8 Nonequilibrium and Transport Phenomena : Summary

• *Boltzmann equation*: The full phase space distribution for a Hamiltonian system, $\varrho(\varphi, t)$, where $\varphi = (\{q_\sigma\}, \{p_\sigma\})$, satisfies $\dot{\varrho} + \dot{\varphi} \cdot \nabla \varrho = 0$. This is not true, however, for the one-particle distribution $f(q, p, t)$. Rather, $\dot{f}$ is related to two-, three-, and higher order particle number distributions in a chain of integrodifferential equations known as the BBGKY hierarchy. We can lump our ignorance of these other terms into a *collision integral* and write

$$
\frac{\partial f}{\partial t} = \overbrace{- \dot{r} \cdot \frac{\partial f}{\partial r} - \dot{p} \cdot \frac{\partial f}{\partial p}}^{\text{streaming}} + \overbrace{\left(\frac{df}{dt} \right)_{\text{coll}}}^{\text{collision}} \quad .
$$

In the absence of collisions, the distribution evolves solely due to the streaming term with $\dot{r} = p/m$ and $\dot{p} = -\nabla U_{\text{ext}}$. If $\dot{p} = F_{\text{ext}}$ is constant, we have the general solution

$$
f(r, p, t) = \phi \left(r - \frac{p\,t}{m} + \frac{F_{\text{ext}} t^2}{2m} , \, p - \frac{F_{\text{ext}} t}{m} \right) \quad ,
$$

valid for any initial condition $f(r, p, t = 0) = \phi(r, p)$. We write the *convective derivative* as $\frac{D}{Dt} = \frac{\partial}{\partial t} + \dot{r} \cdot \frac{\partial}{\partial r} + \dot{p} \cdot \frac{\partial}{\partial p}$. Then the Boltzmann equation may be written $\frac{Df}{Dt} = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}$.

• *Collisions*: We are concerned with two types of collision processes: single-particle scattering, due to a local potential, and two-particle scattering, due to interparticle forces. Let Γ denote the set of single particle kinematic variables, *e.g.* $\Gamma = (p_x, p_y, p_z)$ for point particles and $\Gamma = (p, L)$ for diatomic molecules. Then

$$
\left(\frac{df}{dt} \right)_{\text{coll}} = \int d\Gamma' \left\{ w(\Gamma \,|\, \Gamma') f(r, \Gamma'; t) - w(\Gamma' \,|\, \Gamma) f(r, \Gamma; t) \right\}
$$

for single particle scattering, and

$$
\left(\frac{df}{dt} \right)_{\text{coll}} = \int d\Gamma_1 \!\int d\Gamma' \!\int d\Gamma_1' \left\{ w(\Gamma \Gamma_1 \,|\, \Gamma' \Gamma_1') f_2(r, \Gamma'; r, \Gamma_1'; t) - w(\Gamma' \Gamma_1' \,|\, \Gamma \Gamma_1) f_2(r, \Gamma; r, \Gamma_1; t) \right\}
$$

$$
\approx \int d\Gamma_1 \!\int d\Gamma' \!\int d\Gamma_1' \left\{ w(\Gamma \Gamma_1 \,|\, \Gamma' \Gamma_1') f(r, \Gamma'; t) \, f(r, \Gamma_1'; t) \right.
$$

$$
\left. - w(\Gamma' \Gamma_1' \,|\, \Gamma \Gamma_1) f(r, \Gamma; t) \, f(r, \Gamma_1; t) \right\} \quad .
$$

for two-body scattering, where f_2 is the two-body distribution, and where the approximation $f_2(r, \Gamma'; r', \Gamma'; t) \approx f(r, \Gamma; t) \, f(r', \Gamma'; t)$ in the second line closes the equation. A quantity $\mathcal{A}(r, \Gamma)$ which is preserved by the dynamics between collisions then satisfies

$$
\frac{d\mathcal{A}}{dt} \equiv \frac{d}{dt} \int d^d r \, d\Gamma \, \mathcal{A}(r, \Gamma) \, f(r, \Gamma, t) = \int d^d r \, d\Gamma \, A(r, \Gamma) \left(\frac{df}{dt} \right)_{\text{coll}} \quad .
$$

Quantities which are conserved by collisions satisfy $\dot{A} = 0$ and are called *collisional invariants*. Examples include $\mathcal{A} = 1$ (particle number), $\mathcal{A} = p$ (linear momentum, if translational invariance applies), and $\mathcal{A} = \varepsilon_p$ (energy).

