[SQUEAKING]

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**JUEJUN HU:** OK. So in this lecture, we are going to start our discussion about viscoelasticity and relaxation. Now, I want to mention that this type of organization is uncommon in most textbooks about glass science. They typically treat viscoelasticity and relaxation in two completely different sections there. I decided to put them together for a few reasons.

One is that they both occur during the glass transition regime, and they have a very similar structural origin. They essentially all relate to relaxation of the glass structure. And as you also see later, they can be described using identical mathematical formalisms. So it helps a lot if we develop mathematical models and then use it as a way to lead to the discussion about relaxation kinetics. OK. OK.

So as I mentioned, both of these phenomena are characters of the glass transition regime. So the glass transition regime scientifically is probably the most intriguing part about the whole glassy state. So as one example here, what I'm showing you here, this is the *Journal of Science* in their 125th anniversary. They posted the list of 125 questions that summarizes some of the most significant outstanding challenges in all fields of science.

So one of them is about glass, and it's right about glass transition. So what it says is, "what is the nature of the glassy state? Molecules in a glass are arranged much like those in liquids, but are more tightly packed. Where and why does liquid end and glass begin?" That's glass transition. OK.

So there has been lots of advances in this field, obviously, over the past 20 years after the question was posed. But suffice it to say that this is still an area of very active scientific investigation. In fact, I also want to quote the physicist David Weitz from Harvard University, where he says, "there are more theories of the glass transition than there are theorists who propose them."

So what we are going to do in this lecture here-- I'm actually not going to try to take a deep dive into the microstructure nature of glass transition. Instead, what I want to do is I want to focus on what I consider as a defining feature of glass transition regime, which is the relaxation.

Now, to look into relaxation, let's step back a little bit. Let's take a look at this slide, which I quoted, actually, from a previous lecture, that essentially looks at the mechanical characteristics, or rheological characteristics, of glasses across different temperatures. We mentioned that at low temperature, glasses is basically an elastic solid, exhibit all the characteristics of a solid that has instantaneous response, follows Hookean's law, and such.

At high temperature, where it becomes a super cool liquid, it is obviously liquid, so it will flow viscously, and it can be described more or less as a Newtonian fluid.

Now, if you look at things in between, this is where the glass transition comes in, OK? And in between regime here, there will exhibit properties that combine both solid and liquid, which is viscoelasticity. And this is also the regime where you actually see significant structural relaxation.

So before I move on to the next slide, I just want to quickly mention one thing. Throughout this entire slide deck, I'm using this kind of a color coding scheme here. Anything that's red is associated with a solid or elasticity. Anything that's blue is basically the liquid or viscous contribution. OK? All right.

So I made the statement that relaxation is only significant in the glass transition regime. Why? Let's see what happens if you go through the liquid phase. So previously, when we were talking about the laboratory definition of glass transition, we said that the liquid regime is essentially ergodic. All the molecules or atoms, they have sufficiently high energy, they can easily move around, and therefore, they can access all the possible microscopic states.

What that also means is the system tends to stay in the "equilibrium" state, OK? "Equilibrium" with the quotation marks. I'm going to talk about that later.

But the idea is that because molecular motion is so efficient and so swift, the relaxation is actually very, very fast. Any structure change is almost instantaneous. That's why it tends to stay at the state that corresponds to the lowest Gibbs free energy, which is the "equilibrium" state, as we are talking about here. So liquid, by definition, is always in the equilibrium state.

Now, what about solid? If you cool it down, then all the atomic motion becomes very sluggish. Then kinetically, any relaxation is getting inhibited despite that, in this case, you have a very large thermodynamic driving force towards relaxing to the equilibrium state. But kinetically, it won't happen. So that's why, in the glassy state, you also don't see a lot of structural relaxation.

Right in between, the glass transition, is where you have the right condition to induce significant relaxation. Kinetically, it is sufficiently fast. It will take place during the duration of our experiment. And thermodynamically, that's also adequate driving force. The glass line has already deviated from supercooled liquid line. So there is actually thermodynamic driving force for such relaxation.

So we can characterize the significance of this kind of relaxation phenomena by again comparing two quantities here. So tau with the subscript ie, this is the time scale for structural relaxation. And t obs, this would be the time of observation or basically the duration of the experiment.

So in the glass transition regime, we have the two time scales more or less are comparable. This is where you will see significant relaxation. OK.

Quantitatively, people define this quantity here called Deborah Number-- it's basically a ratio of tau over the t observation. So it's equivalent to saying that the Deborah number has to be of the order of unity in order to see significant structural relaxation, which correspond to glass transition regime.

