[SQUEAKING]

[RUSTLING]

[CLICKING]

JUEJUN HU:

OK, so let's start. So in the last lecture, we discussed about essentially glass manufacturing techniques, more for volume production. So we're going to switch gears a little bit. We're going to start by talking about caneworking, which is really more for artworks. People do this manually. It's more of a skill, rather than for any kind of industrial-scale production. This is how they actually make all kinds of beautiful art pieces out of glass.

I want to mention that glass has always been a very important material for artists. It has many striking properties that make it very attractive. You can exhibit all kinds of colors. It can go from optically, perfectly transparent, all the way to opaque or translucent.

Also, from the processing side, the fact that you have this continuous viscosity-temperature curve allows you to easily shape glasses into many different kinds of geometries that otherwise can be quite challenging, if you're trying to do it using crystalline materials. That's why, for a long time, back from ancient Romans to today, people have always been using glasses as one of the dominant materials for art pieces.

So what I'm going to show you here is essentially a technique that people have been adopting to essentially make different kinds of glass pieces. It's called caneworking. And I'm showing you here, this is actually just a few photos of examples of artwork coming from caneworking there.

You can notice the names here-- reticello, zanfirico, millefiori. These all have Italian origin. This is not surprising because a lot of these techniques were actually developed in medieval times by essentially glass workers in Venice. In fact, at the time, back in the 13th century, Venice actually had essentially grouped all the glass workers, put them on one isolated island, called Murano island. That's where they actually made the glasses.

And the motivation is pretty clear. Firstly, glass-making is considered dangerous industry because of all the high-temperature furnaces. And trying to do that in wooden houses is not a very perfectly safe practice. So they figured that they should just isolate them, put them all in an island, so in case something happens, nothing's going to spread to [INAUDIBLE].

Second reason, glassmaking is actually one of the most profitable businesses at the time. So Venice were able to get lots of profit out of it through essentially, basically a monopoly. They keep all the secrets about glassmaking as trade secrets, so they can essentially have all the profits to their own. In fact, at the time, the glassmakers, they were actually not allowed to leave Venice. They had to stay on the island. So it makes sense to essentially put them all in one single island there.

In compensation, they get lots of privileges. The glassmakers, they can actually wear swords. They don't get prosecuted by the republic. So they have lots of privileges [INAUDIBLE]. But anyways, over time, I mean, the technology eventually spread out. So now you see glass workshops across the world. But still, lots of techniques originally from those types, from essentially the glassworks in Venice.

So now for caneworking, the whole idea of caneworking is that you can create essentially these long, thin glass rods called canes. They can have different kind of colors and patterns. You can then merge them together to form all kinds of beautiful appearances.

There are two different ways we essentially still use these canes. Some of them, you can use them to essentially look at from the side. This is one example of zanfirico. You can see that these kind of twisted patterns, those are actually embedded in the glass case. And you're looking at them from the side.

You have another example here. This one is millefiori. We're going to see a little video about how this is made. But you can see that there are actually many sections of canes, where you're actually looking at the cross-sectional patterns on the canes. So these are two primary ways how the canes can be used in decoration.

Now, specifically, how you actually make a cane? So the way it works is that you start it out by using essentially a long steel rod to gather a gob of glass, a big chunk of glass from the furnace. So this is the goal. The large steel rod you use to actually gather the glass is called pontil, one of those terminologies specific for glassworking.

So once you have that, what you do next is then you try to roll that piece of glass gob on a bench, workbench with a stainless steel flat surface. So that bench is called a marver. So you roll it until you get this kind of cylindrical shape. And then next thing is that you actually have another person, or sometimes you can do it yourself, essentially fit another pontil to the other end of this gob there.

So then you essentially have this cylindrical shape of the glass now attached to two rods. You can then pull it on the two ends. This is usually done by two person, but you can also do it by yourself. So this glass can now actually deform viscously and then get extended into a thin strand. So once that thin strand cools down, this is your cane.

So the typical cane has a diameter, I would say, maybe like five millimeters, give or take. And there are a lot of tricks you can actually do while you're actually creating a cane. You can essentially, for example, merge different kind of glasses and colored glasses into one single cane.

You can also twist it while you're actually doing the cane joint, so you get these kind of twisted patterns, sort of like what you have here for zanfirico. And then in the end, you can further merge the canes together, stack them together, bundle them together, then do another cane joint process to get all the complex patterns, composite patterns.

So for a long time, this kind of canemaking process is pretty much a trial-and-error process. People make somewhat informed guesses about what cane may be looking like after a certain process, but [INAUDIBLE] there's a lot of guessing and trial and error there. We are MIT, so we like to quantify things. So that's why, a few years back, the MIT Glass Lab actually developed this Virtual Glass software package that allows you to now actually mathematically model how the cane is going to come out, depending on processing parameters.

So I'm going to show you a little video here. In the video, it is also going to show you how the canemaking process is actually done. So that helps explain a lot of things here. So let me just play this video.

[VIDEO PLAYBACK]

- The idea of glass cane is to heat and stretch colored glass into long rods that can, after cooling, be cut into shorter lengths, combined, and then reheated to make various geometric designs. The use of cane goes back far into the history of glass, at least 2,000 years, to Roman times. It is still one of the most popular methods of decoration used by glass artists today.

One of the reasons for the continuing popularity of cane among glass artists is the almost endless variety of possibilities afforded by changing a few basic variables, such as color, the geometry of the design within each cane, and the way the cane is then put together and included in a finished glass piece. For many hundreds of years, the main way to find out what a new cane design might look like has been to go into the studio and try it, perhaps after sketching some ideas on paper. In other words, a lengthy process of trial and error.

- Virtual Glass is a free, open-source software program that allows anyone, at any skill level, to explore the world of cane design. While ultimately there's still no substitute for trial and error in the studio as a way of proving what a design will actually look like in glass, Virtual Glass allows the user to rapidly try many different kinds of approaches to designing glass cane, all at the speed of thought, without having to spend hours manipulating and heating glass.