● *Time reversal, parity, and detailed balance*: With $\Gamma = (\boldsymbol{p}, \boldsymbol{L})$, we define the actions of time reversal and parity as

$$\Gamma^T = (-\boldsymbol{p}, -\boldsymbol{L}) \qquad , \qquad \Gamma^P = (-\boldsymbol{p}, \boldsymbol{L}) \qquad , \qquad \Gamma^C = (\boldsymbol{p}, -\boldsymbol{L}) \quad ,$$

where $C = PT$ is the combined operation. Time reversal symmetry of the underlying equations of motion requires $w\big(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1\big) = w\big(\Gamma^T\Gamma_1^T \,|\, \Gamma'^T\Gamma_1'^T\big)$. Under conditions of *detailed balance*, this leads to $f^0(\Gamma)\,f^0(\Gamma_1) = f^0(\Gamma'^T)\,f^0(\Gamma_1'^T)$, where f^0 is the equilibrium distribution. For systems with both P and T symmetries, $w\big(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1\big) = w\big(\Gamma^C\Gamma_1^C \,|\, \Gamma'^C\Gamma_1'^C\big)$, whence $w(\boldsymbol{p}', \boldsymbol{p}_1' \,|\, \boldsymbol{p}, \boldsymbol{p}_1) = w(\boldsymbol{p}, \boldsymbol{p}_1 \,|\, \boldsymbol{p}', \boldsymbol{p}_1')$ for point particles.

● *Boltzmann's $\mathcal{H}$-theorem*: Let $h(\boldsymbol{r}, t) = \int d\Gamma\, f(\boldsymbol{r}, \Gamma, t) \ln f(\boldsymbol{r}, \Gamma, t)$. Invoking the Boltzmann equation, it can be shown that $\frac{\partial h}{\partial t} \le 0$, which means $\frac{d\mathcal{H}}{dt} \le 0$, where $\mathcal{H}(t) = \int d^dr\, h(\boldsymbol{r}, t)$ is Boltzmann's $\mathcal{H}$-function. $h(\boldsymbol{r}, t)$ is everywhere decreasing or constant, due to collisions.

● *Weakly inhomogeneous gas*: Under equilibrium conditions, f^0 can be a function only of collisional invariants, and takes the Gibbs form $f^0(\boldsymbol{r}, \boldsymbol{p}) = C e^{(\mu + \boldsymbol{V}\cdot\boldsymbol{p} - \varepsilon_\Gamma)/k_{\mathrm{B}}T}$. Assume now that μ, $\boldsymbol{V}$, and T are all weakly dependent on $\boldsymbol{r}$ and t. f^0 then describes a *local equilibrium* and as such is annihilated by the collision term in the Boltzmann equation, but not by the streaming term. Accordingly, we seek a solution $f = f^0 + \delta f$. A lengthy derivation results in

$$\left\{ \frac{\varepsilon_\Gamma - \mathsf{h}}{T}\, \boldsymbol{v}\cdot\boldsymbol{\nabla}T + m\, v_\alpha v_\beta\, \mathcal{Q}_{\alpha\beta} - \frac{\varepsilon_\Gamma - \mathsf{h} + T c_p}{c_V/k_{\mathrm{B}}}\, \boldsymbol{\nabla}\cdot\boldsymbol{V} - \boldsymbol{F}^{\mathrm{ext}}\cdot\boldsymbol{v} \right\} \frac{f^0}{k_{\mathrm{B}}T} + \frac{\partial\,\delta f}{\partial t} = \left(\frac{df}{dt} \right)_{\mathrm{coll}} \quad ,$$

where $\boldsymbol{v} = \frac{\partial\varepsilon}{\partial\boldsymbol{p}}$ is the particle velocity, h is the enthalpy per particle, $\mathcal{Q}_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial V^\alpha}{\partial x^\beta} + \frac{\partial V^\beta}{\partial x^\alpha} \right)$, and $\boldsymbol{F}^{\mathrm{ext}}$ is an external force. For an ideal gas, $\mathsf{h} = c_p T$. The RHS is to be evaluated to first order in δf. The simplest model for the collision integral is the *relaxation time approximation*, where $\left(\frac{\partial f}{\partial t} \right)_{\mathrm{coll}} = -\frac{\delta f}{\tau}$. Note that this form does not preserve any collisional invariants. The scattering time is obtained from the relation $n\bar{v}_{\mathrm{rel}}\sigma\tau = 1$, where σ is the two particle total scattering cross section and $\bar{v}_{\mathrm{rel}}$ is the average relative speed of a pair of particles. This says that there is on average one collision within a tube of cross sectional area σ and length $\bar{v}_{\mathrm{rel}}\tau$. For the Maxwellian distribution, $\bar{v}_{\mathrm{rel}} = \sqrt{2}\,\bar{v} = \sqrt{\frac{16\,k_{\mathrm{B}}T}{\pi m}}$, so $\tau(T) \propto T^{-1/2}$. The *mean free path* is defined as $\ell = \bar{v}\tau = \frac{1}{\sqrt{2}\,n\sigma}$.

