Introduction to Polymer Physics
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Lecture-49
Continuum Mechanics- II

Hello everyone, so in this lecture we will review the continuum mechanics part that we have been doing and then we will take it further and try to analyze the behavior of rubber that is a polymer network. So, just to recall what we have been doing in the last class is we are talking about continuum mechanics and we defined what is known as the stress tensor and the way we have defined it is we have defined a material point P that is fixed to the material and then a volume around this material point and then I talked about a small area on that volume so the 3 dimensional volume around material point and we talked about a surface ds on that volume which has an outward normal n and there is a force that is acting on this small surface given by a stress tensor sigma dotted with the normal vector multiplied by the area.

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

So, now if I take these ideas further before just to write the same thing in Einstein's notation this would be something like this-

$$d F_{\alpha} = \sigma_{\alpha\beta} n_{\beta} dS$$

If I want to take this idea further and try to find the total force acting on the volume around the material point the control volumes are to speak, the total force can be found by integrating the dF’s and this will be given by something like this –

$$F_{\alpha} = \int \sigma_{\alpha\beta} n_{\beta} dS$$

So, now we will make use of what is known as the divergence theorem you probably have done this in math courses that is for any function f of (r) I can write the integration over the volume of its derivative as equal to the integration over the surface of F that is dotted with the n or if I want to work in Einstein notation I will use an r alpha here and an n alpha here. So, if we use this idea in the equation for F_α what I do get is a derivative of the stress tensor with respect to r of β. It is –

$$Divergence\, Theorem\, f(r): \int d\vec{r} \frac{\partial f}{\partial r_\alpha} = \int dS\, f\, n_\alpha$$

So, now going back to the equation of motion that we discussed in the last lecture we had something that is counterpart of mass times acceleration the density multiplied by volume is the mass and the acceleration can be written as the current position as a function of previous position, the second derivative of that and this must be equal to the forces acting on this which can be the forces due to the stress that we talked about and the force is due to the gravity or other body forces which are present in the system. So, this can be for example a gravity force, now we will use divergence theorem so this becomes an integration over the volume. So, the integration over the volume of the derivative is the integration over the surface of the stress tensor multiplied by the normal vector. So, I will use the volume integration here, so we get and then we have certain body forces acting on the system –

$$\rho V \frac{\partial^2 \tilde{r}_\alpha(r_0,t)}{\partial t^2} = \int d\vec{r} \frac{\partial \sigma_{\alpha\beta}}{\partial r_\beta} + \rho V g_\alpha$$

So, if I look at this we have three terms the first term ($\rho V \frac{\partial^2 \tilde{r}_\alpha(r_0,t)}{\partial t^2}$) is the term that defines the inertia of the system. The second term defines ($\int d\vec{r} \frac{\partial \sigma_{\alpha\beta}}{\partial r_\beta}$) the force due to stress and the last term ($\rho V g_\alpha$) defines the body forces.

It turns out that in most cases of interest in polymer physics the inertia and body forces are not so dominant. So, if we neglect inertia and body forces other way of saying that is the inertia and body forces are smaller in comparison to the forces because of a stress then we can drop both terms and then if I use the idea that the volume is small over which I am doing this integration what I can write is –

$$\frac{\partial \sigma_{\alpha\beta}}{\partial r_{\beta}}=0$$

This is what is known as the condition of mechanical equilibrium that is only true when the inertia and body forces are small in comparison to the forces because of stress.

Now the analysis so far is completely general in nature we have not specified what kind of material it is and the specification of the kind of material would come in the definition of my stress tensor σ we have not said what the stress tensor is. It turns out that we can write the stress tensor in terms of the history of deformation of material and that dependence would be different for example for a liquid solid polymer and so on. So, what these dependencies are called is constitutive laws or constitutive relations they relate the stress tensor with the history of deformation.

