[SQUEAKING]

[RUSTLING]

[CLICKING]

JUEJUN HU: In the last lecture, we discussed about this. I'll give you a brief introduction about this topological constraint theory. The main takeaway message there is that you want to have essentially this isostatic network that strikes a balance between having sufficiently large barrier to prevent kinetically fast relaxation to the crystalline state. And also, you don't have a very deep global minimum such that thermodynamic force doesn't become too large and induces a very rapid crystallization.

So now the question of identifying the most stable glass network becomes essentially looking for-- essentially counting for the number of constraints and equating to the number of degrees of freedom to get isostatic condition. So now let's take a look at how we can actually do that. So what we will do next is then let's consider a kind of atom that has the N-- essentially forms N chemical bonds or N nearest neighbors.

And what we'll do is let's try to count essentially-- well, actually, let's use r, sorry. r. This will represent the number of chemical bonds one atom forms with its neighbors. Now let's start to count what's the number of constraints we have in the system here. So let's start with the bond-bending constraints. Sorry, bond-stretching constraints. So these are essentially the bond length.

So if you have r number of chemical bonds, what we want to argue is that for this particular atom, it contributes r divided by 2 number of bond-stretching constraints. Now the reason we include these two vectors there is because any chemical bond, this is always formed between two atoms. So effectively, it's shared between two atoms.

So if you count the number of constraints contributed by the center atom, this is really r divided by 2. OK? All right. That's a straightforward one. Now what about bond-bending constraints. We are talking about, essentially, bond angles. So for bond-bending constraints, you need to have at least two chemical bonds in order to have a bond angle coming from the same atom.

So what we'll do, let's take a look at a few cases here. Most simple case, suppose you have two chemical bonds. This is, in this case, r equals to 2. What will be the bond-bending constraint in this case? If it's r equal to 2, that's actually very straightforward. You get one bond angle. So there's only one bond-bending constraint. Easy.

Now what if we add another chemical bond? We have a 3, 4 coordinated atom. There are a couple of ways of looking at this. One is just to count the number of, essentially, bond angles you have. You can actually have three different pairs. You can have this bond angle here between these two chemical bonds. You have this one between these two chemical bonds. You also have another one between these two. So in this case, r equal 3. Then the bond-bending constraint would be 3.

Now the other way to think about it is, starting from this case here, you have two neighboring atoms. Then you add the third one. So anytime you add a new chemical bond, what the bond angle does is basically specifies the relative orientation of that chemical bond with respect to other chemical bonds. Now, geometrically, let's translate to a problem of defining the orientation of a vector in three-dimensional space.

So the orientation of a vector in a three-dimensional space can be specified fully using two parameters. If you think about a spherical coordinate system, or a polar coordinate system, you can define the orientation by using essentially one of the polar angle and then also the azimuthal angle. So two parameters fully defines the orientation. So that's why, when you add a third bond, you actually add two more bond angles effectively or bond-bending constraints.

So same thing. Now if you have another one, if you now go to 4 chemical bonds, it will start from essentially the r equal to 3 case. This is already 3. The new one added, you also need two more new parameters in order to fully specify the orientation of the chemical bond. So this will be a 5. And that's where the generic expression comes in.

This will be 2r minus 3 here for any r that's greater or equal than 2. This then defines the number of angles you will need to fully specify the relative orientation between the different atoms here and the chemical bonds. Make sense? All right.

So now, the next part, we have been talking about one single kind of atom that has a r coordination number. So if you're looking at a glass network, it consists of different kinds of atoms. To count the number of constraints, you need to essentially add it up over all the constituent atoms. So the total number of constraints-- total number of constraints-- this will be essentially you're summing over all the atoms.

So in your network, if you have a total of N number of atoms, then for each atom you have essentially r divided by 2 plus 2r minus 3, which gives you pretty straightforwardly this is just a 2.5r minus 3. Just arithmetic sum of all the constraints where we have assigned the constraint essentially to associate with each of the atoms there.

All right. Now next thing, let me introduce one parameter here. This is what we call the essentially average coordination number. Specifically, it's called mean coordination number. Mean Coordination Number, MCN. It's basically just the average, weighted average, of the coordination number weighted by, essentially, a fraction of the atoms in the solid.

So what we will do for this one, by definition, you are summing over all the atoms in the solid and then dividing by N. This is the total number of chemical bonds, basically, divided by N. So now comes back here. We can simplify the expression a little bit because we are looking at here. The sum of a sum, you can directly put the N in there because, for example, you're summing over constant.

So what you have here? You have a constant factor of 2.5. You can pull it out of the summation. It becomes Nr minus. 3 is just a constant. So it's the same for all the atoms. So it's basically 3N. Now look at this factor here, r summing over N. You can now apply that expression there. And now write it as 2.5 mean coordination number times N minus 3N.

Now, last part, we need to equate it to the number of degrees of freedom. What's the number of degrees of freedom? You have N atoms. Each atom, you need to specify its location with xyz coordinates in 3D space. So total number of geometric degree of freedom is 3N. You equate the two together. You cancel out N. It becomes very straightforward to see that r, this mean coordination number or average r, equals to 6 divided by 2.5, which is 2.4.

Now, what we have seen here up to this point is that the whole problem of glass network stability reduces to one single number. The mean coordination number of the glass network should equal to 2.4. Topologically, this also makes sense. Why is mean coordination number important? It gives you the connectivity between neighboring atoms, which, of course, relates to the number of constraints and the isostatic condition. So we do expect that this has a very important impact on the topological behavior of the glass network, this number.

So this number, this is also known as the Phillips' magic coordination number. JC Phillips is the physicist who first proposed this whole concept of topological constraint theory. And it's also a very popular number. If you go to glass conferences, they will be talking about this r equals 2.4 all the time. OK.

All right. So if you're happy with that, now what we want to do next? Let's look at some examples, how we actually apply this condition to gauge the glass-forming ability of different composition of glasses. So let's start with a-- I'll pick a random glass. I have on the slides germanium selenide. Let's see what we can do. Let's say germanium sulfide. I'm not being very creative.