● *Transport coefficients*: Assuming $F_\alpha^{\mathrm{ext}} = \mathcal{Q}_{\alpha\beta} = 0$ and steady state, Eq. 8 yields

$$\delta f = -\frac{\tau(\varepsilon - c_p T)}{k_{\mathrm{B}}T^2}\, (\boldsymbol{v}\cdot\boldsymbol{\nabla}T)\, f^0 \quad .$$

The energy current is given by

$$j_\varepsilon^\alpha = \int d\Gamma\, \varepsilon_\Gamma\, v^\alpha\, \delta f = -\overbrace{\frac{n\tau}{k_{\mathrm{B}}T^2}\, \big\langle v^\alpha v^\beta\, \varepsilon_\Gamma(\varepsilon_\Gamma - c_p T) \big\rangle}^{\text{thermal conductivity } \kappa^{\alpha\beta}}\, \frac{\partial T}{\partial x^\beta} \quad .$$

For a monatomic gas, one finds $\kappa^{\alpha\beta} = \kappa \, \delta^{\alpha\beta}$ with $\kappa(T) = \frac{\pi}{8} n \ell \bar{v} c_p \propto T^{1/2}$. A similar result follows by considering any intensive quantity ϕ which is spatially dependent through the temperature $T(\boldsymbol{r})$. The ϕ-current across the surface $z = 0$ is

$$
\boldsymbol{j}_\phi = n\hat{\boldsymbol{z}} \int\limits_{v_z > 0} d^3v \, P(\boldsymbol{v}) \, v_z \, \phi(z - \ell \cos\theta) + n\hat{\boldsymbol{z}} \int\limits_{v_z < 0} d^3v \, P(\boldsymbol{v}) \, v_z \, \phi(z + \ell \cos\theta) = -\tfrac{1}{3} n \, \bar{v} \, \ell \, \frac{\partial \phi}{\partial z} \, \hat{\boldsymbol{z}} \quad .
$$

Thus, $\boldsymbol{j}_\phi = -K\boldsymbol{\nabla}T$, with $K = \frac{1}{3}n \, \ell \, \bar{v} \, \frac{\partial \phi}{\partial T}$ the associated transport coefficient. If $\phi = \langle \varepsilon_\Gamma \rangle$, then $\frac{\partial \phi}{\partial T} = c_p$, yielding $\kappa = \frac{1}{3}n\ell\bar{v}c_p$. If $\phi = \langle p_x \rangle$, then $j_{p_x}^z = \Pi_{xz} = -\frac{1}{3}nm\ell\bar{v}\frac{\partial V_x}{\partial z} \equiv -\eta\frac{\partial V_x}{\partial z}$, where η is the shear viscosity. Using the Boltzmann equation in the relaxation time approximation, one obtains $\eta = \frac{\pi}{8}nm\ell\bar{v}$. From κ and η, we can form a dimensionless quantity $\mathrm{Pr} = \eta c_p/m\kappa$, known as the *Prandtl number*. Within the relaxation time approximation, $\mathrm{Pr} = 1$. Most monatomic gases have $\mathrm{Pr} \approx \frac{2}{3}$.

