[SQUEAKING]

[RUSTLING]

[CLICKING]

JUEJUN HU: All right, so I will start by quickly just talking a little bit about the p set. So for the first problem, that's relatively straightforward. What you would do is just do a weighted average of the number, coordination number, essentially, with respect to the atomic fraction. So what you would do is basically, as I am listing here, you start by computing, essentially, atomic fraction of each of the components and then, essentially, calculate, what is the average coordination number?

In this case, it goes directly to 2.4, which is what I have commented as something that's quite remarkable, that we are able to-- sort of by trial and error, people were able to come up through this composition that coincides with the most stable glass composition there. So that's the first one. Now, for the second question here, this is about glass batching.

So batching essentially refers to a process where you essentially mix different ingredients of glasses with the right amount and then send them into a furnace to melt the glass. So I just want to comment a little bit more about the batching process. So in the class, I have already shown you a few YouTube videos that depicts how the batching process takes place, in a large glass plant. So that's for high-volume industrial manufacturing process.

Now, if you are looking for, essentially, making small amount of glasses, for example, in the lab, or maybe you are trying to do it for some specialty glasses that supply only in small volume, then the process is a little bit different. What I'm showing here, this is actually an example of how you actually make small amount of glasses in the lab.

Basically, what you do for oxide glasses is you just mix all the ingredients, put them into a crucible, heat them up to high temperature, and then you can then cast them or do whatever you like. So for oxide glasses, because they are usually stable in ambient air because they are already oxidized, so you can do this, essentially, in an exposed environment.

Now, if you're trying to process other kind of non-oxide glasses that potentially can be oxidized, then what you will have to do is you use a setup like what I'm illustrating here. You start it out by essentially mixing all the ingredients and then seal them in a cross tube. You put in a little bit of either inert gas or leave it in vacuum, just so that you don't have any risk of oxidation.

Then what you do is you put that cross tube into this so-called rocking furnace. So rocking furnace is basically like a furnace, but it constantly vibrates over time. And the purpose of that is to essentially homogenize the glass composition to ensure that there is no-- any kind of compositional segregation. So this melting process usually takes anywhere from 12 to 24 hours, just to ensure everything's perfectly homogenized.

And then in the end, you bring it out, anneal it. So that will remove any kind of internal stress. All right, so that's sort of more like a small-scale lab glass production process. So now in terms of batching about calculating the composition ratios, there are a few general rules that I want to mention here, which are quoted from [INAUDIBLE] book.

Basically, it says that because of the high temperature during the glass batch-- processing, in the glass process, all the hydrated crystals do lose their water completely. Organics burn off completely. Again, same thing, due to high temperature. Carbonates, sulfates, sulfites, nitrates, nitrites, et cetera, they all change to the corresponding metal oxide. The cation is kept. But carbon, sulfur, or nitrogen, because their oxide is essentially in a gaseous form, they will all get released into them during the glass fabrication process.

Fluoride, chloride bromides, iodines, these are also, essentially, volatile. So most of the halide elements essentially goes away. What's left behind is the cation, the oxide corresponding to cation. And, finally, pure element added convert to equivalent oxide form. They all get oxidized in this strongly oxidizing high-temperature environment. And all the metal ions, aluminum, silicate, phosphate, the anion essentially get kept. The refractory three oxides is what stays behind.

So simply put, refractory oxides and metal oxides remain in the final glass composition. Everything else essentially, if they are volatile or gaseous, they all get released into the environment during the glass fabrication process because of the high temperature and strong oxidizing environment. So then to actually calculate the glass composition, what I prefer to do is using a table, like what I'm showing here.

But, basically, the idea is you start out by calculating, what is the-- starting from the, essentially, composition, calculate, what is the wave fraction? You then convert it to the amount of cation because cation is what kept-- essentially conserved in the glass fabrication process. And then you calculate, what is the amount of cation you need within one kilogram of glass? And then based on that, you calculate, for each ingredient, what is the amount of ingredient that contains that corresponding amount of the cation?

So that's the idea. Now, I also want to show you another, a little bit more complicated example here. In this case, we are trying to make some borosilicate glass. And then the ingredient we are trying to use here is sodium fluorosilicate, SiO_2, sand, as well as Borax. Now, this example is a bit more unique because the cations come from not just one single ingredient. They come from multiple sources.

So if you think about, for example, boron, it comes from both-- sorry, if you think about, for example, silicon, it comes from both sand, as well from sodium fluoride silicate. Same thing happens with sodium. Both Borax and sodium fluorosilicate, they both contain sodium. So if you come up with a question like this, asking about, essentially, what is the composition of the ingredients?

What you will do, same thing. You start with the table, but you have to be careful about sequence here. You start it out by trying to calculate the amount of ingredient you have to add for the cation that come from-- for the ingredient that contains only the supplies that only supplies the particular type of a cation.

So in this case, more specifically, boron comes from only Borax. So if you know the amount of boron you need in the final glass, you can use that to actually determine how much Borax you will need. So that's what you determine first because boron only comes from Borax. Then what you do in the process, once you determine the amount of Borax, you can also compute, what's the amount of sodium that Borax also introduced into the mix?

You then subtract that sodium from the total amount of sodium you need. Then the remaining will be the sodium that has to come from sodium fluorosilicate. That sodium fluorosilicate also supplies some of the silicon there. So, similarly, you subtract the silicon coming from sodium borosilicate. And the remaining amount silicon has to come from SiO_2, quartz. So that's basically a process you can use to essentially infer the glass batch amount in this more complex glass-making process.

Now, Zachariasen's rules, this will also be also be pretty straightforward. For barium oxide, it has a sodium chloride structure. Then you can quickly identify the coordination number around oxygen and barium. In this case, both are six. So that's why they violate the first rule and second rule. About the polyhedron around the cation, in this case, it is this kind of an octahedral. And these octahedrals, they actually share edges for the neighboring octahedrals. So same thing, they also violate the third rule.

Finally, three corners are indeed shared. Otherwise, you cannot find this-- form this three-dimensional structure. That is obeyed. But the four-- three rules are violated. So that's why this is not a good glass formula. I just want to show you another example here. In this case, this is actually a sodium oxide. Sodium oxide has an antifluorite structure, like what I'm illustrating here, where the oxygen essentially occupies this blue lattice point here. And sodium is what-- represented as red atoms here, actually.

