Contents

Chapter 8

Nonequilibrium Phenomena

8.1 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* (3$^{\rm rd}$ edition, North-Holland, 2007)
This is a very readable and useful text. A relaxed but meaty presentation.

8.2   Equilibrium, Nonequilibrium and Local Equilibrium

Classical equilibrium statistical mechanics is described by the full N-body distribution,

$$f^0(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N; \boldsymbol{p}_1, \ldots, \boldsymbol{p}_N) = \begin{cases} Z_N^{-1} \cdot \frac{1}{N!}\, e^{-\beta \hat{H}_N(\boldsymbol{p}, \boldsymbol{x})} & \text{OCE} \\[2mm] \Xi^{-1} \cdot \frac{1}{N!}\, e^{\beta \mu N} e^{-\beta \hat{H}_N(\boldsymbol{p}, \boldsymbol{x})} & \text{GCE}\,. \end{cases} \tag{8.1}$$

We assume a Hamiltonian of the form

$$\hat{H}_N = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i=1}^{N} v(\boldsymbol{x}_i) + \sum_{i<j}^{N} u(\boldsymbol{x}_i - \boldsymbol{x}_j), \tag{8.2}$$

typically with $v = 0$, *i.e.* only two-body interactions. The quantity

$$f^0(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N; \boldsymbol{p}_1, \ldots, \boldsymbol{p}_N) \frac{d^d x_1\, d^d p_1}{h^d} \cdots \frac{d^d x_N\, d^d p_N}{h^d} \tag{8.3}$$

is the probability, under equilibrium conditions, of finding N particles in the system, with particle #1 lying within $d^3 x_1$ of $\boldsymbol{x}_1$ and having momentum within $d^d p_1$ of $\boldsymbol{p}_1$, *etc.* The temperature T and chemical potential μ are constants, independent of position. Note that $f(\{\boldsymbol{x}_i\}, \{\boldsymbol{p}_i\})$ is dimensionless.

Nonequilibrium statistical mechanics seeks to describe thermodynamic systems which are out of equilibrium, meaning that the distribution function is not given by the Boltzmann distribution above. For a general nonequilibrium setting, it is hopeless to make progress – we'd have to integrate the equations of motion for all the constituent particles. However, typically we are concerned with situations where external forces or constraints are imposed over some macroscopic scale. Examples would include the imposition of a voltage drop across a metal, or a temperature differential across any thermodynamic sample. In such cases, scattering at microscopic length and time scales described by the *mean free path* ℓ and the *collision time* τ work to establish *local equilibrium* throughout the system. A local equilibrium is a state described by a space and time varying temperature $T(\boldsymbol{r}, t)$ and chemical potential $\mu(\boldsymbol{r}, t)$. As we will see, the Boltzmann distribution with $T = T(\boldsymbol{r}, t)$ and $\mu = \mu(\boldsymbol{r}, t)$ will not be a solution to the evolution equation governing the distribution function. Rather, the distribution for systems slightly out of equilibrium will be of the form $f = f^0 + \delta f$, where f^0 describes a state of local equilibrium.

We will mainly be interested in the one-body distribution

$$f(\boldsymbol{r}, \boldsymbol{p}; t) = \sum_{i=1}^{N} \left\langle \delta\big(\boldsymbol{x}_i(t) - \boldsymbol{r}\big)\, \delta(\boldsymbol{p}_i(t) - \boldsymbol{p}) \right\rangle$$
$$= N \int \prod_{i=2}^{N} d^d x_i\, d^d p_i\, f(\boldsymbol{r}, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N; \boldsymbol{p}, \boldsymbol{p}_2, \ldots, \boldsymbol{p}_N; t)\,. \tag{8.4}$$

In this chapter, we will drop the $1/\hbar$ normalization for phase space integration. Thus, $f(\boldsymbol{r}, \boldsymbol{p}, t)$ has dimensions of h^{-d}, and $f(\boldsymbol{r}, \boldsymbol{p}, t)\, d^3 r\, d^3 p$ is the average number of particles found within $d^3 r$ of $\boldsymbol{r}$ and $d^3 p$ of $\boldsymbol{p}$ at time t.

In the GCE, we sum the RHS above over N. Assuming $v = 0$ so that there is no one-body potential to break translational symmetry, the equilibrium distribution is time-independent and space-independent:

$$f^0(\boldsymbol{r}, \boldsymbol{p}) = n\, (2\pi m k_{\mathrm{B}} T)^{-3/2}\, e^{-\boldsymbol{p}^2/2m k_{\mathrm{B}} T}\,, \tag{8.5}$$

where $n = N/V$ or $n = n(T, \mu)$ is the particle density in the OCE or GCE. From the one-body distribution we can

compute things like the particle current, $\boldsymbol{j}$, and the energy current, $\boldsymbol{j}_\varepsilon$:

$$\boldsymbol{j}(\boldsymbol{r},t) = \int d^d p \, f(\boldsymbol{r},\boldsymbol{p};t) \, \frac{\boldsymbol{p}}{m} \tag{8.6}$$

$$\boldsymbol{j}_\varepsilon(\boldsymbol{r},t) = \int d^d p \, f(\boldsymbol{r},\boldsymbol{p};t) \, \varepsilon(\boldsymbol{p}) \, \frac{\boldsymbol{p}}{m} \ , \tag{8.7}$$

where $\varepsilon(\boldsymbol{p}) = \boldsymbol{p}^2/2m$. Clearly these currents both vanish in equilibrium, when $f = f^0$, since $f^0(\boldsymbol{r},\boldsymbol{p})$ depends only on $\boldsymbol{p}^2$ and not on the direction of $\boldsymbol{p}$. In a *steady state* nonequilibrium situation, the above quantities are time-independent.

Thermodynamics says that

$$dq = T \, ds = d\varepsilon - \mu \, dn \ , \tag{8.8}$$

where s, ε, and n are entropy density, energy density, and particle density, respectively, and dq is the differential heat density. This relation may be case as one among the corresponding current densities:

$$\boldsymbol{j}_q = T\boldsymbol{j}_s = \boldsymbol{j}_\varepsilon - \mu \, \boldsymbol{j} \ . \tag{8.9}$$

Thus, in a system with no particle flow, $\boldsymbol{j} = 0$ and the *heat current* $\boldsymbol{j}_q$ is the same as the energy current $\boldsymbol{j}_\varepsilon$.

When the individual particles are not point particles, they possess angular momentum as well as linear momentum. Following Lifshitz and Pitaevskii, we abbreviate $\Gamma = (\boldsymbol{p},\boldsymbol{L})$ for these two variables for the case of diatomic molecules, and $\Gamma = (\boldsymbol{p},\boldsymbol{L},\hat{\boldsymbol{n}} \cdot \boldsymbol{L})$ in the case of spherical top molecules, where $\hat{\boldsymbol{n}}$ is the symmetry axis of the top. We then have, in $d = 3$ dimensions,

$$d\Gamma = \begin{cases} d^3 p & \text{point particles} \\ d^3 p \, L \, dL \, d\Omega_L & \text{diatomic molecules} \\ d^3 p \, L^2 \, dL \, d\Omega_L \, d\cos\vartheta & \text{symmetric tops} \ , \end{cases} \tag{8.10}$$

where $\vartheta = \cos^{-1}(\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{L}})$. We will call the set Γ the 'kinematic variables'. The instantaneous number density at $\boldsymbol{r}$ is then

$$n(\boldsymbol{r},t) = \int d\Gamma \, f(\boldsymbol{r},\Gamma;t) \ . \tag{8.11}$$

One might ask why we do not also keep track of the angular orientation of the individual molecules. There are two reasons. First, the rotations of the molecules are generally extremely rapid, so we are justified in averaging over these motions. Second, the orientation of, say, a rotor does not enter into its energy. While the same can be said of the spatial position in the absence of external fields, (i) in the presence of external fields one must keep track of the position coordinate $\boldsymbol{r}$ since there is physical transport of particles from one region of space to another, and (iii) the collision process, which as we shall see enters the dynamics of the distribution function, takes place in real space.

8.3 Boltzmann Transport Theory

8.3.1 Derivation of the Boltzmann equation

For simplicity of presentation, we assume point particles. Recall that

$$f(\boldsymbol{r},\boldsymbol{p},t) \, d^3 r \, d^3 p \equiv \begin{cases} \text{\# of particles with positions within } d^3 r \text{ of} \\ \boldsymbol{r} \text{ and momenta within } d^3 p \text{ of } \boldsymbol{p} \text{ at time } t. \end{cases} \tag{8.12}$$

We now ask how the distribution functions $f(\boldsymbol{r}, \boldsymbol{p}, t)$ evolves in time. It is clear that in the absence of collisions, the distribution function must satisfy the continuity equation,

$$\frac{\partial f}{\partial t} + \boldsymbol{\nabla} \cdot (\boldsymbol{u} f) = 0 \ . \tag{8.13}$$

This is just the condition of number conservation for particles. Take care to note that $\boldsymbol{\nabla}$ and $\boldsymbol{u}$ are *six*-dimensional *phase space* vectors:

$$\boldsymbol{u} = (\ \dot{x}\ ,\ \dot{y}\ ,\ \dot{z}\ ,\ \dot{p}_x\ ,\ \dot{p}_y\ ,\ \dot{p}_z\ ) \tag{8.14}$$

$$\boldsymbol{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}, \frac{\partial}{\partial p_x}, \frac{\partial}{\partial p_y}, \frac{\partial}{\partial p_z} \right) \ . \tag{8.15}$$

The continuity equation describes a distribution in which each constituent particle evolves according to a pre-scribed dynamics, which for a mechanical system is specified by

$$\frac{d\boldsymbol{r}}{dt} = \frac{\partial H}{\partial \boldsymbol{p}} = \boldsymbol{v}(\boldsymbol{p}) \qquad , \qquad \frac{d\boldsymbol{p}}{dt} = -\frac{\partial H}{\partial \boldsymbol{r}} = \boldsymbol{F}_{\text{ext}} \ , \tag{8.16}$$

where $\boldsymbol{F}$ is an external applied force. Here,

$$H(\boldsymbol{p}, \boldsymbol{r}) = \varepsilon(\boldsymbol{p}) + U_{\text{ext}}(\boldsymbol{r}) \ . \tag{8.17}$$

For example, if the particles are under the influence of gravity, then $U_{\text{ext}}(\boldsymbol{r}) = m\boldsymbol{g} \cdot \boldsymbol{r}$ and $\boldsymbol{F} = -\boldsymbol{\nabla} U_{\text{ext}} = -m\boldsymbol{g}$.

Note that as a consequence of the dynamics, we have $\boldsymbol{\nabla} \cdot \boldsymbol{u} = 0$, *i.e.* phase space flow is *incompressible*, provided that $\varepsilon(\boldsymbol{p})$ is a function of $\boldsymbol{p}$ alone, and not of $\boldsymbol{r}$. Thus, in the absence of collisions, we have

$$\frac{\partial f}{\partial t} + \boldsymbol{u} \cdot \boldsymbol{\nabla} f = 0 \ . \tag{8.18}$$

The differential operator $D_t \equiv \partial_t + \boldsymbol{u} \cdot \boldsymbol{\nabla}$ is sometimes called the 'convective derivative', because $D_t f$ is the time derivative of f in a comoving frame of reference.

Next we must consider the effect of collisions, which are not accounted for by the semiclassical dynamics. In a collision process, a particle with momentum $\boldsymbol{p}$ and one with momentum $\tilde{\boldsymbol{p}}$ can instantaneously convert into a pair with momenta $\boldsymbol{p}'$ and $\tilde{\boldsymbol{p}}'$, provided total momentum is conserved: $\boldsymbol{p} + \tilde{\boldsymbol{p}} = \boldsymbol{p}' + \tilde{\boldsymbol{p}}'$. This means that $D_t f \neq 0$. Rather, we should write

$$\frac{\partial f}{\partial t} + \dot{\boldsymbol{r}} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \dot{\boldsymbol{p}} \cdot \frac{\partial f}{\partial \boldsymbol{p}} = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} \tag{8.19}$$

where the right side is known as the *collision integral*. The collision integral is in general a *function* of $\boldsymbol{r}$, $\boldsymbol{p}$, and t and a *functional* of the distribution f.

After a trivial rearrangement of terms, we can write the Boltzmann equation as

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t} \right)_{\text{str}} + \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} \ , \tag{8.20}$$

where

$$\left(\frac{\partial f}{\partial t} \right)_{\text{str}} \equiv -\dot{\boldsymbol{r}} \cdot \frac{\partial f}{\partial \boldsymbol{r}} - \dot{\boldsymbol{p}} \cdot \frac{\partial f}{\partial \boldsymbol{p}} \tag{8.21}$$

is known as the *streaming term*. Thus, there are two contributions to $\partial f / \partial t$: streaming and collisions.

8.3.2 Collisionless Boltzmann equation

In the absence of collisions, the Boltzmann equation is given by

$$\frac{\partial f}{\partial t} + \frac{\partial \varepsilon}{\partial \boldsymbol{p}} \cdot \frac{\partial f}{\partial \boldsymbol{r}} - \boldsymbol{\nabla} U_{\text{ext}} \cdot \frac{\partial f}{\partial \boldsymbol{p}} = 0 \ . \tag{8.22}$$

In order to gain some intuition about how the streaming term affects the evolution of the distribution $f(\boldsymbol{r}, \boldsymbol{p}, t)$, consider a case where $\boldsymbol{F}_{\text{ext}} = 0$. We then have

$$\frac{\partial f}{\partial t} + \frac{\boldsymbol{p}}{m} \cdot \frac{\partial f}{\partial \boldsymbol{r}} = 0 \ . \tag{8.23}$$

Clearly, then, *any* function of the form

$$f(\boldsymbol{r}, \boldsymbol{p}, t) = \varphi\big(\boldsymbol{r} - \boldsymbol{v}(\boldsymbol{p}) \, t \, , \, \boldsymbol{p}\big) \tag{8.24}$$

will be a solution to the collisionless Boltzmann equation, where $\boldsymbol{v}(\boldsymbol{p}) = \frac{\partial \varepsilon}{\partial \boldsymbol{p}}$. One possible solution would be the Boltzmann distribution,

$$f(\boldsymbol{r}, \boldsymbol{p}, t) = e^{\mu/k_{\text{B}}T} e^{-\boldsymbol{p}^2/2mk_{\text{B}}T} \ , \tag{8.25}$$

which is time-independent[1]. Here we have assumed a ballistic dispersion, $\varepsilon(\boldsymbol{p}) = \boldsymbol{p}^2/2m$.

For a slightly less trivial example, let the initial distribution be $\varphi(\boldsymbol{r}, \boldsymbol{p}) = A \, e^{-\boldsymbol{r}^2/2\sigma^2} e^{-\boldsymbol{p}^2/2\kappa^2}$, so that

$$f(\boldsymbol{r}, \boldsymbol{p}, t) = A \, e^{-\left(\boldsymbol{r} - \frac{\boldsymbol{p}t}{m}\right)^2/2\sigma^2} \, e^{-\boldsymbol{p}^2/2\kappa^2} \ . \tag{8.26}$$

Consider the one-dimensional version, and rescale position, momentum, and time so that

$$f(x, p, t) = A \, e^{-\frac{1}{2}(\bar{x} - \bar{p}\,\bar{t})^2} \, e^{-\frac{1}{2}\bar{p}^2} \ . \tag{8.27}$$

Consider the level sets of f, where $f(x, p, t) = A \, e^{-\frac{1}{2}\alpha^2}$. The equation for these sets is

$$\bar{x} = \bar{p}\,\bar{t} \pm \sqrt{\alpha^2 - \bar{p}^2} \ . \tag{8.28}$$

For fixed $\bar{t}$, these level sets describe the loci in phase space of equal probability densities, with the probability density decreasing exponentially in the parameter α^2. For $\bar{t} = 0$, the initial distribution describes a Gaussian cloud of particles with a Gaussian momentum distribution. As $\bar{t}$ increases, the distribution widens in $\bar{x}$ but not in $\bar{p}$ – each particle moves with a constant momentum, so the set of momentum values never changes. However, the level sets in the $(\bar{x}, \bar{p})$ plane become elliptical, with a semimajor axis oriented at an angle $\theta = \text{ctn}^{-1}(t)$ with respect to the $\bar{x}$ axis. For $\bar{t} > 0$, he particles at the outer edges of the cloud are more likely to be moving away from the center. See the sketches in fig. 8.1

Suppose we add in a constant external force $\boldsymbol{F}_{\text{ext}}$. Then it is easy to show (and left as an exercise to the reader to prove) that any function of the form

$$f(\boldsymbol{r}, \boldsymbol{p}, t) = A \, \varphi\left(\boldsymbol{r} - \frac{\boldsymbol{p}\,t}{m} + \frac{\boldsymbol{F}_{\text{ext}}t^2}{2m} \, , \, \boldsymbol{p} - \frac{\boldsymbol{F}_{\text{ext}}t}{m}\right) \tag{8.29}$$

satisfies the collisionless Boltzmann equation (ballistic dispersion assumed).

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[1]Indeed, any arbitrary function of $\boldsymbol{p}$ 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.
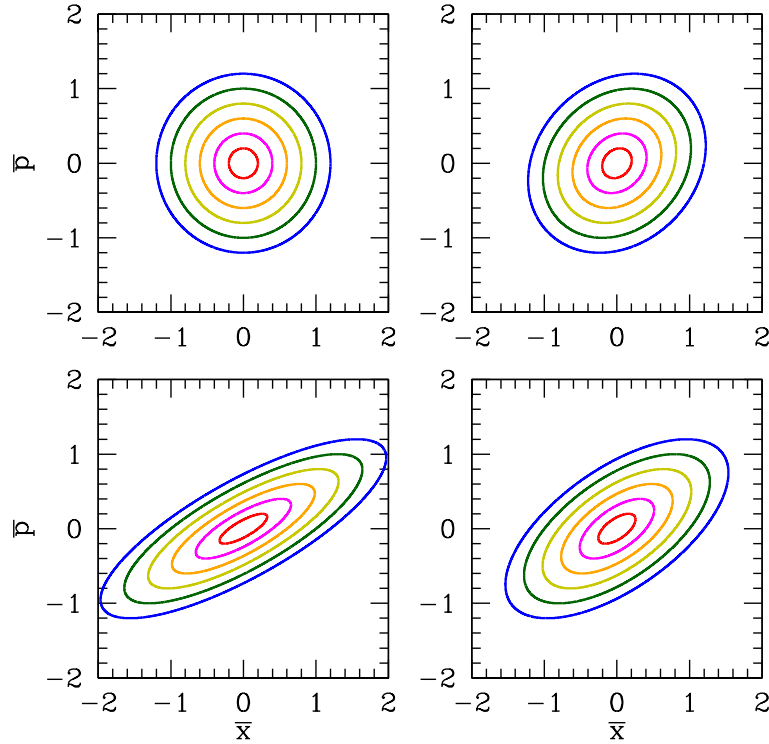
Figure 8.1: Level sets for a sample $f(\bar{x}, \bar{p}, \bar{t}) = A\,e^{-\frac{1}{2}(\bar{x}-\bar{p}\bar{t})^2}\,e^{-\frac{1}{2}\bar{p}^2}$, for values $f = A\,e^{-\frac{1}{2}\alpha^2}$ with α in equally spaced intervals from $\alpha = 0.2$ (red) to $\alpha = 1.2$ (blue). The time variable $\bar{t}$ is taken to be $\bar{t} = 0.0$ (upper left), 0.2 (upper right), 0.8 (lower right), and 1.3 (lower left).

8.3.3   Collisional invariants

Consider a function $A(\boldsymbol{r}, \boldsymbol{p})$ of position and momentum. Its average value at time t is

$$A(t) = \int d^3r\, d^3p\, A(\boldsymbol{r}, \boldsymbol{p})\, f(\boldsymbol{r}, \boldsymbol{p}, t)\,. \tag{8.30}$$

Taking the time derivative,

$$
\begin{aligned}
\frac{dA}{dt} &= \int d^3r\, d^3p\, A(\boldsymbol{r}, \boldsymbol{p})\, \frac{\partial f}{\partial t} \\
&= \int d^3r\, d^3p\, A(\boldsymbol{r}, \boldsymbol{p}) \left\{ -\frac{\partial}{\partial \boldsymbol{r}} \cdot (\dot{\boldsymbol{r}} f) - \frac{\partial}{\partial \boldsymbol{p}} \cdot (\dot{\boldsymbol{p}} f) + \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \right\} \\
&= \int d^3r\, d^3p \left\{ \left(\frac{\partial A}{\partial \boldsymbol{r}} \cdot \frac{d\boldsymbol{r}}{dt} + \frac{\partial A}{\partial \boldsymbol{p}} \cdot \frac{d\boldsymbol{p}}{dt} \right) f + A(\boldsymbol{r}, \boldsymbol{p}) \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \right\}\,.
\end{aligned}
\tag{8.31}
$$

Hence, if A is preserved by the dynamics between collisions, then[2]

$$\frac{dA}{dt} = \frac{\partial A}{\partial \boldsymbol{r}} \cdot \frac{d\boldsymbol{r}}{dt} + \frac{\partial A}{\partial \boldsymbol{p}} \cdot \frac{d\boldsymbol{p}}{dt} = 0\,. \tag{8.32}$$

---

[2] Recall from classical mechanics the definition of the *Poisson bracket*, $\{A, B\} = \frac{\partial A}{\partial \boldsymbol{r}} \cdot \frac{\partial B}{\partial \boldsymbol{p}} - \frac{\partial B}{\partial \boldsymbol{r}} \cdot \frac{\partial A}{\partial \boldsymbol{p}}$. Then from Hamilton's equations $\dot{\boldsymbol{r}} = \frac{\partial H}{\partial \boldsymbol{p}}$ and $\dot{\boldsymbol{p}} = -\frac{\partial H}{\partial \boldsymbol{r}}$, where $H(\boldsymbol{p}, \boldsymbol{r}, t)$ is the Hamiltonian, we have $\frac{dA}{dt} = \{A, H\}$. Invariants have zero Poisson bracket with the Hamiltonian.

We therefore have that the rate of change of A is determined wholly by the collision integral

$$\frac{dA}{dt} = \int d^3r\, d^3p\, A(\boldsymbol{r}, \boldsymbol{p}) \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} . \tag{8.33}$$

Quantities which are then conserved in the collisions satisfy $\dot{A} = 0$. Such quantities are called *collisional invariants*. Examples of collisional invariants include the particle number ($A = 1$), the components of the total momentum ($A = p_\mu$) (in the absence of broken translational invariance, due *e.g.* to the presence of walls), and the total energy ($A = \varepsilon(\boldsymbol{p})$).

8.3.4   Scattering processes

What sort of processes contribute to the collision integral? There are two broad classes to consider. The first involves potential scattering, where a particle in state $|\Gamma\rangle$ scatters, in the presence of an external potential, to a state $|\Gamma'\rangle$. Recall that Γ is an abbreviation for the set of kinematic variables, *e.g.* $\Gamma = (\boldsymbol{p}, \boldsymbol{L})$ in the case of a diatomic molecule. For point particles, $\Gamma = (p_x, p_y, p_z)$ and $d\Gamma = d^3p$.

We now define the function $w(\Gamma'|\Gamma)$ such that

$$w(\Gamma'|\Gamma)\, f(\boldsymbol{r}, \Gamma; t)\, d\Gamma\, d\Gamma' = \begin{cases} \text{rate at which a particle within } d\Gamma \text{ of } (\boldsymbol{r}, \Gamma) \\ \text{scatters to within } d\Gamma' \text{ of } (\boldsymbol{r}, \Gamma') \text{ at time } t. \end{cases} \tag{8.34}$$

The units of $w\, d\Gamma$ are therefore $1/T$. The differential scattering cross section for particle scattering is then

$$d\sigma = \frac{w(\Gamma'|\Gamma)}{n\, |\boldsymbol{v}|}\, d\Gamma' , \tag{8.35}$$

where $\boldsymbol{v} = \boldsymbol{p}/m$ is the particle's velocity and n the density.

