Basic Statistical Mechanics
Prof. Biman Bagchi
Department of Chemistry
Indian Institute of Technology, Bombay
Indian Institute of Science, Bangalore

Lecture - 57
Polymers in Solution and Polymer Collapse Part 3

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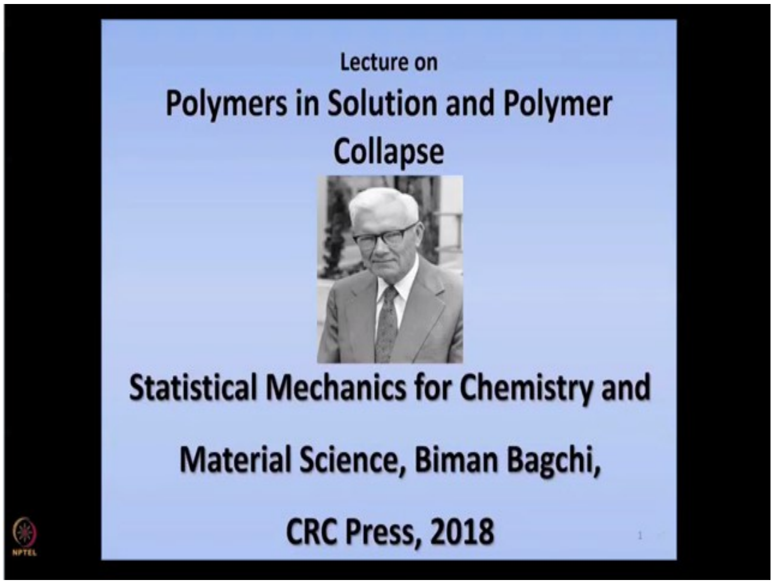

Lecture on

Polymers in Solution and Polymer Collapse

Statistical Mechanics for Chemistry and Material Science, Biman Bagchi, CRC Press, 2018

Good morning or good afternoon everybody depending whatever is your time frame and welcome back to this course on Statistical Mechanics for Chemistry and Material Scientists, this is a course for equilibrium Statistical Mechanics and we have been studying the physical chemistry of polymer and the picture that you see on the slide in front of you is that of Paul Flory who played an enormous role in fashioning this subject.

Before I proceed further, let me tell you this course will be little different from the earlier courses which were recorded in Bombay IIT studio, this one is because of the Corona virus epidemic I am recording it from home, so you will not be able to see me, but rest of the things will be okay you be able to see the slides and you will be able to follow, and what I do go to revise the course first 5-10 minutes of what I did in the last class and then we will go in to do some new things.

This might be a bit of a longest class, but there will be some expressions and derivations but will not derive the lengthy equations, but I will sketch the derivation and you will find the derivations in my book on the same title of the course and there are two other books I want to bring to your attention, one is the book by Paul Flory Principles of Polymer Chemistry and other is book by P-G de Gennes on Scaling Concepts in Polymer Science.

These two books together will be more than enough and as I was telling you about Paul Flory who created almost the much of what we know about polymer science today and he is rightfully called the father of polymer chemistry, he got Nobel prize in 1974 and there are many, many things that he did in polymer and he did both theory and experiment that which is remarkable because he did theory at a very high level.

Paul Flory was born in 1910 in Illinois near Chicago and he graduated from Ohio State University and then joined industry and from industry, he then moved to Cornell University and at the Cornell where he did much of his pioneer work and he also published his book from the Cornell University.

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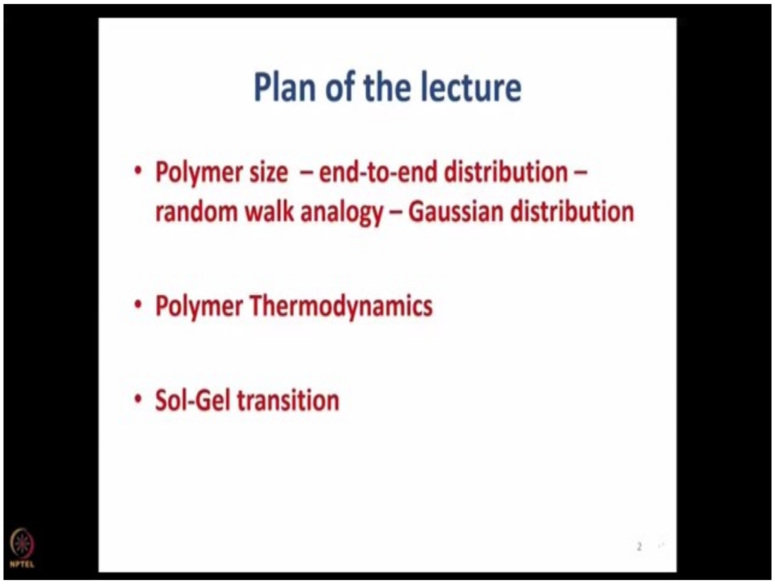

Plan of the lecture

- Polymer size – end-to-end distribution – random walk analogy – Gaussian distribution
- Polymer Thermodynamics
- Sol-Gel transition

Now the next slide I give the plan of the lecture, so this is something we did in the last lecture polymer size, end to end distribution and with a random walk analogy it takes you to Gaussian distribution and then we started Polymer Thermodynamics, we will do little bit more of Polymer Thermodynamics and we will talk two kinds of phase transitions in polymer.

One is a Sol-Gel transition by the reason of doing it is that it bears close similarity to Mayer's theory of condensation gas to liquid transition. It is just is a kind of a cluster indentation here, sol means solution of monomers the monomers connect together to form a branched polymer and which is then become a highly viscous solution, it is a very important industrial process and used widely as I have told you already that polymer is one of the most important part of our daily life.

