

8 Nonequilibrium and Transport Phenomena : Summary

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

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

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

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

valid for any initial condition $f(\mathbf{r}, \mathbf{p}, t=0) = \phi(\mathbf{r}, \mathbf{p})$. We write the *convective derivative* as $\frac{D}{Dt} = \frac{\partial}{\partial t} + \dot{\mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{r}} + \dot{\mathbf{p}} \cdot \frac{\partial}{\partial \mathbf{p}}$. 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 $\Gamma = (\mathbf{p}, \mathbf{L})$ for diatomic molecules. Then

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

for single particle scattering, and

$$\begin{aligned} \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} &= \int d\Gamma_1 \int d\Gamma' \int d\Gamma'_1 \left\{ w(\Gamma\Gamma_1 | \Gamma'\Gamma'_1) f_2(\mathbf{r}, \Gamma'; \mathbf{r}, \Gamma'_1; t) - w(\Gamma'\Gamma'_1 | \Gamma\Gamma_1) f_2(\mathbf{r}, \Gamma; \mathbf{r}, \Gamma_1; t) \right\} \\ &\approx \int d\Gamma_1 \int d\Gamma' \int d\Gamma'_1 \left\{ w(\Gamma\Gamma_1 | \Gamma'\Gamma'_1) f(\mathbf{r}, \Gamma'; t) f(\mathbf{r}, \Gamma'_1; t) \right. \\ &\quad \left. - w(\Gamma'\Gamma'_1 | \Gamma\Gamma_1) f(\mathbf{r}, \Gamma; t) f(\mathbf{r}, \Gamma_1; t) \right\} . \end{aligned}$$

for two-body scattering, where f_2 is the two-body distribution, and where the approximation $f_2(\mathbf{r}, \Gamma'; \mathbf{r}', \Gamma'_1; t) \approx f(\mathbf{r}, \Gamma; t) f(\mathbf{r}', \Gamma'_1; t)$ in the second line closes the equation. A quantity $\mathcal{A}(\mathbf{r}, \Gamma)$ which is preserved by the dynamics between collisions then satisfies

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

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

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

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

where $C = PT$ is the combined operation. Time reversal symmetry of the underlying equations of motion requires $w(\Gamma' \Gamma'_1 | \Gamma \Gamma_1) = w(\Gamma^T \Gamma_1^T | \Gamma'^T \Gamma_1'^T)$. 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, $w(\Gamma' \Gamma'_1 | \Gamma \Gamma_1) = w(\Gamma^C \Gamma_1^C | \Gamma'^C \Gamma_1'^C)$, whence $w(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1) = w(\mathbf{p}, \mathbf{p}_1 | \mathbf{p}', \mathbf{p}'_1)$ for point particles.

- *Boltzmann's H-theorem:* Let $h(\mathbf{r}, t) = \int d\Gamma f(\mathbf{r}, \Gamma, t) \ln f(\mathbf{r}, \Gamma, t)$. Invoking the Boltzmann equation, it can be shown that $\frac{\partial h}{\partial t} \leq 0$, which means $\frac{dH}{dt} \leq 0$, where $H(t) = \int d^d r h(\mathbf{r}, t)$ is Boltzmann's H-function. $h(\mathbf{r}, t)$ 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 $f^0(\mathbf{r}, \mathbf{p}) = C e^{(\mu + \mathbf{V} \cdot \mathbf{p} - \varepsilon_\Gamma) / k_B T}$. Assume now that μ , \mathbf{V} , and T are all weakly dependent on \mathbf{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

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

where $\mathbf{v} = \frac{\partial \varepsilon}{\partial \mathbf{p}}$ 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 \mathbf{F}^{ext} is an external force. For an ideal gas, $h = c_p T$. The RHS is to be evaluated to first order in δf . The simplest model for the collision integral is the *relaxation time approximation*, where $\left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = -\frac{\delta f}{\tau}$. Note that this form does not preserve any collisional invariants. The scattering time is obtained from the relation $n \bar{v}_{\text{rel}} \sigma \tau = 1$, where σ is the two particle total scattering cross section and \bar{v}_{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 $\bar{v}_{\text{rel}} \tau$. For the Maxwellian distribution, $\bar{v}_{\text{rel}} = \sqrt{2} \bar{v} = \sqrt{\frac{16 k_B T}{\pi m}}$, 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 $F_\alpha^{\text{ext}} = \mathcal{Q}_{\alpha\beta} = 0$ and steady state, Eq. 8 yields

$$\delta f = -\frac{\tau(\varepsilon - c_p T)}{k_B T^2} (\mathbf{v} \cdot \nabla T) f^0 \quad .$$