The second class is that of two-particle scattering processes, *i.e.* $|\Gamma\Gamma_1\rangle \rightarrow |\Gamma'\Gamma_1'\rangle$. We define the scattering function $w(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1)$ by

$$w(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1)\, f_2(\boldsymbol{r}, \Gamma; \boldsymbol{r}, \Gamma_1; t)\, d\Gamma\, d\Gamma_1\, d\Gamma'\, d\Gamma_1' = \begin{cases} \text{rate at which two particles within } d\Gamma \text{ of } (\boldsymbol{r}, \Gamma) \\ \text{and within } d\Gamma_1 \text{ of } (\boldsymbol{r}, \Gamma_1) \text{ scatter into states within} \\ d\Gamma' \text{ of } (\boldsymbol{r}, \Gamma') \text{ and } d\Gamma_1' \text{ of } (\boldsymbol{r}, \Gamma_1') \text{ at time } t , \end{cases} \tag{8.36}$$

where

$$f_2(\boldsymbol{r}, \boldsymbol{p}; \boldsymbol{r}', \boldsymbol{p}'; t) = \Big\langle \sum_{i,j} \delta\big(\boldsymbol{x}_i(t) - \boldsymbol{r}\big)\, \delta(\boldsymbol{p}_i(t) - \boldsymbol{p})\, \delta\big(\boldsymbol{x}_j(t) - \boldsymbol{r}'\big)\, \delta(\boldsymbol{p}_j(t) - \boldsymbol{p}') \Big\rangle \tag{8.37}$$

is the nonequilibrium two-particle distribution for point particles. The differential scattering cross section is

$$d\sigma = \frac{w(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1)}{|\boldsymbol{v} - \boldsymbol{v}_1|}\, d\Gamma'\, d\Gamma_1' . \tag{8.38}$$

We assume, in both cases, that any scattering occurs *locally*, *i.e.* the particles attain their asymptotic kinematic states on distance scales small compared to the mean interparticle separation. In this case we can treat each scattering process independently. This assumption is particular to rarefied systems, *i.e.* gases, and is not appropriate for dense liquids. The two types of scattering processes are depicted in fig. 8.2.
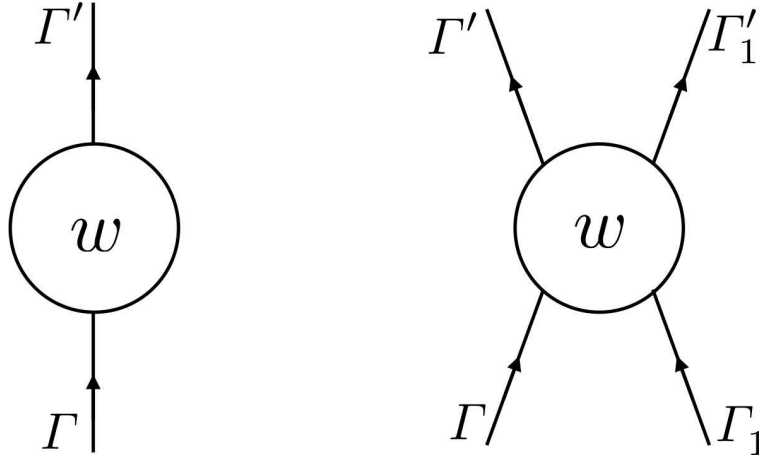
Figure 8.2: Left: single particle scattering process $|\Gamma\rangle \rightarrow |\Gamma'\rangle$. Right: two-particle scattering process $|\Gamma\Gamma_1\rangle \rightarrow |\Gamma'\Gamma_1'\rangle$.

In computing the collision integral for the state $|r, \Gamma\rangle$, we must take care to sum over contributions from transitions *out of* this state, *i.e.* $|\Gamma\rangle \rightarrow |\Gamma'\rangle$, which reduce $f(r, \Gamma)$, and transitions *into* this state, *i.e.* $|\Gamma'\rangle \rightarrow |\Gamma\rangle$, which increase $f(r, \Gamma)$. Thus, for one-body scattering, we have

$$\frac{D}{Dt}\, f(r, \Gamma; t) = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = \int d\Gamma' \left\{ w(\Gamma \,|\, \Gamma')\, f(r, \Gamma'; t) - w(\Gamma' \,|\, \Gamma)\, f(r, \Gamma; t) \right\} . \tag{8.39}$$

For two-body scattering, we have

$$\begin{aligned}
\frac{D}{Dt}\, f(r, \Gamma; t) &= \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \\
&= \int d\Gamma_1 \!\int d\Gamma' \!\int d\Gamma_1' \left\{ w(\Gamma\Gamma_1 \,|\, \Gamma'\Gamma_1')\, f_2(r, \Gamma'; r, \Gamma_1'; t) \right. \\
&\qquad\qquad\qquad\qquad\qquad \left. - w(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1)\, f_2(r, \Gamma; r, \Gamma_1; t) \right\} .
\end{aligned} \tag{8.40}$$

Unlike the one-body scattering case, the kinetic equation for two-body scattering does not close, since the LHS involves the one-body distribution $f \equiv f_1$ and the RHS involves the two-body distribution f_2. To close the equations, we make the *approximation*

$$f_2(r, \Gamma'; \tilde{r}, \tilde{\Gamma}; t) \approx f(r, \Gamma; t)\, f(\tilde{r}, \tilde{\Gamma}; t) . \tag{8.41}$$

We then have

$$\begin{aligned}
\frac{D}{Dt}\, f(r, \Gamma; t) = \int d\Gamma_1 \!\int d\Gamma' \!\int d\Gamma_1' \left\{ w(\Gamma\Gamma_1 \,|\, \Gamma'\Gamma_1')\, f(r, \Gamma'; t)\, f(r, \Gamma_1'; t) \right. \\
\left. - w(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1)\, f(r, \Gamma; t)\, f(r, \Gamma_1; t) \right\} .
\end{aligned} \tag{8.42}$$

8.3.5   Detailed balance

Classical mechanics places some restrictions on the form of the kernel $w(\Gamma\Gamma_1 \,|\, \Gamma'\Gamma_1')$. In particular, if $\Gamma^T = (-p, -L)$ denotes the kinematic variables under time reversal, then

$$w(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1) = w(\Gamma^T\Gamma_1^T \,|\, \Gamma'^T\Gamma_1'^T) . \tag{8.43}$$

This is because the time reverse of the process $|\Gamma\Gamma_1\rangle \to |\Gamma'\Gamma_1'\rangle$ is $|\Gamma'^{\mathsf{T}}\Gamma_1'^{\mathsf{T}}\rangle \to |\Gamma^{\mathsf{T}}\Gamma_1^{\mathsf{T}}\rangle$.

In equilibrium, we must have

$$w\big(\Gamma'\Gamma_1'\,|\,\Gamma\Gamma_1\big)\,f^0(\Gamma)\,f^0(\Gamma_1)\,d^4\Gamma = w\big(\Gamma^{\mathsf{T}}\Gamma_1^{\mathsf{T}}\,|\,\Gamma'^{\mathsf{T}}\Gamma_1'^{\mathsf{T}}\big)\,f^0(\Gamma'^{\mathsf{T}})\,f^0(\Gamma_1'^{\mathsf{T}})\,d^4\Gamma^{\mathsf{T}} \tag{8.44}$$

where

$$d^4\Gamma \equiv d\Gamma\,d\Gamma_1\,d\Gamma'd\Gamma_1' \quad , \qquad d^4\Gamma^{\mathsf{T}} \equiv d\Gamma^{\mathsf{T}}\,d\Gamma_1^{\mathsf{T}}\,d\Gamma'^{\mathsf{T}}d\Gamma_1'^{\mathsf{T}}\;. \tag{8.45}$$

Since $d\Gamma = d\Gamma^{\mathsf{T}}$ etc., we may cancel the differentials above, and after invoking eqn. 8.43 and suppressing the common r label, we find

$$f^0(\Gamma)\,f^0(\Gamma_1) = f^0(\Gamma'^{\mathsf{T}})\,f^0(\Gamma_1'^{\mathsf{T}})\;. \tag{8.46}$$

This is the condition of *detailed balance*. For the Boltzmann distribution, we have

$$f^0(\Gamma) = A\,e^{-\varepsilon/k_{\mathrm{B}}T}\;, \tag{8.47}$$

where A is a constant and where $\varepsilon = \varepsilon(\Gamma)$ is the kinetic energy, *e.g.* $\varepsilon(\Gamma) = p^2/2m$ in the case of point particles. Note that $\varepsilon(\Gamma^{\mathsf{T}}) = \varepsilon(\Gamma)$. Detailed balance is satisfied because the kinematics of the collision requires energy conservation:

$$\varepsilon + \varepsilon_1 = \varepsilon' + \varepsilon_1'\;. \tag{8.48}$$

Since momentum is also kinematically conserved, *i.e.*

$$p + p_1 = p' + p_1'\;, \tag{8.49}$$

any distribution of the form

$$f^0(\Gamma) = A\,e^{-(\varepsilon - p\cdot V)/k_{\mathrm{B}}T} \tag{8.50}$$

also satisfies detailed balance, for any velocity parameter V. This distribution is appropriate for gases which are flowing with average particle V.

In addition to time-reversal, parity is also a symmetry of the microscopic mechanical laws. Under the parity operation P, we have $r \to -r$ and $p \to -p$. Note that a pseudovector such as $L = r \times p$ is unchanged under P. Thus, $\Gamma^P = (-p, L)$. Under the combined operation of $C = PT$, we have $\Gamma^C = (p, -L)$. If the microscopic Hamiltonian is invariant under C, then we must have

$$w\big(\Gamma'\Gamma_1'\,|\,\Gamma\Gamma_1\big) = w\big(\Gamma^C\Gamma_1^C\,|\,\Gamma'^C\Gamma_1'^C\big)\;. \tag{8.51}$$

For point particles, invariance under T and P then means

$$w(p',p_1'\,|\,p,p_1) = w(p,p_1\,|\,p',p_1')\;, \tag{8.52}$$

and therefore the collision integral takes the simplified form,

$$\begin{aligned}
\frac{Df(p)}{Dt} &= \left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}} \\
&= \int\! d^3p_1\!\int\! d^3p'\!\int\! d^3p_1'\,w(p',p_1'\,|\,p,p_1)\,\big\{f(p')\,f(p_1') - f(p)\,f(p_1)\big\}\;,
\end{aligned} \tag{8.53}$$

where we have suppressed both r and t variables.

The most general statement of detailed balance is

$$\frac{f^0(\Gamma')\,f^0(\Gamma_1')}{f^0(\Gamma)\,f^0(\Gamma_1)} = \frac{w\big(\Gamma'\Gamma_1'\,|\,\Gamma\Gamma_1\big)}{w\big(\Gamma\Gamma_1\,|\,\Gamma'\Gamma_1'\big)}\;. \tag{8.54}$$

Under this condition, the collision term vanishes for $f = f^0$, which is the equilibrium distribution.

8.3.6 Kinematics and cross section

We can rewrite eqn. 8.53 in the form

$$\frac{Df(\boldsymbol{p})}{Dt} = \int d^3p_1 \int d\Omega \, |\boldsymbol{v} - \boldsymbol{v}_1| \, \frac{\partial \sigma}{\partial \Omega} \left\{ f(\boldsymbol{p}') \, f(\boldsymbol{p}_1') - f(\boldsymbol{p}) \, f(\boldsymbol{p}_1) \right\} , \tag{8.55}$$

where $\frac{\partial \sigma}{\partial \Omega}$ is the *differential scattering cross section*. If we recast the scattering problem in terms of center-of-mass and relative coordinates, we conclude that the total momentum is conserved by the collision, and furthermore that the energy in the CM frame is conserved, which means that the magnitude of the *relative* momentum is conserved. Thus, we may write $\boldsymbol{p}' - \boldsymbol{p}_1' = |\boldsymbol{p} - \boldsymbol{p}_1| \, \hat{\boldsymbol{\Omega}}$, where $\hat{\boldsymbol{\Omega}}$ is a unit vector. Then $\boldsymbol{p}'$ and $\boldsymbol{p}_1'$ are determined to be

$$\boldsymbol{p}' = \tfrac{1}{2}\big(\boldsymbol{p} + \boldsymbol{p}_1 + |\boldsymbol{p} - \boldsymbol{p}_1| \, \hat{\boldsymbol{\Omega}}\big)$$
$$\boldsymbol{p}_1' = \tfrac{1}{2}\big(\boldsymbol{p} + \boldsymbol{p}_1 - |\boldsymbol{p} - \boldsymbol{p}_1| \, \hat{\boldsymbol{\Omega}}\big) . \tag{8.56}$$

8.3.7 H-theorem

Let's consider the Boltzmann equation with two particle collisions. We define the local (*i.e.* $\boldsymbol{r}$-dependent) quantity

$$\rho_\varphi(\boldsymbol{r}, t) \equiv \int d\Gamma \, \varphi(\Gamma, f) \, f(\Gamma, \boldsymbol{r}, t) . \tag{8.57}$$

At this point, $\varphi(\Gamma, f)$ is arbitrary. Note that the $\varphi(\Gamma, f)$ factor has $\boldsymbol{r}$ and t dependence through its dependence on f, which itself is a function of $\boldsymbol{r}$, Γ, and t. We now compute

$$\begin{aligned}
\frac{\partial \rho_\varphi}{\partial t} &= \int d\Gamma \, \frac{\partial(\varphi f)}{\partial t} = \int d\Gamma \, \frac{\partial(\varphi f)}{\partial f} \, \frac{\partial f}{\partial t} \\
&= -\int d\Gamma \, \boldsymbol{u} \cdot \boldsymbol{\nabla}(\varphi f) - \int d\Gamma \, \frac{\partial(\varphi f)}{\partial f} \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \\
&= -\oint d\Sigma \, \hat{\boldsymbol{n}} \cdot (\boldsymbol{u} \, \varphi f) - \int d\Gamma \, \frac{\partial(\varphi f)}{\partial f} \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} .
\end{aligned} \tag{8.58}$$

The first term on the last line follows from the divergence theorem, and vanishes if we assume $f = 0$ for infinite values of the kinematic variables, which is the only physical possibility. Thus, the rate of change of ρ_φ is entirely due to the collision term. Thus,

$$\begin{aligned}
\frac{\partial \rho_\varphi}{\partial t} &= \int d\Gamma \int d\Gamma_1 \int d\Gamma' \int d\Gamma_1' \left\{ w(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1) \, f f_1 \, \chi - w(\Gamma\Gamma_1 \,|\, \Gamma'\Gamma_1') \, f' f_1' \, \chi \right\} \\
&= \int d\Gamma \int d\Gamma_1 \int d\Gamma' \int d\Gamma_1' \, w(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1) \, f f_1 \, (\chi - \chi') ,
\end{aligned} \tag{8.59}$$

where $f \equiv f(\Gamma)$, $f' \equiv f(\Gamma')$, $f_1 \equiv f(\Gamma_1)$, $f_1' \equiv f(\Gamma_1')$, $\chi = \chi(\Gamma)$, with

$$\chi = \frac{\partial(\varphi f)}{\partial f} = \varphi + f \, \frac{\partial \varphi}{\partial f} . \tag{8.60}$$

We now invoke the symmetry

$$w(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1) = w(\Gamma_1'\Gamma' \,|\, \Gamma_1\Gamma) , \tag{8.61}$$

which allows us to write

$$\frac{\partial \rho_\varphi}{\partial t} = \tfrac{1}{2} \int d\Gamma \int d\Gamma_1 \int d\Gamma' \int d\Gamma_1' \, w(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1) \, f f_1 \, (\chi + \chi_1 - \chi' - \chi_1') . \tag{8.62}$$

This shows that ρ_φ is preserved by the collision term if $\chi(\Gamma)$ is a collisional invariant.

Now let us consider $\varphi(f) = \ln f$. We define $\mathsf{h} \equiv \rho\big|_{\varphi = \ln f}$. We then have

$$\frac{\partial \mathsf{h}}{\partial t} = -\tfrac{1}{2} \int d\Gamma \int d\Gamma_1 \int d\Gamma' \int d\Gamma_1' \, w \, f' f_1' \cdot x \ln x \,, \tag{8.63}$$

where $w \equiv w(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1)$ and $x \equiv f f_1 / f' f_1'$. We next invoke the result

$$\int d\Gamma' \int d\Gamma_1' \, w(\Gamma'\Gamma_1' \,|\, \Gamma\Gamma_1) = \int d\Gamma' \int d\Gamma_1' \, w(\Gamma\Gamma_1 \,|\, \Gamma'\Gamma_1') \tag{8.64}$$

which is a statement of unitarity of the scattering matrix[3]. Multiplying both sides by $f(\Gamma) \, f(\Gamma_1)$, then integrating over Γ and Γ_1, and finally changing variables $(\Gamma, \Gamma_1) \leftrightarrow (\Gamma', \Gamma_1')$, we find

$$0 = \int d\Gamma \int d\Gamma_1 \int d\Gamma' \int d\Gamma_1' \, w \, (f f_1 - f' f_1') = \int d\Gamma \int d\Gamma_1 \int d\Gamma' \int d\Gamma_1' \, w \, f' f_1' \, (x - 1) \,. \tag{8.65}$$

Multiplying this result by $\tfrac{1}{2}$ and adding it to the previous equation for $\dot{\mathsf{h}}$, we arrive at our final result,

$$\frac{\partial \mathsf{h}}{\partial t} = -\tfrac{1}{2} \int d\Gamma \int d\Gamma_1 \int d\Gamma' \int d\Gamma_1' \, w \, f' f_1' \, (x \ln x - x + 1) \,. \tag{8.66}$$

Note that w, f', and f_1' are all nonnegative. It is then easy to prove that the function $g(x) = x \ln x - x + 1$ is nonnegative for all positive x values[4], which therefore entails the important result

$$\frac{\partial \mathsf{h}(\boldsymbol{r}, t)}{\partial t} \leq 0 \,. \tag{8.67}$$

Boltzmann's H function is the space integral of the h density: $\mathsf{H} = \int d^3 r \, \mathsf{h}$.

Thus, everywhere in space, the function $\mathsf{h}(\boldsymbol{r}, t)$ is monotonically decreasing or constant, due to collisions. In equilibrium, $\dot{\mathsf{h}} = 0$ everywhere, which requires $x = 1$, *i.e.*

$$f^0(\Gamma) \, f^0(\Gamma_1) = f^0(\Gamma') \, f^0(\Gamma_1') \,, \tag{8.68}$$

or, taking the logarithm,

$$\ln f^0(\Gamma) + \ln f^0(\Gamma_1) = \ln f^0(\Gamma') + \ln f^0(\Gamma_1') \,. \tag{8.69}$$

But this means that $\ln f^0$ is itself a collisional invariant, and if 1, $\boldsymbol{p}$, and ε are the only collisional invariants, then $\ln f^0$ must be expressible in terms of them. Thus,

$$\ln f^0 = \frac{\mu}{k_{\mathrm{B}} T} + \frac{\boldsymbol{V} \cdot \boldsymbol{p}}{k_{\mathrm{B}} T} - \frac{\varepsilon}{k_{\mathrm{B}} T} \,, \tag{8.70}$$

where μ, $\boldsymbol{V}$, and T are constants which parameterize the equilibrium distribution $f^0(\boldsymbol{p})$, corresponding to the chemical potential, flow velocity, and temperature, respectively.

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[3]See Lifshitz and Pitaevskii, *Physical Kinetics*, §2.

[4]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.

8.4   Weakly Inhomogeneous Gas

Consider a gas which is only weakly out of equilibrium. We follow the treatment in Lifshitz and Pitaevskii, §6. As the gas is only slightly out of equilibrium, we seek a solution to the Boltzmann equation of the form $f = f^0 + \delta f$, where f^0 is describes a local equilibrium. Recall that such a distribution function is annihilated by the collision term in the Boltzmann equation but not by the streaming term, hence a correction δf must be added in order to obtain a solution.

The most general form of local equilibrium is described by the distribution

$$f^0(\boldsymbol{r}, \Gamma) = C \exp\left(\frac{\mu - \varepsilon(\Gamma) + \boldsymbol{V} \cdot \boldsymbol{p}}{k_{\mathrm{B}} T}\right) , \tag{8.71}$$

where $\mu = \mu(\boldsymbol{r}, t)$, $T = T(\boldsymbol{r}, t)$, and $\boldsymbol{V} = \boldsymbol{V}(\boldsymbol{r}, t)$ vary in both space and time. Note that

$$\begin{aligned}
df^0 &= \left(d\mu + \boldsymbol{p} \cdot d\boldsymbol{V} + (\varepsilon - \mu - \boldsymbol{V} \cdot \boldsymbol{p})\frac{dT}{T} - d\varepsilon\right)\left(-\frac{\partial f^0}{\partial \varepsilon}\right) \\
&= \left(\frac{1}{n}\, dp + \boldsymbol{p} \cdot d\boldsymbol{V} + (\varepsilon - h)\frac{dT}{T} - d\varepsilon\right)\left(-\frac{\partial f^0}{\partial \varepsilon}\right)
\end{aligned} \tag{8.72}$$

where we have assumed $\boldsymbol{V} = 0$ on average, and used

$$\begin{aligned}
d\mu &= \left(\frac{\partial \mu}{\partial T}\right)_p dT + \left(\frac{\partial \mu}{\partial p}\right)_T dp \\
&= -s\, dT + \frac{1}{n}\, dp ,
\end{aligned} \tag{8.73}$$

where s is the entropy per particle and n is the number density. We have further written $h = \mu + Ts$, which is the enthalpy per particle. Here, c_p is the heat capacity per particle at constant pressure[5]. Finally, note that when f^0 is the Maxwell-Boltzmann distribution, we have

$$-\frac{\partial f^0}{\partial \varepsilon} = \frac{f^0}{k_{\mathrm{B}} T} . \tag{8.74}$$

The Boltzmann equation is written

$$\left(\frac{\partial}{\partial t} + \frac{\boldsymbol{p}}{m} \cdot \frac{\partial}{\partial \boldsymbol{r}} + \boldsymbol{F} \cdot \frac{\partial}{\partial \boldsymbol{p}}\right)(f^0 + \delta f) = \left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}} . \tag{8.75}$$

The RHS of this equation must be of order δf because the local equilibrium distribution f^0 is annihilated by the collision integral. We therefore wish to evaluate one of the contributions to the LHS of this equation,

$$\begin{aligned}
\frac{\partial f^0}{\partial t} + \frac{\boldsymbol{p}}{m} \cdot \frac{\partial f^0}{\partial \boldsymbol{r}} + \boldsymbol{F} \cdot \frac{\partial f^0}{\partial \boldsymbol{p}} = \left(-\frac{\partial f^0}{\partial \varepsilon}\right)\Bigg\{&\frac{1}{n}\frac{\partial p}{\partial t} + \frac{\varepsilon - h}{T}\frac{\partial T}{\partial t} + m\boldsymbol{v}\cdot\Big[(\boldsymbol{v}\cdot\boldsymbol{\nabla})\,\boldsymbol{V}\Big] \\
&+ \boldsymbol{v}\cdot\left(m\frac{\partial \boldsymbol{V}}{\partial t} + \frac{1}{n}\boldsymbol{\nabla}p\right) + \frac{\varepsilon - h}{T}\,\boldsymbol{v}\cdot\boldsymbol{\nabla}T - \boldsymbol{F}\cdot\boldsymbol{v}\Bigg\} .
\end{aligned} \tag{8.76}$$

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[5]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.

To simplify this, first note that Newton's laws applied to an ideal fluid give $\rho \dot{\boldsymbol{V}} = -\boldsymbol{\nabla} p$, where $\rho = mn$ is the mass density. Corrections to this result, *e.g.* viscosity and nonlinearity in $\boldsymbol{V}$, are of higher order.

