Basic Statistical Mechanics
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Lecture -55
Polymers in Solution and Polymer Collapse Part-1

Welcome back to this course on statistical mechanics and what we are trying to do here is to develop an understanding of basic phenomena from the point of view of statistical mechanics. And as I repeatedly tell that the undergraduates understanding our undergraduate studies or physical chemistry is wonderful going through all different phenomena which then finds use in biology, biophysical chemistry in materials in organic chemistry, all kinds of things that physical chemistry.

Physical chemistry is sometimes called the soul of chemistry but it is certainly the basic understanding of chemistry and also that branch of physics which interfaces with physics and chemistry. During my course and travel to the world I found one very interesting thing. That what we studied in physical chemistry in universities of the United States, that what we call physical chemistry, theoretical physical chemistry, liquids, polymers.

And all other aspects of biophysics protein folding they are all studied in the phase departments in Europe. Like in Japan in that not only Europe in Japan, Europe in France in German they are very much, so theory of liquid is the physics department and chemistry used to be the traditional chemistry colloids, organic, syntheses things like that. The reason is that the understanding of physical chemistry.

Or the things that in undergraduates require a lot of mathematics and the concepts which are very common and already existed in physics, Lioville equation I told you, which came to be Bogoliubov-BornGreen-Kirkwood-Yvon (BBGKY), BBGKY theory Bogolyuvbov and Born they are physicists, Yvon physicist, Kirkwood was a physical chemist in chemistry department, Green was physicist. Ornstein was a physical chemist trained as a chemical engineer.

And other great guys like Zernike they had in the chemistry department. So Sterling is chemist and he is a physicist. So this branch of statistical mechanics has physics and chemistry working together to unravel to understand these rather complex systems. Now, we now start one thing for next 40 minutes or so we will try to do very interesting things which is a big subject by itself just like in theory of liquids there are books on theory of liquids.

Here also there is endless number of books on polymers but our emphasis here is to introduce to students the concepts of statistical mechanics. To understand polymers and there are some beautiful work has been done several Nobel Prizes have come. The picture that we have here is that a Paul Flory and Paul Flory are considered the father of polymer chemistry or polymer physics.

And we have this chapter in my book in statistical mechanics chemistry and material science and we have taken this picture from his book and Paul Flory and with many other people many other big names are there in that field.

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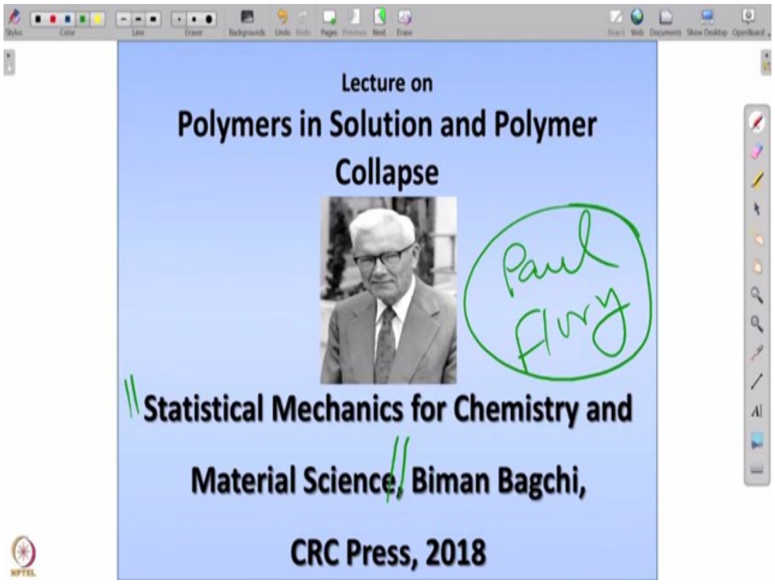

Lecture on

Polymers in Solution and Polymer Collapse

Paul Flory

Statistical Mechanics for Chemistry and Material Science, Biman Bagchi,

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But he introduced the concepts of statistical mechanics, concepts of probability and he modernized the polymer science that is why one has, he got a single Nobel Prize for this I think 1960s or 1970s sometime like that and so what will do many today is many of the things that

Flory did and he did pioneering contributions on the distribution of polymer science into a distribution of polymer.

