[SQUEAKING] [RUSTLING] [CLICKING]

PROFESSOR: All right. So in the last lecture, we discussed about essentially-- give you an overview of different kinds of inorganic network glasses. What we'll focus on in this lecture-- we'll start by essentially wrapping up the introduction of different glass categories. And then we'll move on to actually my favorite part of this class, which is talking about glass-forming theories and how topology actually impacts glass network stability. All right.

So the next class I'm going to discuss here, these are essentially amorphous semiconductors. In particular, we are mostly talking about group four elements, so amorphous silicon, amorphous germanium, amorphous carbon. If you look at some literature, people sometimes call it tetrahedral "glasses." I put a quotation mark there because these are really not glasses.

So we talk about what constitutes glass. A glass needs to have a metastable disordered structure. And then you also need to have glass transition. So for these amorphous semiconductors, they are definitely amorphous. But they lack glass transition. In fact, in order to form these semiconductors, unlike conventional glass where you start from a melt, you then cool down. And then a supercooled liquid, then go through glass transition, and then become the glassy state.

For these materials, the way to prepare them is to usually go directly from the gas phase. You do a vapor phase deposition, whether it's physical vapor deposition or chemical vapor deposition to directly form amorphous-thin film. You simply skip that glass transition step, Also, when you heat them up, if it's traditional glass, when you heat it up, it's going to soften, and then eventually goes back into essentially a supercooled liquid.

Whereas for these amorphous semiconductors, when you heat them up, they crystallize well before they exhibit any signature of glass transition. And that's why they are considered as amorphous. But they are not the glass, at least not in the traditional sense. So now if you look at the structure for this kind of amorphous group for semiconductors, silicon-- if you think about silicon, you have diamond cubic structure.

Each silicon for four coordinated form this kind of periodic network. When it becomes amorphous, you still get a little bit of distortion of the bond angles. And you also change local coordination structure. One of the key structure signatures in this amorphous semiconductor is that you tend to have some silicon with what's called a dangling bond. A dangling bond basically means that you have essentially your one electron that does not pair with other electrons. So the silicon becomes basically three or four coordinated with one lone electron sitting there.

So these dangling bonds actually has a profound impact on the electronic properties of these amorphous semiconductors. If you look at the density of states-- so this is the density of states-- so this is basically the energy. And then this will be the density of states. So what's going to happen there is that if it's a conventional semiconductor, then you will have your valence band, your conduction band. Inside the band gap, there's nothing.

But with the introduction of these dangling bonds, they tend to form what's called a mid gap defect. So close to the middle of the end gap, you then have a number of states that actually correspond to these dangling bonds. Now this is very harmful in terms of electronic properties or semiconductors, because if you have some states in there-- so this is EC. This is EV.

Suppose you have some electrons excited into the conduction band. It can then very quickly relax into these mid-gap states, and then recombine with a hole in the valence band. So you quickly annihilate, essentially, any kind of excited electrons in the conduction band. Well, amorphous silicon, people know that amorphous silicon exists for decades, for a very long time,

For quite a while, people consider it as a useless material for any kind of electronics, exactly because of this-- this is known as a Shockley-Read-Hall recombination, SRH recombination mechanism. So the change comes in when people start to realize that they can actually use introducing hydrogen to passivate these defects. So before, the way people used to actually prepare this amorphous silicon, is to do things like evaporation, for example.

So you have essentially a piece of silicon. You heat it up to well above its melting point. And it actually essentially vaporizes and then deployed into a cold substrate to form amorphous film. In the process, because these atoms is coming into contact with this very cold substrate, so effectively, it gets quenched quickly.

So it cannot essentially form this crystalline structure. But instead, atoms essentially randomly pack to form amorphous structure. But the problem with that amorphous silicon is that it's pure amorphous silicon. There's nothing else. This is one of the cases where being pure is actually not good.

If you go to a chemical vapor deposition process, for example, the key trick here is that he's introducing a hydrogen, lots of hydrogen. So if you think about a chemical reaction here in a chemical vapor deposition, you start it out with silane, which is basically SiH4. You also use a hydrogen actually as a carrier gas. So there's lots of hydrogen around.

You then go to a plasma. This plasma then helps you to break down this SIH4 into different kinds of radicals. So radicals essentially means that you have this excited state molecules where the SIH4, SIH2, SIH, also like mobile hydrogen ions. Then those then cluster onto the substrate surface and then eventually form the [INAUDIBLE] film, when they actually are coalesced together.

So now you notice that because the structural unit we use to form the thin film are these radicals. And these radicals contain lots of hydrogen. So the resulting film also incorporate lots of hydrogen atoms. So the customary way to label this kind of chemical composition is like what I'm showing you on the board there. It's amorphous silicon, h. So this is called hydrogenated amorphous silicon.

Because hydrogen is such a small atom-- it's very mobile. It easily moves around in the entire lattice. And hydrogen also has one excess electron. So that electron, it can then combine with these dangling bonds and form these SIH bonds. In the process, it helps to annihilate this mid-gap defect state.

And that's what then made amorphous silicon becoming useful electronic material. So nowadays, amorphous silicon processing is used quite widely in a lot of electronic devices, in particular when you're dealing with so-called macro electronic devices. So you're all familiar with microelectronic devices like computer chips.

But there are also another class of devices where the figure of merit is not about trying to make very small line width or very high speed. But rather you would need to make, essentially, a large area devices, such as a display or solar cell. So for those kind of microelectronic devices, the figure of merit is basically a cost per area. So amorphous silicon is actually particularly good for that because, number one, unlike crystalline silicon, if you want to grow crystalline silicon, you need to go to a single crystalline furnace and then actually pull the crystals. So the size of the area you can get is actually constrained by the wafer size, wafer diameter.

Versus amorphous silicon, later on, we all have one lecture dedicated to talking about amorphous silicon layer. You can actually deposit them on huge glass sheets, like meters in width. So each glass sheet can be easily the size of this entire classroom right in one single deposition. So it can be very efficient and very high throughput. So that's what gives you a low cost.

Also, unlike crystalline silicon, if you want to grow single crystal silicon you need to do epitaxy. You need to start with single crystal substrate. You then grow the film. So they inherit the single crystal nature of the substrate. Amorphous film does not have that constraint. You can deposit it on any substrate, including glass, which is what you use for displaying solar cells, those kind of things.

OK, so there's processing benefits is what lead to essentially this widespread adoption of amorphous silicon in the microelectronics industry. Any kind of large-area electronic devices, you tend to see a lot of amorphous semiconductor coming in. Yes.

AUDIENCE: So with the effect through hydrogenation, does it function very comparably to a standard crystalline semiconductor?

PROFESSOR: Yeah, so the question is about, if you eliminate mid-gap state, then how does the electronic property look like? So it will behave somewhat similar to crystalline semiconductors. You can, essentially, you have conduction band or valence band. You would dope it. You can change it to p and n type. You can form p injunctions. So in that regard, it becomes very similar to crystalline semiconductors.

