Introduction to Polymer Physics
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Lecture-10
Probability Density of an Ideal Chain
Part II

In the last class we have been discussing the 1 dimensional random walk but now the objective was to look at the probability distribution of the end to end distance and we have been able to is derive this particular relation for the probability of having certain end to end distance R_e for a walk of M steps of the drunkard as-

$$\ln P(R_e, M) = \ln M! - M\ln 2 - 2\ln\left(\frac{M}{2}!\right) - \frac{R_e^2}{2M}$$

So, what we will do is will use what is known as the sterling approximation for the factorial when the value of M is very high. This really works only at high value of M and the reason why we have been doing this again is because the factorials of large numbers are difficult to evaluate that is one reason and the other reason is we want to go to towards the continuum limit when M is very high. So, if we do this, this particular approximation is given like this, so I can approximate and you can try to see how it works for large values of M. So, it really works well for M higher than 20 or 50 and so on particularly our polymers are really larger values of M.

Using Stirling approximation we get:

$$M! \approx \sqrt{2\pi M}\left(\frac{M}{e}\right)^M$$

$$\ln M! \approx \ln\sqrt{2\pi M} + M\ln M - M$$

(*)

After simplification we get:

$$\ln P(R_e, M) = \ln\sqrt{2\pi M} + MlnM - M - Mln\,2 - 2\left[\ln\sqrt{\pi M} + \frac{M}{2}\ln\frac{M}{2} - \frac{M}{2}\right] - \frac{R_e^2}{2M}$$

Further simplifying we get:

$$\ln P(R_e, M) = \ln\sqrt{2\pi M} + MlnM - M - Mln\,2 - 2\ln\sqrt{\pi M} + Mln\,M - Mln2 - M - \frac{R_e^2}{2M}$$

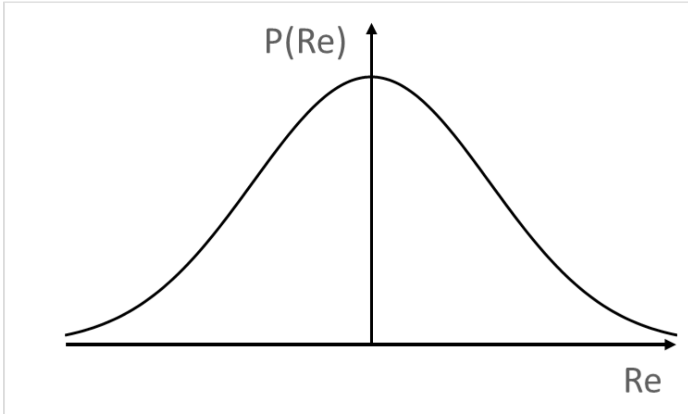
After certain cancellations, we get:

$$\ln P(R_e, M) = \ln\sqrt{2\pi M} - 2\ln\sqrt{\pi M} - \frac{R_e^2}{2M}$$

$$P(R_e, M) = \sqrt{\frac{2}{\pi M}}\exp\left(\frac{-R_e^2}{2M}\right)$$

This equation happens to be in the form of what is known as a Gaussian distribution, so now we can see from here when the R_e value is very large. Then the probability to find that R_e will be smaller because the Re appears in the exponential with the negative sign and so the configurations will have which are like more stretched or having a higher value of R_e will be less probable. The smaller values of Re for the same reason will be more probable but essentially mean is a folded configuration of a polymer is more probable compare to an stretched configuration.

If I plot this particular relation against R_e what we do get is the distribution that is the Gaussian or normal distribution.



So, we can compare this with the standard form of the Gaussian distribution and we realise that the prefactor in this tendered form slightly different. Let's look at that so the general form of Gaussian distribution is given as for a random variable x that is sum of random variables x_i for i going from 1 to M. We can write P (X, M) that is now the probability density:

$$P(X,M)=\frac{1}{\sqrt{2\pi M\sigma^2}}\exp\left[\frac{-(X-M\acute{x})^2}{2M\sigma^2}\right]$$

Using, $\vec{R}_e=\sum\vec{b}_i$ and $\langle\vec{b}_i\rangle=0$ and $\sigma=1$, we get:

$$P(R_e,M)=\sqrt{\frac{1}{2\pi M}}\exp\left(\frac{-R_e^2}{2M}\right)$$

So, this will give you and the reason why this happened is not because we derived it wrongly, the reason why this happened is we have to normalise the probability density just like for a discrete distribution the sum of the probabilities of all the possible events must be equal to 1.

