Lecture 11: Coupled Current Equations: and thermoelectric devices

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basic equations of thermoelectricity

\[ \mathcal{E}_x = \rho_n J_x + S_n \frac{dT_L}{dx} \]
\[ J^q_x = \pi_n J_x - \kappa_n \frac{dT_L}{dx} \]

Four transport coefficients:

1) resistivity (Ω-cm) = 1/conductivity (S/cm)
2) Seebeck coefficient (V/K)
3) Peltier coefficient (W/A)
4) Electronic heat conductivity (W/m-K)

Note: These equations describe electric and heat currents due to electrons in the diffusive limit and in 3D.
physics of Peltier cooling

contacts 1 and 2

Electrons absorb thermal energy, $E - E_{F1}$

Electrons dissipate energy, $E - E_{F2}$

Net power dissipated: $P_D = IV$

$E_{F2} = E_{F1} - qV$

Electrons enter contact 1 at the Fermi energy, $E_{F1}$

Electrons leave contact 2 at the Fermi energy, $E_{F2}$
a closer look at contact 1

energy channel

“evaporation” of the electron liquid
Monte Carlo simulation

“It is interesting that the thermoelectric cooling and heating regions are contained in the highly doped contact layers.”

1) Introduction
2) Coupled flow equations
3) Thermoelectric devices
4) Discussion
5) Summary
for bulk 3D semiconductors

\[ J_x = \sigma \mathcal{E}_x - \sigma S \frac{dT_L}{dx} \]

\[ J^q_x = T_L \sigma S \mathcal{E}_x - \kappa_0 \frac{dT_L}{dx} \]

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

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

(diffusive transport)

\[ \sigma = \int \sigma'(E) dE \]

\[ \sigma'(E) = \frac{2q^2}{h} \lambda(E) \frac{M(E)}{A} \left( - \frac{\partial f_0}{\partial E} \right) \]

\[ S = -\frac{k_B}{q} \int \left( \frac{E - E_F}{k_B T_L} \right) \sigma'(E) dE \]

\[ \pi = T_L S \]

\[ \kappa_0 = T_L \left( \frac{k_B}{q} \right)^2 \int \left( \frac{E - E_F}{k_B T_L} \right)^2 \sigma'(E) dE \]

\[ \kappa_e = \kappa_0 - \pi S \sigma \]
transport parameters (3D, diffusive)

1) Assume parabolic energy bands

2) Assume power law scattering

\[ \lambda(E) = \lambda_0 \left[ \frac{(E - E_C)}{k_B T_L} \right]^\gamma \]

Ionized impurity scattering: \( r = 2 \)
Acoustic phonon scattering: \( r = 0 \)

\[ \sigma = \int \sigma'(E) \, dE \]

\[ \sigma'(E) = \frac{2q^2}{h} \frac{\lambda(E)}{A} \frac{M(E)}{A} \left( - \frac{\partial f_0}{\partial E} \right) \]

\[ S = -\frac{k_B}{q} \int \left( \frac{E - E_F}{k_B T_L} \right) \sigma'(E) \, dE / \int \sigma'(E) \, dE \]

\[ \pi = T_L S \]

\[ \kappa_0 = T_L \left( \frac{k_B}{q} \right)^2 \int \left( \frac{E - E_F}{k_B T_L} \right)^2 \sigma'(E) \, dE \]

\[ \kappa_e = \kappa_0 - \pi S \sigma \]
transport parameters

\[
\sigma = \frac{2q^2}{h} \left[ g_v \frac{m^* k_B T_L}{2\pi \hbar^2} \mathcal{F}_0(\eta_F) \right] \left\{ \lambda_0 \frac{\Gamma(r+2) \mathcal{F}_r(\eta_F)}{\Gamma(2) \mathcal{F}_0(\eta_F)} \right\}
\]

\[
S = -\left( \frac{k_B}{q} \right) \left\{ \frac{(r+2) \mathcal{F}_{r+1}(\eta_F)}{\mathcal{F}_r(\eta_F)} - \eta_F \right\}
\]

\[
\pi = T_L S
\]