Still it has some unique electronic properties that crystalline does not possess. We are going to talk about it later. Let me just delegate to the future lecture. We have one lecture dedicated to essentially amorphous silicon. For now, just keep in mind that you need to understand that hydrogen is actually really important in passivating these amorphous silicon.

All right. So now next one, I've been talking about metallic glass for a while. I will just give you one slight heads up about what's going to come up for metallic glasses or amorphous metal. So metal is quite different from the network glass we were talking about in terms of bonding nature. We said that network glass like Oxides or Chalcogenides, they can form amorphous network easily because the directionality of the covalent bond, which gives you a lot of space between the atoms, which allow you to distort the network and accommodate the structure disorder.

Metal, on the other hand, you have metallic mode. Metallic bond come from interaction between outer shell electrons and the atomic nuclei. So for metallic bonds, if you want to lower energy, you want to increase the packing density.

That's why lots of metals, if you look at it, they all have fairly close or close-packed structures or close to close-packed structures, near close-packed structures. Now, if you think about elemental metal, for elemental metal, all the atoms have the same size. If you are managing, you have a lot of hard spheres that has exactly the same diameter.

If you shake it a little bit, and then if you look at it, locally, you're likely going to see this kind of periodic packing. So same idea if you're looking for elemental metal. Turns out it crystallizes so readily that for a long time, people do not believe that you can make metal in amorphous form. So it's only till like 1960s when people actually developed ways to essentially do a very rapid quench of a metal belt. Then people start to essentially prepare this kind of amorphous metal.

And then later, this group in [INAUDIBLE] is from Japan. So this scientist, he essentially developed what's known as bulk metallic glass. So it's no longer like early days of this metallic glass. They are all in the form of thin foil which limit, of course, limit the application. But it was first developed for metallic glasses so that you can have millimeter thick or even centimeter thick of metallic glass components.

So in order to develop this kind of bulk metallic glass, you need to enhance the glass-forming ability. That's called the glass-forming ability. It essentially gauges the ability for the glass composition to resist crystallization and form amorphous structure. Now to maximize glass forming ability, he proposes three empirical rules.

So the first one, it says that it has to be a multi component system consisting of three or more elements. And the second one actually closely related to that, saying that there must be a significant size difference between the three constituent atoms. Now, the first two rules, they are actually both topological in nature. It does not talk about the chemical nature, electron affinity, chemical reactivity, whatever, of the constituent atoms. It only talk about size.

OK, why? Because as I said, in metal, in order to low energy, you need to maximize the packing density. Now in order to avoid going to this kind of close-packed periodic structure, what you want to have is this kind of hierarchical structure like what I'm showing here. Suppose you have some large atoms. You can explode it with smaller atoms.

And if you get the right size ratio, you can imagine that these small atoms can exactly surround these large atoms without leaving a gap in between them. Now between these larger spheres, you can also have smaller interstitials, tetrahedral, octahedral interstitials, if you want to maximize packing density, you then also want to find some other atoms that can exactly fit in those interstitials without leaving any gaps.

So by having atoms with different sizes, you can satisfy that geometric constraint. So you can get a close-packed structure without introducing a conventional structure order. So later on we are going to talk about a topological theory that specifically discuss about the stability of metallic glass formation. And we'll see. It all boils down to essentially how sphere packing. It becomes geometric problem.

You can determine the radius ratio of different atoms, as well as the atomical fraction that maximizes packing density, which also give rise to the best glass stability. All right. So that's the first two conditions there. Now the last condition, it says that you need to have a negative enthalpy of mixing. That's actually quite easy to understand.

This is coming from thermo dynamic perspective. If you have a negative enthalpy of mixing, it means it's going to stay together rather than stay segregated. So that's it, simple. So as I said, we're going to discuss about a more quantitative theory that elaborates on this close-packing condition for metallic glasses later. All right.

Now in terms of properties, the most important difference between amorphous metal and crystalline metal comes in the fact that amorphous metal does not have a lot of defects like dislocations or grain boundaries, because it doesn't have a lattice structure. We know that these kind of lattice defects play a very significant role in dictating the property of a conventional polycrystalline glasses.

So, for example, if grain boundaries, grain boundaries are where you get a lot more structural disorder. So the atoms inevitably are slightly higher Gibbs-free energy compared to inside the crystalline grain. So if you dip a metal, a polycrystalline metal, for example, into a chemical agent, usually it's the grain boundary that's getting selectively attacked. That's the weak link. So amorphous metal does not have that problem. So it's actually a lot more chemically resistant compared to its polycrystalline counterpart. So that's one reason why they are of interest.

Second reason is for mechanical properties. When you're trying to introduce plastic deformation in conventional metal, what happened there is that dislocation essentially moves. You have [INAUDIBLE] to solutions slide. That's actually what happens. Again, in amorphous metal, you get no dislocations. So that kind of plastic deformation mechanism is completely absent in amorphous metal. So as a result, amorphous metal tend to have a much higher elastic limit compared to traditional polycrystalline metal.

So it means that it will stay essentially elastic without introducing any plastic deformation up to much higher stress. You have taken your mechanics class, so you know that essentially relates to your strength of the material. Your strength essentially represents a material's ability to resist plastic deformation.

So amorphous metal tend to have much higher yield strength, like an order of magnitude higher compared to crystalline counterpart. And that's also the reason why, for example, Apple has always been thinking about you may be able to use amorphous metal to actually make some components where we require high mechanical strength in that case. OK, question?

AUDIENCE: So does it just not exhibit classic behavior pretty much at all?

PROFESSOR: It does. If you give it enough stress, eventually it will yield, by yielding a very different way compared to conventional metal. It actually yields catastrophically.

AUDIENCE: So like brittle fracture?

PROFESSOR: No, it's called strain localization. We going to talk about it. If it doesn't yield, then it's perfect. But if it starts to yield, it tends to have essentially all the strain localized in a very small region, so, essentially, this fracture in one region. OK, we're going to talk about it later. For now just keep in mind that the big difference there is that you need to have the absence of this crystalline defense. So that's why their property is quite different. All right.

I also want to mention that I have only really scratched the surface about different classes of amorphous materials you can see around the world. You can have other kind of oxide glasses like phosphate glasses, where phosphorus is the glass-forming element. They are actually quite useful in bioactive glasses. They tend to dissolve in body fluids. They are also biocompatible. So it's quite important glass ingredient for that kind of application.

You have heavy metal oxides. These are essentially compounds of oxygen with essential elements like tellurium, or other kind of transition metal elements. So some of them, heavy metal oxides, they can form glasses. Some others, for example like titanium dioxide that you can easily form amorphous titanium dioxide film. But they are usually not considered as a glass, as well, because when you heat them up, they tend to crystallize when it goes to glass transition, so similar to amorphous silicon.

