

LECTURE 10. TAO FAN. METHODS AND APPROXIMATIONS FOR COMPUTING THERMOELECTRIC

Section 1.

The First question, what key parameters we need to know in order to evaluate thermoelectric performance of a material.

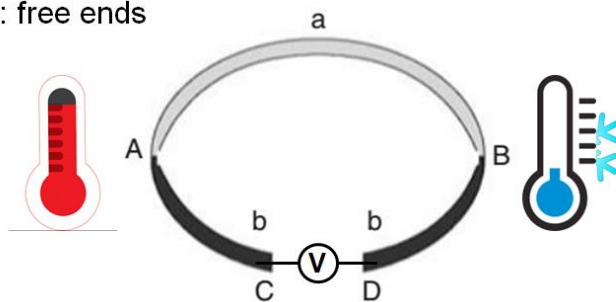
Let's briefly retrospect the definition of thermoelectric materials and the physical scheme under it.

Thermoelectric material is a kind of functional material which can achieve conversion between heat and electricity using its internal carrier movement.

The advantages of thermoelectric devices are: solid device, no moving part, low noise, reliable performance, size adjustable, ideal for small scale, distributed electric generator.

The physics scheme that analyzes thermoelectric energy conversion is based on the Seebeck effect and Peltier effect.

a, b: conductors
A, B: joint points
C, D: free ends



Differential Seebeck coefficient:

$$\alpha_{ab} = \frac{V}{\nabla T}$$

Differential Peltier coefficient:

$$\pi_{ab} = \frac{q}{I}$$

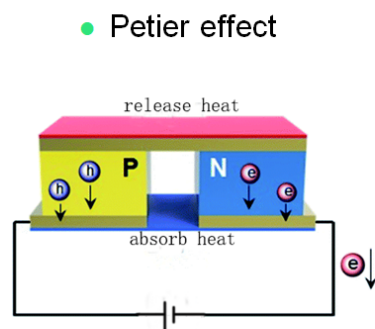
Kelvin relationship:

$$\pi_{ab} = \alpha_{ab} T$$

The physical principles underlying the thermoelectric energy conversion are the Seebeck effect and the Peltier effect. As a simple schematic shown in Fig., it can be considered as a circuit formed from two different conductors a and b (referred to as thermocouple legs in a thermoelectric device), which are connected in series. Two junction points are A and B. Conductor b is divided into two parts (the breaking

points are C and D). Supposing a temperature difference ΔT is established between the two junctions while the two free ends of conductor b are maintained at the same temperature, if we insert a voltmeter in the gap., a potential difference V will be observed between points C and D. this is the Seebeck effect and here we define the differential Seebeck coefficient α_{ab} , as the ratio of V to ΔT . Instead, if we insert a power source to points C and D so as to drive electric current in the circuit, then the junction A will be heated and junction B be cooled. This is the Peltier effect and we define the relative Peltier coefficient π_{ab} is equal to the ratio of the rate of heating or cooling q at each junction to the electric current I . the differential seebeck coefficient and differential Peltier coefficient can be related by Kelvin relationship.

Let's see the thermoelectric refrigerator first.



the rate of absorption of heat from the source:

$$q_1 = \underbrace{(\alpha_p - \alpha_n)IT_1}_{\text{Peltier cooling}} - \underbrace{(T_2 - T_1)(K_p + K_n)}_{\text{heat conduction}} - \underbrace{I^2(R_p + R_n)/2}_{\text{Joule heating}}$$

the rate of expenditure of electrical energy:

$$w = \underbrace{(\alpha_p - \alpha_n)I(T_2 - T_1)}_{\text{rate of working to overcome the thermoelectric voltage}} + \underbrace{I^2(R_p + R_n)}_{\text{resistive loss}}$$

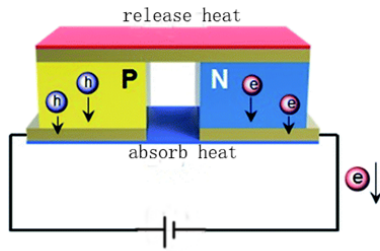
coefficient of performance $\text{COP} = \frac{\text{heat absorbed}}{\text{electrical power input}} = \frac{q_1}{w}$

K_p, K_n are the thermal conductance of the branches; R_p, R_n are the electrical resistances of the branches; T_1 is the temperature at the heat source, while T_2 is at the heat sink.

