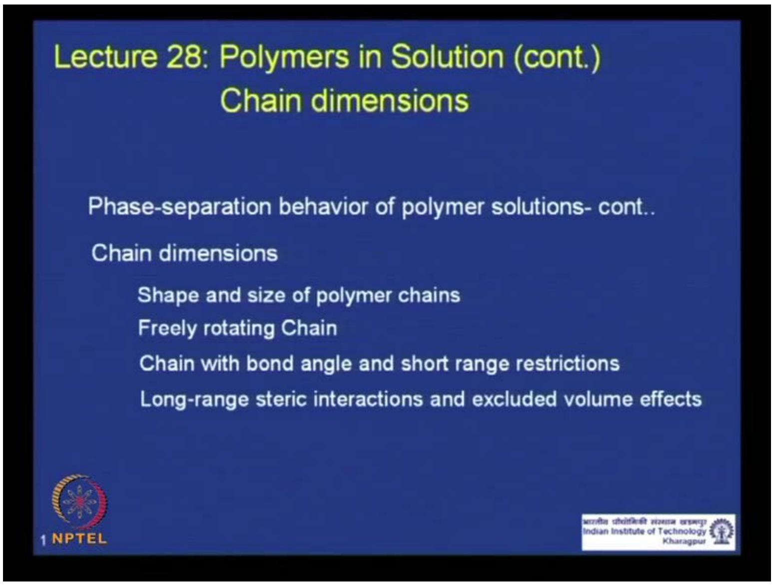

Lecture 28: Polymers in Solution (cont.)
Chain dimensions

Phase-separation behavior of polymer solutions- cont..

Chain dimensions

- Shape and size of polymer chains
- Freely rotating Chain
- Chain with bond angle and short range restrictions
- Long-range steric interactions and excluded volume effects

Welcome back to this course on polymer chemistry. And in this lecture, we will continue our discussion on polymer solutions, the remaining part, and then start a new topic on chain dimensions, polymer chain dimensions. And we planned to just complete the discussion, we were having on phase separation behavior of polymer solutions. And then in chain dimensions, we will talk about size and shape of polymer chains, and take different chains, freely rotating chains, chains with bond angle and short range restrictions. And then finally, with long range steric interaction and excluded volume.

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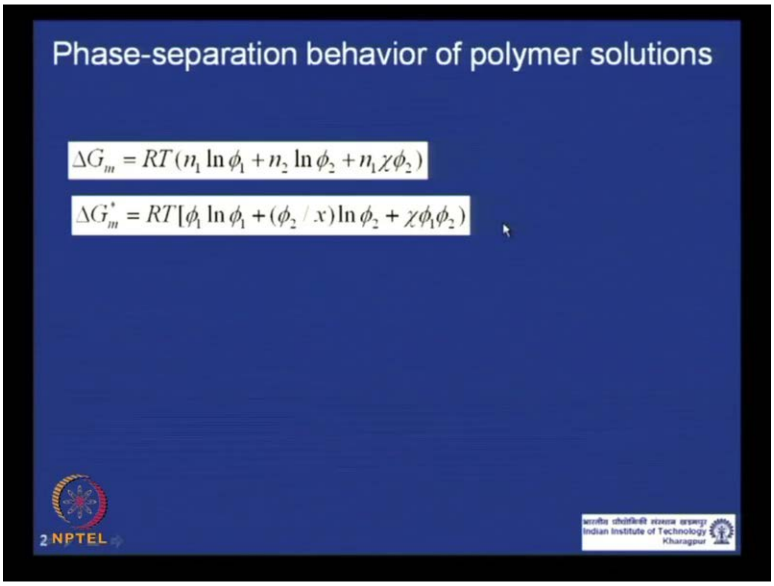

Phase-separation behavior of polymer solutions

$$\Delta G_m = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \chi \phi_2)$$

$$\Delta G_m^* = RT[\phi_1 \ln \phi_1 + (\phi_2 / x) \ln \phi_2 + \chi \phi_1 \phi_2)$$

Now, let us just complete the discussion, we are having in the last lecture, you know, from Flory Huggins equation, we have seen this is a, this is the Flory Huggins expression and then we converted to Gibbs free energy of mixing per segment in the last lecture, and which was turned out to be this. And then we said that if we plot this expression.

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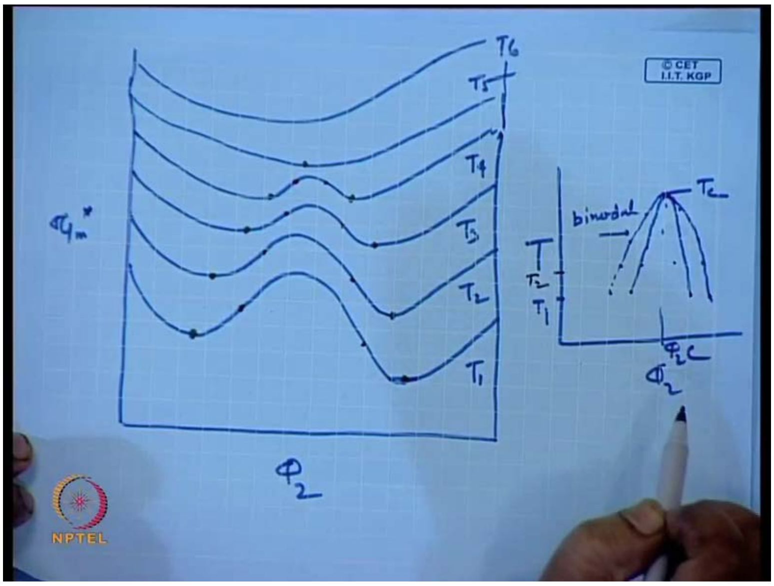

We can, we will find this type of general, this type of general curve. These are corresponding to different temperature. And we discussed that there could be one type where the polymer is soluble in the solvent at any composition, and then there could be another type where you have in left hand side and in this side, you have complete solubility, and you have a region where you have metastability, thermo dynamically unstable, but metastable for small fluctuation in composition, and then you have a completely insoluble region or unstable region.

Now, these are the points to minima, who have the, which has the, which have the common tangent, they are called binodal points or bimodal composition, and the inflection point which is the boundary between metastable unstable region. They are called spinodal points. These are called binodal and these are called spinodal points. And now, you can see that this both the binodal points as well as the spinodal points, they are actually temperature dependent.

If you change the temperature of your polymer solvent mixture, they are, they will change. So, these are the possible different temperature where T 6 is the highest and T 2 greater than T 1 and so on.

Now, what we are going to do, we are going to plot this binodal and spinodal points with respect to temperature. So, if you have t, there are T 1. So, this T 1 you have two binodal points and two spinodal points.

At T 2, you have again, this is the binodal points and these are two are the spinodal points. So, you have binodal points here and you have spinodal points here, like that you plot T 3, and T 4, and T 5, and T 6 and so on. So finally, you will get these, you get these points. Now, you join them, you join to get a line for the binodal points and a line for the spinodal points. So, if I want to join them at different temperature, I will get a line for the binodal points. This is for binodal and then similarly, I get line for the spinodal points which will coincidence or converge in a same temperature, which we call T c, critical temperature and the corresponding composition here is phi 2 c which we discussed in last lecture, here.

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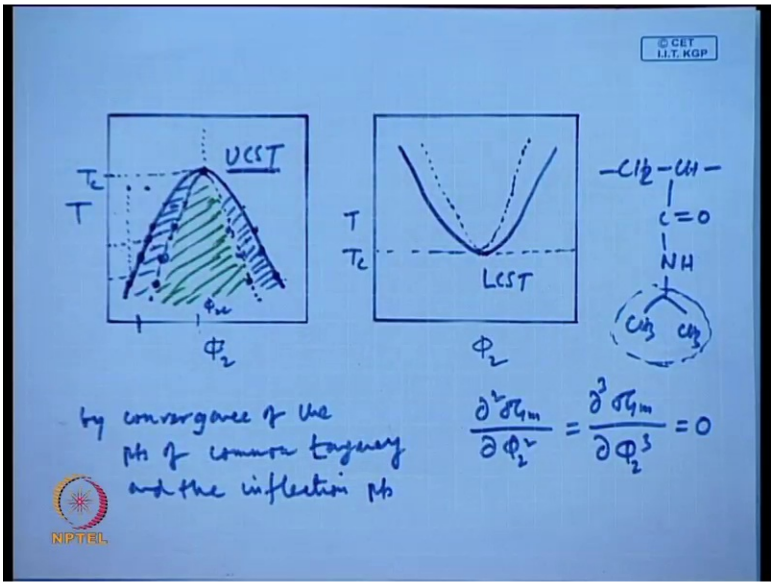

by convergence of the pts of common tangency and the inflection pts

$$\frac{\partial^2 \Delta G_m}{\partial \phi_2^2} = \frac{\partial^3 \Delta G_m}{\partial \phi_2^3} = 0$$

So, you get this is specifically a plot of polymer phases with temperature changing and with different composition. So, If I, this is the region where this is unstable or two phase system, this is a metastable system which is thermodynamically unstable, but metastable and this outside is completely stable. Now, if you start see, if you start from here, a point from here, a composition from here corresponding to this corresponding here.