So some of these transition metal oxides, they are amorphous and are not usually called glass. You can have headlight glasses and alloys similar to chalcohalide and oxides. Now instead of using oxygen or sulfur or selenium, you actually have halides as the other elements. They are also quite often used for infrared transmitting fibers.

One example I'm showing here. ZBLAN, this is a commercially available halide glass composition*for* infrared fibers. you. Also have other kind of amorphous minerals I'm showing here. Opal is one good example. You have also biominerals. In fact, if you read that paper I'm quoting there, it gives you one example about, essentially, a lobster shell.

You have all eaten lobster. So lobster shell is actually very flexible. And one of the main ingredients in lobster shell is actually a calcium carbonate-- limestone, which is rigid and stiff. So that's actually a very interesting paper about how they can actually, essentially, lobster, they engineer the micro structure of calcium carbonate with amorphous network and some hierarchical structure to make it not just flexible, but also strong. OK, quite interesting paper. If you're interested, I'll refer you to that.

All right, so before I wrap up this class, I just also want to quickly mention about what's the convention people use to represent the competition in different classes? So it's quite straightforward. In oxide glasses, the convention is just to list the network modifiers in increasing valence order. And with the glass network formula, putting it last.

So, for example, think about this glass. This is basically alkaline, alkaline Earth oxide. So you have two glass modifiers, calcium and potassium--sorry, potassium and calcium. So you start with a lower valence element, which is potassium and then calcium. And then with the glass formula, which is SiO_2.

You can then write it in terms of either molar fraction or by weight. Just don't confuse one with the other. Make sure that you know what the author is actually referring to when they're using this kind of representation. In metallic glasses, on the other hand, because you don't have glass network formers or network modifiers, you usually just list the elements in the order of decreasing amount.

So this is one example here. This is known as vitreloy. This is one of the most popular, or most widely used metallic glass compositions. Now, I also want to mention that there are always exceptions to the rule. These are just the conventions that people customarily adopt. But if you do see exceptions, that happen all the time.

All right. So just quickly summarize what we've talked about here. For this lecture, and the key thing you want to understand there is that for these oxide glasses, we talk about the concept of glass formers, network modifiers. You need to know how to essentially perform this kind of simple structure analysis. I give you one example, how to determine the structure in an alkaline silicate glass going from essentially a network glass to inverted glass by looking at chemical composition. So you need to be able to perform that kind of simple structure analysis and determine different structural moieties.

The other very important thing that we are also going to revisit later in the semester is actually this boron anomaly. If you are [? borrowing ?] a glass network by introducing alkaline atoms, you can either introduce a non-bridging oxygen or introduce this kind of P3 to P4 conversion. Aluminum has similar kind of peculiarities there. Just keep that in mind. Later on you will see people actually use that for useful applications.

And then I'm not going to go through a table here. But this summarizes, essentially, the key properties of different kind of oxide-based glasses and how they change with different kind of network modifiers. All right. So any more questions about this section here before we move on to talk about, as I said, my favorite section of the entire class? I like topology. That's why.

And as you'll see, glass stability is all about topology, whether it's network glass or it's metallic glass. So in this lecture, we're going to talk about glass forming, how you actually form glasses. Normally I will skip this slides. But for this particular one, I have to highlight one thing. If you are using the *Fundamental Organic Glasses,* the 1994 version, you need to skip this section entirely. That section is incorrect. Simple. All right. They actually fix it in the more recent version. They take out the entire section. But just keep that in mind. If you use the 1994 version, don't look at it.

AUDIENCE: Rip it up.

PROFESSOR: Yes. Oh, well. Don't do that for a library book. All right. So now let's take a look at, essentially, the glass formation process. This is something we have already talked about. So to form glass, you typically start from melt. You quench down. So you bypass crystallization. You then go through a glass transition regime. You end up with solid glass.

Well, this is a process that seems quite simple. There's still a few questions we want to address in this section here, three questions. The first one we are keeping talking about you need to quench this glass melt fast enough in order to avoid crystallization. So how fast is fast enough? What are the quantitative measures we use to calculate this process there? So that's the first question we're going to address. We are going to talk about it using the so-called kinetic theory of glass formation.

Next one is this glass transition here. So we know that this glass transition has a lot of peculiarities. It's thermal history dependent. If you cool down with different rate, you end up with different glassy state. Also, despite it being a smooth transition, it connects two very different-- fundamentally different-- states of matter. supercooled liquid and glass.

And as I said, these two states of matter, they are different because they have different thermal expansion coefficient. They have different heat capacity. So they have different atomic configuration. So what's going on there, during last transition process? That's a pretty profound question that people have not fully elucidated yet. But what I will do is, I will give you a list of what we call the laboratory definition of a glass transition that highlights some of the key features that allows you to essentially explain some of the key features during glass transition process.

Now the last one is what I've been alluding to many times already-- stability. We know there are glasses that are truly stable like silica. You can essentially slowly cool it down for a year without introducing crystallization versus some other glass competition like-- whatever. There, are a lot of unstable glass compositions which easily crystallize under any kind of perturbation.

So what's the structural origin that lead to this vastly different glass-forming ability? It's that glass-forming ability is one of the few properties where it can expand many, many order of magnitude, over 10 to the 15th order of magnitude, which is quite remarkable there. What's the structural origin behind it? So these are the topics of this section here.

As I said, we're going to talk about the kinetic theory. The kinetic theory pretty much is a revisit of the crystallization kinetics that you have learned in kinetics class. But we're trying to do exactly opposite. Instead of trying to get crystallization, we try to avoid crystallization at all costs. Crystallization is like the valley of death for glass scientists.

We're not going to talk about laboratory glass transition and then the structural theories, especially the topological constraint theory, to explain why some glasses are much more stable compared to others. All right. So kinetic theory, as I said, crystallization is the valley of death for glass scientists. This is just one example showing you actual crystallized glass.

So this is a rod of transparent glass. This side is amorphous. This side is like crystallize. You can immediately see the difference because you have crystalline precipitates out of lattice. And then those crystals can actually scatter light, which leads to this kind of a translucent appearance there. So how do we avoid this kind of crystallization? What is the kinetics in the process?

So quick review here, in order to form crystallization from a supercooled liquid you need essentially nucleation and growth right. So for nucleation, this is basically a quick revisit of the thermodynamics of nucleation. What I'm plotting here is the free energy as a function of temperature. Have you all taken kinetics? Then it should be pretty straightforward. I will just quickly go through the concepts here.

We know that liquid and crystal, they have different entropy right. Liquid has more structure to this order. That's why it has more entropy. The slope of this line here, partial derivative of g with respect to t, give you entropy. So that's why liquid has a larger slope. So it has a smaller slope. That's why they must cross over at some point, which defines the melting point.

So now for glass foaming, we are always talking about temperature below melting point. Crystalline lies below the liquid line. So supercooled liquid always has the tendency to relax to crystalline state which is crystallization. The thermodynamic driving force is then this delta G. This is the free energy difference between these two states.