Let's start with the creation and use of a simple white cane, alternating between the software where the cane is designed and the glass studio where the cane is made and used. First, we select the color from a library of colors produced by popular glass manufacturers. The selected color appears in the library on the left, under the New Color heading, ready to be used in cane.

- When making cane in the glass studio, color, here in the concentrated bar form, is broken into appropriately sized chunks and then placed in the pickup oven, where it sits for about 15 minutes to come up to a working temperature of about 1,000 degrees Fahrenheit.

- In Virtual Glass, we create a cane by specifying its cross-section. First we select a template, in this case a colored core surrounded by clear glass. Then we drag a color into the cross-section from the library area on the left. Finally, we adjust the diameter of the colored core in proportion to the clear casing around it.

- In the glass studio, the cane begins by picking up the color previously loaded into the oven onto a metal rod called a punty. The color gets further heated in the glory hole to nearly 2,000 degrees Fahrenheit, allowing it to be shaped into a straight-sided cylinder. Next, we gather clear glass from the furnace, which is the start of the cased layer.

We shape and cool the casing until we can add more clear glass.

After a final shaping pass and heat adjustment, we attach another rod and start to pull the cane.

We slowly stretch the glass, finally pulling it straight as the glass becomes rigid, and set it down when it is cool enough not to bend.

- Next, let's combine the cane we've created into a finished piece. First, we select a template for a pickup. In this case, a simple arrangement that we adjust to contain 24 canes. Then we drag cane from the library area on the left, filling in the template.

Once the first cane has been dragged into the template, subsequent canes can be added by dragging from the canes already in the template. The 3D visualization in the right window can be switched to several common forms, which can be altered by dragging control points. Here, we settle on a bowl shape.

- To make the bowl in the studio, first we cut the cane to uniform lengths, and then we arrange it onto a pre-heated ceramic kiln shelf.

Once the temperature of the cane and the shelf equalize, we heat the pickup further in the glory hole, where it fuses together into a sheet. And then we pick it up onto a blowpipe. We shape the pickup into a cylinder, close it off into a bubble, and then blow and shape it into the final piece.

- Let's look at the creation of a more complex cane that uses two sub-canes. The first sub-cane is a transparent dark green cased in clear, and the second sub-cane is opaque white cased in transparent light green cased in clear. We arrange these two canes around a circular core, alternating light and dark.

We color the core transparent yellow. We add some final clear casing to simulate the final gather of clear glass from the furnace. Finally, we twist the cane.

- In the studio, we create this setup by preheating the sub-canes with a torch.

Then roll them into the hot yellow core.

After casing and shaping, the cane is ready to be pulled. We achieve the twist by constantly spinning the rods during the pull.

Here is the final cane. The top is the virtual drawing from Virtual Glass, and the bottom is a photograph from the studio. We hope you enjoy using Virtual Glass to design your own cane. Thanks for watching.

[END PLAYBACK]

JUEJUN HU: Now, the cane you see there, that's actually one example of how you actually make canes. So actually, you can use the patterns by viewing essentially from the side of the cane. I want to show you another video. This actually shows the making of a millefiori, which essentially means 1,000 flowers. This is another classical example to show how to actually make different canes, and then use the cross-sectional patterns to actually decorate the final pieces.

[VIDEO PLAYBACK]

- This object is made by fusing millefiori canes into the surface of a rather thick bubble of glass. There are two types of canes, canes meant to be viewed from the side and canes meant to be viewed from the end. Millefiori canes are this type. They are usually cut into small sections. A millefiori cane can be cold-worked to reveal a chevron pattern.

In this video, three colored glasses will be used to create a millefiori bead. The first is opaque white. Molten, the glass appears colorless. As the glass cools, crystals form, which create the opacity.

This is an opaque red glass that similarly appears colorless and transparent when molten.

The third is a transparent, intensely colored aqua. When the glass cools to room temperature, the colors reveal themselves.

The first step is gathering glass on the end of a metal rod. To get a sufficient amount, this is done two times. The glass is rolled back and forth on the brass table called the marver. And this elongates the mass of glass.

This is lowered into a different color, here opaque white.

Marvering ensures an even coating.

This is lowered into the transparent aqua glass. Excess is left to drip off. It's marvered, and the excess at the tip is cut away. The goal is to produce a rather thin layer of aqua. This is pressed firmly into the dip or optic mold to create ribs. And as soon as it hardens, it's lowered gradually into the pot of molten opaque white glass.

Excess glass is trimmed free at the end. This is then pressed into a larger optic or dip mold. After slightly cooling, it's lowered gradually into the opaque red glass.

After reheating, it goes into another mold.

The final layer will be opaque white glass.

This is pressed into the dip mold.

And after reheating, the cane is pulled.

No matter how long the cane is pulled, and no matter how small the diameter, the pattern will remain intact.

A simple machine is used to cut the cane into thin slices.

The ball is made by gathering clear glass, marvering it to make the glass even, blowing air into the pipe to create a bubble, and then rolling the bubble over the preheated millefiori slices.

The glass is reheated and the process repeated.

The glass is reheated and marvered to press the canes gently into the surface of the clear glass.

Eventually, the surface becomes smooth.

The goal is to completely cover the bubble with millefiori canes, so the process is repeated.

The canes are embedded in clear glass, so a second gather of glass is made atop the millefiori canes.

Glassblowing now begins.

To separate the bubble from the blowpipe, it's necessary to make a constriction.

Water is dropped on the constriction, the blowpipe tapped, and the ball breaks free.

Only after cooling to room temperature do the colors reveal themselves.

[END PLAYBACK]

JUEJUN HU: So the cane join process has always been quite amazing to me. When I first saw it in the glass workshop, I see people pulling on these very long, thin canes. The immediate analogy that I have in my mind, from a material science perspective, is those tensile tests of materials.

Now, you are all familiar with the tensile test. In tensile test, what usually happens with a very short, somewhat ductile material is that you get this phenomena called necking. Essentially, as you are pulling on the rod, as you increase the stress, due to some kind of inherent randomness or intrinsic non-uniformity, some part of the rod essentially becomes a little bit thinner. And now, when that happens, you actually get higher stress due to the smaller cross-section at that necking region. And then this essentially leads to accelerated deformation of that necking region, which eventually leads to breakage.