Now, you wonder where the Deborah number, this name comes from? It's actually from the Bible. It basically says that the prophetess Deborah, over a time period of billions of years, they observed that the mountains flowed before the Lord. So that's viscoelasticity. It essentially means that if you give it long enough relaxation time, anything that appears like a solid, they can exhibit some viscoelastic response. So that's why people call it the Deborah number.

So as I mentioned, we're going to talk about structural relaxation and viscoelasticity here. Viscoelasticity, in itself, is the manifestation of structural relaxation in glass. That's the microscopic origin. Now, before we go to the microscopic origin here, what we will focus on is focusing on the mathematical description of viscoelasticity. And as I said, this will serve as the basis to derive the mathematical formalism to describe structural relaxation.

I have promised you before that we are going to derive a mathematical theory that allows you to quantitatively predict what is the shape of this curve as the glasses cool down and reheat up, going through the glass transition region. That's what we're going to do in this lecture here. OK. OK.

So speaking of viscoelasticity, what I'm introducing here basically is just a basic mathematical formalism to describe the mechanical properties of solids in a viscoelastic regime. You may have seen this a little bit in 3013. But we will be considering a complex shear modulus rather than a pure real shear modulus, like elastic solids.

And to define a complex elastic modulus, what you would do is considering a stimulus that's applied in a sinusoidal manner. It can be stress or strain. In this case, we actually choose to apply a sinusoidally varying shear strain. OK?

So mathematically, you can describe it using a complex number. And if you think about elastic response, it's pretty straightforward. You just time it with the elastic constant. So what we see here is that the stress from elastic response and the strain, they are always in phase with each other because of instantaneous response.

Now, if it's a viscous response, the constitutive relation, especially given by this one here, this Newtonian flow, now, if you take a time derivative with respect to the strain here, because of the complex differential, when you take the time derivative, you pull out a factor of i omega. So that means, effectively, now the stress differs from the strain by a factor of i. There's an imaginary number coming into play here. The imaginary number in the complex plane means that these two quantities, their phase, differ by 1/2 pi. So therefore, there is a phase lag between the stress and the corresponding strain. They are out of phase if you are looking at the viscous response.

So now, if you combine both together, then phenomenologically, the effective shear modulus would then contain both real part and imaginary part, where the real part comes from the elastic contribution, whereas the imaginary part comes from the viscous contribution.

So that's why the real part is what people call, basically, a shear modulus. Sometimes people also call it a storage modulus, because any elastic response, you are converting the external force, the energy of external force or work done by external force, into elastic energy. So it's stored there. You have elastic energy stored.

But if it's a viscous flow, because it's internal friction, you are moving molecules past each other, any work performed by external shear force would be dissipated in the form of heat. So that's why this is also called the loss modulus, the imaginary part of the shear modulus. It's also considered as a way to dissipate mechanical work. OK. OK.

So that's the high-level framework. Now, to derive the mathematical formalism of how to actually look at relaxation phenomena in a viscoelastic solid, we have to introduce a couple of phenomenological models. Of course, Hookean spring and Newtonian dashpot, which I suppose you have seen in 3013? Yeah.

So Hookean spring-- simple. It's strain equals stress. Dashpot is something characterized ideal properties of a Newtonian fluid. The assumption there is that because we are assuming linear relations-- so practically, we are assuming we are operating in the linear regime. So linear regime, rigorously speaking, applies only when the strain is very small. And so the strain rate is also very small. That's why things stay linear.

And as we will see later, what's really important there is that every time you're introducing one phenomenological model containing a Newtonian dashpot, each dashpot corresponds to one microscopic structural relaxation mechanism.

And so as you'll see later, each Newtonian dashpot is associated with one characteristic relaxation time scale. So different microscopic mechanisms can have very different time scales. So for example, if you think of polymers, when you're actually introducing plastic deformation or a viscoelastic deformation in polymers, the shape change can be introduced by changing the conformation of the polymer chain. You can have a linear chain getting folded or twisted. And then you can also have, for example, bone breaking or having some kind of chemical reaction.

So these two have very different time scales. So one's reflected on the phenomenological model of the material in terms of mechanical property, is that you then need two Newtonian dashpots to correspond to each of these kind of microscopic structure relaxation mechanisms. OK?

So now, in order to introduce in the mathematical formulation here, we look at a few different ways to assemble these basic elements together to describe the viscoelastic response. The most simple one-- Maxwell element. Just put the two in series. If you put them in series, obviously, the stress is constant across the two elements. But the strain is going to be the sum of the strain that's sustained by the spring and the dashpot.