So germanium sulfide. Let's say it's germanium 1 minus x Sx. OK. All right. So how do you calculate the mean coordination number? As I said, this is basically a weighted average of the coordination number of these constituent atoms weighted by this atomic fraction. So in this case, because we already have the total mole number normalized to unity, it just becomes r with two atoms.

Germanium is fourfold coordinated. So it's 4 times its fraction, which is 1 minus x. It has to be atomic fraction, by the way. Don't do it with weight. This has to be atomic fraction when you're trying to apply this method. Sulfur is twofold coordinated. So it's 2 times x. Let's see what we get. This becomes 4 minus 4x plus 2x. This becomes 4 minus 2x.

We then equate to 2.4, which says now x has to be 0.8. So plugging that here, it means that the most stable glass composition in the germanium sulfide family should be-- this one is 0.2, this is 0.8. Yeah. Basically, GeS4. And in fact, it does agree with the experiment. This particular stoichiometry gives you the best glass stability.

Now, one thing you also probably notice, on the slides, I have germanium selenide as an example, versus on the board, I have germanium sulfide. The result is exactly the same because sulfur and selenium, they both have two-- they form two chemical bonds. This is one feature of this kind of topological theory. The chemical nature of the atom actually does not matter. The only thing that really comes into play is the connectivity or the number of chemical bonds they form.

Now one more exercise. Let's try, let's say, arsenic selenide. So same thing, 1 minus x, arsenic, x. So in this case-- this will be pretty straightforward now-- arsenic is group 5. So it's threefold coordinated. It will become 3 1 minus x. Sulfur, same thing twofold coordinated. 2x. It becomes 3 minus x equals to 2.4, which then tells you that x has to be 0.6.

And 0.6, if you come back here, it's basically arsenic 0.4, sulfur 0.6, which you can simplify it as As2S3, which you notice, this happened to be the stoichiometric compound composition. This is a coincidence, but arsenic sulfide indeed is actually a very stable glass. It's probably one of the most commonly used chalcogenide glasses for many applications. It's very stable.

All right. Now, a little bit of exercise for you. What about SiO2? Not SiO2, I mean S, silicon oxide glass. Si, 1 minus x. Oxygen, x. What would that be? You can see the answer, in fact, without even doing the calculation. Because you may have noticed, silicon is the same as germanium. Oxygen is the same as sulfur.

So what does that mean? The most stable composition should be SiO4? That does not agree with the experiment. In fact, SiO2 is one of the most stable glass, as I will talk about repeatedly. So why is that? Well, this has to actually go back to something we actually discussed in the previous lecture.

So in the first section, when we were talking about liquid, I mention that because liquid usually resides at high temperature, at high temperature, the atoms have lots of kinetic energy. They can move around. So it means that some of the constraints can get compromised, can get relaxed. I specifically give you the example here where if you look at this plot, it says that one of the chemical bond angles, specifically Si-O-Si bond angle, it shows a very large dispersion in the glass network. So effectively, at that high temperature, this bond angle is being relaxed.

So if this bond angle is being relaxed, the way we count the constraint has to be modified. This r equals to 2.4 no longer applies. What we have to do, we have to go back to the fundamentals. And let's now redo the bond-counting process, but now specifically distinguishing between the two types of bond angles.

So if you still think about the SiO glass structure-- we have already mentioned about that. This is basically silicon-oxygen tetrahedra. They share corners. And that's how you form the silica glass network. Now keep in mind, the bond angle that's getting relaxed is this one. It's what links between the two neighboring tetrahedrons.

The bond angle, the oxygen-silicon-oxygen bond angle, this one is not getting relaxed because the tetrahedra itself is quite rigid. So it doesn't really deform, even under high temperature. So what that means is when we are calculating the bond-bending constraints, any chemical bond coming from silicon, we still have those constraints intact. But for chemical bonds that originate from this oxygen atom, we should not count the bond-bending constraints. That's how we discount this particular one.

So now let's go back and take a look at the number of constraints. First thing, if you look at the bond-stretching constraints, it's the same. Chemical bond angle doesn't really get changed that much. So the bond-stretching constraints, it will still be 1/2 r. So if you follow the convention we have here-- let's look at the silica glass with Si x, oxygen, 1 minus x. Let's use this particular stoichiometry here.

Now let's consider a bond-stretching constraints. For the bond-stretching constraints, we have 1/2 r here, which for silicon is 4. We then have to times the fraction of silicon in the network. So silicon is x in this case. So if you think about essentially, effectively, one more of this molecule, then the more number of the bond-stretching constraints is going to be what I'm writing here.

So then, for oxygen, again, it's r divided by 2. Oxygen, r is 2. So this is 2 divided by 2. And then times, in this case, 1 minus x. So let's see what we have here. This is basically 2x. This is basically 2 minus-- sorry, 1 minus x. So it's 1 plus x.

So now let's look at bond-bending constraints. For bond-bending constraints, we have already did the calculation that it's given by essentially a 2r minus 3. But in our calculation, this time, we should only account for the chemical bonds that originate from the silicon atom. So when we apply that to r minus 3 equation, we should apply only to the silicon atoms.

So for silicon, it's 2r, which is 4, minus 3. But now we should time it with the fraction of silicon and drop the second term that relates to oxygen. So what we have here, 2 times 4 minus 3. This is 5. 5 times x. That's what we have. 5x. So now, add up together total number of constraints. This would be a sum of the two, which just trivially gives you 1 plus 6x. We similarly equate it to the number of degrees of freedom.

Now, the way we are doing it here, the formula I'm using here, I'm basically assuming that we have one more of these molecules. And then the number of constraints we calculated here, the unit of this one is actually more. This is 1 plus 6x more. So for one more of this molecule here, then the number of degrees of freedom should be 3.

Sorry, it should be just 3. 3 more. I should say one more atom, to be exact. That's confusing. The total number of atoms, silicon plus oxygen, equal to 1 mole. That's the way I'm writing it here. Because x plus 1 minus x equals 1. So we have three more of degree of freedom. If you equate the two, then it's straightforward to see that our x becomes 0.5.