And from textile to rubber to many things that we use every day. For example your diode in many things is organic semiconductor is a polymer MEH-PPV. So and these many of these things are made by some kind of a sol- gel transition. So it is an important thing, so we will just go through this in a rather simple fashion without the blackboard I will be more qualitative but I will show the equations.

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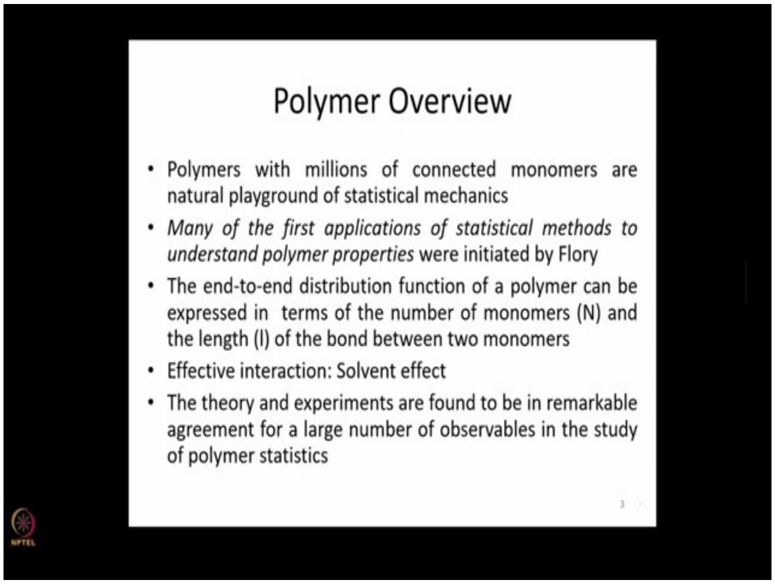

Polymer Overview

- Polymers with millions of connected monomers are natural playground of statistical mechanics
- *Many of the first applications of statistical methods to understand polymer properties* were initiated by Flory
- The end-to-end distribution function of a polymer can be expressed in terms of the number of monomers (N) and the length (l) of the bond between two monomers
- Effective interaction: Solvent effect
- The theory and experiments are found to be in remarkable agreement for a large number of observables in the study of polymer statistics

So in the third slide, I briefly do the overview that a polymer that we think that millions and millions of connected monomers, monomers themselves are somewhat complex molecules and we polymerize them, means we add these monomers together and many of the first applications of, so polymer is since these are many is a large system with a large number of monomers it is a natural playground of statistical mechanics.

And one of the important property of this polymer is end-to-end distribution function of a polymer which is expressed in terms of number of monomers and which is N and in between the monomers, will talk of so effective interaction solvent effect and we talk of several other remarkable properties and some observations that we have got. In the next day we should the random coil polymer chain.

And this kind of Airy bond diagram and you can see the open ends of the polymer and in between that there is a long contour where the connected of monomers is kind of it takes a random zigzag fashion and that is why it is called a random walk. One of the reason that it is so random lies in the basic chemistry and that is when I start with A_0 to A_1 and the beginning to the first bond we did A_0 to A_1 .

That bond many of this is CC single bond carbon-carbon single bond and they can take tetrahedral geometry that means that it can rotate in three dimension, so that bond can take many directions. And then the next one so you join to one bond which already can rotate in many reactions to another bond which again can take many direction so by the time I have gained some bonds connected and each of them tagged many configurations we already have a huge number of configuration space that means rotational configuration space that this polymer can enjoy and that is a very important property of the polymer. This huge number of configuration space the configuration degrees of freedom that a polymer enjoys because of these rotational flexibility or rotational degrees of freedom.

So these different polymer that arise because of the rotational degrees of freedom sometimes there is a preference of certain orientations and then one talk of rotational Isomer and this is a term which was coined by you Russian scientist Valken Stein and which Flory also use later. So in this slide that we are showing that you are starting one then we have these different bonds and the bonds are going a last the other bond it A_N is the red bond.

So this is the ping-pong diagram in order to get end to end distance that would be from A_1 to A_N from 1 to another N that is called R, the universal notation R and that is what we will calculate now and that end to end vector R it can be easily seen is nothing but sum of all these small small vectors and this has one small bond vectors and each of the bond vector has lot of independence from other because of the rotational degree of freedom.

So these bonds arise because the vectorial nature the length is could be the same that is the bond length l but because of the vectorial nature of the bond and the rotational degrees of freedom, R is a random number and that probability distribution of R is a subject of great interest and that is the one which is the Gaussian distribution as we discussed last class and also we discuss today.

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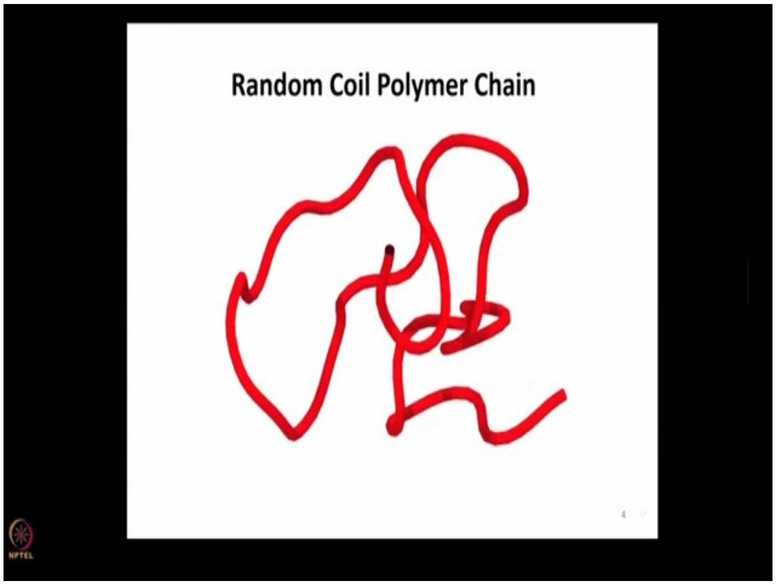

Random Coil Polymer Chain

Now this is we discussed, but let us discuss again this is initially lab caricature of a polymer which is we called is surgery bond diagram, you can see there end-to-end distribution going on here and these end-to-end distribution is you can see from one into the other end that is because of the large intervening conduit going from one into the other end which can take many configurations in sudden way it reminds you of rope what is dangling or dancing rope or snake.