No, actually, the purple one should be sodium. It has eight in a unit cell. And then the red one should be oxygen. It has less. This one. This one is three. So four. Yeah, so red lattice point should be oxygen. Purple should be sodium. It has more sodium sites than oxygen sites. So now look at the coordination number here. Oxygen, oxygen is eight because you look at one of these oxygen atoms here. It connects to four sodium atoms at the bottom. By symmetry, there's also another four on top. So it's eight.

The coordination number for sodium in this case is four. So in terms of the cation polyhedra, in this case, the sodium ion sits within this tetrahedra here. So the tetrahedra, they actually share edges. And three corners are shared. So in this case, similarly, the first three rules of-- three Zachariasen's rules are actually violated. So it's also a poor glass formula. Now, to solve these kind of problems, I also have a link to this kind of website here.

This is actually a very handy website. It not only allows you to show the 3D structure, but you can also actually illustrate, in this case, the-- for example, this is the [INAUDIBLE] cation-- you can see this is the cation polyhedra. This is the anion polyhedra. And it shows that these are actually sharing edges. For example, this one is actually sharing-- these are sharing edges.

So this will be a fairly convenient website if you want to see any of the structures and visualize how-- whether or not they obey the Zachariasen rules. All right, next question about the 2D rigidity percolation threshold or isostatic condition. All of you get it right. I'm not going to talk much about it.

The answer also makes sense. If it's 2, you can form a long polymeric chain. In 2D, because you are not allowed to rotate out of plane, so if you fix the bond angle, and also, you know the bond length, then this completely determines the configuration of the big chain there. That's why it's isostatic. In 3D, it is not because you can actually rotate the chemical bond with-- back to each other out of plane, so that this is still under constraint.

Now, last, this one. This is the more tricky one. So the question is asking about whether or not you can make, essentially, a tunable lens out of these phase change materials, tunable bulk lens. The answer is that, no, because even though optically, indeed, this material can be switched between these two states to give you different optical performance, you will not be able to switch this material reversibly in a bulk form.

So this goes back to the fact that this phase change material, they have very fast crystallization kinetics. That's why they can be used as fast memories to recall data. But what that also means is that it takes a very short time for them to crystallize. So I have actually looked into some literature here. So the typical crystallization time for GST is of the order of 15 nanoseconds. That's what people measured.

With this very fast crystallization, it means that, in order to reamorphize it, you also have to cool down very, very fast. You have to cool down within a time period of less than 50 nanoseconds. Otherwise, you cannot bypass crystallization. Now, the problem with having a bulk piece of glass is that it always takes time for the heat to essentially get dissipated from the interior to the surface.

So it means that for this bulk piece of glass, you can only amortize it on the only very top surface layer, not the inside. So more quantitatively, I did some calculations here. I look up the thermal conductivity with the volume, volumetric heat capacity. You can now actually calculate, what is the thermal diffusivity? Then you know the time of crystallization. So that allows you to calculate the heat diffusion length during that period of time.

So conclusion, 76 nanometer. So what this says is that the thickness of this GST film has to be of the order of a hundred nanometer or less if you want to be able to reversibly switch it. So that's why bulk GST, you cannot switch it. In fact, even thick, thick, thicker GST films, like few hundred nanometers thick, most likely, you cannot completely reamorphize it as well. It will stay in the crystalline state, the inside.

Don't worry too much about making a mistake. I saw people making this mistake all the time. There are always people trying to propose all kinds of novel optical designs out of the GST material. And if you actually read that paper, they tend to ignore this constraint there. The structure can be microns in size or whatever. It doesn't work. If they really try to experimentally make it, they'll find that they will not be able to switch it reversibly.

So now, last question, this is about comparing the property of glass films prepared using different techniques there. The bottom line is, if you are trying to do it through a vacuum deposition, you have much higher effective cooling rate because what you are actually doing is you have, essentially, these glass molecules in the vapor phase or glass atoms in the vapor phase.

They come into contact with a cold substrate and then condense into a solid form. So, effectively, this cooling rate is very, very fast because of the very large heat capacity of the substrate compared to, essentially, the gas phase molecules, which is much smaller amount. So that's why vapor deposition is equivalent to having a very, very high cooling rate.

If you have high cooling rate for most glass materials, essentially, that correspond to essentially higher volume. That also correspond to having a higher enthalpy because, again, if you look at this plot here, faster cooling rate means that this glass line deviates from the supercooled liquid line at an earlier point. So it's in a less equilibrated state, and that's why it corresponds to higher residual enthalpy.

So you would tend to expect that any vapor that deposited films, they are able to reach a state that's much more further away from equilibrium compared to if you do a [INAUDIBLE], quenching, or whatever, any other technique. That's also the reason why vacuum deposition can be used to generate amorphous films that, otherwise, it's very difficult to obtain.

Vacuum deposition is a technique that people first use to actually demonstrate amorphous metal. You can also prepare a lot of transition metal oxides in amorphous form quite easily using vapor deposition, which otherwise you cannot make using bulk glass preparation techniques. Any more questions about the p set before we switch on to today's main content?

So now we're going to return to the topic of relaxation. So in the previous lecture, we have talked about two examples of relaxation, where we talk about stress-strain relaxation in viscoelastic solids. We also discussed about free volume relaxation in glass materials. So what I want to do here is to introduce it in a more generic theory, basically called Tool's theory.

What it describes is it gives you, essentially, a way to characterize the property change of glass materials in the glass transition process, not just for volume. That's what's characterized by free volume theory. But, essentially, any other thermodynamic parameters, how they actually changes during the glass transition, that's what Tool's theory allows you to quantitatively predict.

So the big assumption about Tool's theory is about this parameter, fictive temperature. So we have already talked about fictive temperature in the very first lecture of the class. We said that the definition of fictive temperature is that, if you look at this cooling line, cooling plot of glass here, you extend the glass state line. The point where they intersect with the supercooled liquid line now defines the fictive temperature for the corresponding glassy state.

The more quantitative or maybe more descriptive definition of fictive temperature, it says that the temperature on a supercooled liquid curve, at which the glass will find itself in equilibrium with the supercooled liquid state, if brought suddenly to it. Now, that may be a bit difficult to understand. So let me explain what it actually means.

