GANG CHEN: This course is for pass fail. You should turn in your weekly reading report. And I will give you-- I'll send the email. So I'll give you two buy-outs since I haven't said this before. Two buy-outs means you can skip two reports, but below that, you can't pass this course-- so pass fail, OK? So I'll send that out.

I came back this morning from San Diego. And what I want to show you-- OK, this is my towel bag. And that's all I bring because now I feel one day, my son had a homework assignment-- carbon footprint. And he came back and said we will be below the average, except you travel too much.

So my footprint is just a tremendous release of family carbon dioxide footprint. My way of trying to redeem a little bit is by traveling light. And I was at a meeting in San Diego. This meeting was on the application of thermoelectrics. So we actually, in the last two days, really-- the key people from thermoelectrics area around the world converged in San Diego discussing the application areas.

I'll share some of the meeting findings. Let's see. I want to start by-- some of you read one or both of the papers-- the assignment. One is by crowning one in on the *Inconvenient Truth.* And the story is he attended one of those conferences organized by Al Gore.

And so that was a good title--*Inconvenient Truth's* title. And I know he called me at the time and was asking for some slides. So whether you have any thoughts-- the other the other review by Lambell is more optimistic. So one is the pessimistic one. The other is, I think, the more optimistic one. And I don't know which side you're in. Any thoughts on that, or anyone have any opinion? Yes?

AUDIENCE: They were saying some of the same things with a different tone because they both were saying that if this is going to be useful, it's for low power, niche applications, maybe some covered applications. And then the difference was in terms of-- I think it was-- Bell was saying this is going to be a great impact if we can do these applications.

And Cronin Vining was more like, you can do these applications, but it might not make that much of an impact overall. You're never going to touch the large scale energy sector with thermal objects.

GANG CHEN: OK. Yeah. So I would buy into the-- but still, the two-- in terms of the impact-- conclusions seemed to be a little bit different, right? Probably the same no matter what you do. Thermoelectric won't make a difference in the larger scale. So who raised their hand? Who else?

AUDIENCE: But there's an argument for doing a lot of little things, right? If you were to, for some reason, take over all of the low power applications, that's a lot of things you add efficiency for. It's not a large scale. So it's like, if you replaced every cell phone with something that saves 5%, that's a lot of cell phones that you [INAUDIBLE].

GANG CHEN: I guess the future is very uncertain. And it's very hard to see what technology will win.

AUDIENCE: Exactly.

GANG CHEN: So that's a good perspective. Well, I was asked to serve as a panelist in this meeting. I gave a talk, but they also asked me to serve as a panelist. So I thought of what I would say-- anything during the meeting different from what I was going to talk on the scientific side.

I pulled out the Cronin Vining's paper. I read it again on the airplane and made a few slides I want to share with you. So let me-- this is not in the handout, but I can put it in the website. So I also try to use-- you can help me think about the last time. I say whether it's incorrect conclusion or inconvenient truth.

So I think the erroneous argument is really based on here. This is the efficiency heat source. And they look at, of course, this is the maximum you can get. So there's no mistake in the scientific side. The question is, where do you place the dots? This is fine. This is a cold running cycle. You can even get the 60% if you do the coaching.

And although we-- he has now put in there somewhere between around 25% internal combustion. And solar sturdy-- that's a mistake. Nobody has that kind of efficiency even demonstrated. Nuclear ranking, that's the esteemed solar ranking. So solar, these two dots accompanied [INAUDIBLE]. The solar, if you think about what's currently deployed in solar steam generation is between 15% to 18% efficiency.

And, of course, in the lower target range for this argument here are competitive technology. This is an organic Rankine cycle, for example, where the organic has a lower evaporation temperature. So you can do the steam engine-based cycles. So that's his argument. Basically, you see the thermoelectrics, even [INAUDIBLE] too [INAUDIBLE] be much dense compared to, of course, if you compare with this talk.

Let's say, I thought that the comparison was not on the mark. Because now, if you look at the PV, photovoltaic, and amorphous silicon is about 6% to 8%. The single crystalline silicon deploys about 18% In the real world. Of course, in the lab there has been higher efficiency demonstrated. And the first solar panels generate, that's the fastest growing solar sector is about 10% efficiency.

So, of course, even PV you can make the same argument. Will it make a difference? Because they were at least 30 terawatts in the next 30, 40 years. And PV now the deployment annually is about six, seven gigawatt. You can go to see how much you have to have to catch that.

Let's say, of course, today nobody would really argue against PV. In the long run, this could be a solution. So you look at the PV cell efficiency progress, this is the best. This is the best efficiency progress against the year. And as I said, amorphous silicon-- this is the amorphous silicon there where this is amorphous silicon. And then deployed [INAUDIBLE] 6% to 8% efficiency in the real world.

And single crystalline silicon, 26% here, and deployed is about 8%. And part is [INAUDIBLE]. And so, this is a-- with this low efficiency, you are, of course, competing against the coal generation. And at this stage, it is not competitive. So the government is giving stimulus, trying to promote this technology.

And let's see, I think my argument, if you think about why solar, even nobody probably really will think that in the near future you get a 40% solar cell in the deployed. Of course, concentrating is another option, but there are a lot of problems with multi-junction solar cells. So why solar can make a, say, come to the map and people accept it? I think fundamentally is heated-- solar energy is free. So it's not like coal. Coal, say, any petroleum-based, you have to put in more money to get the fuel. But in the case of solar, you have free fuel come in.

So now you look at the thermal, how we use the energy now, you see, OK, mostly are fossil fuels. And the way we're using is conversion into heat and then into whatever mechanical electrical energy or just a simple heat. So heat is intrinsically connected in almost over 90% of the way we are using energy. So that's the one part, that's the input part.

