Physico - Chemical, Mechanical and Electrical Properties of Polymers

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Lecture - 42
Dielectric Response II

Hello, we will continue our discussion, related to the dielectric response of polymeric systems. In this week, we are spending quite a bit of time, learning about different properties of these polymer systems. And, we have already discussed, the ideas related to conducting polymers, where, mainly the dissipating property of, electrons being delocalized and forming a current is the phenomenon which is of importance.

Then in the last lecture 41, we looked at that polymers, because of the inherent relaxation phenomena which are associated with that always incorporate dissipative phenomena even for a dielectric response. And so therefore, we always have this combination of dielectric and conducting response in case of polymers.

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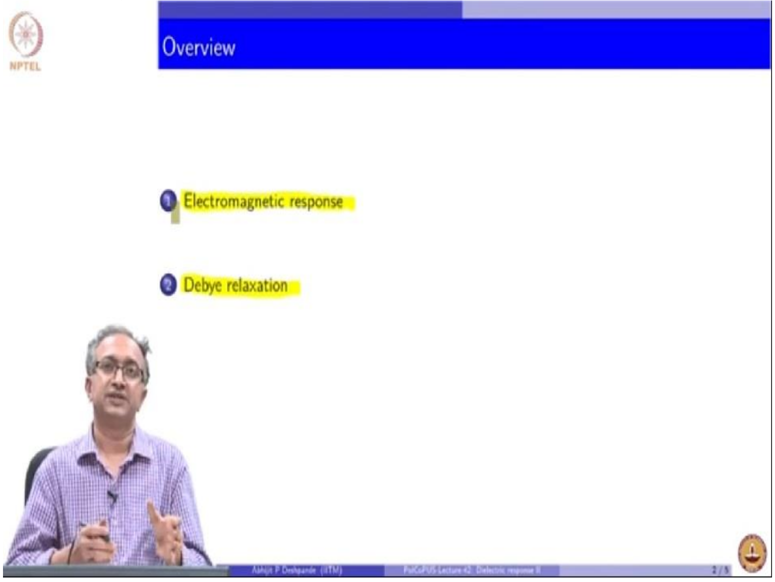

Overview

1. Electromagnetic response
2. Debye relaxation

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So we will see an example of how this happens for dielectric materials by looking at a process called a Debye relaxation. It’s a simple model to describe molecular polarization in polymers. And, before we do that we will look at the overall idea of electromagnetic response. Electromagnetic radiation from very low frequency to very high frequency such as microwave, even high frequency is basically light, visible light and even higher frequencies are radiation like x-rays and so on.

So therefore, electromagnetic radiation forms this vast frequency domain range. And of course for our course purposes, Debye relaxation is of interest generally in a few Hz to kHz to MHz range. And so that is the range where a dielectric response of polymers is also of great interest. But many of the features that I discussed here are common. Even if you look at let us say microwave response of polymers.

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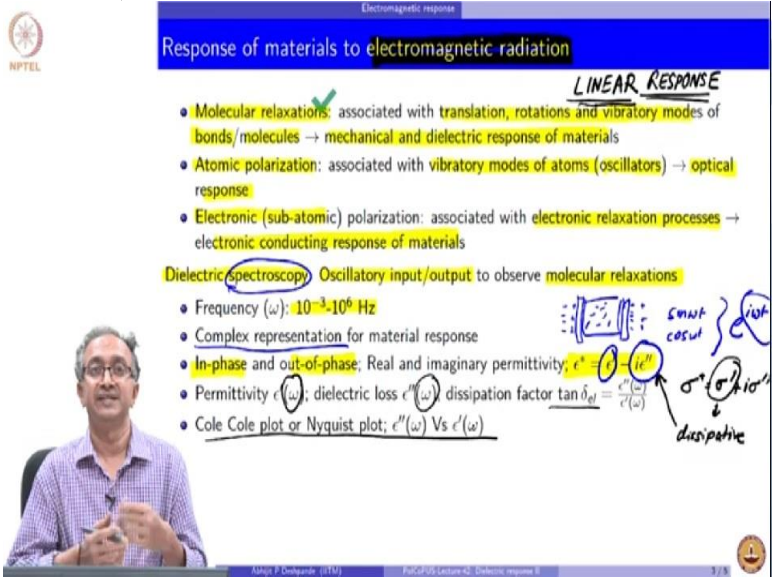