Introduce the concept of excluded volume, nobody thought will be so important and so interesting and then he also went on to do a theory of sol-gel transition and so, that his stamp on the polymer science is really amazingly diverse and he was both a man of experimentation and he did many of the experiments himself and so, he then developed the theory. So this was probably one of the last of that kind of gentleman who did both in physical chemistry.

Both did theory and experiment but of course he had to be on organic chemist also in order to synthesize these large polymers. Now we continue with Paul Flory's work.

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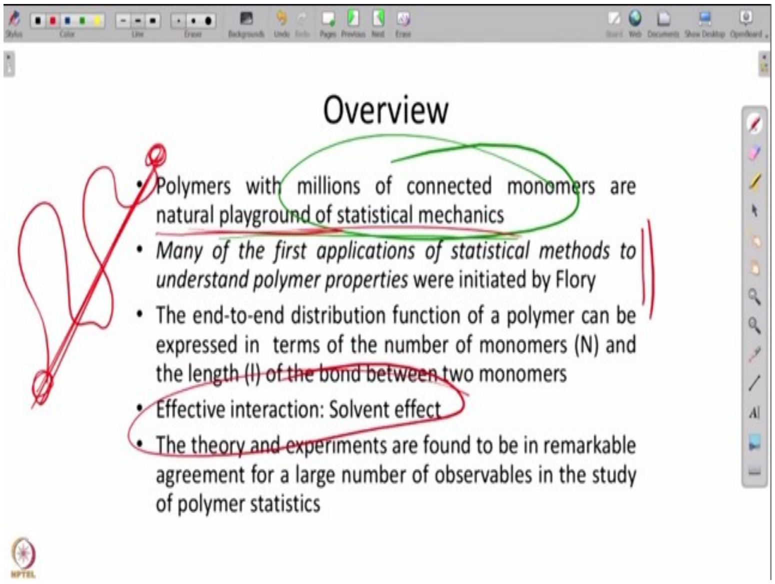

Overview

- 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 with millions of connected so polymers at what we have I remember, there millions, we are not talking of 10 particle or 20 particle things. We are the conventional polymers that we use or everyday nylon and many other things teflon or rubber all these things coming there are millions and millions of monomers connected and this is the natural playground of statistical mechanics because of these the note the term natural playground of statistical mechanics.

That is a very nice way to put into it. Because this, we completely many-body system. These are statistical systems and there are some beautiful things that physicist, talk about like critical phenomena. Where there is a long-range correlation energies that density fluctuation in one region gets correlated fluctuation distance, 1000 Angstrom apart, that means 50-100 molecules apart or 500 molecules apart.

In polymer there is already the correlation because a polymer is a connected thing but then one monomer knows another bond might be ten thousand monomer apart along the chain because they cannot cross. So this excluded volume intervals by Flory. Introduce a long-range correlation into polymer which that is what later Pierre de John and Michael Fisher use the concept of critical phenomena to understand polymer science and polymer physics in a much detailed way.

So while Flory what did, what we use the term polymer chemistry or polymer physical chemistry what it was my confusion, polymer physics but you know they also do same thing. So it was by initiated by statistical applications were initiated by Paul Flory, as I told. So what Paul Flory did and there is some other gentlemen also did the end-to-end distribution. That means if I have a polymer long chain then it, very important to know what is the distribution in end to end?

Because from that then I can get the size and size of a polymer is very important it is not only measured in light scattering, that also plays a role in giving rise to the viscosity of the polymer solution and many other properties of the polymer. And then these effective interactions or excluded follow of interaction, followed by Paul Flory and these remarkable many, many theories is one of the place where theory and experiment agree extremely well.

