

8.8: Nonequilibrium Quantum Transport

Boltzmann equation for quantum systems

Almost everything we have derived thus far can be applied, *mutatis mutandis*, to quantum systems. The main difference is that the distribution f^0 corresponding to local equilibrium is no longer of the Maxwell-Boltzmann form, but rather of the Bose-Einstein or Fermi-Dirac form,

$$f^0(\mathbf{r}, \mathbf{k}, t) = \left\{ \exp\left(\frac{\varepsilon(\mathbf{k}) - \mu(\mathbf{r}, t)}{k_B T(\mathbf{r}, t)}\right) \mp 1 \right\}^{-1}, \quad (8.8.1)$$

where the top sign applies to bosons and the bottom sign to fermions. Here we shift to the more common notation for quantum systems in which we write the distribution in terms of the wavevector $\mathbf{k} = \mathbf{p}/\hbar$ rather than the momentum \mathbf{p} . The quantum distributions satisfy detailed balance with respect to the quantum collision integral

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \int \frac{d^3 k_1}{(2\pi)^3} \int \frac{d^3 k'}{(2\pi)^3} \int \frac{d^3 k'_1}{(2\pi)^3} w \left\{ f' f'_1 (1 \pm f) (1 \pm f_1) - f f_1 (1 \pm f') (1 \pm f'_1) \right\} \quad (8.8.2)$$

where $w = w(\mathbf{k}, \mathbf{k}_1 | \mathbf{k}', \mathbf{k}'_1)$, $f = f(\mathbf{k})$, $f_1 = f(\mathbf{k}_1)$, $f' = f(\mathbf{k}')$, and $f'_1 = f(\mathbf{k}'_1)$, and where we have assumed time-reversal and parity symmetry. Detailed balance requires

$$\frac{f}{1 \pm f} \cdot \frac{f_1}{1 \pm f_1} = \frac{f'}{1 \pm f'} \cdot \frac{f'_1}{1 \pm f'_1}, \quad (8.8.3)$$

where $f = f^0$ is the equilibrium distribution. One can check that

$$f = \frac{1}{e^{\beta(\varepsilon - \mu)} \mp 1} \implies \frac{f}{1 \pm f} = e^{\beta(\mu - \varepsilon)}, \quad (8.8.4)$$

which is the Boltzmann distribution, which we have already shown to satisfy detailed balance. For the streaming term, we have

The wavevectors are now restricted to the first Brillouin zone, and the dispersion $\varepsilon(\mathbf{k})$ is no longer the ballistic form $\varepsilon = \hbar^2 \mathbf{k}^2 / 2m$ but rather the dispersion for electrons in a particular energy band (typically the valence band) of a solid¹⁰. Note that $f = f^0$ satisfies detailed balance with respect to one-body collisions as well¹¹.

In the presence of a weak electric field \mathbf{E} and a (not necessarily weak) magnetic field \mathbf{B} , we have, within the relaxation time approximation, $f = f^0 + \delta f$ with

$$\frac{\partial \delta f}{\partial t} - \frac{e}{\hbar c} \mathbf{v} \times \mathbf{B} \cdot \frac{\partial \delta f}{\partial \mathbf{k}} - \mathbf{v} \cdot \left[e \mathcal{E} + \frac{\varepsilon - \mu}{T} \nabla T \right] \frac{\partial f^0}{\partial \varepsilon} = -\frac{\delta f}{\tau}, \quad (8.8.5)$$

where $\mathcal{E} = -\nabla(\phi - \mu/e) = \mathbf{E} - e^{-1} \nabla \mu$ is the gradient of the ‘electrochemical potential’ $\phi - e^{-1} \mu$. In deriving the above equation, we have worked to lowest order in small quantities. This entails dropping terms like $\mathbf{v} \cdot \frac{\partial \delta f}{\partial \mathbf{r}}$ (higher order in spatial derivatives) and $\mathbf{E} \cdot \frac{\partial \delta f}{\partial \mathbf{k}}$ (both \mathbf{E} and δf are assumed small). Typically τ is energy-dependent, $\tau = \tau(\varepsilon(\mathbf{k}))$.