Hmm? No, no, sorry. It should be 1/3. x is 1/3. So if x is 1/3, then the condition would exactly be SiO2. So now we have agreement with experiment. SiO2 indeed is a very, very, very stable glass.

AUDIENCE: Sorry. Can you just explain the origin of why we're relaxing the oxygen-- or the oxygen is similar?

JUEJUN HU: This comes from experiment. It's actually a bit difficult. In the next slide, I'm going to show you how we actually do that, in a couple of slides. But it's a bit difficult for you to predict a priori which bonding constraint are relaxed, which ones are not. So the way we can discount this Si-O-Si bond-angle constraint is because if you go to experiment, when you actually do the experiment from diffraction, you actually measure the distribution of bond angles in the silica glass network.

What you find out is that instead of having a narrow peak, you get this very, very broad peak. If you have a very broad peak, essentially means that, essentially, between the two chemical bonds, the bond angle is actually not fixed. It's very floppy. You can actually bend it. So if you can bend it over a large range, that constraint is no longer existent. It does not place a constraint in, essentially, the geometric position of atoms.

So that's why we discount it. Basically, it depends on our experimental evidence. And this usually happens actually for oxide glasses, especially for things like silica. if you add network modifiers, you decrease the glass transition temperature, then this phenomena is OK. It's not that severe. The problem with silica is that because it has no network modifiers, its glass transition temperature is very, very high.

So at the glass-forming temperature, some of the constraints will be relaxed because of very high kinetic energy of the atoms. So that's why. So that's why I put the statement on top there. "The constraint number should be evaluated at the glass-forming temperature." Because the temperature range where the glass stability matters is when you're actually trying to form glass. When you're trying to form glass, you need to bypass the crystallization. You need to suppress that. And so that's why the glass stability should also be assessed at that particular temperature.

So for something like silica, that actually makes a difference. Now if you look at chalcogenides, if you look at the example, I'm giving here, I like to use chalcogenides as an example not because I myself work on chalcogenides. It's because chalcogenides, as I mentioned, they usually typically have low glass transition temperature. Their transition temperature is like 100, 200 degrees Celsius.

So at that much lower temperature, most of the constraint is perfectly maintained. So that's why they serve as very good examples to actually illustrate the, essentially, efficacy of the theory there. OK. Make sense?

AUDIENCE: Yes.

JUEJUN HU: OK. Now last point here. I also have a one question there. Why does oxides and chalcogenides make good glasses? Now, if you think about this r equals 2.4 number there, oxygen and sulfur, they have essentially two. They form two chemical bonds. So you have two chemical bonds. If all the atom has two chemical bonds, then you can imagine that the best thing you can do is form essentially long linear chains.

If r equals 2.4, you add some other atoms with higher valence number. Essentially, those atoms can serve as cross-linking points. They then cross-link these long chains to form 3D network. So topologically, that's part of the reason why oxygen and chalcogenides, oxides or chalcogenides, they are preferred as glass constituents because it's very easy to add some additional elements, nonmetal elements, to actually reach that 2.4 number.

OK. So by the way, in the p-set, I'm actually giving you one more example. You remember I mentioned about this soda lime glass composition, something like 16 Na_2O, 10 CaO, 74 SiO_2. In the p-set, which I already posted on the Canvas website, by the way, you can actually go ahead and do the calculation for that particular glass composition. What you'll find out is that r exactly equals 2.4 for that one.

So there's a good reason why people converge to that particular composition-- because it's a glass stability. Again, people do it previously empirically. But now, here's some theoretical insight to see why that actually matters.

Now, building a bit more on this concept of temperature-dependent constraints. So I've already said that as you raise the temperature, some of the constraints will start to relax. So you can further elaborate on this concept. You can assign one onset temperature or one threshold temperature to each of the constraints. Above that temperature, you can consider the constraint as being absent or getting relaxed.

And that temperature will obviously be different for different kind of constraints. So for the more soft bond angles, like Si-O-Sio, this will relax at low temperature. But for this one, this is a much more rigid structure. O-Si-O, this one won't get relaxed. The bond length, the bond-stretching constraints, usually, those are also only relaxed at very high temperature. So then what you can do is that you can actually now derive-- if you know that onset temperature for different constraints, you can now derive the number of constraints as a function of temperature. OK?

Now the other peculiarity I also have to mention here is that the glass structure can also be a function of composition and temperature as well. One good example will be think about borate glasses. So borate glasses, if you put alkaline in there, you can get this essentially nonbridging oxygen. You can get [? BO3-to-BO4 ?] conversion. So if you want to determine the number of constraints, it's quite important to decide what is the structural regime you are located at.

So determining constraints may be a bit more complicated than just simply counting the number of valence states. You need to know what structural moieties actually exists in the gas network. But if you have that information, then what you can generate is a plot, like what I'm showing here. This is quoted from a paper discussing about this.

I have already posted this paper, by the way, on the Canvas website. It's a pretty nice summary about how people use this theory, not just for predicting glass stability. So if you look at this plot here, essentially, what they were doing there is that, using this topological constraint theory with the known onset temperature of different constraints, they can now determine the number of constraints inside this kind of a ternary system. This is actually a alkali-alkaline-earth borate glass.

So now, why is this important? The key thing here is that if you know the number of constraints, you can also actually predict the entropy of the system. Now, that actually makes sense because think about what entropy is. Entropy is the number of microstates the system can access. If you have more constraints, each constraint essentially restricts the geometric configuration your network can actually access.

So it's quite natural that you can actually go from the number of constraints to essentially the number of microstates, which gives you entropy. So if you know entropy, there are a number of statistical theories that allows you to connect entropy to other thermodynamic and rheological parameters. You can calculate, for example, enthalpy. Then you know the forming energy of different glass compositions, which one can be more stable.

You can know the viscosity. Again, it also makes sense. Viscosity essentially is the ability of glass to flow, basically. So if you have a more rigid versus a more floppy network, they will obviously have an impact on essentially the flow behavior or rheological behavior of the glass fluid. So you can actually know lots of very important glass parameters, just based on counting the number of constraints available in the system.

