Introduction to Polymer Physics
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Lecture-60
Maxwell Model- II, Closing Notes

Hello everyone welcome to the last lecture of the introduction to polymer physics course. In this lecture I will go back to the Maxwell model that we have been doing and we do one more example and then we also try to conclude this entire course and give you some future reading if you want to learn more about the polymer physics in general.

So, just to remind what we have been doing, we were doing the spring dashpot model in which we look at the response to an applied stress that give rise to different strains or amount of shear and accordingly give rise to different rates of the same and we can define the net stress because the two elements are in series we can talk in terms of their modulus and viscosity, respectively. The shear and shear rates in the viscous and elastic elements are

$$\gamma_v(t), \acute{\gamma}_v(t) \wedge \gamma_e(t), \acute{\gamma}_e(t)$$

Therefore,

$$\sigma(t) = G_e \gamma_e(t) = \eta_v \acute{\gamma}_v(t)$$

This was the Maxwell model that we have been doing.

So, I want to do one more example to show that why this model explains the viscoelastic behavior and the example is of a constant shear rate as opposed to a constant shear that we discussed in the last class. So, let us say instead of the shear we talk up the of the shear rate at time t = 0. We start applying a constant shear rate-

$$\acute{\gamma} = \acute{\gamma}_0$$

$$\acute{\gamma}(t) = \acute{\gamma}_0 \theta(t)$$

And we want to look at the response of the system as a result of this particular deformation, so we can look at the individual shears and shear rate in the two elements and based on that we can look at the behavior of a system. The key point here is as opposed to the last case where we are doing a constant shear and the stress relaxed to 0. In this case that is not going to happen because even at long times the material is flowing, it's a liquid, and since we are working at a constant shear rate we will have a constant stress in the end as opposed to 0 stress that we had in the last class because the shear rates vanished at long times.

In this case the shear rate is assumed to be constant from time t higher than 0 to infinite times that is the reason we do not go to 0 stress towards the end. So, with this idea I can again look at this system starting from first looking at the overall shear rate that would now be sum of the shear rate in the elastic element and the shear rate in the viscous element. Just remember that when we have been doing earlier we were doing in terms of shear in the last example now we are doing in terms of shear rates because that is what is being held constant.

$$\acute{\gamma}_0=\acute{\gamma}_e(t)+\acute{\gamma}_v(t)$$

So, this would give us –

$$\acute{\gamma}_v(t)=\acute{\gamma}_0-\acute{\gamma}_e(t)$$

Therefore,

$$\sigma(t)=\eta_v\acute{\gamma}_v(t)=G_e\gamma_e(t)$$

We are choosing to write this in terms of $\acute{\gamma}_0$ - $\acute{\gamma}_e$ that would simplify the analysis. So, now you work in γ_e and $\acute{\gamma}_e$ terms. In the last example we worked in γ_v and $\acute{\gamma}_v$ terms. So, this would give me again-

$$\sigma(t)=\left(\frac{\eta_v}{G_e}\right)\left(\acute{\gamma}_0-\acute{\gamma}_e(t)\right)=\gamma_e(t)$$

$$\frac{d\gamma_e}{dt}=\left(\acute{\gamma}_0-\frac{\gamma_e}{\tau}\right)$$

So, in this case in the last case what we had was the viscous element was starting from 0 shear to begin with because we were applying a constant shear. In this case we apply a constant shear rate and so the elastic element starts from 0 and the viscous element starts from the high value. So, it is opposite of what we had in the last example so it is 0 and then finally we will have some $\gamma_e(t)$ and this is my time. So we have –

$$\int_0^{\gamma_e(t)} \frac{d\gamma_e}{\acute{\gamma}_e - \frac{\gamma_e}{\tau}} = \int_0^t dt$$

So, if I do the integration what we have is –

$$\ln\left[\frac{\acute{\gamma}_0 - \frac{\gamma_e}{\tau}}{\gamma_0}\right] = \frac{t}{\tau}$$

Because we will have a τ coming from the integration because we have γ_e/τ here and then this is going to have the on solution what do I get is also a minus sign here. So, what we have is –

$$\acute{\gamma}_0 - \frac{\gamma_e(t)}{\tau} = \acute{\gamma}_0 \exp\left(\frac{-t}{\tau}\right)$$

$$\gamma_e(t) = \tau \acute{\gamma}_0 \left[1 - e^{\frac{-t}{\tau}}\right]$$

Now I can go ahead and find $\acute{\gamma}_e$ which is going to be –

$$\acute{\gamma}_e(t) = \acute{\gamma}_0 e^{\frac{-t}{\tau}}$$

$$\acute{\gamma}_v(t) = \acute{\gamma}_0 - \acute{\gamma}_e(t) = \acute{\gamma}_0 \left[1 - e^{\frac{-t}{\tau}}\right]$$

So, this is what we get from here so we can also get the stress tensor for this case as –

$$\sigma(t) = G_e \sigma_e(t) = G_e \tau \acute{\gamma}_0 \left[1 - e^{\frac{-t}{\tau}}\right] = \eta_v \acute{\gamma}_v(t) = \eta_v \acute{\gamma}_0 \left[1 - e^{\frac{-t}{\tau}}\right]$$

And both are same because we have defined η_v¿G_e as our τ .