Starting out by looking at here, this point here, if brought suddenly to it, so what we're trying to do, we're trying to find a state, a supercooled liquid state, that's in equilibrium with the glass, the specific glass structure. So to determine if two states are in equilibrium with each other, what you can do is, essentially, you put them in contact with each other, see if there's any transition between the two. If they essentially remain-- no transition takes place, it means that they're essentially in equilibrium with each other.

However, if you want to bring a glass state to the supercooled liquid line, if you do it in a normal experimental process, the problem is that this process always involves relaxation. So structure is going to change while you are trying to bring it to the supercooled liquid line, the corresponding temperature. So this relaxation then changes the structure, which essentially defeat the original assumption that we are trying to find some parameters that characterize the glass structure.

So if brought suddenly to it, it essentially means that this is an ideal process. If you can do this quickly so that you avoid any structural relaxation, essentially, you maintain the glass structure, while you bring it into contact with supercooled liquid. So that's what it means. The structure of the glass stays the same when you are changing its temperature. That's the assumption there. If you do this fast enough, it do not change the microscopic structure.

So then what happens if you are changing the temperature of a glass instantaneously? If you change the temperature of glass instantaneously, then what happens? There is no structural relaxation. Then the glass structure will essentially move along this glass line here, these three line. Moving along these three line, the only thing that's really changing here is the volume changes slightly because of thermal expansion.

Now, thermal expansion, we talk about the atomic origin. The reason the material can actually expand as you heat it up is because, essentially, the equilibrium position of atoms changes a little bit in the potential well. That's defined by attractive and repulsive forces between the atoms. So because their process involves, essentially, the interatomic interactions, that's actually very fast. It's an instantaneous process.

So, therefore, even if you do this very quickly, you can still see the thermal expansion there. Thermal expansion can be considered as instantaneous. Structural relaxation, on the other hand, takes time, all right? So when you change this glass structure instantaneously, the glass is going to move along this line.

So imagine, if you try to bring it towards the supercooled liquid, it's going to go along this dotted line here, which says that the glass is not relaxing. It's only changing the volume by thermal expansion. So now, if you bring it to the supercooled liquid, then the glass and the supercooled liquid essentially meets at this point here for this particular glass line, number 3.

So what does this point mean? At this point, the glass and the supercooled liquid has the same volume or the same enthalpy, depending on what vertical axis is. So now, what is the driving force or relaxation? In the previous lecture, we talk about driving force for volume relaxation is essentially a free volume. It's a volume difference between the glassy state and the supercooled liquid state.

Now, with this kind of a system here, where we have this glass and the supercooled liquid both coming into this same point here, the volume difference between them is zero. So there's no driving force. So what that means is that glass is already in equilibrium with the supercooled liquid state. So, essentially, fictive temperature can be used to label the glass structure.

The glass structure, it labels-- essentially, a fictive temperature allow you to define a specific supercooled liquid state. Now, this supercooled liquid state will be in equilibrium with the corresponding glass structure. That's what the fictive temperature means. Again, let me repeat. Fictive temperature allows you to define a specific supercooled liquid state. You can essentially look at the cross-section point, the supercooled liquid state with a specific temperature, with the fictive temperature.

Now, the supercooled liquid at this stage, it will equilibrate with the glass structure that has the same fictive temperature. That's what it means. Now, while this number seems a bit simple, the implication of that can be pretty profound because one thing I'm essentially hinting here is that I can now use, essentially, one single parameter, which is fictive temperature, to describe glass structure.

If you look at all these different glass structures here, they all have their unique fictive temperature. So what we're doing, we are simplifying this very complex problem of describing glass structure into just giving one single parameter, fictive temperature. Obviously, you can probably already suspect that this is a vastly simplified approximation. But what I'll show you is that it actually works pretty well, reasonably well, allows you to predict different glass properties, all based on one single structural parameter.

So if we take this assumption there, then one statement I also want to make here is that the glassy state would now be fully described by thermodynamic parameters, which is, normally, if it's something equilibrium, you can describe it with temperature and pressure. But now we have additional parameter, Tf. With the three parameters, you can now uniquely define the glass structure and, hence, all of its properties.

So if you keep a constant pressure, what that means is that if you are given the temperature, the actual temperature, as well as the fictive temperature, you can now uniquely specify all the glass properties. It's going to be a single value function of Tf. All right, so based on this assumption, now, let's try to take a look at how we can now use this fictive temperature theory to now predict the different glass properties.

So let's take volume as an example. But, really, you can replace it with any kind of variables. It can be enthalpy. It can be entropy. It can be whatever. So what we have mentioned there is that, if you fix the pressure, then the volume is uniquely defined by only two parameters, temperature, the actual temperature of the sample, as well as the fictive temperature, which gives you the structure of the glass sample.

So now, suppose you want to-- in a lot of cases, during glass transition, you may want to predict how this volume changes as a function of temperature during some kind of a process. So, ultimately, what you want to do is you want to try to predict these parameters here, how the volume changes as a function of temperature.

So now, let's see what we have here. So if you are trying to calculate dV, now, dV has two components because it has two variables, T and Tf. The dV change can be caused by temperature change. It can also be caused by a? Fictive temperature change, which is essentially structural change. So we can then write it in two terms here.

Let me write it as, essentially, Ve. In fact, maybe it's a bit easier. Let's just look at dV. Don't worry about the-- let's just look at Dv T, Tf. That's a bit easier. Let's just look at some volume change, small amount of volume change. So there are two terms here. The first term is the volume change due to a temperature variation, while we keep Tf constant. It essentially means that the structure is not changing. You only look at the temperature change. And, of course, there's a dT here.

The second term is same thing. You take the partial derivative now with respect to Tf. You look at volume change due to structure relaxation of the gas, but with temperature constant, dTf. So now, what's the physical significance of the first term here? The first term is how the volume changes with respect to temperature. Suppose the structure stays constant.

We have already mentioned about that. If the structure kept constant, then the only thing that really changes with respect to temperature is thermal expansion. So, therefore, you expect the first term, which just basically gives you the volumetric thermal expansion coefficient. I add the label subscript here, g. This is to ensure that this quantity is associated with the glassy state.

Later on, I'm going to use another subscript, e, which is a quantity associated with the supercooled liquid state. e essentially means equilibrium. So supercooled liquid state is the state we are relaxing towards. So this will be just alpha g dT. That's the first term. Now, the second term, for the second term, we now try to keep temperature constant. But we're trying to see how the volume changes with respect to a fictive temperature.

