[SQUEAKING]

[RUSTLING]

[CLICKING]

**JUEJUN HU:** All right. All right. So now last lecture, we talked about essentially the X-ray diffraction theory for amorphous materials. If you forget about everything I talked about in the last lecture, there's only one thing you really need to remember. It should be this equation here. Again, you don't need to remember specifics, but you need to keep in mind that there is such equation that actually kind of links the X-ray diffraction spectra, or the structure vector, directly to the pair distribution function.

So while that may seem very easy, as I have mentioned, there are actually a number of Corrections you have to carefully perform in order to transform experimentally measured data into the pair distribution function. So what I'm showing here, this is actually a few steps we have to go through to actually process the raw data.

So what I'm showing, this is basically an example of raw data. Normally, if you collect a spectrum from XRD lab, what you will get is essentially the intensity counts as a function of the theta, which you can easily convert into the scattering vector by just following the equation that q equals to 2 k sine theta.

So now the corrections you have to perform, first thing, there are a few corrections you have to execute here to eliminate some of the side effects, OK? So first one is essentially detector dead time.

So what that means is that the detector you use in the XRD machine, there's actually a response time. So if there is a photon comes in, an X-ray photon comes in, it's going to give you a reading. But then it takes a short period of time for that detector to actually recover. If you have a high flux of photons coming in, such that two photons may come in at almost the same time, then the detector basically will only pick up one photon because it does not have enough time to actually recover to read the next photon. So this kind of error becomes essentially more severe as you go to higher and higher X-ray scattering intensity. So that's something you have to correct if you want to get the right line shape.

Second thing is background. And that's quite straightforward. That happens especially when you have thin film samples. The sample itself is in vacuum. You need some kind of holders. If it's a thin film, you also have the substrate. So all of those, that's irrelevant to your actual sample information. They should all be removed, so recalibration.

Now, next one, absorption. This goes back to our assumption where we said that when we go through our derivation, we assume that the attenuation of X-ray in the sample is actually very weak. That's actually not the case. There's always a little bit of absorption and scattering and attenuation due to scattering when you actually go through a sample. So you also have to correct for that.

Similarly, for addition, the entire theory we discussed in last lecture is basically a scalar theory, scalar scattering theory. We have not accounted for the fact that there are actually two orthogonal polarizations for the incident X-ray. So that's something we also have to correct for.

Multiple scattering refers to the fact that the scattered X-ray, by the atoms, they can actually get scattered again as they propagate from the outside sample. So this is what's called multiple scattering.

And finally, inelastic processes mostly are Compton scattering and sometimes also fluorescence, as well. So those are also introducing undesirable background. You also have to subtract. So after you have done all the correction there, what you see is that the curve essentially changes a little bit. There's a minor correction there. The actual shape changes.

For crystalline material, a lot of this actually doesn't really matter, because what you care about is actually fitting the peaks. Versus amorphous material, on the other hand, because you actually have to rely on the shape of the curve in your transformation to get a pair distribution function. So this correction actually becomes a lot more important when it comes to amorphous samples. OK.

All right, next part. We then need to basically normalize the spectrum. Now, what we want to do, if you go back, we actually need to calculate this one, the structure factor here. So the definition of structure effect here, it links to the scatter intensity with this vector here, N times average f sub m squared, where f sub m, as we said, this is the scattering coefficient.

In principle, if you know your sample's composition and you perform a very careful calibration on your experimental setup to know the scattering coefficient for all the constituent atoms, you can determine, essentially, this coefficient just experimentally. In practice, there's actually an easier trick. You don't really have to do that, right?

Now, keep in mind, this scattering coefficient, this scattering coefficient, it depends on the specific sample setup. Different XRD machines have different X-ray collection efficiency, different X-ray intensity. So this vector is actually instrument-dependent. So if you want to get it a priori, you have to do very careful calibrations.

Now, what I want to mention here is that you actually don't have to do that, OK? You can play one trick, avoid having to do that calibration yet still being able to normalize the spectrum converted from intensity to structure factor. This is to leverage on a phenomenon called coherent independent scattering.

So to explain how that works, let's again-- it goes back to the definition of Q here. So we have mentioned that Q, if you just look at the magnitude, forget about direction, it is basically 2 times k sub i times sine theta. You can also write k in terms of lambda. So this would be 4 pi over lambda sine theta.

Now what happens if you look at very large Q? If Q is very large, effectively-- because sine theta maximally is bound by essentially unity, right? So very large Q necessarily means that you're looking at very small wavelength. And when wavelength becomes much smaller than the lattice, then what happens is that the optical path length difference for the X-ray scatter by different atoms will always be differ by many, many wavelengths.

So now if you try to add up this scattered signal from all the different atoms, because of the large path length difference, you essentially lose coherence. Essentially, interference effect gets averaged out. So as a result, instead of adding up the amplitude because of the random phase caused by the the very large path length difference compared to wavelengths, you can simply just add up the intensity, as if interference is nonexistent.

This only applies when Q is very, very large. When Q is small, wavelength becomes comparable to lambda, then you cannot apply this approximation. There's always a definitive phase delay between the X-rays scattered by different atoms. OK? Yes.

**STUDENT:** So what is lambda in this case? It's like a particular--

**JUEJUN HU:** It's a fixed number. It's a fixed number. Well, the X-ray machine, yeah.

But the idea here is that when you actually need to perform this transformation, in the transformation, if you remember, the integration goes from 0 to infinity. If you go back, we can look at the equation again. OK?

**STUDENT:** Right. Yeah.

**JUEJUN HU:** And you're integrating over, Q, which basically means that you're integrating over essentially sine theta effectively.

**STUDENT:** Yes.

**JUEJUN HU:** Right. So in order I will talk about this point actually in a second.

In order to be able to integrate to a very large number-- again, in empirical experiment, you cannot really integrate infinity. You have to cut off at some point. But in order to get a good approximation. So that you collect large enough Q range, you need to ensure that your lambda is actually small enough to start with.

**STUDENT:** OK.

**JUEJUN HU:** Yeah. So then when you actually are looking at this large Q range, effectively you are looking at the range where the interference becomes very weak. If the spacing between the atoms is much larger in wavelengths, let's say 100 lambda, right. So then you can imagine if you differ, that atomic spacing differ by a little bit, you can already change face easily from 0 to 2 pi entirely.

If you average out across the entire solid, essentially any kind of phase difference becomes very-- the effect becomes very negligible. Effectively, you are adding up the scatter X-ray intensity in a coherent way. That's what it means. Does that make sense. Yeah so.

