Thermoelectricity: From Atoms to Systems

Week 2: Thermoelectric Transport Parameters
Lecture 2.6: Boltzmann Transport Equation
Bonus Lecture

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review: coupled charge and heat currents

**electrical current:**

\[ \mathcal{E}_x = \rho J_x + S \frac{dT}{dx} \]

**heat current (electronic):**

\[ J_{Qx} = \pi J_x - \kappa_e \frac{dT}{dx} \]

**heat current (lattice):**

\[ q_x = -\kappa_l \left( \frac{dT}{dx} \right) \]

\[ \sigma = \frac{2q^2}{h} \left\langle \frac{M_{el}}{\mathcal{A}} \right\rangle \left\langle \frac{\lambda_{el}}{} \right\rangle = n_0 q \mu_n \]

\[ S = -\left( \frac{k_B}{q} \right) \left( \frac{E_J - E_F}{k_B T} \right) \]

\[ \pi = TS \]

\[ \kappa_e = T \sigma \mathcal{A} \]

\[ \kappa_l = \frac{\pi^2 k_B^2 T}{3h} \left\langle \frac{M_{ph}}{\mathcal{A}} \right\rangle \left\langle \frac{\lambda_{ph}}{} \right\rangle \]
The TE transport coefficients are traditionally derived by solving the Boltzmann Transport Equation (BTE). This lecture is a short introduction to the BTE approach and a discussion of how it relates to the Landauer approach.

1) Phase space
2) The BTE
3) Solving the s.s. BTE
4) The TE coefficients
5) BTE and Landauer
\[ f(r, k, t) \]

\[ \mathbf{p} = \hbar \mathbf{k} \]

"crystal momentum"

\[ f(x, k_x, t) \]

\[ f_0(x, k_x) = \frac{1}{1 + e^{(E-E_F)/k_BT}} \]

"phase space"
goals

1) Find an equation for $f(r, p, t)$ out of equilibrium.

2) Learn how to solve it near equilibrium.

3) Relate the results to our Landauer approach results – *in the diffusive limit*.

For much more about the BTE, see
ECE 656: L12-17:  [http://nanohub.org/resources/7281](http://nanohub.org/resources/7281)
semi-classical transport

\[
\frac{d(\hbar \vec{k})}{dt} = -\nabla_r E_C(\vec{r}) = -q \vec{E}(\vec{r})
\]

\[
\begin{align*}
\hbar \vec{k}(t) & = \hbar \vec{k}(0) + \int_0^t -q \vec{E}(t') dt' \\
\vec{v}_g(t) & = \frac{1}{\hbar} \nabla_k E[\vec{k}(t)] \\
\vec{r}(t) & = \vec{r}(0) + \int_0^t \vec{v}_g(t') dt'
\end{align*}
\]

Equations of motion for “semi-classical transport”

\(E_C\) varies slowly on the scale of the electron’s wavelength.
trajectories in phase space

\[ p_x = \hbar k_x \]

\[ h k_x (t) = h k_x (0) + \int_0^t -q \mathcal{E}_x (t') dt' \]

\[ x(t) = x(0) + \int_0^t v_x (t') dt' \quad v_x (t) = \left. \frac{dE}{d(h k_x)} \right|_{\tilde{k}(t)} \]

\[ T(t) = \left[ x(t), p_x (t) \right] \]
Boltzmann Transport Equation (BTE)

\[ p_x = \hbar k_x \]

\[ f(x, p_x, t) = f(x - v_x dt, p_x - F_e dt, t - dt) \]

\[ \frac{df}{dt} = 0 \]
BTE

\[ f(x, p_x, t) \quad \frac{df}{dt} = 0 \]

\[ \frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x} \frac{dx}{dt} + \frac{\partial f}{\partial p_x} \frac{dp_x}{dt} = 0 \]

\[ \frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x} v_x + \frac{\partial f}{\partial p_x} F_x = 0 \]

\[ \frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_r f + \vec{F}_e \cdot \nabla_p f = 0 \]