What we can do? Let's take a look at the plot here. So this will be, let's say, volume. This is a temperature. So what we are trying to see here is how the volume changes with Tf. So let's look at two glassy states with different Tf. So suppose this is a supercooled liquid line, and then we-- it then turned into two different glassy states.

Now, these two different glassy states, they have different fictive temperature. So the difference here, this will then give you the dTf. What we are trying to get is, what's the volume change due to the structural transformation at the same temperature? So, basically, what we are trying to get here is, essentially, the length of this segment, this yellow segment here. And how do we correlate it with dTf?

So this is actually relatively straightforward because, what you can do, you can essentially try to look at this region here, which I fill it up into a little rectangle. For this rectangle, this little segment, this little y segment, the length of this little y segment, you see that horizontal displacement is dTf? This vertical segment, essentially, has to be the slope of the glassy line times the horizontal displacement.

The slope of the glass line is, basically, alpha g, the thermal expansion coefficient of glass, times dTf. So that's what calculate this very short vertical segment there. This longer vertical segment, this one, on the other hand, this is only a supercooled liquid line. It should be the horizontal displacement times the slope of your supercooled liquid line.

So as I mentioned, we use the subscript e to describe any quantity associated with the supercooled liquid. e essentially means equilibrium, as I said. So alpha e, this is basically a thermal expansion coefficient of the supercooled liquid line. So then this times dTf, that will give you this vertical line. So now this yellow line, that will be pretty straightforward. It's just going to be the difference of the two.

So that essentially means second term then reduces to alpha e minus alpha g times dTf. That will give you the volume change due to a modification of structure, while keeping the same temperature. So now, if you want to derive, for example, if you want to derive, let's say, dV dT, you want to see how some parameters change with temperature during some kind of glass process, then this just becomes alpha g. The first term essentially just becomes alpha g. The dT cancels out.

The second term is alpha e minus alpha g. We can divide this. It will be something like this. What we can do is we can divide both the numerator and denominator, both with dt, lowercase t, which represent time. So if you do that, then this becomes dTf dTe divided by dT dt.

So this is basically a dV divided by the temperature change. What I'm doing here is I'm dividing both the numerator and denominator with dt, lowercase t, which gives you time. So uppercase T is temperature. Lowercase t is time. So now, if you look at this equation here, alpha g is known. You can easily measure it. Alpha e and alpha g, this is also something you could easily experimentally infer.

dT divided by dt, this is basically your heating rate or cooling rate, which also is a known parameter if you know your process. So the only unknown parameter's this guy, dTf dt, how the fictive temperature changes over time. Or in other words, this is how the glass structure would relaxes over time. So if you know this parameter, you can then plug it back into this equation and then compute, essentially, how the other parameters will then evolve over time.

I'm using volume as an example, but you can fairly straightforwardly also extend this argument into other kinds of parameters here. On the slides, I show you one additional example. In this case, this is actually enthalpy. So for enthalpy, you get this equation here, similarly. If you know dTf dt, you can also use it to actually infer how the enthalpy changes over your process.

So the same thing applies to all the other parameters of classes if you know this one, dTf dt. If you know how the relaxation kinetics of the fictive temperature, then you know all the glass properties. All right, so this is what we are going to do next. We are trying to derive a quantitative expression for how the Tf is going to change with respect to time.

So what we want to do, we want to predict how Tf changes over time, the relaxation kinetics for the structure. So I'm plotting here-- this is a pretty generic diagram that shows how the parameter of a glass essentially varies as a function of temperature during cooling. Now, we don't care about the specific cooling process. What we care about now is just, essentially, the property of the glass with respect to supercooled liquid. So we will focus our attention only on these two lines here. Let's not worry about specific cooling process.

So the cross-point of these two defines Tf, all right? Then we want to examine now as some other temperature not at Tf. What is the structural relaxation kinetics? Let's suppose we are looking at some temperature, labeled by this T here. Now, if the glass is at Tf, then it will be in equilibrium with the supercooled liquid. There will be no structural relaxation.

However, if the glass is at some different temperature, T, then there is actually a driving force towards equilibrium because, if you look at this one here, the glass property has some vertical offset with that of the supercooled liquid. So this purple vertical line here essentially give you the driving force of relaxation.

So I'm using P here to represent some generic parameter. It can be volume. It can be enthalpy. It can be whatever. What I'm going to do on the board is I will just essentially use volume again as an example. But think of it as you can always replace it with any other kind of variable. So let's start by essentially writing an expression for the driving force here, this term here, Pg minus Pe, which, in this case, we focus on volume. It's just going to be Vg minus Ve, basically, free volume. That's what we have.

So what would be this one? What would be this term? So to see what this Pg minus Pe is, in fact, you can look at the plot on top. The plot, what I have on the board here, the yellow line, gives you exactly what this Pg minus Pe is. If you zoom in and look at, essentially, the diagram here, what we are trying to do is we are trying to get, essentially, this vertical offset.

And we know what's the horizontal offset. In this case, the horizontal offset, this is given by Tf minus T. We're trying to get, essentially, this vertical line segment. So this vertical line segment, this is exactly the same as the-- mathematically, exactly the same as what I have there for that yellow segment, except instead of the horizontal displacement, instead of being dTf, it's, basically, Tf minus dt.

So we can use that same expression there. So the expression will give you-- essentially, in this case, it will be an alpha e minus alpha g. And then we will have dTf, which in this case will be replaced by Tf minus T. So then what we are trying to do is we are trying to get a time evolution of Tf. So what we'll do is let's take the time derivative on both sides of the equation.

So we essentially do a dT. So when we do on the left side, we have, essentially, a term that gives you dVg dt. You also have the second term, dVe minus dV dt. But dV dt is actually not changing because, what we're trying to do here is we're trying to calculate, what is the rate of structural relaxation at some fixed temperature t here?

So if we fix temperature, the corresponding supercooled liquid structure is well-defined. It's basically, this point right here. So if the supercooled liquid structure is fixed at that particular temperature, then Ve is not going to change as a function of time in this isothermal process. So, therefore, the only term that's left on the left-hand side here will be the only-- will be the Vg change. The volume of glass is changing over time.