**STUDENT:** Do you want Q to be large so that you get that averaging?

**JUEJUN HU:** Basically, it's when Q is large, the diffraction effect gets smeared out. All the atoms scatter X-ray independently and you just add some intensity.

Now, without the interference between X-rays scattered by different atoms, you don't get essentially like all the peaks and valleys like what you see in a normal X-ray spectrum. You just get a featureless background. And that's actually what we're trying to use here. What we are trying to argue is that when the Q gets very large. S Q has to approach unity.

Essentially, the scatter X-ray intensity will be the sub, just the simple scalar sum of the scatter intensity from all the atoms, which basically is Nf squared. All of these peaks and valleys, this is a consequence of interference due to the different phase of X-ray, we get pitting scatter from different atoms there. But if you no longer have the interference effect, then it's just going to be an f squared scatter intensity, which means that as Q becomes unity.

So the whole idea is that when Q becomes very large, SQ approaches unity, you can use that property to essentially calibrate this curve here to renormalize it. You just use this section of the curve.

**STUDENT:** Oh, OK. I understand.

**JUEJUN HU:** To normalize it. So essentially you just divide it by this part of the curve, divide in high curve by this section here, and you end up getting normalized curve like this. So SQ should converge to unity at very large Q numbers.

So this is one way to avoid having to experimentally determine this Nf squared numbers, which could be a quite challenging experiment actually. You need to know exactly the composition. You need to collect the samples, the atom, the pure atoms with exactly those kind of constituent atoms. You need to perform a scattering experiment, carefully measure intensity. So you need to do that in order to get to this number here.

**STUDENT:** OK.

**JUEJUN HU:** Yes?

**STUDENT:** Wait, I haven't formed my thought yet. So basically, the coherent independent scattering, which is the the N and the fm squared, is not desirable?

**JUEJUN HU:** If you try to extract structural information, it's not desirable.

**STUDENT:** It's not desirable.

**JUEJUN HU:** Yeah.

**STUDENT:** So you go to values where Q is very large.

**JUEJUN HU:** Yes.

**STUDENT:** And thus your SQ gets overpowered.

**JUEJUN HU:** Oh, as SQ actually approach unity, essentially, the interference effect becomes very small. Yeah. If you want to say overpower. Maybe.

**STUDENT:** So N fm squared, so you basically just fit like on this plot from Q into to 16, you fit that line, or fit that--

**JUEJUN HU:** Right, you approach this featureless curve.

**STUDENT:** Gotcha. OK.

**JUEJUN HU:** And then you just divide it by this curve. Divide the original spectrum by this curve here.

**STUDENT:** Because SQ is basically unity. And so therefore i is just your--

**JUEJUN HU:** Nf squared.

**STUDENT:** And then you can apply that to your lower Q values.

**JUEJUN HU:** Right, because Nf squared is a constant.

**STUDENT:** Where your structural data really is.

**JUEJUN HU:** Yes. Yeah. Because Nf squared is a constant, right? It does not depend on Q.

**STUDENT:** OK.

**STUDENT:** It's a constant?

**JUEJUN HU:** Well, no, I mean there's a dependence. There's a specific functional form that people know. Sorry, I should not say it's constant. Yeah. Essentially you know this red curve. You know the shape of the red curve. You just need to essentially offset it to the right level because you need to know what is your actual SQ.

So bottom line is that you can use this feature to normalize SQ. And you can see here, most of the useful structured data actually resides in this region here. When Q becomes very large, essentially it approaches unity, then the data becomes not very useful anymore. OK?

In fact, if you look at the integration equation, it also makes sense, because what's actually in the integrand is SQ minus 1. So when SQ approaches 1, essentially it's 0. So you no longer contribute to the integration. So that's why I said what's really useful is the part where you actually have oscillations. That's what really contributes to the equation there.

All right. So now last thing I also want to mention after you normalize it, there's still always a truncation error. Because even though I mentioned that you have to try to integrate from 0 to infinity according to the equation, in practice, there's always a maximum Q you can reach, which is dictated by when your sine [? theta ?] is equal to unity.

When your sine is equal to unity, your Qmax is given by 4 pi divided by lambda, and lambda is your X-ray source wavelength. So in order for this calculation to be accurate, you want this Qmax to fall in the range where this curve has almost become featureless. You want Q to be somewhere here. You don't want the Qmax to get truncated somewhere, like here.

What that means experimentally is that you want to select an X-ray source with sufficiently small wavelength, so that this truncation error can be minimized. OK? Now this actually has some practical limitations for experiments. If you want to actually analyze the PDF for amorphous material, suppose you want to do it here, you go to the XRD facility here. They use a copper K-alpha source. Turns out copper K-alpha source, the wavelength is actually not short enough. It's 1.54 Angstrom. OK?

If we were to plot it on the plot, it will fall in somewhere around here. OK? So it will not be able to get a very accurate pair distribution function by using an X-ray source with a copper K-alpha source. You have to find alternative sources, melatonin or silver sources, that actually offers much shorter wavelengths in order to get more reliable reconstruction of the PDF. OK?

So this slide basically summarizes the sources of error in this kind of reconstruction process. I already mentioned about this data truncation error coming from the fact that in practice, you will never integrate from 0 to infinity. You always cut off as a maximum Q value dictated by the X-ray source wavelength.

So that's why if you want to minimize this data truncation error, you either have to use less commonly used X-ray sources like melatonin sources or silver sources, that have shorter wavelengths. Or an even better approach is to go to a synchrotron source. Synchrotron source offers X-ray with a wide wavelength range. You can always pick a short wavelength window to perform your diffraction experiment and then get your PDF data. In fact, most of the time, that's what people actually will do when they try to extract this kind of PDF data. They just go to synchrotron.

So that's one source of error, coming from basically the horizontal axis. Now, you can also get some source of error coming from essentially shot noise. So what shot noise means? If you think about X-ray, X-ray is really not a continuous stream of optical intensity, right? It consists of discrete X-ray photons. And when the photons actually arrive at our detector, it's a completely statistical event. You can integrate over a certain period of time, like one second, and you intensity of the source is what it tells you is that there's an average number of photons is going to fall in the detector within that one-second time interval. But it doesn't tell you within that one second, what are the exact time points when all those photons actually hit the detector. OK? Make sense?

So now, if you are trying to measure the intensity, you always have a finite integration time. So this statistical nature of the photons means that the actual number of photons you collected within that finite period of time would also fluctuate. Sometimes it would be more than average number, sometimes maybe a bit less than average number. It's completely statistical. The shorter the integration time is, the larger the fluctuation is going to be. OK, that's called a shot noise. It comes from the intrinsic discrete nature of a photon stream.