The energy current is given by

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

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 $T(\mathbf{r})$. The ϕ -current across the surface $z = 0$ is

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

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

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

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = \int d^3p_1 \int d^3p' \int d^3p'_1 w(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1) \left\{ f(\mathbf{p}') f(\mathbf{p}'_1) - f(\mathbf{p}) f(\mathbf{p}_1) \right\} \quad ,$$

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

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

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

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

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

$$\phi_1(\mathbf{p}) = \frac{1}{\sqrt{n}} \quad , \quad \phi_{2,3,4}(\mathbf{p}) = \frac{p_\alpha}{\sqrt{n m k_B T}} \quad , \quad \phi_5(\mathbf{p}) = \sqrt{\frac{2}{3n}} \left(\frac{\varepsilon(\mathbf{p})}{k_B T} - \frac{3}{2} \right) \quad .$$

When $Y = 0$, the formal solution to $\frac{\partial \psi}{\partial t} = \hat{L} \psi$ is $\psi(\mathbf{p}, t) = \sum_n C_n \phi_n(\mathbf{p}) e^{-\lambda_n t}$. 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 $\mathbf{j} = \langle \mathbf{v} | \psi \rangle$, $\mathbf{j}_\varepsilon = \langle \mathbf{v} \varepsilon | \psi \rangle$, and $\mathbf{j}_q = \langle \mathbf{v} (\varepsilon - \mu) | \psi \rangle$.

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

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

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 ,

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

• *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

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

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

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

Taking the lower limit in each case, we obtain a Prandtl number $\text{Pr} = \frac{\eta c_p}{m \kappa} = \frac{2}{3}$, 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,

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

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

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

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

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

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

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

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

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

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

These results entail

$$\mathcal{E} = \rho \mathbf{j} + Q \nabla T \quad , \quad \mathbf{j}_q = \square \mathbf{j} - \kappa \nabla T \quad ,$$

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

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

These results describe the following physical phenomena:

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

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

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

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

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

$$\rho = \frac{m^*}{ne^2 \tau} \quad , \quad Q = -\frac{\pi^2 k_B^2 T}{2e \varepsilon_F} \quad , \quad \kappa = \frac{\pi^2 n \tau k_B^2 T}{3m^*}$$

with $\square = TQ$, where ε_F is the Fermi energy. The ratio $\kappa/\sigma T = \frac{\pi^2}{3} (k_B/e)^2 = 2.45 \times 10^{-8} \text{V}^2 \text{K}^{-2}$ 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 \mathbf{B} , additional transport effects arise:

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

Ettingshausen effect ($\frac{\partial T}{\partial x} = j_y = j_{q,y} = 0$): 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 $P = \frac{\partial T}{\partial y} / j_x B_z$.

Nernst effect ($j_x = j_y = \frac{\partial T}{\partial y} = 0$): 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 $\Lambda = \mathcal{E}_y / \frac{\partial T}{\partial x} B_z$.

Righi-Leduc effect ($j_x = j_y = \mathcal{E}_y = 0$): 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 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

$$p(t) = p(0) e^{-\gamma t} + \frac{F}{\gamma} (1 - e^{-\gamma t}) + \int_0^t ds \eta(s) e^{\gamma(s-t)} .$$

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

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

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 thermalizes at long times, *i.e.* $\langle \frac{p^2}{2m} \rangle = \frac{1}{2} k_B T$. This fixes $\Gamma = 2\gamma m k_B T$, 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

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

where $D = k_B T / \gamma m$ 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

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

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

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

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 $x \rightarrow x - ut$ 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, $\Delta x_{\text{RMS}} = \sqrt{2D\Delta t}$.