

Lectures 5-6 - Collège de France - Spring 2013

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I. KUBO FORMULA: GENERAL ASPECTS (CONTINUED FROM LECTURE 4)

II. THE ELECTRICAL AND THERMAL CURRENTS

III. SIMPLIFIED EXPRESSION OF THE THERMOELECTRIC COEFFICIENTS

A. Simplifications for local (momentum-independent) cases

B. General expressions

C. Connection to the Boltzmann equation approach

Local distribution function $F(\mathbf{k}; \mathbf{r}, t)$ in momentum (or energy) space.

Boltzmann equation in the relaxation-time approximation:

$$\frac{dF}{dt} = -\frac{F - F_0}{\tau} \quad (1)$$

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} F + \dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}} F \quad (2)$$

Semiclassical equations of motion:

$$\dot{\mathbf{r}} = \frac{1}{\hbar} \nabla_{\mathbf{k}} \varepsilon_{\mathbf{k}} \equiv v_{\mathbf{k}} \quad , \quad \hbar \dot{\mathbf{k}} = -e\mathbf{E} \quad (3)$$

As long as we take into account the spatial variation of the (electro-)chemical potential, we can as well put the external force and hence $\dot{\mathbf{k}}$ to zero.

Assume local equilibrium:

$$F(\mathbf{k}, \mathbf{r}, t) \simeq f\left(\frac{\varepsilon_{\mathbf{k}} - \mu(\mathbf{r})}{k_B T(\mathbf{r})}\right) \quad (4)$$

From now on I will set $k_B = \hbar = 1$ and restore at the end and work with an \mathbf{r} -dependent μ and no explicit electric field.

$$\nabla_{\mathbf{r}} F = \left[-\frac{1}{T} \nabla \mu - \frac{\varepsilon_{\mathbf{k}} - \mu}{T^2} \nabla T \right] f' \quad (5)$$

with $\partial f / \partial \varepsilon = f' / T$, we get the change of the distribution function:

$$\delta F = \left(-\frac{\partial f}{\partial \varepsilon} \right) \tau(\varepsilon_{\mathbf{k}}) \nabla_{\mathbf{k}} \varepsilon_{\mathbf{k}} \cdot \left[(-\nabla \mu) + \frac{\varepsilon_{\mathbf{k}} - \mu}{T} (-\nabla T) \right] \quad (6)$$

We use the simplest expression of the thermal current (neglecting interaction contributions, see above):

$$\mathbf{j}_n^a = 2 \int \frac{d^d k}{(2\pi)^d} v_{\mathbf{k}}^a \delta F \quad , \quad \mathbf{j}_S^a = \frac{1}{T} \mathbf{j}_Q = \frac{1}{T} (\mathbf{j}_E - \mu \mathbf{j}_n) = 2 \int \frac{d^d k}{(2\pi)^d} v_{\mathbf{k}}^a (\varepsilon_{\mathbf{k}} - \mu) \delta F \quad (7)$$

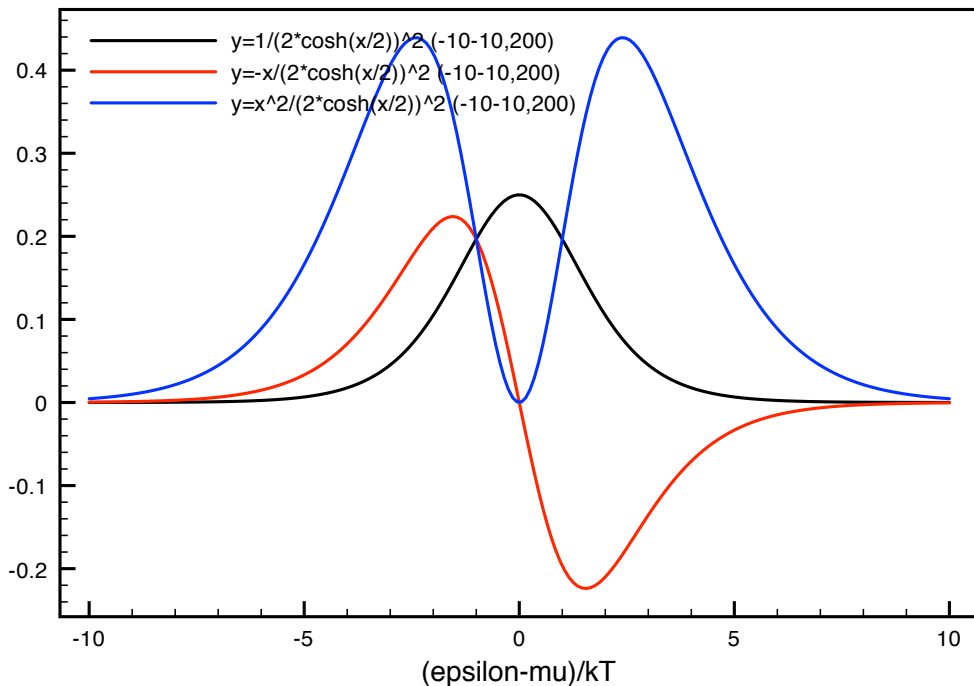


FIG. 1: Statistical weighting factors entering conductivity (black), thermopower (red) and thermal conductivity (blue).