So, this is perfectly consistent with what we had earlier except the profiles look very different here because now we apply a constant shear rate as opposed to a constant shear. So, in this case now if I see I will have different profiles for everything. So, now if I look at my stress, the stress is going to start from 0 and settle to a maximum value that is given by $\eta_v \dot{\gamma}_0(t)$ that is my σ (t). So, instead of stress relaxation now we have a development of a stress. I can do other profiles similarly so if I look at for example our γ_e and γ_v , so γ_e will start from 0 and settle to some $\tau \dot{\gamma}_0$. If I look at the γ_v it is going to be just opposite of that which we can get by integration. So, if I integrate this I will get the expression for $\gamma_v(t)$ which is going to be essentially opposite of what we had for the case of γ_e and the $\dot{\gamma}_e$ will be something like this because I am not doing all the plots but you can see that this kind of works out similar to what we had earlier. Now I want to finally demonstrate that the Maxwell model is also consistent with the idea that we have discussed that the relaxation modulus can be used to find the steady state viscosity that is the viscosity that you have at longer times. So, we want to so that that steady state viscosity is same as the viscosity of the viscous element in the case of a Maxwell model.

So, for that I want to go back to the stress relaxation experiment because that is what is used to define the steady state viscosity. So, for that case the relaxation modulus is given is defined as the ratio of the stress to γ_0 and it turns out to be –

$$G(t) = \frac{\sigma(t)}{\gamma_0} = G_e e^{\frac{-t}{\tau}}$$

And we have defined that the steady state viscosity as –

$$G(t)\,dt = \int_0^\infty G_e e^{\frac{-t}{\tau}}\,dt = \left[-G_e \tau e^{\frac{-t}{\tau}}\right]_0^\infty = G_e \tau = G_e\left(\frac{\eta_v}{G_e}\right) = \eta_v = viscosity\ of\ the\ dashpot$$

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$$\eta_s = \int_0^\infty \text{¿}$$

So, essentially even if we started from a phenomenological model what we have been able to establish is first this very simple model explains the behavior of the viscoelastic material under different circumstances and second the parameters or the material parameters I have defined for this model holds true for the case of the steady state that we can obtain at very long times. So, therefore the Maxwell model is I would say one of the most commonly used models in the treatment of viscoelastic materials for its inherent simplicity and the fact that we can associate meaning to the parameters that we have in the model.

So, there are further extensions for the Maxwell model and there are more detailed constitutive models that apply for different class of polymers in the interest of time I am not going into the details here. So, I want to conclude my, the discussion of the rheology part by saying that we have a whole set of experimental tools nowadays to analyze the flow and deformation behavior of polymeric systems and we need to be able to get and we can get the constitutive laws using those experimental measures and using that constitutive law then I can finally look in detail on the flow and deformation behavior of polymeric systems.

So, with this last point I want to conclude this course on introduction to polymer physics. So, I want to just quickly recap what we have done in this course so we have done three or four major topics.

In the very beginning we looked at statistics of a single polymer chain in terms of random walk models which was essentially a toy model but it contained a lot of physics and a lot of similarity to what we see in polymer chains. Then finally we went to the thermodynamics of polymer solutions we looked at what is known as the Flory-Huggins theory of polymer solutions again it was sort of a model that was a toy model that was able to explain the thermodynamics quantities such as osmotic pressure, chemical potential, Gibbs free energy of the polymer solutions and also to look at the phase separation and mixing behavior of polymer chains then we looked at the Brownian motions of polymer chains in terms of the Langevin equation we discussed the roused models the Zimm models which varied in their level of rigor and then finally we started looking at the flow and deformation of materials.

We first reviewed the principles of continuum mechanics we discussed how they need to be revised in the context of polymer systems and finally we did the rheology of polymer systems mainly looking at the experimental aspects or practical aspects of rheology as opposed to the theoretical aspects.

So, the polymer physics itself is a very I would say a very mature field and there is a lot more that we could not cover in this particular course. Some of the interesting topic if you are further interested is the topic of self assembly of polymers particularly block copolymers. There is lot of research going in the area of polyelectrolytes then there is a lot of work in the in the area of biopolymers such as DNA and other molecules again there, there is lot of similarity with the principles we have covered in this course but we have not really discussed the biophysical principles that works there in those cases and we tried to do the, I would say a significant amount of math that was required to understand the basic principles but you must have noticed that towards the end especially in the discussion of polymer dynamics we have been rather brief for example in the case of a Zimm model and the reason is like it was very difficult to pack in in this in these 30 hours.

If you want to learn more about the derivations that we did you can refer to I would say 2 or 3 books. The first reference is Soft Matter Physics by Doi and I will give a list separately in the course then there' is another book on Introduction to Polymer Physics. I would say that these two books pretty much cover most of the material that we have discussed in the in the class in this particular course although I have not really gone in any particular order. If you want to know more about the derivations used in the polymer dynamics part. I would refer to the book on Theory of Polymer Dynamics by DOI and Edwards and finally at times in the course we alluded to the scaling idea of de Gennes and other although in this course we did not really go into details of any of that that is a whole another approach to look at polymer systems representing a polymer molecules as set of blocks. So, if you want to know more about the scaling theories I would refer to the classical book Scaling Concepts in polymer physics by de Gennes and there is another recent book on Polymer Physics by Rubenstein and of course there are many other books that you can refer to.

So, I hope that you enjoyed this particular course and I hope that this course finds use in the things that you are interested in particularly for people who are research oriented I would say that this is an extremely useful course because this is a rather hot area in in terms of materials research but even those who are working in industry would find use in applying these principles that we have covered in understanding certain aspects of polymer processing in industry and looking at the behavior of different polymeric materials that we use in many industries such as the food and packaging industries.

So, with that I want to conclude the course, thank you.