[SQUEAKING]

[RUSTLING]

[CLICKING]

JUEJUN HU: For this lecture, I'm going to try to do three different things. I will start by wrapping up about the essentially optical properties, optical applications. And then I will talk a little bit about the pset. And after that, I will actually discuss about different characterization methods that can be applied for amorphous materials. Specifically in this lecture, we're going to focus on diffraction techniques.

All right, so in the last lecture, I showed you this video which essentially showed some developments of a higher refractive index glasses, specifically for augmented reality applications. So if you look at the key properties that are desirable for this kind of augmented reality glasses, as I said, high refractive index is basically the number one requirement there. So the reason high refractive index is needed, it basically goes back to essentially the field of view of the system. So we know that the refractive index essentially dictates the range of angles where the light can be trapped inside the waveguide through total internal reflection.

So this is basically the angle theta. So basically, this angle theta has to be greater than the critical angle in order for the light to be able to trap via total internal reflection in the waveguide. So if the index is higher, this critical angle is going to get smaller.

And that means that there's increased angular range where this waveguide can be used to trap light. So that actually translates in the end to a larger angular field of view where people can actually see images coming from the waveguide itself, because that's essentially a larger angular range of light rays that can propagate in the waveguide. And that's quite important for these AI applications, obviously, because we want to make sure that when you actually display something, you'll be able to feel like the large field of view, rather than only a very narrow, angular range.

So that's why there has been a strong push towards high-index materials for this kind of AI applications. And you can see here that many of the glass vendors-- I'm using short as an example here. But many of the glass vendors also have similar glass products, now with a refractive index actually higher than 2.0, which is quite remarkable considering that most silicate oxide glasses only have index of about 1.5.

All right, so that's one property. Now, other things, we also need high transmission for obvious reasons. You want to make sure there's minimal efficiency loss. Low birefringence-- birefringence refers to essentially anisotropy of its optical refractive index in the material. In a glass material, normally it should be isotropic. So there should be zero birefringent.

But birefringence can be caused if there's any kind of residual stress in the material. So low birefringence, essentially, you need to process the material or annealing glass material sufficiently well to annihilate any kind of residual stress. And that will be important to prevent any kind of optical distortions.

Homogeneity is to essentially lower any kind of image distortion, enhance image quality, and prevent scattering. Same thing-- flatness and thickness homogeneity, this is also helps to ensure that optical designers can know very well the parameters of the components, and therefore ensure that optical performance is consistent with all design. Roughness-- low roughness helps to reduce any kind of scattering loss, enhances transmission, and reduces any kind of haze coming from the glass.

The last one here cosmetic-- you notice that the unit is a scratch / dig. So what this means-- the first number called scratch essentially gives you the maximum allowed width of a scratch on the finished glass surface in microns. So it means essentially that the maximum width of the scratch you can find on a glass surface is 40 microns.

Dig, on the other hand, refers to essentially more like point defects, like pinholes, inclusions, maybe like surface. There's a little pit or something. So this number is in 10 microns. So 20 dig means that the maximum size of this point defect you find on the glass component surface is 200 microns maximum. That's what's allowed.

So having a low scratch / dig number also ensures that you have high surface quality. And this minimizes any kind of loss due to essentially optical scattering at those defects. So those are the basic requirements for these kind of optical properties and morphology of the glass.

For form factor, low wafer thickness combined with the high glass strength ensures that you can have a lightweight glass, which helps to reduce the weight for any kind of wearable devices. You also need to have enough mechanical strength so that these glass wafers can be handled in a high-throughput wafer processing systems, which is important for high-volume manufacturing. And finally, wafer size-- most of the state of the art fabrication facilities use wafer sizes of 200 or 300 millimeters, 8 or 12 inch wafers, which is compatible with what glass vendors can offer. So these are the key attributes of this kind of high index glasses for augmented reality.

Now, if you look at specifically the chemistry that people use to realize high-index glasses, not surprisingly, the recipe here is to go with heavy metal oxides. As we have mentioned about lead, there are also alternatives-- non lead-containing oxides, such as zirconium oxide or titanium oxide. People can add them into the glass network to help increase the polarizability, and therefore refractive index.

So if you look at this plot here, this is basically the [INAUDIBLE] plot for the different glass compositions. These glasses typically get crowded in this corner here, essentially with a large letter F. So these are filling glasses, which means that they are doped with heavy metal oxides to boost the refractive index. So that's the basic idea how you chemically formulate these glass materials.

All right, so just to quickly summarize, we have talked about essentially optical fibers and planar waveguides here. For fibers, you need to understand the fabrication process. And for waveguides, it's important to understand the loss mechanisms in this kind of waveguide devices, and what are some of the key applications for waveguides in fiber devices.

All right, so now what I will do is switch gears a little bit. And let's take a look at the pset. All right, so the first question is basically, just essentially look at this figure here and try to calculate the strain, as well as the temperature, at which the thermal stress starts to build up.

So what I mean here is essentially, you just look at this picture. From the picture, you can essentially read out the parameters like the bending radius, as well as the thickness of the wire, using some kind of image processing software. And then you can plug into this basically this bimetallic strip equation. From the equation, if the radius of this band here, you can then use that to actually calculate the strain mismatch, as well as delta T.