And now you look at the output part, useful energy is about 35%. That means 65% is thrown away. And of course, thermodynamics will tell you have to throw away some. Let's say, we threw away a lot more than what's need in terms of thermodynamics. Because if you think about combustion process, right, let's take a 2,000 degree Kelvin. In thermodynamics, most of this is a high temperature combustion. The carbon cycle is over 90% efficiency. And we're throwing away 60%-- more than 60%.

So, in fact, if you think about your free energy, I said the solar is free, but you're throwing a lot of here also free. And if you can take that-- so, of course, you think of where it could be deployed. Is it here or is it here? I don't have a clear answer, but the gut feeling is probably this is where you will have this is a free energy. So you may have more, let's say, easier acceptance.

And of course, there are a lot of you where a lot of heat is free. But let's say, even in the case of heat is not free, I add this into this generated. If you think about the household, and say you burn fuel, but you just take a hot shower, that's where you generate heat. So this is a, say now you're talking about combined heat and power in your household. And fundamentally, of course, the solar is also the heat. So whether we can use it, with thermoelectric, you have to, at the end, calculate the cost.

In the real world, they say solar, even solar is still not competitive because it hasn't reached that cost level. So if you look at what's the solar cost. And per dollar watt, of course, it's progressively decreasing. And now the best, I think, the first solar is claiming they're about slightly below $1 per watt. So to reach the grid part, some people say already it depends on where you are. But I think, let's say, this is ideally equal. So ideally, you say this is where you want to reach the grid. When you say grid parity is really compete against the coal generation type of technology.

So it's a factor of three. And it doesn't sound to be very far, but it is a lot there. Of course, there are a lot of challenges to get there. Let's see. Thermoelectrics, I give one example. I think it's not the-- actually it could have say, even in the large scale for the application. Because this is actually a measurement found in the lab. So it's just a two legs, one and two. Each leg is about 1.5 millimeter cube. And so, this two leg, you have about 190 degree delta t, you generate about 80 milliwatt.

And 80 megawatt, so if I take that, I go to calculate the weight of the two legs and calculate the material price, and calculate the cost for this 80 mega from a material perspective, and they got about $0.10 per watt materials. And that's just to say, this is almost like a bottom line. So you have to pay for the materials. And of course, you have to manufacturer it, you have many other things together.

So the question is, do you go from here, say, to build anything that is cheap enough to be adopted? Of course, the efficiency, there are many constraints. In fact, the biggest constraint for thermoelectrics is, I think, of course, efficiency is the one. But the very different from solar is-- you have to have heat incoming and heat rejection. And those systems, of your systems, could be much more expensive than just a thermoelectric one.

So again, this is where I think a lot of you engineers really think where it could be used, where there are a lot of room for innovation. And the workshop I went to was organized by the Department of Energy, energy efficiency. And the focus there is the automobile, because the automobile now is the biggest driver for thermoelectrics because there's the waste heat from the engine. And so, if you think about 40% of the heat actually goes through the exhaust.

And it's a really government legislation. The government, particularly in Europe, there is legislation, I forgot the year, I have loads, that a few years down the road and the CO2 emission, there's a standard per 100 kilometer. And if you are one gram above that, it's a penalty of 95 euros.

So with the 95 euros-- so if you-- roughly you need a 3% fuel saving to get there, to get that three grams. And so that means the system has to be around 300 euros to have a few hundred, watt of 300 watt, let's say, 300 watt of electric power. So roughly, you have a $1 per watt range they are calculating in there.

I thought it's a-- automobile is the hardest problem. In fact, I was-- a BMW guy was saying the same thing. I was-- I agree with him, and I thought a lot of in the past. And if you can do automobile, you can do anywhere. So if that area is successful, I think there are a lot more impact. But unfortunately, that's also hardest because it has to be very space-constrained, very efficient, weight-constrained. When you add a weight to the system, you actually create a penalty. The efficiency of the automobile drops.

So there are a lot of constraints, but see, the dynamics-- it's there where the government is putting money. So unfortunately, thermoelectrics is very dynamic in terms of dynamic situation where the money came from, automobile, is driving hardest application. And which is not quite sure whether it will be completely successful or not. You are tackling the hardest problem.

But I thought that there are many other areas where you could innovate. Maybe it's not as hard, I think. Of course, the challenge is where the money is. So chicken-egg problem. But I think we need more success to stimulate the interest from both government and the public. And clearly, you see, I'm on the-- which side of the fence because I'm biased.

Now let's come back to designs. So I know that for many of you, it's a very steep dive. We start from nothing. I assume that the-- I hear from the engineers is a lot of those concepts. I was reading your report, a lot of those concepts are foreign, and we should expect it. Let's see. What I'm going to do-- to hope is to bring you to where I was yesterday, in the least today and the next lecture-- will be part of the next lecture. And where I was yesterday, there was talking about the most current topic in thermoelectric research.

So last time we're talking about the energy levels in solids. We talked about the lattice vibration, where the quantum of lattice vibration is a phonon, so basic energy [INAUDIBLE] of vibration. And of course, most of you-- I had a colleague when I was a UCLA faculty member. And he said in my course, three courses down the road, see, I don't still don't understand what is a phonon. It's not a real particle. Phonon is a collective vibration.

And you have a lot more easier acceptance to the name of photon. But if you go to think about what is the photon, it's the same-- you must have the same confusion there. What is a photon? Photon is just people talk. It's the electromagnetic wave, the quantized form of electromagnetic wave, the quanta of the electron.

And I took a course in quantum mechanics, and midway there was a substitute professor at Berkeley. And he asked the class, anybody understood? No student dared to raise their hand, understand the quantum mechanics. That's correct answer. Nobody else it. But see, what I think-- so take it-- let's go from there.