So, if you start a point here; obviously, this is a single phase system soluble, and then if you cool the temperature, what will happen? At this temperature, they will start precipitating. So, they will start forming two phase system, because this is that is metastable, thermodynamically unstable; similarly, if you start from this temperature, this point, this composition then they will start precipitating this temperature. So, if you change the composition; obviously, the temperature at which the two phase or the precipitation starts will vary.

These this points where this two phase actually gets generates or the polymer become insoluble, they are called cloud points; whereas for these composition, at critical temperature it will start forming two phase or polymer become insoluble, above this temperature, you can, you have any composition, they are insoluble.

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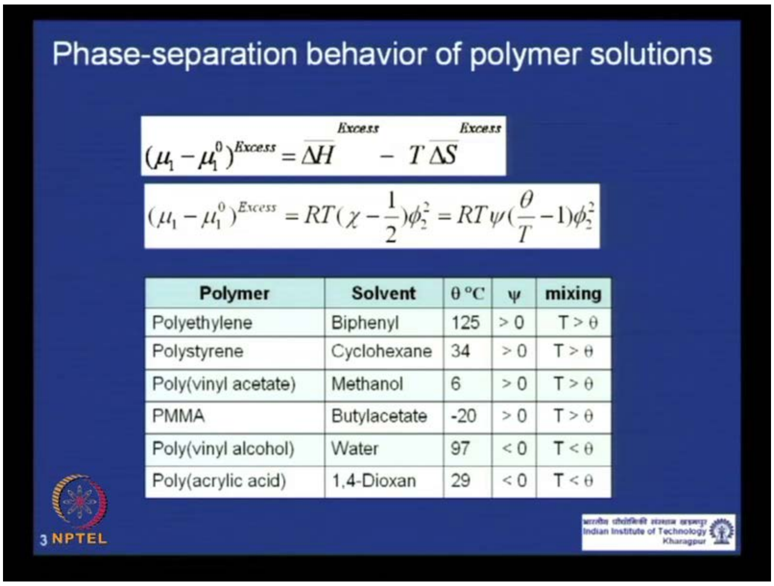

Phase-separation behavior of polymer solutions

$$(\mu_1 - \mu_1^0)^{Excess} = \overline{\Delta H}^{Excess} - T\,\overline{\Delta S}^{Excess}$$

$$(\mu_1 - \mu_1^0)^{Excess} = RT(\chi - \frac{1}{2})\phi_2^2 = RT\psi(\frac{\theta}{T} - 1)\phi_2^2$$

Polymer	Solvent	θ °C	ψ	mixing
Polyethylene	Biphenyl	125	> 0	T > θ
Polystyrene	Cyclohexane	34	> 0	T > θ
Poly(vinyl acetate)	Methanol	6	> 0	T > θ
PMMA	Butylacetate	-20	> 0	T > θ
Poly(vinyl alcohol)	Water	97	< 0	T < θ
Poly(acrylic acid)	1,4-Dioxan	29	< 0	T < θ

So, basically this temperature is called upper critical solution temperature and that happens, because if you remember our excess chemical potential term. Now, it can be expressed, we have expressed earlier in two components, it contains two components; one is enthalpic excess and more enthalpy and one excess and more entropy. Now, both these term excess term also dependent on the temperature as well, and you can also express in terms of polymer solvent interaction parameter and finally, with entropy parameter. Now, chi which is polymer solvent interaction parameter also temperature dependent. Now, most cases, most of the polymers, this entropic term is negative; most of the, in case most of the polymers, as we have seen earlier this entropic term is positive. So, if. So, at some temperature which is higher than theta temperature, this excess term will become positive and you will start getting precipitation. So, these are the corresponding temperature and in those system, you will get a upper critical solution temperature. Now, in some polymer system which are not very frequently observed, you get this type of behavior which is a lower critical solution temperature, where the entropic term entropic term is negative.

One example, very common nowadays used in research is polyanisopropylaclamide. Now, this polymer, polyanisopropylaclamide, this is has a hydrophobic group. Now, if you dissolve this polymer in water, what happened? These two groups participate in hydrogen bonding with water, but because this is hydrophobic group to hide this hydrophobic groups from water, the waters form, water molecules form structured around this hydrophobic group which we call hydrophobic hydration or cage formation and results, you get a negative entropy. The entropy actually comes down because of structuring of the water molecules this hydrophobic groups.

Now, in addition to the combinatorial groups, which is always favorable, favorable in mixing process; in this case, this entropy, because of contact between the polymer and the solvent, which is opposing the mixing process. So, in this case, the entropic parameter is negative. So, psi is negative. So, what happened? Then unless you have the temperature lower than theta, you will not get the solution. So, what happens? As you go down in temperature, you get from insoluble system to soluble system, and when that the particular temperature, when that happens for all composition, we call that temperature l c s t.

L c s t can be observed for this two cases as well, where we have psi parameter negative; another polymer is polyehtyleneglycol, you can have l c s t because you have a strong interaction between the polymer and the solvent.

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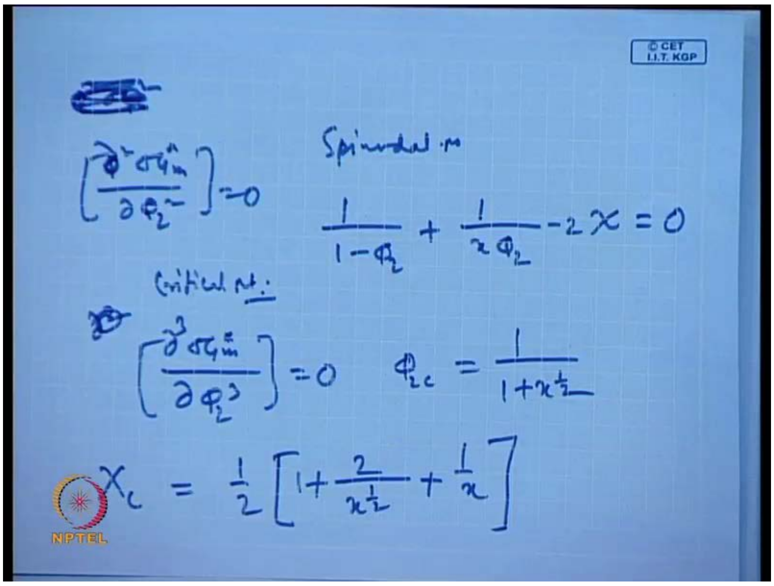

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$$\left[\frac{\partial^2 \Delta G_m}{\partial \phi_2^2}\right] = 0$$

Spinodal pt

$$\frac{1}{1-\phi_2} + \frac{1}{x\phi_2} - 2\chi = 0$$

Critical pt:

$$\left[\frac{\partial^3 \Delta G_m}{\partial \phi_2^3}\right] = 0 \qquad \phi_{2c} = \frac{1}{1+x^{\frac{1}{2}}}$$

$$\chi_c = \frac{1}{2}\left[1 + \frac{2}{x^{\frac{1}{2}}} + \frac{1}{x}\right]$$

Now, what we have seen in last lecture that if you, this spinodal binodal points, for this binodal points, this, you have still first derivative 0, for spinodal points you have second derivative 0, and for the critical point spinodal curve and the binodal curve merges, the third derivative is also 0, and if you just use that formula that gives free energy, this formula and differentiate with phi two, then you will get these expressions.

Now, if you know the dependence of chi with temperature then you can find out the spinodal points; and the critical points is given by this expression. And if you can combine these two, you can get the critical entropy, the polymer solvent interaction parameter by this expression. So, let me write it again.