Now, as you can see from the video there, cane join is pretty much a manual process. So there's really not much you can show about how uniform you apply the stress or strain across the process there. So now my question is that why you are not breaking the cane during this seemingly very crude process? Why they can actually maintain this stable, uniform diameter throughout this join process?

AUDIENCE: Since in a glass you don't have dislocation plates? So plastic deformation generation is from the movement of dislocations?

JUEJUN HU: OK, that's a very good guess. Indeed, glass doesn't have those kind of plastic deformation mechanisms as in like metals. But you can also get viscous flow. So glass is deformable. And naively, one would think if you actually have somewhere happen to get a little bit narrower, then it will, of course, get more stress. Then it will deform faster, then it will break. So something is actually preventing that.

OK. Well, we can do some quantitative analysis to see what actually happens. To see that, the first thing I want to do is that I want to do a little bit of quick scaling analysis. This goes back to what I call the scale invariance of the viscous flow equation. If you recall the governing equation for viscous flow, it basically says that the strain rate is proportional to the shear stress, where the proportionality constant basically gives you by the viscosity if you assume it's a Newtonian fluid.

Now, if you look at the equation, nowhere in the equation does any kind of dimensions or length appears in that equation. So what it means is that this a for viscous flow fluid system, it's supposed to be scale invariant. So what I mean by that is that if you think about, for example we have a section of the rod, you apply some stress on the n sigma, it's going to elongate, OK? And you have some kinetics of how fast it's going to deform.

Now, if you scale the system size by lambda times, so all the linear dimensions essentially get multiplied by a factor of lambda, you still keep the same boundary condition, which means in this case, the same stress. The system is going to deform in exactly the same rate, meaning the strain rate is going to be exactly the same regardless of the size or the scaling factor of the system.

OK? So that's pretty straightforward. It's just same stress gives you the same strain rate, right? So now we can take a look at now what happens. We can essentially look at two segments in the cane. Suppose there's some non-uniformity leading to a segment with slightly different diameter. And so for one of the canes, here we apply axial force of F. Now, because all the different segments essentially they are connected in series, so what's kept constant is actually the force rather than the stress.

So when you increase the diameter of the cane locally, because the force is the same, it means that the stress, which is normalized by area, has to decrease by a factor of lambda squared in a scaled system. OK? So if the stress decreases by lambda squared, we know the strain rate must also decrease by a factor of lambda squared. So what it says is that if you have a larger rod, wider or thicker rod, you are going to have a slower deformation.

So eventually, the thinner sections, it deforms faster. It gets even thinner. So it will break before the thicker sections do. OK? Now, it's actually pretty straightforward to show quantitatively. This can be easily shown like if you think about the strain rate, strain rate is basically given by how the linear dimensions like diameter, in this case D is basically diameter, so this gives you basically a strain rate. If we gauge this trend in terms of the change of the diameter.

So we know that this strain rate, it must be proportional to, in this case, stress, right? And stress scaled with diameter essentially to the inverse squared. So therefore, this must scale with 1 over D squared. OK? So you can cancel out the 1 over D on both sides, which then gives you this very simple condition here. And if you don't want this cane to essentially break, you need to make sure that the strain rate essentially remains a constant, right?

But that's obviously not the case here. What this analysis shows is essentially why necking happens in general materials because of stress concentration. However, one factor we have not taken into account here is that actually a proportionality constant, which is the viscosity eta. OK. So the larger the eta, the slower the deformation. So in order to reach stability, this factor, the strain rate, must be the same.

So what it means, that you must have eta that essentially increases as the diameter gets smaller. You can already probably guess what's actually happening there. What does eta depend on? Eta depends on temperature. So thinner segments, the temperature drops faster. And then that leads to increase viscosity, which then eventually allows you to reach this stability condition there, where the strain rate becomes a constant, which, in this context, is basically the eta times the diameter squared, becomes a constant. That's basically stability theorem, where you have a constant strain rate across the entire rod.

OK. So where might we want to be a quantitative? We want to see if that actually happens. So I did a little bit more analysis looking into essentially trying to model this process. So because our hypothesis is that thinner cane is going to have a faster heat dissipation, so as a result, it cools down faster. That's what prevents essentially breakage.

We have to look into essentially the heat dissipation process. What are the mechanisms there? Generally, there are three kinds of heat dissipation mechanisms. You get conduction. Conduction means essentially heat directly pass from one solid to another solid. It's actually pretty negligible in this case because if you think about cane, it's a pretty long, elongated geometry, right? So the real contact, solid-to-solid contact happens at the end of the cane, which is much smaller compared to essentially the sidewall surfaces.

So conduction is pretty much negligible. You also get convection. Convection is when you have air coming into contact with the rod. And then the heated air essentially gets essentially you get lighter, it moves away, where the cold air comes in. So this process continues. Air is not very good thermal conductor even with a pretty strong convective flow. And in this case, it turns out it's pretty negligible as well, the convective heat flow.

The dominant heat transfer mechanism in this particular case is radiative heat transfer. Essentially due to blackbody radiation, anything when you heat up higher temperature, it emits infrared radiation that carries away energy from the hot body. General rule of thumb, if you're dealing with a hot body, a high temperature above a few hundred degrees Celsius, usually the dominant heat transfer mechanism becomes radiative heat transfer.

So for radiative heat transfer, we have the Stefan-Boltzmann law which basically says here is the heat flux q is proportional to T to the 4th power. This explains what my conclusion, as I said, for high temperature bodies, usually radiative heat transfer dominates because the heat flux scales T to the 4th power. Versus convective and conductive heat flow, where the heat flux scales temperature difference linearly. So that's why eventually at high temperature, radiative heat transfer takes over.

So e is the emissivity. It's a constant between 0 to 1. Sigma is what's called the Stefan-Boltzmann constant. So then if you have that, you can actually write the temperature churn rate if you think about one section of the cane there, with a volume V and the surface area S. So S would be the sidewall surface area, right? So then you can simplify this equation. I'm going to go through the details. It's pretty straightforward. It's basically about the heat removes lead to the temperature reduction of the rod.