The phonon spectra in solids, and what's important in solids is their crystal structure. So in each crystalline directions, there are different, say, mass springs because the spring constant is different, even though it's the same atoms. Say, electrons in solid in different crystallographic directions, there are different energy levels for the electrons.

So we started with the simplest picture. But I said, I want you to get comfortable. If you read any papers, you'll see people show those complicated lines where in each crystallographic direction that's the different crystallographic direction. Very often use the symbols. And those are wave vectors, different wave vectors. Wave vector is 2 pi over lambda. So we think about the wavelengths, the waves. Different wavelengths have different-- each wavelength has a corresponding vibrational frequency. So that's the phonon spectrum.

And also shown at the end here, this is another concept that we introduced, density of states. So it's a number of quantum mechanical modes or quantum mechanical states at, in this case, per frequency interval. So it's a differentiable. So you can integrate this density of states over all frequency to get how many quantum states you have. So that's the phonons.

And the electron, again, you see here, different crystallographic direction, there is a different energy for the electrons, a different wave vector, which means the electron wave different wavelengths have different energy. And this is the case theta bandgap, not bandgap. In the case of silicon, the minimum of the conduction band and maximum of the valence band, the another safe spot, that's the indirect semiconductor.

And it's really this whether you have gap or not that determine whether you are metal, semiconductor, insulator. The insulator is a much larger gap. Semiconductor is a gap that's in the less than 3 electron volts. And gallium arsenide is direct gap, minimum, maximum is at the same wave vector location. And they have very different optical properties.

And then we give an example of how to calculate, again, [INAUDIBLE]. So how to calculate how many electrons we have in the-- so here is the most of those electron is in this region, the minimum of the conduction band. And when we do the calculation, we say this sub-states, that's the number of states per unit energy interval. Of course, we went through the summation to introduce the density of states. And then this is also the number of quantum states. And each quantum state, how many electrons we have, that's the Fermi-Dirac distribution. And they integrate.

So if you do a parabolic event, that's the-- say parabola, we can approximate-- always approximate, not always, but as approximation, when I have a minimum or maximum, I can say the first order derivative is 0. So the Taylor expansion gave me the second order. That's a parabolic band. So with that parabolic band approximation I have-- I can do a [INAUDIBLE] statistics. I can do this integration to get the relation of how many electrons is determined by ec minus mu. That's this guy.

It's this guy is really the [INAUDIBLE] potential. So [INAUDIBLE] potential determine how many the number of particles, electrons. And here is, say, the related to the effective mass, how flat this mass is, the curvature, how flat is this guy. So those are some of the key concepts that we learned in the last lecture.

And today I'm going to-- we learn the phenomenon. You read also Goodsmith's chapter on Seebeck effect. And today we're going to have more mathematics, going to have expressions for those coefficients. What determine the electric conductivity? What determine the Seebeck coefficient? What determine the thermal conductivity? So that's the goal here.

And I will still use the same picture I presented in the first class where I say, I look at how many particles are going from left to right and how many particles are from right to left, and the difference being the flux. And this flux could be heat flux. It could be charge flux. And so, with that, we will derive will have the mathematical expressions for all the transport coefficients.

So let me start with the electrical conduction. And electric conduction, in the simplest picture, would consider an isothermal electrical conductor. So there's isothermal, there is no Seebeck effect, just a simple potential flow. I have an electric field, and the electric field here, this is the most, for mechanical engineering, including me, the most troublesome point is the electron has a negative charge. So when I draw a field and say and charge go that way, that's a talk about electron.

And now, of course, under a field, electron experience a force. So F equals ma. Force of the charge experience is the charge times the electric field. Then you can charge for electrons. F equals ma. And so, that's the simple Newton's law of motion. But the electron will not travel very far because they will collide. They collide with each other. They collide with-- by the phonon, the lattice vibration also distort their motion.

So once in a while, between the collision, they go straight. Under the field, due to one collision they will change direction, trajectory. So the terminal velocity, I can do a integration of this, So I do a integration. I say, OK, this is the collision part where the free acceleration time, you can think that way.

And I say, this is the velocity the electron will get between each collision, the terminal velocity, that's also called the drift velocity. So you integrate that, you get drift velocity. And we can also write the e pi e tau divided by m as a mu. And the mu is called the mobility, it's [INAUDIBLE]. So we have velocity is proportional to electric field, drift velocity proportional to electric field through the proportionality constant the mobility.

And now, once I have the each electron drift velocity, I can calculate current easily. Why? The current is just a-- so let me just add one more. The mean free path is the time between the collision times-- now I don't use this drift velocity. This way I put a thermal velocity.

So what I mean is electron, they have two part velocity. One is they are doing thermal random motion. And in fact, that's a very high speed, 10 to the 6 meter per second. It is very fast. And so, and of course, so they do a random motion, that's a random thermal velocity. And then under field they have superimposed on that thermal velocity is a drift velocity.

And for mechanical engineer, that's the same with convection. Molecules move about 300 meter per second in this room. Let's say, the average velocity is 0. The convection is when the average velocity is not 0. So this is the convection velocity. That's the molecule random velocity.

And now, so this is the mean free path times-- so this is the collision, the distance between successive collision. That's the mean free path.

AUDIENCE: [INAUDIBLE]

GANG CHEN: Yes.

AUDIENCE: So this drift velocity is basically [INAUDIBLE]?

GANG CHEN: Right.

AUDIENCE: And the terminal velocity is already existing between [INAUDIBLE]?