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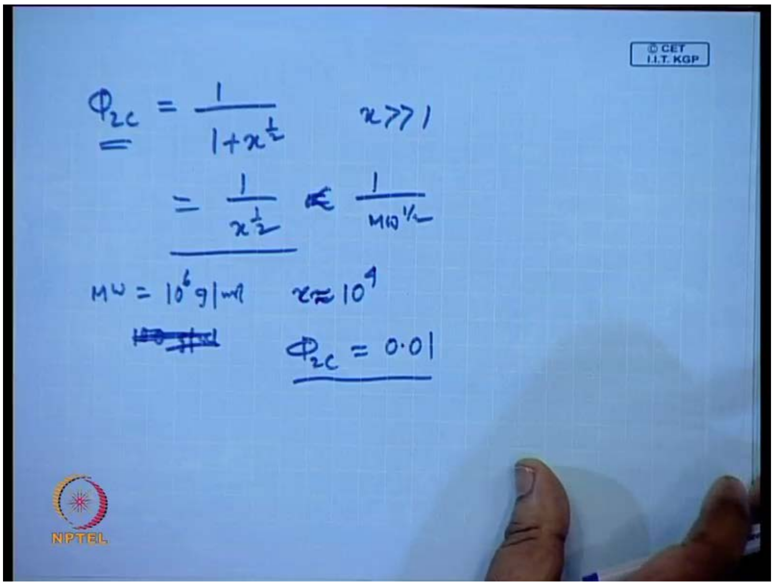

$$\underline{\Phi_{2c}} = \frac{1}{1+x^{\frac{1}{2}}} \qquad x \gg 1$$

$$\underline{= \frac{1}{x^{\frac{1}{2}}}} \propto \frac{1}{Mw^{1/2}}$$

$$Mw = 10^6\ g/mol \qquad x \approx 10^4$$

$$\underline{\Phi_{2c} = 0.01}$$

So, critical composition at which the polymer started, starts a separating out from solution is given by 1 by 1 plus x, x is the number of segments, chain segments which is always very high, x is always much, much greater than 1. So, you can write 1 by x.

So, the critical concentration at which the phase separation first appears going from a two phase region, from one phase region in to two phase region is thus predicted to occur at low polymer concentration, if we have say polymer having a polymer weight of 1 million 10 to the power 6 gram per mole, and then if you have the repeating this molecule to this is hundred, this is the molecular weight, then x would be close to 10 to the power 4 close to ten to the power 4, then phi 2 c would be 0.01.

So, basically if you have very high molecular weight then the concentration at which the polymer starts from going, from becoming one phase system to two phase system is very low, if your polymer molecular comes down then this goes to little higher concentration. Now you also know, second, this is, this shows that the critical composition at which the polymer becomes one phase system to the two phase system is highly dependent on the molecular weight because this is also proportional to molecular weight. So, you can molecular weight to the power half.

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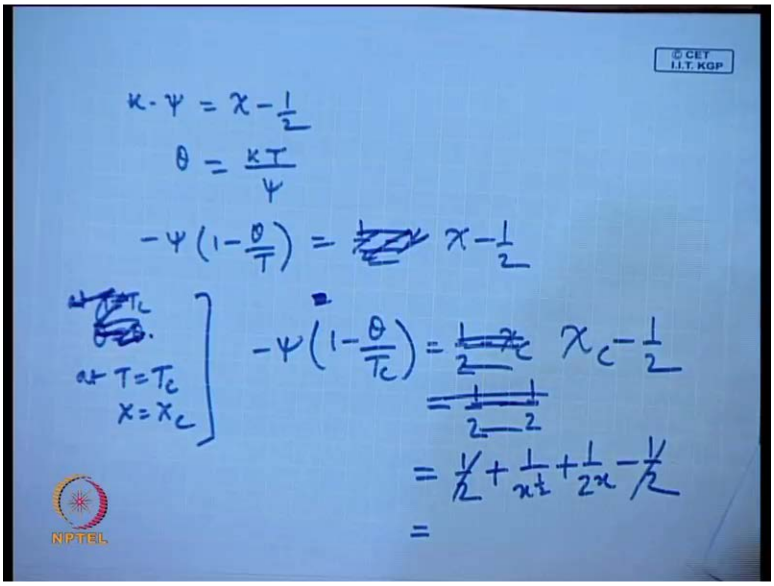

$$\kappa \cdot \psi = \chi - \frac{1}{2}$$

$$\theta = \frac{\kappa T}{\psi}$$

$$-\psi\left(1 - \frac{\theta}{T}\right) = \chi - \frac{1}{2}$$

at $T = T_c$
$\chi = \chi_c$

$$-\psi\left(1 - \frac{\theta}{T_c}\right) = \chi_c - \frac{1}{2}$$

$$= \cancel{\frac{1}{2}} + \frac{1}{x^{\frac{1}{2}}} + \frac{1}{2x} - \cancel{\frac{1}{2}}$$

$$=$$

So, as the molecular increases, this goes to lower and lower composition. Now you can. So, this, you can also write from our previous knowledge that this is the enthalpy parameter, this is the entropic parameter and theta is kappa T psi. So, we can write minus psi 1 by theta by T half minus chi. We can set T is equal to T c and theta is equal to theta c at T is equal to T c chi is equal to chi c, we can write from this, minus psi 1 minus theta T c to half minus chi c. Chi c, we have only the got from last expression. So, that is half, minus half, just one minute, this is chi minus half. Let me do it again, its just some confusion, let us just do it again.

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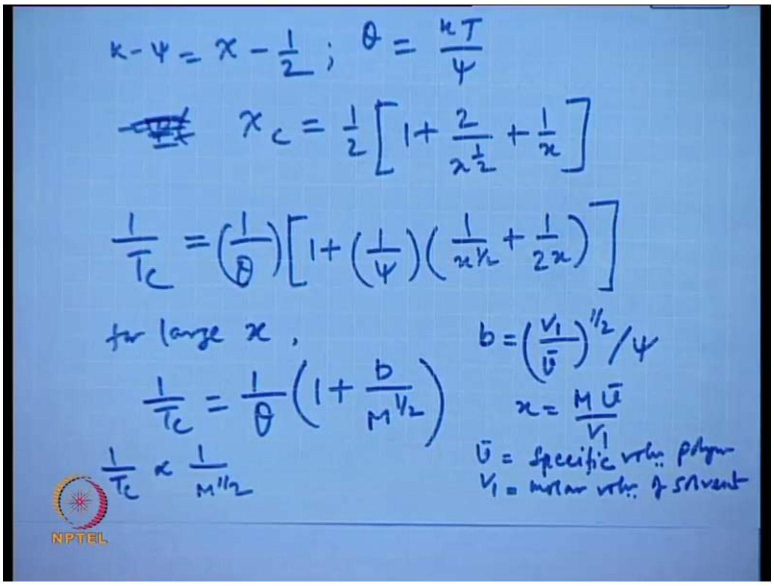

$$\kappa - \psi = \chi - \frac{1}{2} ; \quad \theta = \frac{\kappa T}{\psi}$$

$$\chi_c = \frac{1}{2}\left[1 + \frac{2}{x^{\frac{1}{2}}} + \frac{1}{x}\right]$$

$$\frac{1}{T_c} = \left(\frac{1}{\theta}\right)\left[1 + \left(\frac{1}{\psi}\right)\left(\frac{1}{x^{1/2}} + \frac{1}{2x}\right)\right]$$

for large x,

$$\frac{1}{T_c} = \frac{1}{\theta}\left(1 + \frac{b}{M^{1/2}}\right)$$

$$\frac{1}{T_c} \propto \frac{1}{M^{1/2}}$$

$$b = \left(\frac{V_1}{\bar{v}}\right)^{1/2} / \psi$$

$$x = \frac{M\bar{v}}{V_1}$$

$\bar{v}$ = specific volm. polymer

V_1 = molar volm. of solvent

So kappa minus psi, we know. So, theta is T by psi. So, minus… These are the expressions we know. Now from there, we can write 1 by T c; for large x, we can write one by T c is one by theta one plus b b is b 1. This v bar is specific volume of polymer and v 1 is molar volume of solvent, then we can write the number of segments like this; and we define the term b as this. So, we can, for large x, we can remove or discard this term, ignore this term. So, we can write this. So, which means that one by T c is proportional to M to the power half; that means, the critical temperature is again like the critical composition in this, critical temperature also varies with the molecular weight.

So, if your molecular weight goes up then your critical temperature also will go down. We have seen earlier that your molecular goes up, critical composition also goes down. And in this case, we are seeing that the molecular goes up then critical temperature also comes down.

