GANG CHEN: How about we start by reviewing what we talked in the last lecture. We introduced the thermoelectric effects, including the Seebeck effect. When we have a temperature difference, a voltage is generated. That's the phenomenon. And that will give a microscopic picture of what happens with the diffusion of charge on one side of the path, the charge to the other side.

And the total effect is when we have a junction that made up two different materials, we pass current through it. You will have either cooling or heating effect, depends on the direction of the current. And this is because the charge itself also carry heat. So when the charge flow from one material to another material, if there are more heat flows out, then the junction cools down. And if there are more heat flows in the junction itself and you reverse the current direction, you can see that the effect is reversed.

And Thomson effect is when we have a uniform conductor, or semi-conductor, we have a different imposed time and the flow of current through, then along the material there is uniform cooling, there is a distributed cooling, or heating, that happens along the material. And this is because, really, at each section of the material, because the temperature difference, the charge, the electrons, carry different amount of heat. So that's the Thomson effect.

And then we did the analysis, simple analysis of a device. We have a real device. We pass current through it. There is a thermoelectric effect. There also undesirable side effects. The side effect is one, there's [INAUDIBLE] heating. And two, there is a reverse heat flow conduction, and this diminished degree the device performance.

And if we do the device analysis and find out that the efficiency, or the coefficient of performance, we found that those depends on, eventually, the material property which you will call the figure of merit ZT. And, of course, those are heat engines. So the pre-factor and the caudal factor, hence, something that's less than 1. If it's less than 1, it's dependent on the material property, and that 1 to be larger, as large as possible.

And then we discuss applications. I mentioned that at this stage, the materials is not competitive to replace the main refrigerators, or main power generator, like an internal combustion engine. So there are two directions to go. One, if you're an engineer, think about really using those there. You have to look at the system and the innovation where it makes sense from both the efficiency and, particularly, cost commercial product on the view.

And the other direction is go to improve the materials. So what we'll be talking in the next today's lecture and next lecture is on understanding what really determines the microscopic aspects of the materials, and what are the directions which you go to improve the materials. What are the ideas? So let me, again, start with this figure of merit ZT.

I said that when you do thermoelectric, so people say I work on thermoelectric. So when people ask you what's your ZT, right? That shows you know something about it. And I have three parameters-- the electrical conductivity, the Seebeck coefficient, and the thermal conductivity. And the thermal conductivity, the heat conduction in the material consists of two parts. One is the topical vibration. The lattice in the material, the atoms in the material, vibrate and conduct heat.

And the other is when charge itself, it carries states also conducted. So here, we decompose this k into [INAUDIBLE] and the electron. So those are when you think about ZT, you look at those parameters-- electric conductivity, Seebeck coefficient, and the [INAUDIBLE] contribution to thermal conductivity, electron contribution, thermal conductivity. And what I want to do next is to give you-- go back into more details.

So what are the microscopic pictures determine those properties? And what are the physical more together with some mathematical formulation for those properties? So today, we hope-- I hope you all power those topics. We will first review some basic concepts in solid state. And then using the simplest picture, that's the same picture I talked in the first lecture how we use a three step. I derive [INAUDIBLE], right? It's a really popular going from left and minus particle, from left to right, from right to left.

So with that imbalance, you will see we can come up with expressions for the electric conductivity, Seebeck, thermal conductivity, all those. And then I will do a leap of faith. I'm not going to the detailed derivation from this. You know we go-- we can go to more formal transfer theory and have the more rigorous expressions for the transport coefficients. So let me start. Like I said, this is a review, but I know for most of you it's new.

Because if you are, for example, from mechanical engineering, you have not seen this. So don't worry about it. You just follow-- let's follow through. Some of you will take this other result from wavelengths. Others, I hope the picture is simple enough for you to appreciate those pictures. So let's start with the basic concept. First, in terms of the atomic vibration, because atomic vibration in the solid carries [INAUDIBLE], right?

So now, I think about the bonding between atoms. You can think of this either solid or even just a hydrogen molecule. The bonding between the two atoms, two hydrogen atoms in the molecule, when they are far apart, they are attractive. And when they are too close, they repel each other because the electrons start to overlap, and they-- all the mechanics will say the basic principle is the exclusion principle. It doesn't allow the electron to take this [INAUDIBLE].

So we have a typical potential curve in the far separation between the atoms. It's attractive. And when they close, it's repulsive and the atoms sits in the equilibrium position. So when we have many atoms, they will have constraints on both sides. So they have the most stable position. That's where the energy is the minimum, right? Now, because this curve, the energy is a minimum. If you look at the mathematics, when I have a curve, minimum or maximum, the first derivative is zero.

So when I look at the expansion, I can expand this potential into the minimum point, plus, the first derivative is zero. Then I go to the second derivative. So you can go to higher order. But for the understanding here, we just go to second order, and then the force between the two atoms is just the derivative of the potential. So F equals the potential derivative. So I get a force equals the spring constant between the-- So now, we can take this two atoms vibration as a spring. So it's a mass spring system.

And for mass spring system, we all know the simplest picture is mass print. And there is a natural frequency for this vibration. The vibration frequency is the spring constant and divided by the mass of the atom. This is very relevant when you think about what material you want to choose for thermoelectric. And typically, the larger is the spring constant between the atoms. You look at this, the higher is the frequency, the more vibrational energy, the more-- the bonding of the atoms is stronger. There is a larger spring constant. And this will lead to higher thermal conductivity.