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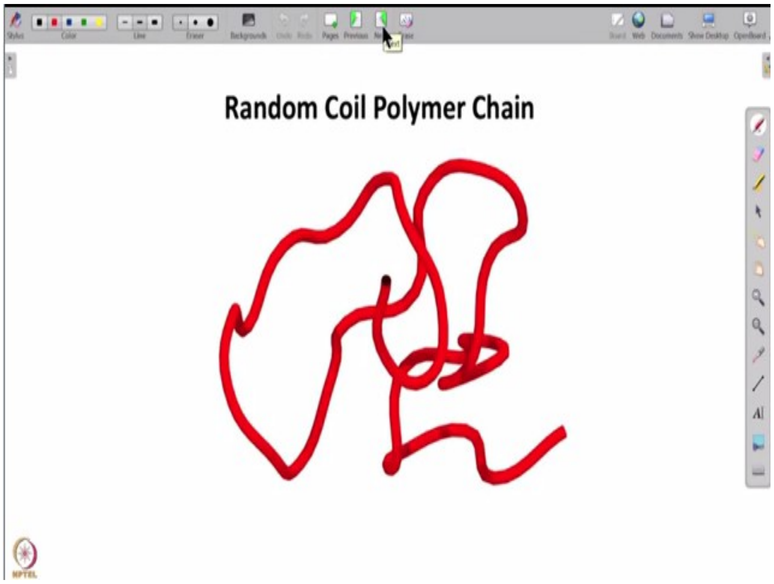

Random Coil Polymer Chain

Here is on us is a polymer is called random coil this is random coil because they are connected and even if the saturated polymer means tetrahedral one C connects to another C but then because they are tetrahedral. So they kind, even at that point it becomes again another tetrahedral but then this coil can rotate around this coil. So by the time you have come 1-2-3-4 fourth monomer that it already has a very large number of conformational spaces.

So because of that these distribution, end-to-end distribution has huge number of configurations space. It can access to that coil you have to coil of a distribution and like statistical mechanics. So, basically this I said is the described here that if we start at one of them.

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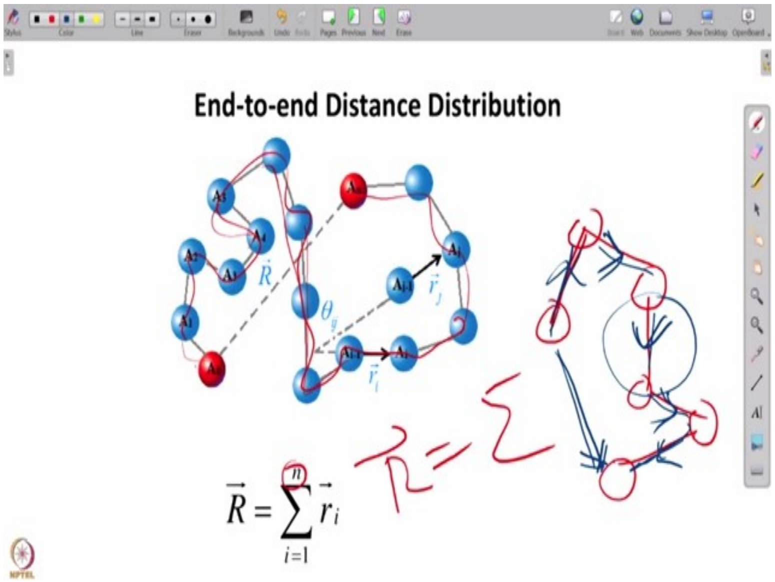

End-to-end Distance Distribution

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

Like it is with this guy then how you go around like that and come back, we start at A then go low like that from here in going like that, then you get essentially beyond a point a random coil. So if I want to know the position of a monomer in it, of specific monomer which N contour distant apart, then all I have to do is to sum over all the vectors. So that is shown here there are some over all the vectors.

And then I add this vector, this vector, with this vector, with this vector, with these vector and then if I have vector. So this if I add this vector, this vector, this vector, this vector then I get that. So if I want to get these distance then I have to sum over all the vectors. That is very nice, these vectors are clearly random because of the tetrahedral T because of the rotation around the bond, we called it black body and that gives rise to a wonderful theory.

