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):

$$q_x = -\kappa_L\left(\frac{dT}{dx}\right)$$

$$\sigma = \frac{2q^2}{h}\langle M_{el}/A\rangle\langle\langle\lambda_{el}\rangle\rangle = n_0 q\mu_n$$

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

$$\pi = TS$$

$$\kappa_e = T\sigma\mathcal{L}$$

$$\kappa_L = \frac{\pi^2 k_B^2 T}{3h}\langle M_{ph}/A\rangle\langle\langle\lambda_{ph}\rangle\rangle$$

lecture 6 topics

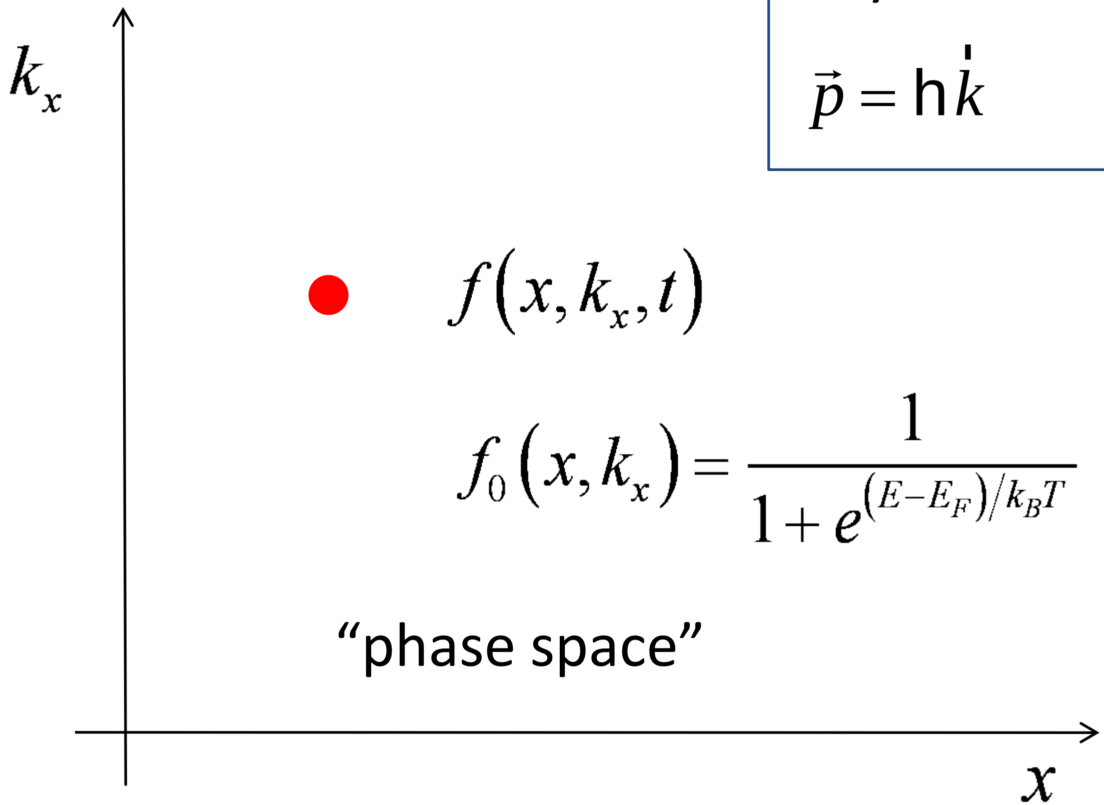
The TE transport coefficients are traditionally derived by solving the Boltzmann Transport Equation (BTE). This lecture is a short introduction to the BTE approach and a discussion of how it relates to the Landauer approach.