We can use Equation [qlbe] to compute the electrical current \mathbf{j} and the thermal current \mathbf{j}_q ,

$$\begin{aligned} \mathbf{j} &= -2e \int_{\Omega} \frac{d^3 k}{(2\pi)^3} \mathbf{v} \delta f \\ \mathbf{j}_q &= 2 \int_{\Omega} \frac{d^3 k}{(2\pi)^3} (\varepsilon - \mu) \mathbf{v} \delta f. \end{aligned}$$

Here the factor of 2 is from spin degeneracy of the electrons (we neglect Zeeman splitting).

In the presence of a time-independent temperature gradient and electric field, linearized Boltzmann equation in the relaxation time approximation has the solution

$$\delta f = -\tau(\varepsilon) \mathbf{v} \cdot \left(e \mathcal{E} + \frac{\varepsilon - \mu}{T} \nabla T \right) \left(-\frac{\partial f^0}{\partial \varepsilon} \right). \quad (8.8.6)$$

We now consider both the electrical current¹² \mathbf{j} as well as the thermal current density \mathbf{j}_q . One readily obtains

$$\begin{aligned} \mathbf{j} &= -2e \int_{\hat{\Omega}} \frac{d^3 k}{(2\pi)^3} \mathbf{v} \delta f \equiv L_{11} \mathcal{E} - L_{12} \nabla T \\ \mathbf{j}_q &= 2 \int_{\hat{\Omega}} \frac{d^3 k}{(2\pi)^3} (\varepsilon - \mu) \mathbf{v} \delta f \equiv L_{21} \mathcal{E} - L_{22} \nabla T \end{aligned}$$

where the *transport coefficients* L^{11} are matrices:

$$\begin{aligned} L_{11}^{\alpha\beta} &= \frac{e^2}{4\pi^3 \hbar} \int d\varepsilon \tau(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|\mathbf{v}|} \\ L_{21}^{\alpha\beta} = T L_{12}^{\alpha\beta} &= -\frac{e}{4\pi^3 \hbar} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|\mathbf{v}|} \\ L_{22}^{\alpha\beta} &= \frac{1}{4\pi^3 \hbar T} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu)^2 \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|\mathbf{v}|}. \end{aligned}$$

If we define the hierarchy of integral expressions

$$\mathcal{J}_n^{\alpha\beta} \equiv \frac{1}{4\pi^3 \hbar} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu)^n \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|\mathbf{v}|} \quad (8.8.7)$$

then we may write

$$L_{11}^{\alpha\beta} = e^2 \mathcal{J}_0^{\alpha\beta}, \quad L_{21}^{\alpha\beta} = T L_{12}^{\alpha\beta} = -e \mathcal{J}_1^{\alpha\beta}, \quad L_{22}^{\alpha\beta} = \frac{1}{T} \mathcal{J}_2^{\alpha\beta}. \quad (8.8.8)$$

The linear relations in Equation (linrel1) may be recast in the following form:


$$\begin{aligned} \mathcal{E} &= \rho \mathbf{j} + Q \nabla T \\ \mathbf{j}_q &= \square \mathbf{j} - \kappa \nabla T, \end{aligned}$$

where the matrices ρ , Q , \square , and κ are given by

$$\begin{aligned} \rho &= L_{11}^{-1} & Q &= L_{11}^{-1} L_{12} \\ \square &= L_{21} L_{11}^{-1} & \kappa &= L_{22} - L_{21} L_{11}^{-1} L_{12}, \end{aligned}$$

or, in terms of the \mathcal{J}_n ,

$$\begin{aligned} \rho &= \frac{1}{e^2} \mathcal{J}_0^{-1} & Q &= -\frac{1}{eT} \mathcal{J}_0^{-1} \mathcal{J}_1 \\ \square &= -\frac{1}{e} \mathcal{J}_1 \mathcal{J}_0^{-1} & \kappa &= \frac{1}{T} \left(\mathcal{J}_2 - \mathcal{J}_1 \mathcal{J}_0^{-1} \mathcal{J}_1 \right), \end{aligned}$$

 A thermocouple is a junction formed of two dissimilar metals. With no electrical current passing, an electric field is generated in the presence of a temperature gradient, resulting in a voltage $V = V_A - V_B$.

A thermocouple is a junction formed of two dissimilar metals. With no electrical current passing, an electric field is generated in the presence of a temperature gradient, resulting in a voltage $V = V_A - V_B$.