Similarly in the case of a probability density what we should have is if I integrate the probability for all possible values of Re we must get it equal to 1.

$$\int P(R_e)\, dR_e = 1$$

Therefore we can correct our probability from function just by multiplying or dividing by a factor of 2 that appears because of this particular normalisation. In any case the factor does not contain the R_e what is essential to us is the fact that the probability density in our case:

$$P(R_e, M) \propto \exp\left(\frac{-R_e^2}{2Mb^2}\right)$$

This is the way we typically proceed keeping in mind that whatever the probability we derive from a discrete distribution has to be normalised again for the continuous distribution and essentially what we were able to show is if I look at the random walk problem, in that case what we actually got was is known as the binomial distribution.

If you think of the coin toss problem and for large values of M for the number of samples the binomial distribution approaches the Gaussian distribution. This is one of the tenets of a statistical mechanics then when the number of samples become large. In that case all the distributions that we get in the discrete space approximates to the Gaussian distribution in the continuous space. This is not really true only for the binomial distribution this is true for the kinds of distributions as well. So, this is related to what we know in a statistical mechanics as the law of large numbers and what we know as the central limit theorem.

We could have started with a simpler Stirling approximation

$$\ln M! \approx \ln\sqrt{2\pi M} + MlnM - M$$

Assuming that the first term is smaller compare to the other. So, many texts you will find the Stirling approximation written something like this and we can see like we can again put the same expression in the equation we had from the last class and see that we will go back to the same equation that we have derived.

$$\ln P(R_e, M) = \ln M! - 2\ln\left(\frac{M}{2}!\right) - Mln2 - \frac{R_e^2}{M}$$

$$\ln M! \approx Mln M - M$$

$$\approx MlnM - M - 2\left(\frac{M}{2}\ln\frac{M}{2} - \frac{M}{2}\right) - Mln2 - \frac{R_e^2}{2M} \approx -\frac{R_e^2}{2M}$$

After applying normalisation we get:

$$P(R_e, M) = \exp\left(\frac{-R_e^2}{2M}\right)$$

$$\int P(R_e, M)\, dR_e = 1$$

$$P(R_e, M) = \frac{1}{\sqrt{2\pi M}}\exp\left(\frac{-R_e^2}{2M}\right)$$

So, now let us think of like what would happen if I think of a 3 dimensional random walk, so you can decompose the 3 dimensional random walk as a random walk in x direction, random walk in y direction and random walk in z direction and why I am saying this is because let us say if I am doing a random walk in two dimensions. Then this a mounts to random walk in x and a random walk in y and the same idea we can extend to random walk in z. In other words my end to end distance vector can be written in terms of it is components we have this and this these are the components in xy and z directions. And ex, eye z are the root vectors in xy and z.

$$\overline{\Re} = Re_x\hat{e}_x + Re_y\hat{e}_y + Re_z\hat{e}_z$$

So, if I think of that three dimensional random walk for Re I can think of it as product of three random walks in each of the three directions. So,

$$P_{3D}\left(\vec{\Re},M\right)=P_{1D}\left(Re_x,M\right)P_{1D}\left(Re_y,M\right)P_{1D}\left(Re_z,M\right)$$

$$¿\sqrt{\frac{1}{2\pi\left\langle Re_x^2\right\rangle}}\exp\left(\frac{-Re_x^2}{2\left\langle Re_x^2\right\rangle}\right)\sqrt{\frac{1}{2\pi\left\langle Re_y^2\right\rangle}}\exp\left(\frac{-Re_y^2}{2\left\langle Re_y^2\right\rangle}\right)\sqrt{\frac{1}{2\pi\left\langle Re_z^2\right\rangle}}\exp\left(\frac{-Re_z^2}{2\left\langle Re_z^2\right\rangle}\right)$$

$$\left\langle R_e^2\right\rangle=Mb^2$$

$$\left\langle Re_x^2\right\rangle+\left\langle Re_y^2\right\rangle+\left\langle Re_z^2\right\rangle=Mb^2$$