And this ability to take many many configurations determined the end-to-end distribution, so roughly the size of the polygon when we see the size of a polymer we essentially talk of two things, how only average how far is my end the average one, what is the average distance and since it is a random quantity that average is a mean square and this is really close analogy random walk.

So as if it has monomer to monomer distances almost have random walk and we will discuss this now immediately little bit. Extremely important to realize that end to end distribution along with the end to end distribution giving you the size of a polymer there is one more quantity is radius of gyration. Radius of gyration is nothing but the kind of moment of inertia that means you take the position and $\sum_i m_i r_i^2$ and you that gives you also a called R_G that also gives you a measure of the size and these 2 quantity is the mean square end-to-end distribute size and the radius of gyration a very closely connected to each other they have the same dependence of number of monomers but they have some numerical factor which make them different from each other. So we can use either radius gyration or root mean square distributed end-to-end distribution.

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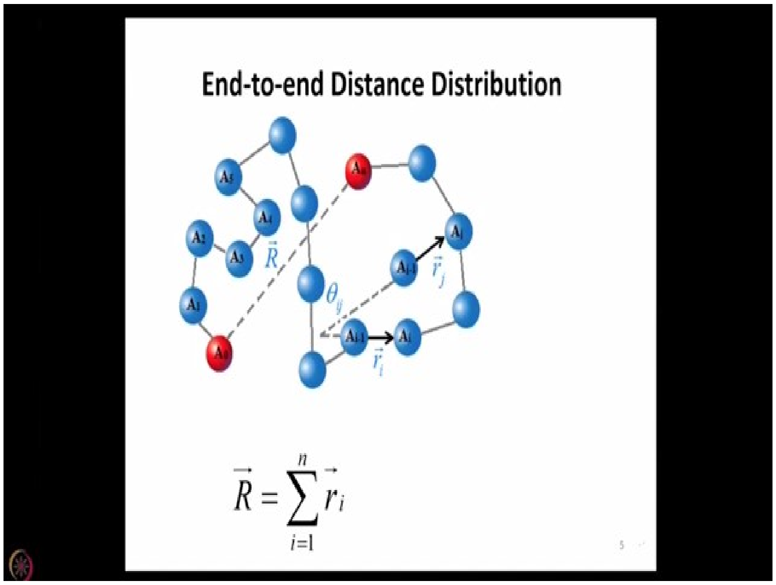

End-to-end Distance Distribution

$$\vec{R} = \sum_{i=1}^{n} \vec{r}_i$$

This is what I was telling that we will be discussing little bit of the random walk scenario and then go to A_1, A_2, A_3 and then go over and go to endpoint that two endpoints are given by two red spheres. And one important thing to know here that when I go from A_0 to A_1 and A_1 to A_2 then A_0 to A_1, fitted can rotate and can take a large number orientations this is not quite 360^o because there is some static hindrance post by a molecular architecture.

But it is fairly flexible that means it can take many orientations, so now you consider that you are orienting one from the other and the other. So by the time you have just 8 or 10 monomers connected, just 10 mark already you can see a huge number of configurations that can this polymer can take, this is extremely important to realize the inherent huge flexibility of a polymer.

A huge number of internal degrees of freedom, the configuration of a degree of freedom that a polymer enjoys and that is this very important part of this property is which Flory realized very early along with Vulcan stein and Vulcan Stein coined name rotational isomer this multiple configurations that polymer gates was recognized by would these two giants polymer chemistry. So now if I want to put end-to-end distance we call it $\vec{R}$.

Then you realize that this is nothing but the sum of the vector just like I want to go one place to another place where that is so finally placed then where I go finally I if I number of shapes then I add up these things the vector and that is why vector is important of depended on orientation, that is why orientation is very important. So you can now see the end-to-end distance both the vector and a scalar is a dynamic quantity and is also hugely random because and you see now in one position.

Then if you are in a solution polymer in a little later and you see in a different position. So it is completely moving around finding and uncoiling at zig zag direction, so the way to say that we try to have an idea is through what appears to be extremely important extremely complicated. But turns out to be not complicated not only not complicated it is a beautiful universality that Flory, Valcan Stein realized, as enormously exploited Physics a community where Polymer Physics the big subject now.

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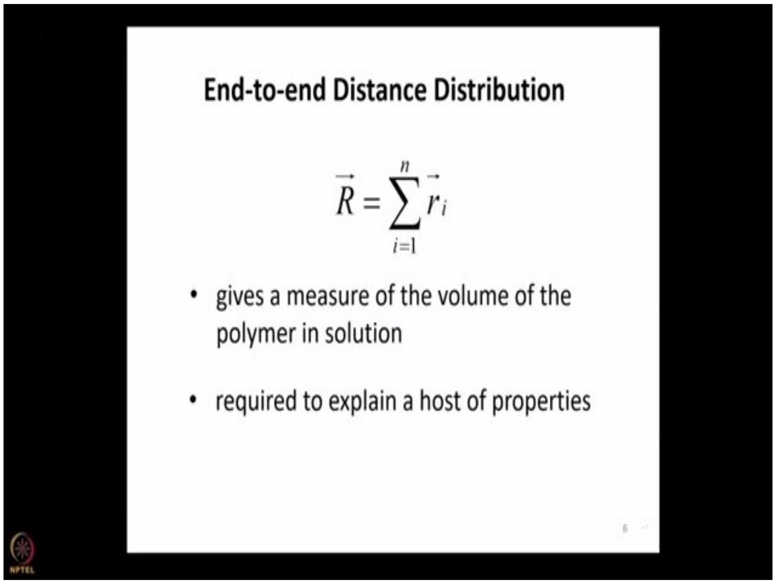

End-to-end Distance Distribution

$$\vec{R} = \sum_{i=1}^{n} \vec{r}_i$$

- gives a measure of the volume of the polymer in solution
- required to explain a host of properties

So this is the sum we get and now we are to get a distribution of this R and $\vec{R}$ as I told you this $\vec{R}$ is a stochastic quantity, is the random quantity.