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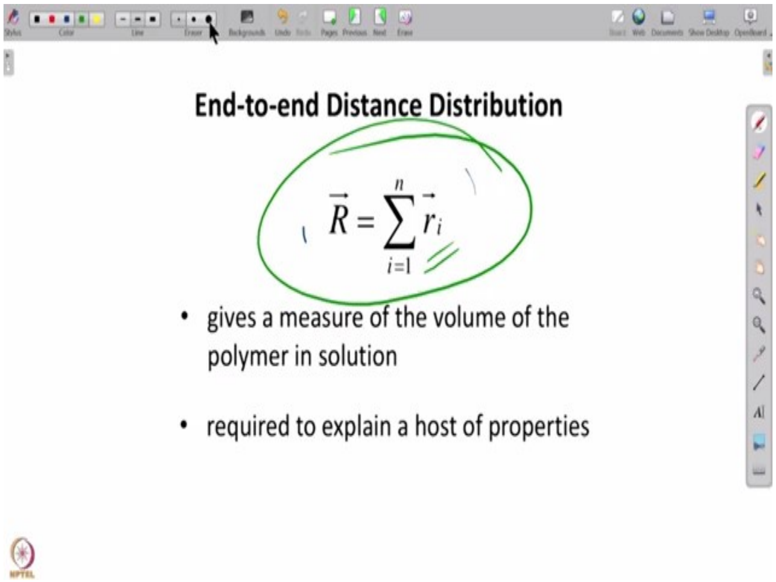

End-to-end Distance Distribution

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

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

Is that, this why end-to-end distribution is sum over these things and these are projections and they can take many values so they are random numbers.

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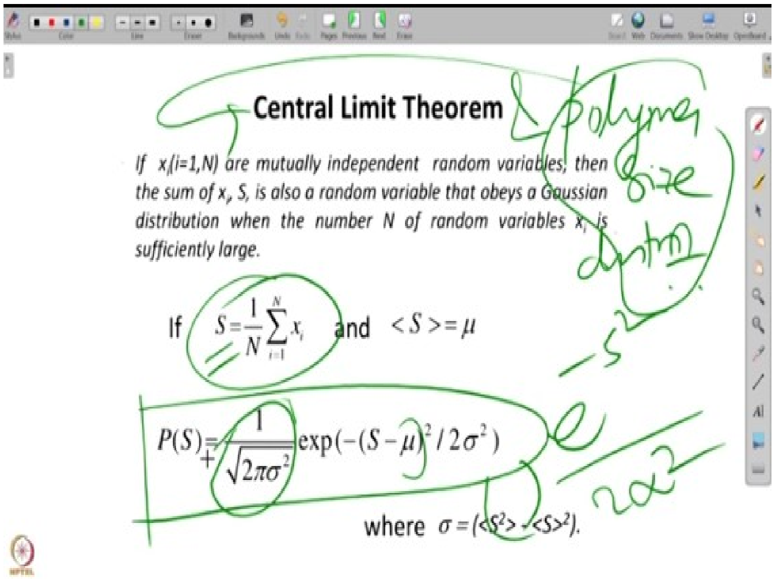

Central Limit Theorem

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

Now that is, now we have if this distribution end-to-end distribution is a beautiful thing from central limit theorem and polymer size distribution. So that should be retired to the central limit theorem and polymer size distribution or polymer size distribution and central limit theorem. So central limit theorem is something we discussed it will be before but let me state again that if having N number of random N number.

If value I have one variable x which takes N number of distributions or I have x_N number of random variables which are taking all values within a certain range and if I add them or sum then if this my random variables which weakly correlated or not correlated random number then the sum becomes a Gaussian equation this is one of the most powerful theorem in the theory of probability and that is our name central limit theorem.

As I always tell in my class that mathematicians are not given to well like sometimes physicists like theory of everything and many other things that we do mathematicians are very conservative people they are not used to give very big, big names they very rarely this a central limit theorem or fundamental like they have a fundamental theorem of algebra and that is the most important theorem value of that you know that which gives you that a polymer optically aim.

As we have N roots and that depending on the coefficients of a signs of a and b the complex conjugates and complex roots have to be in equal number. That is the fundamental theorem which is used everywhere whole complex analysis based on that fundamental theorem. Similarly central limit theorem is a hugely important in the theory of probability it can be derived in many different ways has been derived in many different ways.

