

8.S: Summary

References

- H. Smith and H. H. Jensen, *Transport Phenomena* (Oxford, 1989) An outstanding, thorough, and pellucid presentation of the theory of Boltzmann transport in classical and quantum systems.
- P. L. Krapivsky, S. Redner, and E. Ben-Naim, *A Kinetic View of Statistical Physics* (Cambridge, 2010) Superb, modern discussion of a broad variety of issues and models in nonequilibrium statistical physics.
- E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics* (Pergamon, 1981) Volume 10 in the famous Landau and Lifshitz *Course of Theoretical Physics*. Surprisingly readable, and with many applications (some advanced).
- M. Kardar, *Statistical Physics of Particles* (Cambridge, 2007) A superb modern text, with many insightful presentations of key concepts. Includes a very instructive derivation of the Boltzmann equation starting from the BBGKY hierarchy.
- J. A. McLennan, *Introduction to Non-equilibrium Statistical Mechanics* (Prentice-Hall, 1989) Though narrow in scope, this book is a good resource on the Boltzmann equation.
- F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, 1987) This has been perhaps the most popular undergraduate text since it first appeared in 1967, and with good reason. The later chapters discuss transport phenomena at an undergraduate level.
- N. G. Van Kampen, *Stochastic Processes in Physics and Chemistry* (3rd edition, North-Holland, 2007) This is a very readable and useful text. A relaxed but meaty presentation.

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 $f(\mathbf{q}, \mathbf{p}, t)$. 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 $\frac{Df}{Dt} = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}$

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

$$f(\mathbf{r}, \mathbf{p}, t) = \phi \left(\mathbf{r} - \frac{\mathbf{p}t}{m} + \frac{\mathbf{F}_{\text{ext}}t^2}{2m}, \mathbf{p} - \frac{\mathbf{F}_{\text{ext}}t}{m} \right), \quad (8.S.1)$$

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, $\Gamma = (p_x, p_y, p_z)$ for point particles and $\Gamma = (\mathbf{p}, \mathbf{L})$ for diatomic molecules. Then

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = \int d\Gamma' \left\{ w(\Gamma | \Gamma') f(\mathbf{r}, \Gamma'; t) - w(\Gamma' | \Gamma) f(\mathbf{r}, \Gamma; t) \right\} \quad (8.S.2)$$

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

$$\frac{d\mathcal{A}}{dt} \equiv \frac{d}{dt} \int d^d r d\Gamma \mathcal{A}(\mathbf{r}, \Gamma) f(\mathbf{r}, \Gamma, t) = \int d^d r d\Gamma \mathcal{A}(\mathbf{r}, \Gamma) \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}. \quad (8.S.3)$$

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

$$\Gamma^{\text{ss}} = (\Gamma^{\text{ss}})^{\text{ss}} \quad \Gamma^{\text{ss}} = (\Gamma^{\text{ss}})^{\text{ss}} \quad \Gamma^{\text{ss}} = (\Gamma^{\text{ss}})^{\text{ss}}$$

where $C = PT$ is the combined operation. Time reversal symmetry of the underlying equations of motion requires $w(\Gamma^{\text{ss}}_1, \Gamma^{\text{ss}}_2) = w(\Gamma^{\text{ss}}_2, \Gamma^{\text{ss}}_1)$. Under conditions of *detailed balance*, this leads to $f^0(\Gamma^{\text{ss}}_1) = f^0(\Gamma^{\text{ss}}_2)$, where f^0 is the equilibrium distribution. For systems with both P and T symmetries, $w(\Gamma^{\text{ss}}_1, \Gamma^{\text{ss}}_2) = w(\Gamma^{\text{ss}}_2, \Gamma^{\text{ss}}_1)$, 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 $H(t) = \int d^3r h(\mathbf{r}, t)$ 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 $f^0(\mathbf{r}, \mathbf{p}) = C e^{(\mu + \mathbf{V} \cdot \mathbf{p} - \varepsilon_p)/k_B T}$. 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