• *Linearized Boltzmann equation*: To go beyond the phenomenological relaxation time approximation, one must grapple with the collision integral,

$$
\left(\frac{df}{dt}\right)_{\mathrm{coll}} = \int d^3p_1 \int d^3p' \int d^3p_1' \, w(\boldsymbol{p}', \boldsymbol{p}_1' \,|\, \boldsymbol{p}, \boldsymbol{p}_1) \left\{ f(\boldsymbol{p}') \, f(\boldsymbol{p}_1') - f(\boldsymbol{p}) \, f(\boldsymbol{p}_1) \right\} \quad ,
$$

which is a nonlinear functional of the distribution $f(\boldsymbol{p}, t)$ (we suppress the t index here). Writing $f(\boldsymbol{p}) = f^0(\boldsymbol{p}) + f^0(\boldsymbol{p}) \, \psi(\boldsymbol{p})$, we have $\left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}} = f^0(\boldsymbol{p}) \, \hat{L}\psi + \mathcal{O}(\psi^2)$, with

$$
\hat{L}\psi(\boldsymbol{p}) = \int d^3p_1 \int d\Omega \, |\boldsymbol{v} - \boldsymbol{v}_1| \, \frac{\partial \sigma}{\partial \Omega} \, f^0(\boldsymbol{p}_1) \left\{ \psi(\boldsymbol{p}') + \psi(\boldsymbol{p}_1') - \psi(\boldsymbol{p}) - \psi(\boldsymbol{p}_1) \right\} \quad .
$$

The linearized Boltzmann equation (LBE) then takes the form $\left(\hat{L} - \frac{\partial}{\partial t}\right)\psi = Y$, where

$$
Y = \frac{1}{k_{\mathrm{B}}T} \left\{ \frac{\varepsilon(\boldsymbol{p}) - \frac{5}{2}k_{\mathrm{B}}T}{T} \, \boldsymbol{v} \cdot \boldsymbol{\nabla}T + m \, v_\alpha v_\beta \, \mathcal{Q}_{\alpha\beta} - \frac{k_{\mathrm{B}} \, \varepsilon(\boldsymbol{p})}{c_V} \, \boldsymbol{\nabla}\cdot\boldsymbol{V} - \boldsymbol{F} \cdot \boldsymbol{v} \right\} \quad .
$$

for point particles. To solve the LBE, we must invert the operator $\hat{L} - \frac{\partial}{\partial t}$. Various useful properties follow from defining the inner product $\langle \psi_1 | \psi_2 \rangle \equiv \int d^3p \, f^0(\boldsymbol{p}) \, \psi_1(\boldsymbol{p}) \, \psi_2(\boldsymbol{p})$, such as the self-adjointness of $\hat{L}$: $\langle \psi_1 | \hat{L}\psi_2 \rangle = \langle \hat{L}\psi_1 | \psi_2 \rangle$. We then have $\hat{L}|\phi_n\rangle = -\lambda_n |\phi_n\rangle$, with $\langle \phi_m | \phi_n \rangle = \delta_{mn}$ and real eigenvalues λ_n. There are five zero eigenvalues corresponding to the collisional invariants:

$$
\phi_1(\boldsymbol{p}) = \frac{1}{\sqrt{n}} \qquad , \qquad \phi_{2,3,4}(\boldsymbol{p}) = \frac{p_\alpha}{\sqrt{nmk_{\mathrm{B}}T}} \qquad , \qquad \phi_5(\boldsymbol{p}) = \sqrt{\frac{2}{3n}} \left(\frac{\varepsilon(\boldsymbol{p})}{k_{\mathrm{B}}T} - \frac{3}{2} \right) \quad .
$$

When $Y = 0$, the formal solution to $\frac{\partial \psi}{\partial t} = \hat{L}\psi$ is $\psi(\boldsymbol{p}, t) = \sum_n C_n \, \phi_n(\boldsymbol{p}) \, e^{-\lambda_n t}$. Aside from the collisional invariants, all the eigenvalues λ_n must be positive, corresponding to relaxation to the equilibrium state. One can check that the particle, energy, and heat currents are given by $\boldsymbol{j} = \langle \boldsymbol{v} \,|\, \psi \rangle$, $\boldsymbol{j}_\varepsilon = \langle \boldsymbol{v}\,\varepsilon \,|\, \psi \rangle$, and $\boldsymbol{j}_q = \langle \boldsymbol{v}\,(\varepsilon - \mu) \,|\, \psi \rangle$.