But we do not need that here. So this is what is that that if some is just all these numbers then probability of s.

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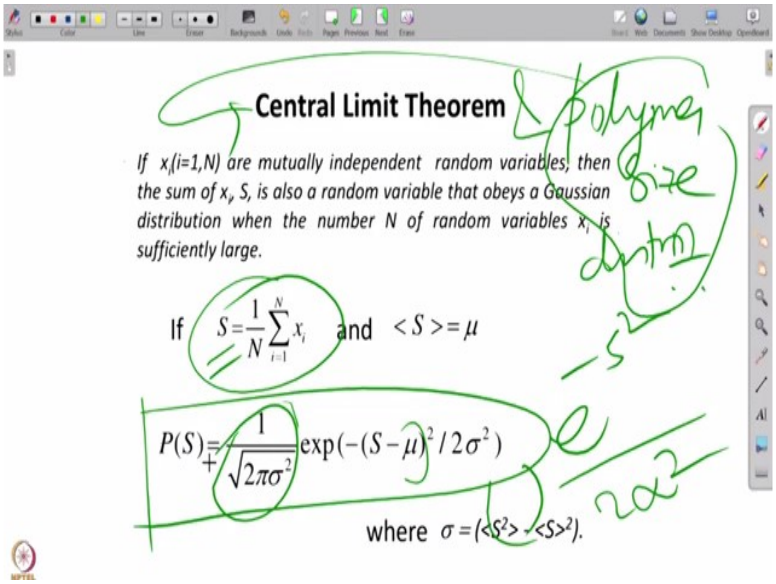

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where $\sigma=(<S^2>-<S>^2)$.

Is this thing, is the culture, so that may have values between + 1 or - 1 randomly picked up. For example, you know in a way we developed it, we generated Gaussian distribution in computer that we call it random number and a random number between this is - 1 + 1 and then we add them up and it is about just about 12. So it is random numbers is it enough that N can be 12. Below 12 it does not work that well.

Sometimes we take 20 but N equal to 12 will give you fairly good Gaussian distribution and this is something in which one should have it is uniformly distributed between + 1 and - 1. Then this average goes to 0 then you just have $e^{-s^2/2\sigma^2}$ and the normalization constant in front. So now we are coming back to polymer in the polymer, we all have this random, we are adding up.

So one bond this one is really not that correlated with that one because it can rotate. So if I think of distance between my central and the final one then it is adding up these projections, which are fairly random. So then in my at that my central limit theorem, I can surmise that the end-to-end distribution is a Gaussian and that exactly what holds under this one of the most is not.

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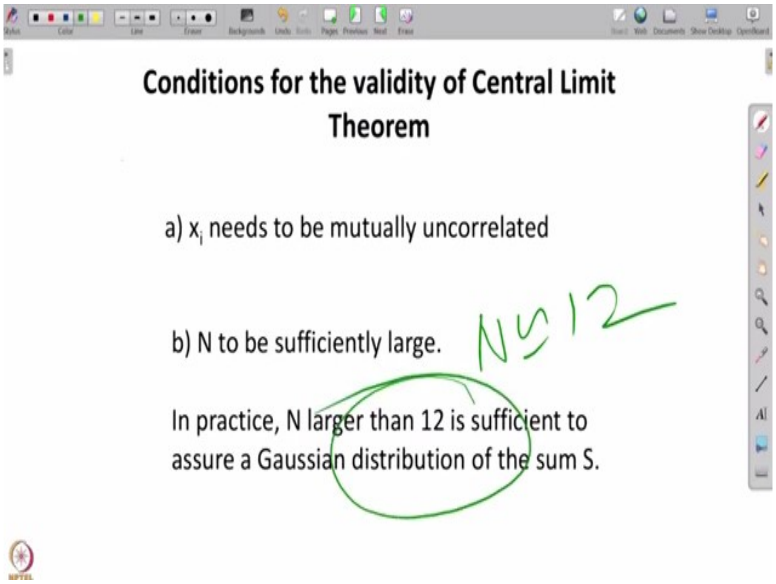

Conditions for the validity of Central Limit Theorem

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.