$$\left\{ \frac{\varepsilon_p - h}{T} \mathbf{v} \cdot \nabla T + m v_\alpha v_\beta Q_{\alpha\beta} - \frac{\varepsilon_p - h + T c_p}{c_p / k_B} \nabla \cdot \mathbf{V} - \mathbf{F}^{\text{ext}} \cdot \mathbf{v} \right\} \frac{f^0}{k_B T} + \frac{\partial \delta f}{\partial t} = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}, \quad (8.S.4)$$

where $\mathbf{v} = \frac{\partial \varepsilon}{\partial \mathbf{p}}$ is the particle velocity, h is the enthalpy per particle, $Q_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial V^\alpha}{\partial x^\beta} + \frac{\partial V^\beta}{\partial x^\alpha} \right)$, 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, $\bar{v}_{\text{rel}} = \sqrt{2} \bar{v}$.

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 $F_{\alpha}^{\text{ext}} = Q_{\alpha\beta} = 0$ and steady state, Eq. [8.S.4] yields

$$\delta f = -\frac{\tau(\varepsilon - c_p T)}{k_B T^2} (\mathbf{v} \cdot \nabla T) f^0. \quad (8.S.5)$$

The energy current is given by

$$j_\varepsilon^\alpha = \int d\Gamma \varepsilon_p v^\alpha \delta f = -\frac{\overbrace{n\tau}^{\text{thermal conductivity } \kappa^{\alpha\beta}}}{k_B T^2} \langle v^\alpha v^\beta \varepsilon_p (\varepsilon_p - c_p T) \rangle \frac{\partial T}{\partial x^\beta}. \quad (8.S.6)$$

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

$$\mathbf{j}_\phi = n \hat{\mathbf{z}} \int_{v_z > 0} d^3v P(\mathbf{v}) v_z \phi(z - \ell \cos \theta) + n \hat{\mathbf{z}} \int_{v_z < 0} d^3v P(\mathbf{v}) v_z \phi(z + \ell \cos \theta) = -\frac{1}{3} n \bar{v} \ell \frac{\partial \phi}{\partial z} \hat{\mathbf{z}}. \quad (8.S.7)$$

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 $\phi = \langle \varepsilon_p \rangle$, 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,

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = \int d^3p_1 \int d^3p'_1 \int d^3p'_2 w(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1) \left\{ f(\mathbf{p}') f(\mathbf{p}'_1) - f(\mathbf{p}) f(\mathbf{p}_1) \right\}, \quad (8.S.8)$$

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

$$\hat{L} \psi(\mathbf{p}) = \int d^3p_1 \int d\Omega |\mathbf{v} - \mathbf{v}_1| \frac{\partial \sigma}{\partial \Omega} f^0(\mathbf{p}_1) \left\{ \psi(\mathbf{p}') + \psi(\mathbf{p}'_1) - \psi(\mathbf{p}) - \psi(\mathbf{p}_1) \right\}. \quad (8.S.9)$$

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

$$Y = \frac{1}{k_B T} \left\{ \frac{\varepsilon(\mathbf{p}) - \frac{5}{2} k_B T}{T} \mathbf{v} \cdot \nabla T + m v_\alpha v_\beta \mathcal{Q}_{\alpha\beta} - \frac{k_B \varepsilon(\mathbf{p})}{c_V} \nabla \cdot \mathbf{V} - \mathbf{F} \cdot \mathbf{v} \right\}. \quad (8.S.10)$$

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:

$$\phi_1(\mathbf{p}) = \frac{1}{\sqrt{n}}, \quad \phi_{2,3,4}(\mathbf{p}) = \frac{p_\alpha}{\sqrt{nmk_B T}}, \quad \phi_5(\mathbf{p}) = \sqrt{\frac{2}{3n}} \left(\frac{\varepsilon(\mathbf{p})}{k_B T} - \frac{3}{2} \right). \quad (8.S.11)$$

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

$$\psi(\mathbf{p}) = \sum_{n \notin \text{CI}} \lambda_n^{-1} \langle \phi_n | Y \rangle \phi_n(\mathbf{p}). \quad (8.S.12)$$