So I'm not going to go through the details here. I think you all get the basic steps. The numbers may not be the same as what I'm showing here, because it turns out everyone has slightly different readings in terms of how thick the wire is, as well as the bending radius.

So there's a pretty large error bar associated with that. So that's why I don't worry too much about the specific numbers there. As long as you get the method right, I give you full credit for that.

So I did my fitting. This is probably not very accurate. I roughly guess that the thickness is about 1 millimeter. And this actually gives a delta T of 926 degrees Celsius, which means that the strains start to build up at 950 Celsius.

It falls somewhere within the working range. So it's somewhat more or less reasonable. You expect the strain start to build up when the glass loses the ability to deform. So you expect that temperature to be falling in maybe somewhere around the working range, and maybe at the lower end of the working range.

But I do want to mention, there's a pretty large error bar associated with this number here. This comes from two parts here. Possibly one is actually the thickness variation.

Two is that we also made the assumption that the borosilicate and the soda-lime has exactly the same width. From the experiment, you know that's actually not exactly the case. One of them is definitely wider than the other.

So I also did some more simulations. Actually, this is basically a Matlab code I used for that. There are two plots here.

So the first one, this is if we assume the two pieces of glass have the same thickness, but you have essentially different thickness values. You see that the delta T actually linearly scales with thickness, which makes sense. The thicker it is, the more strain you need to actually bend it.

Also, some of the minor impacts come into effect if you have varying thickness ratios. In this case, I keep the total thickness to be 2 millimeters by varying the thickness ratios. You see that the thickness ratio again, when it's close to unity, you get actually more or less the minimum delta T. But if you have a different thickness ratio, you can imagine that it gets more difficult to bend it.

If you have a thinner piece, try to bend the thicker piece. So that's why the temperature also increases. But it has a relatively minor impact.

So the main error actually comes from the fact that we cannot read the thickness precisely. So that's something we have to live with basically. All right, so that's the first one.

The second one, this one is asking about whether we can come up with-- or essentially, this one is about the microscopic entities contributing to dielectric constant refractive index. That's quite straightforward. Essentially, depending on the frequency, if it's a relatively low frequency, like microwave, then all the atoms, all the ions, contribute to polarizability, as well as their electrons.

But if you go to high frequencies, like optical frequencies, then it's only the electrons that can actually respond to oscillating electric fields. And then for this equation, this equation actually applies for all the non-magnetic materials. It's quite generic provided that you measure the epsilon r as well as n at the same frequency or the same wavelength.

All right, so now for the next question here, this one is about trying to come up with a glass material that potentially has an even lower loss than silica. Some of you cited ZBLAN, the fluoride glass. I forgot. One of you, I think.

[INTERPOSING VOICES]

JUEJUN HU: Someone. OK. I mean, if you look at some of the online resources or papers, they claim that ZBLAN can have a very low minimum source. I think it's unvalidated. First of all, nobody really achieved it experimentally.

Second of all, I always question whether or not you can get to that low level of loss given that there are so many different ion species. And there's definitely contributions coming from concentration scattering. So my preference here would be let's look at the different sources of loss. If you look at what determines the minimum loss window, it pretty much comes from Rayleigh scattering and phonon absorption.

These are the two mechanisms coming from high and low wavelengths that bound the minimum loss window. So if you want to reduce the loss, what you have to do, number one, you need to have low Rayleigh scattering loss. So for low Rayleigh scattering loss, the first thing, you want to have a single component glass, which allows you to eliminate any of the concentration scattering.

There are some other techniques which I'm going to talk about in a second. Well, maybe I'll just mention it here. So that's one.

The second one is that you also want to decrease the effective temperature of the glass materials. If you remember, when I was talking about the equation that actually gives you the Rayleigh scattering loss, I said that loss actually scales with fictive temperature. Fictive temperature is a measure of structure inhomogeneity.

It's essentially a structural parameter. So the higher the fictive temperature, the higher the structural fluctuation, and therefore higher Rayleigh scattering. So if you're able to control the glass structure, make it essentially have a low fictive temperature, make it essentially closer to the equilibrium state, then you actually have a lower scattering loss.

I want to mention that there is actually a very interesting paper. What I'm showing you here, this one's from last year's OFC conference. A group in Japan basically reported a record low silica fiber propagation loss with the loss down to a 0.14dB/km. This is basically a plot that shows there are two curves, shows for [? R&D ?] lab-grade optical fibers, how the loss evolves over time. And this is the lowest loss in industry scale optical fibers, how it decreases over time for silica-based optical fibers.

Now, the trick they do there is that one is called the fiber core glass. We mentioned that to create index contrast for fiber. There are two ways to do it. You can either dope the core to increase index, or you dope the cladding to decrease index. Which one do you think is preferred if you want to really lower loss?

AUDIENCE: [INAUDIBLE]

JUEJUN HU: Exactly, yeah, because the optical mode or the optical field mostly is confined to the core, less in the cladding. If you're doping the core, essentially, that means you're creating this kind of [? coherent ?] scattering there. So that's why. That's exactly what they do.

The core is almost pure silica. They dope the cladding with fluorine, which is, of course, a very light element with very strong electronegativity. So they tend to have a very low electron polarizability. So only by putting a little bit of fluorine, they were able to create enough in the contrast, and therefore minimize [? coherent ?] scattering.

