Introduction to Polymer Physics

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Lecture-52
Microscopic Definition of Stress Tensor- I

Hello everyone, so in the last couple of lectures we have been discussing the continuum mechanics framework to study polymer networks and we have discussed the shear modulus and Young's modulus of polymer networks and before that we have discussed what is the definition of a stress tensor. So, now I want to combine few ideas that we have developed in the very beginning on random walk models that we further extended while we are doing the Rouse model of the dynamics of a polymer chain to this kind of context when we look at the stress tensor. So, the idea we will discuss is known as the Macroscopic Description of the Stress Tensor where we try to put the polymer models within a fluid and try to find the stress tensor that is somewhat of a macroscopic quantity starting from the models that we have developed which are essentially particle models or microscopic models of the systems.

So, while developing the expression for the stress tensor we defined a cubic control volume around a material point P. The material point P and a plane has an outward normal N and we are interested in the net force acting on this plane for which we had derived the expression as-

$$d\bar{F} = \acute{\sigma} \cdot \hat{n}\, dS$$

Where σ is my stress tensor and is a normal vector and ds is the area of the small plane.

So, now if I look at this from a microscopic perspective the force acting on any given plane has to be because of the molecules that are below the plane and molecules above the plane. So, although they did not come in our analysis because we are looking at a macroscopic description ultimately the forces has to appear from the molecules below and above. Let us see if I look at just that plane containing material point P there will be particles above the plane so there are particles which are above this plane within the control volume and then there are particles which are below the plane. So, what it means is if the plane is at certain height H from bottom then the z coordinates of the particles which are below the plane is less than H and z coordinates of particles which are above the plane is higher than H okay. And these molecules now interact in the in the end the plane is simply a hypothetical idea right. So, we just draw some volume and a surface around a material point and that is what we are calling a plane or a material volume.

The key idea is that whatever forces which are acting between the molecules the net result or a net projection of that onto the plane is the stress that we are eventually getting from here. There is one more component that can give rise to force is because of movement of particles through the plane. So, the particles can eventually move across the plane and they would also add to some contribution to the stress in a microscopic sense. It turns out that that contribution because of the movement of molecules through the plane is relatively less important for polymer segments or polymer molecules then compared to say gaseous molecules or liquid state.

So, what we will develop is a description where we look at the particles of this polymer or large solutes for instance as particles and then we will take into account the effect of the containing liquid or solvent in a continuum sense just like we have done in the macroscopic definition. These particles are of course in a solvent let us say water but that solvent is not explicitly models we do not explicitly modeled we do not really care about the position of say water molecules or whatever solvent there is we look at the position of the part the solute segments that are below and above and the force is acting between them and how they contribute to the stress acting on a given plane or the force acting on a given plane and separately we will look at the forces because of the solvent using the constitutive law we have discussed for the case of a viscous liquid. This is the analysis you can see where it is going ultimately we are going to replace the solute particles by beads connected by springs and then we have a polymer molecule on n molecules actually that are present in the system that is the direction we are going to take. So, we start with solute molecules individually and then we go into details about the polymer models later.

So, we have a plane containing point P and then there are particles which are above the plane and particles which are below the plane. They will have z less than h and they will have z higher than h where h is the height of the plane from the bottom of control volume. So, now if I am looking at the contribution to the stress because of the presence of these solute molecules they will contribute through the forces which are acting between these segments. So, of course there can be interactions between segments below and segments above but these interactions are not expected to affect what is happening in the plane because those interactions are somewhat on a different plane those interactions are not really crossing through the plane containing the particle P.

On the other hand if interactions between the particles which are below and above then those particles interact and their interactions or their field of interaction contains the plane. So, in some sense that will affect the force acting on the plane the total force acting on the plane. So, what we are going to say is the net force acting on the plane is because of the interaction between particles above the plane and particles below the plane. The interactions between only the particles which are below they will have no consequence on the force acting on the plane which is above it only when the line connecting the two particles or to solutes to solutes passes through the plane or crosses the plane then only these forces will contribute to the stress tensor that is not so much of a poor assumption it is actually is reasonable enough.