And diamond, for example, has the highest thermal conductivity among the materials, and that's because the bonding between carbon in diamond is very strong, and the carbon atom is very light. OK. So that's just a-- it has implications for this, even though it's very simple. And this is what we learn in classical mechanics dynamics, the natural frequency of vibration. And if you go to quantum mechanics, what it tells you is just a small addition, you know what I'm saying? The frequency is still the same. New is still the same.

But what it tells you is that energy cannot be any value. We all know quantum mechanics, the basics, the energy is complex. So if your oscillation is either this frequency in classical mechanics, the oscillation amplitude, the velocity, can be any value. And in quantum mechanics, we say the energy must be integer of this [INAUDIBLE]. OK. So that's the new thing coming from quantum mechanics. So it must be multiples of the Ishmael. And so this Ishmael, you can think of this as a basic energy quantum, and that's-- a solid is called a phonon.

And this one-half is also-- is related to the so-called uncertainty principle in quantum mechanics. It's also called the zero point energy. So if you recall before I talk about the photon, right, when we do electromagnetic waves, and this atomic vibration is analogous to the electromagnetic wave. So those are all waves. We'll extend this more to waves in the next step. So that's where the name coming from, photon for electromagnetic wave, and the phonon for lattice vibration. And that's the basic energy quanta of vibration.

OK. So this is a-- we're talking about the individual oscillator. And now, I look at the atomic chain. So when I think about solid, the most simple picture is a crystal. Crystal, a periodic arrangement of atoms. So now, I started with one dimension of atomic chain, and the distance between the atoms is the lattice constant, A. So we have N atoms. So the length of this chain is [INAUDIBLE] A. Now, again, you recall in the electromagnetic wave, the last lecture, I derived the Planck blackbody radiation [INAUDIBLE].

I say that when we consider a cavity in the length direction, I have standing width. I'm going to make the same argument. If I clamp the two ends of this atomic chain, do not move. Again, take a rubber band as an example. You fix this end, you oscillate it. You see the waves, different waves. And the violin is another example. So the length gave me-- those are the wave of the constraint. The wave has to be multiples of lambda, which is the wavelength over 2. So I have-- the length must be more than 2. It could be any integer.

And then the weight vector. Again, I'm talking about because of the weight, so the inverse of the wavelength is the weight vector is 2 pi over lambda. That's the definition. And the fundamentally is like the Fourier transform. If you're an electrical engineer, the time signal, or sine omega t signal. And here is key and frequency is omega. The relation is omega equals 2 pi over t, the same. This is a spatially periodic vibration, so the weight vector and wavelength relation is 2 pi over lambda. So that's a Fourier transform.

And so this is the same picture. I clamped the two ends of the [INAUDIBLE]. I have those other [INAUDIBLE] wave vectors. And I went this pretty fast in the last time I talk about electromagnetic wave. But I did say the standing wave. I did write the mathematics. You go to check. When I wrote the mathematics, I say I can do the summation of two traveling waves. One goes from left to right, the others go from right to left.

So here k is 2 pi over lambda. Those are the values. So now, I do the traveling wave. So rather than clamp the two ends, I say, OK, I don't have that constraint. The waves can go both positive direction and negative direction. OK. So in this case, the weight vector is pi over-- or minus pi over 8, 2 plus pi over 8. And two traveling wave will make a standing wave. So if you have the same wave lengths there. But also, if you compare what I wrote before, OK, I didn't put the [INAUDIBLE] limit, right? | this wave every vector can have any value.

On the other hand, when I think about very logically vector, what it means in a crystal, because the two atoms, the smallest distance is here. Now, if you have wavelengths shorter than that, it doesn't mean much. So that's why I say my wavelength is limited to here. If you look at this, this is a two wave. The two-- one atomic distance is A, so this is the minimum you can have in terms of wavelengths. So those are the region of my weight vector going from negative pi over A 2 plus pi over A.

Now, you think about the frequency. When I talk about the one atom vibrating, the frequency is K or M, square root of K over M. Now, I have the whole lattice, different wave vector. So each wavelength corresponding to one mode of vibration. And the thing about, if my whole atomic chain is one way, one way with pure, one pure, the frequency is higher, or lower, or same as my individual K over M square root. Anybody is making a guess?

AUDIENCE: If an atom was moving fast, yes, I'd say it's the same as the [INAUDIBLE].

GANG CHEN: Well, let's suppose-- again, let me take this as right. Now, all the atoms moving just one pure, all the moves. And then let's say is a one pure, and more pure since the frequency. Do they change, or they don't?

You probably can go back and do an experiment and put some beads or a rubber band, and then you'll find out the relation between the frequency and the wavelength.

In this case, it's changing, right? When all the atoms move in unison, when, say, only one pure, it looks like the whole atoms-- all the atoms in the chain is moving same time. So it's slower. The frequency is smaller. So that's-- in the long wavelengths, this is the weight vector. Long wavelength frequency is smaller. And when you go to larger wavelengths at the end, it's closed. Coming back to here, you can see, here is a K over M square root. So come back to individual atom and high frequency.