They also played some tricks. Essentially, what they concluded is that in the end, they verified that their glasses also have exceptionally low fictive temperature. So they have low structural homogeneity. That's why they get to that number. Anyway, it comes back here.

If you're looking for alternative compositions, of course, as I said, you want a single-component glass. You also want to try to lower the phonon absorption. So an effective way to do it is to go to heavy element glasses, which allow you to push this line essentially to the right-hand side, and therefore push it to a lower minimum loss window. So that's why one potential component could be a germanium oxide.

Or you can go to things like germanium sulfide. Although I have already mentioned for chalcogenides, they may have different structural moieties within the network. So it may not work. So germanium oxide probably is the best option specifically for this problem here. But yeah, as long as you get the main idea right, that's what I'm really looking for here.

All right, last one, comparing polysilicon and amorphous silicon. For any kind of electronic properties, whether solar cells or transistors, you want to have high mobility, long carrier lifetime in those cases, and less degradation. So in those cases, polycrystalline silicon is usually better. For waveguides, amorphous silicon is better because you don't have all the grains. And crystalline grains can contribute very significantly to scattering loss.

In fact, in practice, people make polycrystalline silicon waveguides with a loss of the order like 10db/cm versus less than 1db/cm when it comes to amorphous silicon waveguides, because there is no crystalline grain structures. So potentially, it can be much lower loss. OK, any more questions about the pset here before we move on? All good, OK.

All right, now let's go to the last section before we talk about the topic you proposed, which is biomineralization of amorphous materials, something I'm still making here. So in this section, I'm going to essentially talk about a few different techniques that people use to actually characterize amorphous state. Before I go into more specific details, I do have a few tables here that summarize some of the common methods you use to characterize different attributes of amorphous or glass material.

So I won't go through it. You can just read through the table yourself. But what I just want to mention here is that if you look at-- so for example, one specific thing I want to quickly mention here if you go to optical properties.

So for optical Properties, one of the very important metrics essentially is the loss or attenuation in the material. If you look at the techniques I'm listing here, a lot of them essentially mention that you can actually use measured optical attenuation. However, there's one very important difference here. So there are basically two kinds of methods to measure optical attenuation.

One type is like ellipsometry, or maybe UV-Vis spectroscopy. So if you have a bulk material, that's actually quite straightforward. But if you have a thin field, which is what people use, for example, for waveguides, then when you're trying to use ellipsometry or UV-Vis spectroscopy to measure the absorption, you essentially perform more or less this kind of surface normal measurement.

You essentially shine light from free space. You go through a thin film, you measure the transmission or you measure a reflection. And you use this information to actually fit the attenuation in the field.

Now, if you look at the path length of light in this kind of measurement here, it's actually quite small. It's basically related to the thickness of the film, which is of order of maybe a few hundred nanometers, maybe a few microns. So this is one class of technique. This low short path length also means that intrinsically, it cannot measure films with very low absorption because the attenuation induced by propagation within such a short distance becomes negligible if it's very low loss.

Versus there's another class of techniques that rely on in-plane propagation of light. So in this case, it can be a-- I listed prism coupling or I listed waveguide measurement. But basically, in most cases, the idea is that you want to couple light into the thin film and let it propagate inside the thin film in the form of essentially waveguide mode.

So in this case, the path length can actually be a lot longer. It can be, like, millimeters or centimeters. So because of the much longer path length, you are able to actually measure much smaller optical absorption or scattering losses.

So that's very important information I want to mention here, because it's quite common that you see people make the mistake, saying that they essentially did the absorption measurement, seeing that the K, or the imaginary part of the refractive index, is small enough. And they claim that this is actually transparent material. That's not always the case.

If you want to verify that a material can be used for fiber or for waveguides, practically you have to make a fiber wave out of it and verify it. It's very difficult to verify the low-loss characteristics out of any other techniques. All right, so this is one thing I want to mention quickly here.

Now next let's start by talking about diffraction here, both X-ray electron and neutron diffraction. So different techniques is something that people very routinely use to characterize material structures, which I believe you probably have also learned a little bit in either 3.091 or maybe a 3.010, I think. Yeah, OK, good. So we'll be essentially expanding a little bit on that, but focus specifically on characterization of amorphous materials.

But just to start with, I'm showing you this famous picture here. This is a famous picture taken by the scientist here, Rosalind and Raymond. And this is essentially the first X-ray diffraction spectra of DNA. Rumor says that Watson and Crick, who actually discovered the double-helix structure of DNA, they actually saw this picture. And this is what really inspired them to propose the structural double-helix model of DNA.

Now, you look at the picture here. You see this basically a cross pattern with a few discrete dots going in the two X's. This is a characteristic diffraction pattern if you have a helical structure.

To prove to you that that's actually the case, we can actually do an experiment. I can show you that. I have a helical structure here.

I have my light source, which is my laser pointer. I will show you that the diffraction of a laser light on this spring is going to give you that pattern. That's what I will do.

But what the tricky part here is that if you look at the structure size here, of course, this is pretty big. So it means that the wavelength is actually much, much smaller than the structure feature size here. This is actually very similar to electron diffraction, which we're going to talk about later.

For electron diffraction, the electron wavelength is also much smaller compared to crystalline lattice constant. So as a result, if you go through the [? secondary ?] diffraction theory, it shows you that the differential angle becomes very, very small. So that's why when I want to do this experiment, I want to do it essentially over long distances so that you can see the diffraction pattern going through here.