So now we can consider what is its response of the system to two kinds of external stimuli, OK? Constant stress versus constant strain. Constant stress is relatively straightforward. If you apply a constant stress to a system, because the stress is uniform across both elements-- so same stress applied to both elements-- the stress is going to elongate the spring to a fixed amount dictated by Hookean's law. For the dashpot, a constant stress essentially means constant strain rate. So if you have constant strain rate, it means that the strain is going to grow linearly over time.

So what we're seeing here, basically, is a creep. So this happens in lots of cases in high temperature. For example, lots of materials. If you apply constant stress, then eventually, the material continuously deforms slowly, OK? So that's what happens there.

Now, what's more interesting is actually constant strain. This is more relevant to relaxation there, OK? Because constant strain leads to stress relaxation. So if it's constant strain, let's first take a look at what's going to happen intuitively. If you [? apply ?] constant strain, initially, keep in mind that a dashpot cannot respond to strain immediately. It takes time to elongate the dashpot, because you apply any force, you're introducing a finite strain rate. It's not a finite strain. So it takes time to build up a strain in a dashpot.

So therefore, if you apply a constant strain, then, initially, all the strain is going to get concentrated on this Hookean spring. But then this Hookean spring, when it's stretched, it's then going to apply a stretching force on the dashpot, which then slowly elongates the dashpot. And as the dashpot elongates, because the total strain is constant, the strain distributed on the Hookean spring will now decrease. The equilibrium state will be then this dashpot that's fully stretched, but the spring now experiences no stress. So what we're seeing here is a typical phenomena of relaxation.

You start out from a state that's not in equilibrium. The initial state is when you have the spring getting stretched. The end state, this stress completely goes away. This will be the equilibrium state.

So now what will be the kinetics of this process? So this will also be pretty straightforward. We can just write the total strain. This is the sum of the elastic component plus the viscous component. OK? So for elastic component, we know that the stress would just simply be G times the epsilon E. This would be the stress on the whole system-- on the spring but also the whole system.

So now this stress is also what's driving the viscous flow on the dashpot, yeah? So this should also equal to eta d epsilon v, dt. Because epsilon v is basically epsilon minus epsilon E, so we can plug into the equation here. This becomes negative d epsilon E, dt.

So then if you look at these two terms here, what this says is that the epsilon E will have to follow an exponentially decaying formalism. So epsilon E, this will have to be proportional to exponential. Let's see. So this will be a-- divide over here. Negative g divided by eta. So this would be a negative G divided by eta, t. So the stress would have to decay exponentially.

And we need to determine the specific coefficients of this by looking at the boundary condition where, in this case, is the added stress, initially, when t equals 0, it has to equals to the strain. All the strain is sustained. Sorry, the strain. All the strain is sustained by the Hookean spring. So that's why, initially, it has to equal epsilon. Over time, when t goes to infinity, it decays to 0, OK?

We can now also introduce in this quantity here tau, which would be our relaxation time for this particular system as eta divided by G. Then this one becomes epsilon exponential negative t divided by tau. OK?

So we use a single exponential to describe this kind of relaxation kinetics if there's only one relaxation mechanism involved in the material. OK, every relaxation mechanism corresponds to one relaxation time scale.

Now, we can also further manipulate this equation a little bit, OK? So what's the driving force for this relaxation? The driving force for this relaxation is actually internal stress. It's a stress that's sustained by the spring. This is what's stretching the dashpot, eventually leading to relaxation there, OK, to a deformation relaxation.

So we can write the kinetics here in the form of-- I mean, we can also write sigma. This will also equal to epsilon divided by g, this starting state, and then it exponentially decays. We can write the relaxation kinetics also in the form of the driving force there.

So this is our epsilon E-- this is our stress here. So if you look at how the stress-- let's look at the relaxation rate. So d sigma, dt-- how the stress decays over time. It's complex exponential. So it's actually pretty straightforward. It's actually negative tau, 1 over, sigma.

Now, this is actually a very important mathematical formalism. When we are assuming that we have a single exponential of decay there, what we are basically assuming implicitly is that the kinetics of relaxation scale linearly with the driving force, which makes intuitive sense. The larger the driving force, the faster the relaxation kinetics, the faster the rate of change.

Now, this is the same formalism we are going to use later on when we're deriving the structural relaxation in glass materials. If assuming a single relaxation mechanism, rate proportional to the driving force. OK. All right.

That's sort of the key conclusion I wanted to come to there, that particular equation. So I'm going to leave it on the board. We will be using it later. OK? All right.