And finally, you can also model how the viscosity changes as a function of temperature by using this, basically, a Arrhenius equation. Now rigorously speaking, this delta E, activation energy, should be temperature-dependent. We already learned about it. But for now, for typical glasses, over temperature range we're thinking about here as a first-order approximation, let's treat that as a constant.

So now we can actually do our model. So I actually put a code already on the Canvas website. I put a little Matlab code that actually did the calculation. I'm looking at a simplified case, where we look at essentially two connected sections. It has a slightly difference in diameter. They started out in terms of same temperature. And I made some assumptions here. I assumed that the temperature is uniform across the can cross-section, which for small k is pretty good approximation in any case.

I assume there's no heat or mass exchange between the cane sections, which obviously is wrong. But if the cane is long enough, it's a decent approximation. And then I only consider radiative heat transfer as we have mentioned. And finally, I'm assuming a constant joint speed and hence, essentially, a constant force across the two rods, actually. So now if you look at the simulated results, what I'm plotting here is that both canes or both canes segments started out at the same temperature of 900C. But as you can see here, the smaller cross section 1, it actually decreases, temperature decreases faster than the thicker one.

Basically, if you go back to equation, it goes back to this factor here. It's basically surface-to-volume ratio. If the thinner section you have more surface to volume and therefore, this kind of radiative heat transfer, which scales with surface area, becomes more efficient. So that's why it cools down faster. As it cools down faster, we expect its viscosity to increase. Once its viscosity increases, that resists this deformation, so that this becomes essentially this kind of self-feedback loop that prevents destabilization in the cane joining process.

OK? So that's what I'm putting here thinner section faster, increasing viscosity, which then keeps you to damp out any kind of non-uniformity cane joining process. And that's why when you see the canes join, despite, people, essentially there's no control over the specific joint conditions there, they usually come up with very, very uniform diameters, except at the end when you're close to the pointy. OK

OK? Make sense? Now, this same process, the same mechanism also applies to other cases when you're doing glass deformation as well, for example, when you're doing glass fiber joint. It's basically the same process but with a lot more control and going to much smaller diameter. But the same kind of stability criteria helps you prevent the breakage in that case as well. And that's shown in the simulation result here where the diameter of the two canes eventually converges. So any kind of initial difference, they will damp out in the process.

OK. Questions about this, or this is all good? All right. So now next, besides caneworking, I also want to mention that people are always exploring new ways to actually create all kinds of innovative art structures. And this example, this also comes from MIT, actually comes from Media Lab. They now develop a way to essentially create different art pieces using 3D printing. OK. I will just show the video. It's pretty straightforward.

[VIDEO PLAYBACK]

[MUSIC PLAYING]

[END PLAYBACK]

So at the end of the video, that's actually a display that used to be in the lobby of the Media Lab, the new Media Lab building. I don't know if they still have it, but you can take a look. Also, if you go back a few years back when we actually do the glass lab demo, you actually get to see the printer right in the glass lab. Not anymore. They were doing the printing essentially inside the MIT Glass Lab for a few years, and then later on, they increased demand. So they decided to spin out.

They actually started their own glass workshop somewhere in the vicinity here. So you don't get to see it anymore. That's why I'm playing a YouTube video here. But people are actually extending these techniques. Now, people will only do for oxide glass printing. People even do non-oxide glasses like chalcogenide. They essentially use the same technique to create all kinds of functional components.

OK. So now comes back to more industrial scale process. I want to discuss about processes that people use to structure small glass pieces, especially on precision optical components. This is called a precision glass molding. The idea behind this is pretty straightforward. You have a two-piece mold. When you put them together, there's a cavity forming between the two. So if you put in some glasses, heat it up, press it, the glass will then viscously flow and then fill the entire cavity. So then when you actually release the mold, you can take out the piece. It will conform to the shape of the cavity to the first order. OK.

AUDIENCE: --injection molding?

JUEJUN HU: Great question. These are two slightly different processes. For glass, because we typically do a compression molding. This is called compression molding. Injection molding is a little bit different. The cavity or the mold resides in essentially one piece. You inject the liquid into that cavity to fill in. And then you eventually open up cavity and take it out. Versus in this case, you have two pieces. You use pressure to force the glass to conform to the two pieces. That's why it's called compression molding.

It's very similar. If you go to polymer community, people actually can do both, either compression or injection. The difference is are somewhat minor. Compression molding is a bit easier to handle. The tooling is simpler. You can make large sheets and pieces, like flat-panel pieces with low aspect ratio easier using compression molding. Injection molding is more industrial-scale process, higher throughput. Eventually, you get lower cost with higher volume. So minor differences. But from a material perspective, they are pretty much very similar. They all rely on viscous deformation or viscoelastic deformation of the amorphous materials. Yes.

AUDIENCE: So could you injection-mold glass?

JUEJUN HU: Yes, I do think it's a very common process. People still typically do compression molding, but I believe it's definitely doable. In fact, we are going to see an example when we talk about amorphous metal. People do injection molding of amorphous metal, which is glass. So, yes, you can do it.

AUDIENCE: --you just have to get a lot harder to get it back.

JUEJUN HU:

Injection molding requires lower viscosity compared to compression molding. I mean, if you look at compression molding here, the pressure range we are talking about here is actually well above the working range, because you essentially use pressure to accelerate the viscous flow process. Injection molding, you have to fill in essentially the whole cavity there. That's why it requires, essentially, lower viscosity.

So it means that the material you are trying to mold here, you need to have sufficient resistance to crystallization, because injection molding, you need to raise to higher temperature. So a little caveat that. Maybe that's why people are doing more of the compression molding because it requires a lower temperature and it's easy, a bit easier in terms of all the wear and tear and everything, temperature tolerance and all that stuff. But, yeah, for glass, for inorganic like oxide type of glasses, compression molding is the more common process.

So if you look at the typical compression molding process, what I'm showing on this plot here, this is how the force or the pressure you apply on the mold as the temperature evolves across the entire process. You start out with a purging step. This is optional if you're doing like oxide glasses. If you're doing non-oxide glasses, like chalcogenide, you don't want to get oxidized. You have to purge it with inert gas a bit.