So you may have to take a picture there, because this may be a bit difficult to align. You will have to look at it from the board there. And you can get a bit closer. Do you see anything? Do you see the cross pattern?

AUDIENCE: Yes.

JUEJUN HU: And it looks very similar to that, actually. Yeah.

AUDIENCE: [INAUDIBLE] coming?

JUEJUN HU: Yeah, my hand is not very steady. Let me see. I can see if I can try to-- is this any better?

AUDIENCE: Oh, yeah. That's better, yeah.

JUEJUN HU: Oh.

AUDIENCE: That's cool.

JUEJUN HU: Are you able to take a picture?

AUDIENCE: Yeah.

JUEJUN HU: You see the cross pattern? OK. Good?

AUDIENCE: One more.

JUEJUN HU: Oh, one more. OK. I just have to have very steady hands. Good? OK. All right.

So as you'll see later, this is actually very similar to electron diffraction-- same idea. Electron diffraction also has very small diffraction angles. So essentially, they use a beam blocker to block the center beam and the diffraction pattern right around it at very small angles. So same idea. All right.

Now of course, over time, people are trying to solve more and more complex structures. And then some of these complex structures, you can no longer guess it from intuition. This is just one example of actually a structure factor of some kind of protein's macromolecules.

We'll talk about what structure factor is. But obviously, this is beyond any kind of a simple human intuition. And people actually have to solve it using advanced computer codes.

Now coming back, we are going to focus specifically now on crystalline material, about amorphous material. So for amorphous material, what I'm showing you here is actually a simple differential structure of some kind of metallic glass. This red trace is actually a more fully amorphous metallic glass. This black trace is after annealing, which has partially crystallized.

So you are all familiar with what are actually differential equations look like for crystalline materials. If you plot it essentially intensity or the counts from the detector as a function of 2 times the right angle, you see some very sharp peaks here. Each of the sharp peaks essentially corresponds to some crystalline planes with a specific spacing such as Bragg's equation. Bragg's equation is actually satisfied. And that's why you see a sharp peak there.

For amorphous material, on the other hand, you tend to see this kind of broad background that looks somewhat featureless almost. So the background tends to be a lot weaker compared to these crystalline sharp peaks. This is because when you have one of these sharp peaks here, what actually happens is that you have coherent addition of the scattering from all the atoms in the material in order to generate one of those sharp peaks. Whereas for this amorphous background, you don't have that coherent addition because of irregular structure. And so that's why the intensity tends to be a lot lower there.

And also, one question that will come up is, if you see this kind of spectrum, obviously, this is amorphous. But will we be able to get a bit more information out of this broad spectrum here? Can we get some quantitative information to describe the amorphous structure there? So that's what we're going to do. We're going to try to develop a quantitative theory that allows us to correlate this kind of broad, seemingly featureless spectrum to some quantitative structure descriptors of amorphous materials.

So I will start out by essentially setting up the problem here. So here, basically, we will have essentially some X-rays coming into the material and then get diffracted. For any quantity that's associated with the incident X-ray, I use a subscript i for any quantity associated with the scattered or diffracted X-ray, I use the subscript s.

The position of the atom, atom m, I can label atom using this letter here. So in a solid material, you can have lots of atoms here, from 1 to capital N. M is basically the label to label one each atom here OK. So r will be the position vector of that particular atom here.

Now a few assumptions we want to make before we go through the quantitative derivation is that first thing, we are approximating the incident and diffracted X-ray both as monochromatic plane waves. Now monochromatic, usually that's a pretty good assumption. For X-ray diffraction, you usually have a source that's close to being monochromatic-- copper K-alpha source, for example. They usually are pretty narrow bands, so you can treat them as single wavelengths.

Plane wave essentially means that your X-ray source is sufficiently far away to the sample, so that the distance of the source to a sample is much larger compared to the linear dimension of the sample. So in that case, the angular divergence of the X-ray is actually pretty small. You can treat it more or less as a plane wave.

Now, next one, elastic scattering, means that the scatter in the incident X-ray has exactly the same energy or same wavelength. This essentially means that we are discounting any of the Compton scattering effect. Compton scattering is one very common elastic scattering mechanism where actually, the X-ray wavelength changes.

Last one, we are neglecting any X-ray attenuation in the sample, which obviously is incorrect. Because when the X-ray gets scattered, the initial beam must have some energy getting diverted into the scattered X-ray. What we are assuming there is that the effect is relatively weak.

So essentially, the field amplitude for the incident X-ray is uniform across the entire sample for all the atoms. That's what we're basically assuming. It is a reasonable assumption if the sample is not too thick.

All right, now let's start to take a look at how we actually set up this problem here. So we will start out by essentially trying to write the complex amplitude of the incident wave, which is basically this equation here. I assume you're all familiar with how to represent the waves in a complex amplitude representation.

So you will have essentially the amplitude E. This is basically the real amplitude of the incident X-ray. And this exponential factor then gives you the phase delay for light to propagate from the origin point all the way to this point r here with some kind of position vector. So if you're looking at the field amplitude specifically at one particular atom m, then you just plug in essentially rm into r here. And this is basically field amplitude at that particular atom.

