Introduction to Polymer Physics

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Lecture-09
Probability Density of an Ideal Chain
Part I

In the previous class we have discussed basically the toy models that describe the end to end distances square averaged of a polymer chain we did for a flexible chain models and for a semi flexible chain models. So, now I want to think beyond the mean of the square end to end distance let us say like how the distribution of the end to end distance looks like and using that what I want to ultimately built is the notion of an elastic energy of a polymer chain. So, first we will discuss how the probability of confirmations vary and then finally how can we associate that with the elastic energy of polymer chain.

Let us first discuss the idea of a thing called probability density, so most of you know what a probability is. For example if I am tossing a coin and being unbiased in terms of a how I am tossing it then the probability of having a head or a tail is simply the same and they are equal to ½. So, in this particular case there are only 2 outcomes of the experiment either it is a head or a tail. So, in that case we can say that the random variable takes 2 values head or tail or I can say if I say head is a number+1 and tail refers to some number like -1. Then it can take values like +1 or -1. So this is when we use the idea of probability.

The probability density comes into picture when the random variable can take values in a continuous domain, for example when talk about the end to end distance then the end to distance can really vary from 0 to higher values let us say 10^6 or what not. Actually when we are talking about the end to end distance then we talk about also the sign of it, so it can vary from -10^6 to

10^6 thinking that the chains are very large and it is varying continuously which means that we can take any value in this particular domain not really certain discrete values there. So, in that case what we are talking about is a probability density that is defined in this particular way-

$$P(R_e)\,d(R_e) = \textit{probability that } R_e \textit{ is between } R_e \wedge R_e + d\,R_e$$

This is what I will call a probability density.

The other idea is unlike the coin toss example where there is only one experiment being conducted which has an outcome head or tail, in the case of a polymer chain if we think in terms the toy model and the random variable is not the end to end distance vector the random variable is bond vectors. So, let's say if I have a freely jointed chain what I am actually varying are the bond vectors which are represent like b1, b2, b3 and so on. So, in the end what I am looking at is essentially a sum of random variables each of which can vary and each of which has certain range. So, we looked at the ensemble average of that, that was equal to 0 and we looked at the correlations of that and that varied for different chain models. But for this particular model it was equal to something like this:

$$R_e = \sum \vec{b}_i$$

$$\langle \vec{b}_i \rangle = \vec{0}$$

$$\langle \vec{b}_i \cdot \vec{b}_j \rangle = b^2 \; when\, i = j$$

We will use these 2 ideas will talk about probability density of having a chain end to end distance between R_e and R_e+ dR_e. Here when we say the end to end distance we also a count for it is sign, that means that negative values of R_e are not same as positive values of R_e and the other idea we will use is we are not looking at 1 random variable but a sum of random variables that is giving rise to the end to end distance vector.

So, with this now I want to use the simplest model that we derived the 1 dimensional random walk because in that case we are only moving around 1 dimension that really simplifies our analysis. In that case the end to end distance is only along 1 dimension and we can then extend the idea to higher dimensions or actual 3 dimensions as in the case of a freely jointed chain.

So, let us go back to the 1-D random walk and the question is not that what will be the mean square end to end displacement or distance of the drunkard, but we are interested in like what is the probability that he moves 5 steps to the left or 5 steps to the right after so many steps. So, other way to think about it is we are trying to find whether he will be able to reach his home in certain number of a steps provided the home is around certain number of a steps away.

Let us say he is 10 steps away, so let us say if he starts and go towards his home then he made say 20 or 30 steps what is the probability that he will get home in that particular step that will correspond to having certain end to end distance R_e after let us say M steps. So, we are doing it for the discrete case, in this case we do not talk about probability density. But we will soon go to the limit when the number of the steps become very large and then we have continuous situation. So,

$$P(R_e, M)$$

Here, P = probability that the drunkard moves Re steps to the right after M steps. And just for simplicity we will take b=1 that is at every instant he can move 1 unit in the left or 1 unit in the right and that would equally probable that means that at every time irrespective of how he moved in the previous step, he can move either to the left 1 unit or right 1 unit.

So, let's say in these M steps he moves M_+ steps to right and M_- steps to left then for this to be true for the distance travelled to be equal to R_e to the right what we should have is

$$M_+ - M_- = R_e.$$

Because at every step he is moving like 1 unit, so he moves like M_+ steps total to the right and M_- steps total to the left, so $M_+ - M_-$ is a net distance in the right direction now since the total number of steps is M,

$$M_+ + M_- = M.$$

After solving above two equations we get:

$$+\text{¿}=\frac{M+R_e}{2}$$
$$M_{\text{¿}}$$

$$-\text{¿}=\frac{M-R_e}{2}$$
$$M_{\text{¿}}$$

So, now if I want to know how many ways there are in which he is making this particular combination of a steps then basically what it turns out is we can define a quantity w that is the number of trajectories that give rise to end to end distance Re in M steps at the standard permutation problem:

$$-\text{¿}$$
$$+\text{¿}+M_{\text{¿}}$$
$$M_{\text{¿}}!$$
$$\text{¿}$$
$$M$$
$$\text{¿}$$
$$-\text{¿}$$
$$M^{\square}_{+\text{¿}}$$
$$+\text{¿}+M_{\text{¿}}C_{\text{¿}}$$
$$\text{¿}$$
$$+\text{¿}!M_{-\text{¿}!}=\text{¿}$$
$$M_{\text{¿}}$$
$$\text{¿}$$
$$W(R_e, M)=\text{¿}$$