By N can be even 12 is enough here and as I said in 12 is sufficient.

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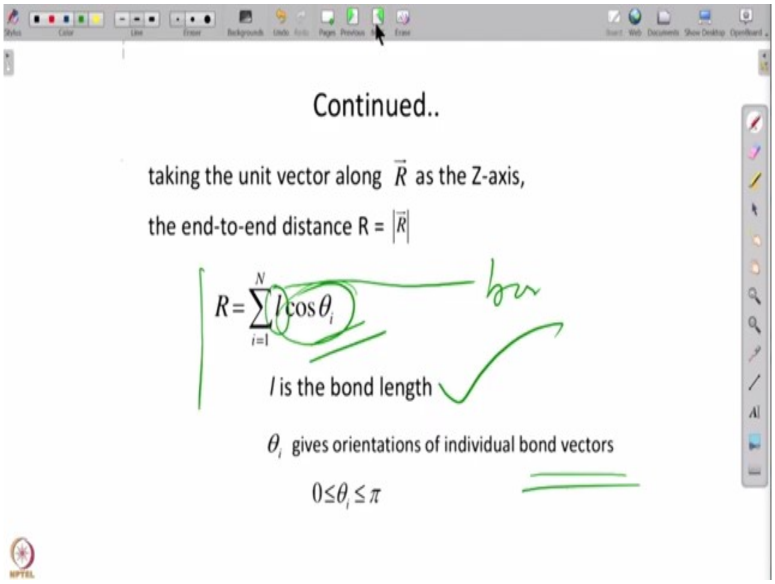

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taking the unit vector along $\vec{R}$ as the Z-axis,

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

$$0 \le \theta_i \le \pi$$

And then we can continue a little bit to make a little bit more, a as I said that it is just angle $\cos\theta$ angle makes with that. So if l is the bond length as it is given here θ_i is the individual bond vectors then this θ_i and $\cos\theta_i$ is random just between - 1 and + 1 as I said so it becomes l^2 and then.

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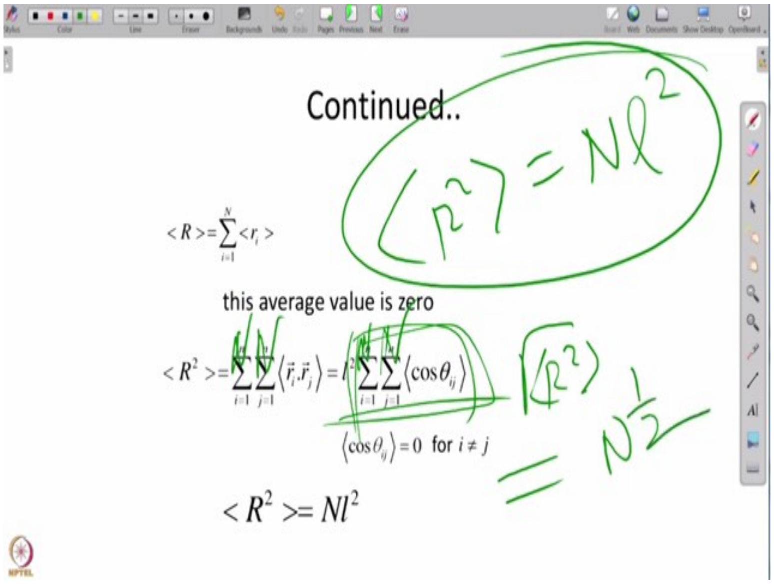

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$$< R >=\sum_{i=1}^{N}< r_i >$$

this average value is zero

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

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

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

$$\boxed{\langle R^2\rangle = Nl^2}$$

$$\sqrt{\langle R^2\rangle} = N^{\frac{1}{2}}$$

I get this is double sum and one of them gives you 0 or 1 then, this double sum become proportional to N, you can do it random number one of them everywhere then do you I do with respect to that and the rest one you can sum. So this should be capital N this should be capital N this should be capital N in this together. So one sum is taken care to give you this random number second and seen from distribution.