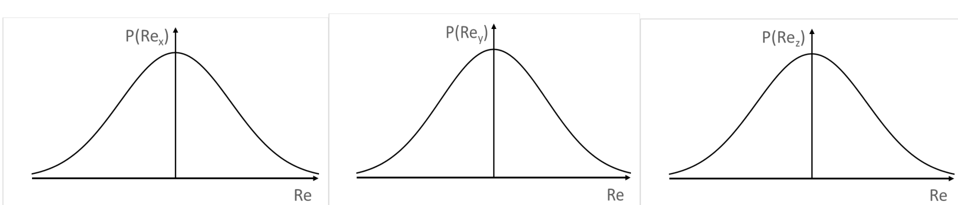
$$\left\langle Re_x^2\right\rangle=\left\langle Re_y^2\right\rangle=\left\langle Re_z^2\right\rangle=\frac{Mb^2}{3}$$

$$¿\left(\frac{3}{2\pi Mb^2}\right)^{\frac{3}{2}}\exp\left(\frac{-3}{2}\left(Re_x^2+Re_y^2+R_e z^2\right)\right)$$

$$¿\left(\frac{3}{2\pi Mb^2}\right)^{\frac{3}{2}}\exp\left(\frac{-3}{2}\frac{R_e^2}{Mb^2}\right)$$

So, we have got this particular look equation again it is the Gaussian the pre factors have changed. And now it is normalised again because we have a started from the continuous distributions so, we do not need to normalise again.

So, what this a mounts to is I can now write my probability distribution or probability density for three dimensional random walk again as Gaussian function. But now along a vector but in reality this is plot with 3 axis verse rdx rdy or rdz. The other way to think about it is this particular distribution is identical to the product of the three random walks that we get along the x y and the z axis.



That is one thing to gain from and this discussion the other thing is and that is what now we will eallude to be we can associate this probability distributions in terms of the elastic energy of the chain and this happens because we know from again from a thermodynamics that the probability to get is state of a system within energy E is proportional to

$$P(E) \propto \exp\left(\frac{-E}{k_b T}\right)$$

Which means is as the energy of the states become larger the probability to find them become a smaller. We can think of this in many ways so, if I think of example an electron the ground state will have the least energy and that's more probable The excited states will have lower energy and they we come progressively higher energy and the we come progressively less probable.

So, if I compare this with what we have obtained so, what we have is:

$$\frac{E}{k_B T} = \frac{3}{2} \frac{R_e^2}{M b^2} = E = \frac{3}{2} k_B T \frac{R_e^2}{M b^2}$$

If we have two confirmations of polymer chain then configuration has a R_e which is lower than the other configuration then the higher then this case this will have more probability. So, you can a start thinking of the analogy with a spring so, if their spring is more stressed it contains more energy if the spring is like less stressed it contains lesser energy. So, in this case this extension of the spring is represented by my end to end distance and I can think of a spring constant and going to the idea of the spring having the energy half of key x square. We can see from here is:

$$u(x) = \frac{1}{2} k x^2$$

$$k = \frac{3 k_B T}{M b^2}$$

This term is called spring constant.

So, in this way I can represent different confirmations of polymer chain as having a length R_e of the spring. And if the k is changing that give rise to a stiffer spring or a flexible spring the higher values of k will correspond to more stiffed spring and now we can see like how it is happening because if M is larger in my case my k becomes a smaller okay. So, as we have a longer polymer chain it will have more flexibility because the value of the spring constant is lesser. In other words since the elastic energy is half k x square. It will cause lesser energy penalty if I try to a stretch the spring then compared to the case when k was higher which will happen for the case when M is lesser. So, in this way we can say that the elastic energy of the polymer chain has entropic origin and we will see like how this particular result become very important in the next class.

Thank you.