OK. So this is the relation between the wave vector. And the frequency is, again, the dispersion. Remember, for photon, for the electromagnetic wave, omega equals [INAUDIBLE] k. That's a linear dispersion.

And here, the real one we have is approximately half of a sine. This is like a sine function. And often, we do a linear approximation, take the slope. So the speed of sound is that that's-- the slope is for the longitudinal wave. That's the speed of sound.

So in solid, you lock one end, propagate to the other end. That's the speed of sound. And that's this slope here. And at a very high frequency, when you go to look at the mass of the atoms, you can see this frequency can go as high as terahertz or tens of terahertz. So very high frequency. Of course, the acoustic wave that we can hear is only a few 100 hertz.

So this is a simple one-- monatomic atomic chain. And now if I extend this a little bit-- suppose my chain has two different atoms. Gallium arsenide has a crystal. One atom is gallium. The other atom is arsenide.

So in this case, this is a white one here. So from the 22 atoms-- the same atom-- that's one here. Of course, this one simple picture is-- the outer atom is moving in unison with this atom. So they form the same face into two sets of subatom lattice. And in this case, the dispersion-- the relation between the wavelength-- wave vector and frequency-- is similar to what we drew before.

And in the other case, we could have this set of atoms moving up and the other set of atoms moving down. So it's a much harder stretch. We are very close. You are forcing them in terms of a different phase. It's much harder [INAUDIBLE] than the higher frequency.

So in this case, we have two type-- I'm going to have two atoms. One is the acoustic branch. That's the bottom part. That's this picture here, roughly. The other is the other phase. That's the [INAUDIBLE] approach. So that's the atomic vibration in one dimension.

And of course, a crystal is not the just one dimension. A solid is just one dimension. It's three dimension. So any direction you look, it look like you got a one-dimensional periodical arrangement. It's just that space in between the atoms will be different.

So how we express it? So here, we'll go back to what I said before-- Fourier transform. And the periodic signal-- if the period is t, We see the frequency is the 2 pi over t. And in terms of wave, we want to mention wavelengths of the lambda. And the Fourier transform is 2 pi lambda.

But in three dimension, each direction has a lambda. If I look at the crystal, a cube-- take a simple cube. Put them periodically arranged. You look at the other direction. The period is cubic 3-- no square root of 3 times the lattice constant a. So that's your periodicity. You look at, say, a different [INAUDIBLE] you have different periodicity.

So what I do is I transform this periodicity in space. Let's say I take a crystal-- and say, here is a, say, face on the structure-- face on the cube. And we add a face on the surface. There is also an atom.

And I do a Fourier transform of this space in three dimensions. That's what it looks like. Now it looks a little bit ugly. But I can say each crystallographic direction here is a p direction, And the shortest distance, L-- this point-- is the longest real space because the k is 2 pi over lambda.

So if I think about this from center to this point, the shortest, I know for a cube, that's a 111 direction. It's the universe of the atomic space.

So this is a way that the physicists like to use the reciprocal space. I joke with them-- I say, you guys don't live in the real world. They like to express things in the reciprocal space.

So now let's look at a simple-- in terms of mathematics-- expression of this, You go to electrical engineers. They like to do signal analysis and frequency. They don't do time signal. Time signal-- you have to plot the time. You do a hard spectral analysis, you can use frequency. It's a much simpler mathematical language.

So now you get to the real world because that-- before, it looked very simple. Now you can start to look at a string. For most mechanical engineers, you look at this, and you'll get the-- what is that, they'll say. It's really looking at the different crystallographic direction, the vibration frequency.

And if you look at this all silicon gallium arsenide or phase-centered cubic, as I do before, different crystal has different-- those different directions-- different reciprocal-- the shape of this basic unit cell in reciprocal space. So I look at the gamma direction. So this is diagonal, from this to this-- diagonal direction.

So if I look at that direction, what's the vibrational situation spectrum? So if I have the lattice wave propagating in the diagonal direction-- so that's from gamma to L. And those are the optical phonons. Those are the acoustic phonons. Acoustic phonons start from 0 here. Optical is from the top of the acoustic.

And why I have different branches-- I have different branches because the vibration-- the sound wave you receive is longitudinal. Here, is longitudinal wave only. But in solid, you can have longitudinal as well as transverse. You can sustain the shear.

So I have a longitudinal wave, transverse wave. And really, transverse-- if you look at the electromagnetic wave, I said there are two polarizations. See, acoustic wave transfers also two.

But in highly symmetric direction, like from gamma to L, in this case, this is [INAUDIBLE] symmetric. So the two directions-- this direction and this direction-- the same wave vector-- they have same frequency. So they become degenerate just for [INAUDIBLE] one.

But in some other direction. It's not highly symmetric. You can say there are three polarizations-- longitudinal, one longitudinal, two latitudinal. So acoustic branches, optical the branches. That's the station from 1D to 3D.

AUDIENCE: What is the spacing between the different wavelength vectors?

GANG CHEN: Different wave vector-- the spacing-- those are experiments. The data is comparing experiment.

AUDIENCE: The frequency should be in hertz or [INAUDIBLE] frequency is in the hertz?

GANG CHEN: Frequency is-- if it's omega-- so this is another thing that, very often, people get really confused because it depends on who likes to plot out what. And sometimes-- here is k-- omega. And sometimes you'll see this one is not [INAUDIBLE] terms of the frequency. This is centimeter inverse.