So again something to capital N, so $\langle R^2\rangle = Nl^2$ a beautiful thing is amazing result. So root mean square now I can say $\sqrt{\langle R^2\rangle} = N^{1/2}l$, this is one of the first results. That is kind of mu the floating systemized it, there are other people who have got this result that size of the polymeric scales of intuitive of this is, we think is a remarkable result because I think of is a remarkable result.

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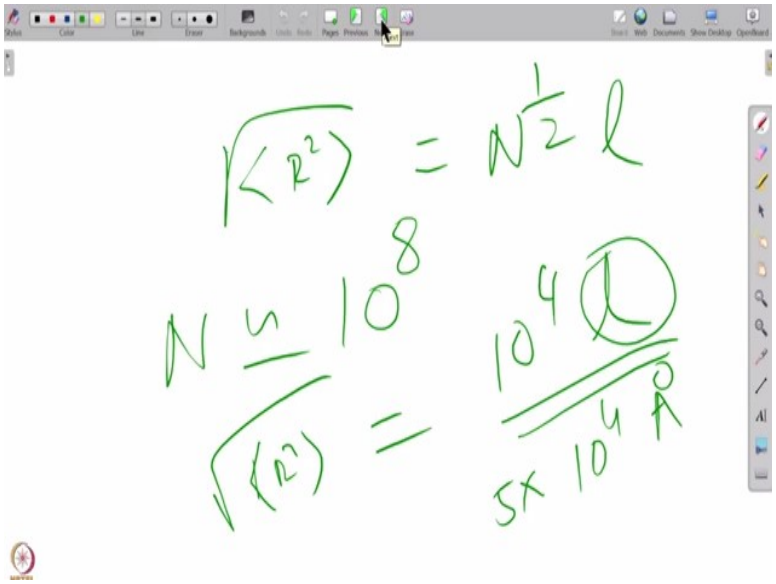

That root over which is size is $\sqrt{\langle R^2\rangle} = N^{1/2} l$ and remembers our aim it can be 100 million. So 10^8 then the size $\sqrt{\langle R^2\rangle} = 10^4 l$. l is say 5 A^0, then this 5×10^4 A^0 that means it is 50,000 A^0. I now know the size of the polymer this is very important because that can be that can be obtained by experiment.

So we almost doing no work because of central limit theorem almost we know what other than this little thing that we have done and that is trivial. So we get that you know if they are correlated that they are not they are equal to 0, then only $i = j$ survives and that is a random number that you want to - 1 to + 1, on that average there should be forward probably a factor of half missing here you get N^2.

So we get this huge result because of the central limit theorem and Rohde did not do it by central limit theorem. He just took them, random numbers and he used probability theory but alternative way he arrived at the same exactly same expression.

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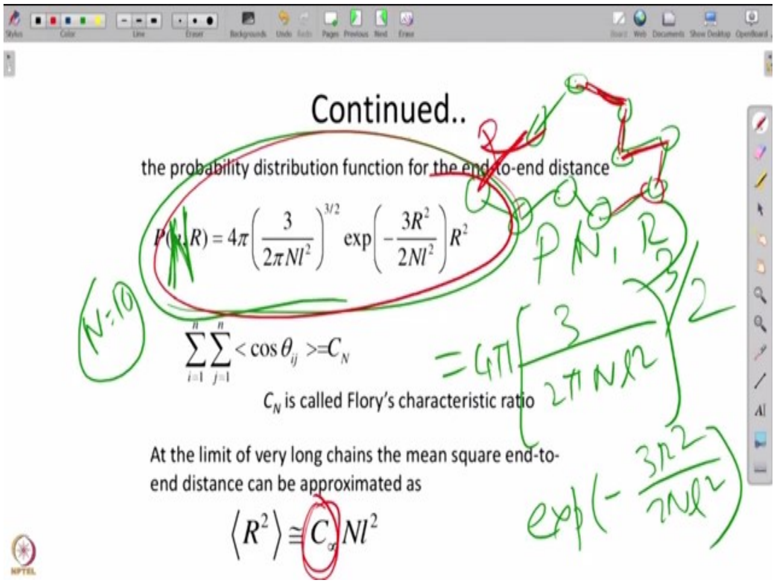