And then you start to heat it. During the heating process, you essentially ramp up the temperature and then you stay there for some time. You apply a very low pressure just to ensure the door is closed. And then you go to a pressing step, where you actually crank up the pressure, allow the things to deform. And then finally, you allow it to slowly cool down while you actually release the stress.

So fairly simple process. Some of the key points here is that in order to improve the throughput and reduce any kind of damage of the mold so you can reuse it, essentially, you need to prevent any kind of mold sticking and damage. So that's why for a lot of these molds, people actually also put the low friction and also refractory coatings on top. Titanium nitride, silicon carbide, that's one very important parameter there.

Also, you need to essentially prevent any kind of non-uniform temperature distribution in this process, because non-uniform temperature diffusion lead to variation in terms of viscosity, which is not desirable in this case. And variation of viscosity leads to a variation of strain rate. So that's why people don't like it. And finally, one very important part also want to mention here is that people develop very elaborate models, trying to essentially simulate this process, to predict any kind of a postmodern shape deformation.

And that mostly come from essentially viscoelasticity of the glass. So we're going to talk about viscoelasticity in the next section there. But basically, a material during the glass transition temperature regime exhibits both elastic properties and also viscous flow properties. So a direct consequence of that is that the final geometry of the structure, now very sensitively depends on the temperature history.

During this modeling process, you expect that you get lots of information. This actually leads to a lot of residual stress. So if you release the mold, now essentially, you allow the surface to freely deform. This residual stress is then going to lead to relaxation and eventually leading to a geometric deviation from your target mold structures. So that's something you have to very carefully model in order to prevent this kind of shape deformation there. So there are tons of papers looking into how to actually model this process to prevent any kind of a shape deformation.

Now, why this is so important, why people care about it, because the most important application for this kind of modeling process is for optical elements. And for these optical surfaces, any kind of a shape deviation can be very harmful. It leads to aberrations, essentially blurs the image you get in your final camera products. So what I'm showing you here, this is actually a table. It's a bit old, but the general features are still there.

It compares two common materials people use for essentially molding process, glass versus plastic or polymer. OK. So if you think about state-of-the-art consumer electronic devices like the phone in your pocket, these lenses here, a lot of the high-end cameras, they now use a mix of glass lenses plus polymer lenses. You sometimes see people seeing like a camera may have 1G6P or maybe like 7P8P.

So essentially, what it means is that your camera lens contains one piece of glass lens and six pieces of plastic lens. Or you can also do like eight pieces of plastic or seven pieces of plastic. So previously, people pretty much just plastic only like this. Recently, people start to transition to this kind of hybrid lenses, where you combine both glass and plastics. The motivation behind that goes back to the properties here.

So for glasses, you get huge amount of varieties where you can easily tailor optical properties. Most importantly, it goes back to this P number, which basically gives you the dispersion of glass. We're going to talk about that later on when we were talking about optical properties. But plastics tend to have very high dispersion. So it means that refractive index changes pretty drastically with wavelength.

And that can be problematic when you're trying to focus all different colors of light into the same point to get a sharp image. So the way to correct for it is to find a material with different dispersion characteristics. And that's actually what exactly glass is actually good for. They can actually compensate, provide different dispersion characteristics to compensate the color performance of the cameras.

And that's why, I mean if you also look at the specific parameters here, glass modeling also tend to be a bit more precise. So essentially you can use, for example, one piece of glass lenses potentially to replace two pieces of polymer lenses while not sacrificing any optical performance. Well, that may sound trivial. It actually gets important because people are always looking for something that's more compact so that you don't have this bump on the cell phone right there.

So those are important considerations people are looking into that. The advantage of polymer is actually cost. Injection-molded polymer lenses are extremely cheap. They basically cost nothing practically. So while glasses, they still get more expensive compared to polymer lenses. So that's why you see essentially this kind of hybrid lenses mostly in high-end cell phone products like iPhone, iPhone Pro Max, something like that. That's where they actually use hybrid lenses to give you the ultimate imaging qualities.

There are also other use cases where glasses is very important, for example in automotive industry. There are lots of cameras on the car. Both outside the car, outside the cabin, inside the cabin to either look at the surrounding environment or to monitor the occupants or drivers in the cabin. For those applications, it's really important that the material you use has to be compatible with the automotive regulations.

Automotive regulations are quite stringent in terms of temperature excursion, in terms of saw, mist, dust, everything. So that's where glass actually excels compared to polymers. Polymers often have challenges, especially meeting those kinds of specifications. And that's why it's almost pretty much a mandated requirement that you actually use glass lenses on those automotive applications. So that's why the glass molding is really picking up in recent years because of the increasing use of, essentially, computer vision systems.

All right, so these are four tiny little lenses, right? What about the huge ones? Telescope ones. So we're looking at telescopes here. I showed you this picture before. This is actually one of the large tactical mirrors made by Corning. This one has a diameter of 2.7 meters, which may appear big. But if you look at this big chart here, that actually shows all the telescopes in the world to scale. They also put, in this case, a tennis court and a basketball court to scale.

So now if you look at this one, this one may seem very big. It's about the size of this Hooker Telescope. It's not the same one, but size-wise very similar. So this tiny little one. Now, if you look at this plot here, now I have a couple of things. I've a couple of observations I made. First thing is about that the astronomers don't seem very creative when it comes to naming because look at it. They have large telescope, very large telescope, extremely large telescope, overwhelmingly large telescope.

AUDIENCE: They're like, no, no, no, it's too big. It's too big. We'll cancel it.

[INTERPOSING VOICES]

JUEJUN HU: They are smart people, right? I wish they come up with more creative names rather than that, but whatever. Now, that's the first thing. Second thing, look at these ones, these big mirrors. Do you notice something?

AUDIENCE: [INAUDIBLE]

JUEJUN HU: Yeah, that's because you need light waves to actually go through the camera in the back. Outside that, look at the size. You notice something there? They're all more or less the same size. In fact, they all have a maximum diameter of 8.4 meters. I mean, wonder where that number comes from. Because they all come from the same place. There's only one big furnace in the world that actually can make such huge mirrors. And the diameter of that furnace is 8.4 meters.