On the right-hand side, alpha e minus alpha g, these are just constant. They should not change over time. So that's why you can pull them out as constants. And then you have dTf dt minus dT dt. All right, next thing, let's take a look at this term here. We have already mentioned about, essentially, the glass structure relaxation, this, how the volume actually changes over time.

So dVg dt, this is the equivalent to the free volume change. And in the previous class, we have already made the assumption that, if you assume a simple single exponential, relaxation kinetics, then the kinetics would then be proportional to the driving force with the proportionality constant being a 1 over tau relaxation. So in this case, the relaxation rate is going to be the driving force-- this is the free volume-- normalized with tau relaxation

Now, we also have this expression here, Vg minus Ve equal to this guy. We can plug it into this equation here. So then it becomes negative 1 over tau relaxation, then times-- so Vg minus Ve, we substitute it with everything on top. It becomes alpha e minus alpha g, and then Tf minus T.

One thing I should also change a little bit is actually here. For this equation, when we take the time derivative, we already mentioned that what we are trying to do here is, essentially, we are looking at the structural relaxation at a constant temperature and see how it changes over time. So because we are actually doing it at constant temperature, this term, dT dt, should really be 0. So I should remove this term here because the temperature is not changing over time. We are only looking at the structural relaxation over time.

So now you can see where I'm trying to combat. These last two equations there, they're both equal to dVg dt. So they should be equal to each other. If you set them equal to each other, this alpha e minus alpha g term actually cancels out. So what you are left behind, now you have dTf dt. Let's see what's left behind. You have a negative tau relaxation. You also have a Tf minus t.

This is Tool's equation. It's actually not really surprising that we come up with this result. You see that it follows the same mathematical formalism. It also follows the simple first order relaxation. You have the kinetics scales with the driving force. So what it says is the driving force for structural relaxation is the difference between Tf and the temperature T, actual temperature T.

So what's the physical significance there? I've already mentioned that if, let's suppose, you conduct your experiment at a temperature equaling to Tf. At Tf, we mentioned that the glass should equilibrate with the supercooled liquid state at that same temperature. So if T equals to Tf, glass and supercooled liquid, they are in equilibrium with each other. There should be no driving force.

So anytime your actual glass temperature deviates from its fictive temperature, then you move away from equilibrium and then you have your relaxation. So that's why, from the perspective of fictive temperature, this difference here, Tf and T, the difference between the two, is the driving force for structural relaxation.

So now if you have this equation, while it looks-- seems very simple, you have this equation. You can now put it back into the generic equation that I'm [INAUDIBLE] listing here. You can put it into this term here. As long as you know how Tf changes with time, you can use it to actually predict the evolution of all the other kind of parameters with respect to the glass.

In fact, what you can do, if you actually substitute Tool's equation back into this particular equation I put on the board here, you will get the free isovolumetric relaxation theory, which is what we talked about in the previous lecture. Again, that's not really surprising because this is all like a circular argument. We derive the two equation by assuming, essentially, the free isovolumetric relaxation theory in this case. But the idea is that it applies to all the other thermodynamic parameters as well.

Now, to show you one example about how to actually originally come up with the theory and how we actually use it to predict glass structural evolution, these are actually some figures quoted from the original paper, published by Tool. At the time, he was a scientist working at the National Bureau of Standards, which is basically NIST today.

So he did some precision measurements, looking into the thermal expansion of glass materials. So that's actually what's plotted here. So vertical axis is, basically, expansion. You can treat it as volume, effectively. Horizontal axis is temperature. He prepared two glass samples that he labeled as 1 and 1 prime. And these thoughts, essentially, give you how the volume of these two samples actually changes over-- when you actually change temperature.

So you can clearly see how it essentially expands, and relaxes, and then kind of comes back up, so fairly typical glass relaxation. So from this plot, you can then go back to this equation here. So in this equation here, now, all these parameters here, you can measure dT dt, how the volume changes with temperature. This is basically represented by this plot here, from experimental data.

So know this parameter. You know all these thermal expansion coefficients. You know the heating rate, dT dt. So you can then use that to calculate, what is the dTf dt? From this experimental data, you can actually predict how the Tf changes over time. So, basically, by looking at experimental data, you can infer how the fictive temperature of these two glass samples changes in your experiment. So that's actually what this plot represents. He basically inferred fictive temperature of the two glass samples, and then as a function of temperature in this case.

So the next thing you do is that, now you know the fictive temperature, you can then use that to actually predict other thermodynamic properties. So in this case, he tried to use that to actually predict enthalpy. So now, you know this term here. You can plug it into this equation here and calculate how the enthalpy changes over the experimental process.

Now, experimentally, what is the physical significance of enthalpy change? Enthalpy change gives you the amount of heat that's absorbed or released by a sample, which you can experimentally measure using calorimetry. So that's what he did in the end, on the right-hand side here. On the right-hand side, he basically did some differential thermal analysis, DTA.

We're going to talk later all about these kind of thermal analysis techniques there. But long story short, it basically is a measure of how the amount of heat that's released and absorbed as a function of temperature will heat up the sample. So these two curves, this is the corresponding amount of, basically, a DTA trace, DTA measure curve, during-- on the right-hand panel, this is actually the theoretical curve that's predicted based on the fictive temperature.

What's on the left-hand side here, this is actually experimentally-measured data. So now you see this striking similarity. The Tools equation, the fictive temperature, now allows you to actually predict, essentially, the enthalpy change based on volume expansion coefficient data. Or, sorry, volume expansion data.

So what this result really shows you, that this remarkable agreement is that you can now-- essentially, all these different parameters, temperature-- sorry, all the different glass properties, volume or enthalpy, they can all be correlated into this one single parameter, which is fictive temperature. That's what this experiment verifies. Essentially, they use fictive temperature as a bridge that allows you to correlate two sets of data that simply would be quite different. One is volume, one is enthalpy.

This comparison shows that both of them can be predicted by using one single parameter, which is fictive temperature. So that goes back to the assumption there. You can label glass structure, which is one single parameter, Tf. All right, so while that looks pretty good, I also want to mention that this theory, obviously, is oversimplified. Glass structure is very, very complex. You don't imagine that you can simply just summarize it with one single parameter there.

So a few years later, there was another experiment carried out by one of his postdocs, one of Tool's postdocs. So this is one of the rare cases where the postdoc actually disproved the theory proposed by his advisor, but whatever. So this is Ritland. It's called Ritland's experiment. So, essentially, what Ritland did is he has two groups of glass samples.

