[SQUEAKING]

[RUSTLING]

[CLICKING]

JUEJUN HU: OK, so let's start. So starting in this lecture, we're going to talk about a different topic here. We are going to discuss about electrical and transport properties in amorphous materials.

The reading materials, they cover ionic transport. There's relatively little coverage on, essentially, electronic structures and electronic transport behavior. You basically just have to more or less rely on the slides, or go to ChatGPT and search for relevant materials.

OK. So to start with, this slide summarizes some of the very basics of electrical conduction. So electrical conduction happens when you apply electric field in a material. The charged particles start to move around. You can have charged particles two different opposite charges. You can have positively-charged ions, negatively-charged ions, or electrons. They will move along different directions in electric field, but both of them will contribute to positive electrical conductivity.

So we can see that from the equation here. This is something you probably have already learned from general physics.

Basically, if you look at the electrical conductivity expression here, n will be the concentration of the charged carriers, Z is the charge number, e is the elementary charge, and mu is basically the mobility.

Now, one thing to keep in mind is that regardless of the sign of the charge, whether it's a positive charge or negative charge, you always get a positive contribution to the electrical conductivity. Which makes sense. Essentially, what happens is if you apply electric fields, the positive- and negative-charged particles, they will move in opposite directions, but the current direction always aligns with the electric field direction. So this is something to keep in mind when you do the summation to get the total electrical conductivity in solid material.

The other thing I also want to mention about this equation here is about this letter here. So for this equation here, v is the velocity. It's basically a product of mobility times electric field. Unfortunately, v looks exactly the same as the Greek letter nu. There's no way to tell the difference on PowerPoint. So that's why any letter v that's in the bold form, this is representing a vector. This is the velocity. OK?

Nu is without the bold. On the board, I'm going to write v with a vector sign. OK? Basically, this is our velocity. This is nu. This is v. This is our velocity. OK?

OK. So the other thing I also want to highlight here, this is also something-- I assume you probably have seen the Einstein relation in kinetics class, yes? Yeah. Essentially, it links two kinds of different kinetic parameters, right? One is diffusion coefficient D, the other is mobility. And the two are naturally linked together because they both describe how these charged particles will actually move under the action of external forces.

In the case of D, it's moving due to a concentration gradient. So essentially, due to a chemical potential gradient. In the case of mu, it's moving under the action of electric field.

So both should be related to how mobile the particle is and the other external force. That's why they are naturally linked together.

And so if you plug everything into the equation here, this is what you end up getting. If you want to get the total electrical conductivity in a material, you just sum up the contribution from each individual charged species. And as I said, because this term here, Z, is squared. And that's why, regardless of whether you have a positive-charge or negative-charge species, you always get a positive contribution to the electrical conductivity. OK? Because the Z here is squared. Make sense? OK? All right.

So what we will do next is let's take a look at now-- essentially, play divide and conquer. Let's look at the contribution to electrical conductivity from both ionic species and the electronic species.

Starting with ionic species, you also probably have learned about the ionic conduction mechanism in crystalline materials in kinetics class. There are two kinds of mechanisms. You can have a vacancy mechanism, where essentially, the ions swap position with neighboring vacancy, and as a result, this will lead to an electric current, or the ions can be staying in interstitial sites, and they can essentially move around from one interstitial moving to a neighboring one, and therefore conduct electricity.

So in amorphous materials, it becomes a little harder to precisely define a lattice site, as well as the vacancy site, because we do have this kind of regular crystalline lattice structure. So instead, the language we want to use here is that there are actually preferred locations or preferred sites.

This size gives, essentially, a low energy when ions are actually populating it. So then, the electrical conduction process becomes, essentially, an ion-hopping process between these low-energy sites. And this low-energy site, obviously, is not periodic. If you look at this plot I'm showing you on the left-hand side here, what I'm showing, essentially, in yellow color, this labels the low-energy sites where the lithium ion, in this case, preferentially sits in the silicate glass.

So you can see that as we increase the lithium ion concentration, the density of this kind of low-energy site actually increases in the glass material. But even for this very high lithium ion concentration, you notice that these sites, still they are separated from each other. They are not completely connected. So then if you want to have the lithium ion move from one end of the material to the other end of material during electrical conduction process, inevitably, it involves the process of the lithium ion hopping from one low-energy site to another low-energy site. And in that process, they have to go through, essentially, barriers in between them.

So you can think of the ionic conduction process also as a thermally-activated process, where the ions will have to essentially overcome the energy barrier between these low-energy sites in order to conduct the current. OK.

So what we will do next is that we will try to essentially develop a model to capture what is the ionic conductivity in solid materials, by looking at this picture here. What we are assuming is we're basically looking at two neighboring low-energy sites. There is some energy barrier in between, that E, this is our energy barrier. And the ion will have to overcome the energy barrier in order to transport the electric current.

Now, one thing I do want to mention here is that because of the statistical nature of glass structure, when we are referring to this parameters of the low-energy sites, such as depths of the well, or the energy barrier separating two neighboring sites, all those numbers should be considered as an ensemble average across solid material. They are not-- unlike crystalline material, they are not well-defined.

OK, so now let's consider how we actually derive the ionic conductivity in this picture here. We will start out essentially with a random walk theory. If you consider an ion will be moving around between neighboring lesser sites, the average distance it will move, r, correlates with the distance for every hop. So d will be the separation between neighboring low-energy sites. So it's essentially the distance where for one atomic hop. OK? And M is the total number of atomic hops.

So from the random walk theory, the total distance within scales quadratically with the number of hops, or square root of number of hops. OK?

Now, the other equation that you probably also have seen in your kinetic class is that the average diffusion distance, this is correlated with the-- this is given by this expression here, where tau is the time of the diffusion, and D is our diffusion coefficient.

So this is basically the definition of the diffusion length. For 1-D, the coefficient is 2, for 3-D, the coefficient is 6, because you have to diffuse along three different directions.

So now, if you combine this equation here, these two equations here, for example, if you take the simple 1-D case, so you have two equations, basically r equals to d square root M, we know that r also equals to square root 2 tau D for the 1-D case, right? So then you can then, essentially, from that you can then calculate D. This would equal to, you do a square on both sides, becomes 1/2 M divided by tau, and then d squared. Right?

Now, M is the number of hops, and tau is the duration, all the time. So M divided by tau essentially gives you the frequency of this kind of atomic hops. So that's where we're now introducing our Greek letter nu d squared. So nu will be the frequency of this successive ionic hops between the neighboring low-energy sites.

OK, so if you look at this equation here, we are essentially simplifying the diffusion coefficient into this hopping frequency, nu, here. So all we need to do in order to derive ionic conductivity, if you look at the expression here, if you know D, you can then use it to actually calculate the ionic conductivity. OK?

So what we need to do is then to predict what is the frequency of successive hops between the neighboring low-energy sites. OK.

Now, this is actually quite straightforward because this is essentially a process where it's thermally activated. Essentially, you have an ion. It's constantly vibrating at this low-energy site with a vibrational frequency of nu 0. Now, every time it vibrates, you attempt to overcome the energy barrier and hop to a neighboring site.

Now, this kind of attempt is not always successful. So the probability of having enough energy for the ion to overcome the energy barrier will be given by the Boltzmann factor here. So according to this Arrhenius law, basically it says that the frequency of successful hops is going to be given by attempt frequency or the vibrational frequency times the [AUDIO OUT]