All we are doing here is since every step can be to the right or to the left, so we can choose M_+ steps out of the total $M_+ + M_-$ steps. So, basically what we are doing is the combinatorial $M_+ + M_-$ C M_+.

So now we will use the idea that both M_+ and M_- has to be very large, if I try to think of this model apply to a polymer chain because the polymer chains has many steps. So, if I try to do that the first thing I will do is I will use the relation that I have find derived earlier-

$$-¿$$
$$+¿+M_{¿}$$
$$M_{¿}!$$
$$¿$$
$$+¿!M_{-¿!}=\frac{M!}{\left(\frac{M+R_e}{2}\right)!\left(\frac{M-R_e}{2}\right)!}$$
$$M_{¿}$$
$$¿$$
$$W(R_e,M)=¿$$

So, now as we can clearly see from here, that of course for a smaller values of M this will be very easy to compute but for larger value the numbers starts to become very huge. So now we can make certain approximations that will apply for larger values of M. So, the approximation we are going to apply goes like this:

$$\ln W(R_e,M)=\ln M!-\ln\left[\left(\frac{(M+R_e)}{2}\right)!\right]-\left[\left(\frac{(M-R_e)}{2}\right)!\right]$$

Let us try to simplify this particular relation,

$$\ln\left[\left(\frac{(M+R_e)}{2}\right)!\right]$$

We get:

$$\ln\left[\left(\frac{M}{2}\right)!\left(\frac{M}{2}+1\right)\left(\frac{M}{2}+2\right)\ldots\ldots\ldots\ldots\ldots\left(\frac{M}{2}+\frac{R_e}{2}\right)\right]$$

$$¿\ln\left(\frac{M}{2}\right)!+\sum_{s=1}^{\frac{R_e}{2}}\ln\left(\frac{M}{2}+s\right)$$

Now we will try to simplify this particular relation,

$$\ln\left[\left(\frac{(M-R_e)}{2}\right)!\right]$$

We get:

$$\ln\left(\frac{\left(\frac{M}{2}\right)!}{\left(\frac{M}{2}-\frac{R_e}{2}+1\right)\left(\frac{M}{2}-\frac{R_e}{2}+2\right)}\cdots\right)$$

$$\ln\left(\frac{M}{2}!\right)-\sum_{s=1}^{\frac{R_e}{2}}\ln\left(\frac{M}{2}+1-s\right)$$

So, I will use these 2 relations that I have derived in here and what I in end up having is:

$$\ln W(R_e,M)=\ln M!-\sum_{s=1}^{\frac{R_e}{2}}\ln\left(\frac{\left(\frac{M}{2}+s\right)}{\left(\frac{M}{2}+1-s\right)}\right)$$

By dividing numerator and denominator by M/2 we get:

$$\ln W(R_e,M)=\ln M!-\sum_{s=1}^{\frac{R_e}{2}}\ln\left(\frac{\left(1+\frac{2s}{m}\right)}{\left(1+\frac{2}{M}-\frac{2s}{M}\right)}\right)$$

So, now we can use again the idea of a Taylor series we get:

$$\ln(1+y)\approx y$$

$$y=\frac{2s}{M}(since\ M\ is\ large)$$

$$\approx \sum_{s=1}^{\frac{R_e}{2}} \left[\frac{2s}{M} - \left(\frac{2}{M} - \frac{2s}{M} \right) \right] = \sum_{s=1}^{\frac{R_e}{2}} \left[\frac{4s}{M} - \frac{2}{M} \right]$$

¿ $\frac{4}{M} \sum_{s=1}^{\frac{R_e}{2}} s - \frac{2}{M} \sum_{s=1}^{\frac{R_e}{2}} 1$

¿ $\frac{4}{M} \frac{\frac{R_e}{2}\left(\frac{R_e}{2}+1\right)}{2} - \frac{2}{M} \cdot \frac{R_e}{2}$

¿ $\frac{R_e^2}{M}$

So, now there is 1 further detail here:

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

Total number of trajectories = 2^M

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

So, we will start from this particular expression that we have derived and we will use the relation that is known as the sterling approximation to get these factorial terms and based on that we will derived the expression of probability distribution for the larger values of M in this case.

Thankyou.