So then the rest I can just very quickly go over it. In addition to this kind of a constant strain, constant stress, you can also apply an oscillatory strain, which, these are the sinusoidally varying strain and stress.

For that, the main quantity I want to mention here is the so-called loss tangent. This tangent theta here. So tangent theta, this is basically defined as the ratio between the imaginary part of the shear modulus and the real part of the modulus.

So physical significance of this loss tangent is that it is the amount of energy loss per cycle in this sinusoidal strain normalized by the elastic energy that's stored in the system. So the higher the loss tangent, the more energy dissipation you get per cycle during the oscillatory strain.

What we are seeing here is that, in this particular case for Maxwell element, this loss tangent monotonically decreases as you increase omega. OK? The horizontal axis here is basically omega times tau, where tau is the relaxation time, which makes sense. Because if you have higher frequency, obviously, a shorter time. In fact, the elastic constant contribution becomes more significant because any kind of elastic-- or sorry, any kind of viscous component, it takes time to respond to external changes.

Also, having a shorter cycle, a shorter period also decreases the amount of energy loss per cycle. So that's why you see this decreasing trend here, OK? But in general, this would be a very general quantity that you can use to gauge whether the system is conserving energy or dissipating energy. OK? All right.

So I'm going to go pretty quickly here. These are some of the other elements. You can also assemble the Hookean spring and the dashpot in different ways. You can put them in parallel with each other. This is called the Voigt-Kelvin element. For this kind of element here, if you apply a constant strain, then all the stress is going to be sustained by the spring here, because dashpot, it doesn't respond to constant strain. For constant strain, the dashpot doesn't give you any friction force, because strain rate is zero.

So that's why all the stress will now be sustained by the spring. That's why we have this equation here. It also exhibits stress relaxation, unlike the Maxwell element. Maxwell element-- sorry, strain relaxation. Maxwell element exhibits stress relaxation whereas for this Voigt-Kelvin element, it exhibits a strain relaxation. If you apply a constant stress, then what happens there is that initially, again, all the stress is going to get sustained by this spring element, but then over time, the stress is then going to lead to elongation of the dashpot.

So in the equilibrium state, if you apply a constant stress, you want to deform the system. But you cannot deform this dashboard immediately, because as I said, it takes time for the viscous element to actually respond to any changes. So initially, the strain is zero. And that's why the spring is not elongating. There's no elastic stress component.

But then over time, this dashpot starts to slowly increase in length, which means that more and more of the stress is actually now getting sustained by the spring instead of dashpot. So in the equilibrium state, the dashboard will stop elongating, but then all the stress will now be sustained by the spring layer. OK? So we can still describe this kind of relaxation phenomena similarly using an exponential decay here, looking at the kinetics. OK? OK.

So now, in the end, if you want to describe a general material that potentially can have many relaxation mechanisms, you can use this kind of generalized Maxwell model. Basically, you put a bunch of these Maxwell elements in parallel with respect to each other. And then the response of the entire material system would then be the sum of the individual components.

Now, the key takeaway message here is that for this kind of system, every dashpot corresponds to one structural relaxation mechanism. So in real material, there can be many complex relaxation mechanisms that occur concurrently. And that's why you need to introduce a large number of these dashpots here to characterize the dispersion of relaxation time.

So now if you look at the actual time domain response, what happens if you have a stress relaxation? Same thing. You apply constant strain, look at how the internal stress of the material relaxes over time. You will get, phenomenologically, an expression like what I'm showing here. OK?

Instead of having one single exponential, you now have to look at the sum of many exponential functions. Each of the tau i here gives you the characteristic relaxation time for one particular microscopic mechanism. OK?

This sum, you can also write it in terms of what's called a Prony series. Sum of single exponentials can be expressed as this so-called stretched exponential function there. In a stretched exponential function, this looks very similar to a single exponential, except that we add the exponents here, beta. OK?

So if you look at, functionally, what this stretched exponential function looks like, let's say this is stress, this is how it varies over time. If it's single exponential, this is what the function would be looking like. And then-- it's not very smooth, but that's OK. When time equals to tau, the stress relaxes to 1 over e of the starting value. OK?

Now, if it's a stretched exponential, when you have beta there, if beta is less than 1, this is what you're going to get. You will have a function that initially relaxes faster. You will have a function that initially relaxes faster compared to a complex exponential. And then eventually, the relaxation is going to get slower, OK? Let's see.

So the reason you get the initial fast relaxation is because now you have many kinds of relaxation mechanisms. They have a difference in terms of relaxation time scale, OK? So there are always some mechanisms that exhibit the faster relaxation than others. So those are what lead to initial fast decay there. And then eventually, the slower decay is when the first components has decayed away. You now are left behind with the slow components. So that's why this with a longer decay tail compared to a conventional exponential decay. OK? OK.