Next, continuity for particle number means $\dot{n} + \boldsymbol{\nabla} \cdot (n\boldsymbol{V}) = 0$. We assume $\boldsymbol{V}$ is zero on average and that all derivatives are small, hence $\boldsymbol{\nabla} \cdot (n\boldsymbol{V}) = \boldsymbol{V} \cdot \boldsymbol{\nabla} n + n \boldsymbol{\nabla} \cdot \boldsymbol{V} \approx n \boldsymbol{\nabla} \cdot \boldsymbol{V}$. Thus,

$$\frac{\partial \ln n}{\partial t} = \frac{\partial \ln p}{\partial t} - \frac{\partial \ln T}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{V} \, , \tag{8.77}$$

where we have invoked the ideal gas law $n = p/k_{\mathrm{B}} T$ above.

Next, we invoke conservation of entropy. If s is the entropy per particle, then ns is the entropy per unit volume, in which case we have the continuity equation

$$\frac{\partial (ns)}{\partial t} + \boldsymbol{\nabla} \cdot (ns\boldsymbol{V}) = n \left(\frac{\partial s}{\partial t} + \boldsymbol{V} \cdot \boldsymbol{\nabla} s \right) + s \left(\frac{\partial n}{\partial t} + \boldsymbol{\nabla} \cdot (n\boldsymbol{V}) \right) = 0 \, . \tag{8.78}$$

The second bracketed term on the RHS vanishes because of particle continuity, leaving us with $\dot{s} + \boldsymbol{V} \cdot \boldsymbol{\nabla} s \approx \dot{s} = 0$ (since $\boldsymbol{V} = 0$ on average, and any gradient is first order in smallness). Now thermodynamics says

$$\begin{aligned} ds &= \left(\frac{\partial s}{\partial T} \right)_p dT + \left(\frac{\partial s}{\partial p} \right)_T dp \\ &= \frac{c_p}{T} dT - \frac{k_{\mathrm{B}}}{p} dp \, , \end{aligned} \tag{8.79}$$

since $T \left(\frac{\partial s}{\partial T} \right)_p = c_p$ and $\left(\frac{\partial s}{\partial p} \right)_T = \left(\frac{\partial v}{\partial T} \right)_{p'}$ where $v = V/N$. Thus,

$$\frac{c_p}{k_{\mathrm{B}}} \frac{\partial \ln T}{\partial t} - \frac{\partial \ln p}{\partial t} = 0 \, . \tag{8.80}$$

We now have in eqns. 8.77 and 8.80 two equations in the two unknowns $\frac{\partial \ln T}{\partial t}$ and $\frac{\partial \ln p}{\partial t}$, yielding

$$\frac{\partial \ln T}{\partial t} = -\frac{k_{\mathrm{B}}}{c_V} \boldsymbol{\nabla} \cdot \boldsymbol{V} \tag{8.81}$$

$$\frac{\partial \ln p}{\partial t} = -\frac{c_p}{c_V} \boldsymbol{\nabla} \cdot \boldsymbol{V} \, . \tag{8.82}$$

Thus eqn. 8.76 becomes

$$\begin{aligned} \frac{\partial f^0}{\partial t} + \frac{\boldsymbol{p}}{m} \cdot \frac{\partial f^0}{\partial \boldsymbol{r}} + \boldsymbol{F} \cdot \frac{\partial f^0}{\partial \boldsymbol{p}} = \left(-\frac{\partial f^0}{\partial \varepsilon} \right) &\left\{ \frac{\varepsilon(\Gamma) - h}{T} \boldsymbol{v} \cdot \boldsymbol{\nabla} T + m \, v_\alpha v_\beta \, \mathcal{Q}_{\alpha\beta} \right. \\ &\left. + \frac{h - T c_p - \varepsilon(\Gamma)}{c_V/k_{\mathrm{B}}} \boldsymbol{\nabla} \cdot \boldsymbol{V} - \boldsymbol{F} \cdot \boldsymbol{v} \right\} \, , \end{aligned} \tag{8.83}$$

where

$$\mathcal{Q}_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial V_\alpha}{\partial x_\beta} + \frac{\partial V_\beta}{\partial x_\alpha} \right) \, . \tag{8.84}$$

Therefore, the Boltzmann equation takes the form

$$\left\{ \frac{\varepsilon(\Gamma) - h}{T} \boldsymbol{v} \cdot \boldsymbol{\nabla} T + m \, v_\alpha v_\beta \, \mathcal{Q}_{\alpha\beta} - \frac{\varepsilon(\Gamma) - h + T c_p}{c_V/k_{\mathrm{B}}} \boldsymbol{\nabla} \cdot \boldsymbol{V} - \boldsymbol{F} \cdot \boldsymbol{v} \right\} \frac{f^0}{k_{\mathrm{B}} T} + \frac{\partial \, \delta f}{\partial t} = \left(\frac{\partial f}{\partial t} \right)_{\mathrm{coll}} \, . \tag{8.85}$$

Notice we have dropped the terms $\boldsymbol{v} \cdot \frac{\partial\, \delta f}{\partial \boldsymbol{r}}$ and $\boldsymbol{F} \cdot \frac{\partial\, \delta f}{\partial \boldsymbol{p}}$, since δf must already be first order in smallness, and both the $\frac{\partial}{\partial \boldsymbol{r}}$ operator as well as $\boldsymbol{F}$ add a second order of smallness, which is negligible. Typically $\frac{\partial\, \delta f}{\partial t}$ is nonzero if the applied force $\boldsymbol{F}(t)$ is time-dependent. We use the convention of summing over repeated indices. Note that $\delta_{\alpha\beta}\, \mathcal{Q}_{\alpha\beta} = \mathcal{Q}_{\alpha\alpha} = \boldsymbol{\nabla}\cdot\boldsymbol{V}$. For ideal gases in which only translational and rotational degrees of freedom are excited, $h = c_{\mathrm{p}}T$.

8.5 Relaxation Time Approximation

8.5.1 Approximation of collision integral

We now consider a very simple model of the collision integral,

$$\left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}} = -\frac{f - f^0}{\tau} = -\frac{\delta f}{\tau} \ . \tag{8.86}$$

This model is known as the *relaxation time approximation*. Here, $f^0 = f^0(\boldsymbol{r}, \boldsymbol{p}, t)$ is a distribution function which describes a *local equilibrium* at each position $\boldsymbol{r}$ and time t. The quantity τ is the *relaxation time*, which can in principle be momentum-dependent, but which we shall first consider to be constant. In the absence of streaming terms, we have

$$\frac{\partial\, \delta f}{\partial t} = -\frac{\delta f}{\tau} \qquad \Longrightarrow \qquad \delta f(\boldsymbol{r}, \boldsymbol{p}, t) = \delta f(\boldsymbol{r}, \boldsymbol{p}, 0)\, e^{-t/\tau} \ . \tag{8.87}$$

The distribution f then relaxes to the equilibrium distribution f^0 on a time scale τ. We note that this approximation is obviously flawed in that all quantities – even the collisional invariants – relax to their equilibrium values on the scale τ. In the Appendix, we consider a model for the collision integral in which the collisional invariants are all preserved, but everything else relaxes to local equilibrium at a single rate.

8.5.2 Computation of the scattering time

Consider two particles with velocities $\boldsymbol{v}$ and $\boldsymbol{v}'$. The average of their relative *speed* is

$$\langle\, |\boldsymbol{v} - \boldsymbol{v}'|\, \rangle = \int\! d^3v \int\! d^3v'\; P(\boldsymbol{v})\, P(\boldsymbol{v}')\, |\boldsymbol{v} - \boldsymbol{v}'|\ , \tag{8.88}$$

where $P(\boldsymbol{v})$ is the Maxwell velocity distribution,

$$P(\boldsymbol{v}) = \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2} \exp\left(-\frac{m\boldsymbol{v}^2}{2k_{\mathrm{B}}T}\right) \ , \tag{8.89}$$

which follows from the Boltzmann form of the equilibrium distribution $f^0(\boldsymbol{p})$. It is left as an exercise for the student to verify that

$$\bar{v}_{\mathrm{rel}} \equiv \langle\, |\boldsymbol{v} - \boldsymbol{v}'|\, \rangle = \frac{4}{\sqrt{\pi}} \left(\frac{k_{\mathrm{B}}T}{m}\right)^{1/2} \ . \tag{8.90}$$

Note that $\bar{v}_{\mathrm{rel}} = \sqrt{2}\,\bar{v}$, where $\bar{v}$ is the average particle speed. Let σ be the total scattering cross section, which for hard spheres is $\sigma = \pi d^2$, where d is the hard sphere diameter. Then the rate at which particles scatter is

$$\frac{1}{\tau} = n\, \bar{v}_{\mathrm{rel}}\, \sigma \ . \tag{8.91}$$
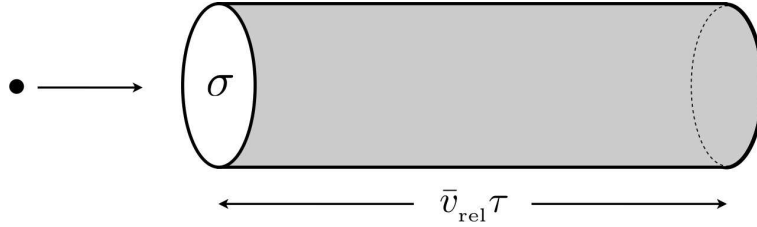
Figure 8.3: Graphic representation of the equation $n \, \sigma \, \bar{v}_{\mathrm{rel}} \, \tau = 1$, which yields the scattering time τ in terms of the number density n, average particle pair relative velocity $\bar{v}_{\mathrm{rel}}$, and two-particle total scattering cross section σ. The equation says that on average there must be one particle within the tube.

The particle *mean free path* is simply

$$\ell = \bar{v} \, \tau = \frac{1}{\sqrt{2} \, n \, \sigma} \; . \tag{8.92}$$

While the scattering length is not temperature-dependent within this formalism, the scattering time *is T-dependent*, with

$$\tau(T) = \frac{1}{n \, \bar{v}_{\mathrm{rel}} \, \sigma} = \frac{\sqrt{\pi}}{4 n \sigma} \left(\frac{m}{k_{\mathrm{B}} T} \right)^{1/2} \; . \tag{8.93}$$

As $T \to 0$, the collision time diverges as $\tau \propto T^{-1/2}$, because the particles on average move more slowly at lower temperatures. The mean free path, however, is independent of T, and is given by $\ell = 1/\sqrt{2} n \sigma$.

8.5.3 Thermal conductivity

We consider a system with a temperature gradient $\boldsymbol{\nabla} T$ and seek a steady state (*i.e.* time-independent) solution to the Boltzmann equation. We assume $F_{\alpha} = \mathcal{Q}_{\alpha\beta} = 0$. Appealing to eqn. 8.85, and using the relaxation time approximation for the collision integral, we have

$$\delta f = -\frac{\tau(\varepsilon - c_p \, T)}{k_{\mathrm{B}} T^2} \, (\boldsymbol{v} \cdot \boldsymbol{\nabla} T) \, f^0 \; . \tag{8.94}$$

We are now ready to compute the energy and particle currents. In order to compute the *local density* of any quantity $A(\boldsymbol{r}, \boldsymbol{p})$, we multiply by the distribution $f(\boldsymbol{r}, \boldsymbol{p})$ and integrate over momentum:

$$\rho_A(\boldsymbol{r}, t) = \int \! d^3\!p \, A(\boldsymbol{r}, \boldsymbol{p}) \, f(\boldsymbol{r}, \boldsymbol{p}, t) \; , \tag{8.95}$$

For the energy (thermal) current, we let $A = \varepsilon \, v_{\alpha} = \varepsilon \, p_{\alpha}/m$, in which case $\rho_A = j_{\alpha}$. Note that $\int \! d^3\!p \, \boldsymbol{p} \, f^0 = 0$ since f^0 is isotropic in $\boldsymbol{p}$ even when μ and T depend on $\boldsymbol{r}$. Thus, only δf enters into the calculation of the various currents. Thus, the energy (thermal) current is

$$\begin{aligned}
j_{\varepsilon}^{\alpha}(\boldsymbol{r}) &= \int \! d^3\!p \, \varepsilon \, v^{\alpha} \, \delta f \\
&= -\frac{n\tau}{k_{\mathrm{B}} T^2} \left\langle \, v^{\alpha} v^{\beta} \, \varepsilon \, (\varepsilon - c_p \, T) \, \right\rangle \frac{\partial T}{\partial x^{\beta}} \; ,
\end{aligned} \tag{8.96}$$

where the repeated index β is summed over, and where momentum averages are defined relative to the equilibrium distribution, *i.e.*

$$\langle \, \phi(\boldsymbol{p}) \, \rangle = \int \! d^3\!p \, \phi(\boldsymbol{p}) \, f^0(\boldsymbol{p}) \Big/ \int \! d^3\!p \, f^0(\boldsymbol{p}) = \int \! d^3\!v \, P(\boldsymbol{v}) \, \phi(m\boldsymbol{v}) \; . \tag{8.97}$$

In this context, it is useful to point out the identity

$$d^3p \, f^0(\boldsymbol{p}) = n \, d^3v \, P(\boldsymbol{v}) \ , \tag{8.98}$$

where

$$P(\boldsymbol{v}) = \left(\frac{m}{2\pi k_{\mathrm{B}}T} \right)^{3/2} e^{-m(\boldsymbol{v}-\boldsymbol{V})^2/2k_{\mathrm{B}}T} \tag{8.99}$$

is the Maxwell velocity distribution.

Note that if $\phi = \phi(\varepsilon)$ is a function of the energy, and if $\boldsymbol{V} = 0$, then

$$d^3p \, f^0(\boldsymbol{p}) = n \, d^3v \, P(\boldsymbol{v}) = n \, \widetilde{P}(\varepsilon) \, d\varepsilon \ , \tag{8.100}$$

where

$$\widetilde{P}(\varepsilon) = \tfrac{2}{\sqrt{\pi}} (k_{\mathrm{B}}T)^{-3/2} \, \varepsilon^{1/2} \, e^{-\varepsilon/k_{\mathrm{B}}T} \ , \tag{8.101}$$

is the Maxwellian distribution of single particle energies. This distribution is normalized with $\int\limits_0^\infty d\varepsilon \, \widetilde{P}(\varepsilon) = 1$. Averages with respect to this distribution are given by

$$\langle \, \phi(\varepsilon) \, \rangle = \int\limits_0^\infty d\varepsilon \, \phi(\varepsilon) \, \widetilde{P}(\varepsilon) = \tfrac{2}{\sqrt{\pi}} (k_{\mathrm{B}}T)^{-3/2} \int\limits_0^\infty d\varepsilon \, \varepsilon^{1/2} \, \phi(\varepsilon) \, e^{-\varepsilon/k_{\mathrm{B}}T} \ . \tag{8.102}$$

If $\phi(\varepsilon)$ is homogeneous, then for any α we have

$$\langle \, \varepsilon^\alpha \, \rangle = \tfrac{2}{\sqrt{\pi}} \Gamma\big(\alpha + \tfrac{3}{2} \big) (k_{\mathrm{B}}T)^\alpha \ . \tag{8.103}$$

Due to spatial isotropy, it is clear that we can replace

$$v^\alpha \, v^\beta \rightarrow \tfrac{1}{3} \boldsymbol{v}^2 \, \delta_{\alpha\beta} = \frac{2\varepsilon}{3m} \, \delta_{\alpha\beta} \tag{8.104}$$

in eqn. 8.96. We then have $\boldsymbol{j}_\varepsilon = -\kappa \, \boldsymbol{\nabla} T$, with

$$\kappa = \frac{2n\tau}{3mk_{\mathrm{B}}T^2} \, \langle \, \varepsilon^2 \big(\varepsilon - c_p \, T \big) \, \rangle = \frac{5n\tau k_{\mathrm{B}}^2 T}{2m} = \tfrac{\pi}{8} n\ell\bar{v} \, c_p \ , \tag{8.105}$$

where we have used $c_p = \tfrac{5}{2} k_{\mathrm{B}}$ and $\bar{v}^2 = \frac{8k_{\mathrm{B}}T}{\pi m}$. The quantity κ is called the *thermal conductivity*. Note that $\kappa \propto T^{1/2}$.

8.5.4   Viscosity

Consider the situation depicted in fig. 8.4. A fluid filling the space between two large flat plates at $z = 0$ and $z = d$ is set in motion by a force $\boldsymbol{F} = F\hat{\boldsymbol{x}}$ applied to the upper plate; the lower plate is fixed. It is assumed that the fluid's velocity locally matches that of the plates. Fluid particles at the top have an average x-component of their momentum $\langle p_x \rangle = mV$. As these particles move downward toward lower z values, they bring their x-momenta with them. Therefore there is a downward ($-\hat{\boldsymbol{z}}$-directed) flow of $\langle p_x \rangle$. Since x-momentum is constantly being drawn away from $z = d$ plane, this means that there is a $-\boldsymbol{x}$-directed *viscous drag* on the upper plate. The viscous drag force per unit area is given by $F_{\mathrm{drag}}/A = -\eta V/d$, where $V/d = \partial V_x/\partial z$ is the velocity gradient and η is the *shear viscosity*. In steady state, the applied force balances the drag force, *i.e.* $F + F_{\mathrm{drag}} = 0$. Clearly in the steady state the net momentum density of the fluid does not change, and is given by $\tfrac{1}{2}\rho V\hat{\boldsymbol{x}}$, where ρ is the fluid mass density. The momentum per unit time injected into the fluid by the upper plate at $z = d$ is then extracted by the
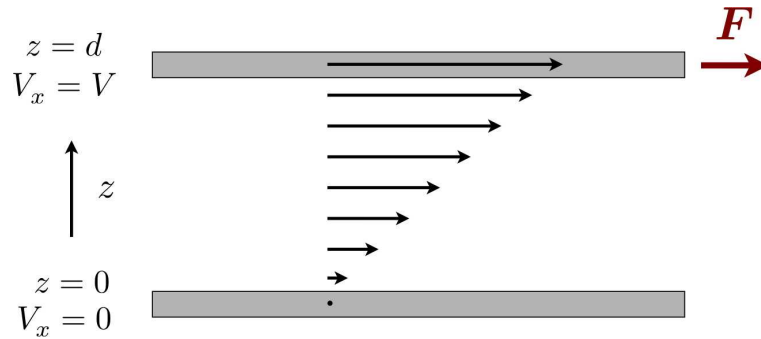
Figure 8.4: *Gedankenexperiment* to measure shear viscosity η in a fluid. The lower plate is fixed. The viscous drag force per unit area on the upper plate is $F_{\mathrm{drag}}/A = -\eta V/d$. This must be balanced by an applied force F.

lower plate at $z = 0$. The *momentum flux density* $\Pi_{xz} = n \langle p_x v_z \rangle$ is the drag force on the upper surface per unit area: $\Pi_{xz} = -\eta \frac{\partial V_x}{\partial z}$. The units of viscosity are $[\eta] = M/LT$.

We now provide some formal definitions of viscosity. As we shall see presently, there is in fact a second type of viscosity, called second viscosity or *bulk viscosity*, which is measurable although not by the type of experiment depicted in fig. 8.4.

The momentum flux tensor $\Pi_{\alpha\beta} = n \langle p_\alpha v_\beta \rangle$ is defined to be the current of momentum component p_α in the direction of increasing x_β. For a gas in motion with average velocity V, we have

$$
\begin{aligned}
\Pi_{\alpha\beta} &= nm \langle (V_\alpha + v'_\alpha)(V_\beta + v'_\beta) \rangle \\
&= nm\, V_\alpha V_\beta + nm \langle v'_\alpha v'_\beta \rangle \\
&= nm\, V_\alpha V_\beta + \tfrac{1}{3}nm \langle \boldsymbol{v'}^2 \rangle \delta_{\alpha\beta} \\
&= \rho\, V_\alpha V_\beta + p\, \delta_{\alpha\beta} \,,
\end{aligned}
\tag{8.106}
$$

where v' is the particle velocity in a frame moving with velocity V, and where we have invoked the ideal gas law $p = nk_{\mathrm{B}}T$. The mass density is $\rho = nm$.

When V is spatially varying,

$$
\Pi_{\alpha\beta} = p\, \delta_{\alpha\beta} + \rho\, V_\alpha V_\beta - \tilde{\sigma}_{\alpha\beta} \,,
\tag{8.107}
$$

where $\tilde{\sigma}_{\alpha\beta}$ is the *viscosity stress tensor*. Any symmetric tensor, such as $\tilde{\sigma}_{\alpha\beta}$, can be decomposed into a sum of (i) a traceless component, and (ii) a component proportional to the identity matrix. Since $\tilde{\sigma}_{\alpha\beta}$ should be, to first order, linear in the spatial derivatives of the components of the velocity field V, there is a unique two-parameter decomposition:

$$
\begin{aligned}
\tilde{\sigma}_{\alpha\beta} &= \eta \left(\frac{\partial V_\alpha}{\partial x_\beta} + \frac{\partial V_\beta}{\partial x_\alpha} - \tfrac{2}{3} \boldsymbol{\nabla}\!\cdot\!\boldsymbol{V}\, \delta_{\alpha\beta} \right) + \zeta\, \boldsymbol{\nabla}\!\cdot\!\boldsymbol{V}\, \delta_{\alpha\beta} \\
&= 2\eta \left(\mathcal{Q}_{\alpha\beta} - \tfrac{1}{3} \mathsf{Tr}\,(\mathcal{Q})\, \delta_{\alpha\beta} \right) + \zeta\, \mathsf{Tr}\,(\mathcal{Q})\, \delta_{\alpha\beta} \,.
\end{aligned}
\tag{8.108}
$$

The coefficient of the traceless component is η, known as the *shear viscosity*. The coefficient of the component proportional to the identity is ζ, known as the *bulk viscosity*. The full stress tensor $\sigma_{\alpha\beta}$ contains a contribution from the pressure:

$$
\sigma_{\alpha\beta} = -p\, \delta_{\alpha\beta} + \tilde{\sigma}_{\alpha\beta} \,.
\tag{8.109}
$$

The differential force dF_α that a fluid exerts on on a surface element $\hat{n}\, dA$ is
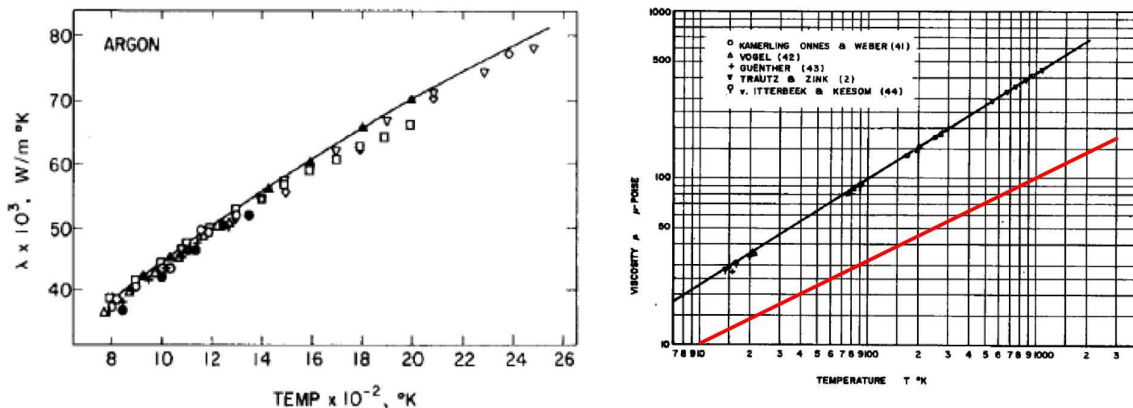
$$
dF_\alpha = -\sigma_{\alpha\beta}\, n_\beta\, dA \,,
\tag{8.110}
$$

Figure 8.5: Left: thermal conductivity (λ in figure) of Ar between $T = 800\,\text{K}$ and $T = 2600\,\text{K}$. The best fit to a single power law $\lambda = aT^b$ results in $b = 0.651$. Source: G. S. Springer and E. W. Wingeier, *J. Chem Phys.* **59**, 1747 (1972). Right: log-log plot of shear viscosity (μ in figure) of He between $T \approx 15\,\text{K}$ and $T \approx 1000\,\text{K}$. The red line has slope $\frac{1}{2}$. The slope of the data is approximately 0.633. Source: J. Kestin and W. Leidenfrost, *Physica* **25**, 537 (1959).

where we are using the Einstein summation convention and summing over the repeated index β. We will now compute the shear viscosity η using the Boltzmann equation in the relaxation time approximation.