And specifically, viscosity is also very important because, in the glass community, the way we define Tg, glass transition temperature, this is defined with respect to viscosity. So Tg in the glass community is defined as viscosity eta equals to 10 to the 12 pascal-second. Later, we are going to elaborate on this concept a bit more when we talk about viscosity of glasses.

But if you can predict the viscosity as a function of temperature and glass composition, you can now actually generate the Tg for all glass composition groups. This is of very significant practical importance because Tg is a very important glass-processing parameter. It defines the processability of the glass. So now you already see that this theory can be actually very powerful.

As I said, if you go and look at this paper, this is a paper from a group in Corning. They're actually already applying this kind of topological constraint theory to guide the design of some of the latest glasses you see in consumer electronic devices. Any more questions about this part?

All right. Now before I move on, I also want to quickly just highlight a few points about how you actually correctly count the number of constraints. We already covered some of this. For bond-stretching constraints, this is a more straightforward one. You can basically just apply the 8 minus N rule for these nonmetal covalent-bonded solids.

If you have group 5, for example, it's 8 minus 5 equals 3. You have three chemical bonds. Group 6, two chemical bonds. And so on and so forth. So that's 3 [INAUDIBLE]. However, there's exceptions here. The exceptions mostly come in for those heavy elements. I'm giving you an example there, tellurium.

Tellurium is notorious because they can actually form any valence-- they form any valence state from minus 2 to plus 6. Anything in between. So if you see any glass containing tellurium, you have to be very careful there. You actually need to perform either structural characterization, like some diffraction techniques to actually ascertain what are the chemical mole numbers, or you have to perform some first-principle calculations to actually determine the actual coordination number. So just be very careful with those heavy elements, where its valence state is subject to change.

All right. For bond-bending constraints, we have covered this. For glasses with low glass-forming temperature, like chalcogenides, that's pretty straightforward. You can safely apply this to r minus 3 equation there. But for glasses with high glass-forming temperatures, you have to account for the fact that some of the bond-bending constraints may get relaxed because of the high energy of the atoms. So in that case, you also have to do either experiment, like diffraction experiments, to look at structure and relaxation of the configuration, or you do simulations to actually predict it. OK?

All right. So in this slide, I also want to highlight another fact that this magic number, 2.4, is not only important for determining the glass network stability, it also impacts the properties of glasses. So many glass properties, they will actually exhibit essentially an extrema that corresponds to this mean coordination number of 2.4. So I'm giving two examples here.

So for example, on the left-hand side, I'm actually showing you how the molar volume varies as a function of mean coordination number in these binary and ternary glasses. In both cases here, you notice that there's a dip right at 2.4. On the right-hand side, this is the actually heat capacity. Again, similarly, you see a little dip here at 2.4.

And later, on when we talk about mechanical properties, you're going to see that all the elastic modulus, they also usually show a extrema right at 2.4. So that's why the glass scientists appreciate the importance of this magic number there. It's definitely quite important.

All right. So now, before we wrap up this part about glass-forming theory, I also want to quickly mention about, practically, how do you actually measure and essentially gauge glass-forming ability? So one of the very common figure of merit many people use to essentially measure the glass-forming ability is this delta T. It's basically the difference between crystallization temperature and glass transition temperature.

So Tx, as we have mentioned, this is the temperature at which you start to see crystallization of a sample under certain annealing conditions. So the higher Tx, the most stable a glass is. And above Tg is where you start to see significant structural relaxation and those kind of things. So the gap in between gives you the ability of the network to resist this kind of relaxation. So that's why it makes sense that this actually a figure of merit to gauge the glass stability.

Now, that said, I do want to mention that this figure of merit is very much an empirical parameter because if you think about Tx, I have already mentioned that Tx itself is an empirical parameter. It depends on how you actually anneal it, how you prepare the glass, and how long you actually anneal it even. So Tx can be varied quite a bit depending on specific experimental conditions.

Now, what about Tg? Tg, depending on who you talk to, you have different definitions. If you talk to a glass scientist, they'll tell you this is the definition. It's defined with respect to viscosity. Now if you go to talk with a polymer scientist, you may get a different answer. They prefer to actually measure Tg from thermal measurements, essentially, or calorimetric measurements.

So for example, you can measure the heat capacity of a glass or polymer, amorphous polymer. And we know that if you think about this plot there where we look at enthalpy as a function of temperature, there's actually a slope change when you go from glass to supercooled liquid. Supercooled liquid tend to have a higher heat capacity because you have more degrees of freedom to access in the network there. So that's why it has higher capacity. And glass tends to have lower heat capacity.

Now the question is, how do you actually connect the two in between? So you may get something like this, which is good. Nice, smooth curve. But practically, you may also get-- well, if it's something like that, that's pretty straightforward. The way you define Tg is you do extension between these two lines there. The crossover point defines you what the Tg is.

Now, you may also get something like that, or you may get something like this. It all depends on relaxation behavior in that regime. I mean, some people still define it. They can, for example, define, if you extend these two lines, the crossover point actually gives you the Tg. But as you can see, this is a bit arbitrary. And it also depends on how you actually perform the thermal measurement there. So that's why.

You have to be careful. When you're trying to compare this delta T number here, you have to essentially compare apples to apples. Make sure you are comparing two sets of experiments that's performed under similar conditions and apply similar criteria. All right.

Now, one quick thing. There are some alternative figures of merit here. This one is called Hruby coefficient. It's very similar. It's basically just normalizing the two melting points of glass to account for that different glass compositions have different melting points. So it's like normalized delta T.

So we can wrap up this chapter here. So we have basically covered three main theoretical aspects of glass transition. We talk about kinetic theory. On that, the most important part is T-T-T diagram. You need to be very proficient about how to read and interpret the T-T-T diagram and use that to actually make informed decisions about the glass-processing temperature conditions.

We talk about glass. We talk about laboratory glass transition. Basically, glass transition is ergodicity breakdown. Liquid is ergodic. Glass network is nonergodic. That can also explain why you have this history dependence of glass properties. And finally, we have seen one example where topology can actually predict glass stability for network glasses. We are going to see that example again when we go to metallic glasses. It's a different kind of topology but same idea. It's not so much about the chemical nature of the atoms, but it's just about essentially coordination and geometric constraint that actually limit the glass stability. All right

So any more questions about this part before we move on to the next one? So now the next lecture, as I mentioned in the first lecture there, the way we organize this class is that we will have one section talking about the fundamental theory, and then we have one section talking about the practical applications, how to actually apply the theories into something with practical significance. So for glass forming, we are going to see some applications, how we can actually use that to guide the design of phase-change materials.