1) Phase space
2) The BTE
3) Solving the s.s. BTE
4) The TE coefficients
5) BTE and Landauer

$f(r, k, t)$

"crystal momentum"

$$\vec{p} = \hbar \vec{k}$$



$$f\left(x, k_x, t\right)$$

$$f_0\left(x, k_x\right) = \frac{1}{1 + e^{\left(E - E_F\right)/k_B T}}$$

"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
Lundstrom, *Fundamentals of Carrier Transport*, Cambridge, 2000.
ECE 656: L12-17: http://nanohub.org/resources/7281

semi-classical transport

$$\frac{d\left(\hbar\vec{k}\right)}{dt} = -\nabla_r E_C(\vec{r}) = -q\vec{\mathcal{E}}(\vec{r})$$

$$\left\{ \frac{d\vec{p}}{dt} = \vec{F}_e \right\}$$

$$\hbar\vec{k}(t) = \hbar\vec{k}(0) + \int_0^t -q\vec{\mathcal{E}}(t')dt'$$

$$\vec{\upsilon}_g(t) = \frac{1}{\hbar}\nabla_k E\left[\vec{k}(t)\right]$$

$$\vec{r}(t) = \vec{r}(0) + \int_0^t \vec{\upsilon}_g(t')dt'$$

equations of motion for "semi-classical transport"

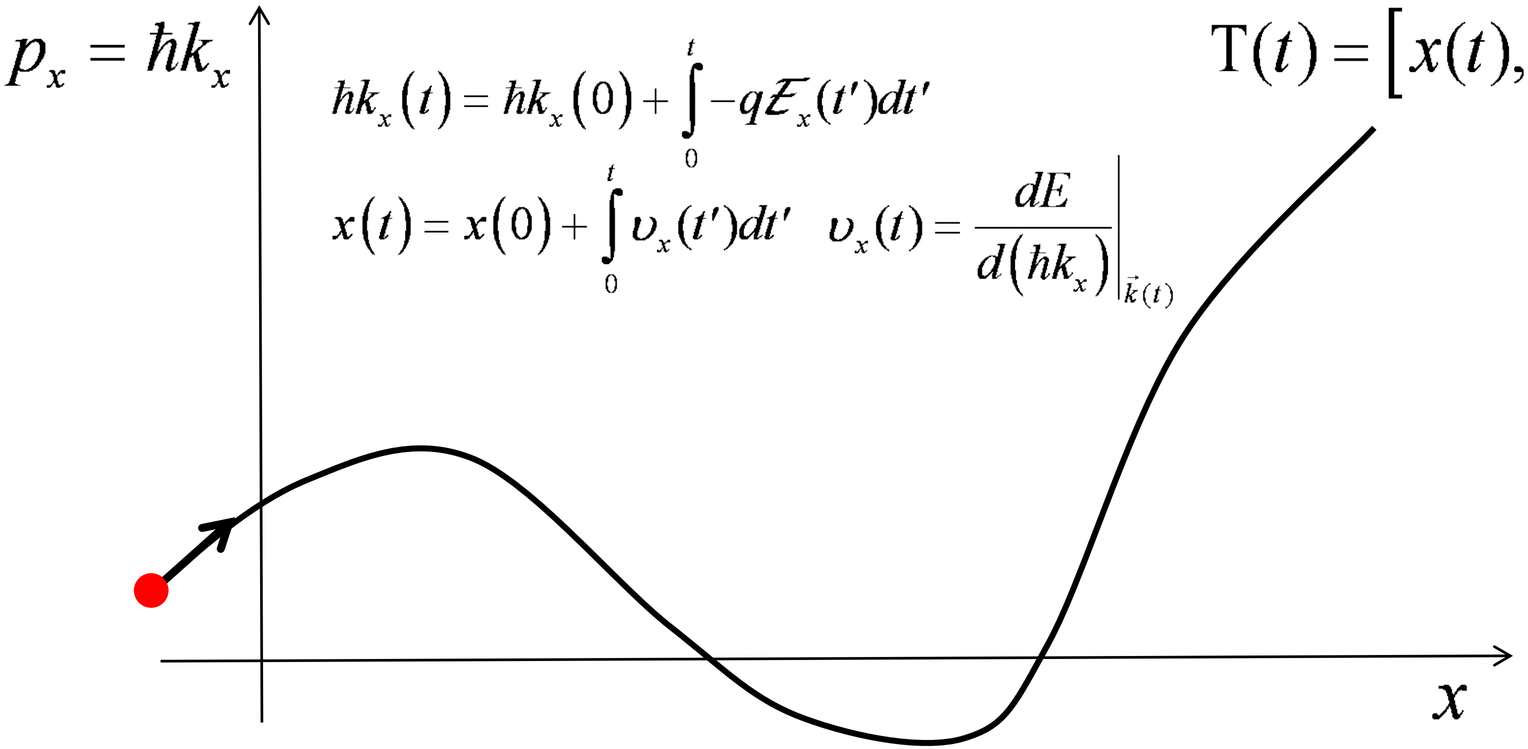
E_C varies slowly on the scale of the electron's wavelength.