GANG CHEN: Right. So even typically drift velocity is much smaller than the thermal velocity. Just the same as when we do convection. You're electric engineer, so that's easier. Let's say when we do convection, it's a meter, 10 meter per second is pretty fast, wind. But the molecule is 300 meter per second is moving around. Of course, the electron thermal velocity could be 10 to the 6. Yes.

AUDIENCE: Why is it the thermal velocity 0?

GANG CHEN: Thermal velocity?

AUDIENCE: Yeah.

GANG CHEN: Ah.

[INTERPOSING VOICES]

GANG CHEN: Anything, unless you go to 0 Kelvin.

AUDIENCE: But the average, not the repeat-- is that like the root mean squared? The average density has to be going in each direction, right?

GANG CHEN: Yeah. So the average of velocity is 0, but the magnitude is not 0. Right?

AUDIENCE: Right. But if any individual electrons use-- which one would that be?

GANG CHEN: This is the magnitude. This is not the vector velocity. It's the magnitude of--

AUDIENCE: So of each, it's not an ensemble property?

GANG CHEN: It's an average. It's a rough thing. So it's an ensemble property.

AUDIENCE: So it's like the root mean squared?

GANG CHEN: Right. So, OK, how you estimate it is 1/2 kvt, we said before, roughly 1/2 mv squared. So that's your thermal, because this is the thermal energy. And the kinetic energy, that's the kinetic velocity.

AUDIENCE: OK.

GANG CHEN: And the mass of electron very small. That's why it's much faster than the molecules. So now it's easy, because the current-- what's a current? Current is the left motion of a charge. So the electron coulomb number density per unit volume, number of electrons per unit volume, times here the drift velocity. This is the convection current. That's the electric current.

And you go to check the unit, you should-- I should have a unit here. I didn't put it there. That's the amp per meter squared. If you do a heat transfer, you will be watt per meter squared. This is a flux. You go to look at the unit. So this is a coulomb per second. Seconds come from here-- gives you amp. Here is a meter cubit, one more meter cubit, here is one meter, so give you a meter squared. So m per meter squared, that's a unit of current.

What is that? That's Ohm's law. So here is a few steps. You get the picture. You learn from high school, this is the Ohm's law. You have your current. It's proportional electric conductivity times the electric potential. The electric potential, if you do electric field, electric field is the electrostatic potential gradient. So that's right into differential form.

And in fact, this is a very similar-- if you take and replace this with a temperature, that's a Fourier law. So even though one is seems like a convection picture, the other seems diffusion picture. But they all collision dominate transport process. It's all collision laws, the diffusion phenomena. So that's the Ohm's law.

And now let's go to the isothermal in the previous case, now I'm putting a temperature gradient. I want to consider coupled transport. Thermoelectric is a heat and charge coupling. And of course, when I have a guilty-- say, a potential, I still got that convection drift part. What's different now is that I have a temperature gradient. So the molecule or the electrons-- and I'm used to talk to mechanical molecule. So electrons here go faster than electron here.

Now there is also diffusion flux of charge. So to consider that diffusion flux, I have from left to right and right to left. That's what I did for heat conduction before. So the electron flux law-- so here I have previous one from previous slide, the Ohm's law. That's the drift part because I have an electrical potential.

But also I have the diffusion part. This is going from left to right. This is from right to left. Again, I carry this negative sign, negative charge. This way should be thermal velocity. I should have been more careful. It should be thermal velocity because they are ranked randomly jiggling from left to right and right to left.

And the left for density, and in this region one mean free path you can go zip through. Longer than one mean free path, it will collide, change directions. So I'm only considering those whizzing by mean free path that can zip through from left to right. And then on the right to left, one mean free path can go half of them only. Because it go equally go in all directions randomly.

So this is the same way I did for Fourier law, the diffusion part. And now I do the Taylor expansion, the different-- expand over at x. So I do the Taylor expansion. I have e v x square tau even vx. And in this part, I'm just talking. I messed up a negative sign. See? That's what I say, I really don't like a negative sign in the electrons-- historical mistake. Can't have that.

And you know that, we just showed before, n is related-- the electron density is related to the temperature and the local chemical potential. ec minus mu is the chemical potential. That's what I reviewed from last lecture.

So now temperature depends on location, space. And ec minus mu, I can think of just mu, chemical potential depends on location. Because n really-- or say, mu determine n. So both depend on location. So if I take the dn, dx derivative, I have dx, dt, dx, give you many x.

AUDIENCE: The velocity is also [INAUDIBLE]?

GANG CHEN: Very good questions. I can't do that simply in here. So I just do 1/3 v square. Otherwise, I'll have to put it inside dm, dx. So that's why my coefficient will not be accurate.

AUDIENCE: How much is the thermal velocity different from Fermi velocity, the temperature?

GANG CHEN: Ah, thermal velocity is very different from Fermi velocity. This is-- OK. So some of you know all those concepts. But if you think about what's a Fermi level-- I briefly mentioned this before. In a metal-- I can take a simplest case. This is the electron energy level. In the metal, Fermi level is here.

So the energy of the electron is close to Fermi level because only those electrons are moving. The electron deep inside don't have any free space to move. So this one is the Fermi velocity. So m vf squared. So that's also-- it turns out this also is the thermal velocity. Those are the electrons, because the electrons do have this much energy. They will move around with this energy.

But in the semiconductor, that's the valence band, that's conduction band. And then you dope, and your ef may be here if you don't have it doped. That's what I was drawing before. So this ef, no electrons have this ef. Electrons only in this region-- because the thermally, a small fraction of electrons go there. So those energy is really-- this is just 1/2 [INAUDIBLE].

This is the relatively-- this kinetic potential is-- let's see, relative to the kinetic energy relative to here, 0. So. So the only is about the [INAUDIBLE] about the 1/2 [INAUDIBLE].