and using the above expression of δF , we obtain the following expression of the transport coefficients (written here for isotropic case). It is convenient to introduce (restoring \hbar):

$$\mathcal{T}(\varepsilon) \equiv \frac{2}{\hbar} \int \frac{d^d k}{(2\pi)^d} \tau(\varepsilon_{\mathbf{k}}) \left[\frac{1}{d} \sum_a (\nabla_{\mathbf{k}}^a \varepsilon_{\mathbf{k}})^2 \right] \delta(\varepsilon - \varepsilon_{\mathbf{k}}) \quad (8)$$

Dimensional analysis: $(E.t).t.L^{-d}(E.L)^2/(E^2 t^2) \sim L^{2-d}$.

$$L_{11} = \frac{1}{\hbar} \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon} \right) \mathcal{T}(\varepsilon) \quad (9)$$

$$L_{12} = \frac{1}{\hbar} \frac{1}{T} \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon} \right) (\varepsilon - \mu) \mathcal{T}(\varepsilon) \quad (10)$$

$$L_{22} = \frac{1}{\hbar} \frac{1}{T^2} \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon} \right) (\varepsilon - \mu)^2 \mathcal{T}(\varepsilon) \quad (11)$$

The L 's have dimension $\frac{L^{2-d}}{\hbar}(1, k_B, k_B^2)$ respectively. We recall that:

$$\sigma = e^2 L_{11} \quad , \quad \alpha = -\frac{L_{12}}{e L_{11}} \quad , \quad \kappa = T \left(L_{22} - \frac{L_{12}^2}{L_{11}} \right) \quad (12)$$

These formula emphasize that the excitations controlling conductivity live right at Fermi level, while those controlling thermopower and thermal conductivity live a few $k_B T$'s away from it (Fig. 1). They also emphasize the importance of particle-hole asymmetry for the thermopower.

D. Formal similarity to the Landauer approach

IV. METALS: IMPURITY SCATTERING

Let us evaluate the above expressions in the low- T limit for a metal, in which $\mathcal{T}(\varepsilon)$ is non-zero at the Fermi level. Using the Sommerfeld expansion:

$$f(\varepsilon) = \Theta(\mu - \varepsilon) - \frac{\pi^2}{6} (k_B T)^2 \delta'(\varepsilon - \mu) + \dots \quad (13)$$

we obtain:

$$L_{11} \simeq \frac{1}{\hbar} \mathcal{T}(\mu) , \quad L_{12} \simeq \frac{\pi^2 k_B^2}{3 \hbar} \mathcal{T}'(\mu) , \quad L_{22} \simeq \frac{\pi^2 k_B^2}{3 \hbar} \mathcal{T}'(\mu) \quad (14)$$

a. Conductivity

$$\sigma \simeq \frac{e^2}{\hbar} \mathcal{T}(\mu) \quad (15)$$

For a free electron gas and energy-independent impurity scattering:

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2m} \Rightarrow \frac{1}{d} \sum_a \left(\frac{\partial \varepsilon_{\mathbf{k}}}{\partial k_a} \right)^2 = \frac{2 \hbar^2}{3 m} \varepsilon \quad (16)$$

we obtain:

$$\mathcal{T}(\varepsilon) = \frac{2 \hbar}{3 m} \varepsilon N(\varepsilon) \tau_i \quad (17)$$

$$N(\varepsilon) = C \sqrt{\varepsilon} \Rightarrow n = C \frac{2}{3} \varepsilon_F^{3/2} , \quad \frac{2}{3} \varepsilon_F N(\varepsilon_F) = n \quad (18)$$

Hence the Drude expression:

$$\sigma = \frac{n e^2 \tau_i}{m} \quad (19)$$

b. Thermopower and the Mott formula

The thermopower is given by (Mott formula):

$$\alpha \simeq -\frac{\pi^2 k_B}{3 e} \frac{\mathcal{T}'(\mu)}{\mathcal{T}(\mu)} k_B T = -\frac{\pi^2 k_B}{3 e} k_B T \frac{\partial}{\partial \mu} \ln \mathcal{T}(\mu) \quad (20)$$

c. Behnia-Jaccard-Flouquet scaling Again for an energy-independent scattering rate and a free electron gas (parabolic band in 3D) , we have:

$$\mathcal{T}(\varepsilon) \sim \varepsilon^{3/2} \Rightarrow \frac{\partial}{\partial \varepsilon} \mathcal{T}(\varepsilon) = \frac{3}{2\varepsilon} \quad (21)$$

Hence using the above relation between n and d.o.s:

$$\alpha = -\frac{\pi^2 k_B}{3 e} \frac{3 k_B T}{2 \varepsilon_F} = -\frac{\pi^2 k_B}{3 e} k_B T \frac{N(\varepsilon_F)}{n} \quad (22)$$

Recalling the specific heat at low- T :

$$C_{el} = \frac{\pi^2}{3} k_B^2 N(\varepsilon_F) T \quad (23)$$

We obtain:

$$\alpha = -\frac{C_{el}/n}{e} \quad (24)$$

This illustrates again the notion that the thermopower measures the entropy per charge carrier. Incidentally, we could also write this in terms of the Hall number (?):

$$\frac{\alpha}{C_{el}} = R_H \quad (25)$$

Question: how does this survive for a more general band dispersion, transport function etc. ?

d. Thermal conductivity and Wiedemann-Franz law The thermal conductivity reads:

$$\kappa \simeq \frac{\pi^2}{3\hbar} \mathcal{T}(\mu) k_B^2 T \quad (26)$$

yielding the Wiedemann-Franz law:

$$\frac{\kappa/T}{\sigma} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 \quad (27)$$

Note: This low- T expansion, however, has been performed assuming that $\mathcal{T}(\varepsilon)$ does not have significant intrinsic T -dependence. If it does, eg if ε/T scaling applies, things have to be reconsidered - see below.