So now the next thing we argue here is m when we are looking at this scattered field amplitude Es, we will argue that, first thing, this scattered field amplitude, it must be proportional to the incident field amplitude. This also makes sense. For any kind of linear scattering phenomena, the more photons coming from the incident light, the more it will scatter proportionally.

So therefore, we postulate that this Es should scale with Ei. And therefore, if we plug in Ei, it essentially just means that E negative ikirm, this will be the scattered field amplitude by the atom m. I did not use negative here.

I used the positive, so this is just-- let me make this positive. So this is basically the incident field. This is the excitation source.

Now, you also need to have a second term here because you are measuring the scattering field. The scattering field, as it propagates away from this atom to your detector, it's also going to accumulate a phase delay as well.

So the phase delay term will scale with the iks r minus rm. So the last term here, r minus rm, is basically the distance the light will travel from your atom to where your detector is or where you are measuring the scattering field.

So the next thing we do, we notice that both of these contains essentially rm here a complex dimension containing rm. So we can regroup the terms a little bit. We can have E, now have iks r.

And then the second term, we have E negative iki. Let's pull out this common term of rm here. And then you now have ks minus ki. I'm just pulling out a common term that contains this rm, the complex measure.

Now, we can also define this new quantity here that we call Q, which is what we call the scattering vector. Q should equal to is minus ks, I should say. This is the difference of the wave vector for the scattered and the incident X-ray waves. So if you do that, the last vector just becomes an exponential negative iQrm.

You'll also notice that in this equation, I did not use equals sign. I use a proportional sign-- proportionality sign. And that's because we actually don't know what is the scattering cross-section for the atom m.

So what we can do in order to eliminate this uncertainty here, we can lump all of the essential atomic scattering cross-section all into one constant layer that we call the fm. Essentially, we are lumping the scattering cross-section, scattering efficiency, as well as this Ee, electric field, and in addition, also this factor here. So this factor is actually a constant if you have a fixed detector partition.

R is basically where you actually measure the scatter field. So you have a fixed detector partition, this is basically a constant there. So we are lumping all these constants together into one single constant. This is what we call the scattering efficiency or scattering factor. So scaling factor is basically about how efficient this atom can use scatter light, scatter X-rays.

All right, so now, next thing we can do, we want to try to add up this. This gives you the full amplitude that's being scattered by one single atom m. In a solid material, you have a group of atoms, a total of N number of atoms-- capital N.

So therefore, we expect that in order to get the total scattered amplitude you need to add everything up. So the total amplitude-- let's see, what letter do I use. The total amplitude, let's write it as E total. Basically, we should sum over all the possible Es.

So summing over all the capital N number of atoms in the solid material, all of the amplitudes here. They add up coherently because we assume this is a monochromatic wave. And therefore, instead of adding up the intensity, which adds up the amplitude because it's a single wavelength.

If it's all single wavelength, then it's always coherent. So it adds up the amplitude. So plug in there. That essentially means that you're summing up m n to all the fm e iQrm.

Now, this is the field amplitude. What you measure is actually the intensity. You actually measure [INAUDIBLE] intensity, not amplitude. So intensity actually scales with amplitude squared. So if you want to measure the scatter intensity I, then what you need to do is take basically the amplitude modulus squared.

So how do you do a modulus squared for a complex number here? A modulus squared essentially is equal to the real part times its imaginary part. That's how you do modulus squared for complex numbers. So therefore, that means that you now have essentially this one, the real part, which I just copy this E negative iQrm then times the imaginary part. The imaginary part, I use a different letter n here-- lowercase n, e now complex.

Essentially, you get rid of the negative sign there because that's a complex conjugate. And I use a different letter n here to indicate that in each of the parentheses, we have a total of uppercase N number of terms. So we have an n terms times also an n terms here. So you actually basically get n squared terms in this product here.

AUDIENCE: What was the significance of the n squared terms? I understand that it's true.

JUEJUN HU: I'm just telling you that [INAUDIBLE]. That's it. [CHUCKLES]

AUDIENCE: But what was that to lowercase n?

JUEJUN HU: Lowercase n is just another way, I can replace it with any letter there. It's basically, this subscript has to cycle from 1 all the way to capital n. You have to sum over all the atoms-- basically independent.

That's what I'm trying to indicate. Yeah, they're independent. OK, so the whole problem of solving the diffraction intensity essentially boils down to solving this equation here.

Also, before I move any further, I want to introduce this additional parameter here. This is called SQ This is called structure factor. By definition, we are saying that this intensity equals to SQ times N times fm squared.

So here, this bracket indicates averaging. So bracket fm, essentially, this is the average scatter factor across the entire solid, across all the atoms. So this is the definition of SQ the structure factor here, just the definition. That's it.

So what we are seeing here is basically the structure factor. This is directly correlated with the measured diffraction intensity. So if you know differential intensity you can immediately calculate structure factor.

Structure factor is also a function of Q. So what is Q? Let's now take a look at Q here. Q is ks minus ki

So suppose this is the solid surface. In a crystalline material, this may be one of the atomic planes. Then you have an X-ray comes in here.

This is the X-ray diffraction angle theta. This is incident X-ray. It will then diffract let's say go to a similar [INAUDIBLE]. This is also theta. So in this configuration here, you can now plot essentially using simple vector identity to see what is the ks and ki.