The question is, what is the energy conversion efficiency of a thermoelectric refrigerator like this one. This is a thermodynamic problem. Supposing that thermal radiation and losses by conduction and convection through the surrounding medium are negligible. for this refrigerator(or heat pump), the efficiency is expressed by coefficient of performance, which is the heat absorbed q divided by electrical power input w . where the rate of absorption of heat from the source includes three part: the Peltier cooling effect at the heat source, which is opposed by the heat conductance in the device, and the Joule heating within the thermoelements. For the rate of expenditure of electrical energy, it includes two terms: the first term is the rate of working to overcome the thermoelectric voltage whereas the second term is the

resistive loss. Since the thermal conductance, the electrical resistances and the temperature are usually fixed, we can see actually q , w and even COP are quadratic functions of current I . For these functions, we are interested in two points :

● Petier effect



L : length
 A : cross-sectional area
 ρ : electrical conductivity
 λ : thermal conductivity

When q_1 is maximized,

$$I_q = (\alpha_p - \alpha_n) T_1 / (R_p + R_n) \quad \text{COP} = \frac{ZT_1^2 / 2 - (T_2 - T_1)}{ZT_2 T_1}$$

When COP is maximized,

$$I_\phi = \frac{(\alpha_p - \alpha_n)(T_2 - T_1)}{(R_p + R_n) \left\{ (1 + ZT_m)^{1/2} - 1 \right\}} \quad \text{COP}_{\max} = \frac{T_1 \left\{ (1 + ZT_m)^{1/2} - (T_2/T_1) \right\}}{(T_2 - T_1) \left\{ (1 + ZT_m)^{1/2} + 1 \right\}}$$

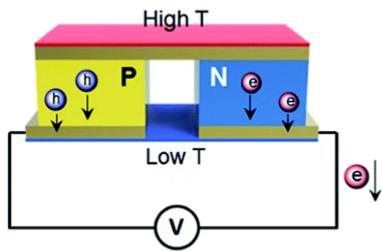
Here
$$Z = \frac{(\alpha_p - \alpha_n)^2}{\left\{ (K_p + K_n)(R_p + R_n) \right\}}$$

If
$$\frac{L_n A_p}{L_p A_n} = \left(\frac{\rho_p \lambda_n}{\rho_n \lambda_p} \right)^{1/2} \quad \text{then} \quad Z = \frac{(\alpha_p - \alpha_n)^2}{\left\{ (\lambda_p \rho_p)^{1/2} + (\lambda_n \rho_n)^{1/2} \right\}^2}$$

The first point, when the q_1 , cooling power is maximized, we get the current corresponding to this maximum q_1 and also, the COP like this. The second point, when the COP is maximized, the corresponding current is expressed as, and the maximum COP is. Here we introduce a new parameter, uppercase Z , named figure of merit, which is expressed by Seebeck coefficient, thermal conductance and electrical resistivity of the two branches. COP depends solely on Z and temperature. As we can see from the formulas, the larger of Z , the better. Since the thermal conductance and electrical resistivity related with the shape of the thermoelement, the factor in the denominator can be minimized, by setting the shape of the two branches satisfy the relationship, then the optimized Z can be expressed as, which is determined by the intrinsic properties of the branches. By the way, one would wish to operate a thermoelectric refrigerator as close to the condition of maximum COP as possible, However, this is sometimes not practical, because the cooling power under this condition can be much less than the maximum value, particularly, when the temperature difference between the source and sink is small. the preferred current will lie somewhere between that for maximum cooling power and optimum COP.

Now for thermoelectric generators, again, we assume that thermal radiation and losses by conduction and convection through the surrounding medium are negligible.

- Seebeck effect



the power delivered to the load:

$$w = I^2 R_L = \left\{ \frac{(\alpha_p - \alpha_n)(T_1 - T_2)}{R_p + R_n + R_L} \right\}^2 R_L$$

the rate of heat flow from the source:

$$q_1 = \underbrace{(\alpha_p - \alpha_n)IT_1}_{\text{Peltier cooling}} + \underbrace{(K_p + K_n)(T_1 - T_2)}_{\text{heat conduction}}$$

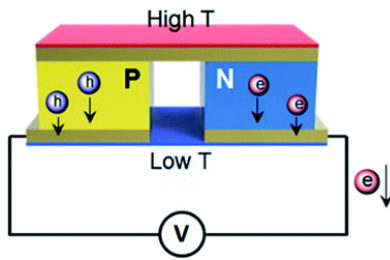
efficiency:

$$\eta = \frac{w}{q_1}$$

K_p, K_n are the thermal conductance of the branches; R_p, R_n are the electrical resistances of the branches, R_L is the resistance of the load; T_1 is the temperature at the heat source, while T_2 is at the heat sink.

The efficiency η is the ratio of the output power w to the rate at which heat is drawn from the source q_1 . where the power delivered to the load is and the rate of heat flow from the source includes two terms: part of the heat drawn from the source is used to balance the Peltier cooling associated with the flow of current. In addition, there is the flow of heat due to thermal conduction along the branches. For generators, the current in the circuit can be adjusted by resistance of the load. There are also two interesting points (pict.).

- Seebeck effect



When w is maximized,

$$R_p + R_n = R_L \quad w_{\max} = \frac{\{(\alpha_p - \alpha_n)(T_1 - T_2)\}^2}{4R_L}$$

When η is maximized,

$$\eta = \frac{(T_1 - T_2)(M - 1)}{T_1(M + T_2/T_1)} \quad M = \frac{R_L}{R_p + R_n} = (1 + ZT_m)^{1/2}$$

If ZT_m were much greater than 1, M would also be very large and the efficiency would approach $(T_1 - T_2)/T_1$, which is the value for the Carnot cycle.