Electromagnetic response

Response of materials to electromagnetic radiation

LINEAR RESPONSE

- Molecular relaxations: associated with translation, rotations and vibratory modes of bonds/molecules → mechanical and dielectric response of materials
- Atomic polarization: associated with vibratory modes of atoms (oscillators) → optical response
- Electronic (sub-atomic) polarization: associated with electronic relaxation processes → electronic conducting response of materials

Dielectric spectroscopy: Oscillatory input/output to observe molecular relaxations

- Frequency (ω): 10^{-3}-10^{6} Hz
- Complex representation for material response
- In-phase and out-of-phase; Real and imaginary permittivity; $\epsilon^* = \epsilon' - i\epsilon''$
- Permittivity $\epsilon'(\omega)$; dielectric loss $\epsilon''(\omega)$; dissipation factor $\tan\delta_{el} = \frac{\epsilon''(\omega)}{\epsilon'(\omega)}$
- Cole Cole plot or Nyquist plot; $\epsilon''(\omega)$ Vs $\epsilon'(\omega)$

And so the response of the polymeric materials to electronic electromagnetic radiation is basically depends on which part of the atomic molecular systems are polarizing or responding to the electromagnetic radiation. Of course, we are only looking at the electrical response for these course purposes, as polymeric materials have a most relevant, properties in the electrical domain. However, in general, materials can be electrical response or can give a magnetic response. And so, in a response to an electromagnetic radiation material can polarize, or it can magnetize also. So, but we are focusing only on the electrical domain. And so therefore, which part of the atoms or molecules or sub atomic entities respond to these electromagnetic radiation, will determine what is the type of response we get. In all of this of course, we are not looking at nuclear processes.

And so the attention most often is to electron or atoms and molecules. So, at, lower frequencies generally, because the timescales that are associated with lower frequencies and the timescales which are associated with molecular relaxations are similar. So therefore lower frequencies we have what are called molecular relaxations which are associated with basically translation, rotation, and vibrations of atoms and molecules. So bond flexibility, molecular flexibility.

You can immediately see a connection between the molecular relaxations and glass transition that we talked about. So using a technique which can capture these molecules relaxation in response to electromagnetic radiation, we should be able to capture the glass transition in the material. So glass transition should be possible to be measured if we can characterize, whether molecule relaxations are present or not.

What do we mean by molecular relaxation? It's the presence of basically a dipole which is along with the bond in the system. And so if these bonds can rotate and vibrate and translate then clearly that implies there is flexibility. But if these dipoles cannot orient themselves then that implies lack of flexibility. So therefore molecule relaxations are very crucial in terms of determining the overall mechanical or dielectric response of the material.

Because the molecular relaxation possible or not possible will make the material rigid or flexible or make the material a good dielectric or not such a good dielectric. On the other hand, if we go to higher frequencies then we have atomic and subatomic polarizations. This is where the atom or sub atom electrons respond. And, so you can have vibrations of the atoms itself. We analyse them as just an oscillator and we can get basically the optical response of the material. So refractive index, if we want to understand, we have to look at the atomic polarization processes. And clearly the frequency range is higher because light, basically the frequency range is 10^{14} and thereabouts. So therefore we are looking at much smaller entities of the material which are responding to that electromagnetic radiation. Electronic relaxation processes on the other hand will lead to conduction of electrons. So we are looking at a subatomic polarization in that case.

So one of the ways in which we can, understand the overall polarization in the material in the form of a molecular relaxation which is what we will focus more on this course is by looking at, the dielectric spectroscopy of the material. When we say spectroscopy, we basically apply different frequencies. So, electromagnetic radiation or current or voltage will be applied in all different frequency. So we can apply one mV as a signal at different frequencies. And that is what we mean by applying electromagnetic radiation to the material.

So basically we are, applying an oscillatory input and then, output is being measured to observe the molecular relaxation. You can think of it this way also that if we have a material which has a certain dipoles and now if we are applying electric field on it, which itself is a oscillating. So which means at some point, this will all be plus and some other point this will all be minus

while at some point this will be minus some other point this will be plus. So these dipoles will have a tendency to either orient in the one direction or the other. And so if oscillating field is applied then these dipoles will also start oscillating. So, depending on what is the frequency of oscillation these dipoles may get enough time to oscillate or they may appear to be frozen. So therefore, spectroscopy is an idea in which we apply the experimental timescales at different rates.
And since material timescales is based on the mechanisms in the material, based on the temperature at which we are, we can therefore then measure the overall dielectric response of the material. And so, given that we have talked about in-phase, out of phase in the 41st lecture also, so, complex notation is very useful, to look at such in-phase out of phase. You can always remember that sin (ωt) or cos (ωt) and then $e^{i\omega t}$.