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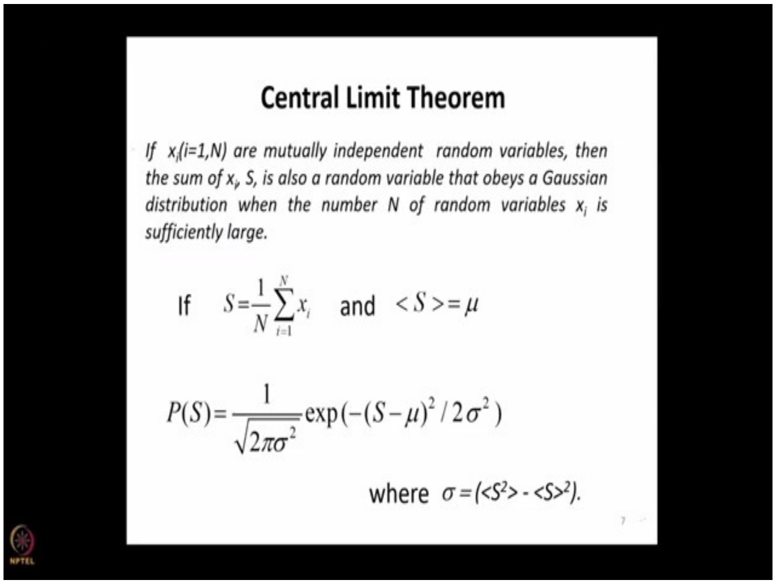

Central Limit Theorem

If $x_i(i=1,N)$ are mutually independent random variables, then the sum of x_i, S, is also a random variable that obeys a Gaussian distribution when the number N of random variables x_i is sufficiently large.

If $S = \frac{1}{N}\sum_{i=1}^{N} x_i$ and $<S> = \mu$

$$P(S) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp(-(S-\mu)^2/2\sigma^2)$$

where $\sigma = (<S^2> - <S>^2)$.

Then in many ways it can be done it can be just applied do not have to do Center Limit Theorem, we can apply to random walk, but Central Limit Theorem gives a very easy way access is a well known theory that I discussed last time that, if I have a quantity S which the sum of N number of random quantities and when I sum it up that sum is a Gaussian distribution that is called Central Limit Theorem.

I do not want to spend too much time on that, but it is a very robust theorem as I told you last time mathematicians are not given to give this kind of name fundamental theorem, Central Limit Theorem that is not, there is more in physics and chemistry we give grandiose name like theory of everything or many great thing but not mathematicians they are very conservative people so when the Central Limit Theorem it is really Central Theorem of Probability Theory.

That if I have N number of random variables I add it up, then that goes over we Gaussian distribution with it mean μ and the, the mean is very easy to understand in this case because it is rotating and so you can easily convince yourself that mean would be zero and but then everything holds on just the width of the distribution which is the standard deviation which gives the size because if I now want to get the size then I have to get the $\left\langle R^2 \right\rangle$ second moment of the distribution.

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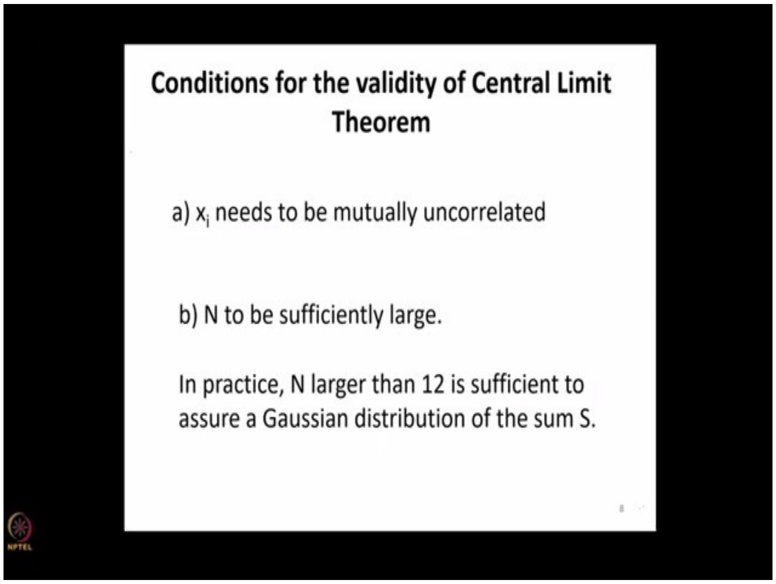

Conditions for the validity of Central Limit Theorem

a) x_i needs to be mutually uncorrelated

b) N to be sufficiently large.

In practice, N larger than 12 is sufficient to assure a Gaussian distribution of the sum S.

So this has one little bit on Central Limit Theorem you can find it on Google, on internet you will find huge amount of things and Center Limit your number the main thing is that N to be large, but as I told you that 10-12 you already have fairly Gaussian distribution, this is one of the thing we always in computed we generate Gaussian distribution, we generate 12 random numbers we add them up and the sum becomes the Gaussian.