So what shot noise will give you essentially means that your curve, there's actually an error bar in the vertical axis direction. The intensity is actually not exactly what you measured. So this can lead to a reconstruction error. Now to decrease the actual noise is actually pretty straightforward. You just increase the integration time. The more you integrate, the more you average out the effect. And then you can actually decrease the noise there OK.

Downside, it takes longer. You have to book your synchrotron machine for a longer period of time. You also make it more accurate practically. Next one, finite resolution, similarly, you also want to measure many, many angular values in order to ensure your structure factor is a precisely constructed function. You have to use slow scan basically, which means that you have to book your source for an even longer period of time. So that's what it boils down to. If you really want to get a good PDF, you have to really spend your time with your X-ray source to collect this high-quality data there.

I also just want to highlight that a lot of these corrections, you don't really have to perform by hand. People have developed software packages where you can actually automatically process the accuracy spectra and give you the PDF data, so, whew, you don't have to worry about integration yourself.

Yeah, but you still want to understand the physics, so you can actually properly apply those kind of corrections, make sure you are actually doing the right thing. That's why I'm talking all about it. OK. So that's about X-ray diffraction. Now, I also want to discuss about you can also use other kinds of waves to probe the internal structure of materials besides X-ray. You can use electrons. You can also use neutrons.

Electrons are used because they have the advantage that they are basically integrated with the electron microscope, typically transmission electron microscope. So it means that you can essentially look at the structure of the materials while also examining the morphology in exactly the same instrument, you can actually do a one-to-one correlation. You can look at the structure, look at the morphology, essentially look at zooming into a specific regime of a region of interest. And then perform a local diffraction experiment just to look at the diffraction spectra from that small region there. OK.

This is basically called the Selected Area Electron Diffraction, or SAED, and it becomes very useful if you're analyzing a sample that's actually not homogeneous, right? You may have, for example, an amorphous matrix with lots of crystalline precipitates. And you don't want to perform a macroscopic diffraction experiment such that your data get contaminated with all the crystalline phases. You just want to look at amorphous matrix. You can easily do that with selected area electron diffraction by focusing your electron beam only to the amorphous phase regime.

OK, so that's one reason why electron diffraction is quite useful there. The other peculiarity about electron diffraction I also want to mention here is that the electron waves has a much smaller wavelength compared to X-rays. And this goes back to the fact that electrons are like photons. It has a non-zero static mass. OK? So you have a non-zero static mass. It means that its momentum tends to be a lot larger compared to X-ray photons.

A larger momentum, according to the de Broglie relation, corresponds to a small wavelength. So if you remember for X-rays, we are talking about wavelengths of angstroms, one angstrom. Electrons have a wavelength that's two orders of magnitude smaller, so much, much smaller.

So for electron diffraction, what that means is that the electron wavelength also becomes much smaller compared to the lattice constant of the material or the atomic spacing. So this is very similar to the demo experiment I did in the last lecture. Remember, I used a laser light to actually illuminate the spring. In that case, the laser wavelength is also much smaller compared to the feature size of the spring there. And what you have seen there is in that case, essentially the deflection angle becomes very, very small. So that's also exactly the case in the case of electron diffraction there.

If you have electron beam coming down right, say this is your sample. Then what happens is that the deflection angle of the scatter or the diffracted electron beam, this angle theta is actually very, very small. Most of the electrons travel pretty much still in this vertical direction there.

So that's why if you look at electron diffraction spectra, what it looks like typically is something like this. You take an image like this. You see this little black shadow there? This is actually the beam blocker. What the beam blocker does is essentially it blocks this undiffracted or unscattered beam. You only focus on information coming from the deflected electron beams there. OK? You look at the surroundings. OK. So the shadow is basically casted by this little beam blocker there.

And if you look at the amorphous sample then the typical electron diffraction pattern would look something like this, you have actually a set of diffused rings OK? Which contains effectively the pair distribution function. If it's crystalline material, then you have essentially discrete dots coming from a coherent scattering by the atoms in a crystalline grid.

So the information contained here is very, very similar to X-ray diffraction, except that you can do a selective area diffraction rather than averaging over macroscopic sample. You can also do neutrons besides electrons. Unlike electrons, electrons mostly when you use electron beam to actually illuminate a sample, electrons mostly interact with electrons, because you have very strong coulombic repulsion.

Neutrons, on the other hand, because it's charged neutral, they tend to interact with atomic nuclei instead of with electrons. It doesn't really interact that much with electrons. It also has a much higher mass. So it means that it's very difficult to actually deflect its trajectory with light-mass electrons. So that's why it only gets scattered with atomic nuclei.

Because it interacts with atomic nuclei, one very interesting feature for neutron diffraction is that you can easily distinguish between the neighboring elements, meaning elements with similar z numbers or even isotopes. If you're trying to use electron diffraction or X-ray diffraction to look at solids containing different isotopes, it will not be able to distinguish between different isotopes, because they have the same electronic structure. But they have a different number of neutrons in the atomic nuclei, which can be picked out by neutron diffraction. So that's quite a unique aspect.

Another consequence is that the neutron diffraction is also a lot more sensitive to light elements. So this goes back to the fact that if you have a light element, say carbon, boron, and lithium, those, they have very few number of outer shell electrons. So smaller number of outer shell electrons means that the diffraction effect of either X-ray or for electrons becomes a lot smaller. So that's why electron diffraction tends to miss out a lot of the light elements, while neutron diffraction can pick them up.

OK. That's about diffraction. Any more questions? Happy with that? All right. Now let's go to another technique, Raman spectroscopy. So Raman spectroscopy, obviously, rely on Raman scattering, which is a phenomenon discovered by the Indian physicist, Raman. And this is just a quote from him saying that he derived inspiration of Raman scattering coming from essentially sailing on the Mediterranean Sea, looking at the wonderful blue opalescence of the Mediterranean Sea, which is basically light scattering.

**STUDENT:** That is inspiring.

**JUEJUN HU:** OK, so what is Raman scattering? Essentially, it's a inelastic interaction of photons with the atoms. OK, always the crystalline lattice. There can be two kinds of Raman scattering processes. In one case, the phonon can get scattered and then it transfers energy to the lattice. Essentially, it loses a phonon or excites a phonon in the lattice. In this case, the photon energy will decrease. This is called a Stokes scattering.

You also have the opposite process where the photon comes in, the lattice actually transfers energy to the photon, so that the lattice essentially excites itself. It goes from excited state back to the ground state. And in this case, photon, actually its frequency actually will shift, go to high energy. This is called anti-Stokes scattering.

