Introduction to Polymer Physics

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Lecture-12
Derivation of Diffusion Equation, Einstein Notation

Alright, so in the last few classes we have learnt about the random walk models and how are they used in polymer physics. In today's lecture I want to introduce is the idea that the random walk descriptions we have derived have certain similarities with the diffusion equations that you may have learned in mass transfer or other courses.

So, just to give you some reminder of the diffusion equation. It looks something like this where for example in Cartesian Coordinates:

$$\frac{\partial c}{\partial t}=D\nabla^2 C$$

$$c(\vec{r},t)$$

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

And, we are solving for the concentration of any species, is a function of a spatial location and time this is what is known as the Fick's law of diffusion.

In fact there are 2 laws 1 that relates the concentration as the derivative of the flux and another law that basically describes the flux J.

$$\frac{\partial c}{\partial t}=-\vec{\nabla}\cdot\vec{J}$$

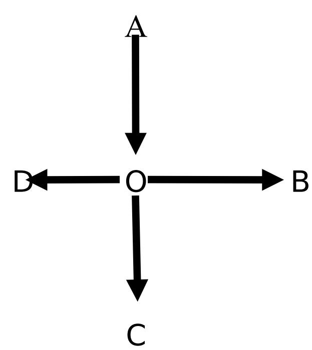
$$\vec{J}=-D\vec{\nabla} c$$

Now you may be surprised that how does the random walk description where about looking at probability of certain end to end distance does relate with this particular relation and you will try to build that in today's lecture. And basically the equation that we will show will have mathematical similarities with these equations and then we can talk about analogy of the variables you see in this equation with whatever equation will go there.

So, let us say I am looking at a z dimensional random walk it is bit of misnomer, so when I say a z dimension it is not like physical dimension what z means is the number of available directions for every segment. So, let us say for example for the 2 dimensional walk that we have discussed the z=4 because we can move in left, right, up and down and so on.

So, if we are doing a z dimensional random walk and let us say I am at a particular end to end displacement R_e or end to end distance R_e after steps M, we have derived that the probability distribution or the probability density for this particular thing to happen goes like a Gaussian function for an ideal chain. But to be here in M steps we must be somewhere near it in the previous step to be more precise I must be at a position R_e-b_i where bi indicates all available directions for the chain movement.

So, let us say for example if I am at A, B, C and D in the figure I can come to the point O in 1 step and then we can have this particular distribution.



So, then we can write that the probability that the end to end displacement is R_e after M steps that must be equal to-

$$P\left(\vec{R}_e, M\right) = \frac{1}{Z} \sum_{i=1}^{Z} P\left(\vec{R}_e - b_i, M-1\right)$$

It means I must be at one of the positions nearby that is it can be in any of the z directions then if suppose I am at A I can of course go to any other direction then coming towards O, so there is the probability of 1/z that I can go from A to O out of all the possible available directions. So if I extend the idea to all the possible neighbours we get this particular relation.

So, now if I look at this particular quantity here and assuming that the bond vector is much smaller than R_e and M is like much higher than 1 we can tailored expand the probability that you see here., so let us just do that:

So, for Taylor expansion in 1 variable goes something like this, so if I want to look at a function value in the neighbourhood of x where h is much smaller than x, this is equal to-

$$f(x+h) = f(x) + f'(x)h + f''(x)h^2$$

Now if we have more than 1 variable we can write this as-

$$f\left(x_1+h_1, x_2+h_2 \ldots\ldots\ldots\ldots x_n+h_n\right)$$

Now we can take a partial derivative with respect x1, x2, x3 and so on. So, we have in total n partial derivatives of first order, so we can write this as-

$$¿ f\left(x_1+x_2+\ldots\ldots\ldots\ldots x_n\right) = \sum_{j=1}^{n} \frac{\partial f}{\partial x_j} h_j$$

The same idea now I apply to the second order derivative. Now second order derivative if you think about it, it is basically 2 first order derivatives. So, now I can apply a first order derivative of any of these x and then I can apply the second derivative for with respect to any of the other x. So, what this comes out to be is basically-

$$f(x_1+x_2+\ldots\ldots\ldots.x_n)=\sum_{j=1}^{n}\frac{\partial f}{\partial x_j}h_j+\sum_{j=1}^{n}\sum_{l=1}^{n}\frac{\partial^2 f}{\partial x_j,\partial x_l}\frac{h_j h_l}{2!}$$

The probability distribution for the random walk of M-1 steps to have the end to end distance is:

$$x_1=\overrightarrow{R_e},h_1=-b_i,x_2=M,h_2=-1$$

$$P(\vec{R}_e-\vec{b}_i,M-1)=P(\vec{R}_e,M)+\frac{\partial P}{\partial R_e}\cdot(-\vec{b}_i)+\frac{\partial P}{\partial M}(-1)+\frac{\partial^2 P}{\partial\vec{R}_e\partial\vec{R}_e}:\vec{b}_i\cdot\vec{b}_i$$

A trick here that since one of the variable is a vector the derivative of probability with respect to Re is also a vector and since a final result is a scalar. So, I take the derivative and a dot with the corresponding value of h, so the end result is a scalar, similarly for M and now we also will have the second order derivatives.