Well, that's not the frequency unit. So what they mean? And in this case, if you want to look at-- the first frequency is 2 pi mil angular frequency. You have to say what exactly is a better plot, the angular frequency or frequency?

And mil is-- if we practice wave vector inverse, we plotted 1 over lambda. So you have to have to convert the frequency equals to c. What about lambda? So people have different habits. Yes.

AUDIENCE: This is speed of sound or speed of light?

GANG CHEN: Huh?

AUDIENCE: Speed of sound or speed of light?

GANG CHEN: This is the speed of sound. Oh, I'm sorry. I'm sorry. Speed of light.

AUDIENCE: OK.

GANG CHEN: Yeah. Not speed of sound. When they do this kind of expression, they always go the speed of light. Speed of sound is different for different materials. So you're asking, what are the wave vector numbers?

So this is where the number of waves-- when I go from here to here-- well, this is called from pi or a minus pi over a to plus pi over a. That's called the first [INAUDIBLE]. And the number of wave vectors, k, equals the number of atoms you have.

So these points-- from here to here-- the number is n. That's actually important later. This number is more important when you do counting. Once you go to microscopic picture, you do the counting.

AUDIENCE: In silicon dispersion relation, we have a mode that seemingly correspond to the optical mode in gallium arsenide. Then what will be-- the mode will look like for the silicon at the top of it?

GANG CHEN: Oh, they'll be optical modes. Well, it turns out silicon is a one lattice point. How many atoms? And the silicon is-- in one lattice point, you have two atoms. So there is another atom-- see that the one quarter, one quarter, one quarter. If you think this is one, there is another-- this is a lattice-- this is the point-- a lattice point.

So there is another atom at the one quarter, one quarter, one quarter. And it's not-- it's an FCC, but there's two atoms. If there are two atoms, that-- say, in the lattice point, if there are two atoms, then there's three acoustic branch-- three acoustic branch. And then there are another-- so two atoms, n minus 1-- so times 3. So there are three optical branch.

If you have three atoms, you have three acoustic [INAUDIBLE] branch, then you have six optical branch. So the total is 3 times n. That's n. At every lattice point on an atom [INAUDIBLE].

AUDIENCE: What's the direction of the two transverse wave?

GANG CHEN: Roughly, it's perpendicular. But when you actually do it, you have to solve the dynamic matrix. You have to solve the matrix to find out the exact direction of the vibration, so the eigenvectors. You can always decompose. But there is an eigenvector that you should go to solve the equation of motion. You can solve the Newtonian equation of motion to get those eigenvectors.

OK. That's all about crystal and vibration. And now let's see the electrons. I started with crystal vibration by hydrogen molecule. I have the two atoms and the separation spreads, [INAUDIBLE]. And when talking about electron, let's also start with hydrogen. This time, I'm starting the hydrogen atom.

And the hydrogen atom-- again, you know quantum mechanics-- this is the energy levels of a hydrogen atom-- electrons, in this case, I'm talking. And the electron-- the energy level-- I didn't even write it down.

You can see I wrote-- so E of the electron is dependent on the n-- is minus 13.6 electron volts n square. So what is the one-- so let me say-- if my electron volt is one electron mode in-- one charge of electron in one mode and one voltage-- for electric field, one voltage.

And that's the energy of the electron. And this is the inverse, 1.6 to the minus 19 charge. So that's the energy of the electrons in the hydrogen atom.

And its electrons are moving in three dimensions. And so when I solve the Schrödinger equation, I'll find the wave function. Again, this is going in quantum mechanics. We're not going to do any quantum-- I'm just introducing the basic concept.

And it turns out because we have a three dimension, r theta phi is in three-dimensional space. So there is three quantum numbers, n, l, m. Those are all results of quantum mechanics, except that in s, you have to go through even relativistic quantum mechanics.

And those n-- you can see now-- all integers. The quantum number-- n is [INAUDIBLE] 1 to 3. All those integers-- L must be less than n. m must be less than L. This is all mathematics-- coming from mathematics.

But what it really means is I wrote down that-- I forgot to write the energy. Energy is minus 13.6 electron volts divided by n squared, so energy doesn't depend on L and n. It depends only on n.

So when n equals 1, I have-- L has-- you look at it. L has to be 0 L has to be 0. And the S could be plus or minus 1/2. So there are two quantum states.

So here, I have two quantum states. So if you look at the theoretical table, that's why you have hydrogen, helium, failed. Helium is stabled. Two failed. And the next quantum level, you go to a plus 2. It's pretty far away from the first level.

So you look at the periodic table again. You fail. This is the one quantum state. One quantum state can only have one electron, [INAUDIBLE]. That's the one I've seen as a different state.

So hydrogen, helium, lithium. Lithium is [INAUDIBLE] 2s now. So when you go to continue to look at the periodic table, you fill in. Here, each energy level is 2n. Once you go to n equals 2, the number of-- total number of electrons you can have, up to filled all the orbital-- the quantum state is n plus 2 is what? 8, right? 11.

So that's the hydrogen atom. And this is a basic model for the periodic table. Look at the periodic table. You can use this and pretty much interpret a lot of those first 30 atoms of [INAUDIBLE].

