8 Nonequilibrium and Transport Phenomena : Summary

• *Boltzmann equation*: The full phase space distribution for a Hamiltonian system, $\varrho(\boldsymbol{\varphi}, t)$, where $\boldsymbol{\varphi} = \big(\{q_\sigma\}, \{p_\sigma\}\big)$, satisfies $\dot\varrho + \dot{\boldsymbol{\varphi}} \cdot \boldsymbol{\nabla}\varrho = 0$. This is not true, however, for the one-particle distribution $\boldsymbol{f}(\boldsymbol{q}, \boldsymbol{p}, t)$. 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

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

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

$$f(\boldsymbol{r}, \boldsymbol{p}, t) = \phi\bigg(\boldsymbol{r} - \frac{\boldsymbol{p}\, t}{m} + \frac{\boldsymbol{F}_{\text{ext}} t^2}{2m} \,,\, \boldsymbol{p} - \frac{\boldsymbol{F}_{\text{ext}} t}{m}\bigg) \quad ,$$

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

• *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 $\mathit{\Gamma}$ denote the set of single particle kinematic variables, *e.g.* $\mathit{\Gamma} = (p_x, p_y, p_z)$ for point particles and $\mathit{\Gamma} = (\boldsymbol{p}, \boldsymbol{L})$ for diatomic molecules. Then

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

for single particle scattering, and

$$\begin{aligned} \left(\frac{df}{dt}\right)_{\text{coll}} &= \int\! d\mathit{\Gamma}_1 \!\int\! d\mathit{\Gamma}' \!\int\! d\mathit{\Gamma}_1' \, \Big\{ w\big(\mathit{\Gamma}\mathit{\Gamma}_1 \,|\, \mathit{\Gamma}'\mathit{\Gamma}_1'\big)\, f_2(\boldsymbol{r}, \mathit{\Gamma}'; \boldsymbol{r}, \mathit{\Gamma}_1'; t) - w\big(\mathit{\Gamma}'\mathit{\Gamma}_1' \,|\, \mathit{\Gamma}\mathit{\Gamma}_1\big)\, f_2(\boldsymbol{r}, \mathit{\Gamma}; \boldsymbol{r}, \mathit{\Gamma}_1; t) \Big\} \\ &\approx \int\! d\mathit{\Gamma}_1 \!\int\! d\mathit{\Gamma}' \!\int\! d\mathit{\Gamma}_1' \, \Big\{ w\big(\mathit{\Gamma}\mathit{\Gamma}_1 \,|\, \mathit{\Gamma}'\mathit{\Gamma}_1'\big)\, f(\boldsymbol{r}, \mathit{\Gamma}'; t)\, f(\boldsymbol{r}, \mathit{\Gamma}_1'; t) \\ &\qquad\qquad\qquad\qquad - w\big(\mathit{\Gamma}'\mathit{\Gamma}_1' \,|\, \mathit{\Gamma}\mathit{\Gamma}_1\big)\, f(\boldsymbol{r}, \mathit{\Gamma}; t)\, f(\boldsymbol{r}, \mathit{\Gamma}_1; t) \Big\} \quad . \end{aligned}$$

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

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

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

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

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

where $C = PT$ is the combined operation. Time reversal symmetry of the underlying equations of motion requires $w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big) = w\big(\varGamma^T\varGamma_1^T \,|\, \varGamma'^T\varGamma_1'^T\big)$. Under conditions of *detailed balance*, this leads to $f^0(\varGamma)\, f^0(\varGamma_1) = f^0(\varGamma'^T)\, f^0(\varGamma_1'^T)$, where f^0 is the equilibrium distribution. For systems with both P and T symmetries, $w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big) = w\big(\varGamma^C\varGamma_1^C \,|\, \varGamma'^C\varGamma_1'^C\big)$, 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 $h(\boldsymbol{r}, t) = \int d\varGamma\, f(\boldsymbol{r}, \varGamma, t) \ln f(\boldsymbol{r}, \varGamma, t)$. 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 $\mathcal{H}(t) = \int d^d\!r\; h(\boldsymbol{r}, t)$ 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 $f^0(\boldsymbol{r}, \boldsymbol{p}) = C e^{(\mu + \boldsymbol{V}\cdot\boldsymbol{p} - \varepsilon_\varGamma)/k_\mathrm{B}T}$. 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

