Nanostructures for Energy Conversion

Thermoelectric devices are semiconductor devices which exploit the Seebeck effect (or equivalently the Peltier effect) to convert heat fluxes to charge fluxes and vice versa. Thermoelectrics are used for power generation based on the Seebeck effect where an applied temperature gradient is turned into a voltage.

Recall that the Seebeck coefficient $S$ was defined by the open circuit voltage due to applied temperature gradient:
\[ J_c = L_u \left( -\frac{d\phi}{dx} \right) + L_{12} \left( -\frac{dT}{dx} \right) \]

\[ J_c = 0 \quad \text{(open circuit)} \]

\[ S = -\frac{d\phi}{dx} = \frac{L_{12}}{L_u} \]

Now we have \( T_h - T_c \) as the temperature drop on each leg.

So the total voltage is

\[ V_s = S_h (T_h - T_c) + S_e (T_c - T_h) \]

\[ = (S_h - S_e)(T_h - T_c) \]

\[ I_c = \frac{V}{R} = \frac{(S_h - S_e)(T_h - T_c)}{R_h + R_e + R_L} \]

\[ W = \text{power delivered to the load} \]

\[ = T^2 R_L = \sum \frac{(S_h - S_e)(T_h - T_c)^2}{R_h + R_e + R_L} \]

Since the Seebeck coefficient is the heat per carrier, the heat absorbed at the hot side into the thermoelectric device is going to be given by the product of \( S_e \).
and the current \( I_{ch} = dQ / dt \)
so that we recall

\[
I_q = TS J_e - K \frac{dT}{dx}
\]

The heat flux out of the hot side \( T_h \) is then simply

\[
J^H_q = (S_h - S_e) T_h J_e + K (T_h - T_c)
\]

we also need to account for

Joule heating due to the flow of current \( J_e \) and resistance \( R_h \) as

\[
\frac{RG}{R_h} \Rightarrow I_e^2 (R_h + R_e) = \frac{I_e^2}{R_h}
\]

The total heat current is then

\[
I_q = (S_h - S_e) T_h I_e + K_{th} (T_h - T_c)
- \frac{1}{2} I_e^2 (R_e + R_h)
\]

The total efficiency is just the ratio of heat absorbed on the hot side to the power delivered to the load

\[
\eta = \frac{W_o}{I_q} = \frac{I_e^2 R_h}{(S_h - S_e) T_h I_e + K_{th} (\Delta T)} = \frac{I_e^2 R_h}{2 I_e^2 (K_{th} / T_h)}
\]
The total thermal conductance of the two segments is

\[ K_{\text{tot}} = \frac{K_h A_h}{H_h} + \frac{K_e A_e}{H_e} \]

and the electrical resistance is

\[ R_{\text{tot}} = R_h + R_e = \frac{H_h}{\sigma_h A_h} + \frac{H_e}{\sigma_e A_e} \]

Maximum efficiency is obtained at \( dn/d\theta = 0 \) since \( R_e \) is the only variable in the system. Note that \( I_c \) depends on \( R_e \)

\[ \eta_{\text{max}} = \left( \frac{\eta \left( \frac{T_h - T_c}{T_h} \right)}{T_h} \right) \frac{1}{\sqrt{1 + 2 \frac{1}{T_h}} - 1} \]

\[ = \eta \text{ cannot} \times \delta_2 \]

where \( \delta_2 = \sqrt{1 + 2 \frac{1}{T_h}} - 1 \)

and \( \bar{T} = \frac{T_h + T_c}{2} \)

\[ z = \frac{(S_h - S_e)^2}{\left[ (K_h/\sigma_h)^2 + (K_e/\sigma_e)^2 \right]^{1/2}} \]
The number $ZT$ is the figure of merit, a unitless quantity which tells us how close we can get to the highest possible efficiency as limited by the Carnot efficiency $\eta_{\text{Carnot}} = \frac{T_H - T_e}{T_H}$.