These equations describe a wealth of transport phenomena:

- ($\nabla T = \mathbf{B} = 0$) An electrical current \mathbf{j} will generate an electric field $\mathcal{E} = \rho \mathbf{j}$, where ρ is the electrical resistivity.
- ($\nabla T = \mathbf{B} = 0$) An electrical current \mathbf{j} will generate a heat current $\mathbf{j}_q = \square \mathbf{j}$, where \square is the Peltier coefficient.
- ($\mathbf{j} = \mathbf{B} = 0$) A temperature gradient ∇T gives rise to a heat current $\mathbf{j}_q = -\kappa \nabla T$, where κ is the thermal conductivity.

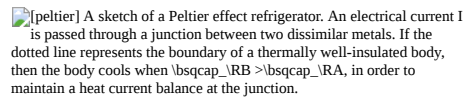
- ($\mathbf{j} = \mathbf{B} = 0$) A temperature gradient ∇T gives rise to an electric field $\mathcal{E} = Q \nabla T$, where Q is the Seebeck coefficient.

One practical way to measure the thermopower is to form a junction between two dissimilar metals, A and B. The junction is held at temperature T_1 and the other ends of the metals are held at temperature T_0 . One then measures a voltage difference between the free ends of the metals – this is known as the Seebeck effect. Integrating the electric field from the free end of A to the free end of B gives

$$V_A - V_B = - \int_A^B \mathcal{E} \cdot d\mathbf{l} = (Q_B - Q_A)(T_1 - T_0). \quad (8.8.9)$$

What one measures here is really the difference in thermopowers of the two metals. For an absolute measurement of Q_A , replace B by a superconductor ($Q = 0$ for a superconductor). A device which converts a temperature gradient into an emf is known as a *thermocouple*.

The Peltier effect has practical applications in refrigeration technology. Suppose an electrical current I is passed through a junction between two dissimilar metals, A and B. Due to the difference in Peltier coefficients, there will be a net heat current into the junction of $W = (\pi_A - \pi_B) I$. Note that this is proportional to I , rather than the familiar I^2 result from Joule heating. The sign of W depends on the direction of the current. If a second junction is added, to make an ABA configuration, then heat absorbed at the first junction will be liberated at the second.¹³

 [peltier] A sketch of a Peltier effect refrigerator. An electrical current I is passed through a junction between two dissimilar metals. If the dotted line represents the boundary of a thermally well-insulated body, then the body cools when $I > 0$, in order to maintain a heat current balance at the junction.

[peltier] A sketch of a Peltier effect refrigerator. An electrical current I is passed through a junction between two dissimilar metals. If the dotted line represents the boundary of a thermally well-insulated body, then the body cools when $\pi_B > \pi_A$, in order to maintain a heat current balance at the junction.

The Heat Equation

We begin with the continuity equations for charge density ρ and energy density ε :

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} &= 0 \\ \frac{\partial \varepsilon}{\partial t} + \nabla \cdot \mathbf{j}_\varepsilon &= \mathbf{j} \cdot \mathbf{E}, \end{aligned}$$

where \mathbf{E} is the electric field¹⁴. Now we invoke local thermodynamic equilibrium and write

$$\begin{aligned} \frac{\partial \varepsilon}{\partial t} &= \frac{\partial \varepsilon}{\partial n} \frac{\partial n}{\partial t} + \frac{\partial \varepsilon}{\partial T} \frac{\partial T}{\partial t} \\ &= -\frac{\mu}{e} \frac{\partial \rho}{\partial t} + c_V \frac{\partial T}{\partial t}, \end{aligned}$$

where n is the electron number density ($n = -\rho/e$) and c_V is the specific heat. We may now write

$$\begin{aligned} c_V \frac{\partial T}{\partial t} &= \frac{\partial \varepsilon}{\partial t} + \frac{\mu}{e} \frac{\partial \rho}{\partial t} \\ &= \mathbf{j} \cdot \mathbf{E} - \nabla \cdot \mathbf{j}_\varepsilon - \frac{\mu}{e} \nabla \cdot \mathbf{j} \\ &= \mathbf{j} \cdot \mathcal{E} - \nabla \cdot \mathbf{j}_q. \end{aligned}$$

Invoking $\mathbf{j}_q = \pi \mathbf{j} - \kappa \nabla T$, we see that if there is no electrical current ($\mathbf{j} = 0$), we obtain the *heat equation*

$$c_V \frac{\partial T}{\partial t} = \kappa_{\alpha\beta} \frac{\partial^2 T}{\partial x^\alpha \partial x^\beta}. \quad (8.8.10)$$

This results in a time scale τ_T for temperature diffusion $\tau_T = CL^2 c_V / \kappa$, where L is a typical length scale and C is a numerical constant. For a cube of size L subjected to a sudden external temperature change, L is the side length and $C = 1/3\pi^2$ (solve by separation of variables).