The first point, when the w output power is maximized, which happens when load resistance equals to the generator resistance. The second point, when the efficiency η is maximized, the ratio M of the resistance of the load to that of the generator fulfills the relationship like this. Here the same Z as that for thermoelectric refrigerator, and T_m is the average temperature between heat source and sink. Thus, the maximum η also depends solely on Z and temperature. If ZT_m were much greater than 1, M would also be very large and the efficiency would approach $(T_1 - T_2)/T_1$, which is the value for the Carnot cycle. Currently, the highest η which was achieved in the laboratory is around 15%.

A short summary, according to the discussion above, for both thermoelectric generator or thermoelectric refrigerator, the energy conversion efficiency of the device is proportional to this parameter, figure of merit for a couple of thermoelement. In the search for improved thermocouples, it is uncommon to investigate a pair of substances at the same time. It would, therefore, be convenient if there is a merit for a single material. Now, we define the figure of merit for a single material, which is α^2 divided by thermal conductivity and electrical resistivity of a material. Although this uppercase Z is different with lowercase z of both n-type and p-type thermoelement, it is found that Z lies close to the average of z_p and z_n so that it is meaningful to select materials on the basis of the single-

material figure of merit. Usually, you see this dimensionless figure of merit in most papers and books, which uses electrical conductivity instead of electrical resistivity, and split thermal conductivity into contributions from lattice vibration and from electrons. Alpha square multiply sigma also called power factor. For now, the commonly used thermoelectric materials are Bi2Te3, PbTe and SnSe, their figure of merit values are 1 or 2, not larger than 3. But for massive commercial deployment, the ZT value is expected to be larger than 4. There is a large space to improve. However, it is hard to optimize these parameters simultaneously because they are interdependent with each other. As this picture shows, both α and σ are related with carrier concentration n . σ is proportional to n , while α is inversely proportional to n (the Pisarenko relation). In addition, according to the Wiedemann-Franz law, $\kappa_e = L\sigma T$, where L is the Lorenz number. Thus, any method increasing σ will also increase κ_e .

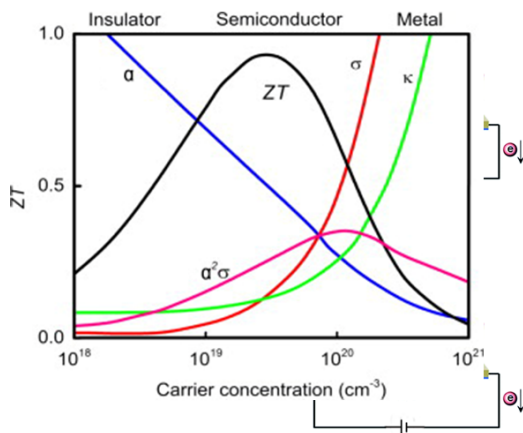


Figure of merit for thermocouple

$$Z = \frac{(\alpha_p - \alpha_n)^2}{\left\{ (\lambda_p \rho_p)^{1/2} + (\lambda_n \rho_n)^{1/2} \right\}^2}$$

Figure of merit for a single material

or

α – Seebeck coefficient,
 σ – electrical conductivity,
 κ_L – lattice thermal conductivity,
 κ_e – electronic thermal conductivity

Reading:

[1] Goldsmid, H. Julian. *Introduction to thermoelectricity*. Vol. 121. Berlin: Springer, 2010.

[2] Rowe, David Michael. *Thermoelectrics handbook: macro to nano*. CRC press, 2018.

Section 2

In this section, I will introduce the physical models which are used to calculate those parameters involved in the figure of merit, which are mainly based on Boltzmann transport theory. I will also mention available software for such calculations.

Let's start from a very simple model, Drude model or say free electron gas model.

Drude model (free electron gas model)

Assumption 1: Ignore the interaction between electrons and ionic cores. This is equivalent to treating the ionic system as a uniform positive charge background that keeps the system neutral, also called "jellium model".

Assumption 2: Ignore the interaction among electrons. This is also called "independent electron approximation".

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \varphi(\mathbf{r}) = \varepsilon \varphi(\mathbf{r}) \quad \longrightarrow \quad -\frac{\hbar^2}{2m} \nabla^2 \varphi(\mathbf{r}) = \varepsilon \varphi(\mathbf{r})$$

with $\varphi(\mathbf{r}) = C e^{i\mathbf{k} \cdot \mathbf{r}}$

This model has been successfully applied to metals. We know a solid compound is composed of ion cores and valence electrons. In the free electron gas model, there are two basic assumptions to clarify the meaning of free: assumption 1, Ignore the interaction between electrons and ionic cores. This is equivalent to treating the ionic system as a uniform positive charge background that keeps the system neutral, also called "jellium model". Since the positive charge is uniformly distributed, there is no interaction with electrons. Assumption 2, Ignore the interaction among electrons. This is also called "independent electron approximation". Thus, based on these two assumptions, from the single electron Schrodinger equation, the equation can be simplified to this second order differential equation, and it has a solution of plane wave format.