So what are phase-change materials? It depends on who you talk to, again. There are actually two main classes of phase-change materials. In the energy storage community, people use phase-change materials to actually store energy. Energy relies on latent heat. The phase-change materials I'm talking about here, these are more for optoelectronic applications, electronic applications. People use them for memory applications. Electronic memories.

So this particular class of Phase-Change Material, or PCM as we call it, they can switch between amorphous and crystalline states. What's really unique about this kind of phase-change material is that while you actually change the atomic arrangement, you also change the electrical and optical properties dramatically. The amorphous state tends to be more electrically insulating. It also tends to have a low optical reflectance, which is basically low refractive index, in this case.

Versus crystalline state, it becomes electrically conductive. It's actually become a degenerate semiconductor. And then it also has a very high optical reflectance and much higher refractive index. This is quite unique behavior. Most of the materials, its electrical and optical properties are largely dictated by the constituent elements. So if you change the structure from amorphous to crystalline, it doesn't really cause such a huge perturbation of electrical optical properties.

So that's why only a handful of materials can be called phase-change materials, despite that practically all materials can switch between amorphous and crystalline state as long as you quench fast enough. We are going to talk about the structural origins, why this material is so peculiar, later on. But for now, you can actually switch these two states reversibly. So you can go from amorphous to crystalline. This is called step process. In a step process, what you do is you try to heat up the material to above its crystallization temperature, Tx, but below the melting point.

And then, within this temperature range here, the thermodynamically stable state is actually crystalline state. So then, if you hold it there for some time, allow the atoms to move around and find the thermodynamically stable position, then you actually induce crystallization. Now if you want to go in the reverse direction-- this is called the reset process in the memory community-- you essentially apply a pulse. Very short, pulse, but intense.

You melt the material so it becomes liquid. You very quickly cool down to essentially bypass crystallization. You then freeze in this kind of liquid-like amorphous state. That's what you get. And you can amorphize the material. So because you can do this kind of reversible switching between the two states here, and these two states has a very large contrast in terms of electrical and optical properties, people are using them as essentially memories.

You can encode digital ones and zeros in the two states of the material, and you can read out, essentially, this kind of information either electrically, by looking at resistance, or optically, by essentially shining a laser on that and looking at reflectance. So this is a material that has already been very widely deployed in commercial data storage. Rewritable CDs, DVDs, they are made of phase-change materials. Companies like Intel or Samsung, they have also developed electronic memories based on this kind of phase-change materials. So that's why this is quite important here.

So now, for this next slide, what I want to do, before I go into more detail description about the properties, I want to first define a few key performance metrics and try to link it to the material properties. Key performance metrics for memory storage applications. So for memory, these are the important parameters here. You want data retention. Basically, it means that if you have stored something in your memory there, you want it to stay for some time. Like for rewritable CDs, DVDs, you probably want it to stay for at least a few years before it gets wiped out.

So now the question-- what is the relevant material property that dictates data retention? Yes?

AUDIENCE: That'd be phase stability.

JUEJUN HU: Yes. Which phase?

AUDIENCE: I'd say amorphous.

JUEJUN HU: Perfect. Yeah. Because crystalline is thermodynamically stable. So it should stay forever. So really, the problem is just amorphous phase. You don't want it to crystallize. So you want some material that has sufficient glass-forming ability. So it doesn't really easily crystallize. Now, next one. What about programming speed? Essentially, it means that you need to be able to write information into the memory quickly.

So there are two processes there. You have set and reset. Which one do you think is the faster process, amorphous to crystalline or crystalline to amorphous?

AUDIENCE: Crystalline to amorphous?

JUEJUN HU: Yes. I mean, you can already read it from the problem there, but the idea is that if you go from amorphous to crystalline, you need to heat it up and hold it there for some time because you need to allow the atoms to move around and actually find the right position, versus crystalline to amorphous, you actually want to do it very, very fast. You just heat it up, quickly quench down. You don't want the atoms to be allowed to relax. So inherently, amorphization is always faster than crystallization. So what that also means is that when you're talking about programming speed, you want the material that can crystallize quickly because that's the rate-limiting step.

All right. So now if you look at the first two conditions there, there's a trade-off. You want something that can retain the data that doesn't want to crystallize. But you also want something that crystallizes very quickly so you can program fast. Can you get something with a balance in between the two? Now, for that, I do want to highlight one thing, very important thing. When you're talking about data retention, you're typically talking about stability of phase at near room temperature, near operating condition.

Even for computer memories, you're probably talking about maybe 100 degree Celsius or something inside your box, mainframe. But for crystallization, when you're actually trying to program it, you do it at much higher temperature. You want to do it actually at the nose temperature of a T-T-T curve because that gives you a shorter crystallization time. And for these chalcogenides glasses-- well, for this PCM. We're going to talk about it. They are chalcogenides. For this kind of phase-change materials, the typical crystallization temperature is of the order of a few hundred degrees Celsius, say 200, 300 degrees Celsius.

So that's considerably higher compared to room temperature. So basically, what we want to do is we want to maintain good glass stability near room temperature, but maximize or expedite the kinetic crystallization at elevated temperature. So how do you engineer that? What is the material parameter that's relevant to that? I mean, effectively what I'm asking is, what material parameter dictates the temperature dependence of kinetics? Or how do you describe the temperature dependence of kinetics?

AUDIENCE: That it's a critical component?

JUEJUN HU: Yes. I mean, that's the parameter you measure eventually, the performance. But think about the temperature dependence of critical cooling rate, for example. Not exactly, but the temperature dependence of the crystallization speed, crystallization time, or temperature dependence of any kinetic process, what equation we use to describe it.

AUDIENCE: Is it the temperature-dependent constraints?

JUEJUN HU: There's something simpler than that. Think about kinetics class. How do you describe, when you change temperature, how fast does the process change?