Now, I'm going to, again, say-- starting from here, I'm going into a [INAUDIBLE] chain because I want to understand electrons in solid. So a [INAUDIBLE] chain-- I'm thinking about hydrogen as a simple example, but the hydrogen [INAUDIBLE] gas, and then thinking about the solid.

And so electrons-- they are waves in quantum mechanics. So both waves and particle characteristics. So waves-- each electron has those wave function as part of [INAUDIBLE]. This is the wave function. Quantum mechanics will give you this function.

And now they are waves. So let's plot a plus 1, approximately. And they spread out-- not just confined to one electron. And now, this is the next atom, a plus 1. They start to overlap with each other.

What happens? And these two electrons from the two atoms both will have the same states because once they start to overlap-- once they start overlapping, the state of the two atoms are the identical states. And the basic quantum mechanics doesn't allow it.

So the state will start to adjust a little bit and form back. So now n equals 1-- this is originally n equals 2, 3, 4. Think about-- they started forming bands. So there are-- if you have n atoms, again, in the chain, between here and here, I have an n point.

And each point now-- they start to-- you can see here [INAUDIBLE] different and those same allowable weight vector-- now electron is a wave, extended through the whole lattice. This is one quantum mechanical state.

So the waves can have different vectors, different period, same as we argued for the lattice. So that's-- a basic quantum mechanics dictate. The energy has to split a little bit, forming, now, a band. It's quasi continuous with [INAUDIBLE] continuous because that k-- there are many k points. But they still return here. So here, the endpoint depends on the n for your number of atoms in a chain.

This is very interesting. because even this simple picture-- I said the hydrogen picture tells you the periodic table. What this picture tells you-- whether you have an insulator or conductor.

Let's think about-- again. If I think of hydrogen as a simple extreme, each hydrogen has one electron, So when the electron field go to the energy, the lowest energy level fails first. They're lazy.

Now, thermodynamics tells you-- everybody wants to go to minimum energy space. So if I have n atoms, I have-- between here and here-- n point. Each point has a spin [INAUDIBLE]. The spin is not reflected in this curve.

So each point has two states-- to spins, s equals plus minus half. So now I start to fill the bottom electrons-- if I have hydrogen, There are really two end quantum states. I have only an electron. Where it goes? It fills about half, right?

So the electron maximum [INAUDIBLE] energy will be somewhere in between the band. So this is where-- it depends on [INAUDIBLE] field here depends on how many electrons you can fill to within the band. And it's either 0 temperature-- 0 Kelvin, this point-- where [INAUDIBLE] just think about the water-filled bucket. The [INAUDIBLE] energy level is [INAUDIBLE].

And so if it's a non-zero temperature, those electrons do not move. They need a lot of energy to move because there is no quantum state in this, here, quantum mechanical-- no state allows energy to move to-- when they move, they change state. The state has to be adjacent, allowable in the solvent. So only electrons in this region are movable.

And in metal-- because the next state-- just close to this point-- they're very close. The energy difference is very close. So the thermal energy is large enough to allow them to go to the next state. So only when your electrons fill to level their empty state in the band it's a conductor. It's [INAUDIBLE]. That's [INAUDIBLE].

And what happens if my number of electron filled here? Then it needs a lot of energy. Depends on the difference of the energy here and here. If this difference is very large, you've got the insulator. Electron cannot move.

So this-- from the [INAUDIBLE] of electrons to the empty state-- that's the band gap. And if this band gap is very large, that's an insulator. How large is large? A few electron volts.

And this is because at room temperature, we said that, in the first class, the energy is about kdt. k is the Boltzmann constant times temperature, thermal energy. And that's about 26 milli-electron volts.

And so if this one is a few electron volts, much larger than kdt. So very, very few chance electron can come over here due to thermal. And that's insulator. But then for this gap, it's not large. Plus, for example, this is an insulator. And the gap is a view of about 4 to 5 electron volts.

Now, silicon-- that gap is about 1.12 electron volts. [INAUDIBLE] So silicon becomes a semiconductor because this gap is not very large. And if you cool silicon to 0 Kelvin, it should be an insulator because there's not enough thermal energy to kick the electrons from here to here.

But at room temperature, the thermal energy, kdt-- because of the thermal energy some electrons are kicked from here to there. And if they are kicked from here to here, what's left behind are some empty states.

Now, those electrons-- those other electrons are happy now. There are some states they can move. And these outer electrons that kicked up is also happy because there are also empty states they can move.

So the motion of those electrons-- those electrons-- it's much easier. So you can think of this-- the thing that's really moving is the electron moving because there are empty states.

But it's much easier to think them as positive charge. So don't think those are electrons. Just think of those empty states as holes. There's no hole. No positive charge. It's electron that's mobile. But we just think this as a whole positive charge, and those are electrons.

And you can even put-- so that's an intrinsic silicon [INAUDIBLE], right? But you could even put the impurities into silicon, into semiconductors to add more electrons or add more holes. So when I add-- for example, if I put a phosphor in silicon, phosphor has 5 charge. Silicon is 4 in the outer shell. So there's one extra pair of silicon.

So that extra-- because it's very close. The energy level of phosphor very close to here. So that electron can easily be excited to this region. So it's an n-type semiconductor.