Appealing again to eqn. 8.85, with $\boldsymbol{F} = 0$ and $h = c_p T$, we find

$$\delta f = -\frac{\tau}{k_{\text{B}}T}\left\{m\,v_\alpha v_\beta\,\mathcal{Q}_{\alpha\beta} + \frac{\varepsilon - c_p\,T}{T}\,\boldsymbol{v}\cdot\boldsymbol{\nabla}T - \frac{\varepsilon}{c_V/k_{\text{B}}}\,\boldsymbol{\nabla}\!\cdot\!\boldsymbol{V}\right\} f^0\;. \tag{8.111}$$

We assume $\boldsymbol{\nabla}T = \boldsymbol{\nabla}\!\cdot\!\boldsymbol{V} = 0$, and we compute the momentum flux:

$$\begin{aligned}
\Pi_{xz} &= n\int\!d^3p\,p_x v_z\,\delta f \\[4pt]
&= -\frac{nm^2\tau}{k_{\text{B}}T}\,\mathcal{Q}_{\alpha\beta}\,\langle\,v_x\,v_z\,v_\alpha\,v_\beta\,\rangle \\[4pt]
&= -\frac{n\tau}{k_{\text{B}}T}\left(\frac{\partial V_x}{\partial z} + \frac{\partial V_z}{\partial x}\right)\langle\,mv_x^2\cdot mv_z^2\,\rangle \\[4pt]
&= -n\tau k_{\text{B}}T\left(\frac{\partial V_z}{\partial x} + \frac{\partial V_x}{\partial z}\right)\;.
\end{aligned} \tag{8.112}$$

Thus, if $V_x = V_x(z)$, we have

$$\Pi_{xz} = -n\tau k_{\text{B}}T\,\frac{\partial V_x}{\partial z} \tag{8.113}$$

from which we read off the viscosity,

$$\eta = nk_{\text{B}}T\tau = \tfrac{\pi}{8}nm\ell\bar{v}\;. \tag{8.114}$$

Note that $\eta(T) \propto T^{1/2}$.

How well do these predictions hold up? In fig. 8.5, we plot data for the thermal conductivity of argon and the shear viscosity of helium. Both show a clear sublinear behavior as a function of temperature, but the slope $d\ln\kappa/dT$ is approximately 0.65 and $d\ln\eta/dT$ is approximately 0.63. Clearly the simple model is not even getting the functional dependence on T right, let alone its coefficient. Still, our crude theory is at least qualitatively correct.

Why do both $\kappa(T)$ as well as $\eta(T)$ decrease at low temperatures? The reason is that the heat current which flows in response to ∇T as well as the momentum current which flows in response to $\partial V_x / \partial z$ are due to the presence of collisions, which result in momentum and energy transfer between particles. This is true even when total energy and momentum are conserved, which they are not in the relaxation time approximation. Intuitively, we might think that the viscosity should *increase* as the temperature is lowered, since common experience tells us that fluids 'gum up' as they get colder – think of honey as an extreme example. But of course honey is nothing like an ideal gas, and the physics behind the crystallization or glass transition which occurs in real fluids when they get sufficiently cold is completely absent from our approach. In our calculation, viscosity results from collisions, and with no collisions there is no momentum transfer and hence no viscosity. If, for example, the gas particles were to simply pass through each other, as though they were ghosts, then there would be no opposition to maintaining an arbitrary velocity gradient.

8.5.5 Oscillating external force

Suppose a uniform oscillating external force $\boldsymbol{F}_{\text{ext}}(t) = \boldsymbol{F}\,e^{-i\omega t}$ is applied. For a system of charged particles, this force would arise from an external electric field $\boldsymbol{F}_{\text{ext}} = q\boldsymbol{E}\,e^{-i\omega t}$, where q is the charge of each particle. We'll assume $\nabla T = 0$. The Boltzmann equation is then written

$$\frac{\partial f}{\partial t} + \frac{\boldsymbol{p}}{m} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \boldsymbol{F}e^{-i\omega t} \cdot \frac{\partial f}{\partial \boldsymbol{p}} = -\frac{f - f^0}{\tau}\;. \tag{8.115}$$

We again write $f = f^0 + \delta f$, and we assume δf is spatially constant. Thus,

$$\frac{\partial\,\delta f}{\partial t} + \boldsymbol{F}e^{-i\omega t} \cdot \boldsymbol{v}\,\frac{\partial f^0}{\partial \varepsilon} = -\frac{\delta f}{\tau}\;. \tag{8.116}$$

If we assume $\delta f(t) = \delta f(\omega)\,e^{-i\omega t}$ then the above differential equation is converted to an algebraic equation, with solution

$$\delta f(t) = -\frac{\tau\,e^{-i\omega t}}{1 - i\omega\tau}\,\frac{\partial f^0}{\partial \varepsilon}\,\boldsymbol{F} \cdot \boldsymbol{v}\;. \tag{8.117}$$

We now compute the particle current:

$$\begin{aligned}
j_\alpha(\boldsymbol{r}, t) &= \int d^3p\,\boldsymbol{v}\,\delta f \\[1mm]
&= \frac{\tau\,e^{-i\omega t}}{1 - i\omega\tau} \cdot \frac{F_\beta}{k_{\text{B}}T}\int d^3p\,f^0(\boldsymbol{p})\,v_\alpha\,v_\beta \\[1mm]
&= \frac{\tau\,e^{-i\omega t}}{1 - i\omega\tau} \cdot \frac{nF_\alpha}{3k_{\text{B}}T}\int d^3v\,P(\boldsymbol{v})\,\boldsymbol{v}^2 \\[1mm]
&= \frac{n\tau}{m} \cdot \frac{F_\alpha\,e^{-i\omega t}}{1 - i\omega\tau}\;.
\end{aligned} \tag{8.118}$$

If the particles are electrons, with charge $q = -e$, then the electrical current is $(-e)$ times the particle current. We then obtain

$$j_\alpha^{(\text{elec})}(t) = \frac{ne^2\tau}{m} \cdot \frac{E_\alpha\,e^{-i\omega t}}{1 - i\omega\tau} \equiv \sigma_{\alpha\beta}(\omega)\,E_\beta\,e^{-i\omega t}\;, \tag{8.119}$$

where

$$\sigma_{\alpha\beta}(\omega) = \frac{ne^2\tau}{m} \cdot \frac{1}{1 - i\omega\tau}\,\delta_{\alpha\beta} \tag{8.120}$$

is the frequency-dependent electrical conductivity tensor. Of course for fermions such as electrons, we should be using the Fermi distribution in place of the Maxwell-Boltzmann distribution for $f^0(\boldsymbol{p})$. This affects the relation between n and μ only, and the final result for the conductivity tensor $\sigma_{\alpha\beta}(\omega)$ is unchanged.

8.5.6 Quick and Dirty Treatment of Transport

Suppose we have some averaged intensive quantity ϕ which is spatially dependent through $T(\boldsymbol{r})$ or $\mu(\boldsymbol{r})$ or $\boldsymbol{V}(\boldsymbol{r})$. For simplicity we will write $\phi = \phi(z)$. We wish to compute the current of ϕ across some surface whose equation is $dz = 0$. If the mean free path is ℓ, then the value of ϕ for particles crossing this surface in the $+\hat{\boldsymbol{z}}$ direction is $\phi(z - \ell\cos\theta)$, where θ is the angle the particle's velocity makes with respect to $\hat{\boldsymbol{z}}$, *i.e.* $\cos\theta = v_z/v$. We perform the same analysis for particles moving in the $-\hat{\boldsymbol{z}}$ direction, for which $\phi = \phi(z + \ell\cos\theta)$. The current of ϕ through this surface is then

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

$$= -n\ell\, \frac{\partial\phi}{\partial z}\hat{\boldsymbol{z}} \int d^3v\, P(\boldsymbol{v})\, \frac{v_z^2}{v} = -\tfrac{1}{3}n\bar{v}\ell\, \frac{\partial\phi}{\partial z}\, \hat{\boldsymbol{z}} \;,$$

$$(8.121)$$

where $\bar{v} = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi m}}$ is the average particle speed. If the z-dependence of ϕ comes through the dependence of ϕ on the local temperature T, then we have

$$\boldsymbol{j}_\phi = -\tfrac{1}{3}\, n\ell\bar{v}\, \frac{\partial\phi}{\partial T}\, \boldsymbol{\nabla}T \equiv -K\,\boldsymbol{\nabla}T \;, \tag{8.122}$$

where

$$K = \tfrac{1}{3}n\ell\bar{v}\, \frac{\partial\phi}{\partial T} \tag{8.123}$$

is the transport coefficient. If $\phi = \langle\varepsilon\rangle$, then $\frac{\partial\phi}{\partial T} = c_p$, where c_p is the heat capacity per particle at constant pressure. We then find $\boldsymbol{j}_\varepsilon = -\kappa\,\boldsymbol{\nabla}T$ with thermal conductivity

$$\kappa = \tfrac{1}{3}n\ell\bar{v}\, c_p \;. \tag{8.124}$$

Our Boltzmann equation calculation yielded the same result, but with a prefactor of $\frac{\pi}{8}$ instead of $\frac{1}{3}$.

We can make a similar argument for the viscosity. In this case $\phi = \langle p_x\rangle$ is spatially varying through its dependence on the flow velocity $\boldsymbol{V}(\boldsymbol{r})$. Clearly $\partial\phi/\partial V_x = m$, hence

$$j_{p_x}^z = \Pi_{xz} = -\tfrac{1}{3}nm\ell\bar{v}\, \frac{\partial V_x}{\partial z} \;, \tag{8.125}$$

from which we identify the viscosity, $\eta = \tfrac{1}{3}nm\ell\bar{v}$. Once again, this agrees in its functional dependences with the Boltzmann equation calculation in the relaxation time approximation. Only the coefficients differ. The ratio of the coefficients is $K_{\mathrm{QDC}}/K_{\mathrm{BRT}} = \frac{8}{3\pi} = 0.849$ in both cases[6].

8.5.7 Thermal diffusivity, kinematic viscosity, and Prandtl number

Suppose, under conditions of constant pressure, we add heat q per unit volume to an ideal gas. We know from thermodynamics that its temperature will then increase by an amount $\Delta T = q/nc_p$. If a heat current $\boldsymbol{j}_q$ flows, then the continuity equation for energy flow requires

$$nc_p\, \frac{\partial T}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j}_q = 0 \;. \tag{8.126}$$

---

[6]Here we abbreviate QDC for *'quick and dirty calculation'* and BRT for *'Boltzmann equation in the relaxation time approximation'*.

Gas	$\eta\,(\mu\text{Pa}\cdot\text{s})$	$\kappa\,(\text{mW/m}\cdot\text{K})$	c_p/k_{B}	Pr
He	19.5	149	2.50	0.682
Ar	22.3	17.4	2.50	0.666
Xe	22.7	5.46	2.50	0.659
H_2	8.67	179	3.47	0.693
N_2	17.6	25.5	3.53	0.721
O_2	20.3	26.0	3.50	0.711
CH_4	11.2	33.5	4.29	0.74
CO_2	14.8	18.1	4.47	0.71
NH_3	10.1	24.6	4.50	0.90

Table 8.1: Viscosities, thermal conductivities, and Prandtl numbers for some common gases at $T = 293\,\text{K}$ and $p = 1\,\text{atm}$. (Source: Table 1.1 of Smith and Jensen, with data for triatomic gases added.)

In a system where there is no net particle current, the heat current $\boldsymbol{j}_q$ is the same as the energy current $\boldsymbol{j}_\varepsilon$, and since $\boldsymbol{j}_\varepsilon = -\kappa\,\boldsymbol{\nabla}T$, we obtain a diffusion equation for temperature,

$$\frac{\partial T}{\partial t} = \frac{\kappa}{nc_p}\nabla^2 T \;. \tag{8.127}$$

The combination

$$a \equiv \frac{\kappa}{nc_p} \tag{8.128}$$

is known as the *thermal diffusivity*. Our Boltzmann equation calculation in the relaxation time approximation yielded the result $\kappa = nk_{\text{B}}T\tau c_p/m$. Thus, we find $a = k_{\text{B}}T\tau/m$ via this method. Note that the dimensions of a are the same as for any diffusion constant D, namely $[a] = L^2/T$.

Another quantity with dimensions of L^2/T is the *kinematic viscosity*, $\nu = \eta/\rho$, where $\rho = nm$ is the mass density. We found $\eta = nk_{\text{B}}T\tau$ from the relaxation time approximation calculation, hence $\nu = k_{\text{B}}T\tau/m$. The ratio ν/a, called the *Prandtl number*, $\text{Pr} = \eta c_p/m\kappa$, is dimensionless. According to our calculations, $\text{Pr} = 1$. According to table 8.1, most monatomic gases have $\text{Pr} \approx \frac{2}{3}$.

8.6 Diffusion and the Lorentz model

8.6.1 Failure of the relaxation time approximation

As we remarked above, the relaxation time approximation fails to conserve any of the collisional invariants. It is therefore unsuitable for describing hydrodynamic phenomena such as diffusion. To see this, let $f(\boldsymbol{r}, \boldsymbol{v}, t)$ be the distribution function, here written in terms of position, velocity, and time rather than position, momentum, and time as befor[7]. In the absence of external forces, the Boltzmann equation in the relaxation time approximation is

$$\frac{\partial f}{\partial t} + \boldsymbol{v}\cdot\frac{\partial f}{\partial \boldsymbol{r}} = -\frac{f - f^0}{\tau} \;. \tag{8.129}$$

The density of particles in velocity space is given by

$$\tilde{n}(\boldsymbol{v}, t) = \int d^3r\, f(\boldsymbol{r}, \boldsymbol{v}, t) \;. \tag{8.130}$$

---

[7]The difference is trivial, since $\boldsymbol{p} = m\boldsymbol{v}$.

In equilibrium, this is the Maxwell distribution times the total number of particles: $\tilde{n}_0(\boldsymbol{v}) = N P_{\mathrm{M}}(\boldsymbol{v})$. The number of particles as a function of time, $N(t) = \int d^3 v \, \tilde{n}(\boldsymbol{v}, t)$, should be a constant.

Integrating the Boltzmann equation one has

$$\frac{\partial \tilde{n}}{\partial t} = -\frac{\tilde{n} - \tilde{n}_0}{\tau} \ . \tag{8.131}$$

Thus, with $\delta\tilde{n}(\boldsymbol{v}, t) = \tilde{n}(\boldsymbol{v}, t) - \tilde{n}_0(\boldsymbol{v})$, we have

$$\delta\tilde{n}(\boldsymbol{v}, t) = \delta\tilde{n}(\boldsymbol{v}, 0) \, e^{-t/\tau} \ . \tag{8.132}$$

Thus, $\tilde{n}(\boldsymbol{v}, t)$ decays exponentially to zero with time constant τ, from which it follows that the total particle number exponentially relaxes to N_0. This is physically incorrect; local density perturbations can't just *vanish*. Rather, they *diffuse*.

8.6.2   Modified Boltzmann equation and its solution

To remedy this unphysical aspect, consider the modified Boltzmann equation,

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} = \frac{1}{\tau}\left[-f + \int \frac{d\hat{\boldsymbol{v}}}{4\pi} \, f \right] \equiv \frac{1}{\tau}(\mathbb{P} - 1)f \ , \tag{8.133}$$

where $\mathbb{P}$ is a projector onto a space of isotropic functions of $\boldsymbol{v}$: $\mathbb{P} F = \int \frac{d\hat{\boldsymbol{v}}}{4\pi} F(\boldsymbol{v})$ for any function $F(\boldsymbol{v})$. Note that $\mathbb{P} F$ is a function of the speed $v = |\boldsymbol{v}|$. For this modified equation, known as the *Lorentz model*, one finds $\partial_t \tilde{n} = 0$.

The model in eqn. 8.133 is known as the *Lorentz model*[8]. To solve it, we consider the Laplace transform,

$$\hat{f}(\boldsymbol{k}, \boldsymbol{v}, s) = \int\limits_0^\infty dt \, e^{-st} \int d^3 r \, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \, f(\boldsymbol{r}, \boldsymbol{v}, t) \ . \tag{8.134}$$

Taking the Laplace transform of eqn. 8.133, we find

$$\left(s + i\boldsymbol{v} \cdot \boldsymbol{k} + \tau^{-1} \right) \hat{f}(\boldsymbol{k}, \boldsymbol{v}, s) = \tau^{-1} \, \mathbb{P} \, \hat{f}(\boldsymbol{k}, \boldsymbol{v}, s) + f(\boldsymbol{k}, \boldsymbol{v}, t = 0) \ . \tag{8.135}$$

We now solve for $\mathbb{P} \, \hat{f}(\boldsymbol{k}, \boldsymbol{v}, s)$:

$$\hat{f}(\boldsymbol{k}, \boldsymbol{v}, s) = \frac{\tau^{-1}}{s + i\boldsymbol{v} \cdot \boldsymbol{k} + \tau^{-1}} \, \mathbb{P} \, \hat{f}(\boldsymbol{k}, \boldsymbol{v}, s) + \frac{f(\boldsymbol{k}, \boldsymbol{v}, t = 0)}{s + i\boldsymbol{v} \cdot \boldsymbol{k} + \tau^{-1}} \ , \tag{8.136}$$

which entails

$$\mathbb{P} \, \hat{f}(\boldsymbol{k}, \boldsymbol{v}, s) = \left[\int \frac{d\hat{\boldsymbol{v}}}{4\pi} \frac{\tau^{-1}}{s + i\boldsymbol{v} \cdot \boldsymbol{k} + \tau^{-1}} \right] \mathbb{P} \, \hat{f}(\boldsymbol{k}, \boldsymbol{v}, s) + \int \frac{d\hat{\boldsymbol{v}}}{4\pi} \frac{f(\boldsymbol{k}, \boldsymbol{v}, t = 0)}{s + i\boldsymbol{v} \cdot \boldsymbol{k} + \tau^{-1}} \ . \tag{8.137}$$

Now we have

$$\int \frac{d\hat{\boldsymbol{v}}}{4\pi} \frac{\tau^{-1}}{s + i\boldsymbol{v} \cdot \boldsymbol{k} + \tau^{-1}} = \int\limits_{-1}^1 dx \, \frac{\tau^{-1}}{s + ivkx + \tau^{-1}}$$

$$= \frac{1}{vk} \tan^{-1}\left(\frac{vk\tau}{1 + \tau s} \right) \ . \tag{8.138}$$

---

[8]See the excellent discussion in the book by Krapivsky, Redner, and Ben-Naim, cited in §8.1.

Thus,

$$\mathbb{P} f(\boldsymbol{k}, \boldsymbol{v}, s) = \left[1 - \frac{1}{vk\tau} \tan^{-1}\left(\frac{vk\tau}{1 + \tau s} \right) \right]^{-1} \int \frac{d\hat{\boldsymbol{v}}}{4\pi} \frac{f(\boldsymbol{k}, \boldsymbol{v}, t = 0)}{s + i\boldsymbol{v} \cdot \boldsymbol{k} + \tau^{-1}} . \tag{8.139}$$

We now have the solution to Lorentz's modified Boltzmann equation:

$$\hat{f}(\boldsymbol{k}, \boldsymbol{v}, s) = \frac{\tau^{-1}}{s + i\boldsymbol{v} \cdot \boldsymbol{k} + \tau^{-1}} \left[1 - \frac{1}{vk\tau} \tan^{-1}\left(\frac{vk\tau}{1 + \tau s} \right) \right]^{-1} \int \frac{d\hat{\boldsymbol{v}}}{4\pi} \frac{f(\boldsymbol{k}, \boldsymbol{v}, t = 0)}{s + i\boldsymbol{v} \cdot \boldsymbol{k} + \tau^{-1}}$$
$$+ \frac{f(\boldsymbol{k}, \boldsymbol{v}, t = 0)}{s + i\boldsymbol{v} \cdot \boldsymbol{k} + \tau^{-1}} . \tag{8.140}$$

Let us assume an initial distribution which is perfectly localized in both $\boldsymbol{r}$ and $\boldsymbol{v}$:

$$f(\boldsymbol{r}, \boldsymbol{v}, t = 0) = \delta(\boldsymbol{v} - \boldsymbol{v}_0) . \tag{8.141}$$

For these initial conditions, we find

$$\int \frac{d\hat{\boldsymbol{v}}}{4\pi} \frac{f(\boldsymbol{k}, \boldsymbol{v}, t = 0)}{s + i\boldsymbol{v} \cdot \boldsymbol{k} + \tau^{-1}} = \frac{1}{s + i\boldsymbol{v}_0 \cdot \boldsymbol{k} + \tau^{-1}} \cdot \frac{\delta(v - v_0)}{4\pi v_0^2} . \tag{8.142}$$

We further have that

$$1 - \frac{1}{vk\tau} \tan^{-1}\left(\frac{vk\tau}{1 + \tau s} \right) = s\tau + \tfrac{1}{3} k^2 v^2 \tau^2 + \dots , \tag{8.143}$$

and therefore

$$\hat{f}(\boldsymbol{k}, \boldsymbol{v}, s) = \frac{\tau^{-1}}{s + i\boldsymbol{v} \cdot \boldsymbol{k} + \tau^{-1}} \cdot \frac{\tau^{-1}}{s + i\boldsymbol{v}_0 \cdot \boldsymbol{k} + \tau^{-1}} \cdot \frac{1}{s + \tfrac{1}{3} v_0^2 k^2 \tau + \dots} \cdot \frac{\delta(v - v_0)}{4\pi v_0^2}$$
$$+ \frac{\delta(\boldsymbol{v} - \boldsymbol{v}_0)}{s + i\boldsymbol{v}_0 \cdot \boldsymbol{k} + \tau^{-1}} . \tag{8.144}$$

We are interested in the long time limit $t \gg \tau$ for $f(\boldsymbol{r}, \boldsymbol{v}, t)$. This is dominated by $s \sim t^{-1}$, and we assume that τ^{-1} is dominant over s and $i\boldsymbol{v} \cdot \boldsymbol{k}$. We then have

$$\hat{f}(\boldsymbol{k}, \boldsymbol{v}, s) \approx \frac{1}{s + \tfrac{1}{3} v_0^2 k^2 \tau} \cdot \frac{\delta(v - v_0)}{4\pi v_0^2} . \tag{8.145}$$

Performing the inverse Laplace and Fourier transforms, we obtain

$$f(\boldsymbol{r}, \boldsymbol{v}, t) = (4\pi Dt)^{-3/2} e^{-r^2/4Dt} \cdot \frac{\delta(v - v_0)}{4\pi v_0^2} , \tag{8.146}$$

where the *diffusion constant* is

$$D = \tfrac{1}{3} v_0^2 \tau . \tag{8.147}$$

The units are $[D] = L^2/T$. Integrating over velocities, we have the density

$$n(\boldsymbol{r}, t) = \int d^3v \, f(\boldsymbol{r}, \boldsymbol{v}, t) = (4\pi Dt)^{-3/2} e^{-r^2/4Dt} . \tag{8.148}$$

Note that

$$\int d^3r \, n(\boldsymbol{r}, t) = 1 \tag{8.149}$$

for all time. Total particle number is conserved!