So suppose this is a ki, this is ks. Then it's straightforward to see that the angle here should be 2 times theta. So now ks minus ki will be the vector that links their endpoints here. And it's pretty straightforward to see that in this case, this Q, which is basically ks minus ki is equal to-- in terms of magnitude should be 2 times the magnitude of ki or ks.

In this case, the magnitude of ki equals to ks because this is the elastic scattering. So they should have the same wavelength, then times sine theta. Because the half length here, this is basically a ki times sine theta. It's 2 times ki sine theta. So that's the magnitude of Q.

So what this equation means is that if you are looking in isotropic solids, which means that the orientation of Q doesn't really matter, then Q is basically synonymous with theta. So what we are saying here is that the structure factor is a function of Q, essentially meaning that it's a function of theta. So if you measure I, the scattered intensity, as a function of a Bragg angle theta, then you can immediately get SQ if you know the scattering vector for all the atoms.

All right, so now this comes back a little bit. Let's think about-- before we talk about amorphous materials, let's actually step back a little bit and talk about what about crystalline materials. What if it's a crystalline material?

So in a crystalline material, you have a periodic lattice. If you want to have a diffraction peak, from what you learned in 3.010 or whatever, you know that need to ensure that the X-ray scattered by the different atoms or from different unit cells should add up coherently. That's how you actually get X-ray diffraction peak.

So now if you look at this equation here, for example, let's look at this one, E total. In order to have coherent addition, you need to make sure that the X-ray scattered by all the different atoms, they add up in phase.

So what that means is that the phase vector here, which is dictated by Q times rm they should all either be the same or differ by integer multiple of 2 pi. So effectively, what I'm saying here is that Q rm, or more rigorously I minus rm, essentially the difference of any of the two, is always equal to an integer multiple of 2 pi. M is just some integer. I neglect the rm here because you can always set the origin-- coincide origin with one of the atoms. In that case, we can essentially drop the second term here. This is fine.

So now let's take a look at what this condition will lead to. So let's first essentially write what Q is. Q from there is basically a 2 times ki. What's ki? K is 2 pi divided by lambda. So it's 2 pi divided by lambda, where lambda is the wavelength.

You also have some set of sine theta. Now times rm-- for rm, if you are looking at, say, two atomic planes. You're looking at scattering from two neighboring atomic planes. Then I minus rm essentially gives you the atomic spacing or the spacing between atomic planes.

So if we want to be consistent with the terminology or the symbols that you use for the Bragg differential equation, essentially rm becomes d, the interatomic spacing, or the atomic plane spacing there. Then on the other side, you can take M the integer as just unity. So now let's see what we have. 2 pi, 2 pi cancels out. It basically tells you that lambda equals to 2D sine theta, which is the Bragg equation that you must have seen in previous lectures.

The other way to look at it is just to look at this equation itself. So rm, this is a vector in real space. It's basically the position vector for some atoms.

Q-- because 2 pi is dimensionless, so it means that the unit of Q must have [INAUDIBLE] of inverse lengths. So Q is actually defined in the reciprocal space. So a reciprocal space vector times a real space lattice vector equals to integer multiple of 2 pi.

This is actually by definition a reciprocal lattice. So it also tells you that you only get a diffraction peak when the scattering vector is one of the reciprocal lattice vectors, which again is probably a conclusion you have learned in your previous lectures, I suppose. Yes? [CHUCKLES]

Well, now you see it, at least. In a crystalline material, if you want to have a diffraction peak, then the diffraction vector should be one of the reciprocal lattice vectors. Especially this is by definition.

This is the definition of reciprocal lattice vector. Or you can always go with Bragg equation. That's a simple way of looking at it.

All right, that's for crystalline material. Now, what about for amorphous material? So for amorphous material, this is probably one of the most mathematically involved derivations throughout the whole semester.

So I need to wipe out the board just to get enough space. I'm going to keep it here because we are going to try to derive SQ. But then I need all the space.

AUDIENCE: Wait, so the Bragg equation came from also derivation of SQ?

JUEJUN HU: Yeah

AUDIENCE: OK.

JUEJUN HU: Essentially, we just assume that the scatter X-ray has to add up coherently. They have to be in-phase for all the atoms. From that, we actually come up with the Bragg equation. That's the only assumption we make. Yeah.

All right, so now before I talk about the amorphous, how to derive it, I do want to revisit one topic there about pair distribution function. Because what we'll see later is that actually, differential function of SQ can be directly correlated with pair distribution function. So this is a slide quoted from the previous lecture. So pair distribution function, judging from its name, is a function that measures the correlation of atomic pairs of certain spacing in between them.

So in our previous slide, we have defined it essentially as-- if you put one of the atoms at the center at the origin. And then it tells you the probability of finding another atom at the spacing r away from the center atom. We also said that we can normalize it.

Essentially, the number density of atoms at distance r is given by rho times gr where gr is our pair distribution function, and rho is the average number density across entire solid. If you do this kind of definition here, go with this kind of definition, then this gr should have these properties here. If the inter-atomic spacing goes to 0, g should go to 0 because no two atoms can occupy exactly the same location as lattice due to Pauli exclusion principle.

Also, if r goes to infinity, meaning that if the two atoms are very, very far away, then you lose any kind of short-range or medium-range order. And this long-range disorder means that g must go to unity because you are seeing essentially a uniform loss matrix if you are very far away from the center. All kinds of near-neighbor information gets completely swept out due to the lack of long-range order.