So from a thermal dynamics or kinetics class, you know that this delta G will scale linearly with the degree of supercooling. So degree of supercooling is basically the melting point minus the temperature at which the crystallization takes place. So it all boils down to this equation here, where the Gibbs free energy scales with the degree of supercooling and also volume of glass.

So this delta S here is the entropy difference between the solid and liquid state per unit volume. And that's why I have a V here. So this is obviously what we call a volumetric term. If you have more glass transition-- sorry-- if you have more liquid transition into crystalline then you have more change of the free energy. Makes sense if your scale is more [INAUDIBLE].

Now we also have a barrier energy barrier for nucleation here. In order to form this nucleus, you are trying to precipitate out some atoms with different structure compared to the surrounding supercooled liquid matrix. Excuse me. So this inevitably creates essentially interface between the solid nucleus and the surrounding supercooled liquid.

So this interface has an interface energy associated with it that we represent as the surface energy here. It's basically area of the nucleus times gamma, which is the surface energy.

So if you plot these two terms here, you have a surface term, which represents the record. You have the volumetric term that I talked about in the last slide in this green curve here, volumetric term scales with volume, so radius cubed, if you think about spherical nucleus. And then the surface term scales with radius squared. So it means that when the nucleus is small, surface term always dominates.

But eventually the volumetric term is going to take over. So this gives rise to essentially a barrier towards nucleation that you have to overcome in order for nuclei to form. So at this very high-- also depends on what kind of nucleation you have there. Homogeneous nucleation always has a higher barrier because you have a larger surface area, a larger volume for nucleus versus heterogeneous nucleation.

By essentially forming the nucleus on some surfaces, you can effectively lower this energy barrier. All right. So that's nucleation. So then, when you talk about kinetics of nucleation, then I won't go through a theory there because you are taking kinetics. But the whole idea is that we're looking at the rate. How fast can the system overcome this energy barrier so that it can essentially go down this slope on the other side, so that the nucleus can then spontaneously grow rather than dissolve back into liquid phase?

The final formalism, there are basically two factors here. So one is the kinetic factor. If you go to higher and higher temperature, the atoms essentially have a higher mobility. They become more mobile. So as a result, the kinetic process is accelerated. So the kinetic factor would grow monotonically with temperature. The higher the temperature, the faster it's going.

But you also have the thermodynamic factor there, where the barrier height essentially depends on the degree of supercooling. The higher the degree of supercooling, the lower the barrier height. So then there essentially is this kind-- that you have to strike a balance there. You want to have enough thermodynamic driving force.

So you need to have enough supercooling. So temperature cannot be too high. But you also don't want temperature to get too low where the atoms become so sluggish they don't move at all. So long story short, if you revisit your kinetics class, it basically says that for nucleation, there's always an optimal temperature. And that optimal temperature, it gives rise to highest nucleation rate. Above that temperature, essentially you get thermodynamic driving force limited.

You don't have enough supercooling. Below that temperature, it's kinetically limited. You don't have enough atomic mobility. Same idea, once you have a nucleus, then you have this grow. The growth process is actually quite similar. You essentially need to allow this atom to hop over the surface energy barrier from liquid state to the crystalline state, so that this crystallization process can proceed. And it's the same dependence there.

You also have, similarly, a thermodynamic factor and kinetic factor. And this gives rise to an optimal temperature where you have the highest growth rate. So because both nucleation and growth, they exhibit similar dependence on temperature. There's always an optimal temperature where you get the maximum nucleation or growth rate. So it means that if you look at the overall crystallization process, there's also an optimal temperature where you have the fastest crystallization.

So if you are [INAUDIBLE] scientist, well, this is the overall crystallization rate. Then the crystallization rate would peak somewhere in between. So if you are a [INAUDIBLE] scientist, you then want to avoid that temperature, because that's where you are going to essentially vitrify your glass. Now quantitatively, how do you actually calculate that? We use the TTD diagram, time, temperature, transformation diagram.

By the way, speaking of TV diagram, this is actually a very important core concept in material science. In fact, at one point, our department was trying to do some revision to the graduate curriculum. We polled all the professors, essentially, which topic they think they should include in the graduate core that all the students should learn. So we talk about all kinds of topics, thermodynamics, kinetics, quantum mechanics, everything. And then the single topic that gets the most votes, which surprise, surprise, TTD diagram.

So everyone agrees this is a very core concept of material science that all of you should know and be proficient with. Now simply put, T diagram is essentially characterize it, have this curve here, this is like this red curve. Under isothermal conditions, how long does it take for crystallization to take place? So, for example, if you look at 800 Kelvin, you draw a horizontal line here, intersect this line at this point. Then you read out the horizontal axis. It means that at this 800k, this particular glass composition to crystallize with about something like, maybe, 200 seconds.

Now the basic feature of this kind of TTD diagram for glass crystallization is that you always get a crystallization region like what I'm showing here. It has this nose because it looks like nose sticking out here, that essentially correspond to a specific temperature where you have the fastest crystallization process, so shortest time to crystallization.

So then, obviously, above that this is the driving force limited. Below that it becomes a diffusion or atomic mobility limited. So now if you want to form a class, you need to make sure that your quenching process completely bypass this crystalline region here. So the way to do it is typically, on a TD diagram, you draw a line that's exactly tangential to this crystallization region. So if you do that, then you can barely bypass the crystallization and end up with a fully amorphous state.

Now this line is what we call the critical cooling line. The slope of this curve-- let me give you this so-called critical cooling rate. It's the lowest cooling rate that you can use to quench your melt, to still avoid crystallization. This is a very important concept in class size. So it's a measure of the glass-forming ability. If a material has a very small glass cooling rate, a critical cooling rate, it means that it's a very stable glass and vice versa.

Now, one caveat, for this particular diagram here, the horizontal axis is in logarithmic time scale. So if it's a linear cooling with a constant cooling rate, it's not supposed to be a linear line there. But if it's a linear scale, then that should be a straight line. So if when you're actually measuring this kind of critical cooling rate, make sure the horizontal axis is actually linear.

So now what I'm doing this next slide here, I'm essentially summarizing the critical cooling rate for some of the common glass-forming components. So you see, for example, like silica, the critical cooling rate is like 10 to the minus 5 Kelvin per second. So that's why you can essentially cool off silica pretty much in any way without worrying about crystallization. It's very, very, very stable.

You also have metal, like steel or other elemental metal. The critical cooling rate is like a billion Kelvin per second. And that's why people used to think it's impossible to make amorphous metal. Now look at this one, vitreloy bulk metallic glass. It has a critical cooling rate of about 1 Kelvin per second, much, much lower crystallization tendency compared to typical elemental metal.