Consider an existence of an external field, for example electromagnetic field.

Under the external field (for example, electromagnetic field), In order to discuss transport property of free electrons:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + e\phi \right] \varphi(\mathbf{r}, t) = i\hbar \dot{\varphi}(\mathbf{r}, t)$$

Assumption 1: electrons experience collision. Such a event happens instantaneously. Between two successive collisions, the electrons move in a straight line, following Newton's laws.

Assumption 2: the collision experienced by electrons can be described by relaxation time τ simply. Within dt time, the probability of any electron getting hit is dt/τ .

Only when the particles have large kinetic energy and when the external field changes slowly, the above assumptions are true.

The behavior of free electrons under an external field should obey the time dependent Schrodinger equation, here ϕ is a scalar potential related to the external electric field. In order to further discuss the transport properties of free electrons under an external field, there are two more assumptions: assumption 1, electrons experience collision or scattering from ion cores. Such an event happens instantaneously. Between two successive collisions, the electrons move in a straight line, following Newton's laws. Assumption 2, the collision experienced by electrons can be described by relaxation time τ simply. Within dt time, the probability of any electron getting hit is dt/τ . So τ generally equals to the average time between two successive collisions. These two assumptions make the problem greatly simplified, but we need to be careful that the conditions of these assumptions are valid. It requires the mean free path of the electron and the scale of the external field should be greatly larger than the uncertainty of the coordinate of the electron. For electrons in metal, it is true, since electrons in metal usually have large momentum, its mean free path around 10 nanometer at room temperature, and larger than its coordinate uncertainty, which usually is several ionic distances. So for metal, the classical model is a good approximation.

Now we can write the kinetic equation of electrons.

Kinetic equation of electrons:

Assume the average momentum of electrons at t moment is $\mathbf{p}(t)$, after dt time, those electrons without getting collision have a contribution to average moment:

$$\mathbf{p}(t+dt) = \left(1 - \frac{dt}{\tau}\right) \left[\mathbf{p}(t) + \mathbf{F}(t) dt \right]$$

Under the first-order approximation:

$$\mathbf{p}(t+dt) - \mathbf{p}(t) = \mathbf{F}(t) dt - \mathbf{p}(t) \frac{dt}{\tau}$$



$$\frac{d\mathbf{p}(t)}{dt} = \mathbf{F}(t) - \frac{\mathbf{p}(t)}{\tau} \quad \text{or} \quad m \frac{d\mathbf{v}(t)}{dt} = \mathbf{F}(t) - m \frac{\mathbf{v}(t)}{\tau}$$

Assume the average momentum of electrons at t moment is $\mathbf{p}(t)$, after dt time, those electrons without getting collision have a contribution to average moment. For those electrons with collision, the probability is dt/τ , and their contribution to the average moment after a dt time will include dt square, and under the first order approximation, this contribution can be neglected. Thus, the kinetic equation of the system can be written as this and the final expression is this. As can be seen, the effect of collision is adding a damping term on the classical equation.

We consider the simplest situation, the external field is constant and the system reaches steady state, at that time, the electric field force equals the damping force and the acceleration stops. The electrons move at constant velocity which can be calculated as v_d , this velocity is called drift velocity.

$$m \frac{d\mathbf{v}(t)}{dt} = \mathbf{F}(t) - m \frac{\mathbf{v}(t)}{\tau}$$

For constant electric field reaching steady state, the electric field force $\mathbf{F} = -e\mathbf{E}$, and equals to damping force. Thus, the acceleration stops and $d\mathbf{v}(t)/dt = 0$. The electrons move at a constant velocity:

$$v_d = -\frac{e\tau\mathbf{E}}{m}$$

The current density:

$$\mathbf{J} = -nev_d = \frac{ne^2\tau\mathbf{E}}{m}$$

According to Ohm's law:

$$\mathbf{J} = \sigma\mathbf{E}$$

Electrical conductivity:

Then the current density in the field can be expressed as this, and according to Ohm's law, current density equals to electrical conductivity multiplying electric field strength. So we get electrical conductivity. Here tau is the electronic relaxation time and m is the mass of electrons.

For the classical model, the average velocity of electrons equals to the average velocity of thermal motion, determined by the temperature of the environment. For quasi-classical model, because of the application of fermi statistics, although the motion of electrons under an external field is treated classically, the average velocity of electrons uses fermi velocity. So it is called quasi-classical model. Thus, to calculate the mean free path of electrons, the fermi velocity should be used.

Classical: average velocity of electrons equals to average velocity of thermal motion

$$v_{th}^2 = k_B T / m$$

Quasi-classical: average velocity of electrons equals to velocity at fermi surface

$$v_F^2 = 2\varepsilon_F / m$$

Mean free path l (the average movement distance between two successive collision of a electron):

$$l = v_F \tau$$

For common metals at room temperature, $\tau \sim 10^{-14}$ s, $l \sim 10$ nm.