\[ \vec{F}_e = -q \vec{E} - q \vec{v} \times \vec{B} \]

\[ \nabla_r f = \frac{\partial f}{\partial x} \hat{x} + \frac{\partial f}{\partial y} \hat{y} + \frac{\partial f}{\partial z} \hat{z} \]

\[ \nabla_p f = \frac{\partial f}{\partial p_x} \hat{p}_x + \frac{\partial f}{\partial p_y} \hat{p}_y + \frac{\partial f}{\partial p_z} \hat{p}_z \]

\[ \vec{p} = \hbar \vec{k} \]
in and out-scattering

\[ p_x = \hbar k_x \]

\[ f(x, p_x, t) \]

\[ \frac{df}{dt}_{\text{coll}} = \hat{C}f = \text{in-scattering - out-scattering} \]

\[ T(t) = [x(t), p_x(t)] \]

position, \( x \), does not change
scattering and the RTA

\[ \frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_r f + \vec{F}_e \cdot \nabla_p f = 0 \quad \Rightarrow \quad \frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_r f + \vec{F}_e \cdot \nabla_p f = \hat{C}f \]

Relaxation time approximation:

\[ \hat{C}f = -\left( \frac{f(\vec{p}) - f_0(\vec{p})}{\tau_m} \right) = -\frac{\delta f(\vec{p})}{\tau_m} \]

See Lundstrom: pp. 139-141. The RTA can be justified when the scattering is \textbf{isotropic and/or elastic} in which case the proper time to use is the “momentum relaxation time.”
steady-state BTE

\[ \frac{\partial f}{\partial t} + \vec{v} \cdot \nabla \cdot f + \vec{F}_e \cdot \nabla_p f = \dot{C}f \rightarrow \frac{\partial f}{\partial t} + \vec{v} \cdot \nabla \cdot f + \vec{F}_e \cdot \nabla_p f = -\frac{\delta f}{\tau_m} \]

\[ f(\vec{p}) = f_0(\vec{p}) + \delta f(\vec{p}) \]

\[ \left| f_0(\vec{p}) \right| \gg \left| \delta f(\vec{p}) \right| \]

"near-equilibrium"

no B-fields for now

\[ \vec{F}_e = -q\hat{\vec{E}} \]

RTA
solving the near eq., s.s BTE

\[ \tilde{v} \nabla_r f - q \tilde{E} \nabla_p f = -\frac{\delta f(\tilde{p})}{\tau_m} \]

\[ \nabla_r f \approx \nabla_r f_0 \quad \nabla_p f \approx \nabla_p f_0 \]

\[ \tilde{v} \nabla_r f_0 - q \tilde{E} \nabla_p f_0 = -\frac{\delta f(\tilde{p})}{\tau_m} \]

\[ \delta f(\tilde{p}) = -\tau_m \tilde{v} \nabla_r f_0 + q\tau_m \tilde{E} \nabla_p f_0 \]
BTE solution

\[ \delta f = -\tau_m \, \tilde{\nabla} \cdot \nabla_r f_0 + q \, \tau_m \, \tilde{\nabla} \cdot \nabla_p f_0 \]

\[ f_0(\tilde{p}) = \frac{1}{1 + e^\Theta} \quad \Theta(\tilde{r}, \tilde{p}) = \frac{[E(\tilde{r}, \tilde{p}) - F_n(\tilde{r})]}{k_B T} = \frac{[E_C(\tilde{r}) + E(\tilde{p}) - F_n(\tilde{r})]}{k_B T} \]

\[ \nabla_r f_0 = \frac{\partial f_0}{\partial \Theta} \nabla_r \Theta \]

\[ \nabla_p f_0 = \frac{\partial f_0}{\partial \Theta} \nabla_p \Theta \]

\[ \frac{\partial f_0}{\partial \Theta} = k_B T \frac{\partial f_0}{\partial E} \]