V. METALS: ELECTRON-ELECTRON INTERACTIONS (CORRELATED METALS WITHIN DMFT)

A. The scattering function

There is a complete formal analogy between the expression of the thermoelectric coefficients in the Boltzmann equation approach and the expressions derived above from the Kubo formula in the local (DMFT) approximation. This is already clear by identifying (fix factors):

$$\mathcal{T}(\omega) = \frac{2}{\hbar} \int d\varepsilon \Phi(\varepsilon) A(\varepsilon, \omega)^2 \quad (28)$$

with $\Phi(\varepsilon) = \int \frac{d^d k}{(2\pi)^d} \left[\frac{1}{d} \sum_a (\nabla_{\mathbf{k}}^a \varepsilon_{\mathbf{k}})^2 \right] \delta(\varepsilon - \varepsilon_{\mathbf{k}})$ the transport function and $A(\varepsilon, \omega)$ the single-particle spectral function (note the switch in notations in integration variables).

For a (correlated) metal at low- T , this similarity can be pushed further by expanding this scattering function at small ω, T . We expand the self-energy $\Sigma = \Sigma_1 + i\Sigma_2$:

$$\Sigma_1(\omega, T) = \Sigma_1(0, T) + \omega \left(1 - \frac{1}{Z}\right) + \dots \quad (29)$$

which leads to the following quasiparticle approximation to the spectral function:

$$A(\varepsilon, \omega) \simeq \frac{Z}{\pi} \frac{\gamma_{qp}}{(\omega - \xi_k^{qp})^2 + \gamma_{qp}^2} \quad (30)$$

with:

$$\xi_k^{qp} = Z[\varepsilon_k - \bar{\mu}] \text{ , } \bar{\mu}(T) \equiv \mu - \Sigma_1(0, T) \text{ , } \gamma_{qp}(\omega, T) = -Z\Sigma_2(\omega, T) \quad (31)$$

Note that the $T = 0$ Fermi surface in the 1-band case is constrained by Luttinger theorem to coincide with the non-interacting one ($\bar{\mu}(0) = \mu_0(n)$) and note the Z -factor entering the quasiparticle lifetime.

At low- T , the scattering rate γ becomes small and quasiparticles close to the FS matter most, hence the change of integration variable: $\varepsilon = \bar{\mu} + \frac{\omega}{Z} + \frac{\gamma_{qp}}{Z} x$, which leads to (I set again $\hbar = 1$):

$$\mathcal{T}(\omega, T) = 2 \frac{Z}{\gamma_{qp}} \int_{-\infty}^{+\infty} dx \Phi \left[\bar{\mu} + \frac{\omega}{Z} + \frac{\gamma_{qp}}{Z} x \right] \frac{1}{\pi^2 (1+x^2)^2} \quad (32)$$

We see that the QP weight Z drops out from the scattering rate, which reads simply:

$$\gamma(\omega, T) \equiv \frac{\hbar}{\tau_{ee}(\omega, T)} = |\Sigma_2(\omega, T)| \simeq C_{\Sigma}^{-1} [(\hbar\omega)^2 + (\pi k_B T)^2] \quad (33)$$

The fact that the scattering rate can be directly related to the self-energy of course stems from the absence of vertex corrections in DMFT. The r.h.s corresponds to a local Fermi-liquid expression, with C_{Σ} a constant having the

dimension of an energy (in Berthod et al PRB 2013 on optics, we defined $C_\Sigma \equiv Z\pi k_B T_0$, with T_0 a characteristic Fermi-liquid scale).

At low ω, T , $\gamma \ll \omega, T$ is small and we can approximate:

$$\mathcal{T}(\omega, T) \simeq \frac{1}{\pi\hbar} \Phi \left[\bar{\mu}(T) + \frac{\omega}{Z} \right] \tau_{ee}(\omega, T) \quad (34)$$

which achieves complete similarity with the Boltzmann equation expression. We have used: $\int_{-\infty}^{+\infty} \frac{dx}{\pi^2(1+x^2)^2} = \frac{1}{2\pi}$.

The low- T expansion of the transport coefficients in this case require more care than above, because the scattering rate obeys ω/T scaling. Hence the T and ω dependence have to be treated on equal footing. We have to set $\omega = xT$ in the integrals defining the Onsager coefficients, and we obtain:

$$\{L_{11}, L_{12}, L_{22}\} = \frac{1}{\hbar} \int_{-\infty}^{+\infty} dx \frac{1}{4 \cosh^2 \frac{x}{2}} \{1, x, x^2\} \mathcal{T}(xT, T) \quad (35)$$

TODO: Check that the lowest-order expansion of \mathcal{T} above is enough also for L_{12} .

B. Conductivity, thermal conductivity and the Wiedemann-Franz law (correlated metal)

The conductivity and thermal conductivity are easier, since only the lowest-order FL form of the scattering rate can be retained (this is not the case for thermopower, which requires also the particle-hole asymmetry of $\tau(\omega, T)$ beyond FL theory, see below - cf. Haule and Kotliar-).