trajectories in phase space

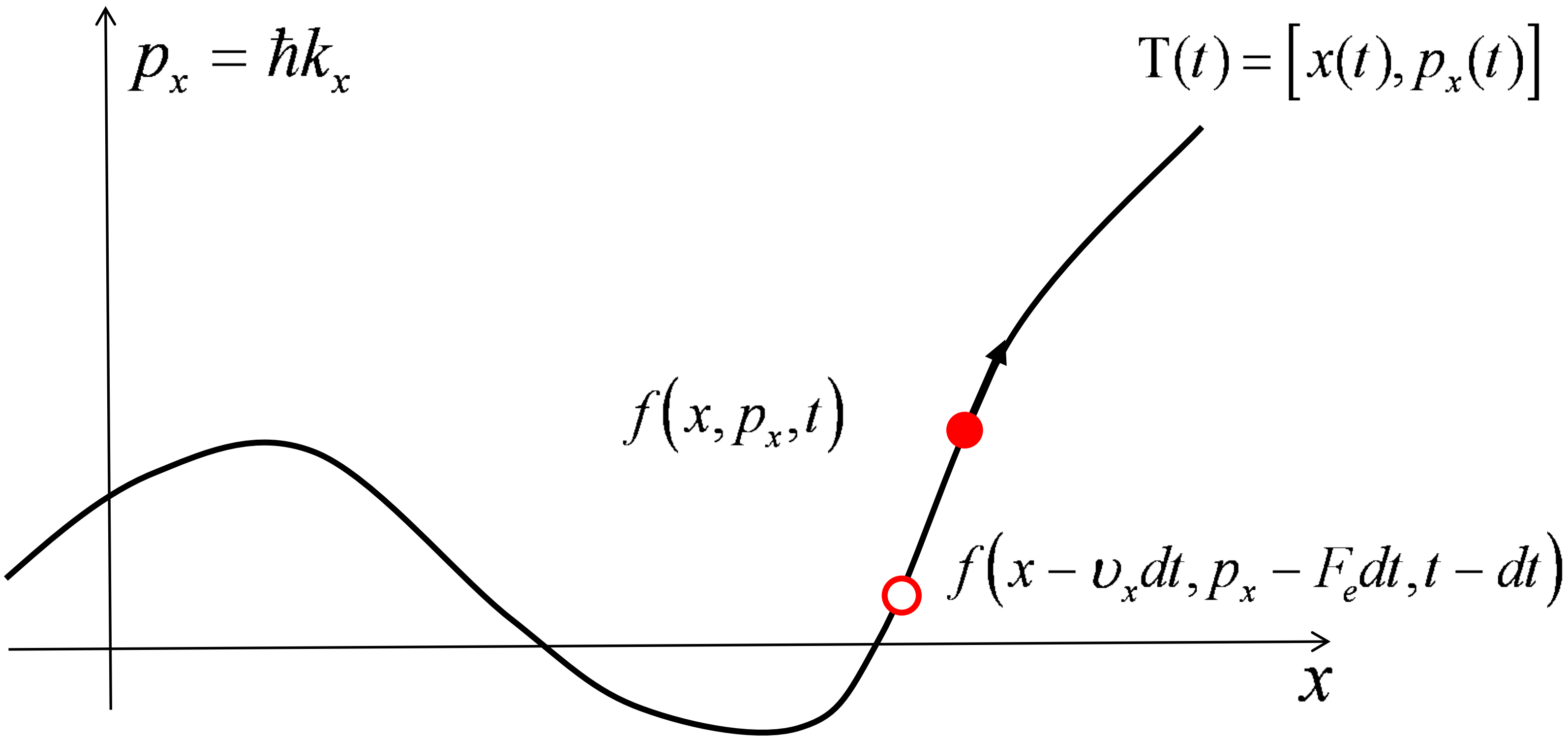
$$T(t) = \left[x(t), p_x(t)\right]$$

$$\hbar k_x(t) = \hbar k_x(0) + \int_0^t -q\mathcal{E}_x(t')dt'$$

$$x(t) = x(0) + \int_0^t \upsilon_x(t')dt' \quad \upsilon_x(t) = \left.\frac{dE}{d(\hbar k_x)}\right|_{\vec{k}(t)}$$



Boltzmann Transport Equation (BTE)



$$f\left(x, p_x, t\right) = f\left(x - \upsilon_x dt, p_x - F_e dt, t - dt\right) \qquad \frac{df}{dt} = 0$$