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 ,

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

• *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

$$\kappa \geq \frac{1}{k_B T^2} \frac{\langle \phi | X_\kappa \rangle^2}{\langle \phi | \hat{H} | \phi \rangle}, \quad \eta \geq \frac{m^2}{k_B T} \frac{\langle \phi | X_\eta \rangle^2}{\langle \phi | \hat{H} | \phi \rangle}. \quad (8.S.13)$$

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

$$\kappa \geq \frac{75 k_B}{64 \sqrt{\pi} d^2} \left(\frac{k_B T}{m} \right)^{1/2}, \quad \eta \geq \frac{5 (m k_B T)^{1/2}}{16 \sqrt{\pi} d^2}. \quad (8.S.14)$$

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,

$$f^0(\mathbf{r}, \mathbf{k}, t) = \left\{ \exp \left(\frac{\varepsilon(\mathbf{k}) - \mu(\mathbf{r}, t)}{k_B T(\mathbf{r}, t)} \right) \mp 1 \right\}^{-1}, \quad (8.S.15)$$

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

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = \int \frac{d^3 k_1}{(2\pi)^3} \int \frac{d^3 k'}{(2\pi)^3} \int \frac{d^3 k'_1}{(2\pi)^3} w \left\{ f' f'_1 (1 \pm f) (1 \pm f_1) - f f_1 (1 \pm f') (1 \pm f'_1) \right\} \quad (8.S.16)$$

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,

$$\frac{\partial \delta f}{\partial t} - \frac{e}{\hbar c} \mathbf{v} \times \mathbf{B} \cdot \frac{\partial \delta f}{\partial \mathbf{k}} - \mathbf{v} \cdot \left[e \boldsymbol{\mathcal{E}} + \frac{\varepsilon - \mu}{T} \nabla T \right] \frac{\partial f^0}{\partial \varepsilon} = - \frac{\delta f}{\tau}, \quad (8.S.17)$$

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

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

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

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

$$\mathcal{J}_n^{\alpha\beta} \equiv \frac{1}{4\pi^3 \hbar} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu)^n \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_{\varepsilon} \frac{v^{\alpha} v^{\beta}}{|\mathbf{v}|}. \quad (8.S.18)$$

These results entail

$$\mathbf{\mathcal{E}} = \rho \mathbf{j} + Q \nabla T, \quad \mathbf{j}_q = \Pi \mathbf{j} - \kappa \nabla T, \quad (8.S.19)$$

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

$$\rho = \frac{1}{e^2} \mathcal{J}_0^{-1}, \quad Q = -\frac{1}{eT} \mathcal{J}_0^{-1} \mathcal{J}_1, \quad \Pi = -\frac{1}{e} \mathcal{J}_1 \mathcal{J}_0^{-1}, \quad \kappa = \frac{1}{T} (\mathcal{J}_2 - \mathcal{J}_1 \mathcal{J}_0^{-1} \mathcal{J}_1). \quad (8.S.20)$$

These results describe the following physical phenomena:

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

($\nabla T = \mathbf{B} = 0$): An electrical current \mathbf{j} will generate a heat current $\mathbf{j}_q = \Pi \mathbf{j}$, where Π 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 $\mathbf{\mathcal{E}} = Q \nabla T$, where Q is the *Seebeck coefficient*.

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

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

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

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

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

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

($j_x = j_y = \mathcal{E}_y = 0$): 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

$$p(t) = p(0) e^{-\gamma t} + \frac{F}{\gamma} (1 - e^{-\gamma t}) + \int_0^t ds \eta(s) e^{\gamma(s-t)}. \quad (8.S.21)$$

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

$$\langle \eta(s) \eta(s') \rangle = \phi(s - s') \approx \Gamma \delta(s - s'), \quad (8.S.22)$$

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, $\langle \frac{p^2}{2m} \rangle = \frac{1}{2} k_B T$. 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

$$\langle x^2(t) \rangle - \langle x(t) \rangle^2 = \frac{2k_B T t}{\gamma m} \equiv 2Dt, \quad (8.S.23)$$

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

$$\delta x(t) \equiv x(t + \delta t) - x(t). \quad (8.S.24)$$

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*,

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x} [F_1(x) P(x, t)] + \frac{1}{2} \frac{\partial^2}{\partial x^2} [F_2(x) P(x, t)]. \quad (8.S.25)$$

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 $P_t = \frac{\partial P}{\partial t}$, $P_{xx} = \frac{\partial^2 P}{\partial x^2}$. 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

$$K(\Delta x, \Delta t) = (4\pi D \Delta t)^{-1/2} e^{-(\Delta x)^2 / 4D \Delta t} \quad (8.S.26)$$

is the *diffusion kernel*. Thus, $\sqrt{\langle \Delta x^2 \rangle} = \sqrt{2D \Delta t}$.