Now the question is how do we quantify the history of deformation so, there are two ways of doing it so the ways to describe history of deformation. The first one is known as deformation gradient tensor then you may have used this kind of a tensor in a solid mechanics course if you have done that. This tensor E is a function of the current time t and a previous time t_0 and given by $E_{\alpha\beta}$ that is a function of t and t_0 as the derivative of r_α with the initial position $r_{0\beta}$.

$$Deformation\,Gradient\,Tensor\,,\acute{E}\left(t,t_0\right):E_{\alpha\beta}\left(t,t_0\right)=\frac{\partial r_{\alpha}}{\partial r_{0\beta}}$$

So, let us say for example we have a deformation going from r_0 to r which in Cartesian coordinates is x_0, y_0 and z_0 not going to x, y and z then E would be a tensor which will have components-

$$\acute{E}=\begin{bmatrix} E_{xx} & E_{xy} & E_{xz} \\ E_{yx} & E_{yy} & E_{yz} \\ E_{zx} & E_{zy} & E_{zz} \end{bmatrix}=\begin{bmatrix} \frac{\partial x}{\partial x_0} & \frac{\partial x}{\partial y_0} & \frac{\partial x}{\partial z_0} \\ \frac{\partial y}{\partial x_0} & \frac{\partial y}{\partial y_0} & \frac{\partial y}{\partial z_0} \\ \frac{\partial z}{\partial x_0} & \frac{\partial z}{\partial y_0} & \frac{\partial z}{\partial z_0} \end{bmatrix}$$

So, the alternate way to look at the history of deformation is known as the velocity gradient tensor which is written as sum Kappa that is only a function of time in the current time not the previous time and this is written as-

$$Velocity\,Gradient\,Tensor\left(\acute{k}(t)\right):k_{\alpha\beta}(t)=\frac{\partial v_{\alpha}}{\partial r_{\beta}}$$

So, it turns out that Kappa tensor become useful for liquids and E tensor becomes useful for solids especially elastic solids and as we have discussed the polymeric systems can be in between the liquid and a solid so this may in turn affect depend on both E and Kappa. We will talk about these details later but for time being keep in mind that there are two ways to quantify one is my deformation gradient tensor that depends on the position at a previous time and the current position and a velocity gradient and tensor that depends on the velocity at correct current point and the position at the current point.

These two tensors can be related the E and Kappa. So, if I do a derivative of $E_{\alpha\beta}$what I do get is-

$$\frac{\partial}{\partial t}E_{\alpha\beta}(t,t_0)=\frac{\partial}{\partial t}\frac{\partial r_{\alpha}}{\partial r_{0\beta}}=\frac{\partial}{\partial t}\frac{\partial r_{\alpha}}{\partial_{r\mu}}\frac{\partial r_{\mu}}{\partial r_{0\beta}}$$

It means that we will sum over all possible values of μ that is 1, 2, 3 in Cartesian coordinates in 3 dimensions. So, if I look at the first term I can move the derivative with respect to time inside and then we have velocity v_{α} coming in there now the first part of it is by definition-

$$¿\frac{\partial v_{\alpha}}{\partial r_{\mu}}\frac{\partial r_{\mu}}{\partial r_{0\beta}}$$

Therefore,

$$\frac{\partial}{\partial t} E_{\alpha\beta}(t, t_0) = k_{\alpha\mu}(t) E_{\mu\beta}(t, t_0)$$

Although we have defined two different measures they are not unrelated they can be related by this equation. So, now I want to take this idea further on how is it ultimately useful because we have reduced the problem of working in terms of stress tensor to working in terms of deformations but we have not yet said how will we relate the stress tensor to the deformations and the answer here is looking at the free energies of the kind that we have discussed while doing the lattice models of polymers. So, when we are doing the lattice model we talked about something like a free energy density of polymer solutions Helmholtz free energy density f (ϕ) and we described the polymer behavior as a function of that free energy density. So, if we can try to connect these deformations or these stresses with that free energy we have now a way to derive the constitutive equation. So, of course the free energies would be different for different types of material. They may depend on the deformation tensor E on Kappa or may be both of them and that is how they will basically give me the dependence of a stress tensor on the deformation and that is the way to derive the constitutive laws that we are interested in.