And that another thing is that these two should be uncorrelated that means from one step to another from monomer 1 to monomer 2 and monomer 2 to 3, so 1 to 2 and 2 to 3 and they have to be independent and that is guaranteed by the rotational degree of freedom.

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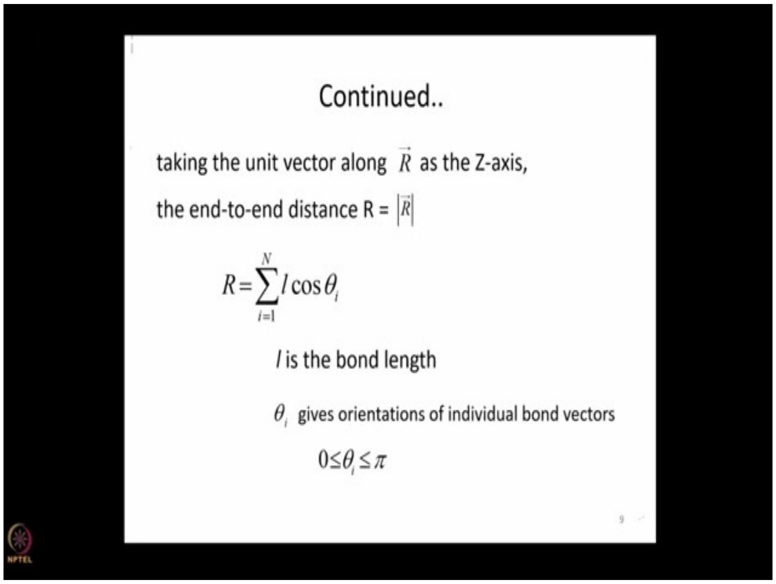

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taking the unit vector along $\vec{R}$ as the Z-axis,

the end-to-end distance R = $|\vec{R}|$

$$R=\sum_{i=1}^{N} l\cos\theta_i$$

l is the bond length

θ_i gives orientations of individual bond vectors

$0\leq\theta_i\leq\pi$

So then one can further quantify these things by taking $\vec{R}$ as the Z-axis, when you predict it on the $\vec{R}$ and you get $l\cos\theta_i$ and then and you take our end to end distance as their axis and we put it on that then $l\cos\theta_i$, l is the monomer length or bond length and θ_i is the one that is what gives you the randomness. So since, θ_i is random, $\cos\theta_i$ is random and now we can do R^2 and I can evaluate the $\cos\theta_i$ from 0 to π and I can evaluate the $\left\langle R^2\right\rangle$.

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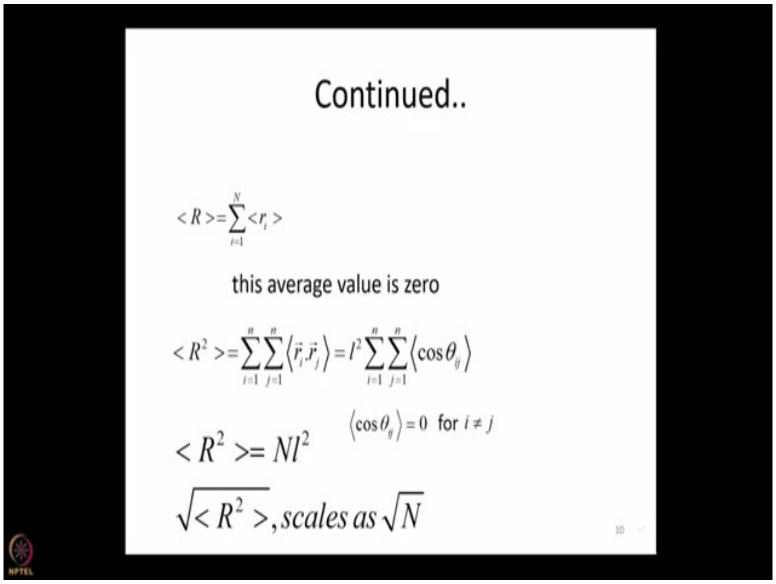

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$$<R>=\sum_{i=1}^{N}<r_i>$$

this average value is zero

$$<R^2>=\sum_{i=1}^{n}\sum_{j=1}^{n}\left\langle \vec{r}_i.\vec{r}_j \right\rangle = l^2\sum_{i=1}^{n}\sum_{j=1}^{n}\left\langle \cos\theta_{ij} \right\rangle$$

$\left\langle \cos\theta_{ij} \right\rangle = 0$ for $i \neq j$

$$<R^2>= Nl^2$$

$$\sqrt{<R^2>}, scales\ as \sqrt{N}$$

And that is exactly done here, when you do the averaging because i, and j these are on bonds, one bond another one is uncorrelated so then I have posted i, j is just one sum because otherwise so then we get N there and so $\left\langle R^2 \right\rangle = Nl^2$ so is the beautiful result which tells you means square is Nl^2, so for that I do not need thee Gaussian distributions for this I do not need this Center Limit Theorem.

But I need this Center Limit Theory to get the distribution of $\vec{R}$ and I can get that there also to random walk. So there are two points here that mean square $\sqrt{\left\langle R^2 \right\rangle}$ is $\sqrt{N}$ which extremely important result is because that gives you the size of the polymer. And then comes the distribution.