Sometimes people like to represent this kind of phenomena with this kind of energy diagram here. The argument is that when this kind of Raman scattering happens, you excite the solid initially to a virtual state, and these virtual states are very short lived. Those are actually not real energy levels, OK? So that's why they must have a very short lifetime dictated by essentially Heisenberg uncertainty principle. So within a very short period of time, it should relax back.

Normally, it will relax back to the same starting level. So there's no change of photon energy. And that's basically the Rayleigh scattering, just all the scattering we talked about previously. Sometimes if you start out from a ground state and relax back to the excited state, then this is basically a Stokes scattering. It will emit a photon with a shorter wavelength. Vice versa, if you start from an excited state, go back to the ground state of the crystalline lattice, then you will end up having a anti-Stokes scattering.

Now if you look at this here, because those scattering, it will interact with the solid that's in the ground state. Anti-Stokes interact with solid at excited state. OK. Now according to Bose Einstein distribution or Boltzmann distribution, either way, excited state population is always much smaller compared to a ground state population. Basically, they differ by the Boltzmann factor, e negative delta E kT.

So that's why Stokes scattering is always a lot stronger compared to anti-Stokes scattering, because there are a lot more excitation at the ground state compared to the excited state. In fact, this actually gives give you a method to quantitatively measure the temperature of a sample in a non-contact manner.

What you will do is you can essentially look at the Raman spectra and compare the intensity of the Stokes line and the anti-Stokes line. From the ratio of the two lines, you can then figure out the Boltzmann factor. And therefore infer the temperature. OK? So this is one unique capability of Raman spectroscopy. You can actually measure temperature in a non-contact way.

I will talk about another method to actually measure temperature using Raman spectroscopy. There are actually multiple ways to measure temperature in Raman spectroscopy. This is one, by looking at the ratio of the Stokes and anti-Stokes lines.

So now Raman is actually very useful for analyzing solids in general, crystalline and amorphous as well. Because as you can see here, the shift of the energy of the photons directly correlates with the phonon energy in the solid material, and phonon energy obviously correlates with the structure of the material. That's why Raman becomes a very useful technique for analyzing solid materials. OK?

So what I'm showing in this slide here, these are the typical Raman setup you would actually use if you go to a lab. Most of the time people now use so-called micro-Raman systems essentially integrating Raman spectroscopy setup with a microscope, optical microscope OK. And the idea there is that you can essentially use the microscope as a way to examine the metrology of the sample, identify a region where you actually want to perform Raman spectroscopy, and then you can use the same microscope objective to focus the excitation laser beam onto the sample. And then collect the backscattered Raman signal also through a microscope objective.

So you can very easily correlate morphology information with the local essentially structured information coming from Raman. It can perform a very high throughput analysis. A lot of the micro-Raman systems are now fully automated. You can essentially tell it to actually scan, for example, multiple spots on the sample surface. And it actually gives you, in the end, essentially a collection of spectrum that allows you to do, for example, structure or elemental mapping across a large area. So it's quite a convenient technique.

Raman also gives you a pretty good spatial resolution in the in-plane direction, the spatial resolution is basically given by the size of the laser spot. So the size of the laser spot can be quite small if you have a high magnification microscope objective, you can have a sub-micron spot in the lateral direction. So you can have high lateral spatial resolution.

You can also enhance the resolution in the depth direction or in the out-of-plane direction by using a so-called confocal setup. OK, so let me explain a little bit about how the confocal microscope works. So for confocal microscope, what you would do is say this is your objective. OK?

It will focus the Raman excitation laser into a small spot and focusing on your sample. So let's say this is your sample. OK. Now in a confocal setup, you actually add a little extra in your path length of laser right at this point here, where the laser beam has the smallest diameter. OK?

So now let's see what happens. Suppose you focus your microscope to write on the sample surface. Then any photon generated from sample surface, it will essentially retrace these light rays here, and then will be able to get through this pink hole or this little aperture easily.

Now what about photons coming from, let's say here? Now keep in mind because your laser continues to diverge, it means that the sample here underneath the surface also can get excited. They can also emit Raman photons. But for these photons, it will also go through the objective. But then because this point is actually getting shifted along the optical axis to this direction, it means that they will now focus at the position, let's shift it towards the objective.

Now you see what happens. Now most of the scattered photons will be blocked by this little aperture there. This is not a very good schematic. Let me try to draw it a little bit better.

So using this method essentially allows you to selectively probe a thin layer within essentially the depth of focus of the system here. So a confocal setup improves the z direction or the out-of-plane direction resolution.

**STUDENT:** The top line is like your viewing field?

**JUEJUN HU:** Top line here, or even this one or this line?

**STUDENT:** Yeah.

**JUEJUN HU:** This line is an aperture. It's basically a little pinhole. It's mostly opaque with a little transparent hole in the middle.

**STUDENT:** How if your focal point is below the surface--

**JUEJUN HU:** And your detector should be here. Detector should be like somewhere sitting here. This is where you actually receive the photons.

**STUDENT:** OK. How does it, if it's not in focus at your aperture, how is it reaching your detector in focus, or is that not an issue?

**JUEJUN HU:** It doesn't have to reach the--

**STUDENT:** Where are you losing information because your focal point is like in front of the aperture? I don't think I understand those lines.

**JUEJUN HU:** Oh, these lines essentially are light rays.

**STUDENT:** So you're losing some of your light rays or they're not crossing right at the aperture.

**JUEJUN HU:** Right. Because then a lot of-- essentially, so think of it like the light comes out as like a cone. It essentially emits, basically, isotropically to all directions. Essentially, that's what happens. But the idea is that if your light source is right here, when it emits, it's going to get all the light. Essentially, the image of this point formed by the lens is right here. So effectively when your detector sees, it's not the light source sitting here. It's the light source sitting right at the pinhole.

So then because it's sitting right at the pinhole, essentially all the light the emitted can actually get to the detector, versus if you have a source coming from this point here. Then the image will be right here. It's actually beneath the pinhole. So then only a very narrow range, angular range of the photons coming from here, could actually reach your detector. Everything else is going to get blocked by this.

**STUDENT:** Yeah. How does that affect that information?

**JUEJUN HU:** You just don't collect it. Essentially, it means that you're collecting very small amount of photons from anything that's actually not at the surface.

**STUDENT:** So your very low signal.

**JUEJUN HU:** You decrease the signal. You suppress the signal. Essentially, if you look at, for example, if you plot this is the intensity of photons you collect, right? This is the depth. You are collecting photons essentially only from near the surface. This is like the z direction, z direction.

**STUDENT:** OK. And you want that?

**JUEJUN HU:** It depends. Sometimes you want this kind of depth resolution. Suppose your sample is inhomogeneous in the depth direction. Like thin film, for example, you only want a signal from your thin film, not from the substrate.