Calculation of Transport Coefficients

We will henceforth assume that sufficient crystalline symmetry exists (cubic symmetry) to render all the transport coefficients multiples of the identity matrix. Under such conditions, we may write $\mathcal{J}_n^{\alpha\beta} = \mathcal{J}_n \delta_{\alpha\beta}$ with

$$\mathcal{J}_n = \frac{1}{12\pi^3 \hbar} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu)^n \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon |\mathbf{v}|. \quad (8.8.11)$$

The low-temperature behavior is extracted using the Sommerfeld expansion,

$$\begin{aligned} \mathcal{I} &\equiv \int_{-\infty}^{\infty} d\varepsilon H(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) = \pi \mathcal{D} \csc(\pi \mathcal{D}) H(\varepsilon) \Big|_{\varepsilon=\mu} \\ &= H(\mu) + \frac{\pi^2}{6} (k_B T)^2 H''(\mu) + \dots \end{aligned}$$

where $\mathcal{D} \equiv k_B T \frac{\partial}{\partial \varepsilon}$ is a dimensionless differential operator.¹⁵

Let us now perform some explicit calculations in the case of a parabolic band with an energy-independent scattering time τ . In this case, one readily finds

$$\mathcal{J}_n = \frac{\sigma_0}{e^2} \mu^{-3/2} \pi \mathcal{D} \csc \pi \mathcal{D} \varepsilon^{3/2} (\varepsilon - \mu)^n \Big|_{\varepsilon=\mu}, \quad (8.8.12)$$

where $\sigma_0 = ne^2 \tau / m^*$. Thus,

$$\begin{aligned} \mathcal{J}_0 &= \frac{\sigma_0}{e^2} \left[1 + \frac{\pi^2}{8} \frac{(k_B T)^2}{\mu^2} + \dots \right] \\ \mathcal{J}_1 &= \frac{\sigma_0}{e^2} \frac{\pi^2}{2} \frac{(k_B T)^2}{\mu} + \dots \\ \mathcal{J}_2 &= \frac{\sigma_0}{e^2} \frac{\pi^2}{3} (k_B T)^2 + \dots, \end{aligned}$$

from which we obtain the low- T results $\rho = \sigma_0^{-1}$,

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \frac{k_B}{e} \frac{\tau}{m^*} \frac{1}{T},$$

and of course $\mathbf{J} = T \mathbf{Q}$. The predicted universal ratio

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \frac{k_B}{e} \frac{\tau}{m^*} = 2.45 \times 10^{-8} \frac{\text{V}^2}{\text{K}^2},$$

is known as the *Wiedemann-Franz law*. Note also that our result for the thermopower is unambiguously negative. In actuality, several nearly free electron metals have positive low-temperature thermopowers (Cs and Li, for example). What went wrong? We have neglected electron-phonon scattering!

Onsager Relations

Transport phenomena are described in general by a set of linear relations,

$$J_i = L_{ik} F_k, \quad (8.8.13)$$

where the $\{F_k\}$ are *generalized forces* and the $\{J_i\}$ are *generalized currents*. Moreover, to each force F_i corresponds a unique conjugate current J_i , such that the rate of internal entropy production is

$$\dot{S} = \sum_i F_i J_i \implies F_i = \frac{\partial \dot{S}}{\partial J_i}. \quad (8.8.14)$$

The Onsager relations (also known as *Onsager reciprocity*) state that

$$L_{ik}(\mathbf{B}) = \eta_i \eta_k L_{ki}(-\mathbf{B}), \quad (8.8.15)$$

where η_i describes the parity of J_i under time reversal:

$$J_i^T = \eta_i J_i, \quad (8.8.16)$$

where J_i^T is the time reverse of J_i . To justify the Onsager relations requires a microscopic description of our nonequilibrium system.