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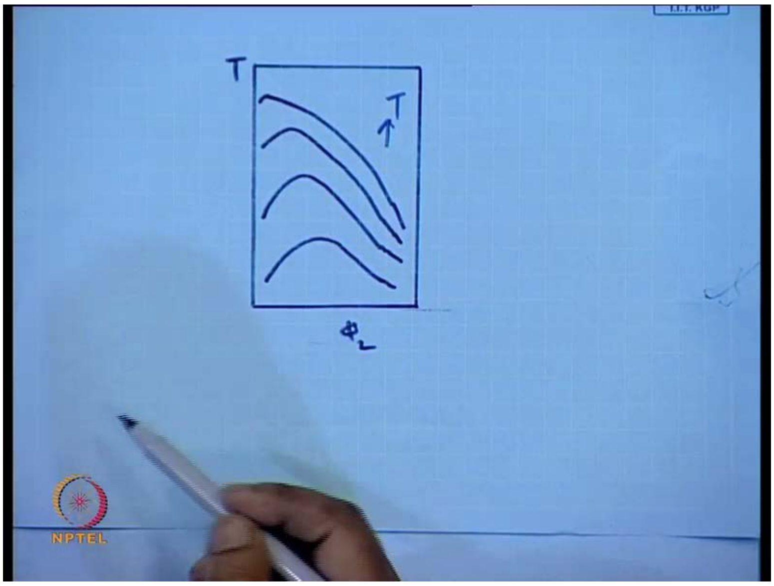

So, we can plot these two. You can see what we have observed, this is experimental curve for observed for solutions having polymer and solvents having upper critical solution temperature. So, as the temperature goes up, this is temperature, as the temperature goes up the critical temperature also goes down and the critical composition at which the phase separation take place, they also become lower, lower; this is experiment cup which we just seen from theoretical calculation that if the temperature goes up both T c goes up and the phi 2 comes down.

Now, these expression is also throws up one more interesting conclusion that if say molecular rate is very high close to infinity then 1 by T c would be equals to theta or theta would be equals to T c.

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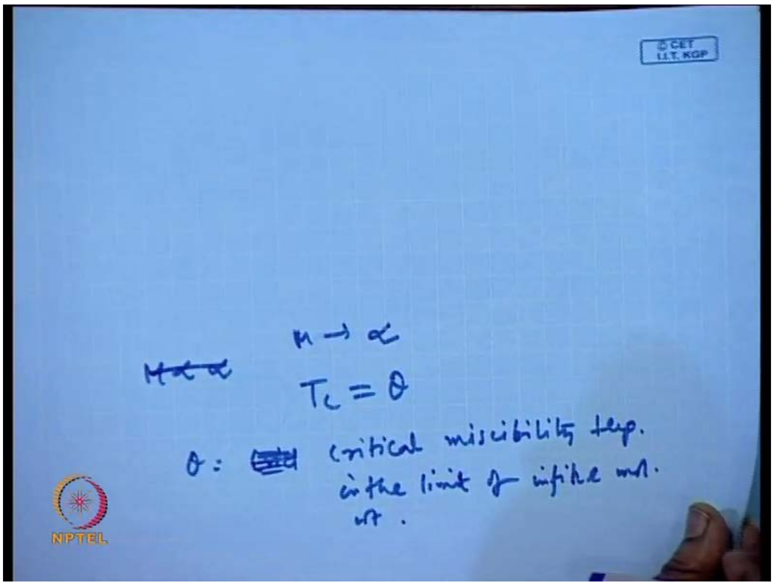

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~~$M \to \infty$~~

$m \to \infty$

$T_c = \theta$

θ : critical miscibility temp. in the limit of infinite mol. wt.

If M is close to infinity or m tends to infinity or T c is equals to theta, which means that critical miscibility temperature, theta is your critical miscibility temperature in the limit of infinite molecular weight. So, that is another observation we can make from this expression.

So now, we completed our discussion on the polymers solutions and in phase separation. Now, what we now, we will shift to the new another topic which is chain dimensions. Now what mean by chain dimension? What we happened in typically, how do you write polymer?

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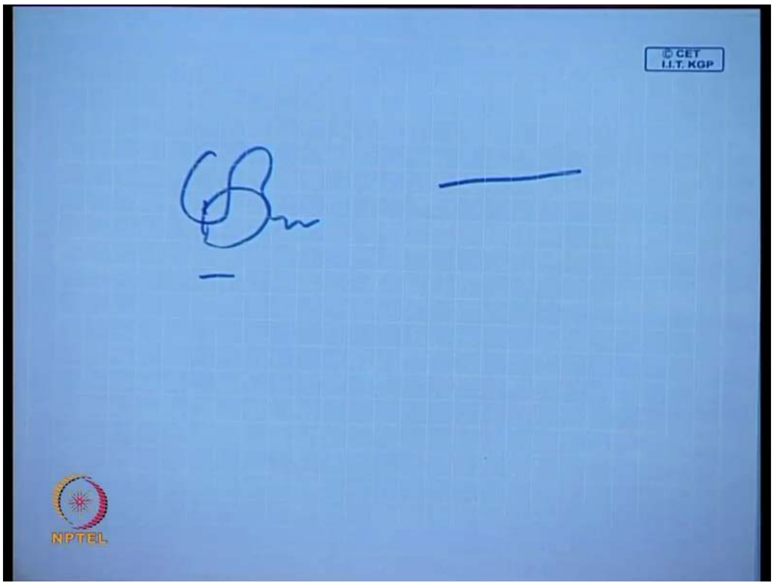

When you have seen in the books, you have seen me always writing polymers like this, something like this, we never write polymers like this, we never write polymers like this, we always write whenever represent polymer, we write a quily chain. Now, that is because that that because the polymers are long chain and you have there is a numerous possible confirmations, because you have a rotational freedom across the backbone and if the polymer chain rotates across the backbone, obviously you will get different chains different confirmations and the backbones are quite flexible in case of polymers. So, that is the reason you get this type of confirmation most of the times.

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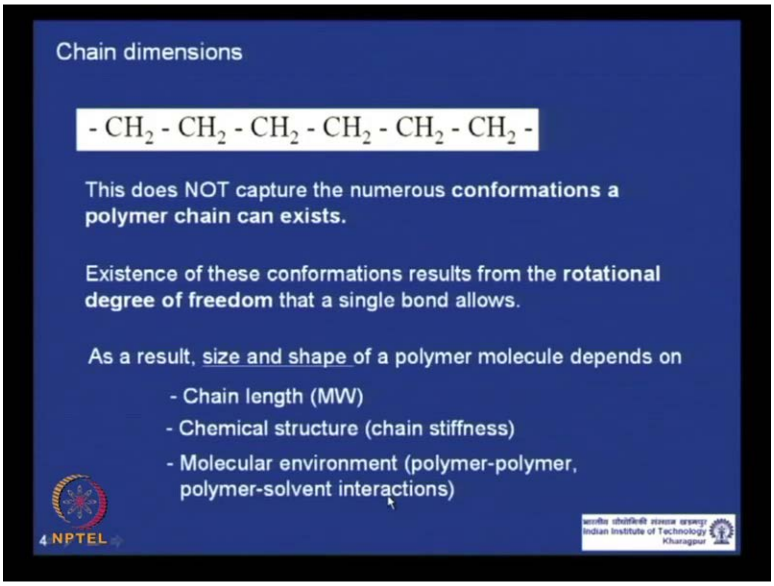

Chain dimensions

$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$

This does NOT capture the numerous **conformations a polymer chain can exists.**

Existence of these conformations results from the **rotational degree of freedom** that a single bond allows.

As a result, size and shape of a polymer molecule depends on

- Chain length (MW)
- Chemical structure (chain stiffness)
- Molecular environment (polymer-polymer, polymer-solvent interactions)

This is a, let us consider a simple polyethylene molecule. This is the chemical expression. Now, this does not capture the numerous confirmations a polymer chain exists. Now, as I said that the existence of the, these numerous confirmation results from the rotational degree of freedom that a single bond allows. You can, depending up on the substitution, the rotational, the rotation across the single bond always allowed

Now, if you have so many bonds in case of, so many single bonds. So, polymer, polymer polyethylene you have so many single bonds. Now, each you can rotate, they are rotatable. So, that is the result you get, so many, so many confirmations. Now, as you have this so many confirmations, the size and shape of the polymer molecule will depends on; obviously, the chain length, now as the chain length goes up, you expect the size also go up; obviously,. Secondly, it depends up on the chemical structure or chain stiffness.

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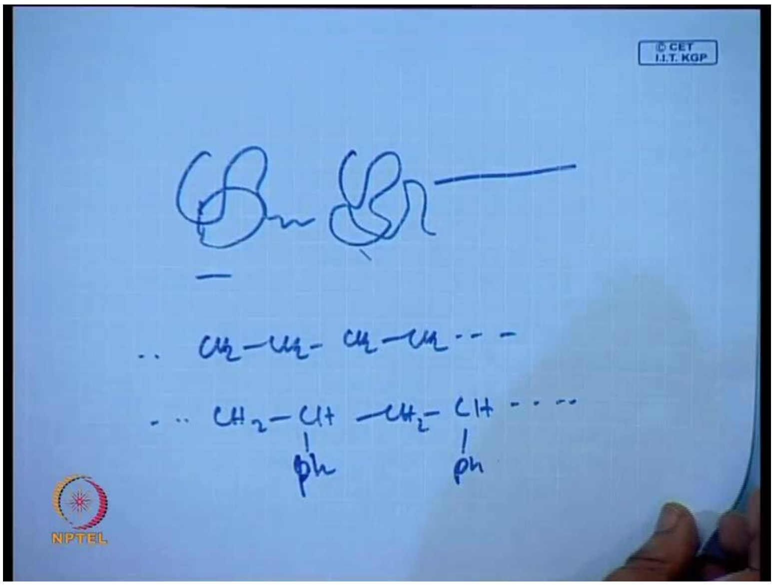

Now, if you have say polyethylene molecule or say polystyrene molecule; obviously, the rotation, the rotational freedom across the single bond will be much lower in case of polyethylene than polystyrene, because of bulky substituent, the rotation across the single bond will be restricted in case of… So, polystyrene is a stiffer chain, we will say that this is the most stiffer chain than the polyethylene, or in other words, polyethylene is a more flexible chain than polystyrene; but still, in spite of being this phenyl in side group, it is still, it is also having significant freedom across the single bond, rotational freedom across the single bond.