AUDIENCE: The key is the difference between the energy of the electron and the chemical potential?

GANG CHEN: No, not even chemical potential, only relative to the bottom of conduction band that you see there.

AUDIENCE: Oh, OK.

AUDIENCE: But can you [INAUDIBLE]?

GANG CHEN: Yes.

AUDIENCE: Yes, so it could be anything. It could be 0 degrees or like--

GANG CHEN: Yeah. Let's say, the average energy of those electrons near that conduction band bottom is about 1/2 [INAUDIBLE].

Yeah. So I'm going to clean this, take a derivative. My sign might be screwed up. Go to check. I mix it up again here. So here is what I have. I have this derivative. And also I have dt, dx derivative. So now I have the chemical potential derivative. Phi is the electrostatic potential derivative. And it turns out, this is when you do a detailed coefficient analysis, this coefficient and this coefficient is the same. So this is the fundamental.

It is also called the Einstein relation, because here is the-- related to mobility, and here is related to the diffusivity. It's chemical potential gradient gives you the diffusion of the charge. And here is the motion. So Einstein didn't do electrons. Einstein did Brownian motion, hypotheses in molecules in liquid. And he derived the relation between the molecular diffusion coefficient and molecular mobility in the liquid. And that relation turns out also to be true between electric conductivity, and here you can think that as an electron diffusivity.

So this is a general for the Einstein relations. And if you generalize even more it is the fluctuation dissipation theorem. So Einstein, that's his PhD thesis. If you were born at that year, you may be writing a paper say it's very important. He did the Brownian motion. And really, it's interesting to read that. He didn't even know there was an experiment on Brownian motion. So he studied statistical thermodynamics, the other branch of statistical thermodynamics. Before that it was Boltzmann. Boltzmann doing gas. Einstein tried to do liquid. And go to read. It's not that difficult.

So there's-- I said, if you say the conductivity is the same here, there's a relationship. And if we combine these two terms-- and I have rewriting this here into this equation here. And the temperature gradient I write into the next term. So I have an electrostatic potential gradient, a chemical potential gradient, and a temperature reading. So that's-- and so this three term that drives my current flow in the case when I have a temperature gradient in a conductor or semiconductor.

And I continue this. I combine some electrostatic potential with the chemical potential. That's called electrochemical potential. Some of you that do battery, you know the electrochemical potential in battery. And in fact, electrical engineers should also know that. It's not the electrostatic potential that drives the current flow, it's the combined electrochemical potential that drives current flow.

And most-- of course, most electrical engineers deal with isothermal. So you don't consider this term, isothermal. But you have to consider this term. So there is always electrochemical potential gradient that drives the current flow. And so, it's a very important concept, and it's hard to understand to some extent. Where is this electrochemical potential?

So I said, the ec, this separation here is the chemical potential. And electrostatic potential, this is when I'm drawing a conductor or semiconductor. And if I draw relative to an absolute reference here, this ec is parallel. So electrostatic potential depends on where you plot your reference. So I can always shift up and down because this is the gradient that determines really the current. So there's a constant reference point. So it's the gradient of this ec that gives you electrostatic potential.

And so I have ec here minus e. The problem is, e energy-- ec is energy. Energy divided by charge is the electrostatic potential. This is always a historical problem, not my problem. So electrostatic is here. Chemical potential is here. So what's left is this electrochemical potential relative to absolute level. It's that gradient that drives current flow.

So now I combine my electrical current. In the front, I just say this electroconductivity I generalized with the coefficient L11. And I combine all the two-- say, electrochemical potential gradient. So this is a typical-- the generalized Ohm's law, it should be this one, electric current proportional to electrochemical gradient is the electric conductivity as a proportionality constant.

And when I have temperature gradient, I have L12, it's the extra term, the coupling between charge and heat. So that's the L12 here due to the temperature gradient. And it's really here what they created the diffusion. Yes.

AUDIENCE: What is the electrostatic potential again?

GANG CHEN: Ah?

AUDIENCE: You're saying it's the same as the gradient of ec?

GANG CHEN: Yeah.

AUDIENCE: But then that cancel out [INAUDIBLE].

GANG CHEN: This one is the chemical potential. This is the electrostatic potential. The difference of these two give you the electrochemical. We can discuss more--

AUDIENCE: [INAUDIBLE]

GANG CHEN: He's the electrical engineer. OK. Now I'm combining everything together. And Seebeck is when there is no current flow. Seebeck voltage is an open circuit. When there is an open circuit, no current flow, you can say there is a temperature gradient, there is corresponding the electrochemical potential gradient. You put a probe there, you do measure electrostatic potential. You measure electrochemical potential.

The metal is connected to a semiconductor. When you connect it, the metal, let's say, is a Fermi level connected to the electrochemical. So you measure-- you can only measure this. But when we are doing one experiment and we really want to measure electrostatic potential, what are we doing? So we are doing, for example, we're trying to do, OK, there is a green boundary, green one, green two. And the green boundary there is an electrostatic potential. We can't measure it with the contact method, but we're putting-- trying to put an atomic force microscope.

And there, when they have-- there is electrostatic potential, it will be electrostatic potential determine the repulsion or attraction. And that's the coulomb's law. When you calculate use the coulomb's law, it's the electrostatic potential. So there's a-- still there are ways to-- I said the content method can't be distinguished, but there are ways to distinguish it.

So that's where the Seebeck coefficient is. Seebeck coefficient is defined as they-- ah. It really should be negative d phi dx divided by dt, dx, should be. So here is negative d phi dx. Then it should be phi dash minus phi z. And you can say, it's related to the Seebeck coefficient now can be expressed in terms of ec minus mu. That's chemical potential. Three, kbt is the thermal energy.