As $Z$ goes to infinity, our system approaches $\eta_{\text{Carnot}}$.

The combined $Z$ of the two P and N segments was given as

$$Z = \frac{(S_n - S_e)}{\left(\frac{K_n}{\sqrt{S_n}} + \frac{K_e}{\sqrt{S_e}}\right)^2}$$

but we typically use an independent $ZT$ for each material as

$$ZT = \frac{S^2 \delta}{K}$$

The thermal conductivity has both phonon and electron contributions, although in practice, one tends to completely dominate. For example,
In metals, $K$ is primarily coming from the electron contribution while in semiconductors it is mostly phonons that carry the heat. Ultimately, both could contribute in different amounts so we set

$$K = K_{\text{el}} + K_{\text{ph}}$$

The goal of increasing efficiency boils down to increasing $ZT$, and that, in turn, can be done in two ways: improving $S$ and $\sigma$ (electrical properties) or decreasing $K$ (thermal properties). Since $S$ and $\sigma$ are closely coupled together ($S = S_{\text{el}}/L_{\text{ph}}$ and $\sigma = L_{\text{ph}}$) it is hard to improve them simultaneously. The most successful approach to improving $Z$ has been to reduce $K_{\text{ph}}$ by reducing physical dimensions of the TE generator.

In the limit of $K_{\text{ph}} = 0$, we can recall the Wiedemann-Franz law

$$K_{\text{el}} = L \sigma T$$

so that

$$ZT = \frac{S^2 \sigma T}{L \sigma T} = \frac{S^2}{L}$$
As a rule-of-thumb, we usually want $ZT > 1$ to be somewhat useful in niche applications. A $ZT > 2$ would be very useful if it could be reached in a cost-effective way. Finally, a $ZT > 3$ would be considered groundbreaking.

Let's guess $T_H = 900 K$ and $T_c = 300 K$. Then $\eta_{carnot} = \frac{600}{900} = 67\%$

$T = 600 K$ and let us try $ZT = 1, 2, 3$

$$\eta = \eta_{carnot} \cdot \frac{\sqrt{1 + 2T} - 1}{\sqrt{1 + 2T} + \frac{T_c}{T_H}}$$

$$= 67\% \cdot \frac{\sqrt{2} - 1}{\sqrt{2} + \frac{1}{3}} \approx 0.77$$
- Seebeck Coefficient

We talked about how thermoelectric conversion and, in general, the coupling between electrons and phonons depends on the Seebeck coefficient (thermopower). Now let us calculate $S$ for a few example systems.

First let us consider a semiconductor material which is non-degenerately doped. We approximate the relaxation time as a function of energy to be

$$\tau(E) = \tau_0 E^\alpha$$

We also assume the effective mass approximation so that

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

and

$$\tilde{V}(k) = \tilde{\rho}_0 \tilde{E}(k) = \frac{\hbar^2}{m^*}$$

Notice that

$$V^2(E) = \frac{\hbar^2 k^2}{(m^*)^2} = \frac{2E}{m^*}$$
Now we go back to our expression for $S$ given as

$$S = -\frac{1}{eT} \int_{E_0}^{\infty} (E-E_0) v^2 \tau \frac{df}{2E} D(E) dE$$

We note right away that constants in $v^2 \tau$ and $D(E)$ will cancel out on top and bottom.