BTE

$$f(x, p_x, t) \qquad \frac{df}{dt} = 0$$

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

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x}\upsilon_x + \frac{\partial f}{\partial p_x}F_x = 0$$

$$\boxed{\frac{\partial f}{\partial t} + \vec{\upsilon} \cdot \nabla_r f + \vec{F}_e \cdot \nabla_p f = 0}$$

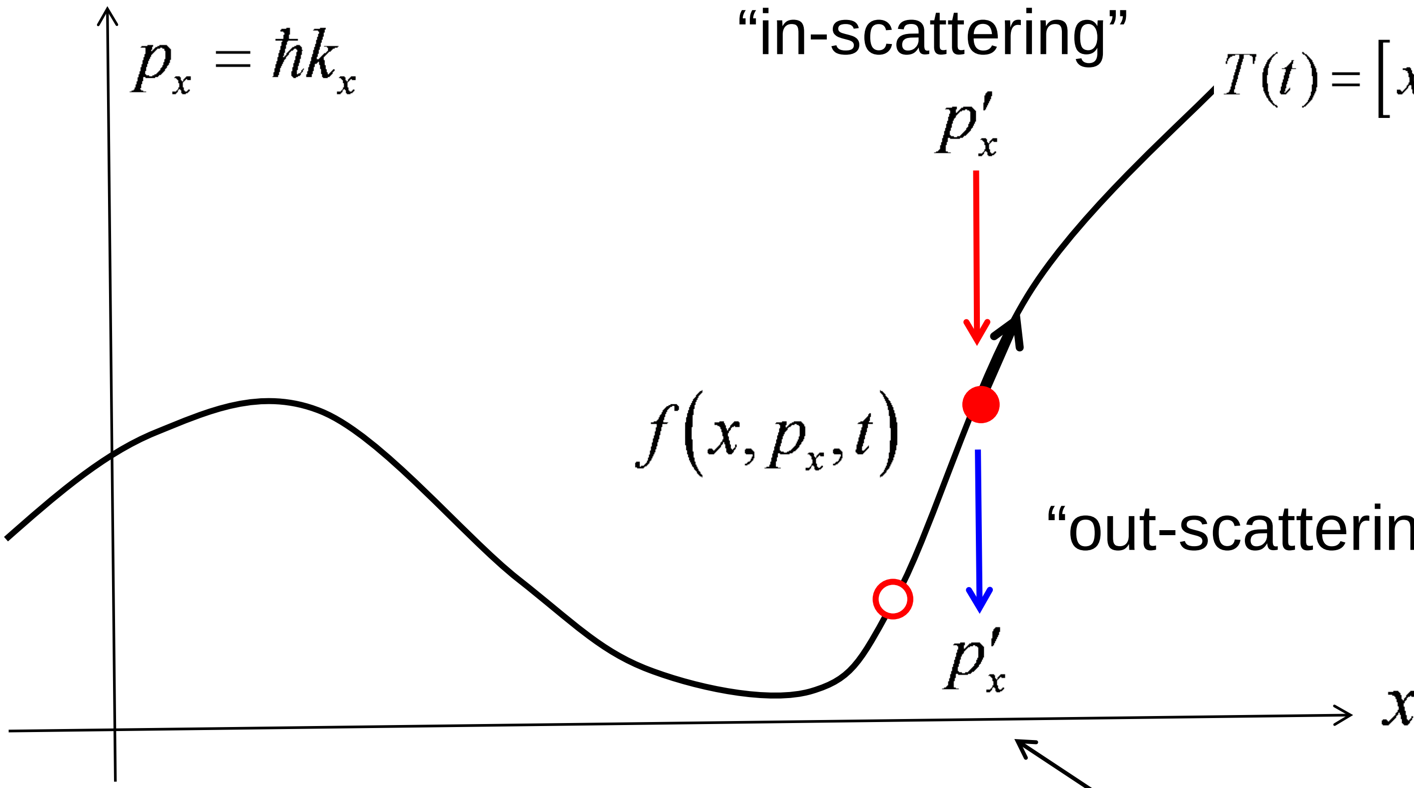
$$\vec{F}_e = -q\vec{\mathcal{E}} - q\vec{\upsilon} \times \vec{B}$$

