NanoEnergy

ECE 597/697 Special Topics: Energy Transport and Conversion at the Nanoscale
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Meeting time and place: MWF 12:20 in Elab 306
*Office Hours*: Tue 10:30am, Fri after class, or by appt
Schedule for the rest of the semester

– Final Project proposal and team members due Friday Nov. 14\textsuperscript{st} (1 page statement of problem, methods, outcomes)

– Reading Assignment Reports Due Monday Nov. 17\textsuperscript{th} (electronic submission preferred).

– Topics left to cover (and 7~8 lectures):
  • Boltzmann transport equation and diffusive transport
  • Thermoelectric and thermionic energy conversion
  • Classical size effects based on the BTE

– Final Project presentations at final exam time Dec. 8\textsuperscript{th}

– Final Reports due Dec. 8\textsuperscript{th} (electronic submission, will accept until Friday Dec. 12\textsuperscript{th})
Recap so far

• We have discussed the transport of energy/heat and charge in a perfect 1-dimensional conductor between 2 reservoirs

• We obtained 4 key results for an ideal 1-d system:
  – Thermal conductance of both phonons AND electrons is \( \frac{\pi^2 k_B T}{3h} \)
  – Charge conductance of electrons is \( \frac{e^2}{h} \)
  – The thermo-electric coupling was zero (no charge current from \( \Delta T \))
  – All of these results were independent of the actual material properties

• Next we move away from the assumption of having quasi-ballistic transport (with constant transmission) between two reservoirs

• We are interested in the regime where we have lots of scattering—conductivity instead of conductance

• We have to consider diffusive rather than ballistic transport
Boltzmann Transport Equation

• The BTE governs the evolution of the transport distribution function

• We “derived” the BTE by counting particles

• There are 3 mechanisms which change the distribution function:
  – Motion in real space due to group velocity
    \[
    \frac{df_T (\vec{r}, \vec{k}, t)}{dt} = - \frac{d\vec{r}}{dt} \cdot \nabla_{\vec{r}} f_T (\vec{r}, \vec{k}, t) = -\vec{v}(\vec{k}) \cdot \nabla_{\vec{r}} f_T (\vec{r}, \vec{k}, t)
    \]
  – Acceleration due to an applied force=change in reciprocal/k-space
    \[
    \frac{df_T (\vec{r}, \vec{k}, t)}{dt} = - \frac{d\vec{k}}{dt} \cdot \nabla_{\vec{k}} f_T (\vec{r}, \vec{k}, t) = -\vec{F}(\vec{r}) \cdot \nabla_{\vec{k}} f_T (\vec{r}, \vec{k}, t)
    \]
  – Scattering from state to state in k-space
    \[
    \frac{df_T (\vec{r}, \vec{k}, t)}{dt} = df_{\text{scat-in}} - df_{\text{scat-out}} = \sum_k \left[ f_T (\vec{r}, \vec{k}', t)S(\vec{k}', \vec{k}) - f_T (\vec{r}, \vec{k}, t)S(\vec{k}, \vec{k}') \right]
    \]

• We simply add up the terms to get the total rate of change of the distribution

\[
\frac{\partial f_T (\vec{r}, \vec{k}, t)}{\partial t} + \vec{v}(\vec{k}) \cdot \nabla_{\vec{r}} f_T (\vec{r}, \vec{k}, t) + \vec{F}(\vec{r}) \cdot \nabla_{\vec{k}} f_T (\vec{r}, \vec{k}, t) = \sum_k \left[ f_T (\vec{r}, \vec{k}', t)S(\vec{k}', \vec{k}) - f_T (\vec{r}, \vec{k}, t)S(\vec{k}, \vec{k}') \right]
\]
Another way to view the RHS of the BTE is to consider what happens if we perturb each of the coordinates slightly by \(dr\), \(dx\), and \(dt\).

