kronIntroduction to Polymer Physics
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Lecture-53
Microscopic Definition of Stress Tensor- II,
Dumbbell Model, Introduction to Rouse Model

Hello everyone, so in the last lecture we have discussed the microscopic definition of a stress tensor. So, I will continue from that point and we will use the Rouse model of polymer chain that we discussed earlier in the context of determining the stress tensor for a polymer solution using the ideas that we have been doing in recent classes.

So, just to quickly recap what we have been doing is I said that there is a plane containing a material point P that plane which is hypothetical in nature that's a small surface around the particle and around the around the material point and we look at the particles which are above this plane and the particles that is solute particles which are below the plane and it is the interaction between the particles above and particles below that gives rise to the stress that we see on the plane containing the material point P. So, essentially we denoted the particles below as i and particles above as j and then there is a force that is acting between the two that is f_{ij} or f_{ji}, f_{ij} acting on the i^{th} particle and f_{ij} until acting under f_{ji} acting on the j^{th} particle in just the opposite direction that is this is going to be - of f_{ij}.

So, for this particular system what we have obtained in the last class is I can write the contribution to the stress tensor because of the solute interactions as-

$$\sigma_{\alpha\beta}^{(p)} = \frac{-1}{V} \sum_{i>j} \langle f_{ij\alpha} r_{j\beta} \rangle$$

Or in the terms of stress I said it is in terms of the vector tensor notation we have the same thing as a diode that is formed with f and r. It is –

$$\acute{\sigma} = \frac{-1}{V} \sum_{i>j} \langle \vec{f}\,\vec{r} \rangle$$

So, then I said that i and j make sort of force dipole having the force f and having the vector connecting the two ends ‘r’ and those force dipoles then give rise to the stress that is acting on the material point actually the plane containing the material point. So, my simple manipulation, we can see that it should be the same for i less than j because we are not differentiating between i and j in a homogeneous system we will have the same number of particles above and below the plane. So, I can write this as-

$$\sigma_{\alpha\beta}^{(p)} = \frac{-1}{2V} \sum_{i,j} \langle f_{ij\alpha} r_{j\beta} \rangle$$

So, this is only the contribution that we get from the solute-solute interactions, we also need to account for the contribution to the stress because of solvent and that we have said that we will assume that it is solvent that is viscous in nature and it is somewhat implicit in the sense that we do not worry about where they are we talk of them in an implicit sense and the effect we assume to be the same as that of a Newtonian liquid. So, this is the contribution to stress from solute that we have handled at a particle level or I can say it is explicitly handled and then there is another contribution that is handled in an implicit manner assuming Newtonian liquid of viscosity η and that contribution as I said earlier will be –

$$\sigma_{\alpha\beta}^{S} = \eta \left(\kappa_{\alpha\beta} + \kappa_{\beta\alpha} \right) - p\,\delta_{\alpha\beta}$$

Where $\kappa_{\alpha\beta} = \frac{\partial v_\alpha}{\partial r_\beta}$

So, now if I add these to the total stress will be given as the sum of these two components-

$$total\ stress : \sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{p} + \sigma_{\beta\alpha}^{s}$$

And this provides a strategy to get the constitutive law because if I know the forces between segments I can get the contribution from the solute interactions and for Newtonian liquid we know from implicit notation that we have just written what the stress tensor contribution is. So, combining those two terms I can get the constitutive law for any fluid that is containing a solute dissolved in a Newtonian liquid. If it is a different kind of a solvent we can take the equivalent constitutive law let us say for a power law fluid and combine that with the contribution from the solute.

So, let us now consider a simpler polymer model and then we go to the Rouse model. In the simpler model that we call the Dumbbell model- we assume that the polymer chain can be represented using only one spring the two beads connected using only one spring. If you think about it what actually it implies, this implies overall relaxation of a polymer chain and it of course does not constitute the local motions that can be present inside the polymer chain but in any case it simplifies the analysis to begin with and then we can extend the idea to a Rouse model.