So, now again basically what you have is you have 2 derivatives now with respect to R_e. So, what you have formed is like a tensor and if you dot with the bi values again there are 2 bi values corresponding to 2h that also is a tensor. So, if you take 2 dot products what you end up having is a scalar again, so this is what we will have-

$$P(\vec{R}_e-\vec{b}_i,M-1)=P(\vec{R}_e,M)+\frac{\partial P}{\partial R_e}\cdot(-\vec{b}_i)+\frac{\partial P}{\partial M}(-1)+\frac{\partial^2 P}{\partial\vec{R}_e\partial\vec{R}_e}:\frac{\vec{b}_i\cdot\vec{b}_i}{2}+\frac{\partial^2 P}{\partial M\partial R_e}\cdot\vec{b}_i+\frac{\partial^2 P}{\partial M^2}\cdot 1$$

Since,

$$|R_e|\ \frac{M^{\frac{1}{2}}\wedge\partial P}{\partial R_e}\gg\frac{\partial P}{\partial M}$$

So, now we get something like this:

$$¿P(\vec{R}_e,M)-\frac{\partial P}{\partial\vec{R}_e}\cdot\vec{b}_i-\frac{\partial P}{\partial M}+\frac{\partial P^2}{\partial\vec{R}_e\partial\vec{R}_e}:\frac{\vec{b}_i\cdot\vec{b}_i}{2}$$

So, now we have some vector derivatives and vector dot products before going to details I want to discuss a particular notation that is called Einstein notation that will help us to write the vectors and tensors in very compact form. We will be using that in all in the entire course, if you about the Einstein notation this is what it is, if you do not about it I will discuss that briefly now. So, let us keep this in mind and we will come back to this in a moment.

So, in the Einstein notation if for example we have a vector v in 3 dimensions it indeed has 3 components in Cartesian coordinates it is looks like this,

$$\vec{v} = v_x \widehat{e}_x + v_y \widehat{e}_y + v_z \widehat{e}_z$$

Where as in Einstein notation we can simple write

$$v_\alpha$$

So alpha note here is what is referred as a free index if the alpha is repeated it is called a dummy index, So, let us say if for example I want to do a.b I can do and complete vector notation as I will decompose the a into 3 terms and I will dot with the b decomposed in 3 terms, it becomes as:

$$\vec{a} \cdot \vec{b} = \left(a_x \widehat{e}_x + a_y + \widehat{e}_y + a_z \widehat{e}_z \right) \cdot \left(b_x \widehat{e}_x + b_y + \widehat{e}_y + b_z \widehat{e}_z \right)$$

$$¿ a_x b_x + a_y b_y + a_z b_z = \sum_{\alpha = x, y, z} a_\alpha b_\alpha$$

Instead of all this we can simply write in Einstein notation as $a_\alpha b_\alpha$

So, in this alpha is a free index that means it is not repeated and in this case alpha is a repeated index or dummy index. Now the advantage of doing this is I will simply count the number of free indices that I have present in the equation and that will tell me the order of the vector. If there are no free indices, so the order is 0 that means it is a scalar. In this case there is 1 free index and the order is 1 that means it is a vector.

If for example I am something like a, b what essentially I mean if I do not put dot or a cross product in between is it is a tensor in the full notation again it is-

$$\vec{a}\vec{b}=\left(a_x\hat{e}_x+a_y+\hat{e}_y+a_z\hat{e}_z\right)\left(b_x\hat{e}_x+b_y+\hat{e}_y+b_z\hat{e}_z\right)$$

¿ $$a_xb_x\hat{e}_x\hat{e}_x+a_yb_y\hat{e}_y\hat{e}_y\ldots\ldots\ldots=\sum_{\alpha,\beta=x,y,z}a_\alpha b_\beta\hat{e}_\alpha\hat{e}_\beta$$

But in Einstein notation it can be simply written as- $a_\alpha b_\beta$ now you can see both alpha, beta are free indices that means the order is 2. So, now we have a tensor okay of second order, so I will use this particular relation in the relationship we have just derived and see like what it turns out to be-

So, let us first the scalar terms and now I should have a term that represents-

$$P\left(\vec{R}_e-\vec{b}_i,M-1\right)=P\left(\vec{R}_e,M\right)-\frac{\partial P}{\partial M}$$

$$\frac{\partial P}{\partial\vec{R}_e}\cdot\vec{b}_i=\frac{\partial P}{\partial R_{e\alpha}}b_{i\alpha}$$

$$\frac{\partial^2 P}{\partial\vec{R}_e\partial\vec{R}_e}:\frac{\vec{b}_i\cdot\vec{b}_i}{2}=\frac{\partial^2 P}{\partial R_{e\alpha}\partial R_{e\beta}}\frac{b_{i\alpha}b_{i\beta}}{2}$$

