Introduction to Polymer Physics
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Lecture-51
Elasticity of Polymer Network

Hello everyone, so in the last lecture we have been discussing the continuum mechanics applied to the case of a polymer network that is rubber and we have obtained the expressions for the stress, the shear modulus and so on we discussed the shear deformation of rubber. So today I will take the discussion further talk about uniaxial deformation for the polymer network and after that I will take you to what is known as a microscopic definition of stress tensor that I will continue in the following lectures.

So, just to recall, we have discussed that the polymer network and the free energy of this network is a function of the deformation tensor, and using that idea we have obtained the shear modulus as-

$$G = n_c k_B T$$

Where n_c is the number of strands per unit volume. And we have been discussing the case for a shear deformation. So, for a shear deformation the stress applied is something like

$$\sigma = G\gamma$$

γ is the shear that is applied and or shear that is obtained after application of a stress of σ, and σ is shear modulus.

So, before we go into uniaxial deformations there is one point I want to make here, that if I want to know the magnitude of this shear modulus how does it compare to other materials it is useful to look at the bulk modulus of an ideal gas for example, so the bulk modulus of an ideal gas is given as something like-

$$K = n k_B T$$

where n is the number of molecules per unit volume which shows some similarity with the expression we have $n_c k_B T$ here also we have something like numbers per unit volume or number density but now we have number of strands per unit volume. But the key idea here is just like the bulk modulus of an ideal gas is very small, ideal gas is not really highly, highly stiff in that sense it is very soft, I would say as soft it can be. So, in same sense the shear modulus of a polymer network is also very small and that explains why the polymer network is very soft that is it will respond to deformation or applied stress much easily than compared to materials like metals which will have much higher shear modulus.

So, if the shear modulus is small that means we are having a material that is very soft in nature. So, this kind of explains that the polymer networks are soft materials as opposed to say hard materials like metals and so on. It is really soft you already have said that it is not quite a solid when I compare that to a metal. If I add a little bit amount of liquid it becomes a gel that is more liquid like so polymer network in solid form is somewhat like a solid but it has very small shear modulus that explains why it is very soft if I apply even little amount of stress it will deform.

In fact if I want to increase the modulus one way is that I can increase the number of cross links the more cross links I am going to have the more stiff the network will become and so the cross link density in some sense is a measure of the elasticity as I increase my n_c I would decrease the elasticity of the material or in other words it is less soft as we increase n_c and this is the way we can obtain materials of different stiffness by varying simply the cross link density and the kind of experiment I proposed to you is we have a polymer solution and we add a cross linker.

So, as I increase the amount of cross linker for given concentration on a polymer solution I will form different kinds of materials to encounter network which will vary in the rigidity or stiffness more cross linkers will give you more stiff materials less cross linkers will give you less stiff material of course in the limit when there is no cross linker we have a liquid and in the limit when there is plenty of cross linker we have a very hard solid that we can think of and of course we are always between these two extremes and we have materials of shear modulus still very small. Although the material keeps is a solid nature as long as the covalent the cross linking is covalent in nature. If it is like a physical cross linking like say entanglements then in that case if I apply some deformation this cross links can really break that is not assumed in the case of covalent cross linking will be stable but the materials will respond to deformations very easily and that is why these materials find a lot of use.

Let us now talk about another type of deformation that is called uniaxial deformation and the idea here is the following- we again start with a material again. So, when I deform this material along the z direction by applying some stress it says σ from both the ends and assuming that we started with unit dimensions that is 1, 1, 1 on all the sides the final state will have some value some length λ along the z direction. And since the material has to conserve volume overall as we stretch in one direction it has to thin in the other two directions. So, if I start from here, I am eventually going to shape like this where we know that the z direction is λ and the other two must be much smaller and since we cannot differentiate between the x and y direction in this case because deformation is being applied in z direction these two must be same. So, this means that the initial volume which is simply 1 = λ multiplied by a^2 that is the final volume. This gives me the value of $a=1/\sqrt{\lambda}$.