So we can use complex notation to describe sinusoidal functions. And so same, tools of a complex algebra are used to describe the permittivity which is in-phase and out of phase has a complex permittivity. So ε' which is related to the energy storage or which is related to the capacitive response of the material is basically that part of material response where dipoles can orient and they can return. While ε'' is related to the dissipative response and therefore that leads to charge displacement or related to loss or related to current in the material. So clearly conductivity and ε'' will be related to each other. So just the way for a dielectric we have in-phase as well as out of phase component for a conductor also, we will have in phase and out of phase component.

And, here the in -hase component is dissipative and this is related to ε''. Now, just to think of why is it that the real part of permittivity is related to imaginary part of conductivity. To think about this, you can just think in terms of the input output variable that are involved, and is there a derivative involved in these relationships. With that you should be able to address this question of why real part of one quantity is related to imaginary part of the other.

$$\epsilon^* = \epsilon' - i\epsilon''$$

But important thing again in all of this is to also think in terms of energy storage, energy loss. If you think in those terms, then you will not be misled into connecting quantities which are let us say not related to each other. So therefore, permittivity and it is complex notation can be used to describe the overall response of the material system. One other thing that we ought to remember here is again, we are discussing all of this for linear response.

And right in this slide, can you see where is the assumption of linear response very evident in the way I have written the response variable? So permittivity is written on the slide, and it is said to be a function of frequency alone. It is not a function of current or voltage or electric displacement or electric field which is being applied. So therefore, we are only looking at linear response.

One other way, in which you can think of this linear and nonlinear response, is the following way that if we apply a frequency ω, and if the response is also in ω, then it is a linear response. But if we get other harmonics, so for example, 2ω, 3ω then we have nonlinear response. So for this course purpose, most often we will confine our attention to linear response. However, nonlinear response is also extremely interesting and whether it is in dynamic mechanical properties, or whether it is in rheology or whether it is dielectric response, a nonlinear response is a fascinating field to understand the material response. Especially because; many of the engineering applications inputs to the system to the material system can be reasonably high where the nonlinear response of polymers is important.

So we can just look at the frequency variation of let us say loss factor or dissipation factor or the other way in which we usually look at these responses is to plot imaginary versus the real. And again those of you who are students of control should be able to see very similar patterns in Bode plot or Nyquist plot being followed in control system also to analyse the system response. In this case, the material itself is our system and we are interested in input output relations by way of stress, strain, current voltage in these material systems.

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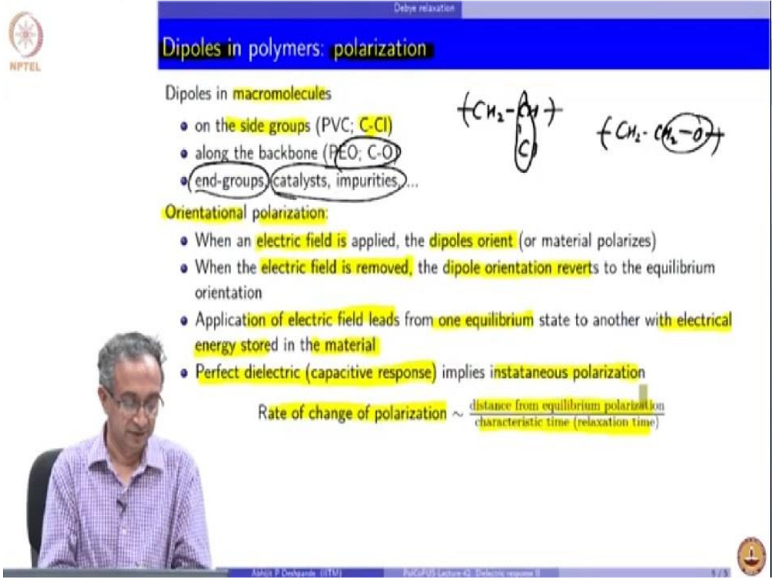

Dipoles in polymers: polarization

Dipoles in macromolecules
- on the side groups (PVC; C-Cl)
- along the backbone (PEO; C-O)
- end-groups, catalysts, impurities, ...