Let's make the model more complex. Still starting from the single electron Schrodinger equation. In the previous model, the potential part V , which represents the ion-electron and electron-electron interaction, is just ignored. We know it is not true, it cannot be omitted. Here, without considering the specific expression of the potential, just consider it has periodicity as the lattice. According to Bloch theorem, the eigen function is Bloch wave function, here the u_k function represents periodicity. The electron's energy spectrum also shows an energy band structure. Talking about the semi-classical model, the external fields dealt with classical way, but electrons are Bloch electrons described by Bloch wave function now. The detailed definition of the model is each electron has a determinate location \mathbf{r} , wave vector \mathbf{k} and band index n . For a specified $\varepsilon_n(\mathbf{k})$, under the external fields, \mathbf{r} , \mathbf{k} and n vary with time by following the rules: Band index n is constant, ignoring the probability of electronic transition; The velocity of electrons is expressed like this; the variation of \mathbf{k} with time expressed like this. This means the wave vector \mathbf{k} can be changed by an external field. The model is valid if the external field varies slowly in the space.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \varphi(\mathbf{r}) = \varepsilon \varphi(\mathbf{r})$$

With periodic potential approximation: $V(\mathbf{r} + \mathbf{R}_n) = V(\mathbf{r})$

According to Bloch theorem: $\varphi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$ and $u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n) = u_{\mathbf{k}}(\mathbf{r})$

Semi-classical model: each electron has determinate location \mathbf{r} , wave vector \mathbf{k} and band index n . For a specified $\varepsilon_n(\mathbf{k})$, under the external fields, \mathbf{r} , \mathbf{k} and n vary with time by following the rules:

1. Band index n is constant, ignoring the probability of electronic transition;
2. The velocity of electron:
3. The variation of \mathbf{k} with time:

From the above model, we can get some important deductions. For example, Full occupied bands don't contribute to the current density \mathbf{J} . Let's express the current density as the total contribution from energy band. Here the integration is for all occupied states. The energy band $\varepsilon_n(\mathbf{k})$ is an even function, then the $v_n(\mathbf{k})$ would be an odd function. Thus, in a full occupied band, the contribution from \mathbf{k} state and

$-k$ state electrons just cancel each other out. The total current density is zero. For a partially occupied band, we can use the fact that the full band doesn't contribute current density, write an expression like this, here the integration is just for the unoccupied level. Move the term to the right. This equation is like, we treated all occupied states by electrons as empty states, while the remaining unoccupied states were occupied by particles with positive e charge. This hypothetical particle is a hole.

1 Full occupied bands don't contribute to the current density J .

Each electron in the band has a contribution of $-ev(k)$ to J , then the total contribution from all electrons is

$$J = -e \int_{\text{occ}} v(k) \frac{dk}{4\pi^3} \quad \text{with} \quad v_n(k) = -v_n(-k)$$

Thus, the contribution from k state and $-k$ state electrons just cancel each other out.

2 Partial occupied bands and the origin of hole.

$$J + (-e) \int_{\text{unocc}} v(k) \frac{dk}{4\pi^3} = 0 \quad \longrightarrow \quad J = e \int_{\text{unocc}} v(k) \frac{dk}{4\pi^3}$$

The above semi-classical model describes the motion of Bloch electrons in the external field. In a real situation, the electrons also experience collision from the lattice. What is the behavior of electrons when external fields and collisions coexist? This problem can be studied based on the distribution function of electrons. In thermal equilibrium condition, the electrons' distribution follows Fermi-Dirac distribution function, the system is uniform and f is unrelated with electron's position r . When external fields exist, and involve collision, the distribution deviates from f_0 , thus having the nonequilibrium distribution function. This term is from the assumption that if there is no collision, the electrons at r, k, t state are from its previous state. The second term is because of the collision. We expand the first term and keep the linear term of dt , get this new equation. When the system reaches steady state, the derivative of f with respect to t would be zero. Thus, we get the final format of the equation, called the Boltzmann equation. The left side is called drift term and the right term is collision term. The meaning of the Boltzmann equation is it connects

the quantum band structure of the materials (reflected in r), the influence of the external field (reflect in derivative of k), the effect of collision with the distribution function f . therefore, this function is the start of dealing with transport properties in solid.

In thermal equilibrium condition, the electrons' distribution follows Fermi-Dirac distribution function f_0

$$f_0(\varepsilon_k) = \frac{1}{e^{(\varepsilon_k - \mu)/k_B T} + 1}$$

When external fields exist, and involving collision, the distribution deviates from f_0 , the nonequilibrium distribution function $f(\mathbf{r}, \mathbf{k}, t)$

$$f(\mathbf{r}, \mathbf{k}, t) = f(\mathbf{r} - \dot{\mathbf{r}}dt, \mathbf{k} - \dot{\mathbf{k}}dt, t - dt) + \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} dt \quad \Rightarrow \quad \frac{\partial f}{\partial t} + \dot{\mathbf{r}} \cdot \frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{k}} \cdot \frac{\partial f}{\partial \mathbf{k}} = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}$$