OK, so that's what we talked about previously. I mean, I'll show this. So if it's a crystalline material, you see a set of delta functions indicating the different coordination shells. If there's amorphous material, it gets broadened out a little bit.

Now, I want to give you a more rigorous mathematical, mathematical definition of a pair distribution function. Don't worry. It's not that complicated, actually. So let's start by looking at the first function here, which we call rho 1. Rho 1 is just the probability density of finding an atom at some particular location.

Now, in our description here, we are essentially assuming that atoms are like geometric points. We can characterize them with a position vector rm. So the probability of finding atoms at a particular location would then be a set of delta functions.

If your position vector happened to coincide with atomic position, then you get one peak. If you're not at that position of the atoms, then you get 0. So you expect that this function rho 1 should just be a sum of a set of delta functions.

And these data functions would only be non-zero if the argument coincides with one of the atomic coordinates. Makes sense? It's a probability non-zero if you happen to hit one of the atoms. Otherwise, it's 0.

Now, we also put this little bracket here. The bracket essentially means that we are doing an ensemble average. We average across the entire solid material. So if you do the averaging, then of course, any kind of this fine structure feature gets smeared out.

What you get is basically just a average density, which is rho. So rho here is just N divided by V. N is the number of atoms, V is the volume, so number density. Makes sense, right? If it's a homogeneous solid, then it should be just uniform, simple.

Now, next one, let's look at the probability density function for finding an atomic pair, one sitting at this location r, the other sitting at location r prime. This is the function we call rho 2. So similarly, you can also represent this with a set [? of other ?] product of delta functions.

In order to find the atom-- one at r, the other r prime, r has to coincide with atomic coordinates for one of the atoms. Same thing-- r prime has to coincide with the atomic coordinates of the other atom. So that's why mathematically, you can see that this can be expressed as, again, the sum of delta functions, and then the product.

So we have this specific condition here where n cannot be equal to m because these two atoms cannot coincide. We are looking for atomic pair, not one single atom OK. That's why n cannot be equal to m. Makes sense?

Now, what we also argue is that if you have a homogeneous and isotropic solid, then the magnitude of this function should not depend on the orientation of the vector of r minus r prime. So this is essentially a vector that connects the two points. If it's isotropic, then the orientation of this vector really doesn't matter.

Also, if it's homogeneous, then it doesn't matter where you set the origin point. And we will argue that this rho 2 should only depend on the spacing of these two atoms-- not the specific location of r and r prime, but only the spacing in between them in a homogeneous isotropic solid. Makes sense? So rho 2 should only be a function of the spacing between the two atoms.

So if you look at now the physical significance, it basically says that rho 2 is a function that describes the probability of finding two atoms with a spacing of r minus r prime, which basically is the definition of pair distribution function. So the only thing we need is to normalize it properly so that it satisfies these requirement here. Especially when r goes to infinity, g has to go to unity. It sets a normalization condition.

So that's why if you look at the rigorous expression here for g, the partition function is basically rho 2 divided by rho squared where rho is the average number density. The reason you do that is because if you look at rho 2 here, it's basically two of the rho 1 functions multiplied together, practically. So you imagine that you have to normalize it by essentially rho 2 squared such that this function, when r goes to infinity, it should also approach infinity. So 1 over rho squared is just a normalization coefficient there. Makes sense?

So then what we are trying to do when we are deriving the diffraction intensity there, the structure factor, is we are trying to essentially write the structure factor expression in a way such that it looks similar to this rho 2 function. That's how we try to build a connection between SQ and the pair distribution function.

All right, now here comes the fun part-- the math. Don't worry about it. This looks complicated. I'm going to go through it step by step to explain what I'm trying to do here.

All right, so let's come back to this board here. What I put on the slide is actually not very detailed. There are a few steps.

Let's skip that. So let's come back and look at what SQ is. So we want to solve for SQ

So by definition, SQ is just N fn squared times the intensity by definition, times I. This is just the definition of SQ. So we can expand this I here because we know what the expression for I is. So this would just be-- I'm just going to copy everything here m N fm e negative iQrn times N n fn e iQrn.

Now, one more thing I want to do is to add this average. Why? Basically, because when we're doing actual experiments. Practically, we are measuring macroscopic-sized samples. Also, even though we mentioned that the X-ray is close to a plane wave, it's not really a plane wave. There's always a small range of angular dispersion of the X-ray source.

And the experiment also takes some time. So it means that during that period, the atoms are undergoing constant thermal vibration. So there are lots of factors together, indicating that we are not measuring one specific snapshot of atomic positions.

But rather, we are doing some kind of ensemble average across the solid material for practical experiments. That's why we put this bracket there. Makes sense? All right.

So now if you look at this bracket here, when I put the bracket, fn basically is a constant for different atoms. When you're doing this averaging effectively, you can pull out the fm essentially as a factor of average fm. Same thing-- fn here, when you do the averaging effectively, you can pull it out as a bracket average fn, which is the same as average FM

So it means that this factor can actually cancel out with this one here Once you do the averaging, they cancel out. So now what do we have?

So now SQ, it makes quite a bit simpler. You have 1 over N And then you have a-- I can take out all the fn there, Qrm, iQrn. All right.

