Introduction to Polymer Physics
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Lecture-50
Kuhn's Theory of Rubber Elasticity

Welcome all of you, so in this lecture we will take the review of continuum mechanics that we have been doing in last couple of lectures to somewhat of a logical conclusion where we are looking at the behavior of rubber. So, what we essentially stated in the last lecture and we took it for granted in the derivation is the free energy of deformation of the rubber is a function of the deformation gradient tensor. We will first establish that by using what is known as the Kuhn's theory of rubber elasticity and then using these ideas we will look at various kinds of deformation of a material and we define what is known as the Shear modulus of a polymer network.

So, we will talk about the Kuhn's theory of rubber elasticity. So, rubber as you know is a polymer network and therefore we can represent the rubber as composed of many polymer chains connected together by some kind of a physical or chemical cross linking typically when it is chemical or covalent cross linking then what that is what we call it a rubber when it is the physical cross linking we call it an entangled polymeric system there is some difference. We also are doing it for the case when there is no solvent when we have a polymer network in a solvent we call it a polymer gel that is somewhat more complicated in terms of formulation then what we are doing here. So, if we take this kind of a network then these junctions are what are known as cross links and between every two of these cross links we will have a polymer strand. The polymer strands in the entire network can vary in their end to end distance and there are number of repeat units because if you think of like how this kind of a thing would be synthesized, you will put polymer solutions in a beaker then you add a cross linker and the cross linker will cross link the polymer chains in a somewhat of a random fashion it is very difficult to get a perfect network that would have fixed number of repeat units between two cross links and of course they will vary with the with regard to the end to end distance because the system can take many, many

confirmations now because every individual segment or a strand can take many, many confirmations.

These strands can also be referred as sub chains because they are not really an entire polymer chain that we started with it is the polymer chain between the two cross links that is somewhat constrained now because it has to move along with the cross links that connects them together. Okay so, because of this cross links the motion of polymer segments become somewhat constrained and that is what give rise to a solid nature to rubber. If it is not cross linked you will have like a polymer solution that can be viscous but not quite like an elastic solid once you cross link it, it starts behaving like a solid. So, let us say we have a certain volume of the network, we can define a number of strands per unit volume that is my n_c and we will use that later.

So, if I now look at the free energy of this particular network one point to start with is we can assume that each of these strand is an ideal chain itself okay that may not necessarily be the case but this is at least a good starting point to start thinking about it. So, we can define we can define a reference configuration that is completely theoretical in nature that is just reference. So, we can talk of free energy with respect to or relative to that reference configuration and that reference configuration contains all ideal chains as strands or all strands or are ideal chains. So, we are going to assume reference, as all strands are ideal and the advantage of doing that is obvious we already know what the elastic energy of an ideal chain is. So, for a strand of end-to-end distance vector R_e and N repeating units or segments we can write the free energy as equal to the elastic energy which is given by this-

$$free\ energy = \frac{3k_BT}{2Nb^2}R_e^2$$

That we have derived for the ideal chain.

Now of course that strand will not really have a fixed number of repeat units. The number of repeat units can change for different strands similarly it will not have a fixed R_e. The R_e value for every strand can be different in fact for the same strand at different time can be different. So, in

reality what we do have is a probability density $P(R_e, N)$ for strand to have end-to-end distance vector R_e and N repeating units. And we have to multiply the free energy with this probability density and integrate over all possible values of N and all possible values of R and then only we can get the total free energy or the average free energy of an strand and if I then multiply that with the number of strands per unit volume we can get the free energy density.

So, I can write the free energy of network as the number of strands per unit volume integral of d R_e that is integral of over all possible values of R_e integral over N and can take values theoretically from 0 to infinity multiplied by the probability density P (R_e, N) and multiplied by the energy that we have for a strand of n repeat units having an end-to-end distance vector R_e

$$\textit{free energy of network} = n_e \int d\vec{R}_e \int_0^\infty dN\, P(R_e, N) \frac{3k_B T}{2Nb^2} R_e^2$$

So, if I look at this term here this is some sort of a joint probability density that is first the probability of the chain having an end to and distance R_e and second the probability that the chain will have N repeat units these two probabilities must be multiplied to get the joint probability P (R_e, N) So, this I can write as P (R_e) and P (N). This we have already derived for the ideal chain it is a Gaussian function-

$$P(R_e) = \left(\frac{3}{2\pi N b^2}\right)^{\frac{3}{2}} \exp\left(\frac{-3R_e^2}{2Nb^2}\right)$$