8.7   Linearized Boltzmann Equation

8.7.1   Linearizing the collision integral

We now return to the classical Boltzmann equation and consider a more formal treatment of the collision term in the linear approximation. We will assume time-reversal symmetry, in which case

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = \int\! d^3p_1 \!\int\! d^3p' \!\int\! d^3p_1'\; w(\bm{p}',\bm{p}_1'\,|\,\bm{p},\bm{p}_1)\left\{f(\bm{p}')\,f(\bm{p}_1') - f(\bm{p})\,f(\bm{p}_1)\right\}. \tag{8.150}$$

The collision integral is nonlinear in the distribution f. We *linearize* by writing

$$f(\bm{p}) = f^0(\bm{p}) + f^0(\bm{p})\,\psi(\bm{p})\,, \tag{8.151}$$

where we assume $\psi(\bm{p})$ is small. We then have, to first order in ψ,

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = f^0(\bm{p})\,\hat{L}\psi + \mathcal{O}(\psi^2)\,, \tag{8.152}$$

where the action of the *linearized collision operator* is given by

$$\begin{aligned}
\hat{L}\psi &= \int\! d^3p_1 \!\int\! d^3p' \!\int\! d^3p_1'\; w(\bm{p}',\bm{p}_1'\,|\,\bm{p},\bm{p}_1)\,f^0(\bm{p}_1)\left\{\psi(\bm{p}') + \psi(\bm{p}_1') - \psi(\bm{p}) - \psi(\bm{p}_1)\right\} \\
&= \int\! d^3p_1 \!\int\! d\Omega\, |\bm{v}-\bm{v}_1|\,\frac{\partial\sigma}{\partial\Omega}\,f^0(\bm{p}_1)\left\{\psi(\bm{p}') + \psi(\bm{p}_1') - \psi(\bm{p}) - \psi(\bm{p}_1)\right\},
\end{aligned} \tag{8.153}$$

where we have invoked eqn. 8.55 to write the RHS in terms of the differential scattering cross section. In deriving the above result, we have made use of the detailed balance relation,

$$f^0(\bm{p})\,f^0(\bm{p}_1) = f^0(\bm{p}')\,f^0(\bm{p}_1')\,. \tag{8.154}$$

We have also suppressed the $\bm{r}$ dependence in writing $f(\bm{p})$, $f^0(\bm{p})$, and $\psi(\bm{p})$.

From eqn. 8.85, we then have the linearized equation

$$\left(\hat{L} - \frac{\partial}{\partial t}\right)\psi = Y, \tag{8.155}$$

where, for point particles,

$$Y = \frac{1}{k_{\text{B}}T}\left\{\frac{\varepsilon(\bm{p}) - c_p T}{T}\,\bm{v}\cdot\bm{\nabla}T + m\,v_\alpha v_\beta\,\mathcal{Q}_{\alpha\beta} - \frac{k_{\text{B}}\,\varepsilon(\bm{p})}{c_V}\,\bm{\nabla}\cdot\bm{V} - \bm{F}\cdot\bm{v}\right\}. \tag{8.156}$$

Eqn. 8.155 is an inhomogeneous linear equation, which can be solved by inverting the operator $\hat{L} - \frac{\partial}{\partial t}$.

8.7.2   Linear algebraic properties of $\hat{L}$

Although $\hat{L}$ is an integral operator, it shares many properties with other linear operators with which you are familiar, such as matrices and differential operators. We can define an *inner product*[9],

$$\langle\,\psi_1\,|\,\psi_2\,\rangle \equiv \int\! d^3p\, f^0(\bm{p})\,\psi_1(\bm{p})\,\psi_2(\bm{p})\,. \tag{8.157}$$

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[9]The requirements of an inner product $\langle f|g\rangle$ are symmetry, linearity, and non-negative definiteness.

Note that this is not the usual Hilbert space inner product from quantum mechanics, since the factor $f^0(\boldsymbol{p})$ is included in the metric. This is necessary in order that $\hat{L}$ be *self-adjoint*:

$$\langle\,\psi_1\,|\,\hat{L}\psi_2\,\rangle = \langle\,\hat{L}\psi_1\,|\,\psi_2\,\rangle\,. \tag{8.158}$$

We can now define the spectrum of *normalized eigenfunctions* of $\hat{L}$, which we write as $\phi_n(\boldsymbol{p})$. The eigenfunctions satisfy the eigenvalue equation,

$$\hat{L}\phi_n = -\lambda_n\,\phi_n\,, \tag{8.159}$$

and may be chosen to be orthonormal,

$$\langle\,\phi_m\,|\,\phi_n\,\rangle = \delta_{mn}\,. \tag{8.160}$$

Of course, in order to obtain the eigenfunctions ϕ_n we must have detailed knowledge of the function $w(\boldsymbol{p}',\boldsymbol{p}_1'\,|\,\boldsymbol{p},\boldsymbol{p}_1)$.

Recall that there are five collisional invariants, which are the particle number, the three components of the total particle momentum, and the particle energy. To each collisional invariant, there is an associated eigenfunction ϕ_n with eigenvalue $\lambda_n = 0$. One can check that these normalized eigenfunctions are

$$\phi_n(\boldsymbol{p}) = \frac{1}{\sqrt{n}} \tag{8.161}$$

$$\phi_{p_\alpha}(\boldsymbol{p}) = \frac{p_\alpha}{\sqrt{nmk_{\mathrm{B}}T}} \tag{8.162}$$

$$\phi_\varepsilon(\boldsymbol{p}) = \sqrt{\frac{2}{3n}}\left(\frac{\varepsilon(\boldsymbol{p})}{k_{\mathrm{B}}T} - \frac{3}{2}\right). \tag{8.163}$$

If there are no temperature, chemical potential, or bulk velocity gradients, and there are no external forces, then $Y = 0$ and the only changes to the distribution are from collisions. The linearized Boltzmann equation becomes

$$\frac{\partial\psi}{\partial t} = \hat{L}\psi\,. \tag{8.164}$$

We can therefore write the most general solution in the form

$$\psi(\boldsymbol{p},t) = {\sum_n}'C_n\,\phi_n(\boldsymbol{p})\,e^{-\lambda_n t}\,, \tag{8.165}$$

where the prime on the sum reminds us that collisional invariants are to be excluded. All the eigenvalues λ_n, aside from the five zero eigenvalues for the collisional invariants, must be positive. Any negative eigenvalue would cause $\psi(\boldsymbol{p},t)$ to increase without bound, and an initial nonequilibrium distribution would not relax to the equilibrium $f^0(\boldsymbol{p})$, which we regard as unphysical. Henceforth we will drop the prime on the sum but remember that $C_n = 0$ for the five collisional invariants.

Recall also the particle, energy, and thermal (heat) currents,

$$\boldsymbol{j} = \int\!d^3p\,\boldsymbol{v}\,f(\boldsymbol{p}) = \int\!d^3p\,f^0(\boldsymbol{p})\,\boldsymbol{v}\,\psi(\boldsymbol{p}) = \langle\,\boldsymbol{v}\,|\,\psi\,\rangle$$

$$\boldsymbol{j}_\varepsilon = \int\!d^3p\,\boldsymbol{v}\,\varepsilon\,f(\boldsymbol{p}) = \int\!d^3p\,f^0(\boldsymbol{p})\,\boldsymbol{v}\,\varepsilon\,\psi(\boldsymbol{p}) = \langle\,\boldsymbol{v}\,\varepsilon\,|\,\psi\,\rangle \tag{8.166}$$

$$\boldsymbol{j}_q = \int\!d^3p\,\boldsymbol{v}\,(\varepsilon-\mu)\,f(\boldsymbol{p}) = \int\!d^3p\,f^0(\boldsymbol{p})\,\boldsymbol{v}\,(\varepsilon-\mu)\,\psi(\boldsymbol{p}) = \langle\,\boldsymbol{v}\,(\varepsilon-\mu)\,|\,\psi\,\rangle\,.$$

Note $\boldsymbol{j}_q = \boldsymbol{j}_\varepsilon - \mu\boldsymbol{j}$.

8.7.3 Steady state solution to the linearized Boltzmann equation

Under steady state conditions, there is no time dependence, and the linearized Boltzmann equation takes the form

$$\hat{L}\psi = Y \, . \tag{8.167}$$

We may expand ψ in the eigenfunctions ϕ_n and write $\psi = \sum_n C_n \, \phi_n$. Applying $\hat{L}$ and taking the inner product with ϕ_j, we have

$$C_j = -\frac{1}{\lambda_j} \, \langle \, \phi_j \, | \, Y \, \rangle \, . \tag{8.168}$$

Thus, the formal solution to the linearized Boltzmann equation is

$$\psi(\boldsymbol{p}) = -\sum_n \frac{1}{\lambda_n} \, \langle \, \phi_n \, | \, Y \, \rangle \, \phi_n(\boldsymbol{p}) \, . \tag{8.169}$$

This solution is applicable provided $|\, Y \,\rangle$ is orthogonal to the five collisional invariants.

Thermal conductivity

For the thermal conductivity, we take $\boldsymbol{\nabla} T = \partial_z T \, \hat{\boldsymbol{x}}$, and

$$Y = \frac{1}{k_{\mathrm{B}} T^2} \, \frac{\partial T}{\partial x} \cdot X_\kappa \, , \tag{8.170}$$

where $X_\kappa \equiv (\varepsilon - c_p T) \, v_x$. Under the conditions of no particle flow ($\boldsymbol{j} = 0$), we have $\boldsymbol{j}_q = -\kappa \, \partial_x T \, \hat{\boldsymbol{x}}$. Then we have

$$\langle \, X_\kappa \, | \, \psi \, \rangle = -\kappa \, \frac{\partial T}{\partial x} \, . \tag{8.171}$$

Viscosity

For the viscosity, we take

$$Y = \frac{m}{k_{\mathrm{B}} T} \, \frac{\partial V_x}{\partial y} \cdot X_\eta \, , \tag{8.172}$$

with $X_\eta = v_x \, v_y$. We then

$$\Pi_{xy} = \langle \, m \, v_x \, v_y \, | \, \psi \, \rangle = -\eta \, \frac{\partial V_x}{\partial y} \, . \tag{8.173}$$

Thus,

$$\langle \, X_\eta \, | \, \psi \, \rangle = -\frac{\eta}{m} \, \frac{\partial V_x}{\partial y} \, . \tag{8.174}$$

8.7.4 Variational approach

Following the treatment in chapter 1 of Smith and Jensen, define $\hat{H} \equiv -\hat{L}$. We have that $\hat{H}$ is a positive semidefinite operator, whose only zero eigenvalues correspond to the collisional invariants. We then have the Schwarz inequality,

$$\langle \, \psi \, | \, \hat{H} \, | \, \psi \, \rangle \cdot \langle \, \phi \, | \, \hat{H} \, | \, \phi \, \rangle \geq \langle \, \phi \, | \, \hat{H} \, | \, \psi \, \rangle^2 \, , \tag{8.175}$$

for any two Hilbert space vectors $|\psi\rangle$ and $|\phi\rangle$. Consider now the above calculation of the thermal conductivity. We have

$$\hat{H}\psi = -\frac{1}{k_{\mathrm{B}}T^2}\frac{\partial T}{\partial x}X_\kappa \tag{8.176}$$

and therefore

$$\kappa = \frac{k_{\mathrm{B}}T^2}{(\partial T/\partial x)^2}\langle\psi|\hat{H}|\psi\rangle \geq \frac{1}{k_{\mathrm{B}}T^2}\frac{\langle\phi|X_\kappa\rangle^2}{\langle\phi|\hat{H}|\phi\rangle} \ . \tag{8.177}$$

Similarly, for the viscosity, we have

$$\hat{H}\psi = -\frac{m}{k_{\mathrm{B}}T}\frac{\partial V_x}{\partial y}X_\eta \ , \tag{8.178}$$

from which we derive

$$\eta = \frac{k_{\mathrm{B}}T}{(\partial V_x/\partial y)^2}\langle\psi|\hat{H}|\psi\rangle \geq \frac{m^2}{k_{\mathrm{B}}T}\frac{\langle\phi|X_\eta\rangle^2}{\langle\phi|\hat{H}|\phi\rangle} \ . \tag{8.179}$$

In order to get a good lower bound, we want ϕ in each case to have a good overlap with $X_{\kappa,\eta}$. One approach then is to take $\phi = X_{\kappa,\eta}$, which guarantees that the overlap will be finite (and not zero due to symmetry, for example). We illustrate this method with the viscosity calculation. We have

$$\eta \geq \frac{m^2}{k_{\mathrm{B}}T}\frac{\langle v_x v_y|v_x v_y\rangle^2}{\langle v_x v_y|\hat{H}|v_x v_y\rangle} \ . \tag{8.180}$$

Now the linearized collision operator $\hat{L}$ acts as

$$\langle\phi|\hat{L}|\psi\rangle = \int d^3p\, g^0(\boldsymbol{p})\,\phi(\boldsymbol{p})\int d^3p_1\!\int d\Omega\,\frac{\partial\sigma}{\partial\Omega}\,|\boldsymbol{v}-\boldsymbol{v}_1|\,f^0(\boldsymbol{p}_1)\Big\{\psi(\boldsymbol{p})+\psi(\boldsymbol{p}_1)-\psi(\boldsymbol{p}')-\psi(\boldsymbol{p}'_1)\Big\} \ . \tag{8.181}$$

Here the kinematics of the collision guarantee total energy and momentum conservation, so $\boldsymbol{p}'$ and $\boldsymbol{p}'_1$ are determined as in eqn. 8.56.

Now we have

$$d\Omega = \sin\chi\,d\chi\,d\varphi \ , \tag{8.182}$$

where χ is the scattering angle depicted in Fig. 8.6 and φ is the azimuthal angle of the scattering. The differential scattering cross section is obtained by elementary mechanics and is known to be

$$\frac{\partial\sigma}{\partial\Omega} = \left|\frac{d(b^2/2)}{d\sin\chi}\right| \ , \tag{8.183}$$

where b is the *impact parameter*. The scattering angle is

$$\chi(b,u) = \pi - 2\int\limits_{r_{\mathrm{p}}}^{\infty}dr\,\frac{b}{\sqrt{r^4 - b^2 r^2 - \frac{2U(r)r^4}{\tilde{m}u^2}}} \ , \tag{8.184}$$

where $\tilde{m} = \frac{1}{2}m$ is the reduced mass, and r_{p} is the relative coordinate separation at periapsis, *i.e.* the distance of closest approach, which occurs when $\dot{r} = 0$, *i.e.*

$$\tfrac{1}{2}\tilde{m}u^2 = \frac{\ell^2}{2\tilde{m}r_{\mathrm{p}}^2} + U(r_{\mathrm{p}}) \ , \tag{8.185}$$

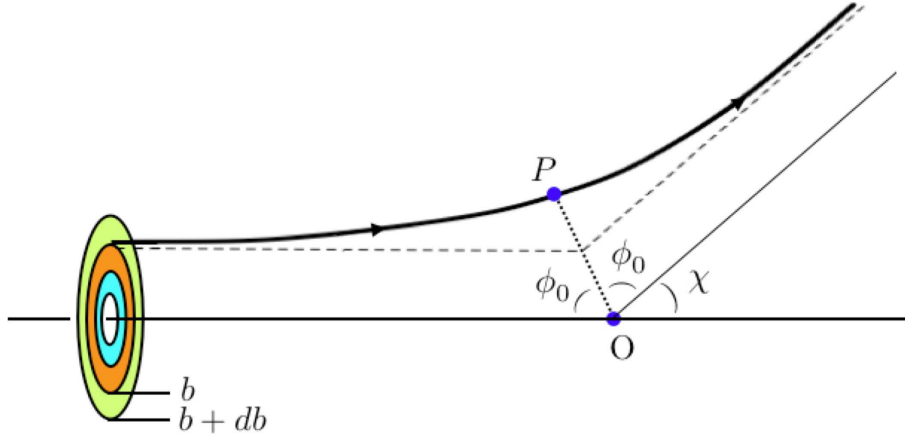where $\ell = \tilde{m}ub$ is the relative coordinate angular momentum.

Figure 8.6: Scattering in the CM frame. O is the force center and P is the point of periapsis. The impact parameter is b, and χ is the scattering angle. ϕ_0 is the angle through which the relative coordinate moves between periapsis and infinity.

We work in center-of-mass coordinates, so the velocities are

$$\boldsymbol{v} = \boldsymbol{V} + \tfrac{1}{2}\boldsymbol{u} \qquad\qquad \boldsymbol{v}' = \boldsymbol{V} + \tfrac{1}{2}\boldsymbol{u}' \tag{8.186}$$

$$\boldsymbol{v}_1 = \boldsymbol{V} - \tfrac{1}{2}\boldsymbol{u} \qquad\qquad \boldsymbol{v}_1' = \boldsymbol{V} - \tfrac{1}{2}\boldsymbol{u}' \qquad , \tag{8.187}$$

with $|\boldsymbol{u}| = |\boldsymbol{u}'|$ and $\hat{\boldsymbol{u}} \cdot \hat{\boldsymbol{u}}' = \cos\chi$. Then if $\psi(\boldsymbol{p}) = v_x v_y$, we have

$$\Delta(\psi) \equiv \psi(\boldsymbol{p}) + \psi(\boldsymbol{p}_1) - \psi(\boldsymbol{p}') - \psi(\boldsymbol{p}_1') = \tfrac{1}{2}\left(u_x u_y - u_x' u_y'\right) . \tag{8.188}$$

We may write

$$\boldsymbol{u}' = u\left(\sin\chi\cos\varphi\,\hat{\boldsymbol{e}}_1 + \sin\chi\sin\varphi\,\hat{\boldsymbol{e}}_2 + \cos\chi\,\hat{\boldsymbol{e}}_3\right), \tag{8.189}$$

where $\hat{\boldsymbol{e}}_3 = \hat{\boldsymbol{u}}$. With this parameterization, we have

$$\int_0^{2\pi} d\varphi\,\tfrac{1}{2}\left(u_\alpha u_\beta - u_\alpha' u_\beta'\right) = -\pi\sin^2\chi\left(u^2\,\delta_{\alpha\beta} - 3u_\alpha u_\beta\right) . \tag{8.190}$$

Note that we have used here the relation

$$e_{1\alpha}\,e_{1\beta} + e_{2\alpha}\,e_{2\beta} + e_{3\alpha}\,e_{3\beta} = \delta_{\alpha\beta} , \tag{8.191}$$

which holds since the LHS is a projector $\sum_{i=1}^{3} |\hat{\boldsymbol{e}}_i\rangle\langle\hat{\boldsymbol{e}}_i|$.

It is convenient to define the following integral:

$$R(u) \equiv \int_0^\infty db\, b\,\sin^2\chi(b, u) . \tag{8.192}$$

Since the Jacobian

$$\left| \det \frac{(\partial\boldsymbol{v}, \partial\boldsymbol{v}_1)}{(\partial\boldsymbol{V}, \partial\boldsymbol{u})} \right| = 1 , \tag{8.193}$$

we have

$$\langle\, v_x v_y \,|\, \hat{L} \,|\, v_x v_y \,\rangle = n^2 \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^3 \int\! d^3V \int\! d^3u \; e^{-m\boldsymbol{V}^2/k_{\mathrm{B}}T}\, e^{-m u^2/4k_{\mathrm{B}}T}\cdot u\cdot \tfrac{3\pi}{2}u_x u_y \cdot R(u)\cdot v_x v_y \;. \tag{8.194}$$

This yields

$$\langle\, v_x v_y \,|\, \hat{L} \,|\, v_x v_y \,\rangle = \tfrac{\pi}{40}\, n^2\, \langle u^5\, R(u)\rangle \;, \tag{8.195}$$

where

$$\langle F(u)\rangle \equiv \int\limits_0^\infty\! du\, u^2\, e^{-m u^2/4k_{\mathrm{B}}T}\, F(u) \Big/ \int\limits_0^\infty\! du\, u^2\, e^{-m u^2/4k_{\mathrm{B}}T} \;. \tag{8.196}$$

It is easy to compute the term in the numerator of eqn. 8.180:

$$\langle\, v_x v_y \,|\, v_x v_y \,\rangle = n\left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2}\!\! \int\! d^3v\; e^{-m\boldsymbol{v}^2/2k_{\mathrm{B}}T}\, v_x^2\, v_y^2 = n\left(\frac{k_{\mathrm{B}}T}{m}\right)^2 . \tag{8.197}$$

Putting it all together, we find

$$\eta \ge \frac{40\,(k_{\mathrm{B}}T)^3}{\pi\,m^2}\Big/\langle u^5\, R(u)\rangle \;. \tag{8.198}$$

The computation for κ is a bit more tedious. One has $\psi(\boldsymbol{p}) = (\varepsilon - c_p T)\, v_x$, in which case

$$\Delta(\psi) = \tfrac{1}{2}m\Big[(\boldsymbol{V}\cdot\boldsymbol{u})\, u_x - (\boldsymbol{V}\cdot\boldsymbol{u}')\, u_x'\Big] \;. \tag{8.199}$$

Ultimately, one obtains the lower bound

$$\kappa \ge \frac{150\, k_{\mathrm{B}}\,(k_{\mathrm{B}}T)^3}{\pi\,m^3}\Big/\langle u^5\, R(u)\rangle \;. \tag{8.200}$$

Thus, independent of the potential, this variational calculation yields a Prandtl number of

$$\mathrm{Pr} = \frac{\nu}{a} = \frac{\eta\, c_p}{m\,\kappa} = \tfrac{2}{3} \;, \tag{8.201}$$

which is very close to what is observed in dilute monatomic gases (see Tab. 8.1).

While the variational expressions for η and κ are complicated functions of the potential, for hard sphere scattering the calculation is simple, because $b = d\sin\phi_0 = d\cos(\tfrac{1}{2}\chi)$, where d is the hard sphere diameter. Thus, the impact parameter b is independent of the relative speed u, and one finds $R(u) = \tfrac{1}{3}d^3$. Then

$$\langle u^5\, R(u)\rangle = \tfrac{1}{3}d^3\langle u^5\rangle = \frac{128}{\sqrt{\pi}}\left(\frac{k_{\mathrm{B}}T}{m}\right)^{5/2}\! d^2 \tag{8.202}$$

and one finds

$$\eta \ge \frac{5\,(mk_{\mathrm{B}}T)^{1/2}}{16\sqrt{\pi}\, d^2} \qquad,\qquad \kappa \ge \frac{75\, k_{\mathrm{B}}}{64\sqrt{\pi}\, d^2}\left(\frac{k_{\mathrm{B}}T}{m}\right)^{1/2} . \tag{8.203}$$

8.8 The Equations of Hydrodynamics

We now derive the equations governing fluid flow. The equations of mass and momentum balance are

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla}\cdot(\rho\,\boldsymbol{V}) = 0 \tag{8.204}$$

$$\frac{\partial(\rho\,V_\alpha)}{\partial t} + \frac{\partial \Pi_{\alpha\beta}}{\partial x^\beta} = 0\,, \tag{8.205}$$

where

$$\Pi_{\alpha\beta} = \rho\,V_\alpha V_\beta + p\,\delta_{\alpha\beta} - \overbrace{\left\{\eta\left(\frac{\partial V_\alpha}{\partial x_\beta} + \frac{\partial V_\beta}{\partial x_\alpha} - \tfrac{2}{3}\,\boldsymbol{\nabla}\cdot\boldsymbol{V}\,\delta_{\alpha\beta}\right) + \zeta\,\boldsymbol{\nabla}\cdot\boldsymbol{V}\,\delta_{\alpha\beta}\right\}}^{\tilde\sigma_{\alpha\beta}}\,. \tag{8.206}$$

Substituting the continuity equation into the momentum balance equation, one arrives at

$$\rho\,\frac{\partial \boldsymbol{V}}{\partial t} + \rho\,(\boldsymbol{V}\cdot\boldsymbol{\nabla})\boldsymbol{V} = -\boldsymbol{\nabla}p + \eta\,\nabla^2\boldsymbol{V} + (\zeta + \tfrac{1}{3}\eta)\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\boldsymbol{V})\,, \tag{8.207}$$

which, together with continuity, are known as the *Navier-Stokes equations*. These equations are supplemented by an equation describing the conservation of energy,

$$T\frac{\partial s}{\partial T} + T\,\boldsymbol{\nabla}\cdot(s\boldsymbol{V}) = \tilde\sigma_{\alpha\beta}\,\frac{\partial V_\alpha}{\partial x^\beta} + \boldsymbol{\nabla}\cdot(\kappa\boldsymbol{\nabla}T)\,. \tag{8.208}$$

Note that the LHS of eqn. 8.207 is $\rho\,D\boldsymbol{V}/Dt$, where D/Dt is the convective derivative. Multiplying by a differential volume, this gives the mass times the acceleration of a differential local fluid element. The RHS, multiplied by the same differential volume, gives the differential force on this fluid element in a frame instantaneously moving with constant velocity $\boldsymbol{V}$. Thus, this is Newton's Second Law for the fluid.