This is all made in Arizona. If you go to University of Arizona, you go to their football stadium, this is under, essentially, audience seats. This is the mirror lab. All those mirrors are melted right there, that big furnace. OK.

AUDIENCE: --just go into the furnace.

[LAUGHTER]

JUEJUN HU: There you go. They probably don't charge you a ticket anyway without hefty price. So maybe a good thing. OK, so now if you look inside this furnace, if you open up, this is actually what it looks like. You're going to pour molten glass into that. And then you see at the bottom here, this mirror is actually not a big solid piece.

They usually put this kind of honeycomb structures at the bottom. This is similar to the kind of patterns, corrugated pattern you have on a waffle iron. So essentially, the created mirrors, instead of having a big solid piece, they are connected by ridges around this honeycomb pieces. And the point of that is that you want to reduce essentially the amount of material used to reduce weight, reduce the cooling time, and also maintain the mechanical stress using the honeycomb structures. Makes sense. Right.

All right. Now, this mirror has a big parabolic surfaces so that you can focus light from distant stars into a spot. So now my question for you, how do you create these huge parabolic surfaces? If you're doing grinding and polishing that's going to take forever. Right, so what--

AUDIENCE: Stamping?

JUEJUN HU: Stamping. Good guess. You need a huge stamp. It has to be very precise. Stamp it.

AUDIENCE: Different cooling/heating rates

JUEJUN HU: You get a parabolic shape.

AUDIENCE: Maybe to like--

JUEJUN HU: Use your wildest guesses.

AUDIENCE: Drip it like [INAUDIBLE].

JUEJUN HU: They spin it. There you go. Very good. Now they should hire you as their-- [LAUGHS] so the way they do it is essentially they spin it while the glass is melted. If you go ahead and calculate it, what you find out is that under gravitational force, if you spin a liquid, its surface obviously is going to rise on the edge. The center is going to sink because of centrifugal force. The surface exactly conforms to a parabolic shape. This is a homework assignment for you.

AUDIENCE: [INAUDIBLE]

JUEJUN HU: No, don't worry about it. But you can do it. It's exactly a parabolic shape.

AUDIENCE: Is the question [INAUDIBLE]?

JUEJUN HU:

PSAT. I'm going to put it on the PSAT. You have to solve it exactly. This is actually one of the questions I recall when I was doing my Physics Olympiad and stuff. That's one of the questions. You have to actually prove it is actually a parabolic shape, which indeed a parabolic shape, by the way. OK, so you basically have that molten glass. It's cooling. We said that glass cooling has to go a long time because you need to release all the stress. So that's a pretty long process.

Over the entire process, you have to spin and spin until it cools down. And actually, it's actually frozen into it. So it's pretty remarkable. Actually that huge, gigantic furnace is actually spinning. And at the end, you get this very nice parabolic shape. You do some fine-tuning. You do a little bit more. Essentially, you're milling and then polishing so that you get it down to a 25-nanometer accuracy, which is remarkable over that 8.4-meter diameter length.

OK, so that's one more example where this kind of viscous flow properties can give you one way to actually structure these gigantic pieces. All right. Any more questions about these inorganic glasses before we move on to talk about metallic glasses?

OK, so now, let's switch gears a little bit and talk about how you actually shape metallic glasses. We'll have one chapter specifically talking about structures and mechanical properties or mechanical glasses later after we talk about mechanical properties. But I want to give you a little preview about how we actually essentially produce all kinds of products with diverse geometries out of metallic glasses. So

We have already talked about some basic attributes of bulk metallic glasses. We mentioned that you have this kind of random packing structure that's free from the typical crystalline defects you would see in a conventional metal, like grain boundaries or crystalline planes or dislocations. So one immediate consequence of that is that this amorphous metal tends to exhibit a much higher yield strength, because there's no way for them to easily deform plastically.

In a conventional metal, plastic deformation usually takes place through a motion of dislocations. You get essentially slip or essentially a climb. So those macroscopic deformation, you don't have any of that. So that's why the lack of plastic deformation mechanism means that it has to deform elastically over a much wider stress range. So now, if you look at the definition of yield stress, you essentially put the stress versus strain. And typically, for material, it will look something like this. You get elastic range, the Hooke and range.

And then it may deviate from that range and eventually, you start to deform plastically. If you're in a less range, if you remove the stress, this curve is going to come back exactly where I come from. But if it is going to a plastic range, then as you unload, then essentially, you come to a point where you leave some residual plastic deformation. So the point where this deformation gets to 0.2%, the corresponding stress is what we define as yield stress.

Now, in amorphous metal, because it doesn't want to deform plastically, it means that this elastic range actually extends much beyond yield, therefore conventional method. So that's one reason people like this amorphous metal there. So what I'm putting on this plot on the right-hand side here, I'm basically comparing the strength of amorphous metal versus unconventional materials. I apologize, the fonts here are tiny. I don't think you can ever read it, but these are essentially magnesium. This is aluminum. This is titanium. This is stainless steel. So compared to conventional crystalline metal.

What you see here is the strength of amorphous metal is much superior compared to all these conventional materials. Again, because you don't have a mechanism to deform plastically. And same thing applies to other things like harness, which is also a measure of how the material can resist deformation. So in terms of those metrics, amorphous metals always win.

However, that also has a problem. If you now come back to processing and trying to use it as a mechanical component. If you are trying to process conventional metal, you typically do a co-working. You can roll it. You can extrude it. You can deform it. It's going to plastically deform. And in that process, the reason the conventional metal can be cold-worked is because of this attribute of so-called strain hardening.

So when you are trying to plastically deform these metals, you actually generate more defects. You generate a lot more dislocations. And then these iterations, as they move around, they are going to interact with each other. And this interaction hampers the further movement of the dislocations. And as a result, the more cold work you put on a conventional metal, the higher the mechanical strength it gets. That's called a strain hardening.