So, it is the deformation in x and y is because of the stress being applied in the z direction and the reason why it is happening is because the material is somewhat incompressible okay. So, now I can write the deformation gradient tensor. In this case again as what we have been doing for the simple shear deformation it will have 9 components like this-

$$\acute{E}=\begin{bmatrix} E_{xx} & E_{xy} & E_{xz} \\ E_{yx} & E_{yy} & E_{yz} \\ E_{zx} & E_{zy} & E_{zz} \end{bmatrix}=\begin{bmatrix} \frac{\partial x'}{\partial x} & \frac{\partial x'}{\partial y} & \frac{\partial x'}{\partial z} \\ \frac{\partial y'}{\partial x} & \frac{\partial y'}{\partial y} & \frac{\partial y'}{\partial z} \\ \frac{\partial z'}{\partial x} & \frac{\partial z'}{\partial y} & \frac{\partial z'}{\partial z} \end{bmatrix}$$

Where again we have assumed that we are going from initial state x y z for every material point in the volume and we are assuming that the deformation is uniform that is the same assumption we have used earlier as well, that is every point is undergoing same deformation or similar kind of deformation. So, then I can write here-

$$x' = \frac{1}{\sqrt{\lambda}} x;\ y' = \frac{1}{\sqrt{\lambda}} y \wedge z' = \lambda z$$

So, this gives me only the diagonal components in the matrix.

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

So, now if I look at the free energy density for deformation we had derived the equation for polymer network as this-

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

Where n_c $k_B T$ is my shear modulus as we just defined, so we can also write it as-

$$\text{¿}\frac{1}{2} G \left[E_{\alpha\beta}^2 - 3 \right]$$

$$\text{¿}\frac{1}{2} G \left[E_{xx}^2 + E_{xy}^2 + E_{xz}^2 + E_{yx}^2 + E_{yy}^2 + E_{yz}^2 + E_{zx}^2 + E_{zy}^2 + E_{zz}^2 - 3 \right]$$

And as we had just noticed all the off diagonal terms are going to be 0 and we are only left with the diagonal terms which you can see for x and y it is 1 over square root of lambda and for z it is lambda. So, the first term is 1 by lambda the second term is 1 by lambda and the third term is lambda squared-

$$\text{¿}\frac{1}{2} G \left[\frac{1}{\lambda} + 0 + 0 + 0 + \frac{1}{\lambda} + 0 + 0 + 0 + \lambda^2 - 3 \right]$$

$$\frac{1}{2} G \left[\lambda^2 + \frac{2}{\lambda} - 3 \right]$$

So, now if I want to find the force that is acting on the surface that is perpendicular to the xy plane, if I look at the force that is acting on the on the surface it will be the stress multiplied by the area. So, we have σ that is now a function of λ that is the force per unit area. If I multiplied by the area that is 1 over λ that gives me the force, that force if I multiply with dλ that tells me the free energy change for a small deformation from λ. So, assuming that the λ is my mechanical equilibrium state and if I do a small deformation then the change in free energy is the force acting at that moment when the deformation is λ that is what we have here. This is the force at deformation λ multiplied by the dλ, the small λ of deformation that is when we go from λ to λ+dλ and this will be equal to the change in the free energy.

$$\sigma(\lambda)\frac{1}{\lambda}d\lambda=df$$

So, this means that the stress can be written something like this and since we have already obtained the expression for F we can get this as that is simply-

$$\sigma(\lambda)=\lambda\frac{\partial f}{\partial\lambda}=\lambda\cdot\frac{1}{2}G\left(2\lambda-\frac{2}{\lambda^2}\right)=\lambda G\left(\lambda-\frac{1}{\lambda^2}\right)=G\left(\lambda^2-\frac{1}{\lambda}\right)$$

Now there is a bit of a problem in this equation since we assume that the free energy varies like the energy of an ideal chain there is no term in this equation that will prevent the stretching of chain to unphysical high values. But in reality if I stretch the polymer network there will be a movement where all the strands are stretched to the maximum possible contour length and beyond which there can be no extension. So, in reality there is a limit on the maximum stretching that can be given by the ratio of the maximum possible contour length of a chain or a strand in this case multiplied by the average length for an ideal chain and this is given by-

$$\lambda=\frac{Nb}{\sqrt{N}b}=\sqrt{N}$$

So, this pose a limit that we can refer as the finite extension limit which is not captured by the model that we have discussed of course we can make corrections to it. So, whatever we have developed is only applicable for a small deformation. It is the same idea that goes to the previous point that in any case the change in free energy on deformation is equal to the work done is something that applies only when we are very close to equilibrium not very far from it very far from equilibrium the whole idea of free energy becomes somewhat crude or I would say not quite accurate, thermodynamics only works near the equilibrium.