Then we can use a Taylor expansion and retain the first terms:

\[
f_T(\vec{r} + d\vec{r}, \vec{k} + d\vec{k}, t + dt) = f_T(\vec{r}, \vec{k}, t) + \nabla_{\vec{r}} f_T(\vec{r}, \vec{k}, t) \cdot d\vec{r} + \nabla_{\vec{k}} f_T(\vec{r}, \vec{k}, t) \cdot d\vec{k} + df_T(\vec{r}, \vec{k}, t)dt
\]

Rearrange this to pull the \(dt\) in front:

\[
f_T(\vec{r} + d\vec{r}, \vec{k} + d\vec{k}, t + dt) = f_T(\vec{r}, \vec{k}, t) + dt \left[ \nabla_{\vec{r}} f_T(\vec{r}, \vec{k}, t) \cdot \frac{d\vec{r}}{dt} + \nabla_{\vec{k}} f_T(\vec{r}, \vec{k}, t) \cdot \frac{d\vec{k}}{dt} + \frac{df_T(\vec{r}, \vec{k}, t)}{dt} \right]
\]

Finally we recognize that the term in brackets is equal to the scattering

\[
f_T(\vec{r} + d\vec{r}, \vec{k} + d\vec{k}, t + dt) = f_T(\vec{r}, \vec{k}, t) + dt \sum_{\vec{k}'} \left[ f_T(\vec{r}, \vec{k}', t)S(\vec{k}', \vec{k}) - f_T(\vec{r}, \vec{k}, t)S(\vec{k}, \vec{k}') \right]
\]

What this means is that the distribution function is conserved along the trajectory of a given particle...unless there is scattering.
BTE: the scattering term

- Motion/acceleration is “easy”: we can compute the group velocity from the dispersion and apply a force via electric and magnetic fields.
- Scattering often poses a challenge and we seek to simplify that term.
- In equilibrium, we know that the rate of change is zero, even with scattering.
- Hence we can write the homogeneous steady-state condition:

\[
\sum_{\vec{k}'} \left[ f_0(\vec{r}, \vec{k}', t) S(\vec{k}', \vec{k}) - f_0(\vec{r}, \vec{k}, t) S(\vec{k}, \vec{k}') \right] = 0
\]

- Here \(f_0\) refers to the equilibrium distribution (Fermi-Dirac for electrons, Bose-Einstein for phonons).
- However, equilibrium also requires that each term in the sum is zero:

\[
f_0(\vec{r}, \vec{k}', t) S(\vec{k}', \vec{k}) - f_0(\vec{r}, \vec{k}, t) S(\vec{k}, \vec{k}') = 0
\]

- This condition is called “detailed balance”.
- For elastic collisions, \(|k| = |k'|\) so we can indeed write \(S(k, k') = S(k', k)\).
BTE: scattering rate vs relaxation time

Using detailed balance, we can simplify the scattering term

$$\frac{df_{\text{scat}}}{dt} = \sum_{\vec{k}} \left[ (f_T' - f_0') S(\vec{k}', \vec{k}) - (f_T - f_0) S(\vec{k}, \vec{k}') \right]$$

Then we can pull the terms that do not have \( k' \) in front to get

$$df_{\text{scat}} = -(f_T - f_0) \sum_{\vec{k}'} S(\vec{k}, \vec{k}') + \sum_{\vec{k}'} (f_T' - f_0') S(\vec{k}', \vec{k})$$

The term \( \Gamma(\vec{k}) = \sum_{\vec{k}'} S(\vec{k}, \vec{k}') \) is usually called the “scattering rate”

Now if our \( df_{\text{scat}} \) were constant (ignoring the in scattering), the distribution would just go back to equilibrium at a constant rate

$$\frac{df}{dt} = -(f_T - f_0) \sum_{\vec{k}'} S(\vec{k}, \vec{k}') = -(f_T - f_0) \Gamma(\vec{k}) = -\frac{f_T - f_0}{\tau(\vec{k})}$$

This rate \( \tau \) is called the “relaxation time” and is the time constant of the exponential decay of the out-of-equilibrium part of the distribution function
BTE: scattering rate vs relaxation time