Now, why is strain hardening important? Strain hardening is the mechanism to prevent essentially localized deformation and failure. Think about the same example as like cane joining. If you're trying to essentially use cold working to, for example, pull a metal wire, if you have some non-uniformity such that locally you get some essentially smaller diameter, it means that you actually get more deformation there.

More deformation lead to more strain hardening. So strength increases. This increased strength then prevents essentially catastrophic failure right at that point. OK? So that's why co-working is a viable way of processing conventional metals. Now, what about amorphous metals? So when amorphous metals-- if you apply lots of stress, it will start to deform at some point plastically. But when it deforms plastically, instead of relying on dislocations, what happens is that essentially, in an intuitive manner, the atomic clusters will have to move past each other directly.

OK? So later on, we're going to talk about the specific mechanism there. And how this actually happens. But essentially, when you have these clusters move past each other, one thing that inevitably happens is it generates excess free volume. So speaking about free volume, where's the wipe? Forget about it. So if you look at the volume-temperature curve that you have seen many, many times, for a crystalline material, you get something like this. Amorphous material, it would be more like this.

So if you allow the liquid to completely relax here, this dotted line, what I'm showing you here, this would be the supercooled liquid line. The definition of the glass says that the glass always try to relax towards the supercool liquid line. So the excess volume we're seeing here, this is what's called a free volume, this delta V here. Because the glass usually has a larger volume compared to its supercool liquid counterpart.

Now, you can imagine that if you have an amorphous metal, if you start to have atom clusters move past each other, you need free volume to induce this kind of deformation. Also, the more information you bring into it, the more free volume you introduce into the system. You are deviating from this very close packed structure there. Now, this creates an issue here. This is called strain softening. The more you deform it, the more excess volume you generate, the more deformable it becomes.

So the strength of the material actually decreases with increasing amount of strain in amorphous metal. And this is very problematic if you're trying to use do cold working on these metals here. You need to essentially shear, so-called shear localization and catastrophic failure. So what happens here, this is one example. This is, basically, amorphous metal rod. You're placing essentially axial compressive strain. And then what happens is that at some point, you start to get this deformation, plastic deformation along one of the planes here.

Now, what happens is strain softens. So it becomes even more deformable. So this actually accelerates local deformation. So that if you look at the deformation, it all localizes in this kind of few localized bands, these lines here. And then it eventually breaks along one of them. So this is called a shear localization. Essentially, all the shear deformation is localized within a very narrow band.

So there will be a problem. That means that you can no longer use cold working to process these materials. They are not stable against perturbations, against deformation. So that's why the way people used to actually process these small metallic glasses are two different methods. One is to essentially you try to heat it up to above the melting point. So you go to a liquid state, and then you cool it down.

You're essentially casting it or essentially put the liquid into some kind of mold, allow it to cool down, and then that allows you to go to the final geometry. So this will be basically the casting process. And there are a few variants there. You can have a suction casting, which basically use vacuum to assist in the filling of the mold. Or you can do a die casting. But all those variants follow the same manner there. You go from liquid phase, pour into a mold, allow you to fill the mold. Eventually, you remove it from a piece.

There is some advantage of doing casting of using metallic glasses compared to conventional metal there. The most important one being that the volume shrinkage is much smaller. So if you look at the volume change during the casting process, for crystalline material, you're essentially from liquid state right to go to the solid state. So the volume change is represented by this vertical line here, that's the first-order phase transition. So there's a certain volume from liquid to solid phase.

Now versus glass. For glass, the liquid phase actually extends a little bit longer, right? Over this supercooled liquid regime, this is still liquid. It still has some viscous flow properties that can still conform to the mold. Also at the end, you see that because of the presence of the free volume, the final density of the amorphous metal also tend to be a little bit smaller compared to a crystalline metal.

So these two factors combined together that this supercritical line extends to lower temperature and also the fact that you have free volume means that the net volume change during the casting process is much smaller for amorphous metal compared to a crystalline metal. Does that make sense? So this leads to this kind of process called a net shape forming.

Essentially means that because the volume shrinkage is sufficiently small, it's about half a percent, versus conventional metal, which is typically a few percent, you don't have to do any kind of a further processing or shaping to fine-tune the shape. You get exactly what you want just from the mold geometry. So quantitatively, this is just one example, comparing this is amorphous metal, this is a volume shrinkage during casting compared to conventional metal, again, aluminum, titanium, steel, copper.

You see that conventional metal has a few percent of volume change versus half a percent for amorphous metal. So that's one advantage for amorphous metal casting there. So the key process parameter you want to control in this process here again is the viscosity. You want to make sure it's induced sufficient viscous flow to completely fill the mold. Also, you are working against crystallization.

The process cannot take forever. You have to essentially complete it with sufficiently fast cooling rate to bypass crystallization, which was indicated by this line here. You have to avoid this crystallization region in order to get amorphous metal. So this also limits essentially geometric dimensioning, if you remember, of the metal you can cast. So that's one way. Now, the second way of doing a bulk metallic glass shaping is to use a process called a thermoplastic forming.

So this really derives from the processing of amorphous polymers. The idea is that you have a piece of polymer. You heat it up to above the glass transition temperature, where it becomes more or less a viscous liquid. You can then use all kinds of molding or deformation techniques to change it to a desired geometry and then you quit out so that you can freeze the final geometry there.

You can do the same thing with bulk metallic glasses. And the thermal history is shown by this curve here. It's actually heat up to somewhere where you have low enough viscosity to allow you to deform it, and then you cool it down to freezing the structure. For this process, the key parameter we want to look at here, again, is crystallization kinetics. You want to make sure you pick a bulk metallic glass component where crystallization is sufficiently slow so that allows you enough time to do the molding or to do the geometric shaping.

So just as one example here, I'm showing you, this is a typical plot people use to essentially gauge which metallic glass composition is suitable for some processing techniques. You essentially look at the essentially viscosity at one end. You have time to crystallization on the other axis. So based on your specific structuring techniques, you know your viscosity window, where your process to take place.