Orientational polarization:
- When an electric field is applied, the dipoles orient (or material polarizes)
- When the electric field is removed, the dipole orientation reverts to the equilibrium orientation
- Application of electric field leads from one equilibrium state to another with electrical energy stored in the material
- Perfect dielectric (capacitive response) implies instataneous polarization

$$\text{Rate of change of polarization} \sim \frac{\text{distance from equilibrium polarization}}{\text{characteristic time (relaxation time)}}$$

So, let’s look at now the molecular relaxations in the polymers. So this is basically polarization of dipoles. So dipoles orienting and for example, dipoles in macromolecule can be there on the side groups such as C-Cl in case of PVC. So this is a dipole which can orient itself. In case of polyethylene oxide, we have a CH2 CH2 O. So therefore the dipole is present along the backbone of the chain. In addition, polymeric systems will sometimes have the end groups, depending on the polymerization reaction which has been used, the end groups are different compared to the bulk of the chain. For example, the end group can be an initiator. If it's a free radical polymerization, initiator starts off reacting with the monomer and then monomers starts attaching. So, therefore one end of the polymer chain will always have initiator. And so initiator can have dipoles. Quite often we also have catalysts and impurities in the material and they might have a certain response.

So therefore, when we talk about dielectric polarization in the material, even for a material where let us say it is polyethylene and there are no dipoles present, we will have certain response due to impurities and catalyst which is present there. So therefore analysis of macromolecular dielectric response, we have to keep this in mind whether we are analyzing the polymer and macromolecule itself or are we analyzing some of the impurities which are present there.

But mind you, the impurities present and their analysis can also tell us about macromolecular flexibility. For example, if there are these catalysts particles and impurities, and they are not able to move that implies that free volume in the polymer is less. So therefore it may be in the glassy state, but if these catalysts and ions and impurities can move about then it may be that there is molecular flexibility in the system and the material has gone to rubbery state. So glass to rubber transition in a macromolecular system could be looked at, by looking at the migration of these impurities. So, which is again a dissipative phenomena associated with motion of these charged entities. So therefore, macromolecular polarization is a broad term in which case, the dipoles on the macromolecules or any other charge system, whether partially charged like a dipole or a ionic species in the form of a catalyst or impurity which is present, all of these respond to the electric field.

So therefore dielectric response is complex depending on whatever is the overall makeup of the macromolecular system. We will right now focus only on the macro molecular dipoles relaxation because it is directly related to segmental motion. So when we apply an electric field, we basically have an orientational polarization that happens in the material. What does it mean?

When we apply the electric field, the dipoles orient, which in other words is saying, that the material polarizes.

Material polarizes is very similar in the mechanical domain to say material deforms. We characterize the deformation using a variable called strain. Similarly, dipoles orientation is being characterized by a variable called electric displacement. When the electric field is removed, the dipole orientation reverts back to equilibrium. And this is again classical idea of energy storage where we say also in a crystal that when we deform the atoms get displaced, but when we release they come back.

Application of electric field leads from one equilibrium state to another with electric energy stored in the material. So, electric energy gets stored as electric displacement. Just the way strain energy gets stored as atom and molecular displacement strain energy in the material. So, perfect dielectric or capacity response implies instantaneous polarization. And, generally for most of the material, the rate of change of polarization will depend on how far away from equilibrium polarization one is. And also there is a characteristic time which we will call the relaxation time of the material. And this we have discussed already in terms of a segmental relaxation or a side group relaxation. So there is a characteristic time associated with each of those relaxations. Larger the macromolecular entity we are talking about larger will be the relaxation time. So for example, whole molecule moving is a relaxation time quite large, maybe hour. If it is a segmental relaxation, then we are talking about seconds or thereabouts.

If it is a subgroup rotating, then we are talking about milliseconds, microseconds. If it is just a bond vibration, we are talking about picoseconds. So you can see that from very small scale to very large scale relaxation times vary. And so, the rate of change of polarization in the material depends on the relaxation time of the dipolar movement which is a material property. Each dipole will have a characteristic timescale. And then how far away from the equilibrium orientation the material is.

