# Rheology of Complex Materials
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## Lecture – 31
## Relaxation time spectrum 2

So, what we have done in this exercise is chosen a different set of relaxation times and we use Maxwell model to you to characterize the relaxation time.

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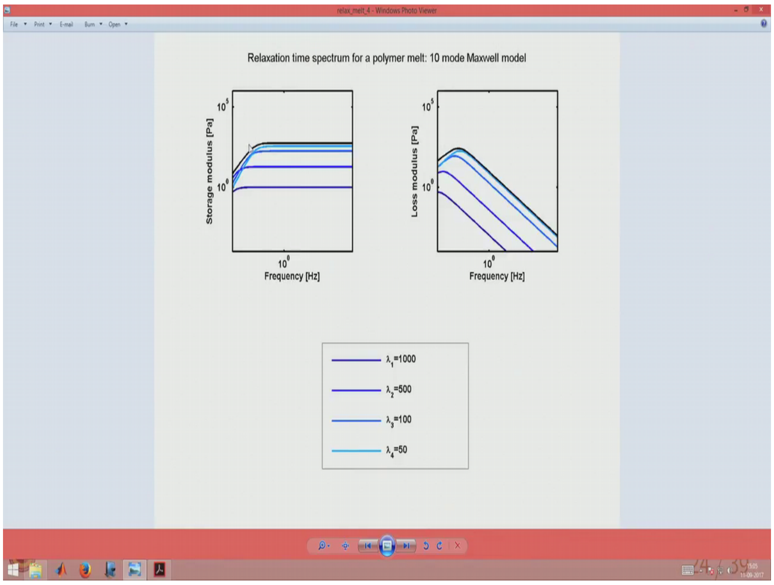

For example, we have chosen let us say lambda 1 equal to 1000 and since this is a very large relaxation time the overall material response is pretty much elastic right because the relaxation time is very large. So, you can see that g double prime is already decreasing and g prime is already constant. Now if I take another relaxation time which is lower right. So, 500 and now what you have to see is the black actually is the one which is sum of the 2. So, the 2 blues are actually the blue and black is on top of each other. So, the other lambda 2 is this 500. So, you can see now that the maybe I will add one more and then you can see it more clearly ok.

Now, you can see that we are shifting the g double prime peak is shifting to the right, because we are going to smaller and smaller lambda that is what we had said if you recall that on the left hand side we are probing the longest relaxation time, when we go to the right we are probing the shortest relaxation times. Now let me add one more and again you can see that you can see how the curve is also changing the black, when I add the all relaxation modes together I now start seeing a response which is.

Student: That means, black is cumulative.

Yeah black is cumulative it is adding all the relaxation modes together and so, initially if you see the response was completely this, where it is almost elastic material I would conclude because that is only one relaxation mode. Now if I add four relaxation modes this particular material when I probe, it looks like it is giving me viscous and elastic both. So, it is viscous for some small frequency range, though I may not be observing terminal viscous response under these conditions because the slope may not be 2.

Student: (Refer Time: 02:23).

Right, but now if I start adding more and more probes you can see that the black curves.

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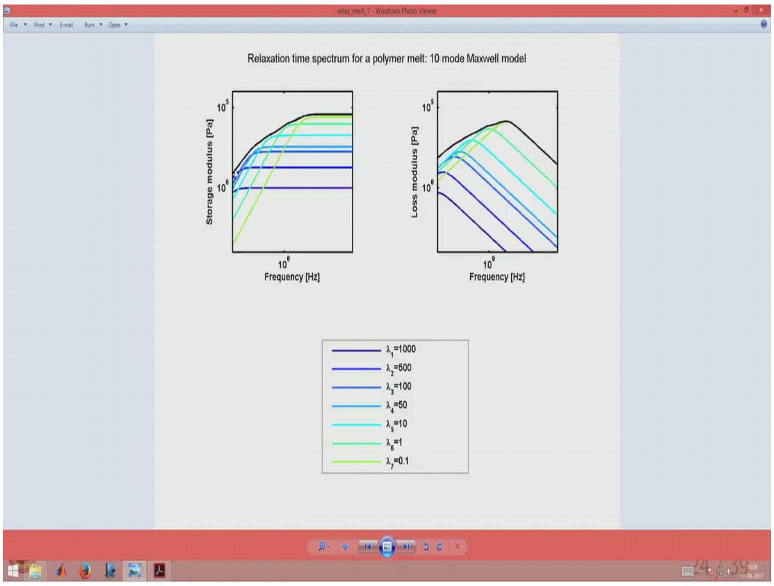