And that's why-- by the way, people can make it into a bulk. So quantitatively, let me talk about it. So this critical cooling rate actually dictates the size or thickness of the sample you can prepare during amorphous state. The equation is listed here. So dmax, this is the maximum thickness of the sample. You can still maintain being amorphous. Alpha is thermal diffusivity. RC is our critical cooling rate and delta T is this guy, is the temperature difference between the melting point, or liquidus point, and the lowest temperature.

So the reason you have a maximum sample thickness is that if you have a material, they tend to crystallize quickly. So if you start to quench a bulk piece of sample, the surface will get quenched very quickly. But it takes time for heat to get dissipated in the interior of the material. It takes time for the heat to escape from inside the material to the surface. So, essentially, that means the larger the thickness of the sample, the slower the effective cooling rate you can get inside center.

So if you have a material that's poor glass stability and you have a large sample thickness, then the inside may never be able to amortize. It will always crystallize because it cannot have heat dissipated fast enough to bypass crystallization.

So that's why now you understand why people call it bulk metallic glass, because in early days, we were dealing with this kind of metal with such a high cooling rate. If you plug it into the equation, the thickness you come up is actually very small. You can only get very thin foil to ensure you have fast quenching throughout the entire piece. Bulk metallic glass, because it's much lower critical cooling rate, you now can afford a maximum thickness of the order of millimeters or centimeters even.

All right. So now, what I have also summarized on the table on the right-hand side is the critical cooling rate or, sorry, it's the cooling rate you can attain using different kind of glass-preparation techniques. So you see air quench, just means that you have a bulk piece of sample leaving on the table that is slowly cooling air. It has a relatively slow cooling rate. Liquid quench is faster.

You can have things like droplet spray or melt spinning. These are actually processes people used to use to make metallic glasses. So, for example, if you are spinning, basically you have a big drum-- big drum kept at room temperature. You then have a little feeder here that then feeds in essentially droplets of metal. So the droplet metal will come up into contact with this drum. And then it will quickly cool down. And essentially-- oh, by the way, this drum is incrase spinning, OK, spinning at very high speed.

So then, due to the centrifugal force, it's then going to essentially spread and form a little foil. And then essentially spin out. So what you end up getting here, you can actually do a continuous production of thin folio of glass of a metallic glass in this case, and with a high cooling rate, much higher cooling rate compared to conventional methods. So, so you can attain a much higher cooling rate here in this kind of techniques.

Now if you go to thin films vapor deposition, you see that vapor deposition gives you a much higher cooling rate compared to bulk material, synthetic techniques. And that's because when you're doing thin film deposition, you essentially have these atoms in atomic state coming into contact in the molecular atomic state, come into contact with the substrate.

The substrate has a much larger thermal mass compared to the individual molecular units. So that's why the effective cooling rate can be very, very high. And that's why, for a lot of the amorphous materials, you can normally only prepare them in a thin film form, not in a bulk form. Examples would be things like amorphous silicon or amorphous TiO_2, amorphous zinc oxide. You can very easily get amorphous materials, thin film. But you typically don't get it in bulk state exactly because of that reason.

So now if you have these two tables in hand, you can then immediately determine for each of these materials, what is the technique you would need to prepare them? What state is still avoid crystallization? So, for example, if you look at silver, you figure that you have to go to vapor deposition in order to ensure it's amorphous. Whereas [INAUDIBLE] you can even afford to just simply do air quench. We're still getting amorphous structures. All right.

So key takeaway message here is to be aware that there is actually a maximum sample thickness where you can actually maintain amorphous structure if you have a limited glass stability. We're going to revisit that very quickly in the next lecture. All right. So that's about basically the kinetic theory of glass formation. What we're going to do next is then I will give you a bit more of a mechanistic explanation about what's actually going on in that glass-forming process.

So in order to formulate such a theory, you need to be able to explain the few key features in the glass transition process. So first key feature is that glasses, its property is always thermal history dependent. If you cool it down at different rates, you get different volume, you get different enthalpy. So your theory need to be able to capture that. Different cooling rate give rise to different structures.

I have another bullet point here which says that we can definitely slow cooling. You have ideal gas state. It's idealization, basically saying that if you have an infinitely slow cooling while still avoid crystallization, then you can imagine that you can-- line is going to continuously trace, super cool liquid line. So it's going to extrapolate.

You can go along this dotted line here. And eventually, it's going to intersect with the solid line. Now the glass line cannot go below the crystalline line because glass need to have a higher enthalpy compared to crystalline solid. Otherwise, it will become thermodynamically stable phase. That's just not right. So it means that for this kind of a ideal glass, it's going to be forced to turn around to inflate and go along this line here. So the glass line will pretty much overlap with the crystalline line.

So that's actually called ideal glass. It applies when this glass has basically almost the same foaming energy as its crystalline counterpart. It's an idealization of practical glasses. Anyway, that's not quite relevant here.

So in order to explain this kind of thermal history dependence of glass structure and properties, let's revisit this concept here. When we're talking about stable glass state, I mentioned that glass structure essentially sits in some kind of metal stable basin, local minimum while crystalline is a global minimum.

So we want to give a more quantitative picture of what we have here. So we want to introduce in this function of so-called potential energy landscape. So in potential energy landscape, the horizontal axis is still the glass structure. But in order to quantitatively represent glass structure, we need to know the position of all the atoms.

Let's say your glass network has a total of n number of atoms. The position of each atom can be represented by a xy d coordinate. So if this know this 3n coordinates, you can then uniquely determine the structure of the glass. If you know the structure of the glass, you also know the interaction potential between the constituent atoms. You then know the interaction potential energy of all the atoms combined together.

OK, so this interaction, this collective, interaction potential energy, is what we call the potential energy here. We label the vertical axis. So what we see here is a well-defined function spanning across these 3n axis. Now if you look at what this function looks like, this is a schematic representation of what it looks like. You must have a global minimum that corresponds to the crystalline state.

You also get many, many, many, many local minima there. Each of these local minima is what we call the laboratory glass state. Essentially means that when you're cooling down from supercooled liquid, the system may relax one of these local minima there. So because each of the minima correspond to one possible state where you may obtain in your laboratory, that's why it's called laboratory glass state.

Then ideal glass, as I mentioned, this is some idealization of the laboratory gassy state. And it should have almost the same enthalpy or energy as the crystal. So that's why ideal glass is almost equally at height as crystal layer. So now what's the difference between glass and supercooled liquid?

So the laboratory definition of glass transition is coming from a statistical mechanics perspective. It basically says that liquid is ergodic and glass is non ergodic. So glass transition is basically *a* ergodicity breakdown. Now let me explain what that *is.* So ergodicity, or ergodic, essentially means that given enough time, a system can transition through all the possible microscopic states. That's called ergodic-- versus if a system is confined only to a small subgroup of states then this is called non ergodic.

We argue that liquid is ergodic because in liquid state, it's high temperature. All the atoms have enough thermal energy. They can easily move around. It doesn't have a well-defined geometry. So it means that if it's a liquid, the system can essentially explore all of these possible combinations of the laboratory glass states.