In steady state, the solution to $\hat{L}\psi = Y$ is $\psi = \hat{L}^{-1}Y$. This is valid provided Y is orthogonal to each of the collisional invariants, in which case

$$\psi(\boldsymbol{p}) = \sum_{n \notin \mathsf{CI}} \lambda_n^{-1} \langle \phi_n | Y \rangle \phi_n(\boldsymbol{p}) \quad .$$

Once we have $|\psi\rangle$, we may obtain the various transport coefficients by computing the requisite currents. For example, to find the thermal conductivity κ and shear viscosity η,

$$\kappa \quad : \quad Y = \frac{1}{k_\mathrm{B} T^2} \frac{\partial T}{\partial x} X_\kappa \quad , \quad X_\kappa \equiv \left(\varepsilon - \tfrac{5}{2} k_\mathrm{B}\right) v_x \quad \Rightarrow \quad \kappa = -\frac{\langle X_\kappa | \psi \rangle}{\partial T/\partial x}$$

$$\eta \quad : \quad Y = \frac{m}{k_\mathrm{B} T} \frac{\partial V_x}{\partial y} X_\eta \quad , \quad X_\eta \equiv v_x v_y \quad \Rightarrow \quad \eta = -\frac{m \langle X_\eta | \psi \rangle}{\partial V_x/\partial y} \quad .$$

• *Variational approach*: The Schwarz inequality, $\langle \psi | -\hat{L} | \psi \rangle \cdot \langle \phi | \hat{H} | \phi \rangle \geq \langle \phi | \hat{H} | \psi \rangle^2$, holds for the positive semidefinite operator $\hat{H} \equiv -\hat{L}$. One therefore has

$$\kappa \geq \frac{1}{k_\mathrm{B} T^2} \frac{\langle \phi | X_\kappa \rangle^2}{\langle \phi | \hat{H} | \phi \rangle} \quad , \quad \eta \geq \frac{m^2}{k_\mathrm{B} T} \frac{\langle \phi | X_\eta \rangle^2}{\langle \phi | \hat{H} | \phi \rangle} \quad .$$

Using variational functions $\phi_\kappa = \left(\varepsilon - \tfrac{5}{2} k_\mathrm{B} T\right) v_x$ and $\phi_\eta = v_x v_y$, one finds, after tedious calculations,

$$\kappa \geq \frac{75\, k_\mathrm{B}}{64\sqrt{\pi}\, d^2} \left(\frac{k_\mathrm{B} T}{m}\right)^{1/2} \quad , \quad \eta \geq \frac{5\,(m k_\mathrm{B} T)^{1/2}}{16\sqrt{\pi}\, d^2} \quad .$$

Taking the lower limit in each case, we obtain a Prandtl number $\mathsf{Pr} = \frac{\eta\, c_p}{m \kappa} = \frac{2}{3}$, which is close to what is observed for monatomic gases.

• *Quantum transport*: For quantum systems, the local equilibrium distribution is of the Bose-Einstein or Fermi-Dirac form,

$$f^0(\boldsymbol{r}, \boldsymbol{k}, t) = \left\{ \exp\left(\frac{\varepsilon(\boldsymbol{k}) - \mu(\boldsymbol{r}, t)}{k_\mathrm{B} T(\boldsymbol{r}, t)}\right) \mp 1 \right\}^{-1} \quad ,$$

with $\boldsymbol{k} = \boldsymbol{p}/\hbar$, and

$$\left(\frac{df}{dt}\right)_{\mathrm{coll}} = \int \frac{d^3 k_1}{(2\pi)^3} \int \frac{d^3 k'}{(2\pi)^3} \int \frac{d^3 k_1'}{(2\pi)^3}\, w \left\{ f' f_1' (1 \pm f)(1 \pm f_1) - f f_1 (1 \pm f')(1 \pm f_1') \right\}$$

where $w = w(\boldsymbol{k}, \boldsymbol{k}_1 | \boldsymbol{k}', \boldsymbol{k}_1')$, $f = f(\boldsymbol{k})$, $f_1 = f(\boldsymbol{k}_1)$, $f' = f(\boldsymbol{k}')$, and $f_1' = f(\boldsymbol{k}_1')$, and where we have assumed time-reversal and parity symmetry. The most important application is to electron transport in metals and semiconductors, in which case f^0 is the Fermi distribution. With $f = f^0 + \delta f$, one has, within the relaxation time approximation,