\[ \delta f = \tau_m \, k_B T \left( -\frac{\partial f_0}{\partial E} \right) \left[ \tilde{\nabla} \cdot \nabla_r \Theta - q \tilde{E} \cdot \nabla_p \Theta \right] \]
BTE solution

\[ \delta f = \tau_m \ k_B T \left( -\frac{\partial f_0}{\partial E} \right) \left[ \tilde{\nu} \cdot \nabla_r \Theta - q \tilde{E} \cdot \nabla_p \Theta \right] \]

\[ \Theta(\vec{r}, \vec{p}) = \left[ E_C(\vec{r}) + E(\vec{p}) - F_n(\vec{r}) \right] / k_B T \]

\[ \nabla_r \Theta = \frac{1}{k_B T} \left[ \nabla_r E_C - \nabla_r F_n \right] + \left[ E_C + E(\vec{p}) - F_n \right] \nabla_r \left( \frac{1}{k_B T} \right) \]

\[ \nabla_p \Theta = \frac{\tilde{\nu}(\vec{p})}{k_B T} \]

\[ \delta f = \tau_m \left( -\frac{\partial f_0}{\partial E} \right) \tilde{\nu} \left\{ -\nabla_r F_n + T \left[ E_C + E(\vec{p}) - F_n \right] \nabla_r \left( \frac{1}{T} \right) \right\} \]
The two forces driving currents are:

1) gradients in the QFL
2) gradients in (inverse) temperature.

In Lecture 1, we saw that \( f_1 - f_2 \) produces currents and that differences in Fermi level and temperature cause differences in \( f \).
what next?

\[ \delta f = \tau_m \left( -\frac{\partial f_0}{\partial E} \right) \vec{v} \cdot \vec{F} \]
moments

\[ f(\vec{r}, \vec{k}) = f_0(\vec{r}, \vec{k}) + \delta f(\vec{r}, \vec{k}) \]

\[ n(\vec{r}) = \frac{1}{\Omega} \sum_{\vec{k}} f_0(\vec{r}, \vec{k}) + \delta f(\vec{r}, \vec{k}) \approx \frac{1}{\Omega} \sum_{\vec{k}} f_0(\vec{r}, \vec{k}) \]

\[ \vec{J}_n(\vec{r}) = \frac{1}{\Omega} \sum_{\vec{k}} (-q) \vec{v}(\vec{k}) \delta f(\vec{r}, \vec{k}) \]

\[ \vec{J}_Q(\vec{r}) = \frac{1}{\Omega} \sum_{\vec{k}} (E - F_n) \vec{v}(\vec{k}) \delta f(\vec{r}, \vec{k}) \]

To evaluate these quantities, we need to work out sums in \( k \)-space.

Recall Lecture 1
\[
\vec{J}_n(\vec{r}) = \frac{1}{\Omega} \sum_k (-q) \vec{v} \delta f(\vec{r}, \vec{k}) \\
\delta f = \tau_m \left( -\frac{\partial f_0}{\partial E} \right) \vec{v} \odot \vec{F}
\]

\[
\vec{F} = -\nabla_r F_n + T \left[ E_C + E(k) - F_n \right] \nabla_r \left( \frac{1}{T} \right)
\]

\[
\vec{J}_n(\vec{r}) = \frac{(-q)}{\Omega} \sum_k \tau_m \left( -\frac{\partial f_0}{\partial E} \right) \vec{v} \odot \vec{F}
\]

\[
\vec{J}_n(\vec{r}) = \frac{(-q)}{\Omega} \sum_k \tau_m \left( -\frac{\partial f_0}{\partial E} \right) (\vec{v} \vec{v}) \odot \vec{F} \quad \text{tensor}
\]
an isotropic, isothermal conductor

\[ J_x = -\frac{dF_n}{dx} \]

isothermal, spatial variations only in x-direction

\[ \delta f = \tau_m \left( -\frac{\partial f_0}{\partial E} \right) v_x J_x \]

solution

\[ J_{nx}(\vec{r}) = \frac{1}{\Omega} \sum_k (-q) v_x \delta f(\vec{r}, \vec{k}) \]