8.9 Nonequilibrium Quantum Transport

8.9.1 Boltzmann equation for quantum systems

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

$$f^0(\boldsymbol{r},\boldsymbol{k},t) = \left\{\exp\left(\frac{\varepsilon(\boldsymbol{k}) - \mu(\boldsymbol{r},t)}{k_{\mathrm{B}}T(\boldsymbol{r},t)}\right) \mp 1\right\}^{-1}\,, \tag{8.209}$$

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

$$\left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}} = \int\!\frac{d^3k_1}{(2\pi)^3}\int\!\frac{d^3k'}{(2\pi)^3}\int\!\frac{d^3k_1'}{(2\pi)^3}\,w\left\{f'f_1'\,(1 \pm f)\,(1 \pm f_1) - ff_1\,(1 \pm f')\,(1 \pm f_1')\right\} \tag{8.210}$$

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. Detailed balance requires

$$\frac{f}{1 \pm f}\cdot\frac{f_1}{1 \pm f_1} = \frac{f'}{1 \pm f'}\cdot\frac{f_1'}{1 \pm f_1'}\,, \tag{8.211}$$

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

$$f = \frac{1}{e^{\beta(\varepsilon-\mu)} \mp 1} \qquad \Longrightarrow \qquad \frac{f}{1 \pm f} = e^{\beta(\mu-\varepsilon)} \ , \tag{8.212}$$

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

$$\begin{aligned} df^0 &= k_{\mathrm{B}}T \frac{\partial f^0}{\partial \varepsilon} \, d\left(\frac{\varepsilon - \mu}{k_{\mathrm{B}}T}\right) \\ &= k_{\mathrm{B}}T \frac{\partial f^0}{\partial \varepsilon} \left\{ -\frac{d\mu}{k_{\mathrm{B}}T} - \frac{(\varepsilon - \mu)\, dT}{k_{\mathrm{B}}T^2} + \frac{d\varepsilon}{k_{\mathrm{B}}T} \right\} \\ &= -\frac{\partial f^0}{\partial \varepsilon} \left\{ \frac{\partial \mu}{\partial \boldsymbol{r}} \cdot d\boldsymbol{r} + \frac{\varepsilon - \mu}{T} \frac{\partial T}{\partial \boldsymbol{r}} \cdot d\boldsymbol{r} - \frac{\partial \varepsilon}{\partial \boldsymbol{k}} \cdot d\boldsymbol{k} \right\} \ , \end{aligned} \tag{8.213}$$

from which we read off

$$\begin{aligned} \frac{\partial f^0}{\partial \boldsymbol{r}} &= -\frac{\partial f^0}{\partial \varepsilon} \left\{ \frac{\partial \mu}{\partial \boldsymbol{r}} + \frac{\varepsilon - \mu}{T} \frac{\partial T}{\partial \boldsymbol{r}} \right\} \\ \frac{\partial f^0}{\partial \boldsymbol{k}} &= \hbar \boldsymbol{v} \frac{\partial f^0}{\partial \varepsilon} \ . \end{aligned} \tag{8.214}$$

The most important application is to the theory of electron transport in metals and semiconductors, in which case f^0 is the Fermi distribution. In this case, the quantum collision integral also receives a contribution from one-body scattering in the presence of an external potential $U(\boldsymbol{r})$, which is given by Fermi's Golden Rule:

$$\begin{aligned} \left(\frac{\partial f(\boldsymbol{k})}{\partial t}\right)'_{\mathrm{coll}} &= \frac{2\pi}{\hbar} \sum_{\boldsymbol{k}' \in \hat{\Omega}} |\langle \boldsymbol{k}' \,|\, U \,|\, \boldsymbol{k} \rangle|^2 \, \big(f(\boldsymbol{k}') - f(\boldsymbol{k})\big) \, \delta\big(\varepsilon(\boldsymbol{k}) - \varepsilon(\boldsymbol{k}')\big) \\ &= \frac{2\pi}{\hbar V} \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \, |\hat{U}(\boldsymbol{k} - \boldsymbol{k}')|^2 \, \big(f(\boldsymbol{k}') - f(\boldsymbol{k})\big) \, \delta\big(\varepsilon(\boldsymbol{k}) - \varepsilon(\boldsymbol{k}')\big) \ . \end{aligned} \tag{8.215}$$

The wavevectors are now restricted to the first Brillouin zone, and the dispersion $\varepsilon(\boldsymbol{k})$ is no longer the ballistic form $\varepsilon = \hbar^2 \boldsymbol{k}^2/2m$ but rather the dispersion for electrons in a particular energy band (typically the valence band) of a solid[10]. Note that $f = f^0$ satisfies detailed balance with respect to one-body collisions as well[11].

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

$$\frac{\partial\, \delta f}{\partial t} - \frac{e}{\hbar c} \boldsymbol{v} \times \boldsymbol{B} \cdot \frac{\partial\, \delta f}{\partial \boldsymbol{k}} - \boldsymbol{v} \cdot \left[e\,\boldsymbol{\mathcal{E}} + \frac{\varepsilon - \mu}{T} \boldsymbol{\nabla} T \right] \frac{\partial f^0}{\partial \varepsilon} = -\frac{\delta f}{\tau} \ , \tag{8.216}$$

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

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[10] We neglect interband scattering here, which can be important in practical applications, but which is beyond the scope of these notes.

[11] The transition rate from $|\boldsymbol{k}'\rangle$ to $|\boldsymbol{k}\rangle$ 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 eqn. 8.215.

We can use eqn. 8.216 to compute the electrical current $\boldsymbol{j}$ and the thermal current $\boldsymbol{j}_q$,

$$\boldsymbol{j} = -2e \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \, \boldsymbol{v} \, \delta f \tag{8.217}$$

$$\boldsymbol{j}_q = 2 \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \, (\varepsilon - \mu) \, \boldsymbol{v} \, \delta f \ . \tag{8.218}$$

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

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

$$\delta f = -\tau(\varepsilon) \, \boldsymbol{v} \cdot \left(e\boldsymbol{\mathcal{E}} + \frac{\varepsilon - \mu}{T} \, \boldsymbol{\nabla} T \right) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \ . \tag{8.219}$$

We now consider both the electrical current[12] $\boldsymbol{j}$ as well as the thermal current density $\boldsymbol{j}_q$. One readily obtains

$$\boldsymbol{j} = -2e \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \, \boldsymbol{v} \, \delta f \equiv L_{11} \, \boldsymbol{\mathcal{E}} - L_{12} \, \boldsymbol{\nabla} T \tag{8.220}$$

$$\boldsymbol{j}_q = 2 \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \, (\varepsilon - \mu) \, \boldsymbol{v} \, \delta f \equiv L_{21} \, \boldsymbol{\mathcal{E}} - L_{22} \, \boldsymbol{\nabla} T \tag{8.221}$$

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

$$L_{11}^{\alpha\beta} = \frac{e^2}{4\pi^3 \hbar} \int d\varepsilon \, \tau(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \, \frac{v^\alpha \, v^\beta}{|\boldsymbol{v}|} \tag{8.222}$$

$$L_{21}^{\alpha\beta} = TL_{12}^{\alpha\beta} = -\frac{e}{4\pi^3 \hbar} \int d\varepsilon \, \tau(\varepsilon) \, (\varepsilon - \mu) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \, \frac{v^\alpha \, v^\beta}{|\boldsymbol{v}|} \tag{8.223}$$

$$L_{22}^{\alpha\beta} = \frac{1}{4\pi^3 \hbar T} \int d\varepsilon \, \tau(\varepsilon) \, (\varepsilon - \mu)^2 \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \, \frac{v^\alpha \, v^\beta}{|\boldsymbol{v}|} \ . \tag{8.224}$$

If we define the hierarchy of integral expressions

$$\mathcal{J}_n^{\alpha\beta} \equiv \frac{1}{4\pi^3 \hbar} \int d\varepsilon \, \tau(\varepsilon) \, (\varepsilon - \mu)^n \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \, \frac{v^\alpha \, v^\beta}{|\boldsymbol{v}|} \tag{8.225}$$

then we may write

$$L_{11}^{\alpha\beta} = e^2 \, \mathcal{J}_0^{\alpha\beta} \qquad , \qquad L_{21}^{\alpha\beta} = TL_{12}^{\alpha\beta} = -e \, \mathcal{J}_1^{\alpha\beta} \qquad , \qquad L_{22}^{\alpha\beta} = \frac{1}{T} \, \mathcal{J}_2^{\alpha\beta} \ . \tag{8.226}$$

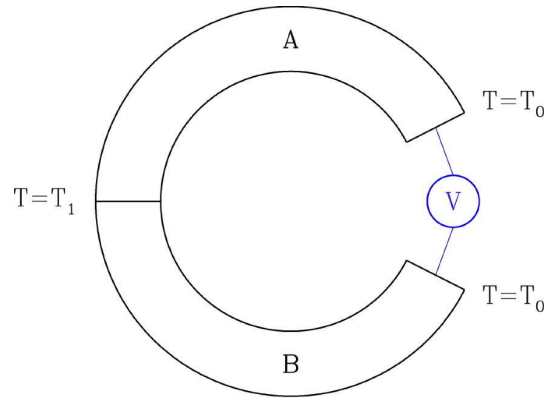The linear relations in eqn. (8.221) may be recast in the following form:

$$\boldsymbol{\mathcal{E}} = \rho \, \boldsymbol{j} + Q \, \boldsymbol{\nabla} T$$
$$\boldsymbol{j}_q = \sqcap \boldsymbol{j} - \kappa \, \boldsymbol{\nabla} T \ , \tag{8.227}$$

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

$$\rho = L_{11}^{-1} \qquad\qquad\qquad Q = L_{11}^{-1} \, L_{12} \tag{8.228}$$

$$\sqcap = L_{21} \, L_{11}^{-1} \qquad\qquad\qquad \kappa = L_{22} - L_{21} \, L_{11}^{-1} \, L_{12} \ , \tag{8.229}$$

---

[12]In this section we use $\boldsymbol{j}$ to denote electrical current, rather than particle number current as before.

$$V = (Q_B - Q_A)(T_1 - T_0)$$

Figure 8.7: A thermocouple is a junction formed of two dissimilar metals. With no electrical current passing, an electric field is generated in the presence of a temperature gradient, resulting in a voltage $V = V_A - V_B$.

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

$$\rho = \frac{1}{e^2}\,\mathcal{J}_0^{-1} \qquad\qquad\qquad Q = -\frac{1}{eT}\,\mathcal{J}_0^{-1}\,\mathcal{J}_1 \tag{8.230}$$

$$\sqcap = -\frac{1}{e}\,\mathcal{J}_1\,\mathcal{J}_0^{-1} \qquad\qquad\qquad \kappa = \frac{1}{T}\left(\mathcal{J}_2 - \mathcal{J}_1\,\mathcal{J}_0^{-1}\,\mathcal{J}_1\right)\,, \tag{8.231}$$

These equations describe a wealth of transport phenomena:

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

- Peltier effect ($\nabla T = \boldsymbol{B} = 0$)
  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 ∇T gives rise to a heat current $\boldsymbol{j}_q = -\kappa\nabla T$, where κ is the thermal conductivity.

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

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

$$V_A - V_B = -\int\limits_A^B \boldsymbol{\mathcal{E}} \cdot d\boldsymbol{l} = (Q_B - Q_A)(T_1 - T_0)\,. \tag{8.232}$$

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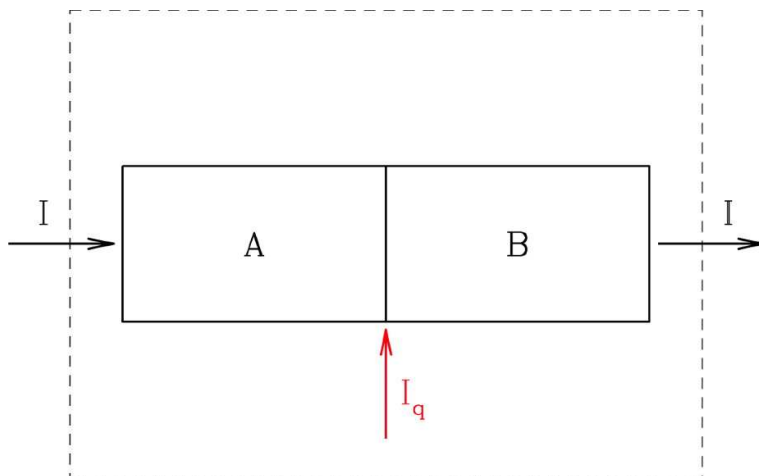
$$I_q = (\Pi_B - \Pi_A) \cdot I$$

Figure 8.8: A sketch of a Peltier effect refrigerator. An electrical current I is passed through a junction between two dissimilar metals. If the dotted line represents the boundary of a thermally well-insulated body, then the body cools when $\Pi_B > \Pi_A$, in order to maintain a heat current balance at the junction.

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

8.9.2   The Heat Equation

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

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j} = 0 \tag{8.233}$$

$$\frac{\partial \varepsilon}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_\varepsilon = \boldsymbol{j} \cdot \boldsymbol{E}\,, \tag{8.234}$$

where $\boldsymbol{E}$ is the electric field[14]. Now we invoke local thermodynamic equilibrium and write

$$\frac{\partial \varepsilon}{\partial t} = \frac{\partial \varepsilon}{\partial n}\frac{\partial n}{\partial t} + \frac{\partial \varepsilon}{\partial T}\frac{\partial T}{\partial t}$$
$$= -\frac{\mu}{e}\frac{\partial \rho}{\partial t} + c_V \frac{\partial T}{\partial t}\,, \tag{8.235}$$

---

[13]To create a refrigerator, stick the cold junction inside a thermally insulated box and the hot junction outside the box.

[14]Note that it is $\boldsymbol{E} \cdot \boldsymbol{j}$ and *not* $\boldsymbol{\mathcal{E}} \cdot \boldsymbol{j}$ which is the source term in the energy continuity equation.

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

$$c_V \frac{\partial T}{\partial t} = \frac{\partial \varepsilon}{\partial t} + \frac{\mu}{e} \frac{\partial \rho}{\partial t}$$

$$= \boldsymbol{j} \cdot \boldsymbol{E} - \boldsymbol{\nabla} \cdot \boldsymbol{j}_\varepsilon - \frac{\mu}{e} \boldsymbol{\nabla} \cdot \boldsymbol{j}$$

$$= \boldsymbol{j} \cdot \boldsymbol{\mathcal{E}} - \boldsymbol{\nabla} \cdot \boldsymbol{j}_q \; . \tag{8.236}$$

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

$$c_V \frac{\partial T}{\partial t} = \kappa_{\alpha\beta} \frac{\partial^2 T}{\partial x^\alpha \, \partial x^\beta} \; . \tag{8.237}$$

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

8.9.3 Calculation of Transport Coefficients

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

$$\mathcal{J}_n = \frac{1}{12\pi^3 \hbar} \int d\varepsilon \, \tau(\varepsilon) \, (\varepsilon - \mu)^n \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \, |\boldsymbol{v}| \; . \tag{8.238}$$

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

$$\mathcal{I} \equiv \int\limits_{-\infty}^{\infty} d\varepsilon \, H(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) = \pi \mathcal{D} \csc(\pi \mathcal{D}) \, H(\varepsilon) \Big|_{\varepsilon = \mu} \tag{8.239}$$

$$= H(\mu) + \frac{\pi^2}{6} (k_{\text{B}} T)^2 \, H''(\mu) + \dots \tag{8.240}$$

where $\mathcal{D} \equiv k_{\text{B}} T \frac{\partial}{\partial \varepsilon}$ is a dimensionless differential operator.[15]

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

$$\mathcal{J}_n = \frac{\sigma_0}{e^2} \mu^{-3/2} \pi \mathcal{D} \csc \pi \mathcal{D} \, \varepsilon^{3/2} \, (\varepsilon - \mu)^n \Big|_{\varepsilon = \mu} \; , \tag{8.241}$$

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

$$\mathcal{J}_0 = \frac{\sigma_0}{e^2} \left[1 + \frac{\pi^2}{8} \frac{(k_{\text{B}} T)^2}{\mu^2} + \dots \right]$$

$$\mathcal{J}_1 = \frac{\sigma_0}{e^2} \frac{\pi^2}{2} \frac{(k_{\text{B}} T)^2}{\mu} + \dots \tag{8.242}$$

$$\mathcal{J}_2 = \frac{\sigma_0}{e^2} \frac{\pi^2}{3} (k_{\text{B}} T)^2 + \dots \; ,$$

---

[15]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.

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

$$Q = -\frac{\pi^2}{2}\frac{k_{\mathrm{B}}^2 T}{e\,\varepsilon_{\mathrm{F}}} \qquad\qquad \kappa = \frac{\pi^2}{3}\frac{n\tau}{m^*}k_{\mathrm{B}}^2 T \;, \tag{8.243}$$

and of course $\sqcap = TQ$. The predicted universal ratio

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3}\,(k_{\mathrm{B}}/e)^2 = 2.45\times 10^{-8}\,\mathrm{V}^2\,\mathrm{K}^{-2} \;, \tag{8.244}$$

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

8.9.4   Onsager Relations

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

$$J_i = L_{ik}\,F_k \;, \tag{8.245}$$

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

$$\dot{S} = \sum_i F_i\,J_i \quad\Longrightarrow\quad F_i = \frac{\partial\dot{S}}{\partial J_i}\;. \tag{8.246}$$

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

$$L_{ik}(\boldsymbol{B}) = \eta_i\,\eta_k\,L_{ki}(-\boldsymbol{B}) \;, \tag{8.247}$$

where η_i describes the parity of J_i under time reversal:

$$J_i^T = \eta_i\,J_i \;, \tag{8.248}$$

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

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

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

$$\rho_{\alpha\beta}(\boldsymbol{B}) = \rho_{\beta\alpha}(-\boldsymbol{B}) \tag{8.249}$$

$$\kappa_{\alpha\beta}(\boldsymbol{B}) = \kappa_{\beta\alpha}(-\boldsymbol{B}) \tag{8.250}$$

$$\sqcap_{\alpha\beta}(\boldsymbol{B}) = T\,Q_{\beta\alpha}(-\boldsymbol{B})\;. \tag{8.251}$$

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

$$\rho_{\alpha\beta}(\boldsymbol{B}) = \rho\,\delta_{\alpha\beta} + \nu\,\epsilon_{\alpha\beta\gamma}\,B^\gamma \tag{8.252}$$

$$\kappa_{\alpha\beta}(\boldsymbol{B}) = \kappa\,\delta_{\alpha\beta} + \varpi\,\epsilon_{\alpha\beta\gamma}\,B^\gamma \tag{8.253}$$

$$Q_{\alpha\beta}(\boldsymbol{B}) = Q\,\delta_{\alpha\beta} + \zeta\,\epsilon_{\alpha\beta\gamma}\,B^\gamma \tag{8.254}$$

$$\sqcap_{\alpha\beta}(\boldsymbol{B}) = \sqcap\,\delta_{\alpha\beta} + \theta\,\epsilon_{\alpha\beta\gamma}B^\gamma\;. \tag{8.255}$$

Onsager reciprocity requires $\sqcap = T\,Q$ and $\theta = T\,\zeta$. We can now write

$$\boldsymbol{\mathcal{E}} = \rho\,\boldsymbol{j} + \nu\,\boldsymbol{j} \times \boldsymbol{B} + Q\,\boldsymbol{\nabla} T + \zeta\,\boldsymbol{\nabla} T \times \boldsymbol{B} \tag{8.256}$$

$$\boldsymbol{j}_q = \sqcap\,\boldsymbol{j} + \theta\,\boldsymbol{j} \times \boldsymbol{B} - \kappa\,\boldsymbol{\nabla} T - \varpi\,\boldsymbol{\nabla} T \times \boldsymbol{B}\ . \tag{8.257}$$

There are several new phenomena lurking:

- <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 $R_{\mathrm{H}} = \mathcal{E}_y/j_x\,B_z = -\nu$.

- <u>Ettingshausen effect</u> ($\frac{\partial T}{\partial x} = j_y = j_{q,y} = 0$)
  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 $P = \frac{\partial T}{\partial y}\big/j_x\,B_z = -\theta/\kappa$.

- <u>Nernst effect</u> ($j_x = j_y = \frac{\partial T}{\partial y} = 0$)
  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 $\Lambda = \mathcal{E}_y\big/\frac{\partial T}{\partial x}\,B_z = -\zeta$.

- <u>Righi-Leduc effect</u> ($j_x = j_y = \mathcal{E}_y = 0$)
  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 temperature gradient $\frac{\partial T}{\partial y}$. The Righi-Leduc coefficient is $\mathcal{L} = \frac{\partial T}{\partial y}\big/\frac{\partial T}{\partial x}B_z = \zeta/Q$.

8.10 Stochastic Processes

A *stochastic process* is one which is partially random, *i.e.* it is not wholly deterministic. Typically the randomness is due to phenomena at the microscale, such as the effect of fluid molecules on a small particle, such as a piece of dust in the air. The resulting motion (called *Brownian motion* in the case of particles moving in a fluid) can be described only in a statistical sense. That is, the full motion of the system is a *functional* of one or more independent random variables. The motion is then described by its averages with respect to the various random distributions.

8.10.1 Langevin equation and Brownian motion

Consider a particle of mass M subjected to dissipative and random forcing. We'll examine this system in one dimension to gain an understanding of the essential physics. We write

$$\dot{p} + \gamma p = F + \eta(t)\ . \tag{8.258}$$

Here, γ is the damping rate due to friction, F is a constant external force, and $\eta(t)$ is a *stochastic random force*. This equation, known as the Langevin equation, describes a ballistic particle being buffeted by random forcing events. Think of a particle of dust as it moves in the atmosphere; F would then represent the external force due to gravity and $\eta(t)$ the random forcing due to interaction with the air molecules. For a sphere of radius a moving with velocity $\boldsymbol{v}$ in a fluid, the *Stokes drag* is given by $\boldsymbol{F}_{\mathrm{drag}} = -6\pi\eta a\boldsymbol{v}$, where a is the radius. Thus,

$$\gamma_{\mathrm{Stokes}} = \frac{6\pi\eta a}{M}\ , \tag{8.259}$$

where M is the mass of the particle. It is illustrative to compute γ in some setting. Consider a micron sized droplet ($a = 10^{-4}\,\mathrm{cm}$) of some liquid of density $\rho \sim 1.0\,\mathrm{g/cm^3}$ moving in air at $T = 20°\,\mathrm{C}$. The viscosity of air is

$\eta = 1.8 \times 10^{-4}\,\text{g/cm} \cdot \text{s}$ at this temperature[16]. If the droplet density is constant, then $\gamma = 9\eta/2\rho a^2 = 8.1 \times 10^4\,\text{s}^{-1}$, hence the time scale for viscous relaxation of the particle is $\tau = \gamma^{-1} = 12\,\mu\text{s}$. We should stress that the viscous damping on the particle is of course due to the fluid molecules, in some average 'coarse-grained' sense. The random component to the force $\eta(t)$ would then represent the fluctuations with respect to this average.