\[
\kappa_0 = T_L \left( \frac{k_B}{q} \right)^2 \frac{2q^2}{h} g_v \frac{m^* k_B T_L}{2\pi \hbar^2} \lambda_0 \times \left[ \Gamma(r+4) \mathcal{F}_{r+2}(\eta_F) - 2\eta_F \Gamma(r+3) \mathcal{F}_{r+1}(\eta_F) + \eta_F^2 \Gamma(r+2) \mathcal{F}_r(\eta_F) \right]
\]

\[
\kappa_e = \kappa_0 - \pi S \sigma
\]
transport parameters in a different form

$$\sigma = \frac{2q^2}{h} \langle M \rangle \langle \langle \lambda \rangle \rangle$$

$$S = -\left( \frac{k_B}{q} \right) \int \left( \frac{E - E_F}{k_B T_L} \right) \sigma'(E) dE$$

$$\pi = T_L S$$

$$\kappa_0 = T_L \left( \frac{k_B}{q} \right)^2 \int \left( \frac{E - E_F}{k_B T_L} \right)^2 \sigma'(E) dE$$

$$\kappa_e = \kappa_0 - \pi S \sigma$$
Wiedemann-Franz “Law”

\[ \frac{\kappa_0}{\sigma} = T_L \left( \frac{k_B}{q} \right)^2 \left\{ \left( \frac{E - E_F}{k_B T_L} \right)^2 \right\}_{\text{ave}} = T_L L' \quad \text{“Wiedeman Franz Law”} \]

\[ \frac{\kappa_e}{\sigma} = \left( \frac{k_B}{q} \right)^2 \left\{ \left\langle \left( \frac{E - E_F}{k_B T_L} \right)^2 \right\rangle - \left\langle \left( \frac{E - E_F}{k_B T_L} \right) \right\rangle^2 \right\} T_L = L T_L \quad \text{Wiedeman Franz “Law”} \]
electronic heat conductivity

\[ \kappa_n = \sigma_n T_L L \quad L \text{ is the “Lorenz number”} \]

The Lorenz number depends on details of bandstructure, scattering, dimensionality, and degree of degeneracy, but for a constant mfp and parabolic energy bands, it is useful to remember:

- For non-degenerate, 3D semiconductors:
  \[ L \approx 2 \left( \frac{k_B}{q} \right)^2 \]
- For fully degenerate, e.g. 3D metals:
  \[ L \approx \frac{\pi^2}{3} \left( \frac{k_B}{q} \right)^2 \]

a “rule of thumb” not a “law of nature”

Peltier and Seebeck coefficient

\[ \pi_n = T_L S_n (T_L) \]  
“Kelvin relation”

“Onsager relations” for coupled flows

\[ \mathcal{E}_x = \rho_n J_{nx} + S_n \frac{dT_L}{dx} \]

\[ J_{Qx} = \pi_n J_{nx} - \kappa_n \frac{dT_L}{dx} \]
Onsager relations

\[ J_x = L_{11} \frac{dF_n}{dx} + L_{12} \frac{d}{dx} \left( \frac{1}{T_L} \right) \]

\[ J_x = L_{21} \frac{dF_n}{dx} + L_{22} \frac{d}{dx} \left( \frac{1}{T_L} \right) \]

\[ J_1 = L_{11} \left( \vec{B} \right) F_1 + L_{12} \left( \vec{B} \right) F_2 \]

\[ J_2 = L_{21} \left( \vec{B} \right) F_1 + L_{22} \left( \vec{B} \right) F_2 \]

\[ J_1, J_2 \quad \text{“generalized fluxes”} \]

\[ F_1, F_2 \quad \text{“generalized forces”} \]

\[ L_{12} = L_{21} \quad \text{Onsager relation} \]
Onsager relations: example

1) temperature differences produce heat currents

2) pressure differences produce matter currents

→

3) heat flow per pressure difference = matter flow per temperature difference

http://en.wikipedia.org/wiki/Onsager_reciprocal_relations
1) Introduction
2) Coupled flow equations
3) Thermoelectric devices
4) Discussion
5) Summary
1) How much heat can be converted into electricity? (what determines the efficiency?)
1) What determines the maximum temperature difference?
2) How much heat can be pumped?
3) What is the coefficient of performance?
inside view of heat absorption/emission
simplified TE device (one leg)

\[ R_n = \frac{1}{\sigma_n} \frac{L}{A} \]

\[ I^2 R_n / 2 \]

\[ I^2 R_n / 2 \]
simplified TE cooling device (one leg)