**STUDENT:** So it's not that you're getting two different spectra from the top surface and down. It's just you are--

**JUEJUN HU:** You're restricting. Yeah, you're restricting the z range where you're collecting the signal from.

**STUDENT:** OK. Yeah.

**JUEJUN HU:** At the expense that you get lower signal. So that's why this kind of confocal microscopy, confocal Raman microscopy is used when you're analyzing things like thin films or if you're trying to analyze surface. OK? If you're trying to analyze the bulk sample, the recommendation is to just use the regular Raman. Don't worry about confocal because otherwise you are essentially losing signal by just cutting off the light. OK?

Now this is some examples that shows what the Raman structure actually looks like for actual amorphous materials. Left-hand side, this is for single crystalline silicon. It has a well-defined Raman peak centering about 520 inverse centimeter. Now notice the unit here. The unit is in Raman shift. It's defined as the change of wave number from the excitation source.

So you can think of the horizontal axis basically as the frequency shift or effectively the wavelength shift. OK? So from the position of the peak what you can infer is basically the phonon energy. The larger the wave number, it means that there is larger energy difference between the incident photon and the scattered photon, and therefore, it means that the solid has a higher phonon energy. Essentially, this latter offset gives you the phonon energy. It's a measure of the phonon energy.

So for single crystal solid silicon, it has a very well defined peak because it has this periodic structure. Its photon energy is also very well-defined. That's basically what it says. OK, versus amorphous material, this is in this case as in sulfide glass. You see this kind of broad peaks here. And that comes from multiple factors. So one is that, of course, you have this dispersion of local structures. Every location, the atomic arrangement is slightly different from others. And this gives rise to dispersion of phonon energy. OK?

Another factor that contributes to this kind of complexity of Raman spectra is the breakdown of selection rules. So selection rules basically coming from Fermi's golden rule, essentially means that there are some certain transitions that despite that a transition exists but has a transition probability of zero because the transition matrix elements is zero. OK?

Now usually that's caused by symmetry. It means that, for example, you cannot easily transition from a symmetric state into a mirror symmetric state because the overlap integral of that two-wave function is zero. That's what happens with selection rule. Now selection rule applies in crystalline solids because you have crystalline lattice, you have symmetry in place.

In amorphous material, you no longer have lattice, no symmetry. So essentially, a lot of these selection rules will just break down. And what that means is that sometimes some of the inhibitor transitions in the crystalline solid now becomes allowable in amorphous materials. And those photon transitions will then show up on this spectrum here, which is another reason why this is a lot more complex compared to the case of a crystalline solid.

OK. So now the question is what information can you extract from this seemingly again featureless spectrum? I'm not going to derive equations. Instead, I will show you one example about what are the information you can extract just looking at Raman spectra. So this is actually some example. This is actually something we did from my own group in collaboration with Lincoln Labs. What we are trying to do is we are trying to look at phase change materials. You know what phase change material is, right? They switch between amorphous and crystalline states.

So we perform this kind of switching by using essentially in this case a microheater, resistive heater. We basically have this kind of silicon wafer structure. It's called silicon on insulator. It has a layer of single crystalline silicon sitting on top of silicon substrate, separated by a layer of silicon dioxide. And silicon, this is actually a doped silicon layer. Once you dope it, they become electrically conductive. We can pass current through it, and therefore, we can introduce a controllable crystallization of this layer of phase change materials.

So now if you look at using Raman, I've schematically shown to you this is what the Raman excitation beam would look like. This is the volume where you have Raman interaction with the sample. Now notice here this interaction volume is actually pretty large. It covers the phase change material itself. It also covers this silicon layer here. That's a heater. And it also overlaps a little bit with the substrate.

So now let's see what information we can get. First thing is that we can monitor the peak position from the silicon Raman peak, signal increase and silicon Raman peak. What we have noticed that is that initially you have one silicon Raman peak. As you increase the voltage through this two electrodes here, it essentially means that you're heating up the heater.

As you heating up, you start to see a shift of the Raman peak. And then at some point, you see that the silicon Raman peak split into two. Now the shift can be explained by the fact that the position of the Raman peak is actually a function of temperature.

So that's actually another method to use Raman to actually do a non-contact measurement of temperature on samples. If you have a crystalline silicon substrate, you can monitor temperature by just looking at the shift. Now, the reason there is actually a split here, it's actually because our probing beam overlaps with both this silicon layer as well as the silicon substrate. As you can imagine, when you pass current through it, this heater is going to go to much higher temperature. The substrate, on the other hand, will set a much lower temperature because it's basically a heat sink.

And that's why you see that at some point, these two silicon peaks will split, indicating that this layer of silicon is now at a much higher temperature compared to the silicon substrate. So now we can essentially now determine what is the temperature of the heater as well as the phase change material. So we can know temperature. This is one thing.

This is actually an actual experimental data. The line is basically our simulation results using finite element methods. The thoughts actually experimentally measure data, showing that how we actually increase the voltage, how the temperature of the heater actually increases. So now you know temperature, we can now try to analyze the temperature dependent structural transformation as well as the kinetics of the transformation.

So to analyze the Raman spectra what I'm showing here, this is the raw spectra that's is collected for amorphous phase of the phase change material. This is for crystalline phase of the phase change material. OK, again, seems quite like featureless. You all this kind of featureless things. OK, but some general features you can tell is that if it's a crystalline phase, there's a dominant peak at this wave number here. This is actually about 100 and I think this was 120 inverse centimeter wave number.

But for amorphous space, there's another peak coming up at around 160 inverse centimeter. So if you want to get more quantitative information, what you have to do is you have to first correct the spectrum and then do some fitting there. The first correction you have to do is to correct for absorption and scattering. So this comes into play because similar to X-ray, when the excitation laser goes through the sample it gets absorbed. It gets scattered. So its intensity actually changes as you penetrate into the sample. So this is a factor that has to be corrected to get the Raman spectra there. So you first perform this correction here to get this corrected structure.

Next part is then we need to eliminate this broad background here. The broad background is caused by so-called a Boson peak. The origin of the Boson peak is still somewhat under debate. But in general, people agree that this is a common phenomena in amorphous materials. It's a consequence of the medium range order in the solids that lead to this Boson peak. Now, fortunately, people already have a pretty well-defined function for this Boson peak here. So you can essentially use that function to actually subtract this background and leaving behind this information did actually come from the Raman scattering of the sample.