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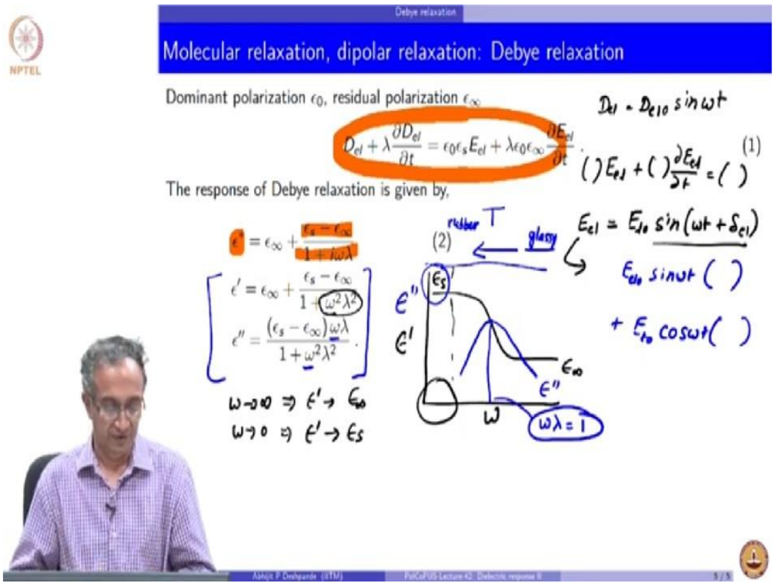

Debye relaxation

Molecular relaxation, dipolar relaxation: Debye relaxation

Dominant polarization ϵ_0, residual polarization ϵ_∞

$$D_{el} + \lambda \frac{\partial D_{el}}{\partial t} = \epsilon_0 \epsilon_s E_{el} + \lambda \epsilon_0 \epsilon_\infty \frac{\partial E_{el}}{\partial t}. \qquad (1)$$

$D_{el} = D_{el0} \sin \omega t$

$(\ ) E_{el} + (\ ) \frac{\partial E_{el}}{\partial t} = (\ )$

The response of Debye relaxation is given by,

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + i\omega\lambda} \qquad (2)$$

$$\left[\begin{aligned} \epsilon' &= \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\lambda^2} \\ \epsilon'' &= \frac{(\epsilon_s - \epsilon_\infty)\omega\lambda}{1 + \omega^2\lambda^2}. \end{aligned}\right]$$

$\omega \to \infty \Rightarrow \epsilon' \to \epsilon_\infty$

$\omega \to 0 \Rightarrow \epsilon' \to \epsilon_s$

$E_{el} = E_{el0} \sin(\omega t + \delta_{el})$

$E_{el0} \sin \omega t (\ )$

$+ E_{el0} \cos \omega t (\ )$

So to capture this idea, we have the Debye relaxation model and, if the electric displacement is directly proportional to the electric field, then we have a perfect dielectric. And so when we learn in schools about a capacitor, we have the model where D ∝ E. So, electric displacement is proportional to electric field. But as the Debye relaxation model makes a hypothesis that the rate of change of polarization in the material is depends on how far away from you are and that immediately implies that rate of change is proportional to the equilibrium, the difference between equilibrium and current and therefore immediately you get the derivatives. And so the rate of change of electric displacement is also related. And, in case of Debye relaxation, what we have is also an additional polarization. So if we do not include this term then what we are saying is the material is able to polarize and that polarization is called the dominant polarization which is ε_s.

And so, when low frequency is there ε_s is the response of the material. When high frequency is there a polarization stops happening. But in a real material, even at very high frequency, some residual polarization in the form of ε_∞ is there. And that is what is included in the Debye model also. So therefore, in the Debye model, the assumption is the following that we have, let's say all these dipoles and the dipoles have a certain characteristic relaxation time, λ, that defines the rate at which they orient. If $\lambda = 0$, then this model falls back to perfect dielectric. So, which means if they respond instantaneously, there is no relaxation time associated with it, then they fall back. If lambda is infinity, then in fact this material is going to be more like a resistive material, and they, it will not have any dipoles to store any energy.

$$D_{el} + \lambda \frac{\partial D_{el}}{\partial t} = \epsilon_0 \epsilon_s E_{el} + \lambda \epsilon_0 \epsilon_\infty \left(\frac{\partial E_{el}}{\partial t} \right)$$

So this is the model of a molecular relaxation which can be used for smaller molecules, as well as for large molecules for macromolecular system. And, the response of Debye relaxation is given by the complex permittivity in a complex notation based on this. So if we solve this differential equation using a sinusoidal input where let's say we apply an electric displacement and then we solve.