AUDIENCE: Like to activate them?

JUEJUN HU: Exactly. Arrhenius law. So yeah, if you think about Arrhenius law, you go through the math, you can fairly easily find out that what you want is actually a high activation energy. Activation energy basically goes into exponent in the exponential law. So if you have a high activation energy, then you create a very large drastic change. As you change the temperature, the kinetic rate changes very, very fast.

So effectively, I mean, most of the actual practical phase-change materials, they tend to have a fairly high nominal activation energy for crystallization. And that's why, in terms of crystallization at high temperature, they can crystallize within a matter of a few tens of nanoseconds. So very, very fast. But at room temperature, they can retain data for 10 years. That's all because of this dependence of crystallization rate as a function of temperature.

Now that's a somewhat simplified explanation. I do want to mention that it turns out, the viscosity, and hence crystallization velocity of phase-change materials, they do not obey Arrhenius law. They do not exactly obey Arrhenius law. But that's a good approximation. We'll stay for that for now. We'll talk about it when we actually talk about the viscosity of glass-forming fluids. But for now, we want something with high activation energy barrier.

All right. Now, next thing, recording density. Recording density means that you want to put as much information as possible, as large a number of bits as possible into one single area. So that has to do with essentially the scaling behavior of the material. If you want to make your memory element very, very small, each bit, for example, each unit cell in state of the art phase-change memories, they are tens of nanometers. So it's a very, very small cell.

So it's important to identify, do you have any kind of size dependence or material properties? Does it change crystallization behavior? Does surface or interface actually matter at that scale? So those are the things that actually come into play when you determine the recording density.

Another factor that also comes in there is actually the driver size. This has to do with electronics. You need to have electronics actually drive the memory. So the size of that driving electronics also matters there. And finally, last thing is that you can potentially increase the recording density in this kind of phase-change materials there by doing a so-called multi-bit operation.

So it means that, in one single unit cell, you now only have two endpoint states. This is fully crystalline. This is fully amorphous. You have lots of states in between that give you essentially partial crystallization. And those intermediate states allow you to essentially store multiple bits within one single unit cell. So if you read the literature, people have done 3-bit, for example, recording. Essentially, it means that you define 8 states instead of 2 states within one single unit cell. 8 different levels of crystallization. So that's one benefit, actually, for this kind of phase-change memory. You can do multi-level operation or multi-bit operation.

All right. Next one, endurance. Endurance is a terminology people using a memory community to describe cycling lifetime-- how many times you can essentially write and erase your information in the memory before it starts to fail. So to boost endurance, this has to do with-- essentially, you have to know the failure mechanism. What causes failure and degradation in this kind of phase-change material over repeated amorphization and crystallization cycles?

In general, for electronic memories, there's two main mechanisms that actually lead to a failure. One is electromigration because, as I will show you later on, the way we actually apply this kind of energy pulses to crystallize it and amorphize it, to essentially heat it up, is by passing current through it, by joule heating. But when you pass current through it, it means that you apply electric field across the material.

If you apply electric field to the material, you get so-called electromigration. The atoms can move in electric field. And eventually, this leads to segregation and failure of the device. You can even get voids, nanovoids, at some point because of the atomic migration, which then lead to, essentially, open circuits. So that's one mechanism of failure.

The second one is actually a phase stability. We will go into a bit more details later, but some of these phase-change memory materials, when they actually melt, they do not melt congruently. They phase-segregate when they go to liquid phase. So over time, that can actually accumulate. Essentially, it means you have essentially composition segregation, which harm the stability of the material.

All right. Last part, power consumption. You want the energy-efficient memories. So what dictates the power you will need to crystallize the amorphous? For amorphization, you need to melt it. So what that means you need to do is, first thing, you need to heat it up. You need to heat it up to melting point. So this has to do with essentially the volume, as well as the heat capacity of the material.

Second part is that there's the latent heat. You need to supply the enthalpy of melting to actually melt it into liquid. So for the amorphization process, the overall power consumption has to do, essentially, with the heat capacity as well as enthalpy of melting. it's sort of like, basically, the total heat you need to essentially melt it is the sum of two terms there.

For crystallization, heat capacity also matters, obviously, but for crystallization, what matters more is actually crystallization speed, because you want to heat it up and hold it there for some time until it crystallizes. The longer you hold there at elevated temperature, the more power you have to consume. So in that regard, you want a composition that can crystallize fast so that you can crystallize it quickly and have a lower power consumption.

Now, another thing that also relates to power consumption that's not directly related to a property of phase-change materials is actually a heat conductivity, thermal conductivity. So if you are surrounded with materials with very good thermal insulation properties, you can confine the heat pretty much only to your phase-change material rather than dissipating the heat to a much larger surrounding medium. So that helps you essentially limit the amount of thermal mass, and therefore make it more energy efficient. So that's also something to account for there.

All right. So if we keep that in mind, now let's actually take a look at a specific example of phase-change materials. The most commonly used phase-change material, they all come from this chalcogenide family. It's a ternary alloy. It's germanium antimony tellurium, or people call it GST. It was discovered by a few groups in Japan back in 1970s, 1980s. They found that this composition allows you to crystallize very, very quickly, which satisfies this property for, essentially, fast memories.

Now, specifically, if you look at the composition there, what I'm showing here is like ternary diagram of a germanium antimony tellurium system. Most of the phase-change memory material come from this pseudobinary system. It's this tie-line between the germanium tellurium and antimony telluride. So one particular composition that's probably the most prevalent is this one, Ge2, antimony 2, tellurium 5. This is called GST 225. This is the most widely used composition for this kind of phase-change memory applications.

But then you can, of course, tailor it to go to other compositions to engineer its properties. So now, if you think about the-- apply the glass-forming theory to this particular composition here, we need to think about the, essentially, glass stability. This is one of the cases you actually don't want good glass stability. Because good glass stability-- or let's say you don't want too good glass stability. Too good glass stability means it takes forever to crystallize, which is bad if you want a fast memory.