In the steady state, $\partial f / \partial t = 0$,

$$\underbrace{\dot{\mathbf{r}} \cdot \frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{k}} \cdot \frac{\partial f}{\partial \mathbf{k}}}_{\text{drift term}} = \underbrace{\left(\frac{\partial f}{\partial t} \right)_{\text{coll}}}_{\text{collision term}}$$

Even now, the Boltzmann equation cannot be solved fully. Several approximations have to be used. The first approximation is The nonequilibrium function f just has a small deviation from f_0 , f_1 is a small quantity. Also, as talked before, using relaxation time approximation to express the collision term. Then for a situation with an electromagnetic field and collision, the transport equation looks like this. In the simplest case, there is only a constant electrical field, the equation can be finally simplified to this form. Once we know the expression of f_1 , we can calculate the current density

The nonequilibrium function f just has a small deviation from f_0

$$f = f_0 + f_1$$

The relaxation time approximation

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = -\frac{f - f_0}{\tau} = -\frac{f_1}{\tau}$$

For a situation with electrical field, magnetic field and collision,

$$\dot{\mathbf{r}} \cdot \frac{\partial f_0}{\partial \mathbf{r}} - \frac{e\mathbf{E}}{\hbar} \cdot \frac{\partial f_0}{\partial \mathbf{k}} = -\frac{f_1}{\tau} + \frac{e}{\hbar} (\mathbf{v}_k \times \mathbf{B}) \cdot \frac{\partial f_1}{\partial \mathbf{k}}$$

A simple case, only constant electrical field.

$$-\frac{e\mathbf{E}}{\hbar} \cdot \frac{\partial f_0}{\partial \mathbf{k}} = -\frac{f_1}{\tau} \quad \text{or} \quad f_1 = \frac{e\tau\mathbf{E}}{\hbar} \cdot \frac{\partial f_0}{\partial \mathbf{k}}$$

The equilibrium distribution has no contribution to the total current, the current solely from the deviated distribution. Substituting it into the formula, this integration is for all wave vectors in the Brillouin zone and difficult to calculate. Here we define a transport distribution function, by this function, τv^2 as a function of band index n and wave vector \mathbf{k} is converted to that as a function of band energy. Further, we define this generalized transport coefficient, which converts $\sigma \epsilon$ to a function of chemical potential μ and temperature. It turns out all experimentally measurable transport properties such as electrical conductivity, Seebeck coefficient, electronic thermal conductivity can be expressed by a series of generalized transport coefficients. In these coefficients, the band energy $\epsilon(n, \mathbf{k})$, electron velocity can be computed by modern first-principle method, such as DFT, the only trouble is this electronic relaxation time $\tau(n, \mathbf{k})$, which is hard to calculate.

Current density \mathbf{J} :
$$\mathbf{J} = -\frac{1}{4\pi^3} \int \mathbf{e}\mathbf{v}_k f d\mathbf{k} = -\frac{1}{4\pi^3} \int \mathbf{e}\mathbf{v}_k (f_0 + f_1) d\mathbf{k}$$

Since
$$\int \mathbf{e}\mathbf{v}_k f_0 d\mathbf{k} \equiv 0$$

Then
$$\mathbf{J} = -\frac{1}{4\pi^3} \int \mathbf{e}\mathbf{v}_k f_1 d\mathbf{k} = -\frac{1}{4\pi^3} \int \mathbf{e}\mathbf{v}_k \frac{e\tau\mathbf{E}}{\hbar} \frac{\partial f_0}{\partial \mathbf{k}} d\mathbf{k} = \boldsymbol{\sigma} \cdot \mathbf{E}$$

Define transport distribution function
$$\sigma_{\alpha\beta}(\varepsilon) = \frac{e^2}{N_k \Omega} \sum_{n,\mathbf{k}} \tau_{n,\mathbf{k}} v_\alpha(n,\mathbf{k}) v_\beta(n,\mathbf{k}) \delta(\varepsilon - \varepsilon_{n,\mathbf{k}})$$

Generalized transport coefficients
$$L^{(\lambda)}(\mu; T) = \int \sigma(\varepsilon) (\varepsilon - \mu)^\lambda \left(-\frac{\partial f_0(\varepsilon; \mu, T)}{\partial \varepsilon} \right) d\varepsilon$$

$$\sigma = L^{(0)} \quad S = \frac{1}{eT} \frac{L^{(1)}}{L^{(0)}} \quad \kappa_e = \frac{1}{e^2 T} \left[\frac{(L^{(1)})^2}{L^{(0)}} - L^{(2)} \right]$$

The electronic relaxation time equals to the inverse of the scattering rate γ , which can be calculated as a summation of scattering probability W . when only consider electron-phonon scattering process, the scattering probability involves both phonon emission and absorption processes can be expressed as this. Here $g_{\mathbf{m}\mathbf{n}\mathbf{v}}(\mathbf{k}, \mathbf{q})$ are the electron-phonon matrix elements which quantify the probability amplitude for an electron to scatter from an initial state $|\mathbf{n}\mathbf{k}\rangle$ to the final state $|\mathbf{m}\mathbf{k}+\mathbf{q}\rangle$, by emitting or absorbing a phonon with wavevector \mathbf{q} and mode index v ; $N_{\mathbf{v}\mathbf{q}}^0$ are equilibrium Bose-Einstein phonon distribution functions. For transport properties' calculation, most of the time is spent on calculating matrix elements, because, in order to converge the transport with the Boltzmann transport equation, the e-ph matrix element need to be computed on a extremely-dense \mathbf{k} - and \mathbf{q} -point grid in the Brillouin zone, usually over 1 million points. Therefore, this is where the approximation has to be introduced. Many models exist differentiating by level of approximation.