And the other term P (N) should satisfy the normalization because ultimately the probabilities must normalize to 1. So it must be –

$$\int_0^\infty P(N)\, dN = 1$$

So, now if I look at the deformation of this material we can talk about deformation from this reference state and again I want to emphasize here the reference state is hypothetical in nature because we have to define some reference to compute the free energy difference. So, we have defined the strands being ideal as the reference state and then we are talking above changes from that reference state. So, if we think of a deformation in the material the deformation will result in

changes in the R_e of individual strands. In fact the R_e will become some R_e' and I can write this R_e' in terms of the language of deformation tensors that we have discussed because just to recall the deformation tensor is the derivative of the current position with respect to reference position or initial position. So, we can write as-

$$E_{\alpha\beta} = \frac{\partial R_{e\alpha}'}{\partial R_{e\beta}}$$

Therefore,

$$R_e \rightarrow \vec{R}_e' = \acute{E} \cdot \vec{R}_e$$

So, now if I talk of the free energy change just to keep in mind that the free energy we have defined here is already normalized. So, it is free energy per unit volume because we have defined the number of strands per unit volume. So, if I now talk of the free energy in the final state where the strands have an end-to-end distance R_e' as opposed to R_e assuming that the elastic free energy expression that we have derived for the ideal chain still applies that in fact is only true for small deformations. We can get the final energy as-

$$\vec{f} = n_c \int dR_e \int_0^\infty dN\, P(R_e, N) \frac{3k_B T}{2Nb^2} \left(\acute{E} \cdot \vec{R}_e\right)^2$$

And from there I can take now the free energy difference between the final state and the reference state and using that I can get the free energy of deformation. So,

$$\textit{free energy of deformation}: \tilde{f} - \tilde{f}_0 = n_c \int dR_e \int_0^\infty dN\, P(R_e, N) \frac{3k_B T}{2Nb^2} \left[\left(\acute{E} \cdot \vec{R}_e\right)^2 - R_e^2\right]$$

So, now we have a clear motivation that why for polymer networks we can write the free energy of deformation as a function of the deformation gradient tensor. And again to recall this is similar to f of ϕ because just like we can think of the initial position with respect to previous position or the reference position we can also think of the final volume fraction relative to the initial volume fraction and that would be what we had for the Helmholtz free energy density we used while

talking about thermodynamics of polymer solutions similar idea is at work here again we are doing thermodynamics the only thing is we are looking at a polymer Network where only the elastic energy is important.

If we are doing for the gel we also have to include the χ terms the effect of solvent into the model and then we can look at what is known as the swelling behavior and collapse behavior of polymer gels but I am not going into details of that now. So, I will not completely derive this equation but keep in mind that we have the probability density function that we have defined to be a Gaussian function multiplied by P (N) that is being normalized in a particular way and on solving what we do get is the following-

$$f(\acute{E}) = \frac{1}{2} n_c k_B T \left[E_{\alpha\beta}^2 - 3 \right]$$

So, when we have done the work done in the previous lecture we have assumed that F is a function of ϕ we did not take the functional form into consideration because we did not know it back then but now we have a functional form so now I can go back to the work done as a function of free energy relations and then try to look in more detail the stress tensor and so on for this polymer network. So, going back to what we derived in last lecture we had the stress tensor as-

$$\sigma_{\alpha\beta} = E_{\beta\mu} \frac{\partial f(\acute{E})}{\partial E_{\alpha\mu}} - p\delta_{\alpha\beta}$$

Now since we have derived-

$$f(\acute{E}) = \frac{1}{2} n_c k_B T \left[E_{\alpha\beta}^2 - 3 \right] = \frac{1}{2} n_c k_B T \left[E_{\alpha\beta}^2 - 3 \right]$$

I can equivalently write this as because anyway β is repeated in the relation its dummy index. So, I can change with μ just as we have been doing in other examples. So, now we can get the derivative as-

$$\frac{\partial f(\acute{E})}{\partial E_{\alpha\mu}} = n_c k_B T \, E_{\alpha\mu}$$

And therefore we have-

$$\sigma_{\alpha\beta} = n_c k_B T E_{\alpha\mu} E_{\beta\mu} - p \delta_{\alpha\beta}$$

So we will identify $(¿¿\overset{n}{c} k_B T)$ as my shear modulus G and therefore we have-

$$\sigma_{\alpha\beta} = G E_{\alpha\mu} E_{\beta\mu} - p \delta_{\alpha\beta}$$

So, now let us assume a shear deformation because we have identified this G as a shear modulus. So, let us assume a shear deformation and see what the expressions become that would explain the idea that why we have identified (n_c k_BT) as the shear modulus.