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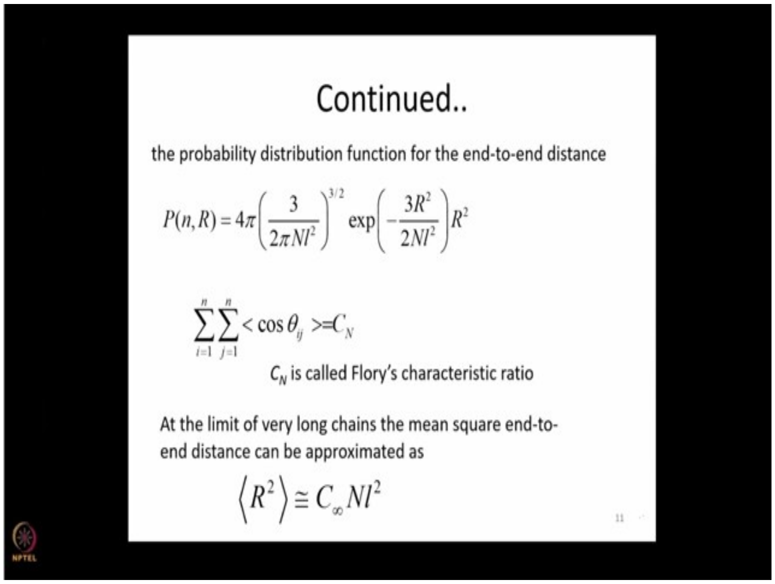

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the probability distribution function for the end-to-end distance

$$P(n,R) = 4\pi\left(\frac{3}{2\pi Nl^2}\right)^{3/2}\exp\left(-\frac{3R^2}{2Nl^2}\right)R^2$$

$$\sum_{i=1}^{n}\sum_{j=1}^{n} < \cos\theta_{ij} >= C_N$$

C_N is called Flory's characteristic ratio

At the limit of very long chains the mean square end-to-end distance can be approximated as

$$\left\langle R^2\right\rangle \cong C_\infty Nl^2$$

So distribution is Gaussian as I said here there is R^2 factor here you know I am asking what is the probability that a little bit problem here that gain should be N would be side or small and on both the two sides but did you see this move my mistakes are not in the book but there are little bit mistakes here and there in these slides. But we go back and look so they distribute the end-to -end distance R is for NR should be there.

This is distribution they the probability that you have N within a distance R and because of the spherical symmetry of the system. So it is in a volume element in a shell that shell is $4\pi R^2$ so at a position R it is $e^{-3R^2/2Nl^2}$ plus the normalization but you have to multiply by $4\pi R^2$.

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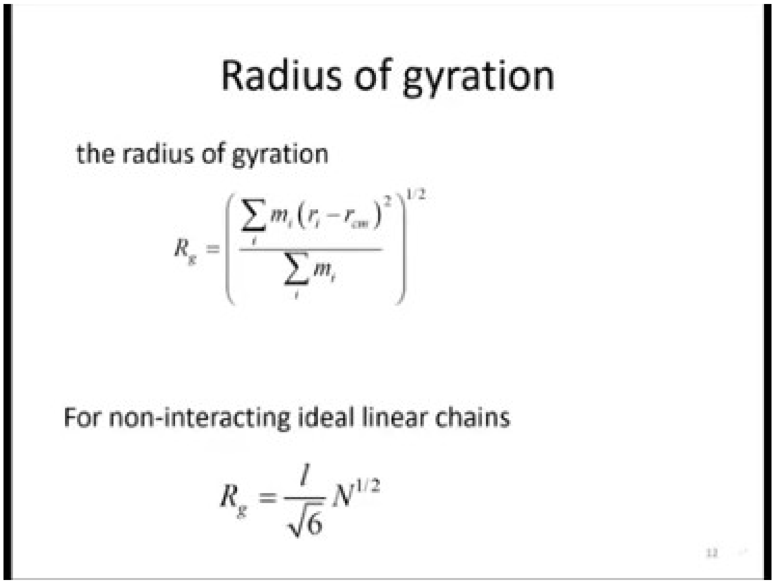

Radius of gyration

the radius of gyration

$$R_g = \left(\frac{\sum_i m_i (r_i - r_{cm})^2}{\sum_i m_i} \right)^{1/2}$$

For non-interacting ideal linear chains

$$R_g = \frac{l}{\sqrt{6}} N^{1/2}$$

So these result, $N^{1/2}$ and that side is then equal to the radius of gyration that these we are exactly same way you can derive because also the second moment you just change your central of your coordinate system and you again see that it is our $R_g \sim \sqrt{N}$, so but basic Center result is the following that the power distribution is Gaussian with $e^{-3R^2/2Nl^2}$.

And so standard deviation or the width of the distribution scale as $\sqrt{N}$ and that is what we concise so as told you before radius of gyration which gives a good measure of the size of the polymer and the mean square end to end distribution they are essentially simply and so as I told you already a polymer is millions and millions of monomers that means N is upwards of 10^7 or 10^8.

Now if l is couple of angstrom then you can imagine that $\sqrt{N}$ is 10^4 this is 2 A^0, then 10,000 into 2 A^0, this is a essentially 20,000 A^0, so radius of gyration is 20,000 A^0 that is essentially roughly a huge here, so you can understand this monster, monster a polymer is sitting in solution and they are not one polymer like that there are many polymers.

So this monsters 10,000 and 20,000 A^0 with the radius here are the spherical things are suspended in solution, so that is what makes the polymer solution thermodynamic so interesting it is a binary mixture but is the binary mixture where one guy is 10,000 times larger than the other guy it is very important to get the sense of number that what makes polymer so unique that polymer solution floating around.

And many of them would specified it, if they are not if preferably solvated, and we see these situations in proteins you know in a folded protein is almost again the polar protein is really spherical but there of course much smaller there a few, and they both of them yeah and so they are much smaller but even then in solution is a very interesting area, so polymer solution stands out from many times you say they are the same.

It is not quite the same polymer solution is the polymers are much bigger quantities. So we do where the protein into your polymer and use the language of polymer science, polymer chemistry to explain proteins.