The assumption that is more critical here is that we have already mentioned. The first one we assume that stress due to motion of solutes across the plane are neglected which are important for gas and liquid and second we are only interested in the contribution to stress due to forces acting between solute particles above and below the plane.

So, let us introduce some language here we will call the particles below using an index i and the particles above using an index j. The force acting on i due to j is given by the vector f_{ij} and there should be an equal and opposite force acting on j due to i that is f_{ji} that is the language we are going to use.

So, then we can write the expression for the contribution to the stress tensor as sum over i and j f ij α looking at α component and then we have to find a way to differentiate between the particles below and above and we can do that using the step function represent using θ. It means-

$$\sigma_{\alpha z}=\frac{1}{S}\sum_{i,j} f_{ij\alpha}\theta\left(h-r_{iz}\right)\theta\left(r_{jz}-h\right)$$

So, for r_{iz} that is the location of the i^{th} particle the z component of that if it is less than h then in that case the θ function will give you 1. If it is higher than h then the θ function will give you 0 that would be the case if the particles are below the plane particles below it is going to be 1 particles above it is going to be 0. So, in this way i will represent particles below the plane.

We can do the same idea for the second θ function and what we will see is since we have swapped the sign of the argument here. We are going to have an opposite function here. This term is going to be 0 when the j is below and when j is above the r will be higher than h, r_{jz} and in that case the particles which are higher than above are identified as j. So, j would contain particles above the plane.

So, if I do not differentiate between i and j in the very beginning I put all the particles in the box just I just looking at this two θ functions we have a way to differentiate the particles below and above. This net function will only be nonzero when i is below and j is above the plane. So now if the system happens to be homogeneous then in that case the stress should not depend on the position of the plane.

So, if I move the plane up or down I can move the plane in the z direction and I should get the same stress tensor. This really means that if I now move this plane up or down my stress tensor should not be changing the other way to say that is I can integrate over the z direction and take an average that would be the same value as the stress acting on any particular point. So, using this idea I can write my contribution to the stress tensor due to solute segments as-

$$\sigma_{\alpha z}^{(p)}=\frac{1}{SL}\sum_{i,j}\int_{0}^{L} dh f_{ij\alpha}\theta\left(h-r_{iz}\right)\theta\left(r_{jz}-h\right)$$

Where I have simply moved the height from say 0 to L that is the length of control volume and I am simply integrating it and I am dividing by the length as you get the same quantity that we have.

So, now I can integrate over this θ function keeping in mind that we are now integrating over the control volume while moving this plane up like this and it turns out that this is equal to so SL is of course V something like this-

$$\frac{1}{V}\sum_{i,j} f_{ij\alpha}\left(r_{jz}-r_{iz}\right)\theta\left(r_{jz}-r_{iz}\right)$$

So, this function $\theta\left(r_{jz}-r_{iz}\right)$ will be one when r_{jz} is higher than r_{iz} so, this will ensure that j is always above i and then this will ensure that j is above and i is below and the reason why this to be the case is because this plane it starts to move up in the very beginning if suppose some particle is above and some is below then we have a particle here at say r_{jz} and a particle below I would say r_{iz}, so I can move the plane starting from a plane parallel to the plane zone that contains r_{ij} until a plane parallel to that zone containing rj or the particle j because once I am after this once I have moved further up then both i and j are below the plane and then they do not affect. So, the integration reason is essentially r_{jz} - r_{iz}. So, if I have to look at the net averaged interaction between particle i and j. I can start from a plane containing i, keep on going up until I hit a plane that contains particle j, once I cross that then both i and j are below their interactions will not affect the force acting on the plane if I go down below i then also both i and j are above and their interactions will not affect the force that is the reason why I am putting $r_{jz} – r_{iz}$. So, now if I define $\vec{r}_{ji}$ as the difference between $\vec{r}_j$ and $\vec{r}_i$ vectors

$$\vec{r}_{ji}=\vec{r}_j-\vec{r}_i$$

then I can write my contribution to stress tensor as –

$$\sigma_{\alpha z}^{\phi}=\frac{1}{V}\sum_{j} f_{ij\alpha} r_{jiz}\theta\left(r_{jiz}\right)$$