You then look at what is the time to crystallization. And then you can tell for yourself whether or not this composition gives you enough time window to complete the process. So for example, actually here, this zirconium-based alloy obviously is a lot better than this palladium-based alloy in terms of this kind of processing. It's a lot more stable. Gives you more time to complete your process.

The other factor. I also want to mention here is this phenomenon called thermal embrittlement. So thermal embrittlement essentially means that if you have a piece of bulk metallic glass, you go through this thermoplastic forming, it typically becomes more brittle. And the reason for that is because when you heat it up, reheat it up to glass transition, pass the glass transition region, you essentially introducing structural relaxation in the material.

So any kind of glass is always trying to relax towards its corresponding supercooled liquid state. Now once it relaxes, it means that you actually decreasing the free volume there. In amorphous metal, you need free volume to essentially default to introducing information. So the fact that after the process you have less free volume means that the material essentially becomes more brittle. Its ability to deform plastically decreases. So that's one thing to keep into account that the material property after the thermoplastic forming could be different from the starting material.

OK. Outside that, this process, you can essentially use almost any kind of techniques that people have developed for processing polymers and apply them to a bulk metallic glasses. It can be molding, extrusion, rolling, whatever. But one advantage of doing thermoplastic forming on these bulk metallic glasses compared to conventional polymers, I want to mention here, is that it has basically two advantages here.

One, in terms of a liquid fragility. So what I'm plotting on this curve here, this is the Angell plot, now contains a lot of this bulk metallic glasses, these ones. Compared to this last one, these crosses, this is actually for a typical polymer or organic liquid. What you notice here is that these bulk metallic glasses, they are definitely somewhat fragile. They don't follow straight lines, but they are a lot closer to a strong liquid compared to organic fluids.

So it means that they have a reduced fragility compared to typical polymers. As I mentioned before, reduced fragility is actually advantageous for processing because it means that its viscosity dependence on temperature is less. So it's more tolerant to any kind of temperature variations without causing too much viscosity excursion. OK? So that's an advantage for this process here. You have a better control over the viscosity.

The second advantage that comes in is that these bulk metallic glasses, they are metal. So they are a lot more thermally conductive. So it means that temperature uniformity tend to be much better chemical polymers. And this could be useful if you want to prevent any kind of inhomogeneity in the temperature and viscosity developed in your process.

So the next few slides is just a quick overview of some of the common techniques people use to structure bulk metallic glasses. They are all borrowed from the plastic processing community. You can do compression modeling. Same idea as to how you do the glass. The main difference here is that in the glass, you typically have basically like a parison or preform, essentially a big, single solid piece where you use to do the compression modeling.

In bulk metallic glasses. Instead of using a parison, you actually use beads, small beads. When you apply pressure and heat it up, they essentially fuse together. So it's a slightly different way of doing the process there. Other than that, it's pretty similar. It's typically used to create open structures with relatively low aspect ratio, which also makes sense. Because you have two pieces, you cannot have, essentially, sealed cavity where you cannot take it out. So they typically are used to create large sheets, more like flat pieces.

You have injection molding, as I promise you. [CHUCKLES] It's very, very similar to the process illustrated here. The main difference here being that essentially you're more essentially forms a cavity shape on one pieces. You have a plunger. You essentially put one piece of this liquid metal in there, amorphous metal in there and then deform it during the heating process. So I, again, have another quick video that shows you how this is actually implemented in industry.

[VIDEO PLAYBACK]

[MUSIC PLAYING]

[END PLAYBACK]

So fairly straightforward process. Same thing, this also applies to open structures because you need to be able to essentially take it out from the mode. So you need to be able to find a way to open it up. But as I said, this usually applies to typically with lower viscosity. So in terms of essentially glass stability, it places a more stringent requirement compared to if you do a compression model because of the high temperature processing temperature.

Now, you can also do blow molding. In glasses, we mentioned that you can use this to create things like bottles. Same idea here, you can use compressed air to conform a piece of a parison into the final geometry. So this is actually one example. This is actually a starting preform or parison. This is the final shape. They essentially blow-mold it against the Chanel perfume bottle. So that's what it ended up being.

The advantage of this blow molding is that it allows you to create structures with very high aspect ratio, essentially thin wall components. The challenge there is that because of the wall gets very thin, it means that it gets a lot more sensitive to any kind of non-uniformity. If a local stress concentrates, you may concentrate a strain and eventually leads to breakage. This is one example where if you don't have good control, that's what actually happens.

So in this regard, if you compare plastic with bulk metallic glasses, this is where bulk metallic glasses has some advantage there because of their much higher thermal conductivity. So this leads to a more uniform temperature distribution, potentially less tendency for localized temperature variations. And then these are local failure. Another thing I also want to mention here, if you compare these two plots, is in terms of maximum strain.

For plastics, the maximum strain is listed as infinity because they basically don't crystallize. They have very strong resistance to crystallization. So you can essentially stay there at this relatively low viscosity state for a very extended period of time. So you can get lots of deformation there. However, for bulk metallic glasses, they do crystallize at some point. So this eventually limits maximum strain and maximum deformation. So that's what limit the expiration we are actually showing here, crystallization or glass-forming ability.

All right, so last quick piece, I just also want to mention here is that people can also do a 3D printing of bulk metallic glasses. There are lots of variants of this technique there. The example I'm giving here is called fused filament fabrication. It's fairly straightforward. You have essentially a filament of metallic glasses. It's essentially fed into this nozzle where it is heated. So it goes into this kind of molten state, glass forming liquid. You then apply a voltage across this nozzle and your conductive substrate.

Now, this voltage drop mostly takes place at this nozzle right here because you have this reduced cross-section. So this is where you have most electrical resistance. So this is where all the voltage drop actually takes place. So all the heating is confined right in this little filament there. As soon as it comes into contact with the bulk piece, its cross-section increases. So it means that you have current spreading. This decreases the voltage drop, and therefore you get much less joule heating.

Also, the heat dissipation becomes very efficient because of the bulk volume there. So it quickly solidifies. So using this, you can then essentially translating the nozzle. You can then print all kinds of geometries in this technique there. So that's the last slide I have here. Any more questions about shaping of amorphous materials? All good? All right. Thank you.