So then next step is that you can perform a peak decomposition to decompose the Raman spectra into a few discrete peaks. Now to further analyze what are causing these discrete peaks, what you have to do now is to actually perform some simulation. So we did some density functional theory, first principle atomic calculations. And according to the density functional theory, there are many, many vibrational modes. Each is represented by essentially one of these peaks here

So the peak position basically indicates the vibrational frequency of each of the vibrational modes of the lattice. And the width of these peaks indicates structural disorder. The more structural disorder you have, the larger the dispersion of the local structure, the wider the peak gets.

So you can see that our simulation actually gives pretty good agreement compared to experiment. There are actually two peaks. The blue curve is actually what's predicted by density functional theory. The black curve is what we actually get from experiment. OK. So you get pretty nice agreement. So now you can unequivocally start to assign structural entities to each of the corresponding peaks.

So for example, this green one actually is associated with germanium 6 selenium octahedral structure. This one is actually germanium sitting in tetrahedral, selenium tetrahedra. This one is antimony sitting in selenium octahedral. OK, so now you will be able to identify what is the structure entity that caused all the peaks.

You also see some useful information here. So for example as you go from crystalline phase to amorphous phase, you are seeing that germanium is actually shifting location. Initially, most germanium actually sits in octahedral site. Now they move to a tetrahedral site as you move to amorphous phase. OK, so that's the useful information. Now you can actually extract from this kind of a data here. OK.

But basically, that's how you actually analyze the Raman spectra quantitatively. You have to compare it with literature or with first principle simulations to identify the specific nature, the origin for all the Raman scattering peaks. All right. So now you can identify essentially the temperature dependent structure of the material.

Next thing you can also do is that it actually gives you a way to actually measure the phase transition kinetics. So phase transition kinetics is captured by this TTT diagram. So to do a TTT diagram, what you have to do is you have to perform a set of isothermal experiments, if you remember how a TTT diagram is derived. You fix the temperature. You look at how long does it take to actually induce some phase transition. And then you connect all those points on the graph. Then you get a diagram.

So that's exactly what we can do now with this technique. Because we know temperature from the Raman peak shift of silicon. We know the structure. So we can know exactly what's the fraction of material we have actually crystallized by analyzing Raman spectra there.

So then if you collect those data, you can generate this TTT diagram here. It may look a little bit different from the TTT diagram, because what we do, this is actually a discrete version of the diagram. What we did is we have the heater. We can turn on the heater, heat up to certain temperature, hold it there for some period of time. And we're now examining whether or not the material has crystallized or not.

So each data point essentially corresponds to one of these experiments. And what we are seeing here is that you're only introducing crystallization when you actually force within this dotted line range here. This is when you actually see crystallization of the PCM. So this total line basically then corresponds to the crystalline region that you normally see in 3D diagram. And this is where essentially the noise temperature is basically.

It's like a discrete version of a normal TTT diagram. Does that make sense? So this is in fact, I believe this is actually the first time a true TTT diagram was actually measured in PCM. Otherwise, it can be pretty tricky, right? Because it crystallizes so fast. And you also need a way to actually accurately identify temperature and also identify the structure there. So Raman is actually a pretty perfect candidate to do both things, killing two birds with one stone. OK. All right. So that's Raman.

Now, last technique I'm going to discuss here is thermal analysis or basically a calorimetry. So you're probably all familiar with calorie numbers that you normally see in essentially any kind of food packages. You will see all those numbers listing calories. Have you ever wondered how those numbers come from? They come from calorimetry measurements. And there's actually an equation I'm listing down here that actually defines rigorously how those calorie numbers are actually calculated or measured.

So it should be equalling to the energy in the food minus the energy that gets carried away in basically a human waste. So now if you want to actually measure the actual calories contained in food ingredient, what you have to do is you have to perform this kind of calorimetric measurements. So a calorimeter basically is you have your chamber here. You then perform oxidation of food or whatever sample it is, basically burning it.

So when you burn it, it generates heat coming from oxidation. The heat is passed around to this water bath here and everything is enclosed in thermally insulating containment. So then the temperature rise of the water will indicate how much heat is generated in oxidation process. So to complete the equation, you need to measure the energy contained in food. You also need to burn human waste to get the actual energy carried away by those materials.

So that's not a particularly pleasant experiment. And as you can imagine, people will not do that. I mean, like will McDonald's try to actually burn the burger to actually measure it, the actual heat? No. Most of the time when you actually see those numbers on food packages, what they did, they took a shortcut. They just look at how much protein, how much fiber, how much fat is contained in each kind of food.

And there's a standard conversion table that tells you that this amount of fat corresponds to this amount of calories. They simply add it together and that's the number they actually reported. So now actually you can imagine that's grossly inaccurate that kind of method. It completely ignores any kind of difference in terms of how you actually process the food.

As you can imagine, if you have a steak, you have basically a raw steak compared to something that's perfectly well done. The amount of energy human body can extract is completely different. The human body requires a lot more energy to assimilate, essentially a raw steak compared to well-done steak. But that difference is completely ignored in this kind of calculation.

So now you realize you should not really trust those numbers too much. They are just simply not very accurate. OK? Now as scientists, we want to be a bit more accurate when it comes to analyzing amorphous materials. So that's why we are introducing two techniques here-- differential scanning calorimetry or DSC or differential thermal analysis, DTA.

First of all, these two methods, they basically more or less reveal similar information. DTA was the first technique that was developed because it's configurationally a lot easier, and that's why people like to use it, especially in early days. But as I'll show you later, DSC can be a lot more quantitative. And that's why people are basically progressively transitioning from DTA to DSC. But if you read all the literature, you're still going to see a lot of DTA data. So that's why you need to understand the technique.

So what does the DSC measure? A DSC essentially you put your sample along with a reference in two separate heating ovens, OK, or two separate heaters. The reference should be an inert material with known thermal characteristics. So for inert, it means that the reference should not undergo any kind of phase transition in the entire temperature range of interest. Its thermal properties, which basically is the heat capacity, should also be very well calibrated across the entire temperature range. OK, that's for the reference.

Now in your actual analysis, what you will do, you create two identical ovens with two identical heaters. You put your sample on one, you put the reference on the other. And they are thermally insulated. There is no crosstalk in between the two. You now start to pass current through the heaters to heat them up. For DSC, you essentially ensure that the temperature of the sample and the reference is always the same throughout the entire heating cycle. And you do this through a feedback loop computer control. You change the instantaneous power you feed into the two heaters, just so that the temperature is always the same for the reference and for your sample.

So what you are measuring here for DSC is basically the difference of heat flow into the sample versus into reference.