We can easily integrate this equation:

$$\frac{d}{dt}\left(p\,e^{\gamma t}\right) = F\,e^{\gamma t} + \eta(t)\,e^{\gamma t}$$

$$p(t) = p(0)\,e^{-\gamma t} + \frac{F}{\gamma}\left(1 - e^{-\gamma t}\right) + \int\limits_0^t ds\,\eta(s)\,e^{\gamma(s-t)} \tag{8.260}$$

Note that $p(t)$ is indeed a functional of the random function $\eta(t)$. We can therefore only compute averages in order to describe the motion of the system.

The first average we will compute is that of p itself. In so doing, we assume that $\eta(t)$ has zero mean: $\langle \eta(t) \rangle = 0$. Then

$$\langle p(t) \rangle = p(0)\,e^{-\gamma t} + \frac{F}{\gamma}\left(1 - e^{-\gamma t}\right). \tag{8.261}$$

On the time scale γ^{-1}, the initial conditions $p(0)$ are effectively forgotten, and asymptotically for $t \gg \gamma^{-1}$ we have $\langle p(t) \rangle \to F/\gamma$, which is the terminal momentum.

Next, consider

$$\langle p^2(t) \rangle = \langle p(t) \rangle^2 + \int\limits_0^t ds_1 \int\limits_0^t ds_2\, e^{\gamma(s_1-t)}\, e^{\gamma(s_2-t)}\, \langle \eta(s_1)\,\eta(s_2) \rangle. \tag{8.262}$$

We now need to know the two-time correlator $\langle \eta(s_1)\,\eta(s_2) \rangle$. We assume that the correlator is a function only of the time difference $\Delta s = s_1 - s_2$, so that the random force $\eta(s)$ satisfies

$$\langle \eta(s) \rangle = 0 \tag{8.263}$$
$$\langle \eta(s_1)\,\eta(s_2) \rangle = \phi(s_1 - s_2). \tag{8.264}$$

The function $\phi(s)$ is the *autocorrelation function* of the random force. A macroscopic object moving in a fluid is constantly buffeted by fluid particles over its entire perimeter. These different fluid particles are almost completely uncorrelated, hence $\phi(s)$ is basically nonzero except on a very small time scale τ_ϕ, which is the time a single fluid particle spends interacting with the object. We can take $\tau_\phi \to 0$ and approximate

$$\phi(s) \approx \Gamma\,\delta(s). \tag{8.265}$$

We shall determine the value of Γ from equilibrium thermodynamic considerations below.

With this form for $\phi(s)$, we can easily calculate the equal time momentum autocorrelation:

$$\langle p^2(t) \rangle = \langle p(t) \rangle^2 + \Gamma \int\limits_0^t ds\, e^{2\gamma(s-t)}$$

$$= \langle p(t) \rangle^2 + \frac{\Gamma}{2\gamma}\left(1 - e^{-2\gamma t}\right). \tag{8.266}$$

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[16]The cgs unit of viscosity is the *Poise* (P). $1\,\text{P} = 1\,\text{g/cm}\cdot\text{s}$.

Consider the case where $F = 0$ and the limit $t \gg \gamma^{-1}$. We demand that the object thermalize at temperature T. Thus, we impose the condition

$$\left\langle \frac{p^2(t)}{2M} \right\rangle = \tfrac{1}{2} k_{\mathrm{B}} T \qquad \Longrightarrow \qquad \Gamma = 2\gamma M k_{\mathrm{B}} T \quad , \tag{8.267}$$

where M is the particle's mass. This determines the value of Γ.

We can now compute the general momentum autocorrelator:

$$\langle p(t)\, p(t') \rangle - \langle p(t) \rangle \langle p(t') \rangle = \int\limits_0^t ds \int\limits_0^{t'} ds'\, e^{\gamma(s-t)}\, e^{\gamma(s'-t')}\, \langle \eta(s)\, \eta(s') \rangle \tag{8.268}$$

$$= M k_{\mathrm{B}} T\, e^{-\gamma|t-t'|} \qquad (t, t' \to \infty\,,\ |t-t'|\ \text{finite})\,.$$

The full expressions for this and subsequent expressions, including subleading terms, are contained in an appendix, §8.14.

Let's now compute the position $x(t)$. We find

$$x(t) = \langle x(t) \rangle + \frac{1}{M} \int\limits_0^t ds \int\limits_0^s ds_1\, \eta(s_1)\, e^{\gamma(s_1 - s)}\,, \tag{8.269}$$

where

$$\langle x(t) \rangle = x(0) + \frac{Ft}{\gamma M} + \frac{1}{\gamma}\left(v(0) - \frac{F}{\gamma M} \right)\left(1 - e^{-\gamma t} \right)\,. \tag{8.270}$$

Note that for $\gamma t \ll 1$ we have $\langle x(t) \rangle = x(0) + v(0)\,t + \tfrac{1}{2} M^{-1} F t^2 + \mathcal{O}(t^3)$, as is appropriate for ballistic particles moving under the influence of a constant force. This long time limit of course agrees with our earlier evaluation for the terminal velocity, $v_\infty = \langle p(\infty) \rangle / M = F/\gamma M$. We next compute the position autocorrelation:

$$\langle x(t)\, x(t') \rangle - \langle x(t) \rangle \langle x(t') \rangle = \frac{1}{M^2} \int\limits_0^t ds \int\limits_0^{t'} ds'\, e^{-\gamma(s+s')} \int\limits_0^s ds_1 \int\limits_0^{s'} ds_1'\, e^{\gamma(s_1 + s_2)}\, \langle \eta(s_1)\, \eta(s_2) \rangle$$

$$= \frac{2k_{\mathrm{B}}T}{\gamma M}\, \mathsf{min}(t, t') + \mathcal{O}(1)\,.$$

In particular, the equal time autocorrelator is

$$\langle x^2(t) \rangle - \langle x(t) \rangle^2 = \frac{2k_{\mathrm{B}} T\, t}{\gamma M} \equiv 2D t\,, \tag{8.271}$$

at long times, up to terms of order unity. Here,

$$D = \frac{k_{\mathrm{B}} T}{\gamma M} \tag{8.272}$$

is the *diffusion constant*. For a liquid droplet of radius $a = 1\,\mu\mathrm{m}$ moving in air at $T = 293\,\mathrm{K}$, for which $\eta = 1.8 \times 10^{-4}\,\mathrm{P}$, we have

$$D = \frac{k_{\mathrm{B}} T}{6\pi \eta a} = \frac{(1.38 \times 10^{-16}\,\mathrm{erg/K})\,(293\,\mathrm{K})}{6\pi\,(1.8 \times 10^{-4}\,\mathrm{P})\,(10^{-4}\,\mathrm{cm})} = 1.19 \times 10^{-7}\,\mathrm{cm}^2/\mathrm{s}\,. \tag{8.273}$$

This result presumes that the droplet is large enough compared to the intermolecular distance in the fluid that one can adopt a continuum approach and use the Navier-Stokes equations, and then assuming a laminar flow.

If we consider molecular diffusion, the situation is quite a bit different. As we shall derive below in §8.10.3, the molecular diffusion constant is $D = \ell^2/2\tau$, where ℓ is the mean free path and τ is the collision time. As we found in eqn. 8.91, the mean free path ℓ, collision time τ, number density n, and total scattering cross section σ are related by

$$\ell = \bar{v}\tau = \frac{1}{\sqrt{2}\,n\sigma}\ , \tag{8.274}$$

where $\bar{v} = \sqrt{8k_{\mathrm{B}}T/\pi m}$ is the average particle speed. Approximating the particles as hard spheres, we have $\sigma = 4\pi a^2$, where a is the hard sphere radius. At $T = 293\,\mathrm{K}$, and $p = 1\,\mathrm{atm}$, we have $n = p/k_{\mathrm{B}}T = 2.51 \times 10^{19}\,\mathrm{cm}^{-3}$. Since air is predominantly composed of N_2 molecules, we take $a = 1.90 \times 10^{-8}\,\mathrm{cm}$ and $m = 28.0\,\mathrm{amu} = 4.65 \times 10^{-23}\,\mathrm{g}$, which are appropriate for N_2. We find an average speed of $\bar{v} = 471\,\mathrm{m/s}$ and a mean free path of $\ell = 6.21 \times 10^{-6}\,\mathrm{cm}$. Thus, $D = \frac{1}{2}\ell\bar{v} = 0.146\,\mathrm{cm}^2/\mathrm{s}$. Though much larger than the diffusion constant for large droplets, this is still too small to explain common experiences. Suppose we set the characteristic distance scale at $d = 10\,\mathrm{cm}$ and we ask how much time a point source would take to diffuse out to this radius. The answer is $\Delta t = d^2/2D = 343\,\mathrm{s}$, which is between five and six minutes. Yet if someone in the next seat emits a foul odor, your sense the offending emission in on the order of a second. What this tells us is that diffusion isn't the only transport process involved in these and like phenomena. More important are *convection* currents which distribute the scent much more rapidly.

8.10.2 Langevin equation for a particle in a harmonic well

Consider next the equation

$$M\ddot{X} + \gamma M\dot{X} + M\omega_0^2 X = F_0 + \eta(t)\ , \tag{8.275}$$

where F_0 is a constant force. We write $X = \frac{F_0}{M\omega_0^2} + x$ and measure x relative to the potential minimum, yielding

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = \frac{1}{M}\eta(t)\ . \tag{8.276}$$

At this point there are several ways to proceed.

Perhaps the most straightforward is by use of the Laplace transform. Recall:

$$\hat{x}(\nu) = \int_0^\infty dt\, e^{-\nu t}\,\eta(\nu) \tag{8.277}$$

$$x(t) = \int_{\mathcal{C}} \frac{d\nu}{2\pi i}\, e^{+\nu t}\,\hat{x}(\nu)\ , \tag{8.278}$$

where the contour $\mathcal{C}$ proceeds from $a - i\infty$ to $a + i\infty$ such that all poles of the integrand lie to the left of $\mathcal{C}$. We then have

$$\frac{1}{M}\int_0^\infty dt\, e^{-\nu t}\,\eta(t) = \frac{1}{M}\int_0^\infty dt\, e^{-\nu t}\left(\ddot{x} + \gamma\dot{x} + \omega_0^2 x\right)$$

$$= -(\nu + \gamma)\,x(0) - \dot{x}(0) + \left(\nu^2 + \gamma\nu + \omega_0^2\right)\hat{x}(\nu)\ . \tag{8.279}$$

Thus, we have

$$\hat{x}(\nu) = \frac{(\nu + \gamma)\,x(0) + \dot{x}(0)}{\nu^2 + \gamma\nu + \omega_0^2} + \frac{1}{M}\cdot\frac{1}{\nu^2 + \gamma\nu + \omega_0^2}\int_0^\infty dt\, e^{-\nu t}\,\eta(t)\ . \tag{8.280}$$

Now we may write

$$\nu^2 + \gamma\nu + \omega_0^2 = (\nu - \nu_+)(\nu - \nu_-) \,, \tag{8.281}$$

where

$$\nu_\pm = -\tfrac{1}{2}\gamma \pm \sqrt{\tfrac{1}{4}\gamma^2 - \omega_0^2} \,. \tag{8.282}$$

Note that $\mathrm{Re}\,(\nu_\pm) \le 0$ and that $\gamma + \nu_\pm = -\nu_\mp$.

Performing the inverse Laplace transform, we obtain

$$
\begin{aligned}
x(t) &= \frac{x(0)}{\nu_+ - \nu_-}\left(\nu_+\,e^{\nu_- t} - \nu_-\,e^{\nu_+ t}\right) + \frac{\dot{x}(0)}{\nu_+ - \nu_-}\left(e^{\nu_+ t} - e^{\nu_- t}\right) \\
&\quad + \int_0^\infty ds\, K(t-s)\,\eta(s)\,,
\end{aligned}
\tag{8.283}
$$

where

$$K(t-s) = \frac{\Theta(t-s)}{M\,(\nu_+ - \nu_-)}\left(e^{\nu_+(t-s)} - e^{\nu_-(t-s)}\right) \tag{8.284}$$

is the *response kernel* and $\Theta(t - s)$ is the step function which is unity for $t > s$ and zero otherwise. The response is *causal*, *i.e.* $x(t)$ depends on $\eta(s)$ for all previous times $s < t$, but not for future times $s > t$. Note that $K(\tau)$ decays exponentially for $\tau \to \infty$, if $\mathrm{Re}(\nu_\pm) < 0$. The marginal case where $\omega_0 = 0$ and $\nu_+ = 0$ corresponds to the diffusion calculation we performed in the previous section.

8.10.3 Discrete random walk

Consider an object moving on a one-dimensional lattice in such a way that every time step it moves either one unit to the right or left, at random. If the lattice spacing is ℓ, then after n time steps the position will be

$$x_n = \ell \sum_{j=1}^n \sigma_j \,, \tag{8.285}$$

where

$$\sigma_j = \begin{cases} +1 & \text{if motion is one unit to right at time step } j \\ -1 & \text{if motion is one unit to left at time step } j \,. \end{cases} \tag{8.286}$$

Clearly $\langle \sigma_j \rangle = 0$, so $\langle x_n \rangle = 0$. Now let us compute

$$\langle x_n^2 \rangle = \ell^2 \sum_{j=1}^n \sum_{j'=1}^n \langle \sigma_j \sigma_{j'} \rangle = n\ell^2 \,, \tag{8.287}$$

where we invoke

$$\langle \sigma_j \sigma_{j'} \rangle = \delta_{jj'} \,. \tag{8.288}$$

If the length of each time step is τ, then we have, with $t = n\tau$,

$$\langle x^2(t) \rangle = \frac{\ell^2}{\tau}\,t \,, \tag{8.289}$$

and we identify the diffusion constant

$$D = \frac{\ell^2}{2\tau} \,. \tag{8.290}$$

Suppose, however, the random walk is *biased*, so that the probability for each independent step is given by

$$P(\sigma) = p\,\delta_{\sigma,1} + q\,\delta_{\sigma,-1} \,, \tag{8.291}$$

where $p + q = 1$. Then

$$\langle \sigma_j \rangle = p - q = 2p - 1 \tag{8.292}$$

and

$$\begin{aligned}
\langle \sigma_j \sigma_{j'} \rangle &= (p-q)^2 \left(1 - \delta_{jj'}\right) + \delta_{jj'} \\
&= (2p-1)^2 + 4\,p\,(1-p)\,\delta_{jj'} \,.
\end{aligned} \tag{8.293}$$

Then

$$\langle x_n \rangle = (2p-1)\,\ell n \tag{8.294}$$

$$\langle x_n^2 \rangle - \langle x_n \rangle^2 = 4\,p\,(1-p)\,\ell^2 n \,. \tag{8.295}$$

8.10.4   Fokker-Planck equation

Suppose $x(t)$ is a stochastic variable. We define the quantity

$$\delta x(t) \equiv x(t + \delta t) - x(t) \,, \tag{8.296}$$

and we assume

$$\langle \delta x(t) \rangle = F_1\big(x(t)\big)\,\delta t \tag{8.297}$$

$$\big\langle [\delta x(t)]^2 \big\rangle = F_2\big(x(t)\big)\,\delta t \tag{8.298}$$

but $\big\langle [\delta x(t)]^n \big\rangle = \mathcal{O}\big((\delta t)^2\big)$ for $n > 2$. The $n = 1$ term is due to *drift* and the $n = 2$ term is due to *diffusion*. Now consider the conditional probability density, $P(x, t \,|\, x_0, t_0)$, defined to be the probability distribution for $x \equiv x(t)$ given that $x(t_0) = x_0$. The conditional probability density satisfies the composition rule,

$$P(x_2, t_2 \,|\, x_0, t_0) = \int\limits_{-\infty}^{\infty} dx_1\, P(x_2, t_2 \,|\, x_1, t_1)\, P(x_1, t_1 \,|\, x_0, t_0) \,, \tag{8.299}$$

for any value of t_1. This is also known as the *Chapman-Kolmogorov equation*. In words, what it says is that the probability density for a particle being at x_2 at time t_2, given that it was at x_0 at time t_0, is given by the product of the probability density for being at x_2 at time t_2 given that it was at x_1 at t_1, multiplied by that for being at x_1 at t_1 given it was at x_0 at t_0, integrated over x_1. This should be intuitively obvious, since if we pick any time $t_1 \in [t_0, t_2]$, then the particle had to be *somewhere* at that time. Indeed, one wonders how Chapman and Kolmogorov got their names attached to a result that is so obvious. At any rate, a picture is worth a thousand words: see fig. 8.9.

Proceeding, we may write

$$P(x, t + \delta t \,|\, x_0, t_0) = \int\limits_{-\infty}^{\infty} dx'\, P(x, t + \delta t \,|\, x', t)\, P(x', t \,|\, x_0, t_0) \,. \tag{8.300}$$

Now

$$\begin{aligned}
P(x, t + \delta t \,|\, x', t) &= \big\langle \delta\big(x - \delta x(t) - x'\big) \big\rangle \\
&= \left\{ 1 + \langle \delta x(t) \rangle \,\frac{d}{dx'} + \tfrac{1}{2}\big\langle [\delta x(t)]^2 \big\rangle\, \frac{d^2}{dx'^2} + \dots \right\} \delta(x - x') \\
&= \delta(x - x') + F_1(x')\,\frac{d\,\delta(x - x')}{dx'}\,\delta t + \tfrac{1}{2} F_2(x')\,\frac{d^2\delta(x - x')}{dx'^2}\,\delta t + \mathcal{O}\big((\delta t)^2\big) \,,
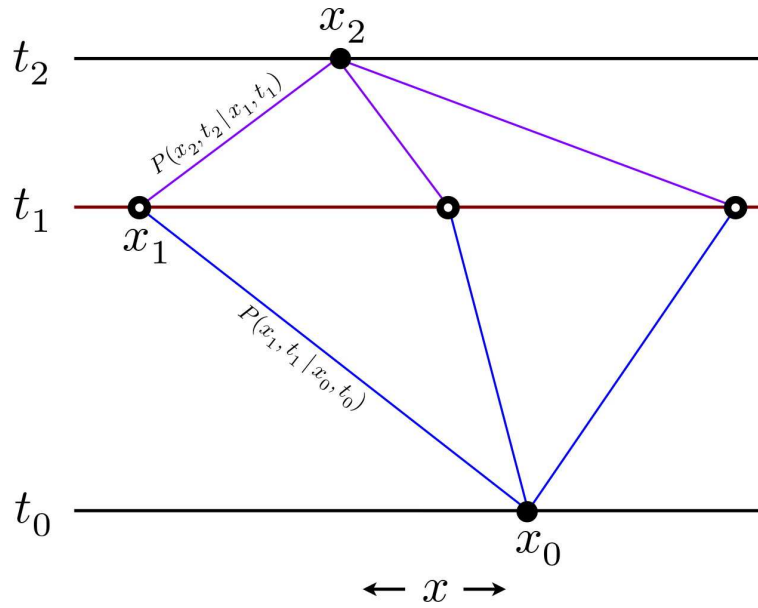\end{aligned} \tag{8.301}$$

Figure 8.9: Interpretive sketch of the mathematics behind the Chapman-Kolmogorov equation.

where the average is over the random variables. We now insert this result into eqn. 8.300, integrate by parts, divide by δt, and then take the limit $\delta t \rightarrow 0$. The result is the Fokker-Planck equation,

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\big[F_1(x)\, P(x,t)\big] + \frac{1}{2}\frac{\partial^2}{\partial x^2}\big[F_2(x)\, P(x,t)\big]\ . \tag{8.302}$$

8.10.5 Brownian motion redux

Let's apply our Fokker-Planck equation to a description of Brownian motion. From our earlier results, we have

$$F_1(x) = \frac{F}{\gamma M} \qquad , \qquad F_2(x) = 2D\ . \tag{8.303}$$

A formal proof of these results is left as an exercise for the reader. The Fokker-Planck equation is then

$$\frac{\partial P}{\partial t} = -u\,\frac{\partial P}{\partial x} + D\,\frac{\partial^2 P}{\partial x^2}\ , \tag{8.304}$$

where $u = F/\gamma M$ is the average terminal velocity. If we make a Galilean transformation and define

$$y = x - ut \qquad , \qquad s = t \tag{8.305}$$

then our Fokker-Planck equation takes the form

$$\frac{\partial P}{\partial s} = D\,\frac{\partial^2 P}{\partial y^2}\ . \tag{8.306}$$

This is known as the *diffusion equation*. Eqn. 8.304 is also a diffusion equation, rendered in a moving frame.

While the Galilean transformation is illuminating, we can easily solve eqn. 8.304 without it. Let's take a look at this equation after Fourier transforming from x to q:

$$P(x,t) = \int\limits_{-\infty}^{\infty} \frac{dq}{2\pi} \, e^{iqx} \, \hat{P}(q,t) \tag{8.307}$$

$$\hat{P}(q,t) = \int\limits_{-\infty}^{\infty} dx \, e^{-iqx} \, P(x,t) \, . \tag{8.308}$$

Then as should be well known to you by now, we can replace the operator $\frac{\partial}{\partial x}$ with multiplication by iq, resulting in

$$\frac{\partial}{\partial t} \hat{P}(q,t) = -(Dq^2 + iqu) \, \hat{P}(q,t) \, , \tag{8.309}$$

with solution

$$\hat{P}(q,t) = e^{-Dq^2 t} \, e^{-iqut} \, \hat{P}(q,0) \, . \tag{8.310}$$

We now apply the inverse transform to get back to x-space:

$$
\begin{aligned}
P(x,t) &= \int\limits_{-\infty}^{\infty} \frac{dq}{2\pi} \, e^{iqx} \, e^{-Dq^2 t} \, e^{-iqut} \int\limits_{-\infty}^{\infty} dx' \, e^{-iqx'} \, P(x',0) \\
&= \int\limits_{-\infty}^{\infty} dx' \, P(x',0) \int\limits_{-\infty}^{\infty} \frac{dq}{2\pi} \, e^{-Dq^2 t} \, e^{iq(x-ut-x')} \\
&= \int\limits_{-\infty}^{\infty} dx' \, K(x-x',t) \, P(x',0) \, ,
\end{aligned}
\tag{8.311}
$$

where

$$K(x,t) = \frac{1}{\sqrt{4\pi Dt}} \, e^{-(x-ut)^2/4Dt} \tag{8.312}$$

is the *diffusion kernel*. We now have a recipe for obtaining $P(x,t)$ given the initial conditions $P(x,0)$. If $P(x,0) = \delta(x)$, describing a particle confined to an infinitesimal region about the origin, then $P(x,t) = K(x,t)$ is the probability distribution for finding the particle at x at time t. There are two aspects to $K(x,t)$ which merit comment. The first is that the center of the distribution moves with velocity u. This is due to the presence of the external force. The second is that the standard deviation $\sigma = \sqrt{2Dt}$ is increasing in time, so the distribution is not only shifting its center but it is also getting broader as time evolves. This movement of the center and broadening are what we have called *drift* and *diffusion*, respectively.