- If there is no in-scattering (the first term is zero), then the relaxation time is just the inverse of the scattering rate
- Sometimes this is called the “single-mode relaxation time” because it assumes only the mode k (an none of the other k’) is out of equilibrium
- For elastic scattering, we can use the symmetry of \( S(k,k') = S(k',k) \)

\[
df_{scat} = -\frac{f_T - f_0}{\tau(\bar{k})} = -(f_T - f_0) \sum_{\bar{k}'} S(\bar{k}, \bar{k}') - \frac{(f_T' - f_0')}{(f_T - f_0)} S(\bar{k}, \bar{k}')
\]

- From this we can define the relaxation time as

\[
\tau^{-1}(\bar{k}) = \sum_{\bar{k}'} S(\bar{k}, \bar{k}') \left[ 1 - \frac{(f_T' - f_0')}{(f_T - f_0)} \right] = \sum_{\bar{k}'} S(\bar{k}, \bar{k}') \left[ 1 - \frac{\Delta f_T'}{\Delta f_T} \right]
\]

- Where \( \Delta f_T \) is the departure from equilibrium \( \Delta f_T = f_T - f_0 \)
Solving the BTE

- If $\Delta f_T$ (the departure from equilibrium $\Delta f_T = f_T - f_0$) is small, we can simplify the RHS by assuming the derivatives of $\Delta f_T$ are negligible, so that

$$\nabla_{\vec{r}} f_T(\vec{r}, \vec{k}, t) \approx \nabla_{\vec{r}} f_0(E, T) \frac{\partial f_0}{\partial T} \nabla_{\vec{r}} T(\vec{r}) - \frac{\partial f_0}{\partial E} \nabla_{\vec{r}} E_F(\vec{r})$$

$$\nabla_{\vec{k}} f_T(\vec{r}, \vec{k}, t) \approx \nabla_{\vec{k}} f_0(E, T) = \hbar \frac{\partial f_0}{\partial E} \vec{v}(\vec{k})$$

- Note that this implies “quasi-equilibrium”: the distribution is changing so it is not in equilibrium but locally in any small region of space it looks like it is in equilibrium

- Now we write the BTE in the RTA and in quasi-equilibrium

$$\frac{\partial f_T(\vec{r}, \vec{k}, t)}{\partial t} + \vec{v}(\vec{k}) \left[ \frac{\partial f_0}{\partial T} \nabla_{\vec{r}} T(\vec{r}) - \frac{\partial f_0}{\partial E} \nabla_{\vec{r}} E_F(\vec{r}) \right] + \vec{F}(\vec{r}) \left[ \hbar \frac{\partial f_0}{\partial E} \vec{v}(\vec{k}) \right] = -\Delta f(\vec{r}, \vec{k}, t) \tau^{-1}(\vec{k})$$

- From this expression, in steady state ($df/dt=0$) we can solve for $\Delta f(r,k)$
Conductivities from BTE

- In steady state ($\frac{df}{dt} = 0$) we can solve for $\Delta f(r,k)$

$$\Delta f(\bar{r}, \bar{k}, t) = -\tau(\bar{k})\tilde{\nu}(\bar{k}) \cdot \left[ \nabla_{\bar{r}} T(\bar{r}) \frac{\partial f_0}{\partial T} - \nabla_{\bar{r}} E_F(\bar{r}) \frac{\partial f_0}{\partial E} \right] + e\tau(\bar{k})\nu(\bar{k}) \cdot \nabla_{\bar{r}} V(\bar{r}) \frac{\partial f_0}{\partial E}$$

- The total solution $f(r,k)$ is the sum of the equilibrium distribution function $f_0(E,T)$ and the $\Delta f(r,k)$;

$$f_T(\bar{r}, \bar{k}) = f_0(E,T) + \Delta f_T(\bar{r}, \bar{k})$$

- Now we can compute the energy and charge currents produced by this solution; however, the equilibrium distribution does not contribute to current:

$$\bar{Q}_H(\bar{r}) = \frac{1}{L^d} \sum_{\bar{k}} (\hbar \omega)\tilde{\nu}(\bar{k}) \left[ f_0(\hbar \omega, T) + \Delta f_T(\bar{r}, \bar{k}) \right] = \frac{1}{L^d} \sum_{\bar{k}} (\hbar \omega)\tilde{\nu}(\bar{k}) \Delta f_T(\bar{r}, \bar{k})$$