They have the same composition. They go through two different heat treatment process. And in the end, they get the same refractive index. So what does that mean? According to Tool's theory, all the parameters correlates with, essentially, just one single parameter here, which is Tf. So if the two glass samples have the same refractive index, refractive index actually correlates with probability, which then relates to density. It's an amount of polarizable electrons within a certain volume that can respond to oscillating electromagnetic field.

But, anyway, this is a parameter of the glass. So if the two glass samples have the same fictive temperature at the same temperature, it means that they must have the same fictive temperature. The two glass must have the same structure. So now, if you look at how you obtain these two groups, one of them, you essentially just keep it at some temperature for a long period of time.

So after the long period of time, you assume this sample has already reached equilibrium state. The sample should already equilibrate with the supercooled liquid, also at the same 530 degrees Celsius. So, therefore, by definition, for group A, this glass, it should have a fictive temperature of 530 degrees Celsius. That's just the definition of fictive temperature. If you leave it at such a long, long time when you reach equilibrium, the T should then equal to Tf.

So then what about the second group? The second group goes through, essentially, some process, cool at some certain rate, whatever. It doesn't matter. But based on Tool's theory, the second group should also have the fictive temperature of 530 degrees Celsius. So now, what happens if you put both of them in a furnace that's held at 530 degrees Celsius? What would Tool's theory predict?

Tool's theory would predict that, because both samples has a Tf that exactly equals to T, 530 degrees Celsius, so no structural relaxation should take place. Both samples should exhibit no change whatsoever because the Tf both equal to actual temperature, T. So according to this equation, no structural relaxation should take place for both samples. Does that make sense?

AUDIENCE: Because group B has been cooled down to reach 530?

JUEJUN HU: Cooled down for 530 degrees Celsius, yeah.

AUDIENCE: Stays there.

JUEJUN HU: Yeah, and, essentially, because they have the same refractive index, what we're trying to infer here, according to our theory, is that they should have the same structure.

AUDIENCE: Wait, so for group B, they basically cooled it all the way down?

JUEJUN HU: You just cool it all the way down.

AUDIENCE: Based on the slope of the line, it should have fictive temperature of 530?

JUEJUN HU: I think they just cool it down to 530 degrees Celsius. For a melt, that's a much higher temperature. They cool down with a specific rate to 530. So then the refractive index at 530 is the same as the group A.

AUDIENCE: How is that different from group A?

JUEJUN HU: Oh, it's just thermal history. It's just cool down immediately to 530, and then that's it. You don't sit there for a long period of time.

AUDIENCE: So group A is at equilibrium and group B is--

JUEJUN HU: Is not. It's just like as cooled, essentially.

AUDIENCE: It's passing through.

JUEJUN HU: It's passing through 530, yeah, basically. It's not staying there for a long time. At 530, with that cooling rate, it also gives you the refractive index. Essentially, there are two sets of samples with different thermal history with the same refractive index.

AUDIENCE: Yes.

JUEJUN HU: Yeah, one is that you confirm it's equilibrated. The second one is that you tune the thermal history. So it also happens to have the same refractive index, but it does not go through the same equilibrium process. But according to our theory, they should be the same because they have the same fictive temperature. They have the same index. So there should be no structural relaxation whatsoever because they are the same.

Now, that's obviously not the case. This is actually a refractive index, how the refractive index changes for the second sample, this trace there. You can clearly see, it actually continues to drop a little bit after keeping at 530 C. And then it goes back up. Eventually it will, of course, goes back to the same temperature because it then converges to the same state as in glass A.

But the fact that you are seeing the time evolution of the refractive index says that the structure of these two glasses, despite they have the same refractive index, is different, which should not be something that comes as a surprise because you imagine, glass structure is so complicated, you just cannot describe it with one single parameter.

Or another way to understand it is you can think of, that for different parameters, they have different Tf. In this case, for refractive index, they may have the same Tf. But then the glass structure still can be different when it comes to other parameters. So bottom line is that you can calculate glass structure fully using just one single parameter, Tf.

In fact, sort of a quick way to explain the Ritland experiment is that there are actually multiple relaxation mechanisms that can currently take place. They have different kinetic constants. So that if you superimpose these two curves together, you get a shape like this. You have a faster relaxation that goes this way. You have another slow relaxation that goes in the opposite direction.

So takeaway message from relaxation experiment is that structural glass is very complex. You cannot simply characterize it using one single parameter, Tf, even though it's a pretty good approximation, as in the case that's proved by 2. The more refined theory is called a Tool-Narayanaswami-Moynihan, or TNM model.

I've included a link there that talks a little bit more about the theory. It's outside the scope of this lecture. But if you really want to study the relaxation, this is the theory people use in, essentially, scientific investigations or industrial applications. In fact, the authors of this theory, originally, they were all affiliated with General Motors.

So General Motors has a very large glass research center. They actually look into relaxation because, of course, they worry about relaxation of windshield glasses over a long period of time. So that's why. They actually come up with this kind of a very fundamental scientific investigation in this model there. So that's actually all I want to cover here in this lecture about relaxation.

AUDIENCE: Love it.

JUEJUN HU: That's from ChatGPT.

[LAUGHTER]

So now, question for you? What is relaxation? Obviously, that's not our definition. So what do you think is the relaxation? So the formal definition of relaxation, which, interestingly, we have not talked about throughout the entire lecture here. We just give you descriptive terms. Relaxation is the return of a perturbed system into equilibrium.

If you look at this definition here, there are actually three key things you have to know about the relaxation process. You need to know, what is the equilibrium state the system is returning to? You need to know, what is the driving force for this process? And, finally, you need to know, what are the kinetics of the process? These are three key parameters you need to know anytime you deal with a relaxation, equilibrium state, driving force, as well as the kinetics.

We mentioned that this kind of a relaxation process, this is obviously time dependent. It occurs in the glass transition regime, where the Deborah number is of the order of unity. We talk about three different examples here, stress-strain relaxation in viscoelastic solids, free volume relaxation, as well as the more general structural relaxation, which is Tool's theory.

In all three examples, you can look at what the three elements are. So for the equilibrium state, strain-stress relaxation is when the residual strain or stress completely goes to 0. That's equilibrium state. And the driving force for the relaxation process, obviously, would be the residual strain or stress. For free isovolumetric relaxation, the equilibrium state is the supercooled liquid state.