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

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

$$\vec{p} = \hbar\vec{k}$$

in and out-scattering



$$\left.\frac{df}{dt}\right|_{coll} = \hat{C}f = \text{in-scattering - out-scattering}$$

position, *x*, does not change

scattering and the RTA

$$\frac{\partial f}{\partial t} + \vec{\upsilon} \cdot \nabla_r f + \vec{F}_e \cdot \nabla_p f = 0 \rightarrow \frac{\partial f}{\partial t} + \vec{\upsilon} \cdot \nabla_r f + \vec{F}_e \cdot \nabla_p f = \hat{C} f$$

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 **isotropic and/or elastic** in which case the proper time to use is the "momentum relaxation time."

steady-state BTE

$$\frac{\partial f}{\partial t} + \vec{\upsilon} \cdot \nabla_r f + \vec{F}_e \cdot \nabla_p f = \hat{C} f \rightarrow \frac{\partial f}{\partial t} + \vec{\upsilon} \cdot \nabla_r f + \vec{F}_e \cdot \nabla_p f = -\frac{\delta f}{\tau_m}$$

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

$$|f_0(\vec{p})| >> |\delta f(\vec{p})|$$

"near-equilibrium"

no B-fields for now

$$\vec{F}_e = -q\vec{\mathcal{E}}$$

RTA

solving the near eq., s.s BTE

$$\vec{\upsilon} \cdot \nabla_r f - q\vec{\mathcal{E}} \cdot \nabla_p f = -\frac{\delta f(\vec{p})}{\tau_m}$$

$$\nabla_r f \approx \nabla_r f_0 \qquad \nabla_p f \approx \nabla_p f_0$$

$$\vec{\upsilon} \cdot \nabla_r f_0 - q\vec{\mathcal{E}} \cdot \nabla_p f_0 = -\frac{\delta f(\vec{p})}{\tau_m}$$

$$\delta f(\vec{p}) = -\tau_m \vec{\upsilon} \cdot \nabla_r f_0 + q\tau_m \vec{\mathcal{E}} \cdot \nabla_p f_0$$

BTE solution

$$\delta f = -\tau_m \vec{\upsilon} \cdot \nabla_r f_0 + q\tau_m \vec{\mathcal{E}} \cdot \nabla_p f_0$$

$$f_0(\vec{p}) = \frac{1}{1+e^{\Theta}} \qquad \Theta(\vec{r},\vec{p}) = \left[E(\vec{r},\vec{p}) - F_n(\vec{r})\right]/k_B T$$

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

$$\nabla_r f_0 = \frac{\partial f_0}{\partial \Theta} \nabla_r \Theta$$

$$\nabla_p f_0 = \frac{\partial f_0}{\partial \Theta} \nabla_p \Theta$$

$$\frac{\partial f_0}{\partial \Theta} = k_B T \frac{\partial f_0}{\partial E}$$

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

BTE solution

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

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

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

$$\delta f = \tau_m\left(-\frac{\partial f_0}{\partial E}\right)\vec{\upsilon}\cdot\left\{-\nabla_r F_n + T\left[E_C + E(\vec{p}) - F_n\right]\nabla_r\left(\frac{1}{T}\right)\right\}$$

generalized force

$$\delta f = \tau_m \left(-\frac{\partial f_0}{\partial E} \right) \vec{\upsilon} \bullet \vec{\mathcal{F}}$$