- If we only apply a temperature gradient, we get a heat current as

$$\bar{Q}_H(\bar{r}) = -\frac{1}{L^d} \sum_{\bar{k}} \hbar \omega(\bar{k})\tau(\bar{k})\tilde{\nu}(\bar{k}) \left[ \tilde{\nu}(\bar{k}) \cdot \nabla_{\bar{r}} T(\bar{r}) \right] \frac{\partial f_0}{\partial T}$$
Thermal conductivity from BTE

- Finally we can compare this to Fourier law \( \vec{Q} = -\vec{k} \nabla T \) to define the thermal conductivity tensor as
  \[
  \kappa_{\alpha\beta} = \sum_{\vec{k}} \hbar \omega(\vec{k}) \tau(\vec{k}) v_\alpha(\vec{k}) v_\beta(\vec{k}) \frac{\partial f_0}{\partial T}
  \]
- Here alpha and beta are the components of the 3x3 tensor
- In crystals with cubic symmetry, the tensor is diagonal
- For an isotropic dispersion, the diagonal components are equal (\( k_{xx} = k_{yy} = k_{zz} \))
- In such a case we can replace the product of the velocity components with their average
  \[
  \kappa(T) = \frac{1}{dL^d} \sum_{\vec{k}} \hbar \omega(\vec{k}) \tau(\vec{k}) v^2(\vec{k}) \frac{\partial f_0}{\partial T}
  \]
- Finally we can take the usual step of replacing the sum with an integral over the energy, multiplied by the DOS
  \[
  \kappa(T) = \frac{1}{d} \int_0^{\omega_{\text{max}}} \hbar \omega \tau(\omega) v^2(\omega) \frac{\partial f_0(\omega, T)}{\partial T} D(\omega) d\omega
  \]
Connection to Landauer and kinetic formalisms

- If we recognize the product of velocity and DOS as the channel number and the product of the velocity and lifetime tau as the mean free path, we obtain

\[ \kappa(T) = \frac{1}{2\pi} \int_0^{\omega_{\max}} \hbar \omega \Lambda(\omega) \frac{\partial f_0(\omega,T)}{\partial T} M(\omega) d\omega \]

- Defining conductance as \( K = \kappa / L \), we see that the BTE solution is exactly the same as the Landauer solution, with transmission being \( T = \Lambda / L \)
- The BTE conductivity is what we got from Landauer in the long \( L \) limit!
- On the other hand, we can, in 3d, recognize the heat capacity as

\[ C(T) = \int_0^{\omega_{\max}} \hbar \omega \frac{\partial f_0(\omega,T)}{\partial T} D(\omega) d\omega \]

- Then, the BTE solution is telling us the kinetic formula is correct, on the average

\[ \kappa(T) = \frac{1}{3} \int_0^{\omega_{\max}} v(\omega) \Lambda(\omega) C(\omega,T) d\omega \approx \frac{1}{3} v \Lambda C(\omega,T) \]
Ohm’s Law from BTE

- We can also obtain the charge current in response to an electric field; again, the equilibrium distribution does not contribute to current:

\[ \vec{Q}_c(\vec{r}) = \frac{e}{L^d} \sum_{\vec{k}} \vec{v}(\vec{k}) \left[ f_0(\hbar \omega, T) + \Delta f_T(\vec{r}, \vec{k}) \right] = \frac{e}{L^d} \sum_{\vec{k}} \vec{v}(\vec{k}) \Delta f_T(\vec{r}, \vec{k}) \]

- Writing this current in terms of the electric field as

\[ \vec{Q}_H(\vec{r}) = \frac{e^2}{L^d} \sum_{\vec{k}} \tau(\vec{k}) \vec{v}(\vec{k}) \left[ \vec{v}(\vec{k}) \cdot \vec{E}(\vec{r}) \right] \frac{\partial f_0}{\partial E} \]

- This is equivalent to Ohm’s Law \( \vec{Q}_H(\vec{r}) = \bar{\sigma} \vec{E}(\vec{r}) \) if we define our conductance as

\[ \sigma_{\alpha\beta} = \frac{e^2}{L^d} \sum_{\vec{k}} \tau(\vec{k}) v_{\alpha}(\vec{k}) v_{\beta}(\vec{k}) \frac{\partial f_0}{\partial E} \]

- In the isotropic case, this becomes a function of energy only so we write

\[ \sigma = \frac{e^2}{d} \int_{E_0}^{\infty} \tau(E) v^2(E) \frac{\partial f_0}{\partial E} D(E) dE \]
But that’s not all...