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

where $\boldsymbol{v} = \frac{\partial \varepsilon}{\partial \boldsymbol{p}}$ is the particle velocity, h is the enthalpy per particle, $\mathcal{Q}_{\alpha\beta} = \frac{1}{2}\Big(\frac{\partial V^\alpha}{\partial x^\beta} + \frac{\partial V^\beta}{\partial x^\alpha}\Big)$, 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 $\big(\frac{\partial f}{\partial t}\big)_\mathrm{coll} = -\frac{\delta f}{\tau}$. 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 $F^\mathrm{ext}_\alpha = \mathcal{Q}_{\alpha\beta} = 0$ 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

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

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

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

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 $j^z_{p_x} = \Pi_{xz} = -\frac{1}{3}nm\ell\bar{v}\frac{\partial V_x}{\partial z} \equiv -\eta\frac{\partial V_x}{\partial z}$, 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 $\mathsf{Pr} = \eta c_p/m\kappa$, known as the *Prandtl number*. Within the relaxation time approximation, $\mathsf{Pr} = 1$. Most monatomic gases have $\mathsf{Pr} \approx \frac{2}{3}$.

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

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

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 $\big(\frac{\partial f}{\partial t}\big)_{\rm coll} = f^0(\boldsymbol{p})\,\hat{L}\psi + \mathcal{O}(\psi^2)$, with

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

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

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

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 $\langle\psi_1|\psi_2\rangle \equiv \int\! d^3\!p\, f^0(\boldsymbol{p})\,\psi_1(\boldsymbol{p})\,\psi_2(\boldsymbol{p})$, 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:

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

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,

$$\begin{aligned} \kappa \quad &: \quad Y = \frac{1}{k_{\rm B} T^2} \frac{\partial T}{\partial x} X_\kappa \quad , \quad X_\kappa \equiv \big(\varepsilon - \tfrac{5}{2} k_{\rm B}\big) \, v_x \quad \Rightarrow \quad \kappa = -\frac{\langle \, X_\kappa \, | \, \psi \, \rangle}{\partial T / \partial x} \\ \eta \quad &: \quad Y = \frac{m}{k_{\rm B} T} \frac{\partial V_x}{\partial y} X_\eta \quad , \quad X_\eta \equiv v_x \, v_y \quad \Rightarrow \quad \eta = -\frac{m \, \langle \, X_\eta \, | \, \psi \, \rangle}{\partial V_x / \partial y} \quad . \end{aligned}$$

• *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

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

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

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

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,

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

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

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

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,

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

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

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

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

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

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

These results entail

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

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:

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

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

<u>*Thermal conduction*</u> ($\boldsymbol{j} = \boldsymbol{B} = 0$): 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*.

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

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

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

with $\sqcap = TQ$, where $\varepsilon_{\rm F}$ is the Fermi energy. The ratio $\kappa/\sigma T = \frac{\pi^2}{3}(k_{\rm B}/e)^2 = 2.45 \times 10^{-8}\,{\rm V}^2{\rm K}^{-2}$ 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:

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

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 $P = \frac{\partial T}{\partial y}\Big/ j_x\,B_z$.

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 $\Lambda = \mathcal{E}_y\Big/\frac{\partial T}{\partial x}\,B_z$.

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 $\mathcal{L} = \frac{\partial T}{\partial y}\Big/\frac{\partial T}{\partial x} B_z$.

• *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

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

in which case one finds $\langle p^2(t)\rangle = \langle p(t)\rangle^2 + \frac{\mathit{\Gamma}}{2\gamma}(1 - e^{-2\gamma t})$. 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 $\mathit{\Gamma} = 2\gamma m k_{\mathrm{B}}T$, where m is the particle's mass. One can integrate again to find the position. At late times $t \gg \gamma^{-1}$, one finds $\langle x(t)\rangle = \text{const.} + \frac{Ft}{\gamma m}$, corresponding to a mean velocity $\langle p/m\rangle = F/\gamma$. The RMS fluctuations in position, however, grow as

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

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 $\big\langle [\delta x(t)]^2\big\rangle = F_2\big(x(t)\big)\delta t$, but that $\big\langle [\delta x(t)]^n\big\rangle - \mathcal{O}(\delta t^2)$ 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 $P(x,t) = \int\limits_{-\infty}^{\infty} dx'\, K(x - x', t - t')\, P(x', t')$, 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, $\Delta x_{\mathrm{RMS}} = \sqrt{2D\Delta t}$.