Now, I have to go to higher and higher frequency to actually see elastic response, because now I am adding even the relaxation mode, which is point one which is very small and so, this is the 10 mode Maxwell model.

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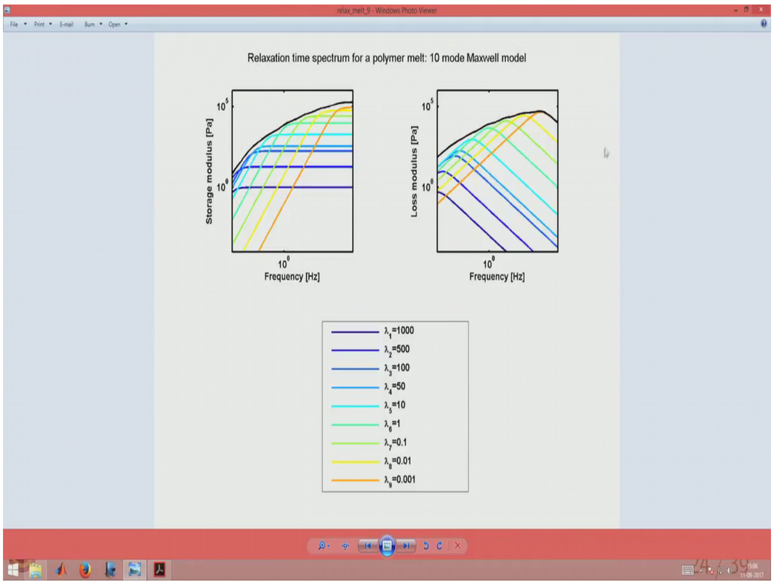
Relaxation time spectrum for a polymer melt: 10 mode Maxwell model

So, we have now added 10 relaxation modes and in fact, now if you see g prime and g double prime it is very similar.

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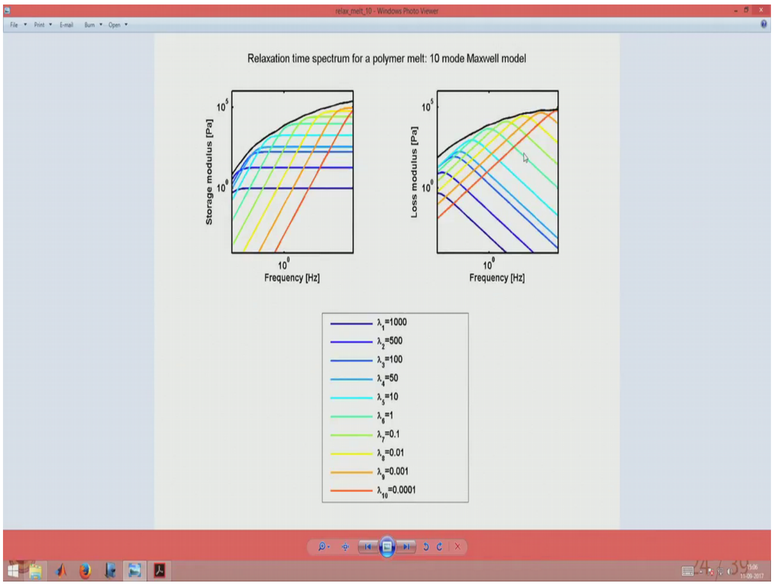
Relaxation time spectrum for a polymer melt: 10 mode Maxwell model

To what we actually talked about for polymer melt right just to remind us.