Now for DTA, DTA is a lot easier. DTA you only have one oven. You have this kind of symmetrically configured oven. You have one heater, single heater. You have a sample, you have a reference. You put it in this mirror symmetric configuration, so that the assumption is that the thermal conductance from the heater to the sample and to reference is the same, more or less identical.

So then if you assume the heat conductance is same, it means that the heat flux going from the heater to the sample. And from the heater to the reference is more or less the same. So if heat flux is same, the sample and the reference, they may have different heat capacities. So different heat capacities will then lead to a different temperature. So what DTA measures is the temperature difference between the sample and the reference.

So now you can see why DTA is a lot easier to prepare because it's very simple. It's just one single furnace. Put things in there and just measure the temperature, very straightforward. Versus DSC, you need actually some pretty complicated computer control to ensure that you always have the same temperature between the sample and the reference.

Now let's start by taking a look at DSC first, and I'll explain DTA. So in a DSC structure essentially the vertical axis will be the difference of the heat flow to the sample versus to the reference. OK? There are different conventions as to which side is the positive axis, which side is negative axis. What I'm assuming here is that if you go along, the positive axis essentially correspond to endothermic reaction in your sample. Endothermic essentially means that the sample is actually absorbing heat.

If you go in the negative axis, it's an exothermic reaction. It means your sample is releasing heat. So effectively, if you have a curve that goes somewhere up here, it means that either your sample is releasing heat or your sample has a very small heat capacity, or smaller heat capacity compared to the reference.

All right. So now we can take a look at the spectra here. So if you have a glass sample, amorphous sample, you go through DSC. Initially, you get more or less a flat line. What a flat line represents, in a steady state we are measuring the heat flux difference. The heat flux in an isobaric experiment, which means the constant pressure that's the case for most experiments, is basically the change of enthalpy. The heat flux is basically a change of enthalpy of the sample. So the heat flux is basically this differential here, dH dT That's enthalpy change as a change rate in your sample.

You're looking at a difference between the sample and the reference. So subscript S is basically your sample. Subscript R is basically reference. Now we also know that enthalpy change can be directly correlated with heat capacity of the material. So essentially this heat flux difference can be trivially connected to this equation here. It's the difference of heat capacity between the two samples here, between the sample and the reference, as well as times the heating rate.

So now you can tell why people like DSC, right? You have this very clean, simple expression. You can directly extract what is the heat capacity just from this measurement here.

**STUDENT:** So the dHS dT minus dHR dT, that's just the y-axis?

**JUEJUN HU:** This is basically the y-axis. It's a heat flux difference. The y-axis is basically measuring the difference of heat flow to the sample and to the reference.

If your sample doesn't undergo any kind of phase transition then you expect this DSC trace will pretty much be a flat line. It just gives you the heat capacity difference between the sample and the reference.

All right. Now go to the first step here. This first step corresponds to glass transition. The reason there's a step there is because as you go from glassy state to go to a supercooled liquid state, the heat capacity changes. The supercooled liquid state, the material has access to more degrees of freedom, and therefore, it should have a high heat capacity. This can also be explained by looking in how the enthalpy changes as a function of temperature for glass materials, if you remember.

And so we change as a function of temperature. Essentially, the curve starts out with a smaller slope. As you go through glass transition, it becomes steeper. Right? That's basically showing up in essentially the different heat capacities here. That's the two plateaus. This is basically heat capacity of the glass. This is the heat capacity of supercooled liquid.

Now if you continue to heat up, there's going to be a dip or negative peak that actually comes up. This corresponds to crystallization. So when the amorphous sample crystallizes, the crystalline state actually has a lower enthalpy compared to the amorphous state. So therefore in the crystallization process, the sample actually releases heat when it transitions to this low enthalpy crystalline state. So that's why that's basically an exothermic peak that comes up. There's excess amount of all enthalpy that's released to the environment as you go through this enthalpy state.

Then if you keep going to high temperature, at some point you go to essentially a melting point. And in order to melt a crystalline material, you need to supply the latent heat. And that's why it shows up as a endothermic peak. And you need to absorb heat in order to transition it from solid state to liquid state.

So this is typically what the DSC trace is going to look like for an amorphous material, for glassy material.

**STUDENT:** That first piece that would have been a lot easier with this.

**JUEJUN HU:** Oh Yeah. Now you remember that one. Yes, exactly. I'm trying to prepare you for this. OK. Maybe I should have done this after this lecture. But now, one thing I also want to quickly mention here, the reason I said DSC people like it is because it's very quantitative. The area under each of these peaks can be directly correlated with the enthalpy change.

You can, for example, from the area under the peak, under the melting peak, you can directly calculate what is the latent heat or what is the enthalpy of melting. Same thing, area under the crystallization peak gives you the enthalpy of crystallization or the enthalpy difference between crystalline and amorphous state.

So you can not only measure the crystallization temperature, the melting point, or the glass transition temperature, you can also quantitatively determine some thermodynamic parameters of your material. And that's why I said people like DSC, exactly for that reason. Because you can quantitatively determine your sample parameters.

Now I want to also mention one caveat here. This is basically your p set, your first p set. About this part of the curve, so I have used this very simple curve here just a smooth curve just to connect the glass regime and the supercooied liquid regime. In reality, usually you don't get this kind of very simple curve. In fact, what you're going to get is a curve more like this, because you have a relaxation.

As you go through a glass transition regime, we know that it's going to relax towards a supercooled liquid state. And the slope of this line basically gives you the heat flux, exactly the p set OK. And that's why you will have this kind of complicated shape of the heat flow there. So this is what our DSC trace is actually going to look like.

Now one immediate consequence here is that it becomes quite difficult to unequivocally determine a glass transition temperature just by looking at the DSC trace here. I mentioned about this kind of ambiguity there, that Tg, glass transition temperature, has different definitions when we talk to different communities. You talk to a glass community. People will tell you that Tg is basically when viscosity equals 10 to the 12th Pascal-seconds-- simple, very well defined.

If you talk to people working on the thermal analysis community, things become a bit fuzzy there. They try to measure the glass transition temperature by essentially looking at when this transition happens on the DSC trace. Now you can tell it's quite difficult to determine. In fact, what people would normally do is they try to extend some of these two lines here and look at the crossover point, and then use that crossover point to define the Tg.

It's not very rigorous, as you can tell. If you have different heating rates, different sample preparation conditions, it's going to be very, very different. So that's why Tg determined from DSC, it's at best, maybe a semi-quantitative measure. If you fix your experimental condition like the same heating rate, you can use it to compare different samples, but you should be very, very careful not to compare your Tg to some other people's Tg measured on two different DSC machines. That may not be comparable.