So basically, what we have discussed here up to this point is that we have shown you that there are three types of response we can look at here, OK? We have classic elastic response, we have viscous response, and the combination of them gives you the viscoelastic response.

If it's an elastic response, that everything is instantaneous, if you apply a stress on a profile like what I'm showing you on the top there, you see the strain profile essentially replicates exactly what you have for the stress. OK? With a proportionality constant given by your elastic constants, OK?

For stress, the strain rate will be proportional to the stress. So then a constant stress gives rise to a linearly varying strain here. When you remove the stress, any strain that has already been induced will be permanent. It will stay there.

Whereas for viscoelastic strain, it's sort of the combination of the two. If you apply a stress like what I'm showing here, as soon as you apply the stress, you're introducing a little bit of an elastic response that's instantaneous. But then over time, you have relaxation. OK? You get a time-varying strain response.

When you remove the stress, you are going to get, again, some instantaneous response. But then as time proceeds, you get some additional variation there. OK? So the key feature for the viscoelastic response is that this is time-dependent.

The state of a material at one particular instant of time not only depends on the instantaneous stress that's applied right at that time point, but it also depends on the history of the stress that's applied on the material.

So this slide shows you some examples where you have the material exhibiting typical viscoelastic response. A lot of them are essentially some kind of amorphous material, where the operation temperature resides right along the glass transition regime. This is where the viscoelasticity is most pronounced. Of course, mozzarella cheese. You all have experienced when they're hot, when you try to remove them from the oven. They will deform continuously even if you're not trying to stretch them.

Human skin. It's quite obvious that human skin has a sort of time-dependent, delayed response, OK? If it's a baby, then the response will be more elastic. If someone like me, you see a significant viscous component. That's a good sign that I'm actually getting old, OK?

Turbine blades. These are things that were traditionally-- if it's a low temperature, this is basically an elastic solid. But when they're operating at very high temperature, you start to see responses like creep kicking in, which is due to the viscoelasticity.

Volcanic lava. This is a good example. Basically, glass-forming fluids, OK? That's why they exhibit the viscoelastic response.

In terms of practical applications of these viscoelastic materials, people use them for things like propellers for naval ships because having the viscous component is helpful in that they can actually absorb a lot of the vibrations or dampen those vibrations through dissipating the energy. And that's important for things like naval ships, because they want to make sure that they remain quiet, they produce less amount of noise, so they don't get easily spotted by sonar by ships from the adversaries.

In terms of everyday applications, I have to scratch my head a little bit to think about what is the actual practical use of a viscoelastic material? But that's one-- memory foam. That is also a classical example of a viscoelastic material in your everyday life. OK? OK.

The last main point I want to make here about viscoelasticity is this Boltzmann superposition principle. So we have discussed about some very simple formulogical models and how those elements, like Maxwell elements, would respond to simple forms of strain or stress variation-- oscillatory strains, constant strain, constant stress. But eventually, we may have to deal with more complex problem where you're given the viscoelastic solid material, you know it's viscoelastic characteristics, and then we may apply some very complex form of strain or stress on the material. And you will be asked to solve, what is the corresponding time domain response? OK?

So the way to deal with that is to use the Boltzmann superposition principle, OK? So the starting point of the Boltzmann superposition principle, it lies on the linearity of the constitutive relations. If you think about the Hookean spring, think about the Newtonian viscous flow equations, both equations are completely linear. For Hookean springs, strain and stress, they are proportional with respect to each other. For the viscous flow, the strain rate always linearly scales with stress.

So if you have equations that are linear, it means that if you have a composite stimuli, you have combined two stimuli, then the resulting response will also be the sum of the response from the individual stimulus. So that's what I'm showing here.

If you think about, in this case, applying some kind of strain, this is a strain step at time t1, you suddenly apply this strain, delta epsilon 1 there. Then obviously, because it's viscoelastic, you're going to get instantaneous response in terms of the stress. And then it will all relax. So the blue part will then be the viscoelastic relaxation. So generically, we can write a stress response as two parts here. You have the instantaneous response given by the real part of the elastic constant. Then you have this time-dependent function here that gives you the kinetics of the relaxation.

So in the most simple case, if you only have one microscopic mechanism responsible for relaxation, then this function would be a simple exponential decay function. But this is a more generic case. This can be a Prony theory, for example. It can be a stretched exponential, right? Or any arbitrary function you can define with respect to the material, OK?