Defining:

$$I_k^n \equiv \int_{-\infty}^{+\infty} dx \frac{1}{4 \cosh^2 \frac{x}{2}} \frac{x^n}{(x^2 + \pi^2)^k} \quad (36)$$

Numerical values (check): $I_1^0 = 0.083, I_1^2 = 0.178, I_2^0 = 0.007, I_2^2 = 0.011, I_2^4 = 0.067$.

We obtain (with $\varepsilon_F = \bar{\mu}(0) = \mu_0(n)$ the bare Fermi energy):

$$\left\{ L_{11}, \frac{1}{k_B^2} L_{22} \right\} = \frac{1}{(k_B T)^2} \frac{C_\Sigma}{\pi\hbar} \Phi(\varepsilon_F) \{I_1^0, I_1^2\} \quad (37)$$

Hence the resistivity (note: Φ has dimension $L^{2-d} \times E$, C_Σ of E):

$$\rho = AT^2, \quad A = \frac{\hbar}{e^2} \frac{\pi k_B^2}{I_1^0 C_\Sigma \Phi(\varepsilon_F)} \quad (38)$$

and the Lorenz number:

$$\mathcal{L}_{ee} \equiv \frac{\kappa/T}{\sigma} = \left(\frac{k_B}{e} \right)^2 \frac{I_1^2}{I_1^0} \simeq 2.14 \left(\frac{k_B}{e} \right)^2 \quad (39)$$

which *differs* from the $\pi^2/3$ value valid for impurity scattering.

We can take into account both impurity and electron-electron scattering in the local approximation by substituting in the calculations above (the 2π factor comes from the conventions used above):

$$\frac{1}{\tau_i} \rightarrow \frac{1}{\tau_i} + \frac{2\pi}{\tau_{ee}} \quad (40)$$

which leads to the resistivity and Lorenz number:

$$\rho(\bar{T}) = \rho_i \frac{I_0(0)}{I_0(\bar{T})}, \quad \mathcal{L}(\bar{T}) = \left(\frac{k_B}{e} \right)^2 \frac{I_2(\bar{T})}{I_0(\bar{T})} \quad (41)$$

In these expressions:

$$I_{\{0,2\}}(\bar{T}) \equiv \int_{-\infty}^{+\infty} dx \frac{1}{4 \cosh^2 \frac{x}{2}} \frac{\{1, x^2\}}{1 + \bar{T}^2(x^2 + \pi^2)} \quad (42)$$

and \bar{T} is a dimensionless temperature defined by:

$$\bar{T}^2 \equiv 2\pi \frac{(k_B T)^2}{\gamma_i C_\Sigma} \quad (43)$$

It is easily checked that the low-T (dominated by impurity scattering) and hi-T (dominated by e-e scattering) limits of these expressions are fully consistent with the above, namely:

$$\rho(\bar{T} \ll 1) = \rho_i = \frac{\hbar}{e^2} \frac{\gamma_i}{2\Phi(\varepsilon_F)} \quad , \quad \rho(\bar{T} \gg 1) = A T^2, \quad A = \frac{\hbar}{e^2} \frac{\pi k_B^2}{I_1^0 C_\Sigma \Phi(\varepsilon_F)} \quad (44)$$

Using these relations, we can express the dimensionless temperature in terms of the (impurity) residual resistivity ρ_i and the A -coefficient of the e-e contribution to the resistivity:

$$\bar{T} = \sqrt{I_1^0} \sqrt{\frac{A T^2}{\rho_i}} \simeq 0.29 \sqrt{\frac{A T^2}{\rho_i}} \quad (45)$$

The temperature-dependence of the Lorenz number is plotted in Fig. 2. The crossover is seen to take place at $\bar{T} \simeq 0.25$, i.e. when the electron-electron contribution to ρ becomes comparable to the residual (impurity) resistivity.

Now, this calculation has been using a local Fermi-liquid approach, and the simplest form of the thermal current (all assumptions justified in DMFT). It would be interesting to know how these conclusions are changed in a more general context.

C. Thermopower (correlated metal)

VI. HEAVILY-DOPED SEMICONDUCTORS

I now consider the theory of thermoelectric transport in heavily-doped semiconductors, as relevant to many materials of practical interest, including of course the most prominent of all Bi_2Te_3 .

Useful references (books): HJ Goldsmid *Introduction to thermoelectricity*; GS Nolas et al. *Thermoelectrics: Basic Principles and New Materials Developments*; V.I. Fistul *Heavily doped semiconductors*; A.F.Ioffe *Semiconductor Thermoelements and Thermoelectric cooling*.

A. General expressions

The theoretical analysis will be based on the expression (9) of the Onsager coefficients in terms of the scattering function (8).

We start with the simplest case: an intrinsic semiconductor with a single-valley valence band and conduction band. We consider separately the contribution to the transport coefficients of doped carriers in the conduction and valence bands (calculations are detailed for the former).