So liquid is ergodic. Now if you start to cool down, if you go to gassy state because it's a low temperature, now the system does not have enough energy to move around between these different local minima there. Basically, you get trapped in one, or maybe just a few, neighboring local minima.

That's when you have a glass. So glass is non-ergodic. So what happens during glass transition is that you are transitioning from this ergodic system into a non ergodic system. So it's a ergodicity breakdown.

All right. So I mentioned that this theory needs to be able to explain the property difference, how the property of glasses depend on its thermal history. So we can take a look at it. So what happens if you do slow cooling versus fast cooling? If you do slow cooling, then liquid, or the molecules or the atoms, still has time to move around a little bit.

And you will try to settle at one of the deeper local minima just to minimize the system energy. So the resulting glass will then have a lower potential energy and therefore lower enthalpy, versus if you do a very rapid cooling. If you do a fast cooling, then the system does not really have the time to essentially explore many of the possible states.

It quickly get trapped in one of the accessible states, which may not be giving you the low energy. So as a result, your system will be more likely ending up in a state that actually has a higher enthalpy compared to the slow, cool glass. So that's how you actually explain why you have this cooling rate difference in terms of glass properties.

Basically, the range of microstates you can access is different. It depends on the cooling rate. More quantitatively, the transition between these different microstates is characterized by this time scale here called intervalley transition time. So if you look at the definition of intervalley transition time,

[INAUDIBLE] this is basically the attempt frequency, or the vibration frequency of the structure between different minima. B gives you the average barrier height between the neighboring local minima there. And this exponential dependence essentially says that this process is thermally activated. It follows Arrhenius law.

The higher the temperature, the more vigorous the atomic motion, the more likely the system is going to transition from one state to the neighboring state, and so on and so forth.

So now with the introduction of this intervallic transition time tau, we can now define a criteria to determine whether you have a glass or liquid for your particular system. So the criteria is this one, t observation is less than tau.

So t observation, this is basically a time of your experiment, the duration of your experiment or what we should observe in the sample. So if your duration of experiment is less than tau, it means that during your experiment, your system will likely get trapped in one of those local minima.

So then you have a non-ergodic system. And then we then define the system you're examining there in your experiment as being a glass, versus if you have opticase, then the system can have enough time during the experiment to hop between different microstructures. Then we consider it as a supercooled liquid.

OK, this is the working definition of glass transition, this one, T observation less than tau. Questions? one interesting aspect of this definition is that whether or not you have a glass depends on your T observation. Or in other words, depends on the experiment duration.

So you can be doing different experiments at lots different time. For example, if you are doing, say that you are trying to measure the mechanical property of [INAUDIBLE] glass. You are doing some tensile experiments, which may take you a few minutes.

So provided that within that few minutes, your structure sits in one valley. You are OK. You have glass. You could also be doing some experiments that you are looking at long-term relaxation of your sample, which may take years. So in that case, the criteria for being glass becomes a lot more stringent. You need to make sure that over the time span of few years, your system is localized in one of the minimum.

So what you see here is whether you get glass or you get supercooled liquid, it depends on your experiment, depends on what you're trying to observe there. That's why I call it. This is a working definition of a glass transition. This is called laboratory glass transition. It comes from this very practical perspective. If the condition is satisfied, you can essentially worry about this kind of structure transformation inside the glass during your experiment. Then you can see as a glass.

So in the end, whether or not you call coil system a glass depends on your experimental condition in this case. Does that make sense? Yes. I expect you have questions. Yeah.

AUDIENCE: Sorry. So is it also a consequence of this that glass cooled at a given cooling rate might have different properties, depending on which--

PROFESSOR: Yes, basically that means the glass structure is always stochastic in nature, always stochastical. So you have exactly the same glass composition. You try to cool it down at exactly the same temperature, same cooling rate. The structure you're going to get is not going to be microscopically identical, because it's basically a stochastic process, the system trying to explore different local minima. And you have two different systems obviously are going to see different structures. So it's going to be different.

AUDIENCE: But macroscopically, we still observe like the same.

PROFESSOR: Macroscopic, they still have similar properties, very similar, usually.

AUDIENCE: And then compared to this [INAUDIBLE], just correspond to different local minima at the same--

PROFESSOR: Similar energy levels because of the same cooling kinetics. And that's why. Later, we're going to talk about, for example, how you can potentially-- using this one single parameter, the fictive temperature, to label the glass structure, which is essentially this simplification.

If you can label it just with a cooling rate, and from that, you can determine the glass structure like a single variable function. It's an approximation because later we're going to show you that that's a vast simplification. There are cases where you-- glasses have the same effective temperature. But you actually get different properties.

But to the first order, I mean, that's what it is. And that's also what give rise to this inhomogeneity of glass, even for the one glass sample, the bulk glass sample. If you look at different locations, you still get this kind of a little bit slight dispersion of the properties. And that's exactly because of that. The kinetic process, even though it goes through the same cooling rate, statistically, there's always some variation there in the glass local structure.

All right. Now let's come to the part-- as I said, my favorite part. Now let's discuss a little bit about now what is the structure that give rise to the highest glass network stability to resist crystallization? We have already shown you this kind of diagram here. This is when we're talking about, glass network formers and modifiers. We see that the network formers and modifiers, they are all clustered on this periodic table.

For glass formers, they tend to be this kind of non metal element forming covalent bonds. And the basic idea behind it is that you want to have, essentially, like open-network structure so that you can accommodate a lot of structure deformation. OK, so this kind of observation is what lead to so-called absence rules.

So Zachariasen is a scientist that actually proposed this random network theory, the structure of the glass materials. We mentioned that in the first lecture. On top of that, he also gave rise a few empirical rules that specifies what kind of compounds will be glass former versus being a glass modifier, network modifier.

For this Zachariasen's rules, a few things I want to mention before I go into that. One is that this empirical rule, it means that there are two exceptions. It applies to most compounds, but not all of them. Also it's only applicable to oxide glasses. So we will be talking about some kind of oxides with the stoichiometry given by Amon. So this will be just an oxide. And the topic of the discussion will be this element A. Is the glass former or is it a network modifier? That's what Zachariah tells you.

So now let's look at the four rules here. The first one, it says that an oxygen atom is linked to no more than two atoms of eight. So it means that the coordination number of oxygen should be 2, which sounds like trivial. But if you think about close packed structures like ionic solids, that's often violated. That's one reason why solids tend to be poor performance.

Now second one, the oxygen coordination around eight. So we talk about the first rule. We'll talk about coordination number, oxygen. The second rule is about coordination number of this element. It should be small, say three or four. So if you combine the first two rules here-- or is this that you need to have a small coordination number around both oxygen and the [INAUDIBLE]. A small coordination number is the typical feature of a covalent solid.