So, it will also be a (( )), but the degree of (( )) may be lower than most flexible chain like polyethylene. So, if the third one is of course the molecular involvement which depends up on where the polymer is if the polymer is in a solvent then obviously, if the interaction between polymer and solvent is higher than or main interaction between solvent-solvent and polymer-polymer, then the polymer solvent interaction will be preferred. So, the polymer will try to expand its chain. So, bigger in size and if the polymer solvent interaction is lower compared to the main interaction of polymer-polymer and solvent-solvent, then it will try to contract and avoid the solvent molecules.

Now, if you, if the polymer present in a concentrated solution then one polymer will come close to another polymer molecules. So, that will in effect not allow polymer to expand. So, they will again try to contract. So, these are the factors where the polymer is in dilute solution or concentrate solution, this is a good solvent or poor solvent or theta solvent that will dictate the size and shape of the molecules polymer molecule.

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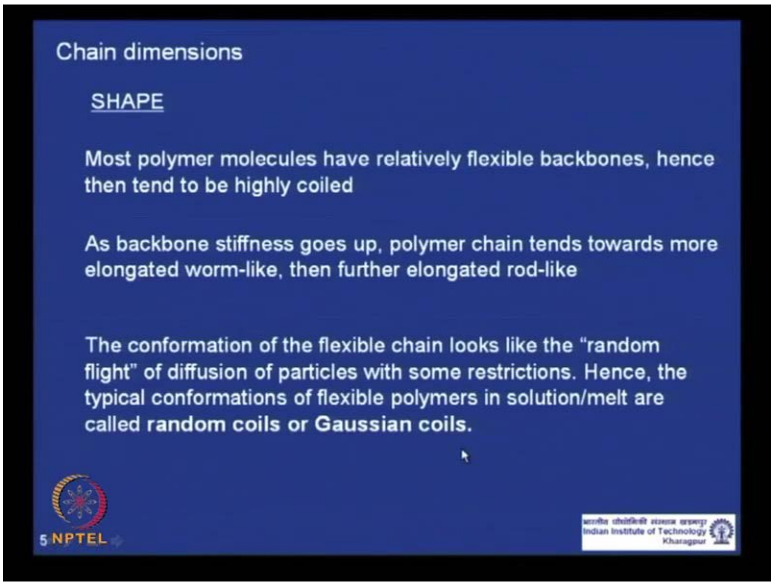

Chain dimensions

SHAPE

Most polymer molecules have relatively flexible backbones, hence then tend to be highly coiled

As backbone stiffness goes up, polymer chain tends towards more elongated worm-like, then further elongated rod-like

The conformation of the flexible chain looks like the "random flight" of diffusion of particles with some restrictions. Hence, the typical conformations of flexible polymers in solution/melt are called **random coils or Gaussian coils.**

Now, let us talk about shape first. We are using the terms size and shape. What do we mean by shape? As we mentioned in most cases, we write polymer chains like this or something like this, never we write this, because polymer chains as we have seen, they are having single bond where rotation occurs in bond are possible. So, you get a flexible a chain and in most cases we highly coiled these are coiled structure. So, we get highly coiled chains. Now, if the stiffness goes up, if you make more stiff, the coiling, the flexibility comes down, coiling will not be possible.

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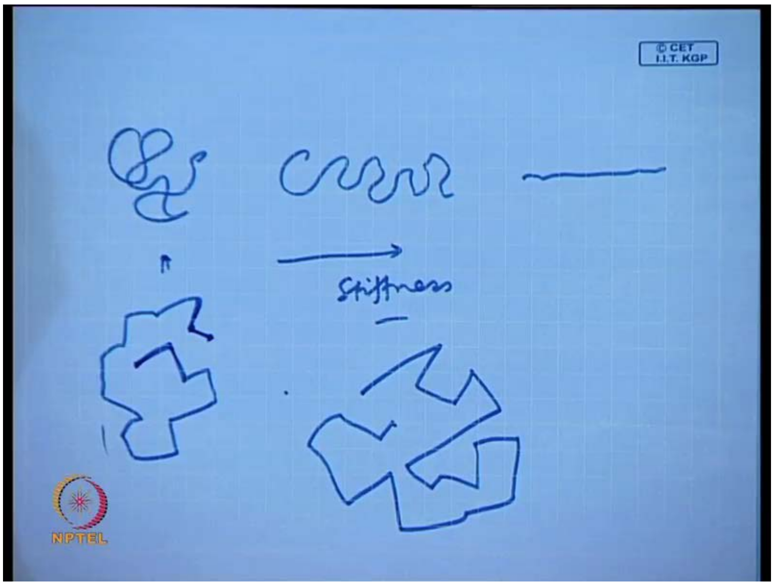

So, if the, if the say this is like a coiled structure, if the stiffness goes up, it may be like something like a worm like, because it is not so flexible to become a coil; and if the chain becomes, even more steep then finally, it will be like a rod. So, this is stiffness goes up, stiffness of the backbone goes up; most polymers, we will deal in this class and we come across in application, they are falling in this category where the polymer is enough flexible to reclose to a random coil than a worm like than a rod like. So, the confirmation the confirmation of a flexible chain looks like random flights of division of particles, when particle say, gas particle diffuse then what happens?

Moves here randomly, random fly, random flight. Now, polymer segments or polymer bonds cannot be so random because you have restriction of this lengths, each gas molecules can move like this. So, it can take any steps wherever it wants, any direction, but in case of polymer molecule, states are fixed as the bond length of the, each of the bond length of the backbone, repeating unit; and there are restriction of each bond angle, and there are restriction of also in rotational, we will come and talk about those in details; what I am telling it is, in case of polymer also, it takes the segment takes random flight, random walk, but not as freely as a gas molecules do in case of diffusion; because it takes random walk or random flight, we call this the confirmations of flexible polymer in solution are in melt as random coils or Gaussian coil.

Now, let us talk about size. We have talked about shape, it could be random like, worm like looks, like rod like and most cases, we deal with their enough flexible to become closer to a random coil. So, we will deal, we will discuss only about random coil, not about the other two confirmations of polymer molecules. Now, let us talk about size. What is size? When you write a polymer chain like this, as we saying all the time, we write polymer chains like this. Now, what we, what do you mean by size?

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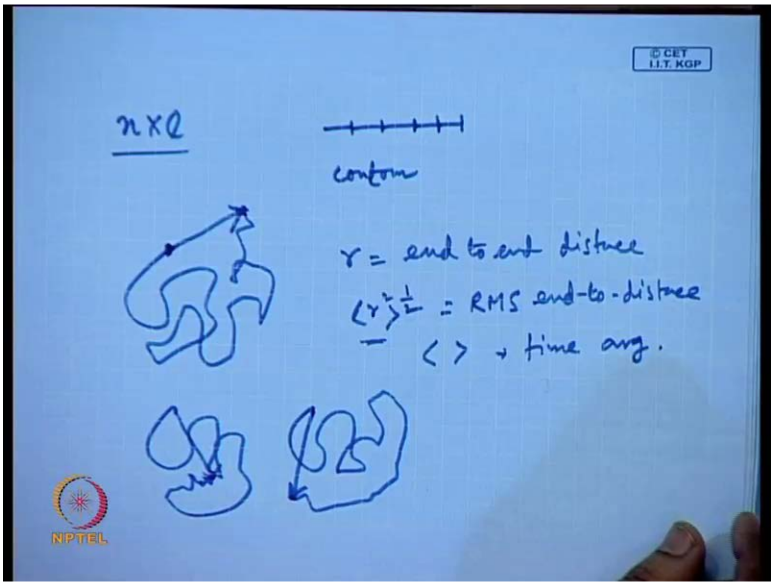

Of course, one of the basic size is contour length, contour length is basically n multiplied by l, n is the number of bonds and l is the, n is the number of bonds and l is the length of each bonds. So, basically of, you arrange all the bonds one after one, all the bonds, the length will give you the contour length. Now, which is in practical, in a polymer chain or any chemical chain will not be, will not have this type of arrangement. So, this is just theoretical number. So, as the maximum theoretically possible length one polymer can have, if just put all the bonds, all bonds in straight line one after one.