In contrast to metals, the important excitations are now close to the bottom of the conduction band (denoted ε_c). Hence, we make the following change of variable in the transport integrals:

$$\varepsilon = \varepsilon_c + k_B T x \quad , \quad \mu = \varepsilon_c + \delta\mu \quad , \quad \frac{\delta\mu}{k_B T} \equiv \eta \quad (46)$$

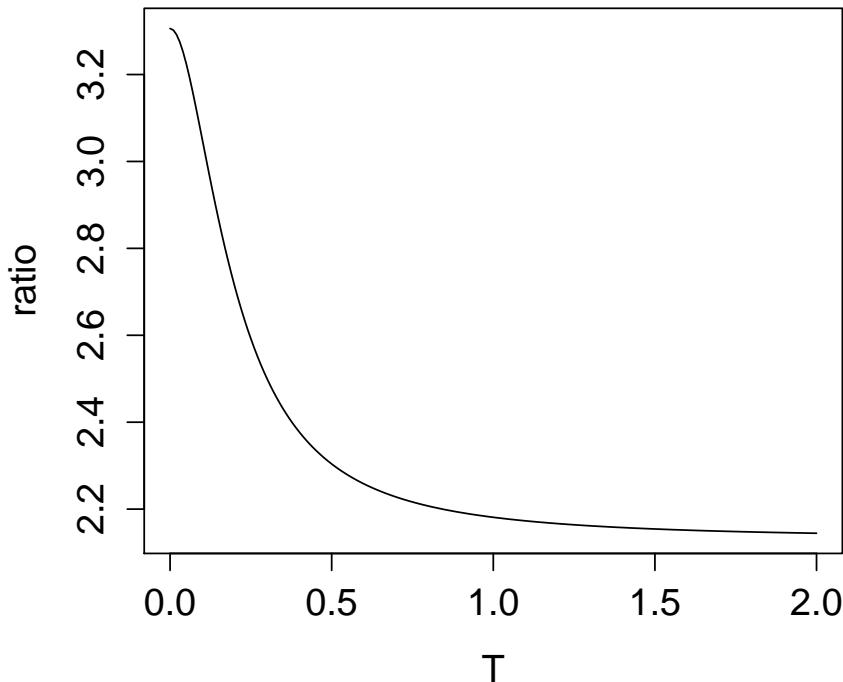


FIG. 2: Lorenz number in a metal with strong electronic correlations: crossover from impurity-scattering to electron-electron scattering as a function of the dimensionless temperature defined in the text (local Fermi-liquid theory, e.g. DMFT).

The following assumptions are made for the behaviour of the transport function and scattering time near the band edge:

$$\Phi(\varepsilon) \simeq C_{\Phi} (\varepsilon - \varepsilon_c)^{\phi} , \quad \tau(\varepsilon) \simeq C_{\tau} (\varepsilon - \varepsilon_c)^r , \quad \mathcal{T}(\varepsilon) = \frac{2}{\hbar} \tau(\varepsilon) \Phi(\varepsilon) = C_t (\varepsilon - \varepsilon_c)^{r+\phi} , \quad (C_t = \frac{2}{\hbar} C_{\Phi} C_{\tau}) \quad (47)$$

The constants C_{Φ}, C_{τ} have bizarre dimensions, but will be eliminated in favour of more physical variables later. The scattering rate is assumed (as is done in all textbooks on the subject) to depend on energy only: the intrinsic temperature dependence is ignored. As shown in the appendix, this is actually usually justified (e.g. for electron-phonon scattering) but this may need to be reconsidered in some cases. For electron-electron scattering in a metal, we have seen that ω/T scaling applies and such an assumption is not valid.

Standard values of the r -parameter are nicely summarized in Table 3.2 of Fistul's book (note: I use standard notation for r in the recent literature, eg Goldsmid. Ioffe and Fistul define $r_{IF} = r + 1/2$):

- Scattering by neutral impurities: $r = 0$ (of course - elastic scattering)
- Scattering by ionized impurities in a semiconductor: $r = +3/2$ (see Appendix B)
- Scattering by acoustic phonons in a semiconductor: $r = -1/2$ (see Appendix C)

As we now show, $\phi = \frac{3}{2}$ for a parabolic band. However, we keep ϕ whenever the effort is not too large below. Consider a parabolic dispersion of the conduction band around the Γ -point:

$$\varepsilon_{\mathbf{k}} = \varepsilon_c + \frac{\hbar^2 \mathbf{k}^2}{2m_c} + \dots \quad (48)$$

in which m_c is the effective mass (assumed isotropic). Then:

$$\frac{1}{3}(\nabla_{\mathbf{k}}\varepsilon_{\mathbf{k}})^2 = \frac{2}{3}\frac{\hbar^2}{m_c}(\varepsilon_{\mathbf{k}} - \varepsilon_c) \quad (49)$$

The density of states reads (for a *single* spin component):

$$g_c(\varepsilon) = \frac{m_c^{3/2}}{\sqrt{2}\pi^2\hbar^3}\sqrt{\varepsilon - \varepsilon_c} \quad (50)$$

and the transport function (again for a single spin component):

$$\Phi(\varepsilon) = \frac{2}{3}\frac{\hbar^2}{m_c}(\varepsilon_{\mathbf{k}} - \varepsilon_c)g_c(\varepsilon) = \frac{\sqrt{2}}{3}\frac{\sqrt{m_c}}{\pi^2\hbar}(\varepsilon - \varepsilon_c)^{3/2} \quad (51)$$

So that for a parabolic and isotropic band:

$$\mathcal{T}(\varepsilon) \simeq C_t(\varepsilon - \varepsilon_c)^{r+3/2}, \quad C_t = \frac{2}{3}\frac{\sqrt{2m_c}}{\pi^2\hbar^2}C_\tau \quad (52)$$