1) heat extracted from the cold side
2) heat pumped by Peltier effect
3) heat diffusing down the thermal gradient
4) heat generated by Joule heating
simplified TE cooling device (one leg)

$$Q_C = \pi_n \frac{I}{A} - \kappa \frac{dT_L}{dx} - \frac{I^2 R_n}{2A} \left( \frac{\text{W}}{m^2} \right)$$

$$\frac{dQ_C}{dI} = 0 \rightarrow I_{\text{max}}, Q_{C,\text{max}}$$

$$Q_{C,\text{max}} = 0 \rightarrow \Delta T_{\text{max}}$$

$$\Delta T_{\text{max}} = \frac{1}{2} Z T_{LC}^2 \quad Z = \frac{S_n^2 \sigma_n}{\kappa}$$

TE figure of merit (FOM)
cooling efficiency (COP)

\[ Q_c = \pi_n \frac{I}{A} - \kappa \frac{dT_L}{dx} - \frac{I^2 R_n}{2A} \left( \frac{W}{m^2} \right) \]

\[ \frac{dQ_c}{dI} = 0 \rightarrow I_{\text{max}}, Q_{c_{\text{max}}} \]

\[ \eta = \frac{Q_{c_{\text{max}}}}{P_{\text{in}}} \]

COP at maximum cooling power:

\[ \eta = \frac{Q_{c_{\text{max}}}}{P_{\text{in}}} = f(T_{LC}, T_{LH}, Z) \]
Similarly, an analysis of the power conversion efficiency,

\[ \eta = \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{I^2 R_L}{A Q_{\text{in}}} \]

shows that it is also determined by the TE figure of merit, \( Z \).
The higher the ZT figure of merit, the more efficient a TE device.

1) What material properties are needed for a high ZT?  
2) Given a material, how can we optimize ZT?
FOM

\[ ZT = \frac{S_n^2 \sigma_n T_L}{\kappa} \]

**Numerator:**

\[
S_n(T_L) = \left( \frac{k_B}{-q} \right) \left\{ \frac{(E_C - F_n)}{k_B T_L} + \delta_n \right\}
\]

Mostly determined by position of band edge and \( E_F \). Similar for most materials.

\[
\sigma_n = \left( \frac{2q^2}{h} \right) \langle M \rangle \langle \lambda \rangle
\]

Need a large no. of channels (large \( M, E_F \)). Need large m.f.p. (mobility)

**Denominator:**

\( \kappa_L \gg \kappa_n \)

Mostly determined by lattice thermal conductivity. (Lecture 9 in notes)
FOM: PF vs. Fermi level

\[ ZT = \frac{S_n^2 \sigma_n T_L}{\kappa} \]
The peak PF occurs when $E_F$ is near the band edge.

$$ZT = \frac{S_n^2 \sigma_n T_L}{\kappa}$$

$$PF = S_n^2 \sigma_n$$
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basic equations of thermoelectricity

\[ E_x = \rho_n J_x + S_n \frac{dT_L}{dx} \]
\[ J^q_x = \pi_n J^x_n - \kappa_n \frac{dT_L}{dx} \]

We can write these equations in **vector notation** as:

\[ \vec{E} = \rho_n \vec{J} + S_n \vec{T}_L \]
\[ \vec{J}_q = \pi_n \vec{J} - \kappa_n \vec{T}_L \]

or in **indicial notation** as:

\[ E_i = \rho_n J_i + S_n \partial_i T_L \]
\[ J^q_i = \pi_n J^i - \kappa_n \partial_i T_L \]

\[ i = x, y, z \]
transport tensors

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

\[ \vec{J}_q = \pi \vec{J} - \kappa_n \vec{\nabla} T_L \]

\[ \vec{J}_q = [\pi] \vec{J} - [\kappa_n] \vec{\nabla} T \]

\[
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix} =
\begin{bmatrix}
\rho_{11} & \rho_{12} & \rho_{13} \\
\rho_{21} & \rho_{22} & \rho_{23} \\
\rho_{31} & \rho_{32} & \rho_{33}
\end{bmatrix}
\begin{bmatrix}
J_x \\
J_y \\
J_z
\end{bmatrix}
\]

\[ \mathcal{E}_i = \sum_{j=1}^{3} \rho_{ij} J_j \]

\[ \mathcal{E}_i \equiv \rho_{ij} J_j \quad \text{“summation convention”} \]
coupled current equations again

\[ \vec{E} = [\rho] \vec{J} + [S] \vec{\nabla} T \]
\[ \vec{J}_q = [\pi] \vec{J} - [\kappa_n] \vec{\nabla} T \]

\[ \mathcal{E}_i = \rho_{ij} J_j + S_{ij} \partial_j T \]
\[ J^q_i = \pi_{ij} J_j - \kappa^n_{ij} \partial_j T \]