Now, we said this the polymers behave like this in random coil. So, another dimension we can have, it is like end to end distance say, if this is one end and this is another end, where we have r, we call end to end distance. Now, is this polymer confirmation is fixed? No, it is not fixed because there are continuous rotation across the single bond.

So, you may have one now and immediately after next moment you may have these are apart, or next moment you can have something like this, where we insert like this. So, as the polymer confirmation is changing all the time, you cannot have a fixed value of end to end distance, because this might have some value which is defined from this value, which is defined from this value.

So, what we do statistically, we find probability of finding one length, how much and then use this term where this represent time average. So, you with time, what is the average? r square to the power half. So, that is the root mean square end to end distance. So, this because the polymer change is always changing with confirmation, you cannot write a fixed r, you have to write statistical parameter which is given by a root mean square end to end distance.

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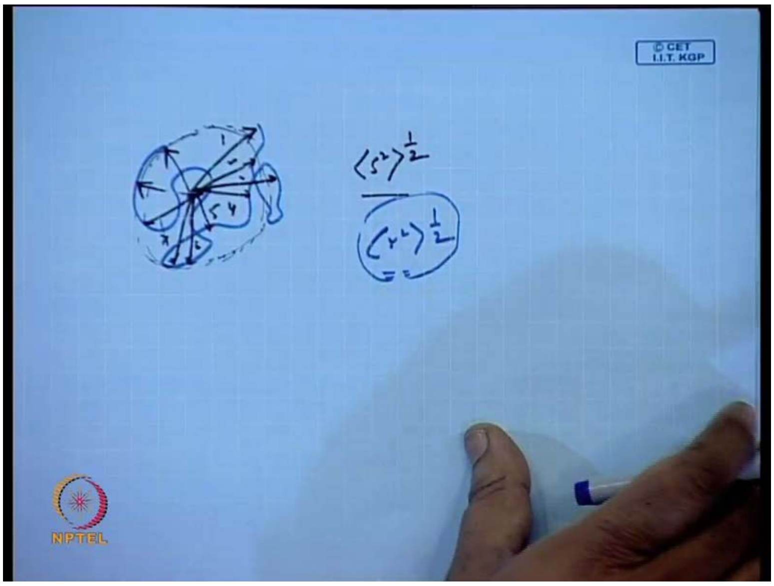

Now the third parameter which we can mention is like a radius of gyration. This radius of gyration is defined as the root mean square of distance of the elements of chain from center of gravity of the coil.

So, if you have a coil and if this is the center of gravity then all the segments. So, these are the distance of all the segments, all the elements, numerous numbers. So, 1, 2, 3, 4, 5, 6, 7, 8. So, root if this is one is s, again the root mean square distance of the elements of the chain from the center of gravity or center of mass of the coil is called the radius of gyration.

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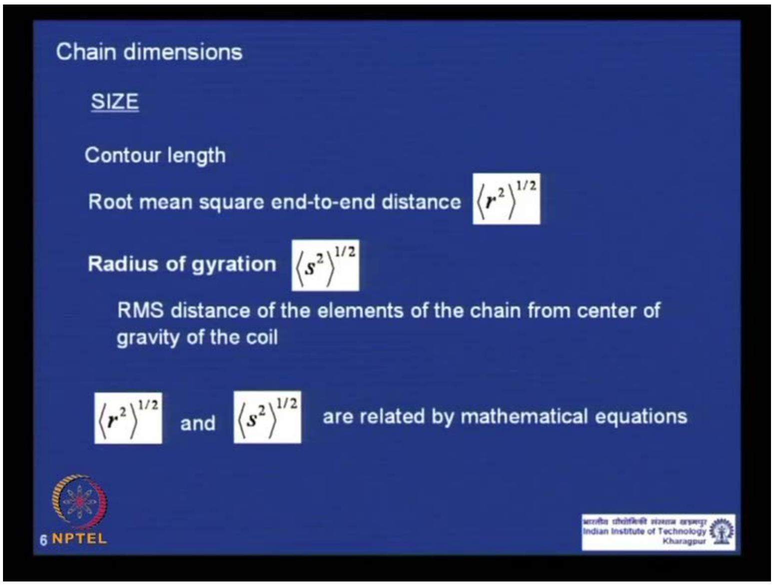

Chain dimensions

SIZE

Contour length

Root mean square end-to-end distance $\langle r^2 \rangle^{1/2}$

Radius of gyration $\langle s^2 \rangle^{1/2}$

RMS distance of the elements of the chain from center of gravity of the coil

$\langle r^2 \rangle^{1/2}$ and $\langle s^2 \rangle^{1/2}$ are related by mathematical equations

Now fortunately, there is a, this two term root mean square end to end distance and root mean square or radius of gyration are mathematically related. So, if you find one, the other would be, you can get easily from that expression which both connects each other.

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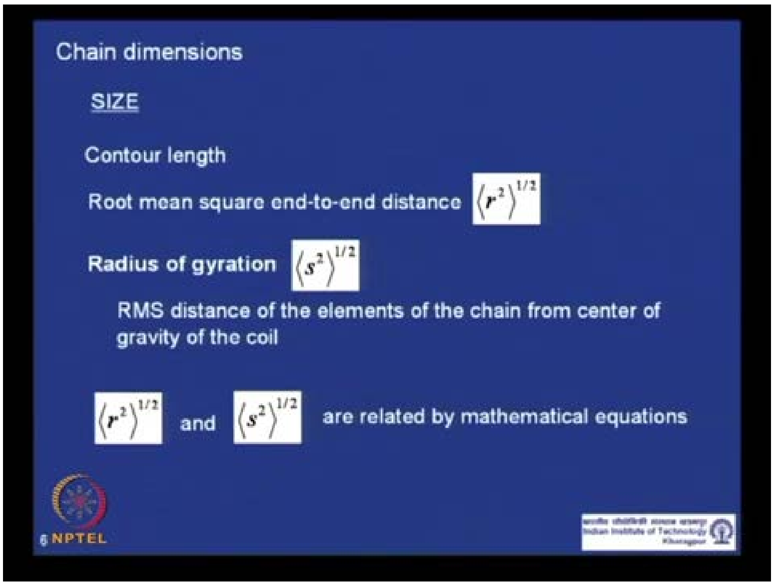

Chain dimensions

SIZE

Contour length

Root mean square end-to-end distance $\langle r^2 \rangle^{1/2}$

Radius of gyration $\langle s^2 \rangle^{1/2}$

RMS distance of the elements of the chain from center of gravity of the coil

$\langle r^2 \rangle^{1/2}$ and $\langle s^2 \rangle^{1/2}$ are related by mathematical equations

Now, out of these two, this radius of gyration is similar to almost like the radius, if you consider the polymer coil as sphere, if you consider coils as a sphere then this radius of gyration is similar to or proportional to the radius of this sphere. So, the solution properties of the polymer chain and light scattering behavior as well is mostly dictated by the radius of gyration value; and is also useful, if you have more than one ends like if you have branched polymer then you have more than two ends, then which, end to end distance is not existing.

Now, which end will take. So, in that case or if you have a cyclic polymer where there is no ends, then end to end distance is also not possible. So, in those cases, it is useful to use the radius gyration is more useful; whereas, in there, the root mean square end to end distance is more useful for describing the rubber elasticity behavior of a polymer coil. So, the radius of gyration gives more, or gives the solution, the solution behavior of polymer coil is mostly dependent on the radius of gyration, where the rubber elasticity is covered by the root mean square end to end distance.

Now, we, let us find out the size of a simplest molecular model. Now, what we will first consider, we now want to find out this values, or these values, now if we can find one of them, we know that both these are related mathematically. So, you can find this easily, the other one. Now, you mainly calculate, how you find information about these and we will know the expression for this and then find out what is relation in how to get this. Now, let us first consider the simplistic, very simple model where you have freely jointed chain with no restriction.