So, with this kind of a framework if I now want to find the Young's modulus in the earlier case when we are doing the shear strain and we are when we are applying a shear we looked at the shear modulus. Now we are like stressing the material like this. So, we are applying a strain normal to the plane as opposed to tangential to your plane. So, now we can define what is known as the Young's modulus. We can write as-

$$\lambda=1+\epsilon$$

$$\sigma=G\left[\lambda^2-\frac{1}{\lambda}\right]=G\left[(1+\epsilon)^2-\frac{1}{1+\epsilon}\right]$$

So, for small epsilon or small strains I can write this as-

$$small\,\epsilon=G\left[\left(1+\epsilon^2+2\epsilon\right)-\left(1-\epsilon+\epsilon^2\right)\right]$$

$$\sigma=3G\epsilon$$

Now since Young's modulus is defined as the ratio of the stress to the strain the Young's modulus = 3 times G for the case of a polymer network.

$$Youn\,g^{'}s\,Modulus=\frac{\sigma}{\epsilon}=3G$$

So, this is like the procedure that we can adopt once we know the expression for the free energy we can go ahead and try to find constitutive law based on the ideas we have discussed and using that we can look at the governing equation of motion and then we have the complete picture of the dynamics of the polymeric system or any system for that matter.

Although we have discussed the case of polymer network you can apply similar analysis for the case of a gas or a liquid or any material. The only problem you will have is you will have to have different expressions for the free energy, they may depend on the deformation gradient tensor as well as the velocity gradient tensor or may be like either of them. In any case both of them are also related by an equation we have discussed and then what we have is what is known as the constitutive equation and this completes the continuum mechanics framework for the study of any system all we need is a constitutive law that relates the stress with the deformation or the history of deformation of a system.

So, although I will not derive it but you may have done these kind of things in solid mechanics or fluid mechanics or transport phenomena of course depending on your background. I am just producing some of the results that apply for different class of materials. For example if we have an ideal elastic material, the constitutive law is for compressible substances-

$$\sigma_{\alpha\beta} = K \epsilon_{rr} + \delta_{\alpha\beta} + G \left[\epsilon_{\alpha\beta} + \epsilon_{\beta\alpha} - \frac{2}{3} \epsilon_{\gamma\gamma} \delta_{\alpha\beta} \right]$$

If it is incompressible then we can have simplifications to this expression.

And if you have an ideal viscous fluid or what is known as a Newtonian fluid the expression we have something like this-

$$\sigma_{\alpha\beta} = \eta \left(k_{\alpha\beta} + k_{\beta\alpha} \right) - p \delta_{\alpha\beta}$$

So, we have discussed the constitutive laws for different class of materials we have done a derivation for the case of a polymer network. We looked at the shear modulus bulk modulus and so on. I am not going in details about other polymeric systems for the lack of time in this course but the analysis can be applied with some generalizations using the idea that we have to first write the free energy of the system and then from there we have to get the constitutive law and from there we can do a continuum mechanics framework.

So, I want to remind you here one thing that we did earlier also we were doing dynamics using the idea of Brownian motion we talked about the Langevin equation and we talked about the Rouse models and Zimm models of polymer chains looking at the diffusion behavior. All of them where for things at equilibrium but now the similar models can now take some of the framework that we have now discussed in the continuum mechanics and using that we can then look at the effect of deformation on these materials in the context of dynamics beyond equilibrium although close to equilibrium but beyond equilibrium and this is how this dynamics would be different from the motion of polymer segments for example by Brownian motion.

So, earlier we could get the diffusion coefficients for example and in these cases we can get viscosities for example okay and then there are a whole lot of detailed models for various kinds of polymer polymeric systems there is a whole literature on the constitutive laws that applies to different polymeric systems like polymers gels, polymer solutions and polymer melts and so on. But the basic framework starts from the thermodynamic descriptions of those systems and then trying to a couple it with the continuum mechanics frame that we have discussed and we will do one of these analysis in the next lecture when we look at what is known as the macroscopic definition of the stress tensor.

So, with that I want to conclude here, thank you.