Relaxation time :

$$\tau_{n,k} = \Gamma_{nk}^{-1} \quad \Gamma_{nk}^{-1} = \frac{1}{N_q} \sum_{m,vq} W_{nk,mk+q}^{vq}$$

$$W_{nk,mk+q}^{vq} = \frac{2\pi}{\hbar} |g_{mnv}(\mathbf{k}, \mathbf{q})|^2$$

$$\times [\delta(\varepsilon_{nk} - \hbar\omega_{vq} - \varepsilon_{mk+q})(1 + N_{vq}^0 - f_{mk+q}^0) + \delta(\varepsilon_{nk} + \hbar\omega_{vq} - \varepsilon_{mk+q})(N_{vq}^0 - f_{mk+q}^0)]$$

Here N_q is the number of \mathbf{q} -points and $g_{mnv}(\mathbf{k}, \mathbf{q})$ are the e-ph matrix elements quantifying the probability amplitude for an electron to scatter from an initial state $|nk\rangle$ to the final state $|mk + \mathbf{q}\rangle$, by emitting or absorbing a phonon with wavevector \mathbf{q} and mode index v ; N_{vq}^0 are equilibrium Bose-Einstein phonon distribution functions.

In the table, I list the commonly used software for calculating electronic transport properties, ranked by complexity of the model.

Table 1 The commonly used software for calculating electronic transport properties

	Complexity	link
AICON	Low	https://github.com/Baijianlu/AICON2.git
BoltzTrap2	Normal	https://gitlab.com/sousaw/BoltzTraP2
BoltzWann	Normal	https://doi.org/10.1016/j.cpc.2013.09.015
EPA	A bit high	https://doi.org/10.1002/aenm.201800246
EPIC STAR	A bit high	https://doi.org/10.1038/s41524-020-0316-7
AMSET	A bit high	https://github.com/hackingmaterials/amset
PERTURBO	High	https://perturbo-code.github.io/
elphbolt	High	https://github.com/nakib/elphbolt

Among them, AICON is a program developed by our group, which uses the Kane band model to describe the energy band and deformation potential theory to calculate the electron-phonon coupling matrix element. I will introduce this program detailly later. BoltzTrap2 and BoltzWann use constant relaxation time approximation. Users need to calculate band energy and velocity on a dense mesh with first principle method, then the program will interpolate the energy and velocity and combine with a constant relaxation time to calculate Generalized transport coefficients. EPA, EPIC STAR and AMSET use some semi-empirical and simpler

models to calculate the electron phonon matrix elements, thus avoiding calculating them on extremely dense mesh. PERTURBO and elphbolt engage purely first principle calculation for matrix elements, thus their calculations are time-consuming and only affordable for simple systems.

For phonon transport properties such as lattice thermal conductivity, similar to electronic transport properties, it can also be solved from the Boltzmann transport equation. In the presence of a temperature gradient ∇T , the phonon distribution function deviates from f_0 which is Bose–Einstein distribution. Two factors affect the phonon distribution: diffusion due to ∇T and scattering arising from allowed processes. In the steady state, the rate of change in the distribution must vanish, the condition is expressed as. where λ comprises both a phonon branch index n and a wave vector q , v_λ is the group velocity of phonon mode λ . Usually, the norm of ∇T is small enough that f_λ can be expanded to first order in ∇T , here g_λ looks like this form. For scattering process, the most important way is phonon–phonon interaction, so

In the presence of a temperature gradient ∇T , the phonon distribution function f deviates from f_0 (Bose–Einstein distribution), and this deviation can be obtained from the BTE. In the steady state, the rate of change in the distribution must vanish,

$$\frac{df_\lambda}{dt} = \left. \frac{\partial f_\lambda}{\partial t} \right|_{\text{diffusion}} + \left. \frac{\partial f_\lambda}{\partial t} \right|_{\text{scattering}} = 0 \quad \text{and} \quad \left. \frac{\partial f_\lambda}{\partial t} \right|_{\text{diffusion}} = -\nabla T \cdot v_\lambda \frac{\partial f_\lambda}{\partial T}$$

where λ comprises both a phonon branch index n and a wave vector q , v_λ is the group velocity of phonon mode λ .