For a parabolic effective mass band structure we have the DOS as

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

Combining everything and removing the constants gives

$$S = -\frac{1}{eT} \int_{E_0}^{\infty} (E-E_0) E^{8+3/2} \frac{df_0}{2E} dE$$

$$= -\frac{1}{eT} \left\{ \int_{E_0}^{\infty} E^{8+5/2} \frac{df_0}{2E} dE - EF \right\}$$
For a non-degenerate semiconductor, the Fermi level is inside the gap, so we can approximate the Fermi-Dirac distribution function by the Maxwell-Boltzmann distribution:

\[ f_0(E) \approx \exp \left( -\frac{E - E_F}{k_B T} \right) \]

In that case, the integrals become much simpler, and we obtain:

\[ S = -\frac{1}{eT} \left[ \sum E - \frac{E_F}{k_B T} \left( \frac{1}{2} + 1 \right) \right] \]

\[ = -\frac{k_B}{e} \left[ \sum \frac{E_F}{k_B T} - \left( 1 + \frac{3}{2} \right) \right] \]

or in terms of the carrier concentration:

\[ S = -\frac{k_B}{e} \left[ \ln \left( \frac{n}{N_c} \right) - \left( 1 + \frac{3}{2} \right) \right] \]

From this, we see that \( S \) goes down as \( n \) increases. However, the decrease is counterbalanced by the increase in \( \sigma = \sigma_0 n \) from \( n \) so that a maximum in \( S^2 \sigma \) is reached, usually around \( n = 5 \times 10^{17} \) cm\(^{-3} \).
At such high doping the non-degenerate assumption breaks down so let us go back and remove it. We had written the Seebeck coefficient as

\[ S = -\frac{1}{eT} \left\{ \int_0^\infty E^{y+5/2} \frac{\partial f_0}{\partial E} dE - \int_0^\infty E^{y+3/2} \frac{\partial f_0}{\partial E} dE \right\} \]

We can write this more generally in terms of integrals \( K \)

\[ K_s = -\frac{8\pi^2}{3} \left( \frac{2}{\hbar^2} \right)^{3/2} \left( m^* \right)^{1/2} T T_0 \int E^{y+3/2} \frac{\partial f_0}{\partial E} dE \]

Then we can integrate by parts using:

\[ \int_0^\infty E^{y+3/2} \frac{\partial f_0}{\partial E} dE = -\left( y+\frac{3}{2} \right) E^{y+\frac{1}{2}} f_0(e) \]

which allows us to convert \( K_s \) into

\[ K_s = \frac{8\pi^2}{3} \left( \frac{2}{\hbar^2} \right)^{3/2} \left( m^* \right)^{1/2} T T_0 \left( y+\frac{3}{2} \right) \left( k_B T \right)^{y+\frac{3}{2}} \]
where the so-called Fermi-Dirac integrals are

\[ F_n (z) = \int_0^\infty \frac{\xi^n}{e^{\xi - z} + 1} \, d\xi \]

and they are only available numerically, but easy to implement on a computer, \( z = E_F/\hbar^2 k_B T \).

Finally, we can now get all of our transport coefficients in terms of \( k_0 \)'s:

\[ \sigma = \frac{e^2}{\hbar} k_0 \]

\[ S = \pm \frac{1}{\hbar c} \left( E_F - \frac{k_1}{k_0} \right) \]

\[ k_e = \frac{1}{\hbar c^2} \left( k_2 - \frac{k_1^2}{k_0} \right) \]

The expression for \( S \) can also be written as

\[ S = -\frac{k_0}{e} \left( \frac{5}{3} \frac{E_F}{k_B T} - \frac{E_F}{k_B T} \right) \]
The treatment of nanostructures can also be done along the same steps, but changing the DOS.

For example, 2D quantum well (made from a very thin layers of material) will have the following electronic structure

\[ E_{\text{h}}(k_x, k_y) = \frac{\hbar^2}{2m^*} \left( k_x^2 + k_y^2 \right) + \frac{\hbar^2 n^2}{2m^* a^2} \]

and the DOS will be \( D(E) \propto E^0 \) i.e. constant instead of \( D(E) \propto \sqrt{E} \) in 3D. Then the Seebeck coefficient will have the same form but with exponents of \( E \) reduced by \( \frac{1}{2} \) so that

\[ S = -\frac{e \hbar}{k_c} \left( \frac{2F}{T_0} - \frac{E_F}{k_B T} \right) \]