To calculate the transport integrals in the expression of the L_{ij} 's, we set $\varepsilon = \varepsilon_c + k_B T x$, $\mu = \varepsilon_c + k_B T \eta$ and expand the moments using: $\varepsilon - \mu = k_B T x - \delta\mu$ and $(\varepsilon - \mu)^2 = (k_B T)^2 x^2 - 2k_B T \delta\mu + \delta\mu^2$. This leads to ($\eta = \delta\mu/k_B T$):

$$\hbar L_{11} = C_t (k_B T)^{r+\phi} D_{r+\phi}(\eta) \quad (53)$$

$$\hbar T L_{12} = -\delta\mu \hbar L_{11} + C_t (k_B T)^{r+\phi+1} D_{r+\phi+1}(\eta) \quad (54)$$

$$\hbar T^2 L_{22} = \delta\mu^2 \hbar L_{11} - 2(k_B T)^{r+\phi+1} \delta\mu C_t D_{r+\phi+1}(\eta) + (k_B T)^{r+\phi+2} C_t D_{r+\phi+2}(\eta) \quad (55)$$

In these expressions, the integrals $D_n(\eta)$ are moments of the derivative of the Fermi function defined in Appendix A, and related there to the so-called Fermi integrals $F_n(\eta)$.

Simplifying, the following expressions are finally obtained:

- Thermopower:

$$\alpha = \frac{k_B}{e} \left[\eta - \frac{r+\phi+1}{r+\phi} \frac{F_{r+\phi}(\eta)}{F_{r+\phi-1}(\eta)} \right] \quad (56)$$

This expression is negative: the sign here being for *n*-type (electrons in the conduction band) - the opposite sign holds for *p*-type.

- Electronic Lorenz number $\mathcal{L}_e = (\kappa_e/T)/\sigma$:

$$\left(\frac{e}{k_B} \right)^2 \mathcal{L}_e(\eta) = \frac{r+\phi+2}{r+\phi} \frac{F_{r+\phi+1}(\eta)}{F_{r+\phi-1}(\eta)} - \left(\frac{r+\phi+1}{r+\phi} \right)^2 \left(\frac{F_{r+\phi}(\eta)}{F_{r+\phi-1}(\eta)} \right)^2 \quad (57)$$

The conductivity reads:

$$\sigma = \frac{e^2}{\hbar} C_t (k_B T)^{r+\phi} (r+\phi) F_{r+\phi-1}(\eta) \quad (58)$$

For a parabolic band ($\phi = 3/2$), this expression can be put in the form:

- Density of carriers (parabolic band):

$$n = 4\pi \left(\frac{2m_c k_B T}{h^2} \right)^{3/2} F_{1/2}(\eta) \quad (59)$$

- Mobility (parabolic band) - not to be confused with chemical potential-:

$$\mu(T, \eta) = \frac{e\tau(T)}{m_c} \frac{2}{3} \left(r + \frac{3}{2}\right) \frac{F_{r+1/2}(\eta)}{F_{1/2}(\eta)}, \quad \tau(T) \equiv \tau(\varepsilon = k_B T) \simeq C_\tau (k_B T)^r \quad (60)$$

- Conductivity (parabolic band):

$$\sigma = n e \mu(T, \eta) = \sigma_0(T) \frac{F_{r+1/2}(\eta)}{\Gamma(r+3/2)}, \quad \sigma_0(T) = \frac{8\pi}{3} \Gamma\left(r + \frac{5}{2}\right) \left(\frac{2m_c k_B T}{h^2}\right)^{3/2} \frac{e\tau(T)}{m_c} \quad (61)$$

B. Non-degenerate limit ($T \ll E_g$)

In this limit $\delta\mu, \eta \ll 0$. We have only a few carriers in the conduction band, which obey almost classical statistics. We can use: $F_n(\eta) \simeq \Gamma(n+1) e^\eta$ and obtain, after some calculations:

$$\alpha = \frac{k_B}{e} [\eta - (r + \phi + 1)] = \frac{k_B}{e} \left[\eta - \left(r + \frac{5}{2}\right) \right] \quad (62)$$

$$\mathcal{L}_e(\eta) = \left(\frac{k_B}{e}\right)^2 (r + \phi + 1) = \left(\frac{k_B}{e}\right)^2 \left(r + \frac{5}{2}\right) \quad (63)$$

where the second expression is for a parabolic band. Note that in this limit the Lorenz number takes a different value than the one corresponding to the degenerate metallic case ($\pi^2/3$). As $T \rightarrow 0$, in an intrinsic undoped and clean semiconductor $\eta \sim -E_g/2k_B T$ and α becomes very large as expected.

Can the Lorenz number teach us about the dominant scattering mechanism (and/or the shape of the band) ?

Carrier density and mobility (parabolic band):

$$n = 2\pi^{3/2} \left(\frac{2m_c k_B T}{h^2}\right)^{3/2} e^\eta, \quad \mu(T) = \frac{e\tau(T)}{m_c} \frac{4}{3\sqrt{\pi}} \Gamma\left(r + \frac{5}{2}\right) \quad (64)$$

Conductivity (with $\sigma_0(T)$ defined above):

$$\sigma = \sigma_0(T) e^\eta \quad (65)$$

C. Degenerate (metallic) limit

In the opposite limit $k_B T \gg E_g$, the relation between density and chemical potential is that expected for a metal (using the appropriate expansion of the F_{r+n} 's, see Appendix 1), $\delta\mu \rightarrow \varepsilon_F$ and $\eta \simeq \varepsilon_F/k_B T$:

$$n = 4\pi \left(\frac{2m_c k_B T}{h^2}\right)^{3/2} \frac{2}{3} \eta^{3/2} \Rightarrow n = \frac{8\pi}{3} \left(\frac{2m_c}{h^2}\right)^{3/2} \delta\mu^{3/2} \quad (66)$$

Expanding the expressions for the theropower and Lorenz number, we obtain:

$$\alpha = -\frac{k_B}{e} \frac{\pi^2}{3} (r + \phi) \frac{k_B T}{\varepsilon_F}, \quad \mathcal{L}_e \rightarrow \left(\frac{k_B}{e}\right)^2 \frac{\pi^2}{3} \quad (67)$$

The first expression is precisely consistent with the Mott formula, and the second is the standard value.