And the driving force would be the free volume, the difference of the glass volume with respect to the volume of the supercooled liquid. For the general structural relaxation, the equilibrium state, again, is the supercooled liquid state. And the driving force is basically this, the difference of Tf, the glass structure, and the temperature at which the sample actually sits. That's the driving force for structural relaxation.

Now, in terms of kinetics, these are the main equations you can actually use to essentially model all kinds of relaxation kinetics, the most important one being this single first order theory, where you assume the relaxation rate of some parameter p scales with the driving force with the proportionality constant of a negative 1 over tau relaxation. That's the most simple one. And that will give you, essentially, a single exponential decay when a response to a perturbation.

If you want to get a more refined model, you can, of course, take into account that there may be multiple relaxation mechanisms concurrently taking place. And that's where you're actually introducing a stretched exponential there to describe the dispersion of relaxation time. Once you know this relaxation kinetics, in the end, you can then plug this function, psi, that gives you relaxation kinetics into the Boltzmann Superposition Principle, which then gives you the full description about how the relaxation is going to respond as any kind of time-dependent perturbation.

So, basically, what we have-- what you have learned in this lecture, in essence, is that you will be able to cope with any kind of realization problem, the kinetics, as long as you know the relaxation kinetics model, as well as the time-dependent perturbation. By combining them into the Boltzmann Superposition Principle, you can predict all the parameters you need. Yeah, this is just a quick summary of all the other theory, which I'm not going to go through yet. Any more questions about relaxation before I move on to talk about mechanical properties?

All right, so now let's switch gears a little bit and let's talk about mechanical properties. So talking about speaking of mechanical properties, so if you are talking about inorganic network glasses-- so let's exclude metallic glasses for now because they are quite different in terms of mechanical properties. If you think about inorganic network glass, what would be the first word that comes into your mind when talking about mechanical properties?

AUDIENCE: Fragile.

JUEJUN HU: Fragile, brittle, stiff, whatever. Now, is that perspective supported by actual numbers? We are scientists. We go by numbers. So this is what we have. If you look at the ultimate tensile stress, for iron, 35 megapascal, structural steel, 550 megapascal. But for glass, glass fiber, they are like an order of magnitude higher in terms of the tensile strength compared to steel, high-quality steel.

So what does that mean? This contradicts our conventional wisdom. It means glass is actually very, very strong. So, in fact, exactly, that's what we have. Why all the superhero movies, why do they have Iron Man? You should have Glass Man. Glass is a lot stronger than steel. Why do you get Iron Man there? What's wrong?

AUDIENCE: Sell that to Marvel. I said, you can sell that to Marvel.

JUEJUN HU: We can try. [LAUGHS] Yeah?

AUDIENCE: [INAUDIBLE]

JUEJUN HU: Why we have this impression that glass is fragile and brittle, they are much weaker than steel? Well, we have to step back a little bit. And let's start by essentially talking about, essentially, the different measures, how we actually measure the strength of a material. So when we talk about strength, that's a pretty loosely-defined term. In fact, there are two-- when we talk about mechanical properties, there are two parameters we talk about. There's the strength. There's also toughness. We should probably learn in mechanics class.

Strength is basically the amount of stress you apply to a material before it caused some kind of change, like failure. Toughness, on the other hand, is actually measuring the energy the material will absorb before it comes to failure. And that's actually different because we look at, for example, when I'm plotting here, this is basically a strain-stress curve for two different classes of material.

Essentially, our left-hand side, this is a ductile material. Right-hand side, this is a fragile material. Or, actually, brittle material, sorry. So on the left-hand side, this would be for things like polymers and metals, where they can actually produce a significant amount of plastic deformation. So then if you start to apply stress, then what happens there, initially, you get this linear deformation there, linear elastic deformation. This is the [? hooking ?] range.

At some point, you start introducing significant amount of plastic deformation. This is how you define your stress. This is when the plastic deformation reaches 0.2%. If you continue to deform it, at some point, you're going to reach the ultimate strength. Beyond that, you see the stress actually decreases. This is because of necking. So some regions of the sample essentially becomes narrower. The diameter becomes smaller. So as a result, this leads to a concentration of the stress. And that's why you see, essentially, the stress actually sort of decreases and then eventually fractures.

Now, the major toughness, you are looking at the area under the curve. The area under the curve gives you essentially the energy absorbed by the material per unit volume. So, essentially, it's W divided by V, where W is the absorbed energy and V is the volume of the material. So for a ductile material, because there's a very large plastic deformation, the area under the curve is also very large.

It means that this plastic deformation allows you to absorb a lot of the energy before it breaks. And this is in contrast to a brittle material, like glass. For glass, essentially, you have this elastic deformation. And then that very little amount of plastic deformation actually takes place. It just cracks. It just breaks. So because of this small amount of plastic deformation, it means that the area under the curve can be much smaller, even though the stress, strength, can be very high.

Strength is what you measure the stress you need to break the material. So high strength does not always equate to high toughness. Ductile material tend to be tougher, even for the same amount of ultimate strength. So this explains partly why, material like steel, people consider it to be stronger. It's because we are mostly talking about toughness there. Steel can absorb a lot more deformation, a lot more energy, compared to glass, even if they have the same strength. That's one part of the story.

Second part of the story is that the strength of the glass material tend to be also very sensitive to defects. So you can get very high-quality glass fibers with a high strength there. But if you're talking about the glass, well, we use every day, the actual strength is actually much lower compared to glass fiber because of the presence of defects.

So to see, what will be the strength, theoretical strength, of a brittle material, let's take a look at this very simple model here. So what we are trying to predict is we are trying to predict, what is the ultimate strength of glass from a theoretical perspective? So if you look at the process here, when you actually apply a tensile stress on a brittle glass, what you are really doing is increasing the spacing between these atoms. You are stretching the material and, therefore, increasing the average spacing between the atoms.

So in this process, when the average spacing between atoms increases, the attractive forces becomes larger than repulsive forces. So the atoms want to stick together. And that's why you see there's actually a stress accumulating inside the material. And it increases initially with increasing amount of strain. Now, at some point, you imagine that, when atoms become so far apart, you start to pull them so far apart, the interaction between them also starts to get weaker because the longer distance. So the stress will have to decrease after some point.