So, again going back to my plane containing the material point P, now you can imagine that many of these dumbbells will pass through the plane and only those dumbbells will essentially contribute to the stress because of the solute segments which are polymer chains in this case. We will have the plane and then the dumbbells will essentially be crossing in various orientations and of course there can be other dumbbells present they do not contribute to stress on plane containing P and those are crossing will contribute to stress on plane containing P.

Now we can assume that there are a certain number of dumbbells in a continuum volume or we can talk about a number density of them of dumbbells the numbers per unit volume. So, let us assume that n_p is the number density that is number per unit volume of dumbbells. Now if I look at each of these dumbbells they will have the vector representing the spring $\vec{r}$ and then there will be a force acting on the dumbbell. The force will essentially be –

$$\acute{f}=-k\vec{r}$$

$$\acute{\sigma}=n_p\langle\vec{f}\,\vec{r}\rangle$$

And of course this need to be ensemble averaged because the dumbbells can take various orientations in different conformations and we need to somehow multiply this with the number density of the dumbbells and this essentially would give me a contribution of the type-

$$\sigma_{\alpha\beta}^{p}=-n_p k\langle r_\alpha r_\beta\rangle$$

So, using this kind of an idea we can get the contribution from the solute-solute interactions within the system and now you can see that when I am going for the Rouse model it will have multiple strings but that springs but in any case that will also be similar to what I have written for a single spring case. So, let us now do it for the Rouse model keeping in mind that this is the kind of expression that we will have for every spring in the system.

So, let us now consider the Rouse model, so now in this case instead of just one spring I will have many of those springs and only those of the polymer chains which are represented now using a bead spring model the Rouse model that passes through the plane containing P will contribute to the stress on the plane containing P. So, now we will have chains again in various orientations that, passes through the plane. So, the net stress will be because of the many chains and the spring within the chain will contribute to the net stress that is acting on the on the plane containing material point P.

So, now I will not do the complete derivation but outline the key steps but it gives you an idea like where we are going. So, let us assume that we have a velocity field or flow field as represented using something of this sort-

$$Flow\,field: \vec{v}(\vec{r},\vec{t}) = \acute{\kappa} \cdot \vec{r}$$

Kappa of course depends on time and the polymer chain is kept within that field.

So now I want to remind you of the Langevin equation or the equation for the Brownian motion of the polymer chain that I will modify considering that there is an additional flow field present that is of course not present in the case of Brownian motion because then we did not have any external field present in the system. So, in this case we will have the equation for the n^{th} bead r_n will be represented using essentially what we had earlier but then we will have an additional term because of the flow.

$$Modified\ Langevin\,equation: \frac{\partial \vec{r}_n}{\partial t} = \frac{k}{\zeta} \frac{\partial^2 r}{\partial n^2} + \vec{v}_r(n,t) + \acute{\kappa} \cdot \vec{r}_n$$

So, there is a net motion as a result of flow plus the random forces acting on the bead plus the motion due to the springs between the neighboring beads. So, this I would represent in the normalized coordinates –

$$\frac{dX_p}{dt} = \frac{-X_p}{\tau_p} + \vec{f}_P$$

This is what we had earlier but now we will have an additional term because of flow which is going to be like this and I am not deriving it but you can see like how it is coming from so Kappa dot r gives you in normalized coordinate a term Kappa dot X_P in the equation for the Rouse mode.

So, now when the equation is solved what I will get and again I am not solving it completely and just outlining the key steps here what I will get is the contribution because of the polymer chain would be given as something like this-

$$\sigma_{\alpha\beta}^{p} = \frac{C}{N} \sum_{p} k_p \langle X_{p\alpha} X_{p\beta} \rangle - p\,\delta_{\alpha\beta}$$

Where C is the number density of segments and N is the number of repeating units or segments depending on how I define my k_p and we can go further if I assume some kind of a flow situation.