The behaviour of the conductivity however is more problematic. Since $F_{r+\phi-1}(\eta) \sim \eta^{r+\phi} \sim (\varepsilon_F/k_B T)^{r+\phi-1}$, we get from the expression that the conductivity is a constant independent of T . This in my opinion reveals that the form of the scattering rate that we took is not appropriate for a metal, and a better job must be done including T -dependence.

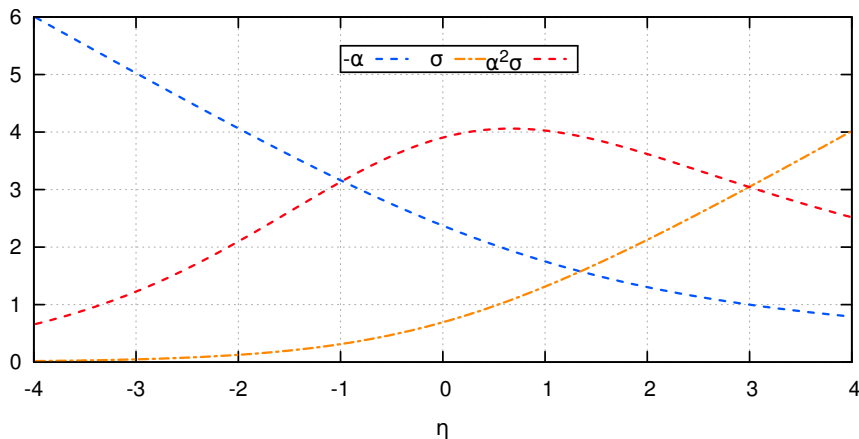


FIG. 3: Dimensionless thermopower ($-\alpha$), normalized conductivity σ/σ_0 and corresponding power factor, vs. the parameter η . Scattering by acoustic phonons $r = -1/2$ is assumed.

D. Considerations on optimal choice of materials

Besides the transport coefficients calculated above, we can also consider the dimensionless figure of merit:

$$ZT = \frac{\bar{\alpha}^2}{\bar{\mathcal{L}}_e + \beta^{-1} \frac{\Gamma(r+3/2)}{F_{r+1/2}(\eta)}} \rightarrow \frac{[\eta - (r + 5/2)]^2}{r + 5/2 + \beta^{-1} e^{-\eta}} \quad (68)$$

in which $\bar{\alpha}$ and $\bar{\mathcal{L}}_e$ are the dimensionless thermopower and electronic Lorenz numbers. β is a material-dependent dimensionless parameter introduced by Chasmar and Stratton which involves the *lattice* thermal conductivity κ_L and the conductivity $\sigma_0(T)$ introduced above:

$$\beta \equiv \left(\frac{k_B}{e} \right)^2 \frac{\sigma_0}{\kappa_L/T} \quad (69)$$

Since σ_0 is the order of magnitude of the conductivity in the relevant regime $\eta \sim 0$, one sees that β^{-1} is some Lorenz number formed from the conductivity in this regime and the lattice thermal conductivity.

The figures below plot a number of quantities:

- Fig.3 displays in a classic way the (dimensionless) thermopower, normalized conductivity σ/σ_0 and corresponding power factor, vs. the parameter η . The plot reveals that there is an optimum value which lies in the range $\eta \in [0, 1]$.
- Figure of merit vs. η
- Density vs. η

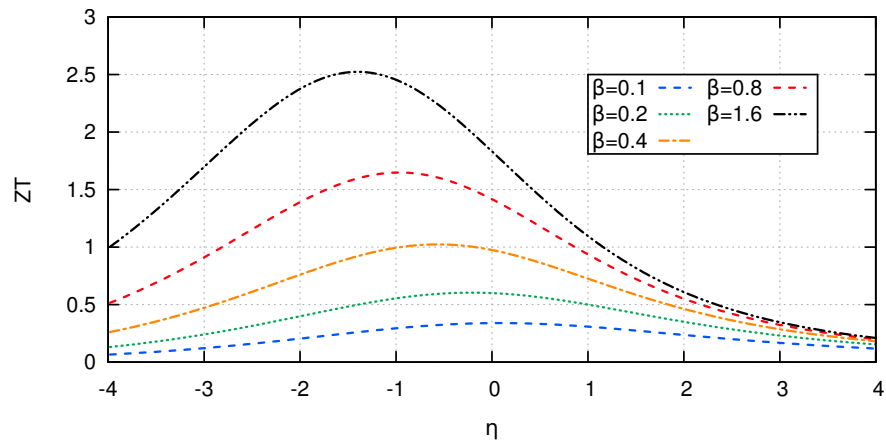


FIG. 4: Dimensionless figure of merit vs. the parameter η , for different values of the parameter β . Scattering by acoustic phonons $r = -1/2$ is assumed.