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

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?

$$\delta f = \tau_m \left(-\frac{\partial f_0}{\partial E} \right) \vec{\upsilon} \bullet \vec{\mathcal{F}}$$

moments

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

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

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

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

Recall Lecture 1

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

current

$$\vec{J}_n(\vec{r}) = \frac{1}{\Omega}\sum_{\vec{k}}(-q)\vec{\upsilon}\,\delta f\left(\vec{r},\vec{k}\right) \qquad \delta f = \tau_m\left(-\frac{\partial f_0}{\partial E}\right)\vec{\upsilon}\circ\vec{\mathcal{F}}$$

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

$$\vec{J}_n(\vec{r}) = \frac{(-q)}{\Omega}\sum_{\vec{k}}\tau_m\left(-\frac{\partial f_0}{\partial E}\right)\vec{\upsilon}\left[\vec{\upsilon}\circ\vec{\mathcal{F}}\right]$$

$$\vec{J}_n(\vec{r}) = \frac{(-q)}{\Omega}\sum_{\vec{k}}\tau_m\left(-\frac{\partial f_0}{\partial E}\right)\left(\vec{\upsilon}\,\vec{\upsilon}\right)\circ\vec{\mathcal{F}}$$

tensor

an isotropic, isothermal conductor

$$\mathcal{F}_x = -\frac{dF_n}{dx}$$

isothermal, spatial variations only in *x*-direction

$$\delta f = \tau_m\left(-\frac{\partial f_0}{\partial E}\right)\upsilon_x \mathcal{F}_x$$

solution

$$J_{nx}(\vec{r}) = \frac{1}{\Omega}\sum_{\vec{k}}(-q)\upsilon_x \delta f\left(\vec{r},\vec{k}\right)$$

current density in *x*-direction

$$J_{nx} = \frac{(-q)}{\Omega}\sum_{k}\upsilon_x\left[\tau_m\left(-\frac{\partial f_0}{\partial E}\right)\upsilon_x\mathcal{F}_x\right] = \left(\frac{1}{\Omega}\sum_{\vec{k}} q\,\upsilon_x^2\tau_m\left(-\frac{\partial f_0}{\partial E}\right)\right)\times\frac{dF_n}{dx} = \sigma\frac{dF_n}{dx}$$

conductivity

$$J_{nx} = \sigma \frac{d\left(F_n/q\right)}{dx}$$

$$\sigma = \frac{1}{\Omega}\sum_{\vec{k}} q^2 \upsilon_x^2 \tau_m \left(-\frac{\partial f_0}{\partial E}\right)$$

To work out this expression, we need to evaluate the sum.

sums and integrals in *k*-space

$$\sum_{\vec{k}} (\circ) \rightarrow \int (\circ) N_k d\vec{k} \qquad N_k = 2 \times \left(\frac{\Omega}{8\pi^2} \right) = \frac{\Omega}{4\pi^3} \qquad d\vec{k} = dk_x dk_y dk_z \qquad \text{3D}$$

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

See:
Lundstrom, Ch. 1, *Fundamentals of Carrier Transport*, Cambridge, 2000.
ECE 656: L2 http://nanohub.org/resources/7281

conductivity

$$\sigma = \frac{1}{\Omega}\sum_{\vec{k}} q^2 \upsilon_x^2 \tau_m \left(-\frac{\partial f_0}{\partial E}\right) \qquad \frac{1}{\Omega}\sum_{\vec{k}}(\circlearrowright) \rightarrow \frac{1}{\Omega}\int(\circlearrowright) N_k d\vec{k} = \frac{1}{\Omega} g_v \frac{\Omega}{4\pi^3}\int_0^\infty (\circlearrowright) 4\pi k^2\, dk$$