And on the other hand, if I put boron into silicon, the outer has three. So the born energy level is somewhere here, close to the bottom of this band. This is the valence band. This is the conduction band.

So the energy levels here-- those electrons are much happier to go here, so left behind holes. So boron becomes an acceptor, entrap the electron. And they create the holes in those bands, anticipating in these bands-- that the electrons [INAUDIBLE].

So that's how you do doping in semiconductor. You create the energy states. Sometimes even impurity-- even frequency could create those additional states. In silicon, we do artificial doping, when we do thermoelectric material's weakened state, a missing atom could create those kind of situation.

So the doping in material-- in thermoelectrics, doping is very important. Of course, this is true for all semiconductor device. Any questions?

Let's move on. Look at the real material now. That's a one-dimensional picture. And I look at, again, three dimensions. Go to the virtual reciprocal space. And 111 is the gamma 2 L point direction. 111-- I only do one half of it because it's symmetric.

Positive wave vector, lengthy wave vector symmetric-- I draw half to save space. So this is a gamma to x that went 00 direction. And it turns out the silicon-- the maximum point where this electron fill to-- at the valence band. And the minimum point-- that's the conduction band. They do not agree in terms of the wave vector. So this is an indirect semiconductor.

And gallium arsenide, on the other hand, is a direct [INAUDIBLE]. There's a big difference in these two materials, direct and indirect.

Microelectronics industry is established on silicon. But the lasers-- semiconductor lasers-- nobody can use silicone to make semiconductors. People are making progress. It's much more difficult to make a laser out of silicon. It's a direct gap. Semiconductor is much easier.

The reason is that in the gallium arsenide device, microelectronic device, you reject the electron here. You eject hole. That's by design. You put a current, and you actually inject it into the material. And then the electrons flow off to the bottom of-- recombine from here and here-- give off a photon.

It's much easier to do that in direct gap because there's no wave vector mismatch. And here it's very difficult for electron recombine with the hole. Well, you see that's good for solar cells, Solar cells-- you don't want recombination, really, if you want to get a charge. But there are various points.

This one-- solar cell is not good. It doesn't absorb well. You can't create-- when photon comes in, a photon-- The wave vector-- the wavelength is about 1 micron. Wavelengths of photon-- a half micron. You think about the visible light-- half micron.

And the wave vector of photon is 2 pi over lambda, 2 pi over a half micron. And here is pi over aa is lattice constant, a few angstrom.

So this is a few angstrom. If it's a 2 pi over a half micron, that's exactly-- almost right at the center. The wave vector of photon, very small. Wave vector hk-- h over lambda is momentum. Momentum of photon is very small.

So in gallium arsenide, the photon comes in and go-- you go from here to-- if the energy is large enough, you can lift the electron from here to here. That was all.

But in silicon, because they interact-- the semiconductor, the photon momentum is here. You cannot leave the electron from here to here. Doesn't have enough momentum. It has enough energy. What can solve that problem? Some method. You solve a huge problem.

See, this is a really-- even in the microscopic world, it's the energy conservation, the momentum conservation. You learn either in continuum or in discrete. That always [INAUDIBLE]. So silicon don't absorb well. Gallium arsenide absorb well.

If you look at a gallium arsenide solar cell, people use the same field. They absorb well. Silicon-- it's very hard to use the same field, because they don't absorb. So your compromise is make thicker for that chance to happen.

AUDIENCE: [INAUDIBLE].

GANG CHEN: Ah, yes. But that's exactly how absorb happens. You need a phonon. Phonon has that wave vector. Phonon doesn't have enough energy. The omega is too small. So phonon plus the photon-- phonon gave you the vector. Photon gave you the energy. Can lift it from here to here. But you've got three particles to work together,

Think about your coordination at MIT. You get three professor together. Much less chance. That's the probability. We'll have that experience.

Now we're going to do a little bit more. That's the basic idea of the energy levels, vibrational energy level, and the electronic energy level in solids. And I'm going to do a little more. And I approximate-- first, I think about the free electron. The kinetic energy-- 1/2 mv square.

And mv square-- quantum mechanics say-- first, m comes away as the momentum. So p squared 2m-- that's the relation from p as the m wave. And in quantum mechanics, p is hk. Oh, I got h squared. Sorry. It should be h squared k squared over 2m. So that's a free electron.

For the electron in the solid, I'm going to do a similar thing. Because this-- here is a maximum. Here is a minimum. Again, the first-order derivative is 0, unless this is a very sharp. There are some cases it's not-- the derivative is not continuous. So the band is not a part of-- what I say is it's not a continuous curvature here.

But see, most of-- this maximum-minimum-- the first derivative is 0. So I have second-order [INAUDIBLE]. Mathematics I extension. So here, if I, for example, take a [INAUDIBLE], of course I put a k. I didn't put a k. This is not 0, so I should put kx minus k0 square. Here, I put the center at the center. So this is the sigma general, not the most general form of doing the mathematics,

And here, it looks very similar to free electron. This is just a second-order derivative of the curvature. Now, if I treat that just as a mass, equivalent of mass-- if I call it effective mass, then it's a free electron. I can do the rest of my work as a free electron.

So mathematical simplification. Here are the effective mass of the electron in the crystal. If I take the effective mass, I write this pretty much like a free electron. So I'm going to do free electron, most of the time, except replacing the mass.