And this I can write as two terms one is when i is higher than j other is when i is less than j. So, theta function will take care of the fact that one has to be above and one is below we have not differentiated in the very beginning. It means-

$$\frac{1}{V}\left[\sum_{i>j} f_{ij\alpha} r_{jiz}\theta\left(r_{jiz}\right)+\sum_{i<j} f_{ij\alpha} r_{jiz}\theta\left(r_{jiz}\right)\right]$$

So, now I can interchange i and j here does not do any harm because I summing over both i and j but what I do get is somewhat of a symmetric expression. This becomes –

$$\text{¿}\frac{1}{V}\left[\sum_{i>j} f_{ij\alpha} r_{jiz}\theta\left(r_{jiz}\right)+\sum_{i>j} f_{ij\alpha} r_{jiz}\theta\left(r_{jiz}\right)\right]$$

Now we can write this expression also as-

$$\frac{-1}{V}\left[\sum_{i>j} f_{ij\alpha} r_{ijz}\left(\theta\left(r_{jiz}\right)+\theta\left(r_{ijz}\right)\right)\right]$$

The first θ function is higher than 0, = 1 when r_{jiz} is positive. The second θ function is 1 when r_{iz} is positive that means r_{jiz} is negative. So, if I sum these two essentially what I get is 1 because one of them has to be positive. So, if j is abovthe θ of r_{jiz} will be 1, if j is below then theta of r_{jiz} will be 1 in any case the sum has to be = 1. So, this means that my contribution to the stress tensor is something like this –

$$\text{¿}-\frac{1}{V}\sum_{i,j} f_{ij\alpha} r_{ijz}$$

So, what we have managed to obtain if you look at the last expression is we have represented the stress acting on this as a multiple of forces between molecules and distances between them right. So, I can write this as in tensor notation I can write this-

$$\acute{\sigma}=\frac{-1}{V}\sum_{i>j}\vec{f}_{ij}\vec{r}_{ij}$$

There is a physical significance attached to it we can think of it as some kind of a force dipole. So, a given plane P containing point P has a particle above and below it and they have a vector connecting them are and then there is a force acting between the two points above and below F and so this kind of forms like a force dipole so as to speak analogous to what we know about an electric dipole. Electric dipole what happens is we have a '+' and a '-'ion for instance. They are forming a dipole and then there is a force acting between them and the net dipole movement is given as something like q_r just like here we have f_r except that in here we are interested in a vector quantity f as opposed to a scalar quantity q in the case of an electric dipole.

The other thing to note here is that there is no dot or cross between f and r there forming a dyad because Sigma is a tensor. So, if I dot f and r we will get a scalar we do not want that even if we cross it we will get a tensor. So, it is like fr and it perfectly came in terms of indices i and j although they are repeated they are not in opposite order. So, if I would have written it like this it may give an impression that it is like a dot product or something of that sort but I want to remind you also that this is not really and Einstein notation at work here. This ij is because of the force acting between the particle i and particle j and we are summing over all possible pairs of particles i and j in the system.

So, so there is one thing that I want to add to this discussion here that in the end the configuration of the solute segments are not going to be fixed with time even at equilibrium. The solvent molecules will of course keep on moving but we are not we are not considering that, but the solute molecules also will keep on moving and forming different conformations and therefore we are not really interested in a particular configuration of the solute molecules where we have obtained the stress tensor we actually interested in the ensemble average of that in the sense of what we have been doing for the random walk models. So, actually the stress tensor is going to be, and ensemble average of this force dipoles and we will start with this particular point in the next class where as you can expect we are going to replace these solute segments by the bead spring model of a polymer chain that we had discussed in the Rouse model and then we can get a more appropriate expression for the contribution to the stress tensor due to solute segments.

So, with that I conclude here, thank you.