So the Seebeck coefficient has a very clear picture here. And this is the-- so you can set up two part. One is the chemical potential here. Between here and here, that's ec minus mu. And the electrons average is thermal energy in this region. But you ask me the vx is a random velocity. So that two-- 3/2 is not good. Because of vx I have to do integration averaging, and it turns out to 5/2 rather than 3/2. I'll show you more exact expressions. So now any question here?

AUDIENCE: Can you go back one slide?

GANG CHEN: Yeah.

AUDIENCE: Why do we have, in the graph, why do we have the position dependent energy level or the potential energy--

GANG CHEN: Ah, here?

AUDIENCE: Yeah. [INAUDIBLE] has a slope.

[INTERPOSING VOICES]

GANG CHEN: That's the potential of the electrons. Potential of electron is divided by electrical charge gives you electrostatic potential. Under current flow, your electron-- and so, the electrostatic potential is going downslope or upslope.

AUDIENCE: OK, I think--

GANG CHEN: When I think about downslope or upslope, I always have to sit there thinking for a long time whether it's positive charge, negative charge so I can [INAUDIBLE]. That's why I don't like the charge, negative sign.

By the way. I don't think, let me see, for a mechanical engineer, to understand this part, I have to sit there many, many times. And I think sometimes when you think you understand it, you have to ask the electric engineer, you understand it is problematic. But it's good to sit there and think through yourself.

Now, I said in the previous part that was the electric current. Now I'm going to do heat current. Peltier coefficient is a heat current. So I have to think about the heat carried by the electrons. And again, we did this in the first lecture.

When I think about the heat flow, Fourier law is from left to right, right to left, diffusion. Here you can see I put an equipotential conductor, low current flow, just a heat diffusion. That's a Fourier law. The Fourier law is valid for electrons and for phonons. I didn't say whether it's electron phonon here in this derivation. So I'm not going to this detail because we're writing down this before. And the thermal conductivity is 1, 0, 3, [INAUDIBLE]. So that's what we did before, diffusion.

And now I'm going to do charge focused on heat carried by electron. And what's the heat carried by electron? And here you have to go back to a little bit of thermodynamics. And the first law tells you that du equals dq. Doesn't look typical thermodynamics. For mechanical engineering you do du dq-- du equals dq minus pv-- pd, pv. There we'll not talk about pdv work. There's no volume change. So we'll talk about chemical potential. So if you're a chemical engineer, this part is easier. So du equals dq plus mu pn. That's a chemical potential term.

And what this tells you, because the du u is n times individual energy e if you have n electrons. So e minus mu is related to q. The heat-- so the energy of a charge consists of two parts. One is the chemical potential. The other is the heat. So e minus mu is the heat carried per charge.

And now, if I take that, I say The heat carried per charge is e minus mu, again, applied to the same picture going from left to right and right to left. So this is a velocity, random velocity, thermal velocity, number density per unit volume. And again, you go to check here, it should be watt per meter squared, the unit. This is a jar. Per second gives you a watt. And then it's a meter and over meter cubed gives you a meter squared.

So here I have left to right, right to left diffusion. I add an extra term here. Because when I do-- when I have a potential gradient, I'm looking at this case. Oh, I forgot to draw one. I should have electrical potential going down. I have current flow. I have temperature potential-- gradient. So that's the-- I'm considering coupled electron heat transport.

So this is the diffusion term. And this is the drift term. Same as I consider, now I go back a few slides, here. Diffusion term for current flow, drift term for current flow. Diffusion and drift. So let's look at it again.

Here is diffusion. And drift is-- this is a drift velocity times the charge density. And each one is carrying e minus mu. So this is the convection term there, convection of the electrons going through the surface we draw.

And now, if I combine-- because this term will give me the same thing as I drew before, electrochemical potential. And the second term I will have also the temperature gradient. So here I draw-- I made some jump. I didn't go through each step derivation, and you can go through that yourself.

And now the heat flux, what I have from this is the heat flux carried by the electron is temperature gradient terms but also is a potential gradient term. So I have, again a couple-- before I have a charge flux electric current, the potential gradient, temperature gradient. Now the heat carried by the charge is also proportional to the potential gradient and temperature gradient. So under equal, say, isothermal case, this is 0, but this is not. This is the Peltier coefficient. When I have heat flows through-- a charge flow through the current, the charge carries heat. So this is the L21 is the Peltier coefficient.

And so, that's the-- now I have the coupled heat and charge flow, and I have the two expression. One, before I wrote the charge-- if you go back to the previous two slides, this jex equals L11 times this plus L12 times this for the current flux. And now, for the heat flux carried by charge, I have Two. 21, L22, and then we'll come back and rewrite this expression-later.

So this is a kinetic. I have not considered the average. That's the question you ask. I cannot do that from this kind of picture. When you want to do the detail, you have to say each charge have different energies, slight different energy. So you have to count more carefully, just like we did before, counting all the modes, counting all the quantum modes. And each one is moving at a velocity-- local velocity, its own velocity. And each mode has this number of charge determined by Fermi-Dirac statistics.

And of course, this e could be either e, minus e, that's when I do current, or E, capital E minus mu, that's when I do heat. So if I do that, I can get the more rigorous expressions. And this is what-- you still get the same format except the coefficient is a little bit different. So I have this relation I've written before, same format. And those cross-terms, these two terms depends on how you write. If you write generalized thermodynamic forces are equal, but this is not generalized thermodynamic force, so it's related. So that's the [INAUDIBLE] relation. And the course term always related.