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

where $\mathcal{E} = -\boldsymbol{\nabla}(\phi - \mu/e) = \boldsymbol{E} - e^{-1}\boldsymbol{\nabla}\mu$ is the gradient of the 'electrochemical potential' $\phi - e^{-1}\mu$. For steady state transport with $\boldsymbol{B} = 0$, one has

$$\boldsymbol{j} = -2e \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\ \boldsymbol{v}\ \delta f \equiv L_{11}\,\mathcal{E} - L_{12}\,\boldsymbol{\nabla}\,T$$

$$\boldsymbol{j}_q = 2 \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\ (\varepsilon - \mu)\,\boldsymbol{v}\ \delta f \equiv L_{21}\,\mathcal{E} - L_{22}\,\boldsymbol{\nabla}\,T$$

where $L_{11}^{\alpha\beta} = e^2\,\mathcal{J}_0^{\alpha\beta}$, $L_{21}^{\alpha\beta} = TL_{12}^{\alpha\beta} = -e\,\mathcal{J}_1^{\alpha\beta}$, and $L_{22}^{\alpha\beta} = \frac{1}{T}\,\mathcal{J}_2^{\alpha\beta}$, with

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

These results entail

$$\mathcal{E} = \rho\,\boldsymbol{j} + Q\,\boldsymbol{\nabla}\,T\quad,\qquad \boldsymbol{j}_q = \sqcap\,\boldsymbol{j} - \kappa\,\boldsymbol{\nabla}\,T\quad,$$

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

$$\rho = \frac{1}{e^2}\,\mathcal{J}_0^{-1}\quad,\quad Q = -\frac{1}{e\,T}\,\mathcal{J}_0^{-1}\,\mathcal{J}_1\quad,\quad \sqcap = -\frac{1}{e}\,\mathcal{J}_1\,\mathcal{J}_0^{-1}\quad,\quad \kappa = \frac{1}{T}\left(\mathcal{J}_2 - \mathcal{J}_1\,\mathcal{J}_0^{-1}\,\mathcal{J}_1\right)\quad.$$

These results describe the following physical phenomena:

Electrical resistance ($\boldsymbol{\nabla}T = \boldsymbol{B} = 0$): An electrical current $\boldsymbol{j}$ will generate an electric field $\mathcal{E} = \rho\boldsymbol{j}$, where ρ is the *electrical resistivity*.

Peltier effect ($\boldsymbol{\nabla}T = \boldsymbol{B} = 0$): An electrical current $\boldsymbol{j}$ will generate an heat current $\boldsymbol{j}_q = \sqcap\boldsymbol{j}$, where $\sqcap$ is the *Peltier coefficient*.

Thermal conduction ($\boldsymbol{j} = \boldsymbol{B} = 0$): A temperature gradient $\boldsymbol{\nabla}T$ gives rise to a heat current $\boldsymbol{j}_q = -\kappa\boldsymbol{\nabla}T$, where κ is the *thermal conductivity*.

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

For a parabolic band with effective electron mass m^*, one finds

$$\rho = \frac{m^*}{ne^2\tau}\quad,\quad Q = -\frac{\pi^2 k_{\mathrm{B}}^2 T}{2e\,\varepsilon_{\mathrm{F}}}\quad,\quad \kappa = \frac{\pi^2 n\tau k_{\mathrm{B}}^2 T}{3m^*}$$

with $\sqcap = TQ$, where ε_{F} is the Fermi energy. The ratio $\kappa/\sigma T = \frac{\pi^2}{3}(k_{\mathrm{B}}/e)^2 = 2.45 \times 10^{-8}\mathrm{V^2K^{-2}}$ is then predicted to be universal, a result known as the *Wiedemann-Franz law*. This also predicts all metals to have negative thermopower, which is not the case. In the presence of an external magnetic field $\boldsymbol{B}$, additional transport effects arise:

Hall effect ($\frac{\partial T}{\partial x} = \frac{\partial T}{\partial y} = j_y = 0$): An electrical current $\boldsymbol{j} = j_x\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield an electric field $\mathcal{E}$. The *Hall coefficient* is $R_{\mathrm{H}} = \mathcal{E}_y/j_x\,B_z$.

Ettingshausen effect ($\frac{\partial T}{\partial x} = j_y = j_{q,y} = 0$): An electrical current $\boldsymbol{j} = j_x \hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z \hat{\boldsymbol{z}}$ yield a temperature gradient $\frac{\partial T}{\partial y}$. The _Ettingshausen coefficient_ is $P = \frac{\partial T}{\partial y} / j_x B_z$.

Nernst effect ($j_x = j_y = \frac{\partial T}{\partial y} = 0$): A temperature gradient $\boldsymbol{\nabla} T = \frac{\partial T}{\partial x} \hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z \hat{\boldsymbol{z}}$ yield an electric field $\boldsymbol{\mathcal{E}}$. The _Nernst coefficient_ is $\Lambda = \mathcal{E}_y / \frac{\partial T}{\partial x} B_z$.