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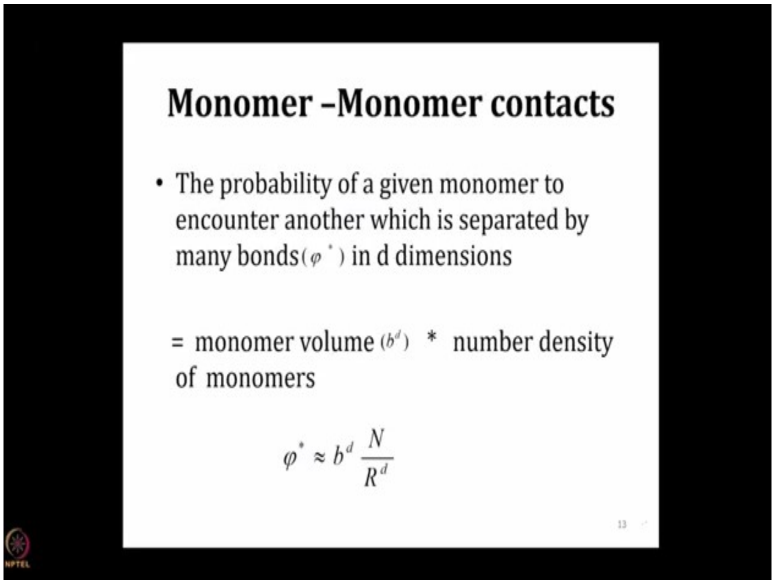

Monomer –Monomer contacts

- The probability of a given monomer to encounter another which is separated by many bonds(φ^*) in d dimensions

= monomer volume (b^d) * number density of monomers

$$\varphi^* \approx b^d \frac{N}{R^d}$$

Now this was done by Valcun Stain and Flory now other beautiful calculations that are Flory and this is just the gimp now Flory said okay, I wanted to find it in d dimension, he of course did it in 3 dimension he said how do I find the size of a polymer in a d dimension? And he said okay, as I told you that this polymer is a monster. It is a big deal, so there is an interaction between monomers, so interaction between monomers depends on the concentration of the monomers, so what is the size of the monomer? Size of the monomer actually will be R^d in d dimension, R^3

3 dimension R^2 in two dimension, now if that is so and if what if monomer has a volume V, then I can consider that a concentration of monomer, why do you need the concentration monomer?

Because I need the density, why do I need the density? I need the density, so that I can consider interaction, why do I need density to consider interaction? Because when the monomers are next to each other they are close to each other they are interacting and they are far from each other they are not interacting, so interaction energy is proportional to square of the concentration i.e., c^2. Now where did you see such logic before that where the interaction energy is ρ^2, where ρ the density of the solution.

Previous class I would have asked you, I would have tested you come up with the answer and you want to be jacked up what do you answer out of you but since I cannot do it now. Let me tell you the answer I did using Van der Waals theory. In Van der Waals theory there is a repulsive term B + B - + B square, N square by B Square that is where exactly same logic Van der Waals seems that in order to interact with both the two molecules should have been a small volume limit.

And in this, what is the probability of the monomer limit if they are independent of each other then one monomer to be there is the concentration or density second monomer is also concentration, okay so that is why concentration is so important which is shown here in N / R_d which is concentration.

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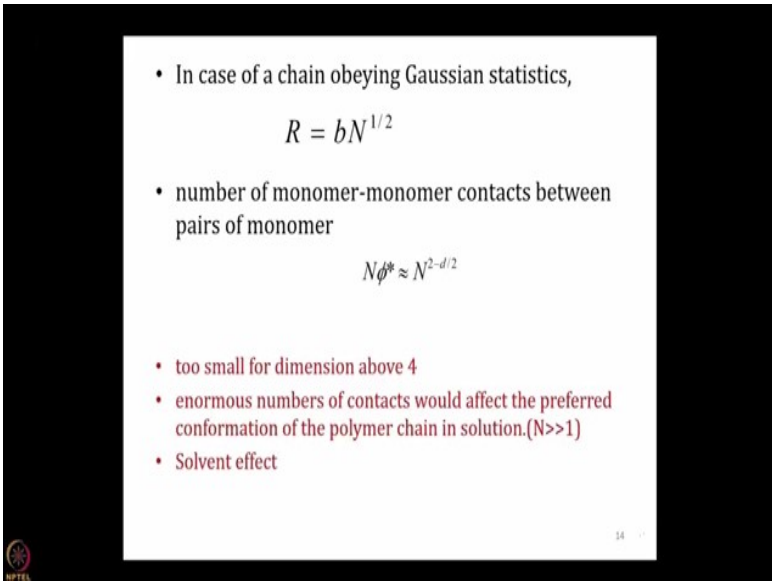

- In case of a chain obeying Gaussian statistics,

$$R = bN^{1/2}$$

- number of monomer-monomer contacts between pairs of monomer

$$N\phi^* \approx N^{2-d/2}$$

- too small for dimension above 4
- enormous numbers of contacts would affect the preferred conformation of the polymer chain in solution.(N>>1)
- Solvent effect

Now in case of chain obeying we know in this case in this R_d, if it is Flory polymer or Gaussian polymer or that is for ideal chain $R \sim bN^{1/2}$, in that case the number of monomer-monomer contacts can be very easily found out to be 5 N square, because there are N number of monomer. So here we contact one monomer in contact with other just this $N^{1-d/2}$. We can find for the earlier one and, however, N is this $2-d/2$.