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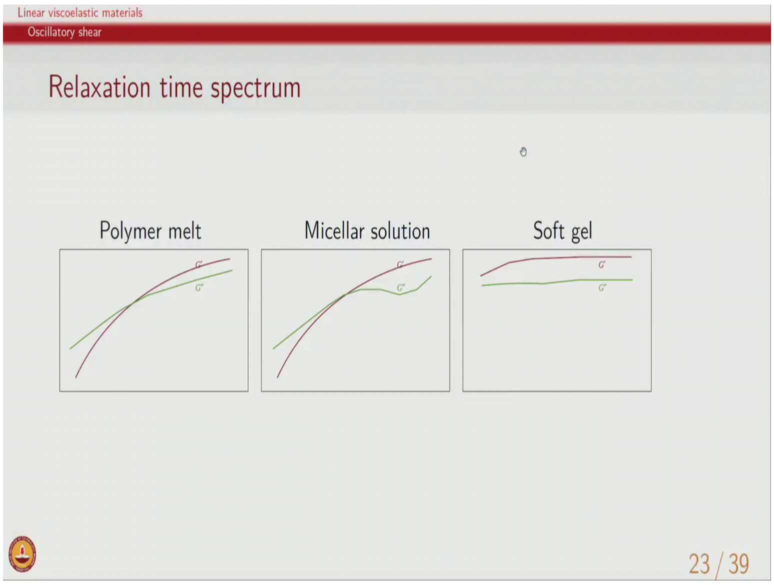

Relaxation time spectrum

Polymer melt

Micellar solution

Soft gel

This is the polymer melt. So, g prime increases, g double prime also increases g prime really does not become constant and g double prime also there is no maximum that is usually there for Maxwell model. So, you can see that how combining 10 relaxation modes we have now described the behavior of polymer melt.

Now, in this we can clearly say that the 1500 those relaxation modes are associated with reputation, then the relaxation modes which may be 50 10 those may be with segmental relaxation, and then they relax 0.1, 0.01 there is may be sub segmental relaxation and so on right and if we go to 10 to the power of minus 5, 10 to the power minus 6, 10 to the power minus 9 is where vibration nanoseconds and all is where bond vibrations and all come in right. So, that is. So, that is how we are probing the material at different frequencies and different time scales.

So, combination; so, if I have to understand polymer melt rheology, I must have a always an idea of what the relaxation modes are. So, that is the power of linear viscoelasticity or the oscillatory shear. I can probe and find out the relaxation time spectrum of the material and of course, it is up to me to now figure out what each of those modes are. So, generally I will have to do some other set of tests also. So, in case of polymer melt maybe I should do some dielectric spectroscopy, maybe I should do some other measurements again where I can probe different types of molecular motions, and then I can confirm that my hypothesis about 1005 being reputation modes the those other ones being segmental modes it can all be justified.

For example one clever experiment which was done was that if the overall molecule response is related to dielectric, while the segmental relaxation is not related to dielectric then if I do both together, I can show that oh look under these timescales I can see the overall reputation motion, while in other case I do not see. So, therefore, there is always a different types of mechanisms that have to be studied by looking at combination of different techniques. In from rheology we can only give a hypothesis it needs to be confirmed using several other techniques.

Now, let us look at the other example that we saw which is a Micellar gel system right where we said that it is a g prime sort of undergoes from viscous to elastic, and then g double prime actually shows a minimum which is associated with breaking and forming and again this can also be explained using.

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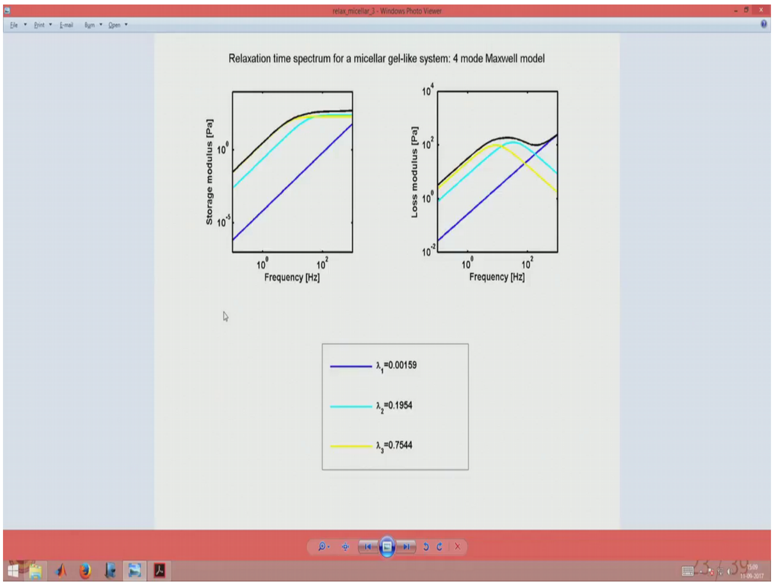