The Onsager relations have some remarkable consequences. For example, they require, for $\mathbf{B} = 0$, that the thermal conductivity tensor κ_{ij} of any crystal must be symmetric, independent of the crystal structure. In general, this result does not follow from considerations of crystalline symmetry. It also requires that for every ‘off-diagonal’ transport phenomenon, the Seebeck effect, there exists a distinct corresponding phenomenon, the Peltier effect.

For the transport coefficients studied, Onsager reciprocity means that in the presence of an external magnetic field,

$$\begin{aligned} \rho_{\alpha\beta}(\mathbf{B}) &= \rho_{\beta\alpha}(-\mathbf{B}) \\ \kappa_{\alpha\beta}(\mathbf{B}) &= \kappa_{\beta\alpha}(-\mathbf{B}) \\ \mathbf{j}_{\alpha\beta}(\mathbf{B}) &= T Q_{\beta\alpha}(-\mathbf{B}). \end{aligned}$$

Let’s consider an isotropic system in a weak magnetic field, and expand the transport coefficients to first order in \mathbf{B} :

$$\begin{aligned} \rho_{\alpha\beta}(\mathbf{B}) &= \rho \delta_{\alpha\beta} + \nu \epsilon_{\alpha\beta\gamma} B^\gamma \\ \kappa_{\alpha\beta}(\mathbf{B}) &= \kappa \delta_{\alpha\beta} + \varpi \epsilon_{\alpha\beta\gamma} B^\gamma \\ Q_{\alpha\beta}(\mathbf{B}) &= Q \delta_{\alpha\beta} + \zeta \epsilon_{\alpha\beta\gamma} B^\gamma \\ \mathbf{j}_{\alpha\beta}(\mathbf{B}) &= \mathbf{j}_{\alpha\beta} \delta_{\alpha\beta} + \theta \epsilon_{\alpha\beta\gamma} B^\gamma. \end{aligned}$$

Onsager reciprocity requires $\mathbf{j}_{\alpha\beta} = T Q_{\beta\alpha}$ and $\theta = T \zeta$. We can now write

$$\begin{aligned} \mathcal{E} &= \rho \mathbf{j} + \nu \mathbf{j} \times \mathbf{B} + Q \nabla T + \zeta \nabla T \times \mathbf{B} \\ \mathbf{j}_q &= \mathbf{j}_{\alpha\beta} \mathbf{j} + \theta \mathbf{j} \times \mathbf{B} - \kappa \nabla T - \varpi \nabla T \times \mathbf{B}. \end{aligned}$$

There are several new phenomena lurking:

- ($\frac{\partial T}{\partial x} = \frac{\partial T}{\partial y} = j_y = 0$) An electrical current $\mathbf{j} = j_x \hat{\mathbf{x}}$ and a field $\mathbf{B} = B_z \hat{\mathbf{z}}$ yield an electric field \mathcal{E} . The Hall coefficient is $R_H = \mathcal{E}_y / j_x B_z = -\nu$.
- ($\frac{\partial T}{\partial x} = j_y = j_{q,y} = 0$) An electrical current $\mathbf{j} = j_x \hat{\mathbf{x}}$ and a field $\mathbf{B} = B_z \hat{\mathbf{z}}$ yield a temperature gradient $\frac{\partial T}{\partial y}$. The Ettingshausen coefficient is $P = \frac{\partial T}{\partial y} / j_x B_z = -\theta / \kappa$.
- ($j_x = j_y = \frac{\partial T}{\partial y} = 0$) A temperature gradient $\nabla T = \frac{\partial T}{\partial x} \hat{\mathbf{x}}$ and a field $\mathbf{B} = B_z \hat{\mathbf{z}}$ yield an electric field \mathcal{E} . The Nernst coefficient is $\Lambda = \mathcal{E}_y / \frac{\partial T}{\partial x} B_z = -\zeta$.
- ($j_x = j_y = \mathcal{E}_y = 0$) A temperature gradient $\nabla T = \frac{\partial T}{\partial x} \hat{\mathbf{x}}$ and a field $\mathbf{B} = B_z \hat{\mathbf{z}}$ yield an orthogonal temperature gradient $\frac{\partial T}{\partial y}$. The Righi-Leduc coefficient is $\mathcal{L} = \frac{\partial T}{\partial y} / \frac{\partial T}{\partial x} B_z = \zeta / Q$.

This page titled [8.8: Nonequilibrium Quantum Transport](#) is shared under a [CC BY-NC-SA](#) license and was authored, remixed, and/or curated by [Daniel Arovas](#).