If you think about ionic solids or think about metallic solids, the chemical bond is non-directional. It's either electrostatic interaction or metallic bonds. So to minimize energy, you want to close packed. You want to have as high a number of coordination as possible around each atom there. As a result, you don't give rise to the open structure that allow you to actually distort the network and accommodate this kind of structure disorder there.

So that's why it's not preferred for glass formation. So as I said, you won't have open structure. So they give rise to a small energy difference between the glassy and crystalline state. If you distort the network, it doesn't cause a huge energy penalty. It doesn't build a lot of stress into a network. All right.

Now next one, the cation polyhedra shares corners, not edges, not faces. Let's take a look at one example here. What's a cation polyhedra? So if you think about silicon glass, the basic structural unit is this kind of SI 04 tetrahedra. So if you look at the tetrahedra with the center as silicon and with surrounded by oxygen atoms, this is what we call the cat-eyed polyhedra. In this case, this is actually a tetrahedron.

If you get boron silicate glass, for example, you get PO3. In that case, you essentially get a triangle, bo3 triangle. That's basically a polyhedron in the BO3, class. Now if you look at two neighboring structure units, what I'm showing you on this plot here, on this one here, this is basically sharing a corner.

You have one non-bridging oxygen that connects to 2, this tetrahedral here. And then you are only sharing-- the two neighboring tetrahedra only shares one bridging oxygen. This is called a corner sharing. Now what about edge sharing? Edge sharing is when you have two neighboring tetrahedra shares two bridging oxygen. This is edge sharing.

You can also have face sharing. If it's face sharing, now I need to really bend it. This is face sharing. So you can see that when we're going from corner sharing to edge sharing and face sharing, the flexibility of the network essentially monotonically decreases.

If you think about this structure, it's actually very rigid. There's no way I can really distort it. Versus if you go to a corner shearing structure, then it gives rise to a lot of potential rooms to distort the network structure by simply just rotating this chemical bonds. Rotation of these chemical bonds give you a much smaller energy penalty compared to like in the case of a edge or corner face sharing. So that's what it means.

If you only have this polyhedron, only shares corners, then you can actually maximize the structural flexibility to accommodate this order. Now finally, last one, at least three corners has to be shared for all the tetrahedra, for all the polyhedra, for silica glass. All four corners are always shared. In silica glass, all the oxygen is bridging oxygen. So essentially means that all the corners are shared.

So let's satisfy this rule. And the reason you have this kind of rule here is because you want to form a 3D network. Yes.

AUDIENCE: Does this apply all the way to the edge?

PROFESSOR: To a surface?

AUDIENCE: Yes.

PROFESSOR: No, we don't worry about surface here. In the summer, you get things like reconstruction and all that stuff. So it's always a little bit different. You get dangling bonds and things. But this is only talking about the bulk.

Yeah, but basically, if you think about bulk, in order to form a 3D network, each of the polyhedra need to share at least three. If you only share two corners, then the best you can get is something like a long linear trade. In order to form a 3D network, you need to share three corners. So that's what the last rule means.

So now before I go to some specific examples of Zachariasen's rules, we notice one thing here. It's that all of these four rules, it does not talk about the chemical nature of the element. It doesn't talk about reactivity. It doesn't talk about electron affinity or electronegativity. There's nothing like that.

The only thing that really goes in there is the valent state, which gives you the number of chemical bonds, one atom forms, as well as the connectivity between the polyhedra. These are all topological features associated with a glass network

So that's why it's exactly because of this nature that people realize the importance of network topology in glass forming. And that's where the topological constraint theory comes in, predicting glass stability, which I'm going to talk about in next few slides. Now, before you go to that, I do want to do a quick practice. Let's see one example of a glass network.

And let's then practice to see whether or not the declaration rule is applied, so OK. Let's look at this simple one here. Let's consider just zinc oxide. This is a crystalline structure for zinc oxide. It has two kind of structural variants. You get zinc blend. You get this kind of a hexagonal structure.

But either way, it turns out the conclusion is the same, because the local connection is the same. It's just stacking of different polyhedra. So now let's try to look at it and see if we satisfy the Zachariasen's rules. So first rule here, so this one this would be zinc. This will be oxygen. So the first rule says that oxygen needs to be two-fold coordinated. It is satisfied.

You can fairly quickly see, what's the coordination on the oxygen? For that, you only look at the nearest neighbors. You look at oxygen linking to zinc. This is the nearest neighbors. Each oxygen links to 4 zinc, so actually violate the first rule, first Zachariasen's rule. What about the second rule? Second rule says that the zinc coordination number has to be three or four. It's actually four. So actually four-- actually obeys the second rule of Zachariasen.

Third rule, neighboring polyhedra need to be sharing corners. So what are the neighboring tetrahedra? So to look at neighboring tetrahedra, you start by looking at the cat-eye, right? So in this case, cat-eye was zinc. So look at this one. You look at the nearest neighbor zinc, which would be this one, for example. So if you look at these two, in this case, the polyhedra is actually a tetrahedra.

So the neighboring tetrahedra, what do they share? They do share the corner. So if a base, this third rule, or the third [INAUDIBLE] rule. Now, however, if you look a bit more closely, it's still pretty rigid network because the two neighboring ones, they share one corner there. But then they are interlinked through the next nearest neighbor. So it's actually still pretty rigid network. But anyway, that's beyond the simple [INAUDIBLE] rule there.

Finally, each polyhedra should share at least three corners. It is satisfied? If you look at polyhedra here, how many corners are shared?

AUDIENCE: All four of them?

PROFESSOR: All four of them. So, yeah. That's why they form a 3D network. However, [INAUDIBLE] still is a poor glass form because it doesn't satisfy all these [INAUDIBLE] rules, which is consistent with experiment. As I mentioned, you can form a thin film, amorphous zinc oxide. But it's quite difficult to prepare zinc oxide in bulk state.

So by the way, when we talk about these Zachariasen's rules, you are typically talking about glass formation for bulk oxide glasses. For thin films, because of the higher quench rate, you can potentially prepare some amorphous state materials that conventionally you would not be able to prepare. All right. So let's see the early days when people are looking at this only applies to oxide glasses, the empirical rules.

Now these Zachariasen's rules definitely heralds the topological constraint theory, which is the more recent theory, or most recent attempt people make trying to explain the glass stability. So the whole concept of this topological constraint theory essentially borrows the concept of a network constraints from basically mechanics.

It classifies the glass network into three kind of topologies. You can have a flexible or floppy or under constrained network. You can have over constrained or what we call stressed rigid network. And what's in between is what people call isostatic or critically constrained network.

Now as I said, the concept comes from mechanics. So if you think about a simple ball and stick model, you simplify the atom and chemical bonds as ball and sticks. You try to put them together, you essentially form mechanical structure. So this network, it can be floppy or flexible. If it's constrained, the number of constraint is less than the number of degrees of freedom.