If you do piezoelectricity, there is also mechanical to electrical coupling coefficient in the case of mechanical motion. Or when you have current flow, quantum mechanical. So the reverse-- this coefficient, cross-coefficient is always related, and that's the also relation-- very fundamental. Also got a Nobel Prize for this. So that's the similar for the charge, flow, and for the charge carry the heat flow.

And now I'm going to write this. You tend to think, this is a thermal conductivity. That's not right. Because when I write, I could write my potential, rewrite it into a jex L12. So I'm replacing my potential in terms of electric current because the electric here, potential is related to temperature gradient.

And now if I substitute into here, I will say the electrical flux, heat flux carried by the charge is proportional to the electrical charge flux and with a proportionality that's a Peltier coefficient. I said this L21 is Peltier coefficient, that's not right, because this is a potential. But the Peltier is really current flux proportional to the charge flux. And this L21 divided by L11 is the Peltier coefficient. And the next term is the temperature gradient.

So only when I write into this form I have the expression for the thermal conductivity. In terms of for electrons, the thermal conductivity involves all four coefficients. L11, L21, L 1.01. Of course, these two coefficients are related. So this is the thermal conductivity.

And now if I write more clearly using the parabolic band approximation, again, here I'm not going to give the derivation, just say the same-- I follow those steps and do, in fact, I need to go forward to my equation. We're not going into that. And here is my final expression. This is a random velocity relaxation time, which could depend on energy. And before when we do it and we didn't say it depends on energy. So we have-- so this is a more rigorous expression. And density of states, and this is the other coefficient.

So with that, you can actually, using those coefficients, you can actually go to model the solid. And what do you have, the solid is really different solid have different density of states. So the band structure is different. And sometimes it has multiple bands, so you have to consider multiple bands' effects. Electrons have holes is another-- so you can see electrons-- negative charge plus the positive charge, and those could all be taken into consideration using this formulations.

Again, I don't expect that you'll fully say, be able to derive it. I didn't derive it. But this is where many people, when they try to interpret the experimental data, they go to those expressions and try to fit the expressions. I say they try to fit because you actually do not know exactly, for example, how to-- what's happening in the solid.

I said the electric conductivity, thermal-- electronic thermal conductivity that's in the previous slide, so those are the electronic conductivity here, electronic thermal conductivity. And the L11 is the electrical conductivity sigma. And the ratio of this, if you go to do Fermi-Dirac statistics in metal, you can do this integral. And turns out the ratio for metal is a constant. And this is a so-called Wiedemann-Franz law. And so that means thermal conductivity is very hard to measure.

So if you measure electric conductivity in metal, as long as the lattice contributions are large, you can roughly-- I say roughly because this is not always valid-- as we measure electric conductivity, you can go to estimate some of it just based on this interpolation Wiedemann-Franz law. So this L is the Lorentz constant, the Lawrence number.

Let's say, if you do semiconductor, it's not a constant. So in thermoelectrics, if you go to actually read thermoelectric literature, many people just take this Lawrence number and say, OK, I measure electric conductivity, and I want to find out what's the electronic thermal conductivity, I calculate. They will take this constant number, and they subtract the total measured thermal conductivity so the rest is due to phonon lattice vibration.

And that often leads to very, I say, varied result. You can't interpret those phonon, because they did a wrong calculation. In semiconductor, L actually depends on-- you have to calculate it. You have to go back to calculate the electronic thermal conductivity using this transport coefficient and the electrical thermal conductivity-- electrical conductivity. I'll give some examples later.

And again, so let's go back to look at what it means. What's the Seebeck coefficient? So if you look at it, that's from the previous expression there. And it's really, the Seebeck coefficient is the weighted average of electron energy relative to ef. ef really is mu, chemical potential. In electrical engineering, the chemical potential and the Fermi level is typically mixed together. They don't distinguish very carefully.

So ef weighed against the electric potential-- electric conductivity at each energy level. And that's really the average energy of the charge relative to the chemical potential. So that's still what I said before. And the electric conductivity is the density of states, velocity, electrical relaxation time, electron relaxation time, and efde. We'll show more later on.

So with that, now you can see why metal is not good. Metal is not a good material for Seebeck, because Seebeck is too small. For wide metal, Seebeck is too small. And this is because in the metal, ef is an in [INAUDIBLE]. And the average energy of electron relative to ef-- so the electron in metal is about half is above, half is below ef.

The electron below-- because the Fermi-Dirac distribution is over-- roughly over kt, that's the electrons. Only on this region kdt, in this region, there are multiple charge. And I draw too wide. It's really just this very narrow. Above is a positive heat, below is a negative heat. When they move together, the positive heat energy above the chemical potential move forward, energy below the-- electron below the chemical potential carry negative heat forward. At the end, they two cancel. So you've got a very small Seebeck coefficient. So metals have very small Seebeck coefficient.

And if anybody has any idea to cut this part off, you can one-- I don't know how to do it. Or cut the upper part off. So in metal, do you have width-- think about width-- how I can place something to scatter potentially half of this. So if you scatter the bottom part, you get a positive Seebeck coefficient, current flow-- heat flow in the same direction as the current flow. You cut the positive part, you get a negative Seebeck coefficient, the heat flow [INAUDIBLE].

So this is where, if you do materials research, you have to think hard on this, how you could potentially manipulate the material to create this asymmetry in the current heat carried by each charge. Semiconductor is better for Seebeck because, of course, here what I'm draw is this [INAUDIBLE]. If you think about this, I said Seebeck is the average energy-- so semiconductor, for example, if I doped it so that Fermi level is here, and the average energy is rapid here. So there is no negative part to pass through.