Usually, the norm of ∇T is small enough that f_λ can be expanded to first order in ∇T

$$f_\lambda = f_0 + g_\lambda$$

g_λ can be chosen to be

$$g_\lambda = -F_\lambda \cdot \nabla T \frac{df_0}{dT}$$

Considering only two- and three-phonon processes, the BTE can be simplified and written as. Again here we use the relaxation time approximation. τ_λ is the relaxation time of mode λ as obtained from perturbation theory. while Δ_λ , with the dimensions of velocity, is the measure of how much the population of a specific

phonon mode – and thus the associated heat current – deviates from the RTA prediction. For phonon relaxation time, it can be calculated by the sum of scattering rate belonging to different types of scattering process. Gamma plus corresponds to absorption processes, resulting in only one phonon with the combination of two incident phonons, while \Gamma minus describes emission processes in which the energy of one incident phonon is split among two phonons. The scattering rate is proportional to the square of scattering matrix element V, which is proportional to third order force constant. After obtaining the uppercase F_λ , the lattice thermal conductivity can be calculated as. In the whole process, the most time consuming part is calculating the high order force constants. Which, even for a simple structure like silicon, needs hundreds of static calculations.

Consider only two- and three-phonon processes, the BTE can be written as

$$F_\lambda = \tau_\lambda^0 (\mathbf{v}_\lambda + \Delta_\lambda) \quad \text{with} \quad \frac{1}{\tau_\lambda^0} = \frac{1}{N} \left(\sum_{\lambda\lambda'} \Gamma_{\lambda\lambda'\lambda''}^+ + \sum_{\lambda\lambda'} \frac{1}{2} \Gamma_{\lambda\lambda'\lambda''}^- \right)$$

$$\Gamma_{\lambda\lambda'\lambda''}^+ = \frac{\hbar\pi}{4} \frac{f_0' - f_0''}{\omega_\lambda \omega_{\lambda'} \omega_{\lambda''}} |V_{\lambda\lambda'\lambda''}^+|^2 \delta(\omega_\lambda + \omega_{\lambda'} - \omega_{\lambda''})$$

$$\Gamma_{\lambda\lambda'\lambda''}^- = \frac{\hbar\pi}{4} \frac{f_0' + f_0'' + 1}{\omega_\lambda \omega_{\lambda'} \omega_{\lambda''}} |V_{\lambda\lambda'\lambda''}^-|^2 \delta(\omega_\lambda - \omega_{\lambda'} - \omega_{\lambda''})$$

$$V_{\lambda\lambda'\lambda''}^- \sim \sum_{ijk} \sum_{\alpha\beta\gamma} \Phi_{ijk}^{\alpha\beta\gamma}$$

Here ω_λ is the angular frequency, N is the number of \mathbf{q} points in the Brillouin zone, f_0' stands for $f_0(\omega_{\lambda'})$, $\Gamma_{\lambda\lambda'\lambda''}^+$ corresponds to absorption processes ($\omega_\lambda + \omega_{\lambda'} = \omega_{\lambda''}$) while $\Gamma_{\lambda\lambda'\lambda''}^-$ corresponds to emission processes ($\omega_\lambda = \omega_{\lambda'} + \omega_{\lambda''}$)

Finally,

$$\kappa_L^{\alpha\beta} = \frac{1}{k_B T^2 N_q \Omega} \sum_{\lambda} f_0 (f_0 + 1) (\hbar \omega_\lambda)^2 v_\lambda^\alpha F_\lambda^\beta$$

In this table, I list the commonly used software for calculating lattice thermal conductivity, ranked by complexity of the model. Our software AICON uses the semi-empirical model, so-called Debye Callaway model, which doesn't need to calculate time consuming high order force constant, thus pretty fast. ShengBTE and phono3py use relaxation time approximation and need to calculate both second order and third order force constant. AFLOW-AAPL uses the same methods as ShengBTE, however, it makes full use of symmetry to reduce the number of static

calculations for force constants. Last but not least, the lattice thermal conductivity can also be calculated by nonequilibrium molecular dynamics or Green-Kubo method. However, these methods require accurate interatomic potentials, which unfortunately are not always available for the studied compounds. Besides, the required simulation time is also very long.

Table 2 The commonly used software for calculating lattice thermal conductivity

	Characteristics	link
AICON	Debye-Callaway model, fast	https://github.com/Baijianlu/AICON2.git
ShengBTE	Iteratively solving BTE starting from RTA, slow	https://www.shengbte.org/
Phono3py	RTA, slow	http://phonopy.github.io/phonopy3py/
AFLOW-AAPL	Iteratively solving BTE starting from RTA, making use of symmetry to reduce the number of static calculation for IFC, a bit slow	http://www.aflow.org/
LAMMPS	nonequilibrium molecular dynamics or Green-Kubo method, require high-quality interatomic potential, slow	https://www.lammps.org/

Assignment:

Assignment 1:

Ziman, John M. *Electrons and phonons: the theory of transport phenomena in solids*. Oxford university press, 2001.

Assignment 2:

Download and install AICON, BoltzTrap2 and ShengBTE, run their examples, familiarize yourself with the process of calculating transport properties.