Endnotes

- Indeed, any arbitrary function of \mathbf{p} alone would be a solution. Ultimately, we require some energy exchanging processes, such as collisions, in order for any initial nonequilibrium distribution to converge to the Boltzmann distribution.
- Recall from classical mechanics the definition of the *Poisson bracket*, $\{A, B\} = \frac{\partial A}{\partial \mathbf{r}} \cdot \frac{\partial B}{\partial \mathbf{p}} - \frac{\partial B}{\partial \mathbf{r}} \cdot \frac{\partial A}{\partial \mathbf{p}}$. Then from Hamilton's equations $\dot{\mathbf{r}} = \frac{\partial H}{\partial \mathbf{p}}$ and $\dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{r}}$, where $H(\mathbf{p}, \mathbf{r}, t)$ is the Hamiltonian, we have $\frac{dA}{dt} = \{A, H\}$. Invariants have zero Poisson bracket with the Hamiltonian.
- See Lifshitz and Pitaevskii, *Physical Kinetics*, §2.
- The function $g(x) = x \ln x - x + 1$ satisfies $g'(x) = \ln x$, hence $g'(x) < 0$ on the interval $x \in [0, 1]$ and $g'(x) > 0$ on $x \in (1, \infty]$. Thus, $g(x)$ monotonically decreases from $g(0) = 1$ to $g(1) = 0$, and then monotonically increases to $g(\infty) = \infty$, never becoming negative.
- In the chapter on thermodynamics, we adopted a slightly different definition of c_p as the heat capacity per mole. In this chapter c_p is the heat capacity per particle.
- Here we abbreviate QDC for 'quick and dirty calculation' and BRT for 'Boltzmann equation in the relaxation time approximation'.
- The difference is trivial, since $\mathbf{p} = m\mathbf{v}$.
- See the excellent discussion in the book by Krapivsky, Redner, and Ben-Naim, cited in §8.1.
- The requirements of an inner product $\langle f|g \rangle$ are symmetry, linearity, and non-negative definiteness.
- We neglect interband scattering here, which can be important in practical applications, but which is beyond the scope of these notes.
- The transition rate from $|\mathbf{k}'\rangle$ to $|\mathbf{k}\rangle$ is proportional to the matrix element and to the product $f'(1 - f)$. The reverse process is proportional to $f(1 - f')$. Subtracting these factors, one obtains $f' - f$, and therefore the nonlinear terms felicitously cancel in Equation [qobc].
- In this section we use \mathbf{j} to denote electrical current, rather than particle number current as before.
- To create a refrigerator, stick the cold junction inside a thermally insulated box and the hot junction outside the box.
- Note that it is $\mathbf{E} \cdot \mathbf{j}$ and not $\boldsymbol{\mathcal{E}} \cdot \mathbf{j}$ which is the source term in the energy continuity equation.
- Remember that physically the fixed quantities are temperature and total carrier number density (or charge density, in the case of electron and hole bands), and not temperature and chemical potential. An equation of state relating n , μ , and T is then inverted to obtain $\mu(n, T)$, so that all results ultimately may be expressed in terms of n and T .
- The cgs unit of viscosity is the *Poise* (P). $1 \text{ P} = 1 \text{ g/cm}\cdot\text{s}$.
- We further demand $\beta_{n=0} = 0$ and $P_{-1}(t) = 0$ at all times.
- A discussion of measure for functional integrals is found in R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals*.
- In this section, we use the notation $\hat{\chi}(\omega)$ for the susceptibility, rather than $\hat{G}(\omega)$.

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