So, this is one relaxation mode what would we say the responses.

Student: Viscous.

Viscous completely right and. So, now, if I increase the relaxation time now I start getting some.

Student: (Refer Time: 05:57).

Elastic response, if I increase further I get further elastic response and I you can also see now in the black curve how the minimum has appeared. So, in this also minimum has appeared.

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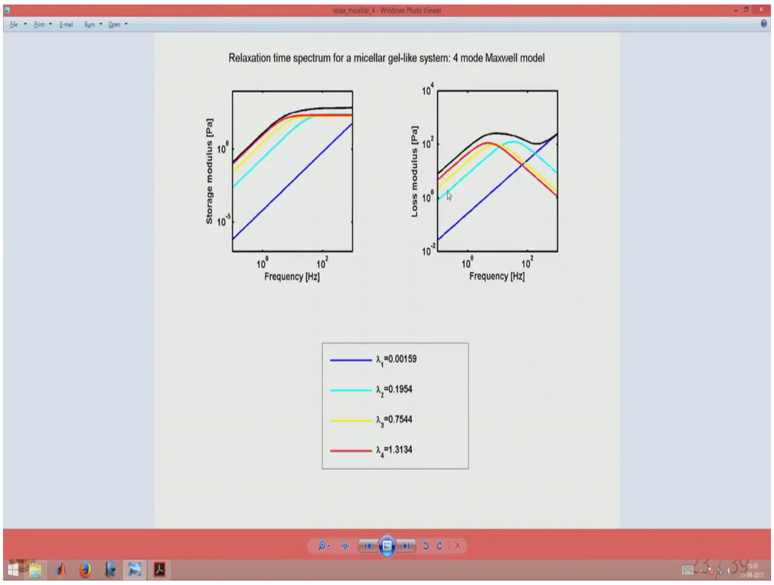

Relaxation time spectrum for a micellar gel-like system: 4 mode Maxwell model

So, clearly in this case I need to combine and in the end now I have a g prime which goes from terminal viscous to terminal elastic, and the g double prime which goes from viscous and then goes through a minimum.

Student: Minimum.

So, this is now a four more relaxation model. So, in this case also then we will have to try to explain what each of these modes might imply.

Student: The way keeping concentration constraint.

This is one material system only you are examining right.

Student: Yes.

This is the black curves supposedly you are getting are by doing experiment on one material, and it is our basic idea that each and every material is has several relaxation modes. Because there are relaxation processes which are happening in the material and by probing the material at very low timescales or high timescales, I am probing different types of relaxation processes. If I say that I have I understand the material well, then I should be able to explain all the relaxation processes.