So now if you plot the stress-strain curve, it should look something like this. It will increase initially and then decreases. And then the top point here will now defines, essentially, the ultimate strength of the material. The slope of this curve when the strain is small, this then defines the elastic constant, Young's modulus. E will be Young's modulus, is the proportionality constant, [? pure ?] in the hooking can range. So if you look from the energy perspective, what happens there? You perform some work. You stretch the glass. Eventually, you break it.

The energy has to turn into something. So in this particular case here, the energy contributes to breaking of the chemical bonds When you break the chemical bonds between the glass or atoms, you essentially create new surfaces. So the work you perform now gets stored in the system in the form of surface energy. So what we argue is that the area under the curve should equate to the surface energy you generated due to the breakage of the glass.

So now, based on this insight, we can then actually quickly try to derive, what is the theoretical strength of the brittle material? We're trying to calculate, what's sigma m? So we can make a first approximation here. If you look at the shape of this curve here, it increases and then decreases. We can approximate it as like a sine curve, just to make it simpler.

So if we approximate it as a sine curve, then the stress should then equals to a sign, some kind of strain. Now, the maximum point is defined by sigma m. Now, the coefficient before strain, this would be essentially related to the period of the sine curve there. So if you define this point here as lambda, then the [? period ?] will basically 2 times lambda.

So we can then write this as, this would be lambda, this would be a pi. So when epsilon equals to 2 lambda, when this train equal to lambda, this becomes 2 pi. You go through a full period of the sine curve. So next thing is that we know that the slope of this curve must equal to the Young's modulus at this point here. So, mathematically, that basically says, when you take the partial-- when you do the d sigma, d epsilon, when your epsilon is 0, this should equal to a? E.

So what would that be? If you take the derivative of the sine at 0, that would just be a sigma m pi lambda. So from that equation, you can now infer what lambda is. Lambda should just be-- let's see. Lambda is pi sigma m divided by E. So now, the next thing, we want to look at the area under the curve. This is absorbed energy, so w divided by v. This would be the area under the curve.

And what you would do, of course you do integration of sigma over d epsilon. You integrate from 0 to lambda. This is a sine curve. So, in fact, the area under the sine curve, there's a fairly simple conclusion, saying that it will be a factor of pi over 2, 2 over pi times the area under the rectangle that covers the entire sine curve. So the area under the rectangle will be just sigma m times lambda. You can also do the integration. You will come up with the same conclusion, basically.

So now you can plug-in the expression there for lambda. Let's see what we get. So it will be sigma m, E. Pi cancels out. And there's another factor, sigma m. Pi cancels out. That's also a factor of 2, so, yeah. So now the final question goes back to, what is the volume here that we should define?

So if you look at the vector w divided by v, w is the surface energy. It's the newly generated surface due to this breaking of the glass. So it can be described as gamma, which is the surface energy, times s. This would be the surface area. This would be the area of, essentially, the cross-section of glass that breaks.

We want to time a factor of 2 there. Why? Because anytime glass breaks, you generate two surfaces instead of one. So divide it by v. So what you see is that this vector now goes back to essentially the surface-to-volume ratio, surface-to-volume ratio. So volume, in this case, here, volume divided by surface area is just going to give you, essentially, the thickness of the glass sample we're talking about here. So this would just be 2 gamma, thickness of the glass.

So what would be the thickness of glass, a0 here? So this would be the thickness of glass that actually generates two fresh, new surfaces. So now, if you think about this process, the way I'm drawing it here can be a little bit misleading because the way I'm drawing it here seems like you have a large piece of glass.

When you start pulling it, only one-- you only get elongation within one of the atomic planes here, which is not the case in the ideal scenario, if it is completely [? defect-free. ?] When you stretch this class, due to symmetry, all the chemical bonds should be stretched proportionally. So when you break, you don't break at just one of these atomic planes there. In fact, all of them. You essentially break the entire glass piece into a set of single atomic plates. They should break all at the same time for the chemical bond, if it's uniform.

So, therefore, what it means is that, to generate two fresh new surfaces, you are really looking at only one single atomic plane. Each atomic plane generate two surfaces. The other way to think about it, just think about simple two-- just a bilayer glass. Start to stretch the bilayer glass, eventually, it's going to break. You generate two flat surfaces.

That's exactly the process, what we're describing here, if you just stretch a bilayer glass. So in this case, the thickness of glass, a0 would just be atomic spacing. If you have a thicker glass, you actually generate more surfaces. So you increase v, but you increase the s proportionally at the same time.

So now you can then finally put it back into the equation here. Now, you know whether w equals to vs. This is 2 gamma divided by a0, which is atomic spacing. You cancel out 2, cancel out 2. So now, finally, your sigma m becomes gamma E a0 square root. So this would be the theoretical strength of a glass. This is the stress you will need to actually break the glass sample to essentially create these fresh new surfaces.

All right, I'm going to quickly just end here. I just want to mention that now you have all these numbers. With this equation, you can go and predict the theoretical strength of glass. You come up with a remarkable number of 35 gigapascal. This is way higher than steel, way higher than any glass you actually measure. Typical glass, you actually get 30 megapascals. So it's like three order of magnitude lower compared to physical strength. However, if you look at silicon nanowire, they do get to the strength at least at the same order of magnitude.

So what it says, basically, is that there's some kind of defects in glass, microscopic defects. The defects compromise the strength of the glass material. However, if you go to a nanowire, because it's so small, the probability of having a defect-free nanowire is much higher compared to bulk glass. So that's why you can approach this theoretical limit in silicon nanowire, but not in a macroscopic glass piece. So we're going to go into a bit more details about the theory later in the next lecture. Let's actually stop here. We are running out of time. Any more questions? Yes?

AUDIENCE: And what will we consider as a defect, defect within [INAUDIBLE] silicon nanowires since there's not any structural bias?

JUEJUN HU: You can still have defects, if you have-- I don't know-- maybe a tiny, little surface dent missing a few atoms. Or you just have non-uniformity. Diameter is non-uniform. There's some atom rearrangement or whatever having some-- one location. Or you have stacking difference. So you can have some defects there. But, again, it's so small.

And the defect we are talking about, as you'll see later, they are essentially microcracks. Those microcracks typically have a length of a few microns, which is much bigger than the nanowire. So that's why. In nanowire, in lots of cases, it can be considered as defect free. And that's why you can really approach the theoretical strength so closely. Any more questions? All right, thank you.