So it turns out, if you look at these kind of compositions here, they are all stressed rigid. They have a mean coordination number that's significantly larger than isostatic condition, which explains why these compositions, they actually crystallize so fast. In fact, being stressed rigid is also beneficial because, as I said, stressed rigid essentially means that you form a very deep valley or deep minimum corresponding to crystalline state.

And in this phase-change materials, in order to induce crystallization, what happens is that there are some atomic arrangements that closely resemble their crystalline configuration. So when crystallization happens, essentially it started out from these kind of arrangements that resemble the crystalline orientation, crystalline arrangement. And then the crystallization speed, growth speed, is actually very, very fast once you have a nuclei.

These represent some of the material that has the fastest crystal growth speed in all material systems. So then, if you have one nuclei, it quickly can propagate through the entire material. And that's how you actually get fast crystallization. So that's why people want to do it specifically in the stressed rigid network.

Now one caveat I do want to mention there is that if you look at this material system, we have two heavy elements that I have specifically listed in the previous slide deck that it's very difficult to determine the coordination number. So if you look at this particular *PRB* paper there, the authors actually did some first-principle calculations to actually predict what's the real coordination number for these elements there.

So it's different from you just use 8 minus N rule. What they have come up is this line here. If you go along this dotted line, this corresponds to the extra isostatic composition. This is, again, different. If you try to apply that simple 8 minus N rule, it's going to get different results. Anything to the right-hand side here, this is stressed rigid.

So if you add more fourfold-coordinated germanium or threefold-coordinated antimony, you actually increase the coordination number. And so what that also means is that if you go along this direction, you get compositions. They are becoming less and less stable. And less stable means faster crystallization. So that's why I have shown here, these are some examples of fast switching compositions, like this one here and this one here. So these fast switching compositions, they all lie to the right side, to this side line there, indicating a reduced glass stability.

Now the other possible way to tailor the composition is sometimes you may want to have high thermal stability alloys. This will be useful if you're trying to use your materials or the memories in high operating temperature environments. So they typically go along this line here, this red line, by increasing the germanium concentration. Now we wonder, if you go along this line, you also increase the mean coordination number. So the network actually becomes less stable.

So why you can have a better thermal stability, or in other words, better Tx? So this actually has to do with the definition of glass-forming ability. So when you're talking about high thermal stability, what you want is the high Tx, high crystallization temperature. But when we actually measure the glass-forming ability, the figure of merit is actually delta T. Tx minus Tg.

So if you go along this axis here, turns out the Tg also increases because germanium, as fourfold coordinated, increased the connectivity of the network. So you also increase Tg. So you actually have decreased glass stability, but the Tx increases as well. So it just has to do with how you actually identify the right figure of merit for specific applications.

All right. So now, last point I also want to make here is that I have already highlighted that this kind of phase-change material is quite unique in that they exhibit a huge contrast of properties between amorphous and crystalline states. This has to do with the chemical bonding nature. In the amorphous network, you have the conventional covalent bond, but when you go to crystalline state, you have the so-called resonant bonding.

So to explain that, let's take a look at the structure of this kind of GST alloy. So GST alloy has a quasicubic structure. It's pretty close to cubic. It's basically sodium chloride structure. So if you look at the sodium chloride structure, you have two penetrating sets of FCC lattices. And tellurium occupies one set of the lattice sites. Germanium antimony combined occupy another set of lattice sites.

But if you look at the stoichiometry, for 225, germanium plus antimony is 4. It's less than tellurium. So it means that this is not a perfect cubic structure. You get lots of native vacancies that comes in the lattice layer. All right. And that's why there's actually distortion through the lattice. So that's why I say it's quasicubic. It's close to cubic.

All right. So now, if you look at the chemical bond configuration, let's look at one plane here, one two-dimensional plane. Let's suppose we're looking at, say, germanium tellurium plane. It can be germanium antimony as well. Doesn't matter. Now, if you think about conventional covalent bonds, in a covalent bond, the two bonding atoms each contribute one electron, and these two electrons are tightly confined between these two atoms there. This is how you actually form the covalent bond.

For phase-change material, on the other hand, if you think about this conventional covalent bond picture, there are two different equivalent ways to arrange the chemical bonds. They are actually energetically equivalent if you look at these two pictures here, this one versus this one. So this solid line, this thicker line, essentially represents an actual chemical bond. So you can essentially generate a chemical bond like what I'm arranging on the left-hand side here. These are the atoms that actually have chemical bonds. Or you can also connect them together in a different manner there.

Now these two, by symmetry, you can easily tell that they should be energetically equivalent. So what actually happens in this process is that these two states are actually going hybridized. So instead of getting a well-defined covalent bond, what you get is this average connection between all the neighboring atoms. And the electrons essentially becomes delocalized. They can now move around between these neighboring atoms here.

Now, in fact, you might have seen one example of resonant bonding when you go to chemistry, if you think about benzene, benzene molecules. This is a six-membered carbon ring. You have some double bonds. You have some single bonds. You probably have learned from chemistry, saying that there are actually two resonant states for this benzene molecule.

You can go from that configuration to this configuration. They are energetically equivalent. So what we actually end up having is that the pi electrons essentially become delocalized. They just move around inside this benzene ring. So the mechanism that leads to electron delocalization in phase-change materials is similar to what you have in the benzene structure there.

Now I do want to highlight that the actual chemical nature is still quite different compared to benzene. And that's why some people like to call it a different name. They actually classify this kind of particular bonding in phase-change materials as a new type of chemical bonding called metavalent bonds. But anyway, that's the terminology people use.

Regardless, what happens if you have this kind of resonant bonding? This resonant bonding, it only exists in the crystalline structure. Why? Because if you look at these two states here, in a crystalline structure, you get this kind of periodic order. So these two, they are structurally equivalent. And that's why they are energetically the same. That's why they hybridize.

Now, if you break this kind of structure order, you introduce structure disorder, then you also break the symmetry between these two types of states. And as a result, in amorphous network, the bonding becomes predominantly covalent. So this kind of a hybridization is the consequence of symmetry and periodicity. If you break that, then you actually lose that nature.