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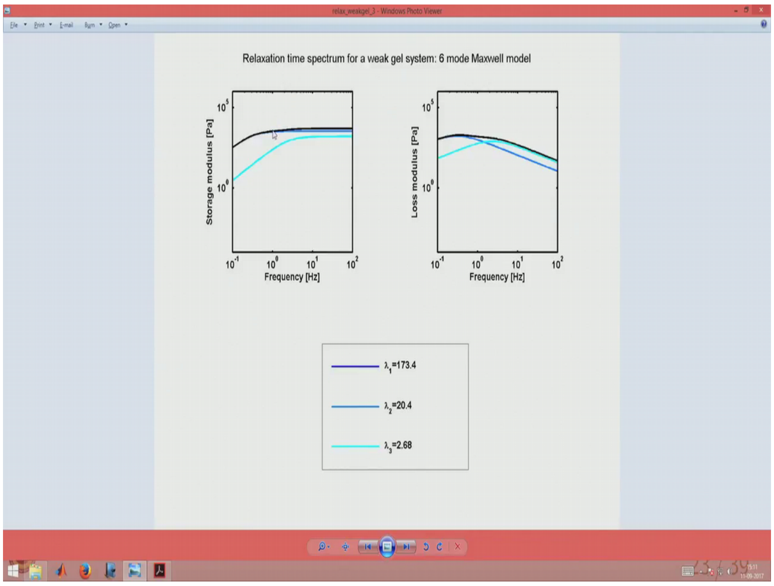

Now, let us look at the other example of the week gel. So, you can see here lambda one very high will get me elastic response and then the second one also pretty much gives me overall elastic response and then because of the elastic response the g double prime is decreasing. Now if I add another relaxation mode in this the g prime still appears to be not changing much, but now g double prime is not decreasing as much.

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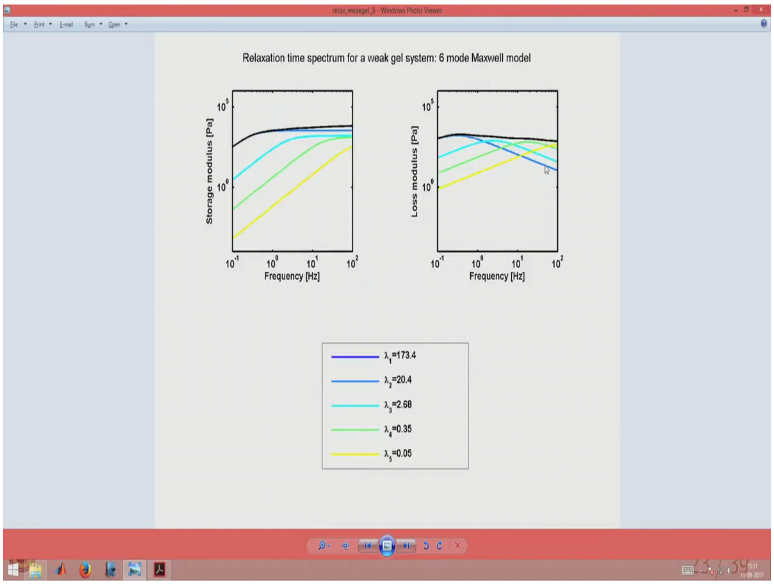
Relaxation time spectrum for a weak gel system: 6 mode Maxwell model

And now by doing this 6 modes of this I get basically g prime is almost independent g double prime also seems to be almost independent.

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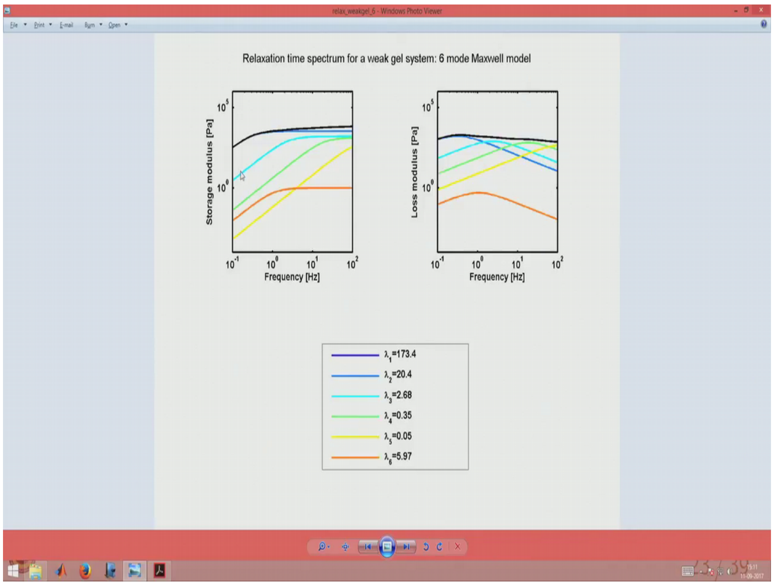
Relaxation time spectrum for a weak gel system: 6 mode Maxwell model

But actually it is a combination of several relaxation modes, and these relaxation modes. In fact, give may be more elastic or more viscous responses it is the sum total of those that appear to be what when we do the experiments, and get these black kind of curves. So, it is always our aim to actually look at the underlying mechanisms, and one important way in which we understand these underlying mechanisms is if we can change them systematically.