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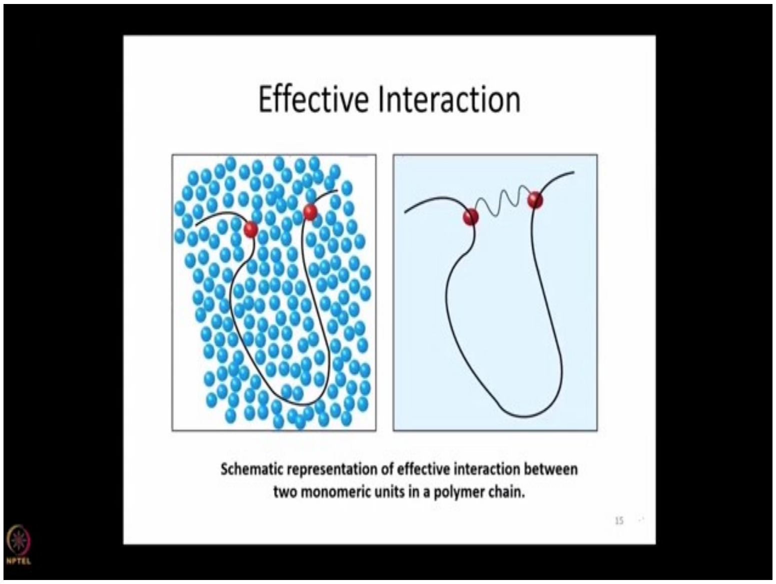

Effective Interaction

Schematic representation of effective interaction between two monomeric units in a polymer chain.

We will continue with the logic in, a minute before that let me consider the a little bit now I want to understand polymer-polymer interaction in solution. As I told you which is suspended in solution, on many occasions typically this solvents considered good solvents it can lies solvent then the polymer and then a lot of solvent molecules come inside one. So it is kind of a porous thing.

So polymer has within itself in it is size R^d in that volume element. It has all these polymer monomer. So the way we sometimes talk of that, if the monomer-monomer likes each other. Then there be more monomer inside then they effectively polymer and polymer are not going to like each other. However, if the monomer of the polymer does not like a solvent molecule then they push these water molecules r, I will find effectively because they solvent molecules will give effective force, then the 2 monomers attract each other.

So I have a situation what divides by Flory where depending on the quality of the solvent, good solvent or bad solvent two monomers effectively this is an effective interaction like each other or they do not like. So this effective interaction is the one which plays a very important role because if I do not want to talk of the solvent I will talk later but not at the beginning so now I do something without that.

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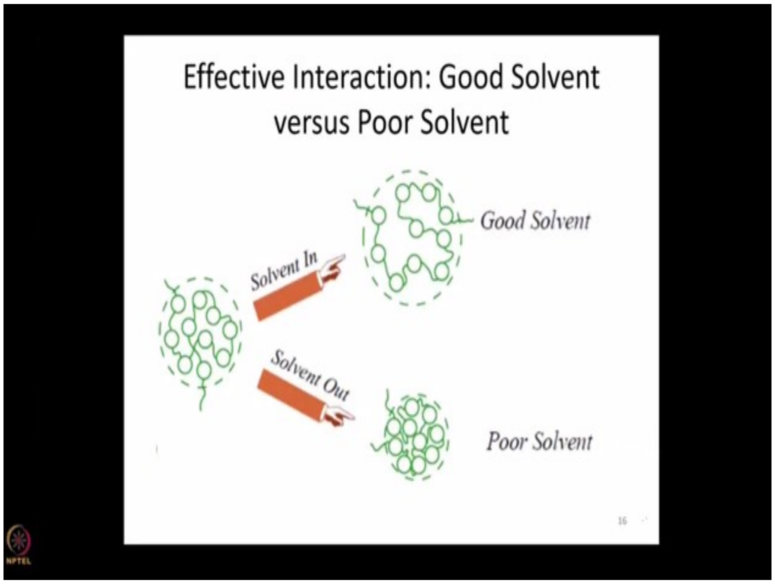

Effective Interaction: Good Solvent versus Poor Solvent

So this is we are saying the good solvent the solvent molecules coming and the polymer gets swell in a bad solvent however collapses. There is actually transition. You can change the quality of the solvent by changing temperature and at certain temperature which transition takes place which is called θ-temperature.

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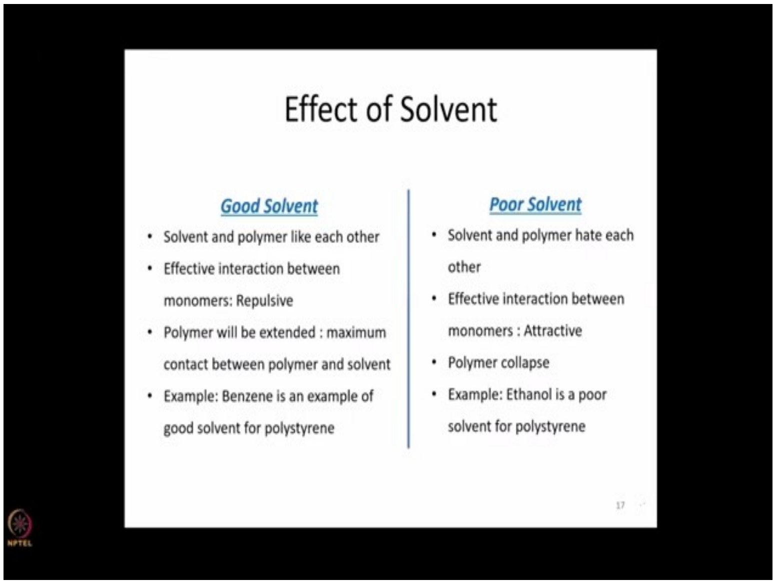

Effect of Solvent

Good Solvent

- Solvent and polymer like each other
- Effective interaction between monomers: Repulsive
- Polymer will be extended : maximum contact between polymer and solvent
- Example: Benzene is an example of good solvent for polystyrene

Poor Solvent

- Solvent and polymer hate each other
- Effective interaction between monomers : Attractive
- Polymer collapse
- Example: Ethanol is a poor solvent for polystyrene

So this is the effect of solvent is very important. You will get the slides along with the talk we did, even look at it and derivations.