Basically, it will be an ordinary differential equation in E where we will have basically some coefficients multiplying E_{el} plus some coefficient multiplying equal to some other coefficients. So this is an ordinary differential equation in E. And, what we will get is a response which is again a sinusoidal function.

$$E_{el} = E_{el0} \sin(\omega t + \delta_{el})$$

Given that we are interested in only the linear domain, the output also will be at the same frequency as the input but there will be a phase lag, which is related to the dissipation factor or the power factor.

And so using this solution then we can decompose this E_{el} into two parts, you know, $\sin(a + b) = sina.cosb + cosa.sinb$. So therefore we can decompose this, overall signal into E_{el0} Sin(ωt) into something plus E_{el0} Cos(ωt) into something. So, I am giving you some of the steps, so you can work out the details based on the solutions of ordinary differential equation and then, you can come up with these solutions to ε′ and ε″. What is interesting here is to see what is the functional form of ε′. At very large frequencies, if $\omega \rightarrow \infty$ then this factor will be very large and therefore $\varepsilon' \rightarrow \varepsilon_\infty$. If ω is very small, then this factor itself will be 0 and then it will be $\varepsilon' = \varepsilon_s$. So, therefore you have this is the response where this is ε_∞, this is ε_s.

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + i\,\omega\lambda}$$

$$\epsilon' = \epsilon_\infty + \frac{(\epsilon_s - \epsilon_\infty)}{(1 + \omega^2 \lambda^2)}$$

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_\infty)\omega\lambda}{1 + \omega^2\lambda^2}$$

$$\omega \rightarrow \infty \Rightarrow \epsilon' \rightarrow \epsilon_\infty$$

$$\omega \rightarrow 0 \Rightarrow \epsilon' \rightarrow \epsilon_s$$

So quite often when we learn in, earlier courses perfect dielectric, we are only interested in low frequency phenomenon and therefore ϵ_s is constant. And therefore we do not need to worry about any other response of the material system. Now in the same, if you look at material, if you look at the dielectric laws, here you can see that depending on the frequency value, we can have it proportional to frequency or inversely proportional to frequency.

So you can, try doing this exercise and then you can justify that ϵ'' will have a peak like structure. So there is dissipation at a frequency maximum and this is $\omega\lambda = 1$. So at the frequency where, which is $1/\lambda$, we will have ϵ'' maximum. So this is a model which is related to molecular relaxation. At very high frequency the dipoles cannot orient themselves because the electric field is being applied very fast. At very low frequencies there is no dissipation and electric displacement and polarization is perfect and it is slow enough that, there is completely storage response. And so somewhere in between is where there is maximum dissipation. And so if now we think in terms of taking the material from a rubbery state to the glassy state, when we are in the rubbery state, we will have the segmental flexibility and the polyvinyl chloride or polyethylene oxide or any of the macromolecular chain the dipoles can orient easily because there is sufficient molecule of flexibility. If we now lower the temperature such that it becomes frozen then basically orientation will not again be possible. So I could have the same plot by actually changing the temperature and keeping the frequency constant. And can you think of the arrow should it be this way or should it be this way when I talk in terms of temperature?

So will ε_s be the permittivity of macromolecule when temperature is high or when the material is rubbery will ε_s be represented or will have ε_s represented when the material is glassy? And if you think in terms of molecular flexibility, you should be able to get the answer that whenever temperature is high, dipoles can orient and therefore, if I do this experiment at a fixed frequency and different temperatures, I will get a rubber response when ε_s is the permittivity in the material and glassy response when the residual permittivity which may be associated with very fast orienting dipoles that can happen even at lower temperature. So therefore you can see now, one of the key ideas that we are talking about in terms of frequency temperature equivalence. The response that I get at high frequency is similar to the response that I get at low temperature.

High frequency very short time, low temperature. High temperature, very low frequency, very large amount of time. So there is this time temperature equivalence in terms of analysis of a molecular relaxation. And this is something we will see recurring in viscoelasticity analysis also.