So, when we when we do let us say one material and get such response and we are making hypotheses about these relaxation modes we should have a systematic way of verifying it, quite often systematic way of verifying it is by saying that by changing concentration, by changing temperature, by changing compositions. So, by doing all that if I am able to explain the phenomena well then yes my hypothesis is stronger and as I said earlier if we of course, probe the material using some other techniques; either molecular techniques or microscopic techniques. So, that we also try to get hints about the same mechanisms by alternate means then our understanding of the material becomes more and more complete. How do we get it will completely depend on the specific material, there is no such general blueprint that if I get this kind of a curve I must be this might be. So, do we know something about the material what is it is microscopic feature.

Student: Yes.

What is the. So, so all that we need to do and then we can start making the hypothesis.

Student: (Refer Time: 09:26) part we get other colors.

Yeah.

Student: (Refer Time: 09:27).

Exactly yeah also by the way this is an ill posed problem in a mathematical sense in the sense that multiple combinations of different lambda can give you the same black curve right. The overall response need not be one unique combinations of relaxation modes. So, that is why it is called an ill posed problem, you cannot just because I get total black curve with complete 100 percent certainty, I can never say that yes these are the only relaxation modes because several combinations of the relaxation modes may still give me the same. So, therefore, it is always a tricky enterprise to try to say that I have the most representative and realistic relaxation time.

The one other thing you can see here is if I start adding relaxation time, I will of course be able to describe any material system, but then I should know because basically when I add more and more relaxation time I have more and more fitting parameters.

Student: Yes sir.

And we know that when we do a curve fitting with very large number of parameters, it is not easy to explain physical significance of all the parameters.

Student: Yes.

So, we should always try to strive hard by achieving the same result with as minimum number of relaxation modes as possible. So, this is like a 2 this thing.

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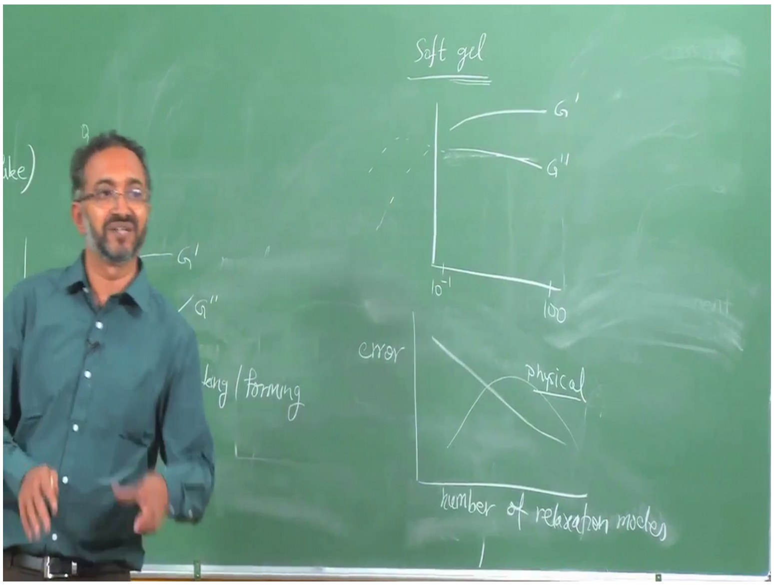

So, the overall error that we get and the number of relaxation time right number of relaxation modes, certainly the error will decrease as I increase the number of relaxation modes. The error between what is my overall prediction of what the material system and then what I experimentally observe. But it does not mean that I continue to increase right because beyond a certain time the physical significance. So, so physical significance probably is like this that if I have. So, this is just a hypothetical picture if I just use one or 2 more relaxation modes then it is difficult to explain the material because I am combining several things and explaining it using one parameter, then it becomes difficult. If I take too many parameters then again to explain physical significance becomes more difficult and. So, therefore, it is somewhere in between is what I need to look at. So, for example, if I have a the hypothesis that certain mode takes milliseconds right.