So each of this electron here is-- relative to the chemical potential is a carrier-- a positive heat relative to chemical potential-- no cancellation. Thermoelectrics are typically not here. They dope actually into here. So the bottom part is actually not good, only the top part is better. Why they want to dope it there is because, when you put your chemical potential here, the number of electrons here is very small. And the number of electrons is very small, so the electric conductivity here is, this is proportional to the number of electrons.

So what do you want? Because at the end, the zt is s squared sigma. Remember, zt figure of merit is the-- s is the Seebeck coefficient, s squared, times the electric conductivity, because you want the enough electron to carry the heat. You just don't want the one electron to carry heat, it just doesn't carry enough heat.

So you see here, this is a-- OK. If I look at this, what is df d? Fermi-Dirac is a very symmetric around the ef. A density of states is here. So it's really, in semiconductor, only this region. This two product is not 0. Only those regions is contributing to electric conduction if you look at this expression. And so, that meaning only this region of charge rather to the chemical potential is the Seebeck coefficient.

So you, later on, we will-- when we talk about quantum structure, people want to say, how you can make this region carry more charge. So you create a peak here. The distance of these states is not good. d is a square root of e minus e, ef, we show-- well, you see before. This is a very small density of states. So don't give you many carriers.

So that's where people do a lot of things when they try to improve electrons. They say, can I create something sharper in this region so I can put more electrons? So remember that, at the end, you want to optimize s square sigma. Not even optimal, just optimize that. You want to optimize ats so there are still some things were missing.

So this is the material side, the basic material physics. And if I go, again, to enforce my statistics, I said that the electrical energy scattering relaxation time depends on electron energy. So there are a lot of different scattering mechanisms. We're not getting into that. You go to do material research, you read literature. But if I do a gamma here, this is a potential power.

For example, due to lattice, due to acoustic phonon scattering, this gamma is negative 1/2. So what it means, negative 1/2 is a low energy electron, has a longer relaxation time. They travel further. High energy electron travel less. You don't like that. If you look at that, your Seebeck have a gamma here. And this is a-- not 3/2. If you do the before, that's 3/2. I said, it's five parts. That's due to this vx squared. This gamma is not good if it's negative, because if I think about acoustics phonon scatter, the high-energy electrons scatter. But I want the high-energy electron travel as far as possible.

But the ionized impurity, it turns out that gamma can be 3/2. That's very good. Of course, ionized impurity, so that means you doped material very heavy, you can have ionized impurity dominant. The problem is your mean free path become very short. Your electric conductivity becomes small. Thermoelectric is always a struggle. You try to sell to one guy, the other guy is not happy. And that's why the material research is very hard.

So and, of course, if I put the ec minus ef [INAUDIBLE] divided by n, and then you will see, because this depends on temperature-- so as the temperature increases, Seebeck coefficient increase. And the reason is that, if you look at this one, you go to check the reason, as you increase temperature, actually the Fermi level shift down. So the average energy now increases relative to the chemical potential-- Fermi level. So that's the reason why the Seebeck coefficient increases with temperature.

Well, I gave you a very simple one-band picture, although I know many of you say, this is pretty complicated already. Let's say, if you want-- if you do materials, you go to look at the real material, this is still the among the simplest picture I can give you.

But say, in real material, for example, I have electrons, I have holes, positive charge. It cancel each other, because when your electron mode see positive energy form of negative energy rather than chemical potential, they cancel each other. So Seebeck, for electron is negative, for hole is positive, and then you combine when you have two different electric conductivity or electron hole.

And what's worse is this thermal conductivity. They just don't not only combine electron hole and lattice vibration, but the combined-- they carry a cluster. This is because when the electron and hole both diffuse from one place to the other, there is an extra energy across the bandgap. That extra energy-- so when electrons go from one diffuse to the next place, they combine with the hole in the next place, they carry a lot more energy. So this is a bipolar contribution of thermal conductivity-- very bad.

And it took me several years to understand the bipolar. So even if you don't understand everything, you can still do research here. When I first wrote the thermoelectric proposal, I didn't know whether a metal was good or semiconductor was good, just to make you feel more comfortable.

Look at this. This is the real material now. And this is actually out of an experiment. This is a Seebeck-- electric conductivity decreases with temperature. Seebeck increases with temperature. I wonder you start to appreciate-- look at the curve, see what the physics, what's [INAUDIBLE] physics? So I said, Seebeck typically increases with temperature. That's all fine, except that now finally start to drop. See, that's-- you said that was wrong. I'll say why.

And if you look at the electrical number-- electron number density, then it will increase with temperature. So you think the electric conductivity should increase with temperature in semiconductor. But this is a completely wrong trend. If you think about n, go to check your n at the fourth slides, second slide I hand out, and that was a review from last lecture. The reason was that we dope this very heavily, and it's not-- almost like a metal. Metal, electric conductivity drop with temperature. So the carrier in the material is somewhere between semiconductor and metal.

Microelectronics, you never dope that-- you seldom dope that. And so, in microelectronics and most semiconductor, the electric conductivity increases with temperature. And Seebeck, when I start to draw, so that's because when I go to higher temperature, I got a holes. Electrons go excited from valence band to conduction band and left behind the empty states, left behind this empty state of holes.

So temperature increase, more excitation, more energy. You reject the electron from valence to the conduction band. You got holes. Holes is detrimental because they're canceling the electron. So when I go to high temperature, I start to drop there. The holes start to cancel. What do you do? You can dope it heavier. So this will have higher electron number, I shift to a higher temperature-- shift here. You can play with doping for different temperature.

But here you see these pics here. You have to optimize it. And you can, if you do mature research, you can just miss the optimization. You may get a goal, throw away. That could happen. And so, there are a lot of details, of course, in doing the material research.

OK, I think I will stop here.