• There is more: we can produce a thermally driven charge current as well as an electrically driven energy (heat) current.

• The whole system of two driving forces and two resulting currents can be written as

\[
\begin{pmatrix}
\vec{Q}_C \\
\vec{Q}_H
\end{pmatrix} =
\begin{pmatrix}
L_{11} & L_{12} \\
L_{21} & L_{22}
\end{pmatrix} \begin{pmatrix}
-\nabla \Theta \\
-\nabla T
\end{pmatrix}
\]

• Where the transport coefficients are defined as

\[
L_{11} = \frac{e^2}{d} \int_{E_0}^{\infty} \tau(E) v^2(E) \frac{\partial f_0}{\partial E} D(E) dE \\
L_{12} = -\frac{e}{d} \int_{E_0}^{\infty} \frac{(E - E_F)}{T} \tau(E) v^2(E) \frac{\partial f_0}{\partial E} D(E) dE
\]

\[
L_{21} = -\frac{e}{d} \int_{E_0}^{\infty} (E - E_F) \tau(E) v^2(E) \frac{\partial f_0}{\partial E} D(E) dE = TL_{12}
\]

\[
L_{22} = -\frac{1}{dT} \int_{E_0}^{\infty} (E - E_F)^2 \tau(E) v^2(E) \frac{\partial f_0}{\partial E} D(E) dE
\]
Connection to the Landauer Formalism

• The transport coefficients can also be connected to the Landauer formalism by recognizing the channel number as \( v(E)D(E) \), \( v(E)\tau(E) = \Lambda(E) \)

\[
L_{11} = \frac{e^2}{d} \int_{E_0}^{\infty} \tau(E)v^2(E) \frac{\partial f_0}{\partial E} D(E) dE \Rightarrow \frac{e^2}{2\pi\hbar} \int_{-\infty}^{\infty} T(E) \frac{\partial f_0}{\partial E} M(E) dE
\]

\[
L_{12} = -\frac{e}{d} \int_{E_0}^{\infty} \frac{(E-E_F)}{T} \tau(E)v^2(E) \frac{\partial f_0}{\partial E} D(E) dE = -\frac{e}{2\pi\hbar T} \int_{-\infty}^{\infty} (E-E_F)T(E) \frac{\partial f_0}{\partial E} M(E) dE
\]

\[
L_{22} = -\frac{1}{dT} \int_{E_0}^{\infty} (E-E_F)^2 \tau(E)v^2(E) \frac{\partial f_0}{\partial E} D(E) dE = -\frac{1}{2\pi\hbar T} \int_{E_0}^{\infty} (E-E_F)^2T(E) \frac{\partial f_0}{\partial E} M(E) dE
\]

• In the “diffusive” limit, we are recognizing that \( T(E) = \Lambda(E)/L \)
• we would write, more generally, \( T(E) = \Lambda(E)/[\Lambda(E)+L] \)
• In the “ballistic” limit, we would write the currents as proportional to differences in the potential and temperature, rather than gradients

\[
\begin{pmatrix}
\bar{Q}_C \\
\bar{Q}_H
\end{pmatrix} =
\begin{pmatrix}
L_{11} & L_{12} \\
L_{21} & L_{22}
\end{pmatrix}
\begin{pmatrix}
-\Delta \Theta \\
-\Delta T
\end{pmatrix}
\]
The Seebeck coefficient