Now, this relaxation only takes place after you have applied the stimuli. That's why the argument here is t minus t1.

Same thing. If you have a time t goes to t2, you apply the second stimulus, then you're going to get some stress response. In the end, the combined response would just be a sum of these two parts there, OK? So that's pretty straightforward.

Now we can move on and discuss about now what happens if you apply an arbitrary profile of a strain. So for any arbitrary profile of a strain, you can always apply the trick of divide and conquer. You divide up the arbitrary strain profile into many, many small time steps. Within each time step, you apply a small variation of the strain. OK?

You then look at the contribution from each individual steps and then sum it up together. So discretely, you can write the total strain as a sum of many individual, little strain steps. Then in terms of response, same thing. You just add up the response. OK?

If you now go into the limit, where each step becomes very, very small, this sum then becomes the integral. Converting a sum to integral, you essentially rely on this relation here, where every step, delta epsilon, you would convert it into d epsilon, dt times dt.

So you use that conversion, you convert your summation sign into an integral, and you will get, basically, the Boltzmann superposition principle that now allows you to infer the response of the viscoelastic solid to any arbitrary time-varying input stimulus. OK.

So basically, what I'm saying here is that if you know the relaxation function, you know the kinetics of structural relaxation, which is this function psi here, if you know this function psi, you would then be able to derive the response of the solid using this superposition principle. OK? All right. So this is for viscoelasticity.

Some of the key characteristics here-- obviously, as I said, this is history-dependent. You can quite clearly see from this superposition principle here, because you have this kind of exponentially decaying tail or this time-varying function part, at any time point, the stress response depends not only on the instantaneous trait, but also the previous history of the strain applied. And the time domain response, of course, is dictated by this function for psi there.

So that's the mathematical formalism we will need in preparation for the discussion when we go to the glass structure relaxation. So what I want to do here, the focus of the remainder of the lecture is to derive the mathematical formalism that now allows us to predict the structural relaxation kinetics in the glass transition regime, OK?

So for that, I will be drawing an analogy between these two kinds of relaxation here. You have a stress relaxation in a simple Maxwell element versus structural relaxation in glasses. Now, I want to mention that this mixture element, obviously, it's an abstraction of real structural relaxation in materials. So it's not surprising at all that these two kind of seemingly different phenomena, they will exhibit the same mathematical formalism there.

So to look at the kinetics of any kind of a relaxation phenomena, we need to look at three things, OK? First is the equilibrium state. So the equilibrium state refers to the state when there's no more time evolution. It becomes static. For the Maxwell element, the equilibrium state is pretty clear if I have stressed relaxation. So when the stress completely dips down to zero stress, then there will be no more relaxation. So this is when you have the dashpot fully stretched and the spring is not elongated at all.

The driving force. The second factor we need to look at here is the driving force. So I have already mentioned, for the stress relaxation, the driving force is basically a residual stress inside the material, OK? We just represent it by the stress exerted by the Hookean spring here.

Now, finally is the realization kinetics. As a first-order approximation, what we have shown here is that the relaxation kinetics, characterized by the rate of change is linearly proportional to the driving force, with the proportionality constant being basically 1 over tau, where tau is the relaxation time.

So now let's try to do the same thing for glass structure relaxation. Let's start out by defining what is equilibrium state. Now, by definition, equilibrium state is crystalline state, obviously. That's where it's thermodynamically stable. However, this is not the equilibrium state we are referring to here. That's why I put the quotation marks on "equilibrium state." OK? In the context of relaxation, the equilibrium state is basically the final state where the material is relaxing towards, where glass is relaxing towards.

So if you look at the definition I give you in the very first lecture, it basically says that glass is always, constantly trying to relax towards its supercooled liquid state. So supercooled liquid state, obviously, when it's below melting point, it's not in thermal equilibrium. But from a structural relaxation perspective, that would be sort of the ultimate state where the glass is trying to relax towards. OK?

So we define the supercooled liquid state as the equilibrium state. So now if we know the equilibrium state, then what about the driving force? The driving force would be the deviation of the state that the glass currently residing from the equilibrium state.

For example, we can take volume relaxation as an example. But this applies to relaxation of other physical parameters as well. So for volume relaxation, let's consider volume as a function of temperature, OK? So for volume as a function of temperature, we know that we have basically this curve here.

So this would be the supercooled liquid. This would be the glass. Now, we have mentioned that the supercooled liquid is basically the equilibrium state of the system. So if you look at the cooling curve here, initially, the system retraces this supercooled liquid. Means that it's actually in equilibrium. At this point here, it starts to deviate from the supercooled liquid state, OK?