Here we had second order derivative and then there are 2 dots which I will write as there was the divided by 2 here again you can see this is now a tensor representing the same tensor we have here this is again a tensor representing this particular tensor when I apply the dot product twice we will have repetition of both alpha and beta which were present as free indices in the 2 tensors and that is why the end result contain no free indices it only has 2 dummy indices alpha and beta and so this particular thing is a scalar. So, let me write that here, so this becomes in Einstein notation-

$$P(\vec{R}_e - \vec{b}_i, M-1) = P(\vec{R}_e, M) - \frac{\partial P}{\partial M} - \frac{\partial P}{\partial R_{e\alpha}} b_{i\alpha} + \frac{\partial^2 P}{\partial R_{e\alpha} \partial R_{e\beta}} \frac{b_{i\alpha} b_{i\beta}}{2}$$

Now if you go back to the initial relation that we have derived we had to sum over this what we were interested in if you remember was P Re, M and as we had derived earlier I can write P, Re, M as sum over the quantities that I have just Taylor expanded. So it becomes:

$$P(\vec{R}_e, M) = \frac{1}{z} \sum_{i=1}^{z} P(\vec{R}_e - \vec{b}_i, M-1) = P(\vec{R}_e, M) - \frac{\partial P}{\partial M} - \frac{\partial P}{\partial R_{e\alpha}} \frac{1}{z} \sum_{i=1}^{z} b_{i\alpha} + \frac{1}{2z} \frac{\partial^2 P}{\partial R_{e\alpha} \partial R_{e\beta}} \sum_{i=1}^{z} b_{i\alpha} b_{i\beta}$$

So what we have got so far is:

$$P(\vec{R}_e, M) = P(\vec{R}_e, M) - \frac{\partial P}{\partial M} + \frac{1}{2z} \frac{\partial^2 P}{\partial R_{e\alpha} \partial R_{e\beta}} \sum_{i=1}^{z} b_{i\alpha} b_{i\beta}$$

So, now if I look at this particular term you should remember from the random walk relation that if alpha is not equal to beta in this case this must be equal to 0. Because the steps in x direction are independent of steps in the y direction or z direction, so this particular quantity will be equal to 0 when alpha is not equal to beta and this quantity will be equal to b_i alpha square when alpha is equal to beta, now alpha can take values of x, y and z, so this can be like b_i x square or b_i y square or b_i z square and for this particular walk in 3 dimensions we know that the sum of these 3 must be equal to b^2. So, this particular quantity must also be equal to $b^2/3$ because the 3 dimensions directions are pretty much equal. So, the b^2 in each of them the 3 directions must be equal and then since the all sum to b^2each of them must be $b^2/3$.

So, I have a shortcut for the writing this particular thing that is:

$$\frac{b^2}{3} \delta_{\alpha\beta}$$

Here $\delta_{\alpha\beta} = Krone\ cker\ delta, it\ is\ equal ¿ 1\ when \alpha = \beta, \wedge 0\ when \alpha \neq \beta$

After all the cancellations our final equation becomes-

$$0=\frac{-\partial P}{\partial M}+\frac{b^2}{6}\frac{\partial^2 P}{\partial R_{e\alpha}\partial R_{e\beta}}$$

$$\frac{\partial P}{\partial M}=\frac{b^2}{6}\frac{\partial^2 P}{\partial \vec{R}_e \partial \vec{R}_e}=\frac{b^2}{6}\frac{\partial^2 P}{\partial^2 R_e}$$

$$\frac{\partial P}{\partial M}=\frac{b^2}{6}\frac{\partial^2 P}{\partial R_e^2}$$

Now if I look at the final answer that we have got and if I compare that to the diffusion equation I wrote in the very beginning which I can write in 1 dimension let us say like this then I can relate the concentration as being analogues to the probabilities. The time as being analogues to the number of segments M and D as being analogues to b^2 /6 and for the dimensional case x as being analogues to R_e. We can extend the idea actually R will be analogues to R_e.

So, apart from this the solution of this equation will be same as that of a diffusion equation we have to look at like what the boundary conditions are and what it turns out is by solving this equation we can also recover the fact that the probability distribution is Gaussian in nature. So, this is I would say a more rigorous way of deriving the fact that the probability distribution is Gaussian. The way we have been done in the past we have done it as looking at a 1 dimensional walk problem then we got binomial distribution and then we took a limit when the number of the steps are very large and then we have got the Gaussian distribution. But we can also get it by using this particular diffusion equation that we have got for the probability. The solution of this will also give you the Gaussian distribution and this particular concept will be very useful as you will discuss in this course.

Thank you.