current density in x-direction

\[ J_{nx} = \frac{(-q)}{\Omega} \sum_k v_x \left[ \tau_m \left( -\frac{\partial f_0}{\partial E} \right) v_x J_x \right] = \left( \frac{1}{\Omega} \sum_k q v_x^2 \tau_m \left( -\frac{\partial f_0}{\partial E} \right) \right) \frac{dF_n}{dx} = \sigma \frac{dF_n}{dx} \]
conductivity

\[ J_{nx} = \sigma \frac{d(F_n/q)}{dx} \]

\[ \sigma = \frac{1}{\Omega} \sum_k q^2 v_x^2 \tau_m \left( -\frac{\partial f_0}{\partial E} \right) \]

To work out this expression, we need to evaluate the sum.
sums and integrals in $k$-space

\[ \sum \langle \psi \rangle \rightarrow \int \langle \psi \rangle N_k d\vec{k} \]

\[ N_k = 2 \times \left( \frac{\Omega}{8\pi^2} \right) = \frac{\Omega}{4\pi^3} \quad d\vec{k} = dk_x dk_y dk_z \quad 3D \]

$N_k$ is the density of states in $k$-space. Note that it is independent of bandstructure.

See:
ECE 656: L2 http://nanohub.org/resources/7281
\[ \sigma = \frac{1}{\Omega} \sum_k q^2 v_x^2 \tau_m \left( -\frac{\partial f_0}{\partial E} \right) \]
\[ \frac{1}{\Omega} \sum_k (\mathcal{C}) \rightarrow \frac{1}{\Omega} \int (\mathcal{C}) N_k dk = \frac{1}{\Omega} g_v \frac{\Omega}{4\pi^3} \int_0^\infty (\mathcal{C}) 4\pi k^2 dk \]

\[ \sigma = \frac{g_v q^2}{\pi^2} \int_0^\infty \nu_x^2 \tau_m (k) \left( -\frac{\partial f_0}{\partial E} \right) k^2 dk \]

\[ \sigma_s = \frac{g_v q^2}{3\pi^2} \int_0^\infty \nu^2 \tau_m (k) \left( -\frac{\partial f_0}{\partial E} \right) k^2 dk \]

\[ \nu^2 = \nu_x^2 + \nu_y^2 + \nu_z^2 \]

\[ \nu^2 = 3\nu_x^2 \]

isotropic bands
conductivity

\[ \sigma = \frac{g_v q^2}{3\pi^2} \int_0^\infty \nu^2 \tau_m(k) \left(-\frac{\partial f_0}{\partial E}\right) k^2 \, dk \]

\[ \sigma = \frac{g_v q^2 (2m^*)^{3/2}}{3\pi^2 \hbar^3 m^*} \tau_0 \int_{E_C}^\infty (E - E_c)^{3/2} \left(-\frac{\partial f_0}{\partial E}\right) \, dE \]

parabolic bands

\[ E = \frac{\hbar^2 k^2}{2m^*} \]

\[ k^2 \, dk = \frac{(2m^*)^{3/2}}{2\hbar^3} (E - E_c)^{1/2} \, dE \]

\[ \nu^2 = \frac{2(E - E_c)}{m^*} \]

constant scattering time

\[ \tau_m(E) = \tau_0 \]
result:

\[ \sigma = q \left( \frac{q \tau_0}{m^*} \right) g_v \frac{1}{4} \left( \frac{2m^* k_B T'}{\pi \hbar^2} \right)^{3/2} \mathcal{F}_{1/2} (\eta_F) \quad \eta_F = \frac{E_F - E_c}{k_B T'} \]

Recall....

\[ n_0 = N_C \mathcal{F}_{1/2} (\eta_F) = g_v \frac{1}{4} \left( \frac{2m^* k_B T'}{\pi \hbar^2} \right)^{3/2} \mathcal{F}_{1/2} (\eta_F) \]

\[ \sigma = n_0 q \left( \frac{q \tau_0}{m^*} \right) = n_0 q \mu_n \]
conductivity from the BTE

\[ \sigma = n_0 q \left( \frac{q \langle \tau_m \rangle}{m^*} \right) = n_0 q \mu_n \]

How does this result relate to the Landauer approach?