Student: Yes.

Or certain mode takes seconds, then I if I do microscopy and I capture either using fluorescence or something I can use the and capture that and that timescale also seems to be the same that I have made a hypothesis out then I can say that the 2 are matching.

For example I have a colloidal system and some particle motion, I have some feature which is associated with let us say few seconds, then I can look at microscopically and make a video out of it, and then look at the motion of a particle and then try to see what is the time scale involved in it is motion. Of course, there will be a very long term timescale in which case the material will the particle would appear to be flowing that is very long time scale, but somewhere in between I will see that oh there seems to be a timescale associated which is few seconds. So, then I say good the hypothesis that I made seems to be matching.

Student: How that a computation error constant like c one c 2 c three various.

Yeah. So, those in fact, if you recall Maxwell model is a 2 parameter model.

Student: Yes.

So, lambda 1 and g or lambda 1 and eta.

Student: Eta.

So, in this case eta is also being manipulated. So in fact, when we say it is a 6 mode Maxwell model we have 12 parameters, and when we said that it is a 10 mode model we have 20 parameters.

Student: (Refer Time: 13:25).

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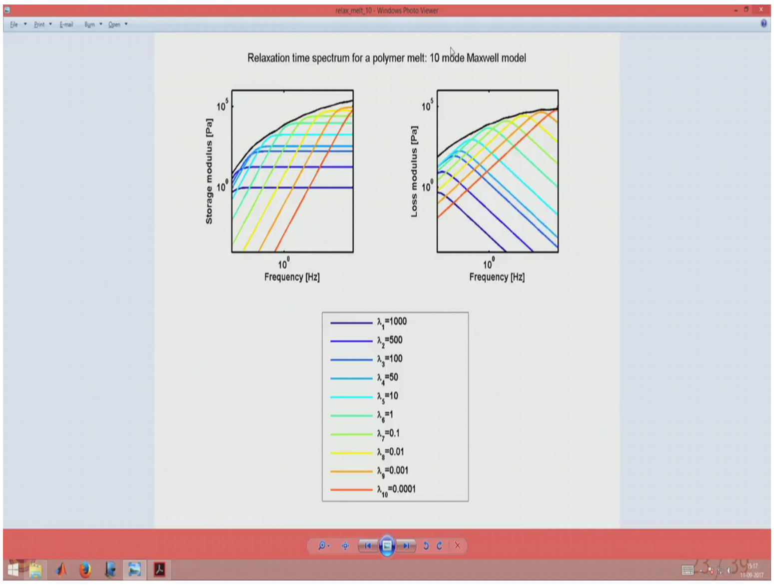

So definitely the larger number of parameters is not very good right in terms of explaining. Sometimes of course, if we want to do we want analytical expression, and we want to do some further work then we use brute force technique to do cu, but in that case we are not looking for physical significance using this for example, if I have to use let us say I have to use this kind of a model to do some other flow simulation, I am trying to simulate let us say flow in a dye and I need as realistic model as possible.

So, I will just take these and then try to simulate because my real interest is in looking at the simulation result, but if I am un explaining if I want to understand you know if I change the molecular weight of the polymer, how will this change. If I change the branching of the polymer will this change. So, if those kind of question then I better understand what each of these modes imply, is any of these modes affected by branching is any of these modes affected by molecular weight. So, then only I will be able to explain ok.

I think maybe this may be a good time to stop we will. So, in the next class we will now look at the idea of time temperature superposition, because the fact that material has different relaxation processes, there are different relaxation times and using temperature we can manipulate those relaxation times. So, keeping the experimental time scale the same we can actually change the material timescales. So, that is the idea behind time temperature superposition, so that we will take a look in the next class.