So, we will use the basic idea that if a system is in equilibrium then if I do a slight hypothetical change near the equilibrium that work done for that change would be equal to the change in free energy we can say that only near the equilibrium because the whole idea of free energy will not become relevant when we go very far from equilibrium. We can talk about thermodynamic measures only near the equilibrium. So, if we talk in a state of mechanical equilibrium and if we do a small deformation in that case we can say that the work done would be same as the change in free energy so we first try to find the work done and then we will relate to a change in free energy and then finally we will apply to the case of a polymer network.

So, if I look at the work done to cause a deformation and that is near equilibrium, it is a small deformation near equilibrium. So, let us say I am at ‘r’ instead of equilibrium and from ‘r’ I deform to r + δu that is a function of r and if I want to find the work done for this deformation that would be simply the force that we have obtained multiplied by the deformation that I am giving to the system. It is a force multiplied by deformation again the force is calculated assuming that we have a state of mechanical equilibrium and that is why I am emphasizing the fact that we must be very near to the equilibrium.

$$\text{taking defromation}\,\text{¿}\vec{r} \rightarrow \vec{r}+\delta\vec{u}(\vec{r})$$

So it is:

$$\delta W=\int dS\,\sigma_{\alpha\beta} n_{\beta}\,\delta u_{\alpha}$$

So, we are also assuming one more thing here that gravity and other body forces are negligible. So, again you can use the divergence theorem I can replace the surface integration with a volume integration and I would have something of this sort-

$$\delta W=\int d\vec{r}\,\frac{\partial}{\partial r_{\beta}}\left(\sigma_{\alpha\beta}\,\delta u_{\alpha}\right)$$

You can see β and α both are repeated now both of them become dummy index which has to be the case because work done is a scalar quantity it does not have the dimensions. So, now if I apply the integration by parts here what I do get is this-

$$\text{¿}\int d\vec{r}\left[\delta u_{\alpha}\frac{\partial\sigma_{\alpha\beta}}{\partial r_{\beta}}+\sigma_{\alpha\beta}\frac{\partial\delta u_{\alpha}}{\partial r_{\beta}}\right]$$

Now you can notice that the first term would be 0 because of the condition of mechanical equilibrium that we had discussed earlier and the second term can be related to what is known as a strain tensor. So, it is the derivative of the small deformation that is being applied with respect to the previous position. So, the second term is strain tensor ($\delta E_{\alpha\beta}$) we have put a δ there just to emphasize that it is a small deformation and then again for the case of small volume around the material point we can drop the integration or if the deformation is uniform we can simply multiply that with the volume And essentially what we do get is something like this-

$$\delta W=V\sigma_{\alpha\beta}\,\delta E_{\alpha\beta}$$

So if I want to relate now the work done to the change in free energy, what we do get is a change in free energy per unit volume as-

$$\delta f = \sigma_{\alpha\beta}\, \delta E_{\alpha\beta}$$

When we are when we are doing this we have made basically a couple of assumptions and that become relevant for the materials one is that we assume that the body force is negligible that may not be true for all class of materials and second we are looking at small deformations around the equilibrium that again will not be true for many classes of materials. So, this is very limited relation that applies to materials such as the polymer networks we will discuss this is not a general relation so, as to speak.