So, if I have a shear deformation in Cartesian coordinates 'r' becoming r' is equivalent to x, y, z becoming x', y', z' and the way to visualize a shear is, we assume some initial state as a rectangle in x, y we also have a z direction but we assume that shear is being applied in the xy, and we apply a shear deformation along the xy plane and then this material deforms and this magnitude is what we know as the amount of shear, so it is per unit the distance in the y direction we have a shear y on the along the x direction this is how we define the shear. So, then the positions actually transform as-

$$x' = x + \gamma y$$

$$y' = y \wedge z' = z$$

Let us say a point moves along x by gamma and it does not move in the y and z direction so it is true for every other point we can draw in the system. So, let us say we had a point here this point retains the same y and z coordinates only changes along the x and we can actually do it for any point in the material even that is not on the edge they will also essentially retain same y and z coordinate only change in the x coordinate.

So given this particular deformation is also called simples shear. We can define the deformation gradient tensor as-

$$\acute{E}=\begin{bmatrix} \frac{\partial x'}{\partial x} & \frac{\partial x'}{\partial y} & \frac{\partial x'}{\partial z} \\ \frac{\partial y'}{\partial x} & \frac{\partial y'}{\partial y} & \frac{\partial y'}{\partial z} \\ \frac{\partial z'}{\partial x} & \frac{\partial z'}{\partial y} & \frac{\partial z'}{\partial z} \end{bmatrix}=\begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

So if I now look at the $\sigma_{\alpha\beta}$ that we have found to be given by this relation-

$$\sigma_{\alpha\beta}=G\,E_{\alpha\mu}\,E_{\beta\mu}-p\,\delta_{\alpha\beta}$$

So if I now look at the $\sigma_{\alpha\beta}$ that we have found to be given by this relation, we know the shear is being applied in the xy direction so there is that is perpendicular to the xy plane so perpendicular to the perpendicular to the y axis. So, essentially we are looking at σ_{xy} that is the only nonzero component in the stress tensor if I for example look at σ_{xx} σ_{xz} and so on all these has to be 0 because stress is only applied perpendicular to the y axis along the x direction that is the direction we have this is; this particular direction. So, if I look at that term that is going to be-

$$\sigma_{xy}=G\left(E_{xx}E_{yx}+E_{x\,y}E_{yy}+E_{xz}E_{yz}\right)$$

$$¿\,G\left(1\cdot 0+\gamma\cdot 1+0\cdot 0\right)=G\gamma$$

So, this is G multiplied by γ that tells me that the stress that is being applied it is only it is just we can call it σ is G multiplied by γ and this is how we define the modulus the stress by strain is a modulus. So, in this case we apply a shear, so stress by the applied shear is my modulus and that is will be a shear modulus and that is the reason why we had identified $n_c\ k_BT$ in that equation as my shear modulus.

So, we can also go ahead try to look at other components of the stress tensor in this case knowing that it is anyway 0 because we know that the stress is only applied in the xy, stress components in all the other directions are 0 okay but knowing that we can try to compute it the advantage of doing this is we can get the value of p from there. So, let us say if I am doing σ_{xx} that is going to be-

$$\sigma_{xx} = G\left(E_{xx} \cdot E_{xx} + E_{xy} \cdot E_{xy} + E_{xz} \cdot E_{xz}\right) - p$$

$$¿ G\left(1 \cdot 1 + \gamma \cdot \gamma + 0 \cdot 0\right) - p$$

$$¿ G\left(1 + \gamma^2\right) - p = 0$$

Therefore,

$$p = G\left(1 + \gamma^2\right)$$

This is how we can analyze the Shear information.

So, we can apply similar kinds of ideas to other kinds of deformation like uniaxial deformation and we will continue a discussion in the next lecture.

So, with that I conclude here, thank you.