No, no, no, no, no. As long as you are consistent using the same DSC machine, compare different things, try the same heating rate, that's OK. Don't worry too much about it. Or if your Tg differs by a much larger temperature window than what I'm showing here, then maybe you don't even care. Anyway, that's just a caveat there. So just be careful when you're actually interpreting DSC data.

All right. Now switch over to DTA. So DTA, as I mentioned, now we are looking at the temperature difference between the two samples. So quantitatively, we can look at the DTA by looking at this equation here. Let me explain what this equation means. So K is the thermal conductance. K is the thermal conductance from your heater to your sample or to the reference. Because it's symmetric, basically, the K is the same for the sample and the reference.

So according to Fourier's law of conduction, the amount of heat flux to the sample or to the reference is given by K thermal conductance times the temperature difference between your heater, which is Tf minus the temperature of your sample, or the reference. It's basically delta T times thermal conductance. That gives you a heat flux. And the heat flux should equal to basically dH dT, the enthalpy change.

So you can take the difference of these two equations. I'm going to skip the math here. We end up getting is that the temperature difference between the sample and reference should also correlate with the heat capacity difference between the sample and the reference.

But notice the sign difference here is CR minus CS. Here is CS minus CR. CS minus CR, CR minus CS. So to the first order, you will see that the DTA curve essentially looks like a DSC curve flipped, flipped upside down because of the negative sign.

Now second thing, I also want to mention that DTA is a lot more difficult to quantify because of the presence of this K in your equation there. K is the thermal conductance from your heater to your sample, which is very difficult to measure. And it's different from one machine to the other machine.

So that's why most of the time when people are using DTA, people are not trying to extract quantitative, thermodynamic parameters like enthalpy. If you want to do that, use DSC. What people use DTA for is just to determine the temperature. Determine, for example, what's Tg, what's Tx, the crystallization temperature, or what's Tm, what's the melting point. So that's what DTA is used for.

So the interpretation of the DTA curve is actually really pretty straightforward. As I said, it's basically the DSC curve more or less flipped upside down. You will see a glass transition. You will similarly now see a positive peak for crystallization and then a dip or negative peak for melting. And you can again use whatever trick you like to do to try to fit the different temperatures there.

All right. Now, one real example of how people actually use DTA to analyze glass materials, so in this case here, people are basically trying to gauge the impact of silicon addition in the amorphous phase stability of arsenic telluride glass. So you can see that you have two decay curves, one without silicon, one with silicon.

And you can now start trying to fit all these different temperature points here. By essentially extending the lines and see where they cross over, and this is how you actually determine all the different temperature points. Again, as I said, this is only semi-quantitative at best.

However, what is legit is that you can actually still look at, if you compare these two samples, measured in the same DTA machine, the relative difference of the temperature still makes sense. In this particular case, what they are trying to determine is the amorphous phase stability. We mentioned that amorphous phase stability can be gauged using different kind figure of merit. For example, the most common one is delta T. Tx minus Tg, where Tx is [? supercooled ?] liquid temperature, Tg is the glass transition temperature.

So essentially, in this case, you can see that you have two samples. Let's see. So this is basically Tx minus Tg. This is Tm minus Tx. So this window essentially tells you which sample is actually more stable. In this case, it seems like the one doped with silicon has a larger difference between Tx minus Tg, and therefore, it should be actually more stable. So the argument is that if you add silicon, you make this glass actually more stable. That's the conclusion you can draw legitimately from this analysis here

All right. So in the remaining five minutes, I just also want to quickly mention that this is actually a new technique people are now developing here called the flash DSC, or ultrafast DSC. The motivation there is that people sometimes want to characterize some material transformation that is very, very fast. And if you use a normal DSC, you will not be able to actually capture that because the sample itself has a finite volume heating up or cooling it down, it all takes time because of the large thermal mass. So you will actually miss a lot of this kind of transient transitions that happens actually in materials.

So in a flash DSC, what people are doing here is they essentially use a special kind of sample data. Instead of being a bulk sample, they essentially use a microfabrication technology to fabricate micro heaters on a silicon substrate. And then they use those micro heaters. They pass current essentially through those resistive micro heaters, and use that to actually quickly heat up and cool down the material. Because a very small sample volume, you can realize much higher heating and cooling rate compared to what you were able to achieve using conventional DSC.

OK, so let me just play that video.

[VIDEO PLAYBACK]

[MUSIC PLAYING]

- Up until now, many physical transitions and chemical reactions could not be investigated simply because no instrument was fast enough to measure the processes involved. The new revolutionary Mettler Toledo Flash DSC, opens up new frontiers in thermal analysis and gives you access to a complete whole new world.

Differential scanning calorimetry, or DSC for short, is a technique that allows you to determine the energy absorbed or released by a sample over a wide temperature range. The standard DSC from Mettler Toledo has a maximum heating rate of 400 Kelvin per minute. In contrast, the new Flash DSC provides heating rates of up to 2,400,000 Kelvin per minute and cooling rates of up to 240,000 Kelvin per minute.

These incredibly high heating and cooling rates present exciting new application possibilities that were previously undreamt of. For example, materials used for injection molding can now be studied under actual processing conditions. The Flash DSC's cooling rates are so high that a sample can be cooled under exactly the same conditions as occur in the process.

The heart of the Flash DSC is the innovative sensor chip based on MEMS technology. This sensor has a very small mass and combines unsurpassed sensitivity with excellent resolution, and--

**JUEJUN HU:** You see the [? better ?] traces. That's actually how you apply--

- On a Flash DSC measurement, the sample is placed directly onto the replaceable sensor. The ergonomic design of the instrument, the touch screen display, and the microscope ensure complete ease of use when working with such very small samples.

The very high heating and cooling rates enable many measurements to be performed in just a few seconds. This generates an enormous amount of new data for evaluation. Mettler Toledo's powerful STARe software offers unrivaled flexibility and almost unlimited evaluation possibilities, and allows you to explore a completely new world with Flash DSC.

**JUEJUN HU:** That's [INAUDIBLE] peaks.

- --innovative technology.

**JUEJUN HU:** So now we know what you have on your T-shirt.

- The Mettler Toledo Flash DSC represents a quantum leap in thermal analysis and revolutionizes fast scanning DSC.

[END PLAYBACK]

**JUEJUN HU:** OK. All right. I show this is just one quick example reference from this paper there. Essentially, this is one example where people actually used ultrafast DSC. In this case is actually the crystallization of phase change material. We know this phase change material actually are essentially poor gasses. They crystallize in very short period of time. You cannot analyze it using conventional DSC. But now you can actually do it with this ultrafast DSC. So we are right on time. And I'm actually going to conclude here. Any last minute questions?