So, now if I am now looking at say a polymer network or rubber is a polymer network, we are doing the case when there is no solvent in there when there is a solvent it is called a polymer gel that will have additional contributions to free energy but in this case it is a solid polymer network the rubber that you know. So, in that case it turns out that the free energy density is a function of E alone the free energy is a function of only the deformation gradient tensor and we will discuss why this is the case we will derive it formally later. But if we take for granted this relation that f is a function of E alone then we can write as-

$$f \equiv f\left(\acute{E}\right)$$

$$\delta f = \frac{\partial f\left(\acute{E}\right)}{\partial E_{\alpha\beta}}\, \delta E_{\alpha\beta}$$

So, now I will I have two relations for δf this one ($\sigma_{\alpha\beta}\, \delta E_{\alpha\beta}$) and another one is ($\frac{\partial f\left(\acute{E}\right)}{\partial E_{\alpha\beta}}\, \delta E_{\alpha\beta}$) and I can compare these two to get the relation that we are interested in that is the definition of the stress tensor. So, you can see here that although both of them contains α and β both of them are dummy indices in the in the two cases. So, we have to be somewhat careful while we are equating these two these two expressions. So, this is equal to-

$$\delta f = \frac{\partial f\left(\acute{E}\right)}{\partial E_{\alpha\beta}} \delta E_{\alpha\mu} E_{\mu\beta}$$

And how do we get this is ultimately-

$$\delta E_{\alpha\beta} = \delta\left(\frac{\partial r_{\alpha}}{\partial r_{0\beta}}\right) = \left(\frac{\partial r_{\alpha}}{\partial r_{\mu}} \frac{\partial r\mu}{\partial r_{0\beta}}\right) = \delta E_{\alpha\mu} E_{\mu\beta}$$

The first term will give me the strain tensor and second term will give me the deformation gradient tensor. So, now I can compare these two because both of them now contain the strain tensor epsilon okay. So, the only problem here is this has an index of α μ and this one has an index of μ α and this one here has an index of α β but keep in mind that both of them are essentially dummy indices. So, there is no harm if I interchange μ with β, so if I interchange μ and β what we do get is-

$$\left(\frac{\partial f\left(\acute{E}\right)}{\partial E_{\alpha\beta}}\right) = \delta \epsilon_{\alpha\beta} E_{\beta\mu}$$

$$\sigma_{\alpha\beta} = E_{\beta\mu}\left(\frac{\partial f\left(\acute{E}\right)}{\partial E_{\alpha\mu}}\right)$$

Now the problem with this particular relation is already although we already relate the stress tensor with the deformation it turns out that it does not take care of the fact that the material is incompressible so if the rubber is incompressible that is there is no change in the density of the material on deformation. So, in that case we have to be somewhat careful here and we have to add an additional term and the reason for that term is the system will respond to external forces-

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

So, if I say apply an external force on rubber it will deform and that deformation is not being captured by the change in the free energy. So, for incompressible materials we have to add an isotropic term where P is the pressure. So, as a rule the constitutive relations we derive using thermodynamic ideas will not really have incompressibility. Incompressibility is enforced by adding a term that is isotropic in nature that will give you a diagonal tensor in the stress matrix and that is will that will that will have terms containing the negative of pressure that is present in the system.

So, with this idea I now have the definition of the stress tensor for a polymer network. So, in the next lecture we will first discuss that what is the motivation for saying that free energy is a function of deformation gradient tensor and then using that we will come back to this relation and try to look at what is known as the elastic modulus of polymer networks and then we can show that if I have a different class of materials, let us say an ideal gas or a liquid their constitutive relations would be different but the approach that we follow to study deformations will remain very similar.

So, in conclusion the basic approach of continuum mechanics is very simple. We are defining a control volume around a material point P then we write essentially a force balance around that control volume. The force balance contains basically an inertia term and stress terms and a body force term and depending on the relative importance or magnitudes of them we can drop the terms which are negligible and then we can write the equation of motion for the system so as to speak that equation of motion is still general in nature what we also need is a constitutive law that relates the stress tensor with the deformation gradients and for the case of polymer networks we have shown that it can be written in terms of free energy that is a function of the deformation gradient tensor that is not a general idea I want to emphasize again that can apply to all types of systems. Okay.

So, I conclude with this here, thank you.