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the probability distribution function for the end-to-end distance

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

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

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

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

$N=10$

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

So we continue then what is the probability if I have $P(N,R)$, he is, I hope these are small mistakes are not in the book. These are the book n and N. $P(N,R) = 4\pi\left[\frac{3}{2\pi Nl^2}\right]^{3/2} e^{-3R^2/2Nl^2} R^2$, so this is number. So this is the full formula of the distribution of N number of end-to-end distribution of N number of, for example, if I do then I have 1,2,3,4,5,6,7,8,9,10.

And then this is N = 10, and these distance then these distance is the end-to-end distance, this is the R. So now this will give me, if I even if I, they told you if you have 20 then that is enough. Then the end-to-end distribution will be given by all of us have done this calculation with a polymer and we have found it out that this it works beautifully well. To extend that this is a universal.

We consider the universal formula and the details of these bonds and the rigidity all these things are somewhat important as but so far the form is concerned. There are certain changes in this rigidity and the kind of restriction on the randomness of the angles that is taken care by introduced in the normalization constant, kind you of feeding parameter here and that is the end of the distribution function rules.

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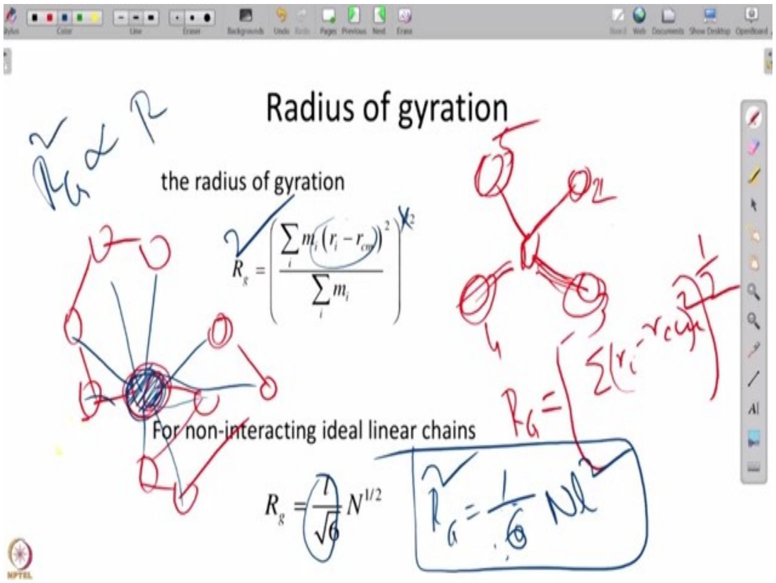

Radius of gyration

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 now one important quantity which is the radius of gyration which is comes in the light scattering and many, many theories and the radius of gyration is nothing but essentially same radius of gyration and moment of inertia that we find in any classical mechanics, like if we have four particles then we find the radius of gyration is they take it as a central point and then we want to find out what is the radius that this guy is rotating.

And that is mass weighted from central. As I was saying from central mass so this is the definition of the radius of gyration, so when these things are we raise that in classical mechanics when these guys are different these are different mass, then different mass then we use this as the if mass is the same everywhere then $R_G = \left[\sum (r_i - r_{cm})^2\right]^{1/2}$ means now I am going to take the distance from a central mass.

So in a polymer I can go to the center of mass of a polymer sorry. So if that is such a polymer then I can go and find out a center of mass here, then now, I want to do about the center of mass what are the other guys are just like in the classical mechanics then a that gives me from the center of mass how the size looks? And then that is this quantity and one can show it is same as these it comes out, do this also a random number.

These distances that I am considering are also random number and then I again gave the central limit theorem to get me these this quantity and again is the fact, if the vector is different I get

$R_G^2 = \frac{1}{6Nl^2}$. So basic thing is the same as R_G^2 square so RG square is same as R^2 with accepting, Michael factor. So the scaling remains the same so the size grows as $\sqrt{N}$.