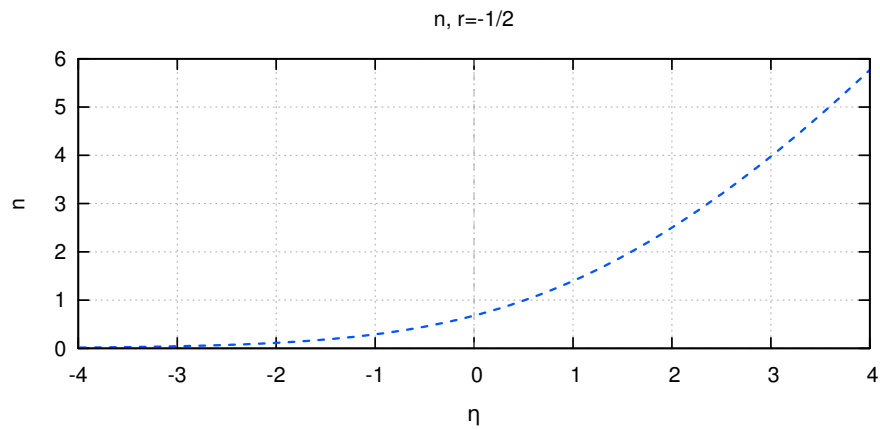


FIG. 5: Normalized carrier density $F_{1/2}(\eta)$ vs. the parameter η .

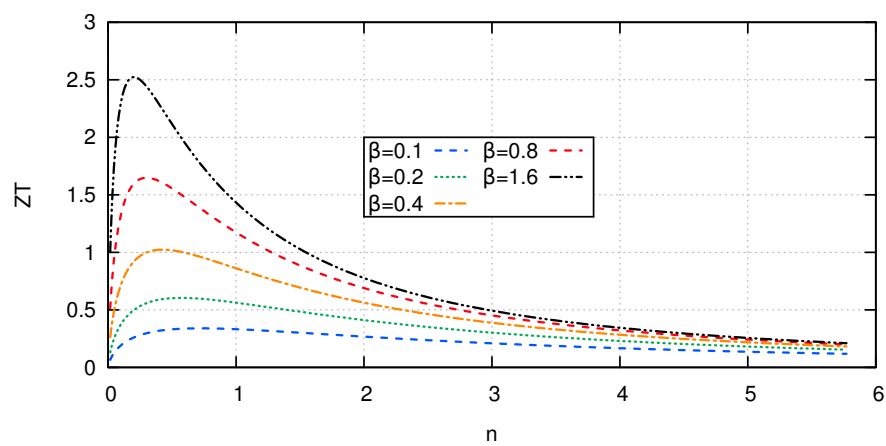


FIG. 6:

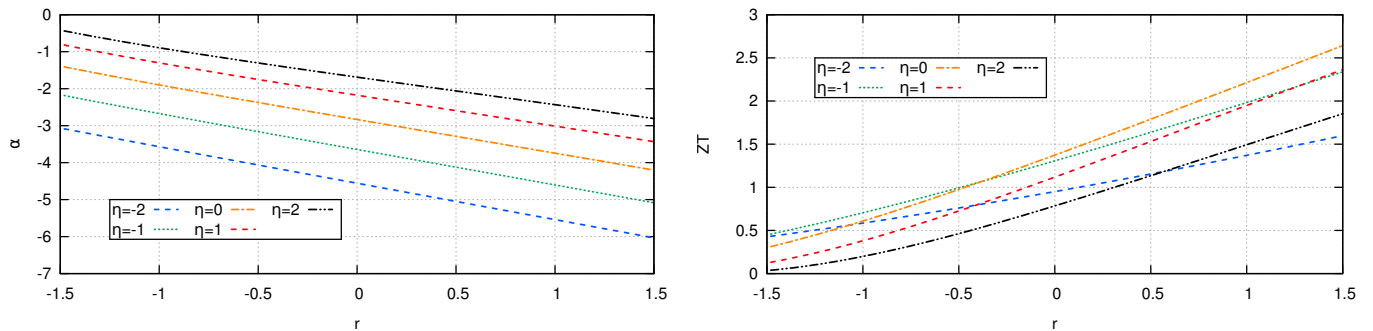


FIG. 7:

E. The case of Bi_2Te_3

Appendix A: Fermi integrals

Fermi integrals:

$$F_n(\eta) \equiv \int_0^\infty dx \frac{x^n}{1 + e^{x-\eta}}, \quad D_n(\eta) \equiv \int_0^\infty dx \frac{x^n}{4 \cosh^2 \frac{x-\eta}{2}} = nF_{n-1}(\eta) \quad (\text{A1})$$

Non-degenerate (classical) regime $\eta \ll 0$:

$$F_n(\eta \sim -\infty) \sim \Gamma(n+1)e^\eta \quad (\text{A2})$$

Intermediate regime:

$$F_n(0) = (1 - 2^{-n}) \zeta(n+1) \Gamma(n+1) \quad (\text{A3})$$

Degenerate (metallic) regime $\eta \gg 0$: D_n behaves better than F_n in this limit, and reads from Sommerfelds' expansion:

$$D_n(\eta) \simeq \eta^n + \frac{\pi^2}{6} n(n-1) \eta^{n-2} + \dots, \quad F_n(\eta) \simeq \frac{\eta^{n+1}}{n+1} + \frac{\pi^2}{6} n \eta^{n-1} + \dots \quad (\text{A4})$$

Appendix B: Scattering by ionized impurities

Appendix C: Scattering by acoustic phonons