So, let us assume that we have shear flow. So, in shear a flow what we will have is the x component of velocity can be represented as something like γ dot of y where γ dot is the shear rate applied along x direction normal to the y plane and in that case the Kappa tensor can be written as in terms of the x, y and z components of velocity –

$$\kappa_{\alpha\beta} = \frac{\partial v_\alpha}{\partial_\beta}$$

$$\acute{\kappa}=\begin{bmatrix}\frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} & \frac{\partial v_x}{\partial z}\\ \frac{\partial v_y}{\partial x} & \frac{\partial v_y}{\partial y} & \frac{\partial v_z}{\partial z}\\ \frac{\partial v_z}{\partial x} & \frac{\partial v_z}{\partial y} & \frac{\partial v_z}{\partial z}\end{bmatrix}=\begin{bmatrix}0 & \acute{\gamma} & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{bmatrix}$$

So in this in this particular flow situation, if I solve the equation what I will get is the equations in terms of normalized coordinates actually the components of that –

$$\frac{d X_{px}}{dt}=\frac{-X_{px}}{\tau_p}+\gamma X_{py}+f_{px}$$

$$\frac{d X_{py}}{dt}=\frac{-X_{py}}{\tau_p}+f_{py}$$

$$\frac{d X_{pz}}{dt}=\frac{X_{pz}}{\tau_p}+f_{pz}$$

To solve it further what we have to do is to define the stress tensor for the Pth Rouse mode and before we go further let us just recall what the rouse modes where, so Rouse modes represented the different levels of motion of chain and by levels I mean the locality of the motion the 0th Rouse mode represents the center of mass. The first Rouse mode represents the correlation of the end-to-end distance of the entire chain. The next rouse mode represents the similar thing for half the chain the next one similar thing for one third of the chain the next higher mode similar thing for one fourth of the chain and so on. So, as we go to higher and higher values of p we look at more and more local motion of the polymer chain and each of these motions will then have a contribution towards the stress tensor and that is what I am defining in terms of normalized coordinates now. So,

$$S_{pxy}=\langle X_{px} X_{py}\rangle$$

And

$$\sigma_{xy}=\frac{C}{N}\sum_p k_p S_{pxy}$$

So, the δ_r term will be 0 for xy The Kronecker δ is 0 and only the first term is what will remain and you can notice here that we have looked at the term containing x and y all the others will be somewhat uncorrelated and that is the reason why we are not writing that. So, using this idea now the kind of math that we have to do is we will multiply the first equation by X_{py} and multiply the second equation with X_{px} and what we then do get is something like on the left hand side we will have is $\frac{d}{dt} S_{pxy}$ So, you can see this is X_{py} $dX_{px}/dt + X_{px}dX_{py}/dt$ by chain rule this becomes d/dt of X_{px} X_{py} which is I represent as S_{pxy} and then this will be equal to on the right hand side I will have -2 S_{pxy} τ_p , so we get the same term on the left on the right hand side for both 1 and 2 and that is why we have a 2 factor here. And then we have-

$$\frac{d}{dt} S_{pxy} = \frac{-2 S_{pxy}}{\tau_p} + \acute{\gamma} \langle X_{py}^2 \rangle$$

I can approximate $\langle X_{py}^2 \rangle$ for weak flow situations that is when the flow rates are not very high. I can approximate this as-

$$\langle X_{py}^2 \rangle = \frac{k_B T}{k_p}$$

Essentially this the result that we obtained for no flow. And now if I go ahead I will have the equation-

$$\frac{d}{dt} S_{pxy} = \frac{-2}{\tau_p} S_{pxy} + \acute{\gamma} \frac{k_B T}{k_p}$$

So this equation now I can solve for S_{pxy} and then I will get the contribution to the stress tensor from the P^{th} Rouse mode, if I plug that in the expression for the stress tensor that I have just obtained so we have we have got the expression for the S_{pxy} that is the contribution to the stress tensor from the P^{th} Rouse mode and if I solve this equation and then plug the results back in the expression for the stress tensor σ_{xy} that I have obtained earlier I would get the constitutive law for the case of Rouse model this is what we will show in the next lecture.

So, with that I conclude here, thank you.