Now, next thing, let's look at these two summations here. As I said, there are a total of n squared number of terms, because in parentheses, each contains n terms. We notice that this n squared terms actually can be classified into two groups.

One group is when n equals to m. The other group is when n doesn't equal to m. What happens if n equals to m? If n equals to m, you can directly take the product of these two there, which is trivial because they cancel each other, becomes unity.

So each of these terms where n is equal to m essentially gives you unity. And you have a total of n capital N number of those similar terms. So if total n number of those terms divided by n, you get unity. So then what you have, you can further simplify it. You now have. m N e negative iQrm times-- now in summation we can write n does not equal to m, N e iQrn.

All right, now next part we try to convert it into a formalism that looks similar to our pattern distribution function, rho 2 function. How do we do that? We have to use this unique property of delta functions

So if you think about any arbitrary function-- any kind of, let's say, any arbitrary function. If you integrate from positive infinity to negative infinity for any kind of arbitrary function, let's say Fx times a delta function of x minus a dx. What do you get?

You're doing integration. It contains delta function. Delta function is 0 everywhere except when x minus a equals 0.

So that means when x minus a equals to 0, then x equals to a. At that point, the integration becomes Fa, and everywhere else is basically zero. So this should be equal to a F-- I don't know. I'll write that on this side here. Fa-- this is a property of delta function.

[LAUGHTER]

This is actually the definition of delta function. Delta functions, if you integrate from 0 to infinity, it's equal to unity. And the function is the only non-zero at the 0 there.

All right, so now next thing we want to do is, let's take this function Fa as e. Essentially, our function f is basically e, for example, negative iQrm. We take this function. And then we take a essentially as our rm, and x essentially as r.

Let's see what we get. So now Fa will becomes e-- basically negative iQrm This should equal to integral of the function itself, which is e negative iQr times the delta function r minus rm dr.

We can actually also do the same thing for rn. I will also write it here-- iQrn. This is a similar e iQr.

Now to be different here, I use r prime, Just to differentiate between the two different integration variables here. This is delta r prime minus rn dr prime.

Essentially, you're integrating this function over the whole space. And the delta function is only non-zero when r equals rm. So what you do is then you plug rm into the equation, the function there. Yeah, same thing with this one. I just changed the integration argument, so it's less confusing as you'll see.

So then what we do, let's plug this back to our equation here. I'm still running out of space. I think 1 over N.

So then what do you have here? This one. You have integration of e negative iQr times delta function r minus rm dr, then times another integration-- e.

Sorry, I need to do some-- I forgot the summation there. I need to sum over m. Here, I need to sum over n. And I also have another integration e iQr prime times delta function r prime minus rn dr prime.

It looks messy. It's fine, because what we can do, let's see what we have here. We essentially have an integral. There are a total of N terms in the integral there. It's a sum of integral times a sum of integral.

This is a linear operation. Summation is a linear operation. So what you can do, because it's linear, you can essentially move this summation into the integration there. It's the same.

So then what you do, you can then do a double integral first, and then you do the summation. Yeah, I don't know if I still need to copy it. But I mean, basically, it then becomes this guy.

And also because this term here e iQr and e iQr prime, you can combine them together to get this one here, e iQr minus r prime. This was combined here. And then you essentially move the summation sign into the integral.

Everything after this is actually pretty straightforward because this part here is exactly our rho 2. All this is basically just rho 2. So I guess I don't have to write it down. I just explain what we have been doing here.

OK, so then the next couple of steps, essentially, you just try to clean up. You essentially put in a proper normalization constant. So you write rho 2 now as g, which is our pair distribution function. And you get this kind of expression here

Now, if you look at the expression, you have a complex exponential times g. Then you do the integration. This is basically the Fourier transform of gr. So basically what it says is that the structure factor directly correlates with the Fourier transform of the pair distribution function. That's the takeaway message on the slide here.

That's a key takeaway message, structure factor relates to Fourier transform of the pair distribution function. And you can mathematically further simplify the equation a little bit, because you notice in this integration here, you still have to integrate over this vector here. R is a vector. You have to integrate over essentially a three-dimensional space r.

But if it's an isotropic solid, you can imagine that it's only the magnitude of r that matters. Its orientation doesn't really matter. So you can then do the integration essentially in a spherical coordinate which allows you to further simplify the equation.

I'm not going to go through the math, but this is what eventually comes out in isotropic material. Then SQ will then directly correlate with this one-dimensional integration over now a scalar r, rather than a vector r. You can then do the inverse transform, which tells you this is how you relate the pair distribution function to the structure vector in an isotropic, homogeneous amorphous material.

So bottom line, if you can measure the diffraction spectra of a material, which usually is given in terms of intensity I as a function of theta, you then convert the I theta into SQ. You can then directly calculate what is the corresponding pair distribution function. By the way, this is known as the Debye scattering equation. It shows that for this kind of even seemingly featureless broad diffraction spectra, you can still extract very useful quantitative information, in this case, pair distribution function, to describe the amorphous structure there.

Now, that may seem simple enough. You can just get your glass sample, go and do X-ray diffraction, and then come back and get a PDF. It's actually quite a bit more tricky than that. We don't have enough time.

In the next lecture, we're going to talk about how you actually correct your experimental data to really implement this equation. It's non-trivial. So I will stop here for this lecture. All right, thank you.