Let’s go back…. (slide 25)

\[ \sigma = \frac{g_v q^2}{3 \pi^2} \int_0^\infty \nu^2 \tau_m(k) \left( -\frac{\partial f_0}{\partial E} \right) k^2 dk \quad \text{change variables to energy} \]
conductivity

\[ \sigma = \frac{g_v q^2}{3 \pi^2} \int_0^\infty \nu^2 \tau_m(k) \left( -\frac{\partial f_0}{\partial E} \right) k^2 dk \]

\[ k^2 dk = \frac{(2m^*)^{3/2}}{2\hbar^3} (E - E_C)^{1/2} dE \]

\[ D_{3D}(E) = g_v \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^3} (E - E_C)^{1/2} \]

\[ \nu^2(E) = 3 \nu_x^2(E) \]

\[ M_{3D}(E) = \frac{\hbar}{4} \nu_x^+(E) D_{3D}(E) \]

\[ \lambda(E) \equiv 2 \frac{\nu_x^2(E) \tau_m(E)}{\nu_x^+(E)} \]

“mfp for backscattering”
So the result from solving the BTE is equivalent to the result from the Landauer approach in the diffusive limit.

Similarly, it is easy to show that the BTE gives the same answers for the Seebeck coefficient and electronic heat conductivity.
the BTE with a B-field...

\[
\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_r f + \mathbf{F}_e \cdot \nabla_p f = \left. \frac{df}{dt} \right|_{\text{coll}}
\]

steady-state, spatially uniform with RTA:

\[
\mathbf{F}_e \cdot \nabla_p f = -\frac{\delta f}{\tau_m}
\]

\[
\mathbf{F}_e = -q\mathbf{E} - q\mathbf{v} \times \mathbf{B}
\]
the coupled current equations ($B = 0$)

\[ \vec{J} = \sigma \vec{E} - s_T \nabla T_L \]

\[ \vec{J}_Q = T_L s_T \vec{E} - \kappa \nabla T_L \]

\[ \vec{E} = \rho \vec{J}_n + S \nabla T_L \]

\[ J^q_x = \pi J_x - \kappa_e \frac{dT}{dx} \]

(diffusive transport)

Transport tensors were \textit{diagonal} for parabolic energy bands.
the coupled current equations \((B \neq 0)\)

\[
\begin{align*}
\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_r f + \vec{F_e} \cdot \nabla_p f &= \frac{df}{dt}_{\text{coll}} \\
\vec{F_e} &= -q\vec{E} - q\vec{v} \times \vec{B}
\end{align*}
\]

\[
\begin{align*}
\vec{J} &= \left[ \sigma(\vec{B}) \right] \vec{E} - \left[ s_T(\vec{B}) \right] \nabla T_L \\
\vec{E} &= \left[ \rho(\vec{B}) \right] \vec{J}_n + \left[ S(\vec{B}) \right] \nabla T_L \\
\vec{J}_Q &= T_L \left[ s_T(\vec{B}) \right] \vec{E} - \left[ \kappa_0(\vec{B}) \right] \nabla T_L \\
\vec{J}_Q &= \left[ \pi(\vec{B}) \right] \vec{J}_n - \left[ \kappa_e(\vec{B}) \right] \nabla T_L
\end{align*}
\]

(diffusive transport)

Transport tensors now depend on the B-field and have off-diagonal terms.
summary

Landauer approach:

- clear physical insight
- works in ballistic limit as well as quasi-ballistic and diffusive regimes
- does not require a bandstructure

BTE approach:

- “easy” to add magnetic field
- anisotropic materials (transport tensors) straight-forward
- can resolve transport spatially
- “off-equilibrium” easy to handle
- ballistic transport can be handled, but not as easily
- not as physically transparent

Bottom line: should know both approaches.