So now, what's the difference in terms of properties? If you think about covalent bonds, the electron is very tightly localized. So it means that it doesn't really move around very far. Versus resonant bonding. Electrons are now allowed to move. They become mobile. They can move much longer distances in the solid. This corresponds to much higher electronic polarizability and conductivity. When you want to conduct electric current, you basically want the electron to move around in a solid. So that's why, when you go to crystalline state, these materials typically have much higher electronic conductivity because of the delocalization of electrons.

In terms of optical properties, refractive index of material actually has to do with the electronic polarizability. Light is basically electromagnetic wave. It's an oscillating electromagnetic field. So if a material has very high electronic polarizability, it means electrons can easily keep up with this oscillating electromagnetic field. So as a result, you have much higher, much stronger optical response. And therefore, you have a higher refractive index. So same thing.

That's why the crystalline state tends to have a much higher refractive index compared to amorphous counterpart. And that's why this material is so unique. You don't see that behavior in typical materials. You only find it in some materials that actually form this kind of a resonant or metavalent bonding.

All right. So our next part, now let's actually take a look at the thermodynamics and kinetics of the phase transition process. For thermodynamics, of course, as a material scientist, we all like phase diagrams. So this is one of probably the more complicated phase diagrams you will see in this kind of binary system. It's actually a pseudobinary system. This is between the germanium tellurium and the antimony telluride. So this gives you all the GST variants along that tie-line there.

So GST 225 is this guy. This is our GST 225. Now notice one thing. It's a line compound. But this solid compound, it doesn't go all the way to the liquid region. There's a little gap right there. So what happens if you reach this temperature? You go into a two-phase region. It essentially means that this solid decomposes into a antimony-rich liquid and a germanium-rich solid. This is called a noncongruent melting. It essentially means that this liquid line-- sorry, this solid line doesn't go all the way to the liquid region there.

So then this is actually-- this can be a concern from a reliability perspective or endurance perspective. If you are trying to melt this material, then you always form essentially different compositional regions. And over repeated cycles, this can eventually lead to a compositional segregation, which then eventually leads to failure. So that's why I'm saying that noncongruent melting and phase stability is one factor that limits endurance.

Now, you can find some other compositions where you actually have congruent melting. And then people have actually shown that those compositions can give you a much better endurance. Now, despite that, this GST 225 is still very remarkable. They can be cycled. If you look at the literature report or even commercial devices, 10 to the 6 to 10 to 8 cycles is very normal.

People were able to get some [INAUDIBLE] results, get 10 to 11, 10 to 12 cycle numbers in laboratory devices. So it's already quite remarkable. Think about it. You to move atoms around, melt it, quench it, melt it, quench it, and crystallize it, so many cycles, while still maintaining this kind of stable performance. So there's a lot of material engineering that goes into engineering this kind of durable materials.

All right. That's for the thermodynamics. Now kinetics. T-T-T diagram, obviously. My favorite. So this is like a schematic T-T-T diagram for GST alloys. A few things here. First thing is, let's look at the nose here. If you look at the nose, there are two regions here. I have two lines. One corresponds to 10% crystallization. The other one corresponds 90% crystallization.

So if you look at near the nose temperature, the time scale we are talking about here is of the order of a nanosecond to tens of nanoseconds. So this is a very, very fast crystallization. You can essentially program these materials within a matter of tens of nanoseconds. Now, this is sort of like a semi-logarithm plot. So the slope here roughly gives you the activation energy or the inverse slope, basically.

If you look at now right this point here, this is near room temperature. At room temperature, we are already talking about crystallization time that's of the order of years. So that's why this material can be essentially very fast in programming, but also very stable over a long period of time. Now, a few of these lines I'm showing here, this line, these two solid lines give you essentially possible routes people use to essentially do the crystallization process, whereas this orange line gives you the temperature trace for amorphization process.

Now, if you look at the cooling rate for this line, it's actually very, very fast. It's of the order of 10 to the 10 kelvin per second. What does this mean? You need to quench your material at this very high speed. How do you do that? Few things. The material has to be sufficiently small. If you have a large volume, you can imagine that it takes time for the heat inside the material to dissipate to the surface and then essentially to cool down.

So as we have mentioned in the previous lecture, this imposes essentially a thickness or linear dimension limit to the unit cell you can have where you can still achieve this reversible switching. You can go ahead and do the calculation. Roughly, for GST 225, the maximum linear dimension you can still quench down without crystallization is of the order of about 100 nanometers. So if you want to reversibly switch it, you really cannot make the material too large because it's such a fast crystallization material.

And it's also quite important to engineer a thermal environment. That's why there's actually a trade-off there. I have previously mentioned that if essentially you enhance thermal conductivity in the surrounding media, actually decrease the thermal conductivity, you can have better heat confinement, and therefore make it more energy efficient. The trade-off there is that you don't want to make it too thermally insulating, otherwise you will not be able to achieve this critical cooling rate.

So there's a fine balance you have to achieve there. You have to quench fast enough to amorphize it, but also be sufficiently insulating to confine the heat within the volume you want to make it more energy efficient. OK. Yes?

AUDIENCE: Yeah. How do you actually quench it that fast at that scale? Especially I assume you have many of these bits next to each other.

JUEJUN HU: It depends on the specific device. So for example, if you are looking at optical storage, your rewritable CDs and DVDs, they basically use a focused laser beam to essentially illuminate a very small spot. And the surrounding material, it still remains at pretty much room temperature. So because the spot is so small, when you actually remove the heat, it can quickly exchange heat with all the surroundings. It has a very large surface-to-volume ratio because it's so small. So then that leads to a very fast heat dissipation. And that's why you can cool down that fast.

For electronic memories, you actually use a resistive heating. You actually have a little cell. You have electrodes. You actually pass current through it. So as soon as you turn off the current, then, again, because a very small volume, it's actually typically of a little wire, you can actually also induce this very fast cooling there. So it all boils down to essentially small volume and high surface-to-volume ratio to expedite this heat dissipation. OK.

OK. In fact, we will probably end the lecture just five minutes earlier. We'll leave essentially all the device sections to next lecture here. Any questions you want to discuss here before we-- all good? OK. So next lecture, we're going to discuss about, essentially, the different device implementations of phase-change materials.