So this is, again, my dispersion relation. Before, I said dispersion relation between frequency and wave vector. And now, if you think about energy relate to frequency, that's new. So frequency, wave vector. Except for electron, people don't talk to a frequency. People like to talk about energy. Close relation between the vector frequency or the vector-- and energy dispersion relations.

AUDIENCE: So the effective mass is different for every direction?

GANG CHEN: It could be different for every direction. In some case, it could be isotropic. Next one-- let me show you. If we take the energy as constant, I do this.

So if you look at this, this is-- OK, what's the constant energy surface looking like? In 3D, If these are the same, it's a sphere. They are different. They are ellipsoid. So this is what's in gallium arsenide. This is a silicon electron. End of story.

So in this case, we say, OK, there, you got six pair of pockets, different directions. And this is just a review. I showed this before. Now we know what is phonon, what is electron. And Fermi-Dirac distribution is for electron. Bose-Einstein distribution for phonon and photon. Most of the time, this [INAUDIBLE] is 0 because phonon and photon are not real particles.

That's another way they are not real. They can disappear. Electron also disappear. But the most of the time-- and not disappear. Electron cannot disappear. Electron is the real part. As we go from conduction band to valence band, we combine-- just [INAUDIBLE] the electron still is there.

OK, now I'm going to do math. The constant. I'm going into more detail constant. I say, OK, I know about semiconductor. Yes.

AUDIENCE: Sorry. Is there any [INAUDIBLE] mass conservation or effective mass conservation [INAUDIBLE]?

GANG CHEN: Mass conservation for-- good question. I don't think we can talk about mass conservation for-- under the effective mass picture. I'm sure this is the only from-- I think mostly from [INAUDIBLE]. Electron-- of course, the true math is still the [INAUDIBLE] 0.1 to 0.31.

But in the solid, when you look at the transport, I see the free electron. Then usually fill the [INAUDIBLE] of the background, lattice. So now they feel either heavier or lighter than the free electron mass, which is 0.1 to 0.31 [INAUDIBLE]. Yes.

AUDIENCE: When people do the [INAUDIBLE] structure calculation for electrons, do they assume independent national approximation? If they include [INAUDIBLE]

GANG CHEN: I think they should include the electron-- for example, you do a density functional theory calculation. They will include the outer electron effect. And you don't do-- just an independent electron. You have electron influence the other electron in the same atom.

So now I'm going to do a spherical-- I'm not going to do parabolic or elliptical, but I'm going to do a spherical [INAUDIBLE]. And it's the same in all directions. So that's a really like a free electron, except that this mass could be different. Like I said, it's good for gallium arsenide,

Let me suppose-- I want to find out-- if I dope the material, how many electrons I have in this conduction band? And I'm going to do counting. This is a strategy that I use. And I use before same for photon. I did that photon in cavity. I count how many photons in the cavity. So now, if you remember, each quantum mechanical state can have one electron.

And in the state, what's the average number of electrons is given by Fermi-Dirac? Maximum one electron, right? We said in the-- this is the average given a certain temperature, quantum potential, average number of electrons in one quantum state.

Now I just need to see how many quantum states I have, right? One quantum state, this is the average number of electrons. So I just need to-- really, all those counting looking very complicated, it's just counting quantum states. And before, when I do electromagnetic wave, I was counting electromagnetic modes. Same way. So all that counting-- counting how many modes, the modes is essentially a state.

So I'm counting. So in the x-- so it's 3D-- kx, ky, kz. And kx, I have nx number, n atoms in the x direction; ky, ny number; kz, nz number. And the factor of 2 is because I have spin, electron spin 1/2, positive/minus-- negative. Electromagnetic wave is a factor of 2. If I want to do full arm, maybe it's a factor of 3 because my [INAUDIBLE] if they are all the same.

And so this is the number of quantum states. And this is, at each quantum state, what's the average number of electrons. You can think that for a phonon or for a photon, it's all the same way, all right?

AUDIENCE: Gang, so it's counting the wave vector, it's counting the number?

GANG CHEN: Ah, well--

AUDIENCE: Why is it number minus the nz over 2?

GANG CHEN: This is a-- yes. It's counting the number. But see, then I do the integration conversion.

AUDIENCE: Yeah. I see you're counting the wave vector.

GANG CHEN: OK. Here is-- I'm counting n. These are the discrete states, right? And then this is a standing wave picture. So everything's positive. And when I do traveling with two directions, I said that these are equivalent, OK? So that's why I go from negative n 1/2 to positive n 1/2. It's just equivalent. OK?

Why I count the numbers? Because my next step is convert the number into integration. Because we're counting states, right? It's better to do integrated states rather than fractional number. This is the number space.

That's where I convert this-- if I think about wave vector, k is a continuous function. And between two states, that delta k is 2 pi over l. So this is converting this integer summation into-- no, this summation into integration, right? I did that same thing when I do electromagnetic modes.

So in the x-direction, if this is the length, but the next two adjacent k-- n is 2 pi over [INAUDIBLE] x, so this is the number converted into here, [INAUDIBLE] down here. So here, I have the integration kx, ky, kz. Those are all mathematics converting-- so the conversion and the counting. And then the reason I want to do this now is I have an integration dkx dky dkz. And 2 pi now, I have is an 8 pi cubic. lx ly lz is the volume, factor of 2.