- Now we can use the transport coefficients to ask questions about the coupling between heat and charge currents
- Setting the charge current to zero (open circuit) produces
  \[ \begin{pmatrix} 0 \\ \vec{Q}_H \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} -\nabla \Theta \\ -\nabla T \end{pmatrix} \Rightarrow \nabla \Theta = -\frac{L_{12}}{L_{11}} \nabla T = -S \nabla T \]
- Where \( S \) is the Seebeck coefficient, defined as
  \[
  S = \frac{L_{12}}{L_{11}} = -\frac{1}{eT} \int_{E_0}^{\infty} (E - E_F) \tau(E) v^2(E) \frac{\partial f_0}{\partial E} D(E) dE
  \]
  \[
  = -\frac{1}{eT} \left\langle E - E_F \right\rangle
  \]
- We note that the Seebeck coefficient is related to a weighted average of the carrier energy above the Fermi level
- Often it is said that \( S \) is the “entropy per particle”
The Peltier coefficient

• The second line of the system of equations can now also be given as

\[
\begin{pmatrix}
\vec{Q}_C \\
\vec{Q}_H
\end{pmatrix} =
\begin{pmatrix}
L_{11} & L_{12} \\
L_{21} & L_{22}
\end{pmatrix}
\begin{pmatrix}
-\nabla \Theta \\
-\nabla T
\end{pmatrix} \Rightarrow \vec{Q}_H = -L_{21} \nabla \Theta - L_{22} \nabla T = \frac{L_{21}}{L_{11}} \vec{Q}_C - \left( L_{22} - \frac{L_{21} L_{12}}{L_{11}} \right) \nabla T
\]

• The first term is related to the Peltier coefficient \( \Pi = \frac{L_{21}}{L_{11}} = T \frac{L_{12}}{L_{11}} = TS \)

• The second term is the electronic contribution to thermal conductivity (or the thermal conductivity of electrons):

\[
\vec{Q}_H = -\left( L_{22} - \frac{L_{21} L_{12}}{L_{11}} \right) \nabla T \Rightarrow \kappa_e = L_{22} - \frac{L_{21} L_{12}}{L_{11}} = L_{22} - T \frac{L_{12}^2}{L_{11}} = L_{22} - S^2 \sigma T
\]

• Usually the electronic contribution to thermal conductivity is small in normal semiconductors, but is dominant in metals and highly doped semiconductors
The Wiedemann Franz Law

- The Wiedemann-Franz law says that the ratio of thermal and electrical conductivity is proportional to temperature

\[ \frac{\kappa_e}{\sigma} = LT \] with the proportionality constant L being the Lorenz number

- This generally holds in metals and when elastic scattering dominates
- Let’s plug in our expressions for conductivities and see what we get

\[ L = \frac{\kappa_e}{\sigma T} = \frac{L_{22}}{L_{11}T} - \left( \frac{L_{12}}{L_{11}} \right)^2 \]

\[ \frac{L_{22}}{L_{11}T} = \left( \frac{k_B}{e} \right)^2 \int_{E_0}^{\infty} \frac{(E - E_F)}{k_B T} \tau(E) v^2(E) \frac{\partial f_0}{\partial E} D(E) dE \]

\[ \frac{L_{12}}{L_{11}} = \left( \frac{k_B}{e} \right)^2 \int_{E_0}^{\infty} \frac{(E - E_F)}{k_B T} \tau(E) v^2(E) \frac{\partial f_0}{\partial E} D(E) dE \]
In a metal, we assume $\tau(T), D(E) = \text{const.}$

We also have $E_F > E_0$, so we can extend the lower limit to infinity.

Then we get $L_{12} = 0$ by symmetry.

In semiconductors, we reach a similar conclusion when we have elastic scattering: every scattering has the same constant probability $S(k,k') = C$.

Then the total scattering rate becomes proportional to the DOS:

$$\tau^{-1}(E) = \Gamma(E) = \sum_{k'} S(k, k') \propto D(E)$$

For this reason, it is typical to write the relaxation time as $$\tau(E) = \tau_0 E^\gamma$$

where the exponent is $-1/2$ for elastic scattering, $-3/2$ for acoustic phonons.

However, inelastic scattering exchanges energy and becomes more difficult to treat (usually done numerically).