For isotropic materials, the tensors are diagonal.

\[ \mathcal{E}_i = \rho_0 J_j + S_0 \partial_j T \]
\[ J^q_i = \pi_0 J_j - K^e_0 \partial_j T \]

"Kronecker delta"

\[ \rho_{ij} = \rho_0 \delta_{ij} \]
\[ \delta_{ij} = \begin{cases} 1 & (i = j) \\ 0 & (i \neq j) \end{cases} \]
form of the transport tensors

\[ \mathcal{E}_i = \rho_{ij} J_j + S_{ij} \partial_j T \]

\[ J^q_i = \pi_{ij} J_j - \kappa^e_{ij} \partial_j T \]

For isotropic materials, such as common, cubic semiconductors, the tensors are diagonal (under low-fields).

For a given crystal structure, the form of the tensors (i.e. which elements are zero and which are non-zero) can be deduced from symmetry arguments. (See Smith, Janak, and Adler, Chapter 4.)

The transport tensors can be readily computed by solving the Boltzmann Transport Equation (BTE).
measuring S

\[ V_{\text{meas}} = \Delta V_s - \Delta V_l \]

\[ \Delta V_s = -S_s \Delta T \]

\[ \Delta V_l = -S_l \Delta T \]

\[ V_{\text{meas}} = -(S_s - S_l)\Delta T \]
what about the valence band?

\[ \mathcal{E}_i = \rho_{ij} J_j + S_{ij} \partial_j T \]

\[ J^q_i = \pi^q_{ij} J_j - \kappa^e_{ij} \partial_j T \]
what about the valence band?

\[ M_{3D}^c = g_v \frac{m_n^*}{2\pi\hbar^2} (E - E_c) \]

\[ M_{3D}^v = g_v \frac{m_p^*}{2\pi\hbar^2} (E_v - E) \]
treating both bands: conductivity

\[ \sigma_{\text{tot}} = \int_{E_1}^{E_2} \frac{2q^2}{h} M_{3D}^{\text{tot}}(E) \lambda(E) \left( -\frac{\partial f_0}{\partial E} \right) dE \]

\[ \sigma_n = \int_{E_C}^{E_2} \frac{2q^2}{h} M_{3D}^c(E) \lambda(E) \left( -\frac{\partial f_0}{\partial E} \right) dE \]

\[ \sigma_p = \int_{E_1}^{E_v} \frac{2q^2}{h} M_{3D}^v(E) \lambda(E) \left( -\frac{\partial f_0}{\partial E} \right) dE \]

\[ \sigma_{\text{tot}} = \sigma_n + \sigma_p \]
treating both bands: \( S \)

\[
S_{\text{tot}} = \frac{\sigma_{\text{tot}}}{E_2 - E_1} \left[ \int_{E_1}^{E_2} \left( \frac{E - E_F}{qT_L} \right) \sigma'(E) dE \right] - \frac{\sigma_{\text{tot}}}{E_C - E_1} \left[ \int_{E_1}^{E_C} \left( \frac{E - E_F}{qT_L} \right) \sigma'(E) dE \right]
\]

\[
S_{\text{tot}} = \frac{S_n \sigma_n + S_p \sigma_p}{\sigma_{\text{tot}}}
\]
treating both bands: $\kappa$

$$M_{3D}^{tot}(E) = M_{3D}^c(E) + M_{3D}^{\nu}(E)$$

“bipolar thermodiffusion”

$$\kappa_n = \sigma_{tot} T_L L_{tot}$$

$$L_{tot} \gg L_n + L_p$$
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summary

\[ \mathcal{E}_i = \rho_{ij} J_j + S_{ij} \partial_j T \]

\[ J^q_i = \pi_{ij} J_j - \kappa^e_{ij} \partial_j T \]
questions

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