As soon as that deviation happens, you now have a driving force towards equilibrium state. So for the driving force, as I said, this is defined as the difference of the current volume versus the equilibrium volume, OK? So the current volume, this is what we label as V, the volume of the supercooled liquid, this is what we label as the V subscript e. So here e essentially refers to equilibrium, OK? This is the equilibrium state we're looking at.

So the difference of the two, V minus Ve, this is the driving force of volume relaxation. Now, you may recall from the last lecture, I gave you the definition of the free volume. Free volume is exactly V minus Ve. This is the excess volume the glass possesses with respect to the supercooled liquid at the same temperature.

So Vf defines how far away your system is away from equilibrium. So in relaxation process, the system will try to minimize Vf. It will try to essentially completely remove the Vf. OK? If you're able to stay at that temperature for a sufficiently long amount of time, it's going to relax towards that point. OK. Finally, kinetics.

We are going to make exactly the same assumption here as in the case of the stress relaxation. We are going to assume that the relaxation rate scales linearly with the driving force. OK? So basically, if you look at how the volume is going to change over time, OK, so at a fixed temperature, then V is basically a constant, right? It's basically you have a well defined this line here that corresponds with the supercooled liquid line. So for every temperature, there's a well-defined volume for the supercooled liquid.

So therefore, for fixed temperature, Ve is considered as a constant. So when you're taking the derivative of volume with respect to t, essentially, you are looking at the change of a free volume with respect to time. Right?

So what we are going to assume here is the same mathematical formalism as what we have for stress relaxation. We have-- it scales inversely with 1 over tau, Vf. I used a different tau here, tau relaxation, just to characterize that. This is the characteristic relaxation time scale in the solid-- in the glass rather than in the Maxwell element, OK?

Now, this gives you relaxation kinetics at one temperature. In the end, if you want to apply this theory to look at the structural relaxation during glass processing, typically, this involves changing the temperature over time. So we would need another equation that then correlates the relaxation rate with temperature, OK?

So this can be done most straightforwardly by looking at the time dependence of the relaxation time scale. So relaxation involves, actually, motion of atoms or motion of molecules. So this motion of atoms or molecules, in a lot of cases, the kinetics can be described by using an Arrhenius equation as a first-order approximation. So if you follow Arrhenius equation, then the relaxation time can also be written with this exponential form. Right?

You can always improve the theory. You can essentially assume a temperature-dependent Ea if you wanted to be a bit more accurate to account for, essentially, a fragile or liquid behavior. But this is an adequate, at least, for the purpose of this theory here. OK, that's all we need.

This equation is really all we need to solve the glass response during any kind of thermal processing. So to see how this can be implemented, let's think about-- for example, you have some kind of process, time-dependent process. To implement the process, you need to know the initial state and you need to know the temperature history. For example, what's the heating rate? What's the cooling rate? And how long it lasts?

So what you would know for this kind of a process is that you have to know that t equals to t1. You need to assign the boundary conditions, right? At t equals to t1, you know the starting volume. OK, volume, V, at t equals to t1, OK? OK, so this is what you would know as your starting boundary condition.

Then we want to predict how this volume is going to evolve as a function of time. It will also be given about how the temperature is going to change over time. That defines your process. So then what you would do is you would apply, basically, a finite difference approach in the time domain, OK? You would look at a very small time step. Let's see what happens at t now equals to t1 plus the little time step dt. OK?

So to get the volume at t1 equals to t1 plus dt, you then first need to calculate what is the dV over that time interval, dt. OK? So you plug into that equation. You have minus tau relaxation 1, and then Vf is the big V minus Ve.

Now look at this equation here. All the quantities are actually known to you. Tau relaxation, you know the temperature at this time point. That's your thermal history. So if you know the temperature, you can plug into this equation here to derive the corresponding relaxation time for that particular instant of time. You know the instantaneous volume. That's given. That's your boundary condition. V is also something that's known, because you know the temperature. Once you know the temperature, the volume of the supercooled liquid is a single-value function of the temperature.

So all the parameters on the right side of the equation is known. Therefore, your V at t1 plus dt would just simply be V at t1 plus dv. I should put the dt here. dV, dt. OK? Now you know the volume at the next time step. You just then need to repeat this process.

And provided, as I said, you know the temperature at all the time points, then you would be able to derive how the volume is going to change as a function of time. Does that make sense? OK?

This may look remarkably simple, but then, in fact, this is also very, very powerful. It allows you to make predictions that agrees with experiments and can predict some of the phenomena, as I mentioned before, about the relaxation, for example, during a reheating of glasses. OK?