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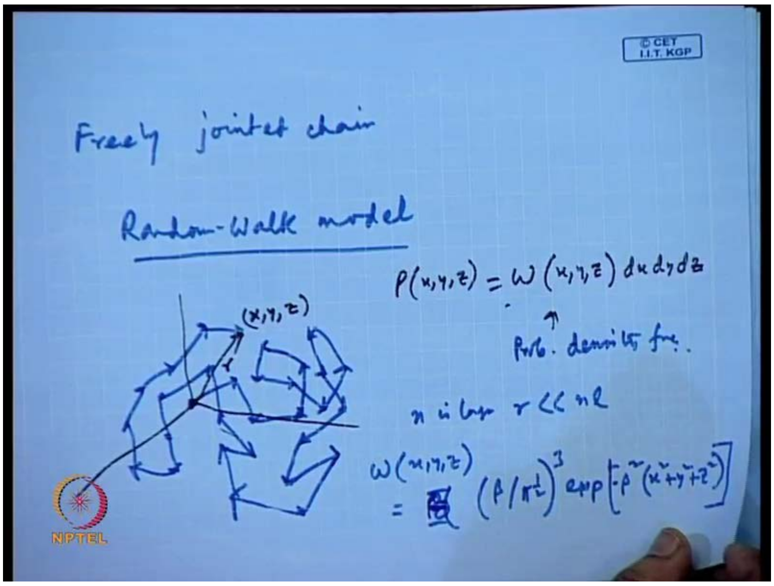

Freely jointed chain

Random-Walk model

$P(x,y,z) = W(x,y,z)\,dx\,dy\,dz$

Prob. density fn.

n is large r << nl

$W(x,y,z) = (\beta/\pi^{1/2})^3 \exp[-\beta^2(x^2+y^2+z^2)]$

So, if you have bonds you can have, you have no restrictions. So, if you consider this as a one bond then the other bond, you can place anywhere without having any restriction of bond angle or the rotational restriction between them. So, this is given by, for this the model is developed and that is again, which is just mentioned is the expression for this chain is given by random walk model, which was first developed for the movement of ideal gas; but here the difference is that, in case of ideal gas, the steps, the gas molecules can take, this does not matter, you can take any value.

But in this case, the each step the polymer can take or the bond can take is the length of the bond. So, you can start from one point, one end and just put the other randomly of course, the chain length the length of the each bond has to be equal. So, you can place, I am placing this randomly. So, you start from one end and you continually adding the further bonds in 3 D specific way, just showing a two d picture here, where you imagine this is in three dimensional. So, this is how the random of model is designed. So, what is, again, continue in a random way. So, one end is here. So, what the model do, you put make a three dimensional coordinate, where the one end is placed as the origin of this coordinate and this is r from the what is found is what is the probability of the other end, be at distance of r from the origin.

The way this model works is that you put the chain end at the origin of the 3 D coordinate and found out what is the probability that the other chain end would be at distance of r from the origin; say, if you put this x y z, then the probability of that the other end would be at point x y z which is having a distance r from the origin would be given by, right. This is, this is probability density function which is the probability unit per volume. So, you are considering one volume, you need volume at a distance r and you are finding out what is the probability of that volume have the other end. When n is large, of course r is the end to end distance much lower than nl, we have this equals to, we have this expression for this, we have this where beta is...

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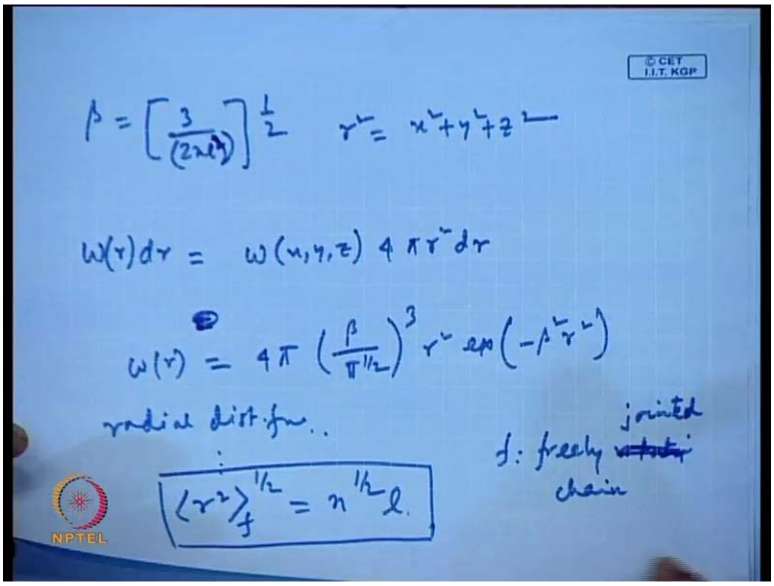

$$\beta = \left[\frac{3}{(2nl^2)}\right]^{\frac{1}{2}} \qquad r^2 = x^2+y^2+z^2$$

$$W(r)\,dr = W(x,y,z)\,4\pi r^2\,dr$$

$$W(r) = 4\pi\left(\frac{\beta}{\pi^{1/2}}\right)^3 r^2 \exp(-\beta^2 r^2)$$

radial dist. fn..

$$\boxed{\langle r^2\rangle_f^{1/2} = n^{1/2} l}$$

f: freely jointed chain

Now, here we are considering one unit volume, in this place. Now, there could be other points which are also having the same distance r; you can have other values r across this three d coordinate. So, you cannot only consider unit volume, you need to consider the volume element at distance r from, say you are not considering one point, you are considering the entire volume element which is having distance r from the origin where you find the probability of ending the other chain end. And that can be written as…

So, we are adding a volume element here with radius of r, 4 pi r squared d r is the volume element. So, you are finding the probability of, this is the probability distribution function. So, total probability of finding the chain, other chain end at a distance r would be the probability distribution function multiplied by the volume element. And this one is w r is then given by… This is radial distribution function and the other case it was Gaussian distribution function. Now, by this, you may not have to remember all this approach, unless you are extremely interested to know the logic behind to get the final expression.

Now, what I am trying to understand, how the approach, how, what the theoretical approach is made to find out the end to end distance, root mean square end to end distance for a random coil; and this is how it is made. And finally, if we, if we neglect or ignore all the steps, we can, that is not required or we cannot have enough time to complete that what we can write that it will finally give the end to end distance like this.

So, if you from these expressions, you finally get an expression, you remember this or you do not have to remember all the steps unless you are required, unless you are interested very much.

Now, if this subscript f, we are mentioning for a freely rotated chain or a freely jointed chain, freely jointed chain; that means, it does not, freely jointed chain does not have any restriction or bond angle and bond protection.

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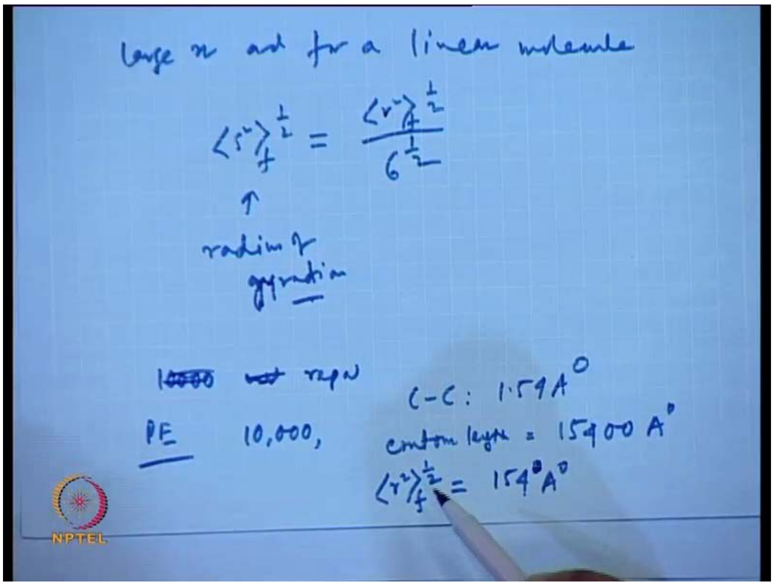

large n and for a linear molecule

$$\langle s^2\rangle_f^{\frac{1}{2}} = \frac{\langle r^2\rangle_f^{\frac{1}{2}}}{6^{\frac{1}{2}}}$$

↑ radius of gyration

~~10000~~ unit repn

PE 10,000,

C-C: 1.54 A°

contour length = 15400 A°

$\langle r^2\rangle_f^{\frac{1}{2}} = 154$ A°

Now, as I said that fortunately there is a relation for large n and for linear molecule. We can write, this is your radius of gyration. So, with this ratios, it can be shown that if you know this. So, for if you put f here, if you put f here. So, freely rotating chain, we can get this expression.

So, by writing for a simple, for a simple model, the molecular model, freely jointed chain for no restriction, we now shown that using Gaussian distribution function or random coil approach, it can be shown that the, it shows this, it has this relation; which means that coil dimensions will be significantly lesser than the contour length, if you have a molecule of say 10000 units 10000 repeating units.