And now the f-- I'm going to just ignore that 1. Plus 1, that's Boltzmann approximation. So the Fermi-Dirac distribution. OK, so I'm plugging this f already here. So that's my number of electrons in this region, in the conduction band.

OK. I encountered this classical problem. My integration is over a wave vector. My function is over energy, right? Same thing in the electromagnetic wave. My function, my integration is over kx, ky, kz. My function is over energy. And I have to choose either energy or wave vector as my variable to do this integration.

I already have the relation between E and k. That's my problem here, E and k, right? So I'm going to do that conversion. In this case, it's much easier for me to convert dkx, dky, dkz into E because you can say that's a Cartesian coordinate. I can convert it into spherical coordinate. And so I'm doing this conversion. Now I do per unit volume number density. And I do that dkx, dky, dkz. In spherical coordinate, k would be magnitude. So it's 4 pi k squared dk.

So that's from Cartesian to spherical function and variant. Now I replace because I know the k, k square is 2 me minus Ecx squared, right? That's the expression. This is a ac squared times k squared. Now, k is my radius, like r, right? So I replace this k square. k square equals 2 pi [INAUDIBLE] minus c over x squared. dk becomes this d. And everything is in [INAUDIBLE].

This will be same thing you do all the time in counting the numbers in crystal. You convert the states-- number of states summation into integration. You choose your integration variable, either in energy or wave vector. And if I group everything all together, this is my f. And this one, I call it the density of states.

OK. It uses-- it's mathematics. [INAUDIBLE] nothing-- physics wise, you don't have much physics. It's just a mathematical way of converting my summation into integration. So this is the number of quantum states per unit volume because I normalize the volume. And per energy interval, because here is d, that's a physical interpretation of my derivation.

And in fact, if you go to look at this one, you can do the integration [INAUDIBLE]. That's why I use the Boltzmann distribution. If I put a Fermi-Dirac-- if I put a, say, 1 over this, not this, plus 1, I can't do this integration, OK? So the reason I use the Boltzmann distribution is that I can do this integration, and this integration gives me-- here is a kpt, and here is E minus c maybe exponent.

So how I determine the chemical potential mu, if you give me the number of dopant-- so I put a phosphor in the semiconductor. Per unit volume, I put how much. I know that. And if I assume each phosphor donates one electron-- assumption, right? And there are more rigorous statistical ways to say how many electrons are activated. But because phosphor energy is so close to silicon, so you can roughly approximate this. So every atom that you put in there donates one electron.

So with that, I know the left-hand side. I can do the inversion. This is where my chemical potential is. So chemical potential is determined by the number of carriers you put in. And then you will see thermoelectrically, you have to optimize this carrier density to get the maximum performance. OK. So let me summarize this, right?

This way of doing the-- converting it to the number counting, you can always start with that summation, I said. But at the end, the most times you will end up with this density of states. It's just that you derive [INAUDIBLE] state. Every time. Once you become comfortable, you can say, OK, this, I can write it directly the number of electrons per quantum state. This is the number of quantum state per unit volume per energy interval times [INAUDIBLE]. That's the number of [INAUDIBLE] quantum states there are. And that gives me the number of electrons near energy E. And I integrate over all possible energy states. That should give me the number of charges.

So once you gone through this a few times, you can just start from the [INAUDIBLE]. And I wrote down for Boltzmann-- so then this is just under Boltzmann distribution. I can do this integration, and that's what we have. And what it means is if I gave a number of dopants to the phosphor, I can see where my potential is, [INAUDIBLE] potential, from here given n [INAUDIBLE] inverse, I know E matches c.

And the Boltzmann-- so this is only valid when this mu is far below Ec. Once the mu gets into here, you have to use the Fermi-Dirac statistics. That's a degenerate semiconductor. This is the only approximation. But here, it's general. You can always do that math to inverse the given number. You can get the [INAUDIBLE].

And the density of states is a mathematical concept. But see, it's very convenient. And really, it's the number of quantum states per energy interval that we-- and in the parabolic band, it's a problem. It's a square root relation. It's obviously increasing as square root.

And of course, below Ec, this is where Ec is. At the bottom here, there's no states in this region, in the forbidden band gap. So that's a typical bulk material [INAUDIBLE] substrates. And then when you fill, it turns out that most of the time, there's only a small region because here is kt. So the electrons are mostly in this region when you do the measurement. Once nE becomes very large, that is [INAUDIBLE] factor very small. Much larger than kt, this is a very small.

OK? So that's what we went through. And I saw that I was going much faster. I will do that next time. This is-- actually, just write down my [INAUDIBLE] in the original syllabus. Any questions? Now, if you're a mechanical engineer, again, I'm sure this is a [INAUDIBLE] normal mechanic [INAUDIBLE] talk about this.

And I don't expect you to completely master it, but I think what you'll get is say, oh, I know the periodic table. I know the metal and dielectric difference. And I know that [INAUDIBLE] vibration in the crystal quantize and the basic unit of that quantization of the phonon.

Now you know electron, you know phonon. And then the thermal conductivity, remember, comes from electron phonon. And in thermal electrics, the s squared comes from electron. So you have to really get this basic picture [INAUDIBLE].

Any other questions? OK.