So I have actually put together a little MATLAB code myself. I can run the MATLAB code, define all kinds of temperature changes, and look at how the glass volume is going to vary as a function of time. OK.

So now what I'm showing here, I'm showing you a few examples-- what's the results of the prediction coming from the code, OK? The first example here, we are considering the same cooling rate but then different reheating rate, OK? So the thermal history-- and so we're starting out from a supercooled liquid. We cool down with a constant cooling rate of 10 degrees Celsius per second. It then going to follow this blue line here. And then once it completely cools down, we then start to reheat it up with a different reheating rate.

So what we're seeing here is that you start to see this kind of a funny shape that I have already mentioned in the very beginning of the semester. So now we explain why you have this kind of interesting shape here. Essentially, what happens is that right here, the glass material is very far from equilibrium. It has a very large excess free volume. So it wants to relax, but it cannot because it's, kinetically, very slow.

So as you start to heat it up, the curve starts to bend downwards, indicating that the system is trying to relax towards the supercooled liquid line. Now, the slower the heating rate, the smaller the heating rate, the more relaxation you see. Basically, it just means that for smaller heating rate, you allow the glass material to dwell at the glass transition regime for a longer period of time.

So if you have longer time, then more structural relaxation is going to take place. And that's why you're seeing the curve dips more. More significant relaxation.

Now, once the curve dips, it's going to hit this supercooled liquid line. Once it starts to approach the supercooled liquid line, then it will try to trace the supercooled liquid line. Because that's equilibrium. That's at the equilibrium state. So as you slowly heat it up, the kinetics of relaxation start to accelerate.

At some point, the kinetics will be sufficiently fast such that your system can now fully remain in the equilibrium state. So that's what happens. The curve starts to dip, and then eventually, you will start to trace this supercooled liquid line there. That means that the system, the kinetics is sufficiently fast to guarantee complete structural relaxation over the process. So that's why you see these different curves with different reheating rates.

Now, this is another example. In this case, I'm looking at now different cooling rates. So same starting glass. I will cool down with different cooling rates here that I have labeled here. And then I use the constant heating rate of 1 degree Celsius per second.

So there are two things we should talk about here. First is that when you are actually cooling it down, initially, the system will trace the supercooled liquid line because it's ergodic. The structural relaxation is fast enough. It can always stay in equilibrium.

Now, at some point, the system will not be able to remain in the equilibrium state because the relaxation kinetics is not fast enough. And this happens first for faster cooling rates, because faster cooling rates, you give it a much narrower time window for it to relax. So therefore, the system will start to deviate from this supercooled liquid line at an earlier point for a faster cooling rate. So the gap here indicates that the system is no longer in equilibrium. Relaxation is not fast enough.

So then once you reach the plateau during reheating here, you see that, for the 100-degree C per second, the faster cooling glass, it exhibits more stronger structural relaxation, which, again, is because it has a much larger driving force. Faster cooling glass has a higher volume, so higher excess free volume. Large free volume gives you a larger driving force. More driving force, the faster relaxation kinetics, according to our assumption there. And that's why you see a much significant dip compared to slower cooling glasses.

So from this plot, you can automatically derive the dependence of a fictive temperature with respect to cooling rate here, just based on the theory.

Now, one thing I also want to mention about this code here is that you may notice, in our typical schematic, the glass line actually has a finite slope. This is associated with thermal expansion of the glass material.

In my code, I basically did not assume any thermal expansion. I basically assumed it's zero. So that's why this line becomes horizontal, but it's fairly easy to correct for it. You just add a linear term over temperature, so that it will go to a linear chain. So that's something you can do if you want for your own code.

Any more questions about this part here? We are actually going to end a little bit early for this lecture. We'll cover up to this point. In the next lecture, we're going to discover the theory about fixed temperature, fictive temperature, and Tool's equations. So that's a different module. I want to wrap up here. But before that, any questions about structural relaxation?

The key point really is this slide. I think this slide is the most important part that covers about the key elements you want to know how to mathematically model structural relaxation using first-order kinetic theory, essentially.

**AUDIENCE:** Can you go back to the-- which slide was it-- the loss modulus, I think, slide, with all the math, breaking down the [INAUDIBLE] like prime? I didn't get it all.

**JUEJUN HU:** Which one? This one?

**AUDIENCE:** I think it was the one before.

**JUEJUN HU:** Oh. This one?

**AUDIENCE:** Yes, that one.

**JUEJUN HU:** OK. OK. Thank you. Any questions about this particular slide or?

**AUDIENCE:** No. I was listening and then didn't actually write it down.

**JUEJUN HU:** Oh.