So, if you have polyethylene molecule with 10000 repeating units, each carbon-carbon length is 1.54 Armstrong. So, the contour length would be multiplied this by the number of bonds. So, it will be less than one intrusions by knowing that. So, it will be contour length; whereas, your r m s end to end distance would be 154 Armstrong which is 100 lower than contour length, and that is coming from this n to the power half term. So, because you have 10000 units, you are getting 100 times lower value of the contour or r m s end to end distance.

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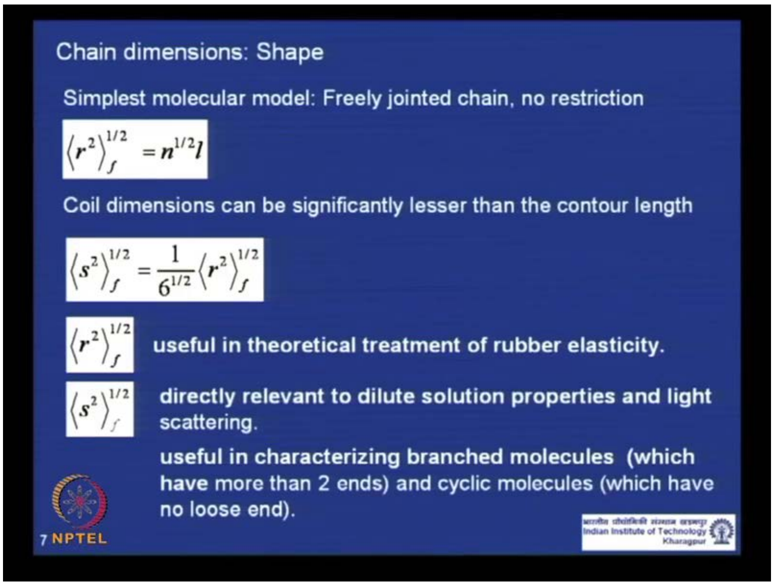

Chain dimensions: Shape

Simplest molecular model: Freely jointed chain, no restriction

$$\langle r^2 \rangle_f^{1/2} = n^{1/2} l$$

Coil dimensions can be significantly lesser than the contour length

$$\langle s^2 \rangle_f^{1/2} = \frac{1}{6^{1/2}} \langle r^2 \rangle_f^{1/2}$$

$\langle r^2 \rangle_f^{1/2}$ useful in theoretical treatment of rubber elasticity.

$\langle s^2 \rangle_f^{1/2}$ directly relevant to dilute solution properties and light scattering.

useful in characterizing branched molecules (which have more than 2 ends) and cyclic molecules (which have no loose end).

Now, you seen that it can be shown that the radius of gyration can be found from the r m s, root mean square, the r m s end to end distance; and as I said earlier, the r m s end to end distance is useful for our elasticity and the radius of gyration useful for directly relevant to dilute solution properties and light scattering and it can also useful for branched molecules and cyclic molecules.

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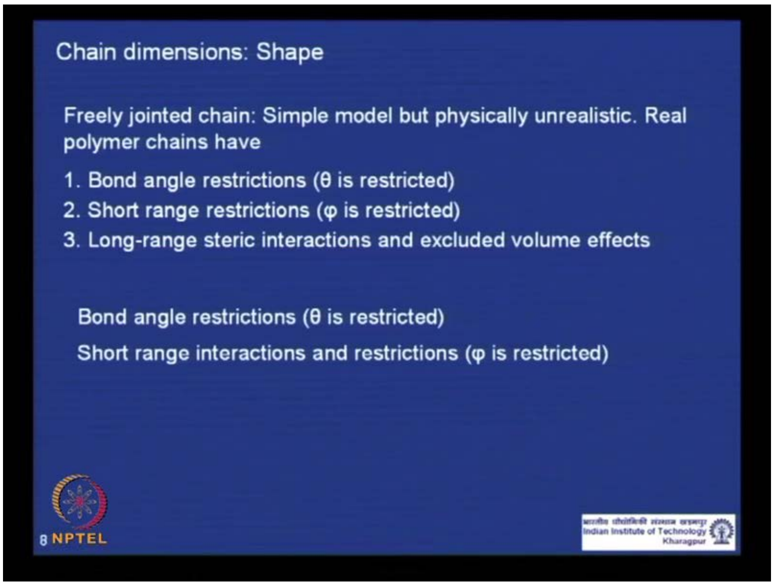

Chain dimensions: Shape

Freely jointed chain: Simple model but physically unrealistic. Real polymer chains have

1. Bond angle restrictions (θ is restricted)
2. Short range restrictions (φ is restricted)
3. Long-range steric interactions and excluded volume effects

Bond angle restrictions (θ is restricted)

Short range interactions and restrictions (φ is restricted)

Now let us, that is not practical, you know, the chain without a restriction, bond angle restriction or bond rotational restriction without is physically unrealistic. So, every real polymer chain will have restriction of bond angle and also restriction for the single rotation around the single bond.

So, there are actually three restrictions, bond angle restriction, short range restriction, restriction which is coming from the single bond rotational restriction, and there is also long range steric interaction, and excluded volume effect which will, which we will encounter 1 by 1 and see how the dimension or the size of the polymer changes, this should be size not shape. So, all this will put in a, all this restriction one after on, found and then r m s end to end distance varies, and once we know the end to end distance and always find the radius of gyration.

Now, let us first consider these two bond angle restriction and short range rotational restriction. Now, let us consider first a single bond; the simple bond, one bond, if you one bond like this; now, the other one, in case of freely rotating, in case of freely rotating chain, you can place it here, you can place it here, or even you can place it here. There is no restriction bond angle, or you can do it in a 3 d, I am just showing a 2 d matrix. So, you can place the other bond here, 180 degree or 90 degree or even 0 degree, there is no, there is no restriction of bond angle, in this case; and as I said, I am just showing a two dimension here a thing, imagine you can think of three dimension as well. So, what would have been the average, if all this 0 to 180 degree is equally probable, then what would be the time average? Time would have been 90 degree.

So, this would have been the time average value. So, what would have been the end to end distance? It would be from this end to this end, this would have been the end to end distance. Now actually, in case of carbon-carbon bond, what is the bond angle? This is the time average, there was no restriction of bond angle; in case actual, you have no 90 degree, you have this 109.5 degree, tetrahedron bond angle, then your actual molecule bond angle would look like this. So, the end to end distance, which was earlier this, now it will become this. So, because of this restriction, you can now understand that the end to end distance or time average end to end distance, root mean square end to end distance will increase from here to here.

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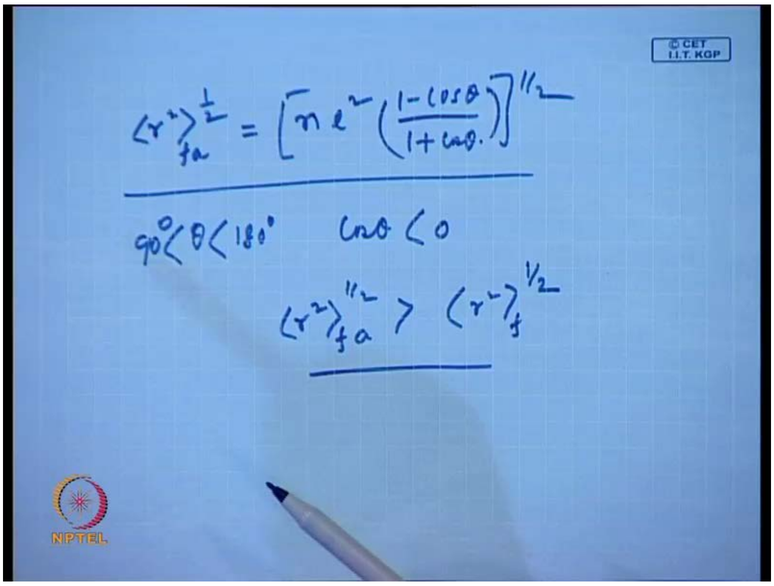

$$\langle r^2\rangle_{fa}^{\frac{1}{2}} = \left[n l^2 \left(\frac{1-\cos\theta}{1+\cos\theta}\right)\right]^{1/2}$$

$90^\circ < \theta < 180^\circ$ $\quad \cos\theta < 0$

$$\langle r^2\rangle_{fa}^{1/2} > \langle r^2\rangle_{f}^{1/2}$$

So for this restriction, you will have increase in the root mean square end to end distance. Now, it can clearly be shown, the these value where the writing f a which is angle restriction from one angle is coming, we are writing these, it can be shown that 1 minus cos theta, it can be shown that… Now, in most cases the carbon-carbon bond are the bonds, theta is between 90 degree and 180 degree, so cos theta is less than 0; so obviously, r square f a would be greater than r square absolute.

Thus, we have just seen from the freely rotating bond. So, this is the expression which now we got from the angle restriction; what we will be the next lecture? We will impose the second restriction and see how this dimension changes.