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

$$\sigma_S = \frac{g_v q^2}{3\pi^2}\int_0^\infty \upsilon^2 \tau_m(k)\left(-\frac{\partial f_0}{\partial E}\right) k^2 dk$$

$$\upsilon^2 = \upsilon_x^2 + \upsilon_y^2 + \upsilon_z^2$$

$$\upsilon^2 = 3\upsilon_x^2$$

isotropic bands

conductivity

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

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

parabolic bands

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

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

$$\upsilon^2 = \frac{2\left(E - E_c\right)}{m^*}$$

constant scattering time

$$\tau_m(E) = \tau_0$$

result:

$$\sigma = q\left(\frac{q\tau_0}{m^*}\right) g_V \frac{1}{4}\left(\frac{2m^* k_B T}{\pi\hbar^2}\right)^{3/2} \mathcal{F}_{1/2}(\eta_F) \qquad \eta_F = \frac{E_F - E_c}{k_B T}$$

✔

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

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

✔

How does this result relate to the Landauer approach ?

Let's go back….(slide 25)

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

change variables to energy

conductivity

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

$$\sigma = \frac{2q^2}{h} \int_0^\infty M_{3D}(E) \lambda(E) \left(-\frac{\partial f_0}{\partial E} \right) dE$$

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

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

$$\upsilon^2(E) = 3\upsilon_x^2(E)$$

$$M_{3D}(E) = \frac{h}{4} \upsilon_x^+(E) D_{3D}(E)$$

$$\lambda(E) \equiv 2 \frac{\upsilon_x^2(E) \tau_m(E)}{\upsilon_x^+(E)}$$

"mfp for backscattering"

finally

$$\sigma = \frac{2q^2}{h} \int_0^{\infty} M(E)\lambda(E)\left(-\frac{\partial f_0}{\partial E}\right) dE = \frac{2q^2}{h} \langle M(E) \rangle \langle\langle \lambda(E) \rangle\rangle \quad ✔$$

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…

$$\frac{\partial f}{\partial t} + \vec{\upsilon} \bullet \nabla_r f + \vec{F}_e \bullet \nabla_p f = \left.\frac{df}{dt}\right|_{coll}$$

steady-state, spatially uniform with RTA:

$$\vec{F}_e \bullet \nabla_p f = -\frac{\delta f}{\tau_m}$$

$$\vec{F}_e = -q\vec{\mathcal{E}} - q\vec{\upsilon} \times \vec{B}$$

the coupled current equations (B = 0)

$$\vec{J} = \sigma\vec{\mathcal{E}} - s_T\nabla T_L$$

$$\vec{J}_Q = T_L s_T\vec{\mathcal{E}} - \kappa\nabla T_L$$

$$\vec{\mathcal{E}} = \rho\vec{J}_n + S\nabla T_L$$

$$J_x^q = \pi J_x - \kappa_e \frac{dT}{dx}$$

(diffusive transport)

Transport tensors were ***diagonal*** for parabolic energy bands.

the coupled current equations ($B \neq 0$)

$$\frac{\partial f}{\partial t} + \vec{\upsilon} \bullet \nabla_r f + \vec{F}_e \bullet \nabla_p f = \left.\frac{df}{dt}\right|_{coll} \qquad \vec{F}_e = -q\vec{\mathcal{E}} - q\vec{\upsilon} \times \vec{B}$$

$$\vec{J} = \left[\sigma\left(\vec{B}\right)\right]\vec{\mathcal{E}} - \left[s_T\left(\vec{B}\right)\right]\nabla T_L \qquad \vec{\mathcal{E}} = \left[\rho\left(\vec{B}\right)\right]\vec{J}_n + \left[S\left(\vec{B}\right)\right]\nabla T_L$$

$$\vec{J}_Q = T_L\left[s_T\left(\vec{B}\right)\right]\vec{\mathcal{E}} - \left[\kappa_0\left(\vec{B}\right)\right]\nabla T_L \qquad \vec{J}_Q = \left[\pi\left(\vec{B}\right)\right]\vec{J}_n - \left[\kappa_e\left(\vec{B}\right)\right]\nabla T_L$$

(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.