A simple example of a floppy network. Let's look at specifically this model I'm holding in my hand here. The constraints we are talking about here, there are two kinds of constraints. you have the bond length and you have the bond angle. The bond length is what we call the bond angle. Sorry, the bond length is what we call the bond-stretching constraint. Bond stretching.

So because we have a well-defined chemical bond length, essentially says that the spacing between these two atoms has to equal to the bond length. So that defines essentially one relation between the spatial coordinates of the neighboring atoms. So that's one thing we consider as a constraint there. That's called bond-stretching constraints.

Now bond angle, this is called bond-bending constraint. Well, this one is basically a bond stretching, bond bending. So if you look at the bond angle, for example, look at this one. This is oxygen, silicon, oxygen [INAUDIBLE] tetrahedra. If it's a rigid chemical bond, it means that I cannot bend this chemical bond here. Then it specifies again the relative spatial location between the two oxygen atoms with respect to central silicon atom.

So if it's rigid, then this is another geometric constraint that this network has to satisfy. So the total number of those constraints summed up together will give you the number of constraints. The number of degrees of freedom. If you have a total of n atoms, each atom you can characterize spatial position with three spatial coordinates. So the total number of geometric degree of freedom is basically given by 3n.

So bottom line, if the constraint number is less than degree of freedom, we call this a flexible network. And as I'm showing, this is indeed a flexible network. I can easily twist and turn to go to different geometric configurations without violating any of the constraints I mentioned. So this is a flexible network.

Now on the other hand, what about a stressed, rigid network? I can give you a very simple example here, our phase sharing. If you think about this phase-sharing tetrahedra here, there's no degree of freedom building. This is a totally rigid network. I cannot deform it at all. In fact, I even have to bend. I have to violate some constraint here in order to fit in here, this kind of network there.

This is one case where the number constraint actually exceeds the number of degrees of freedom. So you have to actually compromise some of the constraints in order to fit in this network structure there. In order to compromise the constraint, what I'm doing here, I'm basically bending the chemical bands. I'm changing the bond angles.

Now, changing the bond angles inevitably increases the Gibb-free energy of the overall system. So as a result, this is what we call the stressed rigid network. It's stressed because actually building stress due to this excess energy we have to apply in order to conform to the structure there.

Oh, all right. Now I break a chemical bond. Actually now I violate a constraint-- literally-- anyway. All right. OK. So now what I want to argue here is that either the floppy network or stress rigid network, they are both bad for glass stability. So let me explain why. If you think about this flexible network, the key visual there is this system can very easily transition from one microscopic state to another microscopic state, because it's all flexible.

So if you look at this potential energy landscape, this is schematically what it's going to look like. The different minimums, the energy barrier separating these different minima is pretty shallow, pretty low. Because this network is flexible, it can easily transition between different microscopic configurations.

So then what that means is that if you have a global minima, which is our crystalline state, because the energy barrier separating this minima is pretty small, kinetically, this system can very easily relax towards the global minimum, which is crystallization. So simply put, a floppy network is kinetically two expedient in relaxing. And it can easily crystallize.

Now what about our stressed rigid network? So first thing I want to mention here, as I'm showing you on the plot, the stressed ridge network is characterized usually by a very deep global minimum of quasi state. The reason it becomes a very deep global minimum is because any kind of deviation from this ideal crystal structure, inevitably, you have to cause lots of distortion because it's already a stressed network. So that distortion is then going to cause a pretty large rise of the Gibbs free energy. And that's why it's a very deep global minima.

Now what does this deep global minima mean? A deep global minima means there's a very large thermodynamic driving force towards crystallization. So if you think about a macroscopically large glass sample, in such a macroscopic large glass sample, because of the statistical fluctuation of the inherent structure in glasses, if you look at one location versus the other, the structure is always a little bit different.

So that means, because it's macroscopic large, almost inevitably at some corner of the glass sample, you're going to see some structure that closely resembles its crystalline state.

So in those regions they can then easily act as the nucleus for subsequent growth. And the problem with the stressed region network is because of this very deep global minima, as long as the structure resembles crystalline, even in a very small location, it can be very easily stabilized. The energy barrier towards nucleation essentially is very, very low because of this huge thermodynamic driving force.

So then, as soon as you have that local cluster that resembles the crystalline structure, it's then quickly going to propagate and introduce the crystallization across the entire sample. So simply put, a stress region network has a poor amorphous stability because of the large thermodynamic driving force.

So what we want to do is the right in between. We need to strike a balance between the kinetic factor and the thermodynamic factor. You want to have a sufficiently high barrier to prevent the crystallization. You also want to make sure that thermodynamic driving force towards crystallization is not too large.

So that's why we argue that what's in between here, the isostatic network, where the number of constraints are exactly equal to the number of the degree of freedom will now give rise to the optimal glass stability. So that's the whole assumption of the topological constraint theory, that you want to find a glass structure that gives you the isostatic network topology. Yes.

AUDIENCE: With the same chemical like network, the same format like formers, as well, if you change the cooling rate, does that change the constraints? The changing, like, the process.

PROFESSOR: OK, that's actually a great question. I have two answers to that. To the first order, it does not. Because if you think about the-- later on we're going to talk about how you actually count the number constraint, how to count the number of basic constraints. The number constraint actually relates to the, essentially, a valent state.

So because, again, the number of bonds, the number of angles, they all relate to a number of chemical bonds it forms, so valent state. So if you have the same chemical constituent regardless of cooling rate to the first order, it doesn't change the number of constraints. And therefore, it doesn't change the topological architecture to the first order.

Now the second order we are also going to talk about it is that some of the constraints can actually get relaxed at different temperatures. So if you have a very drastic change in terms of glass forming, then you may actually have-- some of the constraints may get a little bit relaxed compared to the others. So it does can modify this number constraint a little bit. But usually that's not a significant factor.

So that's why, when we predict the stability of the network we give it essentially as a chemical composition. And the cooling rate is basically a high-order term that we usually neglect. We just say that this chemical composition is more stable against the other one, for example. That's what this theory will tell you, Does that answer your question?

AUDIENCE: Yes.

PROFESSOR: I mean, we are running out of time. So what we will do in the next lecture is to actually go into deriving what are the number of constraints and what is the condition to achieve this isostatic network to maximize stability? Any last minute questions? Yes.

AUDIENCE: I suppose like after processing, is it possible to go make crystalline glass [INAUDIBLE]?

PROFESSOR: You don't say a crystalline glass, right?

AUDIENCE: [INAUDIBLE] glass.

PROFESSOR: Sure, I mean yeah. You could dope it. But, I mean, we're actually going to see it because the number of constraints depend on essentially the valent state. So if you dope it, you actually change the network topology. So you can either increase or decrease glass stability just by doping it. Yeah.

OK, so we're going to talk about it in the next lecture, as you'll see. Later on it becomes-- it's a remarkably simple theory. But it gives very powerful predictions.