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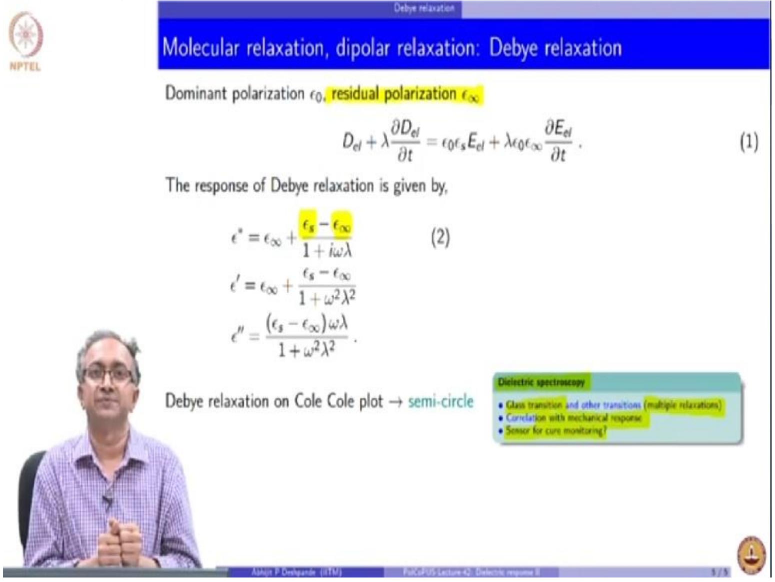

Debye relaxation

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Dominant polarization ϵ_0, residual polarization ϵ_∞

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$$\epsilon'' = \frac{(\epsilon_s - \epsilon_\infty)\omega\lambda}{1 + \omega^2\lambda^2} .$$

Debye relaxation on Cole Cole plot → semi-circle

Dielectric spectroscopy

- Glass transition and other transitions (multiple relaxations)
- Correlation with mechanical response
- Sensor for cure monitoring?

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So, the other way to look at the analysis of the Debye relaxation on a Cole Cole plot, will be to represent ε″=f(ε′). And we get semi-circular response. And quite often, many realistic polymeric materials may have a curve Cole Cole plot which does not seem to be semicircle. However, we could show that this is a combination of several semicircles. Can you try to rationalize what is the meaning of this that we have the real polymer response, which is not a semicircle, but it is a combination of semicircles which implies that several Debye like relaxation processes exist in the material and this is something which we have continuously talked about that a macromolecule being complex from length scale of the overall macromolecule to single bonds there are several relaxation phenomena. And so therefore a combination of several relaxation phenomena can lead to the overall response of the material. So therefore Cole Cole plot can be a very useful way of trying to see what are the kinds of relaxations that are present in the material.

This x axis will not be 0. The intercept here will be epsilon infinity and epsilon s and you can go back and look at the expressions for Debye, put them in an excel sheet or any other software and then try to look at what happens to Cole Cole plot. And look at what is the quantity here

maximum and what is the radius of the semicircle? And you will be able to understand these expressions much better.
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So in all of this, what we have seen is the powerful technique of a dielectric spectroscopy and analysis of the dielectric response of polymeric materials. We have seen that due to the connection between molecular relaxation, dipole orientation and segmental flexibility, we can measure glass transition. Similarly, we can measure other transitions also because that will lead to certain changes in dielectric loss of the material. So therefore multiple relaxations of the materials can be analysed. We can also make a connection to the mechanical response. We already talked about a rubber like response at higher temperature which implies more capacitive and epsilon s being the polarization. In the glassy state only the residual polarization takes place because the molecular flexibility is not there. And glassy state is a stiffer rigid state.

So clearly there is a correspondence between the dielectric electrical response and the mechanical response. And one of the advantages of dielectric response is that you can carry it over such a wide range of frequencies. So from milli hertz and lower to mega hertz and higher, you can explore the timescales which are 9, 10, 12 orders of magnitude. On the other hand, with mechanical response generally we are restricted to smaller frequency domain.

So for example, 100 Hz, 500 Hz is quite a high frequency already. There are some damping analyses which has done with kilo hertz, but that is about it. So therefore the material response that is of relevance in the mechanical domain is in the smaller range. But if we are interested in understanding the structure of the material which can have any of the different responses, then dielectric spectroscopy can be a useful tool.

And, given that we are talking about so much related to how a polymer chain relates to the dielectric response, can you think of dielectric sensor for cure monitoring? In fact, it’s a very commonly used sensor. So if you just search for dielectric cure, you will see that, it’s a standard tool which is used where we measure the dielectric constant of a polymeric material to figure out what is the extent of reaction that is happening.

So with this, we will stop the lecture on dielectric response. Now in the next set of lectures while we are focusing on the properties of material systems, we will start looking at viscoelasticity. But I am sure you have already got a window to looking at viscoelasticity in a very similar way as what we have discussed in terms of energy storage and dissipation, in terms of the dielectric response. Thank you.