Righi-Leduc effect ($j_x = j_y = \mathcal{E}_y = 0$): A temperature gradient $\boldsymbol{\nabla} T = \frac{\partial T}{\partial x} \hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z \hat{\boldsymbol{z}}$ yield an orthogonal gradient $\frac{\partial T}{\partial y}$. The _Righi-Leduc coefficient_ is $\mathcal{L} = \frac{\partial T}{\partial y} / \frac{\partial T}{\partial x} B_z$.

● _Stochastic processes_: Stochastic processes involve a random element, hence they are not wholly deterministic. The simplest example is the Langevin equation for Brownian motion, $\dot{p} + \gamma p = F + \eta(t)$, where p is a particle's momentum, γ a damping rate due to friction, F an external force, and $\eta(t)$ a _stochastic random force_. We can integrate this first order equation to obtain

$$p(t) = p(0)\, e^{-\gamma t} + \frac{F}{\gamma} \left(1 - e^{-\gamma t}\right) + \int\limits_0^t ds\, \eta(s)\, e^{\gamma(s-t)} \quad .$$

We assume that the random force $\eta(t)$ has zero mean, and furthermore that

$$\langle \eta(s)\, \eta(s') \rangle = \phi(s - s') \approx \Gamma\, \delta(s - s') \quad ,$$

in which case one finds $\langle p^2(t) \rangle = \langle p(t) \rangle^2 + \frac{\Gamma}{2\gamma}(1 - e^{-2\gamma t})$. If there is no external force, we expect the particle thermailzes at long times, _i.e._ $\langle \frac{p^2}{2m} \rangle = \frac{1}{2} k_{\mathrm{B}} T$. This fixes $\Gamma = 2\gamma m k_{\mathrm{B}} T$, where m is the particle's mass. One can integrate again to find the position. At late times $t \gg \gamma^{-1}$, one finds $\langle x(t) \rangle = \mathrm{const.} + \frac{Ft}{\gamma m}$, corresponding to a mean velocity $\langle p/m \rangle = F/\gamma$. The RMS fluctuations in position, however, grow as

$$\langle x^2(t) \rangle - \langle x(t) \rangle^2 = \frac{2k_{\mathrm{B}} T t}{\gamma m} \equiv 2Dt \quad ,$$

where $D = k_{\mathrm{B}} T / \gamma m$ is the _diffusion constant_. Thus, after the memory of the initial conditions is lost ($t \gg \gamma^{-1}$), the mean position advances linearly in time due to the external force, and the RMS fluctuations in position also increase linearly.

● _Fokker-Planck equation_: Suppose $x(t)$ is a stochastic variable, and define

$$\delta x(t) \equiv x(t + \delta t) - x(t) \quad .$$

Furthermore, assume $\langle \delta x(t) \rangle = F_1\big(x(t)\big) \delta t$ and $\langle [\delta x(t)]^2 \rangle = F_2\big(x(t)\big) \delta t$, but that $\langle [\delta x(t)]^n \rangle - \mathcal{O}(\delta t^2)$ for $n > 2$. One can then show that the probability density $P(x,t) = \big\langle \delta\big(x - x(t)\big) \big\rangle$ satisfies the _Fokker-Planck equation_,

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x} \big[F_1(x)\, P(x,t) \big] + \frac{1}{2} \frac{\partial^2}{\partial x^2} \big[F_2(x)\, P(x,t) \big] \quad .$$

For Brownian motion, $F_1(x) = F/\gamma m \equiv u$ and $F_2(x) = 2D$. The resulting Fokker-Planck equation is then $P_t = -uP_x + DP_{xx}$, where $P_t = \frac{\partial P}{\partial t}$, $P_{xx} = \frac{\partial^2 P}{\partial x^2}$, *etc.* The Galilean transformation $x \to x - ut$ then results in $P_t = DP_{xx}$, which is known as the *diffusion equation*, a general solution to which is given by $P(x,t) = \int_{-\infty}^{\infty} dx'\, K(x - x', t - t')\, P(x', t')$, where

$$K(\Delta x, \Delta t) = (4\pi D\Delta t)^{-1/2} e^{-(\Delta x)^2/4D\Delta t}$$

is the *diffusion kernel*. Thus, $\Delta x_{\mathrm{RMS}} = \sqrt{2D\Delta t}$.