8.10.6 Master Equation

Another way to model stochastic processes is via the *master equation*, which was discussed in chapter 3. Recall that if $P_i(t)$ is the probability for a system to be in state $|\,i\,\rangle$ at time t and W_{ij} is the transition rate from state $|\,j\,\rangle$ to state $|\,i\,\rangle$, then

$$\frac{dP_i}{dt} = \sum_j \left(W_{ij} P_j - W_{ji} P_i \right) \, . \tag{8.313}$$

Consider now a model in which the states $|\,n\,\rangle$ are labeled by nonnegative integers. Let α_n denote the rate of transitions from $|\,n\,\rangle \to |\,n+1\,\rangle$ and let β_n denote the rate of transitions from $|\,n\,\rangle \to |\,n-1\,\rangle$. The master equation

then takes the form[17]

$$\frac{dP_n}{dt} = \alpha_{n-1} P_{n-1} + \beta_{n+1} P_{n+1} - (\alpha_n + \beta_n) P_n \ . \tag{8.314}$$

Let us assume we can write $\alpha_n = K\bar{\alpha}(n/K)$ and $\beta_n = K\bar{\beta}(n/K)$, where $K \gg 1$. We assume the distribution $P_n(t)$ has a time-dependent maximum at $n = K\phi(t)$ and a width proportional to $\sqrt{K}$. We expand relative to this maximum, writing

$$n \equiv K\phi(t) + \sqrt{K}\,\xi \ , \tag{8.315}$$

and we define

$$P_n(t) \equiv \Pi(\xi, t) \ . \tag{8.316}$$

We now rewrite the master equation in eqn. 8.314 in terms of $\Pi(\xi, t)$. Since n is an independent variable, we set

$$dn = K\dot{\phi}\,dt + \sqrt{K}\,d\xi \quad \Rightarrow \quad d\xi\big|_n = -\sqrt{K}\,\dot{\phi}\,dt \ . \tag{8.317}$$

Therefore

$$\frac{dP_n}{dt} = -\sqrt{K}\,\dot{\phi}\,\frac{\partial \Pi}{\partial \xi} + \frac{\partial \Pi}{\partial t} \ . \tag{8.318}$$

Next, we write, for any function f_n,

$$\begin{aligned}
f_n &= Kf\big(\phi + K^{-1/2}\xi\big) \\
&= Kf(\phi) + K^{1/2}\,\xi\,f'(\phi) + \tfrac{1}{2}\,\xi^2\,f''(\phi) + \dots \ .
\end{aligned} \tag{8.319}$$

Similarly,

$$\begin{aligned}
f_{n\pm 1} &= Kf\big(\phi + K^{-1/2}\xi \pm K^{-1}\big) \\
&= Kf(\phi) + K^{1/2}\,\xi\,f'(\phi) \pm f'(\phi) + \tfrac{1}{2}\,\xi^2\,f''(\phi) + \dots \ .
\end{aligned} \tag{8.320}$$

Dividing both sides of eqn. 8.314 by $\sqrt{K}$, we have

$$-\frac{\partial \Pi}{\partial \xi}\,\dot{\phi} + K^{-1/2}\frac{\partial \Pi}{\partial t} = (\bar{\beta} - \bar{\alpha})\frac{\partial \Pi}{\partial \xi} + K^{-1/2}\left\{ (\bar{\beta}' - \bar{\alpha}')\,\xi\,\frac{\partial \Pi}{\partial \xi} + \tfrac{1}{2}(\bar{\alpha} + \bar{\beta})\frac{\partial^2 \Pi}{\partial \xi^2} + (\bar{\beta}' - \bar{\alpha}')\Pi \right\} + \dots \ . \tag{8.321}$$

Equating terms of order K^0 yields the equation

$$\dot{\phi} = \bar{\alpha}(\phi) - \bar{\beta}(\phi) \ . \tag{8.322}$$

Equating terms of order $K^{-1/2}$ yields the Fokker-Planck equation,

$$\frac{\partial \Pi}{\partial t} = (\bar{\beta} - \bar{\alpha})\frac{\partial}{\partial \xi}(\xi\,\Pi) + \tfrac{1}{2}(\bar{\alpha} + \bar{\beta})\frac{\partial^2 \Phi}{\partial \xi^2} \ , \tag{8.323}$$

where $\bar{\alpha} = \bar{\alpha}\big(\phi(t)\big)$ and $\bar{\beta} = \bar{\beta}\big(\phi(t)\big)$ are to be regarded as functions of t, *i.e.* $\bar{\alpha}(t)$ and $\bar{\beta}(t)$.

If in the limit $t \to \infty$, eqn. 8.322 evolves to a stable fixed point ϕ^*, then the stationary solution of the Fokker-Planck eqn. 8.323, $\Pi_{\text{eq}}(\xi) = \Pi(\xi, t = \infty)$ must satisfy

$$(\bar{\beta} - \bar{\alpha})\frac{\partial}{\partial \xi}(\xi\,\Pi_{\text{eq}}) + \tfrac{1}{2}(\bar{\alpha} + \bar{\beta})\frac{\partial^2 \Pi_{\text{eq}}}{\partial \xi^2} = 0 \quad \Rightarrow \quad \Pi_{\text{eq}}(\xi) = \frac{1}{\sqrt{2\pi\sigma^2}}\,e^{-\xi^2/2\sigma^2} \ , \tag{8.324}$$

where

$$\sigma^2 = \frac{\beta(\phi^*) + \alpha(\phi^*)}{\beta(\phi^*) - \alpha(\phi^*)} \ . \tag{8.325}$$

---

[17]We further demand $\beta_{n=0} = 0$ and $P_{-1}(t) = 0$ at all times.

8.11   Appendix I : Boltzmann Equation and Collisional Invariants

Problem : The linearized Boltzmann operator $L\psi$ is a complicated functional. Suppose we replace L by $\mathcal{L}$, where

$$
\mathcal{L}\psi = -\gamma\,\psi(\boldsymbol{v},t) + \gamma\left(\frac{m}{2\pi k_{\rm B}T}\right)^{3/2}\int d^3 u\,\exp\left(-\frac{m\boldsymbol{u}^2}{2k_{\rm B}T}\right)
$$
$$
\times\left\{1 + \frac{m}{k_{\rm B}T}\,\boldsymbol{u}\cdot\boldsymbol{v} + \frac{2}{3}\left(\frac{m\boldsymbol{u}^2}{2k_{\rm B}T} - \frac{3}{2}\right)\left(\frac{m\boldsymbol{v}^2}{2k_{\rm B}T} - \frac{3}{2}\right)\right\}\psi(\boldsymbol{u},t)\,.
$$
(8.326)

Show that $\mathcal{L}$ shares all the important properties of L. What is the meaning of γ? Expand $\psi(\boldsymbol{v},t)$ in spherical harmonics and Sonine polynomials,

$$
\psi(\boldsymbol{v},t) = \sum_{r\ell m} a_{r\ell m}(t)\,S^r_{\ell+\frac{1}{2}}(x)\,x^{\ell/2}\,Y^\ell_m(\hat{\boldsymbol{n}}),
$$
(8.327)

with $x = mv^2/2k_{\rm B}T$, and thus express the action of the linearized Boltzmann operator algebraically on the expansion coefficients $a_{r\ell m}(t)$.

The Sonine polynomials $S^n_\alpha(x)$ are a complete, orthogonal set which are convenient to use in the calculation of transport coefficients. They are defined as

$$
S^n_\alpha(x) = \sum_{m=0}^{n}\frac{\Gamma(\alpha+n+1)\,(-x)^m}{\Gamma(\alpha+m+1)\,(n-m)!\,m!}\,,
$$
(8.328)

and satisfy the generalized orthogonality relation

$$
\int\limits_0^\infty dx\,e^{-x}\,x^\alpha\,S^n_\alpha(x)\,S^{n'}_\alpha(x) = \frac{\Gamma(\alpha+n+1)}{n!}\,\delta_{nn'}\,.
$$
(8.329)

Solution : The 'important properties' of L are that it annihilate the five collisional invariants, *i.e.* 1, $\boldsymbol{v}$, and v^2, and that all other eigenvalues are *negative*. That this is true for $\mathcal{L}$ can be verified by an explicit calculation.

Plugging the conveniently parameterized form of $\psi(\boldsymbol{v},t)$ into $\mathcal{L}$, we have

$$
\mathcal{L}\psi = -\gamma\sum_{r\ell m} a_{r\ell m}(t)\,S^r_{\ell+\frac{1}{2}}(x)\,x^{\ell/2}\,Y^\ell_m(\hat{\boldsymbol{n}}) + \frac{\gamma}{2\pi^{3/2}}\sum_{r\ell m} a_{r\ell m}(t)\int\limits_0^\infty dx_1\,x_1^{1/2}\,e^{-x_1}
$$
$$
\times\int d\hat{\boldsymbol{n}}_1\left[1 + 2\,x^{1/2}x_1^{1/2}\,\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{n}}_1 + \tfrac{2}{3}\left(x-\tfrac{3}{2}\right)\left(x_1-\tfrac{3}{2}\right)\right]S^r_{\ell+\frac{1}{2}}(x_1)\,x_1^{\ell/2}\,Y^\ell_m(\hat{\boldsymbol{n}}_1)\,,
$$
(8.330)

where we've used

$$
u = \sqrt{\frac{2k_{\rm B}T}{m}}\,x_1^{1/2}\qquad,\qquad du = \sqrt{\frac{k_{\rm B}T}{2m}}\,x_1^{-1/2}\,dx_1\,.
$$
(8.331)

Now recall $Y^0_0(\hat{\boldsymbol{n}}) = \frac{1}{\sqrt{4\pi}}$ and

$$
Y^1_1(\hat{\boldsymbol{n}}) = -\sqrt{\frac{3}{8\pi}}\,\sin\theta\,e^{i\varphi}\qquad\qquad Y^1_0(\hat{\boldsymbol{n}}) = \sqrt{\frac{3}{4\pi}}\,\cos\theta\qquad\qquad Y^1_{-1}(\hat{\boldsymbol{n}}) = +\sqrt{\frac{3}{8\pi}}\,\sin\theta\,e^{-i\varphi}
$$

$$
S^0_{1/2}(x) = 1\qquad\qquad\qquad\qquad S^0_{3/2}(x) = 1\qquad\qquad\qquad\qquad S^1_{1/2}(x) = \tfrac{3}{2} - x\,,
$$

which allows us to write

$$1 = 4\pi \, Y_0^0(\hat{\boldsymbol{n}}) \, Y_0^{0\,*}(\hat{\boldsymbol{n}}_1) \tag{8.332}$$

$$\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{n}}_1 = \frac{4\pi}{3} \left[Y_0^1(\hat{\boldsymbol{n}}) \, Y_0^{1\,*}(\hat{\boldsymbol{n}}_1) + Y_1^1(\hat{\boldsymbol{n}}) \, Y_1^{1\,*}(\hat{\boldsymbol{n}}_1) + Y_{-1}^1(\hat{\boldsymbol{n}}) \, Y_{-1}^{1\,*}(\hat{\boldsymbol{n}}_1) \right] . \tag{8.333}$$

We can do the integrals by appealing to the orthogonality relations for the spherical harmonics and Sonine polynomials:

$$\int d\hat{\boldsymbol{n}} \, Y_m^\ell(\hat{\boldsymbol{n}}) \, Y_{m'}^{l'\,*}(\hat{\boldsymbol{n}}) = \delta_{ll'} \, \delta_{mm'} \tag{8.334}$$

$$\int\limits_0^\infty dx \, e^{-x} \, x^\alpha \, S_\alpha^n(x) \, S_\alpha^{n'}(x) = \frac{\Gamma(n + \alpha + 1)}{\Gamma(n + 1)} \, \delta_{nn'} \,. \tag{8.335}$$

Integrating first over the direction vector $\hat{\boldsymbol{n}}_1$,

$$
\begin{aligned}
\mathcal{L}\psi = &-\gamma \sum_{r\ell m} a_{r\ell m}(t) \, S_{\ell+\frac{1}{2}}^r(x) \, x^{\ell/2} \, Y_m^\ell(\hat{\boldsymbol{n}}) \\
&+ \frac{2\gamma}{\sqrt{\pi}} \sum_{r\ell m} a_{r\ell m}(t) \int\limits_0^\infty dx_1 \, x_1^{1/2} \, e^{-x_1} \int d\hat{\boldsymbol{n}}_1 \left[Y_0^0(\hat{\boldsymbol{n}}) \, Y_0^{0\,*}(\hat{\boldsymbol{n}}_1) \, S_{1/2}^0(x) \, S_{1/2}^0(x_1) \right. \\
&+ \tfrac{2}{3} x^{1/2} x_1^{1/2} \sum_{m'=-1}^1 Y_{m'}^1(\hat{\boldsymbol{n}}) \, Y_{m'}^{1\,*}(\hat{\boldsymbol{n}}_1) \, S_{3/2}^0(x) \, S_{3/2}^0(x_1) \\
&\left. + \tfrac{2}{3} Y_0^0(\hat{\boldsymbol{n}}) \, Y_0^{0\,*}(\hat{\boldsymbol{n}}_1) \, S_{1/2}^1(x) \, S_{1/2}^1(x_1) \right] S_{\ell+\frac{1}{2}}^r(x_1) \, x_1^{\ell/2} \, Y_m^\ell(\hat{\boldsymbol{n}}_1) \,,
\end{aligned}
\tag{8.336}
$$

we obtain the intermediate result

$$
\begin{aligned}
\mathcal{L}\psi = &-\gamma \sum_{r\ell m} a_{r\ell m}(t) \, S_{\ell+\frac{1}{2}}^r(x) \, x^{\ell/2} \, Y_m^\ell(\hat{\boldsymbol{n}}) \\
&+ \frac{2\gamma}{\sqrt{\pi}} \sum_{r\ell m} a_{r\ell m}(t) \int\limits_0^\infty dx_1 \, x_1^{1/2} \, e^{-x_1} \left[Y_0^0(\hat{\boldsymbol{n}}) \, \delta_{l0} \, \delta_{m0} \, S_{1/2}^0(x) \, S_{1/2}^0(x_1) \right. \\
&+ \tfrac{2}{3} x^{1/2} x_1^{1/2} \sum_{m'=-1}^1 Y_{m'}^1(\hat{\boldsymbol{n}}) \, \delta_{l1} \, \delta_{mm'} \, S_{3/2}^0(x) \, S_{3/2}^0(x_1) \\
&\left. + \tfrac{2}{3} Y_0^0(\hat{\boldsymbol{n}}) \, \delta_{l0} \, \delta_{m0} \, S_{1/2}^1(x) \, S_{1/2}^1(x_1) \right] S_{\ell+\frac{1}{2}}^r(x_1) \, x_1^{1/2} \,.
\end{aligned}
\tag{8.337}
$$

Appealing now to the orthogonality of the Sonine polynomials, and recalling that

$$\Gamma(\tfrac{1}{2}) = \sqrt{\pi} \quad , \quad \Gamma(1) = 1 \quad , \quad \Gamma(z+1) = z\,\Gamma(z) \,, \tag{8.338}$$

we integrate over x_1. For the first term in brackets, we invoke the orthogonality relation with $n = 0$ and $\alpha = \frac{1}{2}$, giving $\Gamma(\frac{3}{2}) = \frac{1}{2}\sqrt{\pi}$. For the second bracketed term, we have $n = 0$ but $\alpha = \frac{3}{2}$, and we obtain $\Gamma(\frac{5}{2}) = \frac{3}{2}\Gamma(\frac{3}{2})$, while the third bracketed term involves leads to $n = 1$ and $\alpha = \frac{1}{2}$, also yielding $\Gamma(\frac{5}{2}) = \frac{3}{2}\Gamma(\frac{3}{2})$. Thus, we obtain the simple and pleasing result

$$\mathcal{L}\psi = -\gamma {\sum_{r\ell m}}' a_{r\ell m}(t) \, S_{\ell+\frac{1}{2}}^r(x) \, x^{\ell/2} \, Y_m^\ell(\hat{\boldsymbol{n}}) \tag{8.339}$$

where the prime on the sum indicates that the set

$$\mathrm{CI} = \Big\{ (0,0,0) , \quad (1,0,0) , \quad (0,1,1) , \quad (0,1,0) , \quad (0,1,-1) \Big\} \tag{8.340}$$

are to be excluded from the sum. But these are just the functions which correspond to the five collisional invariants! Thus, we learn that

$$\psi_{r\ell m}(\boldsymbol{v}) = \mathcal{N}_{r\ell m}\, S^r_{\ell+\frac{1}{2}}(x)\, x^{\ell/2}\, Y^\ell_m(\hat{\boldsymbol{n}}), \tag{8.341}$$

is an eigenfunction of $\mathcal{L}$ with eigenvalue $-\gamma$ if (r, ℓ, m) does not correspond to one of the five collisional invariants. In the latter case, the eigenvalue is zero. Thus, the algebraic action of $\mathcal{L}$ on the coefficients $a_{r\ell m}$ is

$$(\mathcal{L}a)_{r\ell m} = \begin{cases} -\gamma\, a_{r\ell m} & \text{if } (r,\ell,m) \notin \mathrm{CI} \\ = 0 & \text{if } (r,\ell,m) \in \mathrm{CI} \end{cases} \tag{8.342}$$

The quantity $\tau = \gamma^{-1}$ is the relaxation time.

It is pretty obvious that $\mathcal{L}$ is self-adjoint, since

$$
\begin{aligned}
\langle\, \phi \,|\, \mathcal{L}\psi \,\rangle &\equiv \int\! d^3v\, f^0(\boldsymbol{v})\, \phi(\boldsymbol{v})\, \mathcal{L}[\psi(\boldsymbol{v})] \\
&= -\gamma\, n \left(\frac{m}{2\pi k_{\mathrm{B}}T} \right)^{3/2} \int\! d^3v\, \exp\left(-\frac{m\boldsymbol{v}^2}{2k_{\mathrm{B}}T} \right) \phi(\boldsymbol{v})\, \psi(\boldsymbol{v}) \\
&\quad + \gamma\, n \left(\frac{m}{2\pi k_{\mathrm{B}}T} \right)^{3} \int\! d^3v \int\! d^3u\, \exp\left(-\frac{m\boldsymbol{u}^2}{2k_{\mathrm{B}}T} \right) \exp\left(-\frac{m\boldsymbol{v}^2}{2k_{\mathrm{B}}T} \right) \\
&\qquad \times \phi(\boldsymbol{v}) \left[1 + \frac{m}{k_{\mathrm{B}}T}\, \boldsymbol{u}\cdot\boldsymbol{v} + \frac{2}{3}\left(\frac{m\boldsymbol{u}^2}{2k_{\mathrm{B}}T} - \frac{3}{2} \right)\left(\frac{m\boldsymbol{v}^2}{2k_{\mathrm{B}}T} - \frac{3}{2} \right) \right] \psi(\boldsymbol{u}) \\
&= \langle\, \mathcal{L}\phi \,|\, \psi \,\rangle ,
\end{aligned}
\tag{8.343}
$$

where n is the bulk number density and $f^0(\boldsymbol{v})$ is the Maxwellian velocity distribution.

8.12 Appendix II : Distributions and Functionals

Let $x \in \mathbb{R}$ be a random variable, and $P(x)$ a probability distribution for x. The average of any function $\phi(x)$ is then

$$\langle \phi(x) \rangle = \int\limits_{-\infty}^{\infty} dx\, P(x)\, \phi(x) \Bigg/ \int\limits_{-\infty}^{\infty} dx\, P(x)\,. \tag{8.344}$$

Let $\eta(t)$ be a random *function* of t, with $\eta(t) \in \mathbb{R}$, and let $P\big[\eta(t)\big]$ be the probability distribution *functional* for $\eta(t)$. Then if $\Phi\big[\eta(t)\big]$ is a functional of $\eta(t)$, the average of Φ is given by

$$\int\! D\eta\, P\big[\eta(t)\big]\, \Phi\big[\eta(t)\big] \Bigg/ \int\! D\eta\, P\big[\eta(t)\big] \tag{8.345}$$

The expression $\int D\eta\, P[\eta]\, \Phi[\eta]$ is a *functional integral*. A functional integral is a continuum limit of a multivariable integral. Suppose $\eta(t)$ were defined on a set of t values $t_n = n\tau$. A functional of $\eta(t)$ becomes a multivariable function of the values $\eta_n \equiv \eta(t_n)$. The metric then becomes

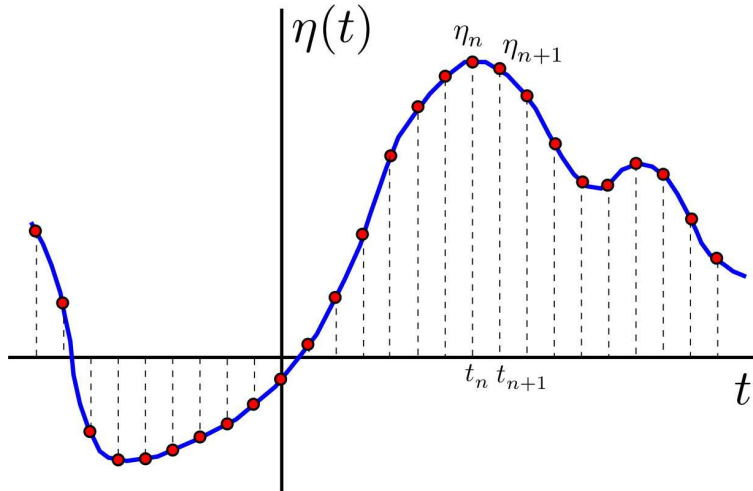$$D\eta \longrightarrow \prod_n d\eta_n\,. \tag{8.346}$$

Figure 8.10: Discretization of a continuous function $\eta(t)$. Upon discretization, a functional $\Phi\big[\eta(t)\big]$ becomes an ordinary multivariable function $\Phi(\{\eta_j\})$.

In fact, for our purposes we will not need to know any details about the functional measure $D\eta$; we will finesse this delicate issue[18]. Consider the *generating functional*,

$$Z\big[J(t)\big] = \int D\eta \, P[\eta] \, \exp\left(\int\limits_{-\infty}^{\infty} dt \, J(t) \, \eta(t) \right) . \tag{8.347}$$

It is clear that

$$\frac{1}{Z[J]} \frac{\delta^n Z[J]}{\delta J(t_1) \cdots \delta J(t_n)} \bigg|_{J(t)=0} = \big\langle \eta(t_1) \cdots \eta(t_n) \big\rangle . \tag{8.348}$$

The function $J(t)$ is an arbitrary *source function*. We differentiate with respect to it in order to find the η-field correlators.

Let's compute the generating function for a class of distributions of the Gaussian form,

$$P[\eta] = \exp\left(-\frac{1}{2\Gamma} \int\limits_{-\infty}^{\infty} dt \, \big(\tau^2 \, \dot\eta^2 + \eta^2\big) \right) \tag{8.349}$$

$$= \exp\left(-\frac{1}{2\Gamma} \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \big(1 + \omega^2\tau^2\big) \, \big|\hat\eta(\omega)\big|^2 \right) . \tag{8.350}$$

Then Fourier transforming the source function $J(t)$, it is easy to see that

$$Z[J] = Z[0] \cdot \exp\left(\frac{\Gamma}{2} \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \frac{\big|\hat J(\omega)\big|^2}{1 + \omega^2\tau^2} \right) . \tag{8.351}$$

Note that with $\eta(t) \in \mathbb{R}$ and $J(t) \in \mathbb{R}$ we have $\eta^*(\omega) = \eta(-\omega)$ and $J^*(\omega) = J(-\omega)$. Transforming back to real time,

---

[18]A discussion of measure for functional integrals is found in R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals*.

we have

$$Z[J] = Z[0] \cdot \exp\left(\frac{1}{2} \int\limits_{-\infty}^{\infty} dt \int\limits_{-\infty}^{\infty} dt' \, J(t) \, G(t-t') \, J(t') \right) , \tag{8.352}$$

where

$$G(s) = \frac{\Gamma}{2\tau} \, e^{-|s|/\tau} \qquad , \qquad \widehat{G}(\omega) = \frac{\Gamma}{1+\omega^2\tau^2} \tag{8.353}$$

is the *Green's function*, in real and Fourier space. Note that

$$\int\limits_{-\infty}^{\infty} ds \, G(s) = \widehat{G}(0) = \Gamma . \tag{8.354}$$

We can now compute

$$\left\langle \eta(t_1) \, \eta(t_2) \right\rangle = G(t_1 - t_2) \tag{8.355}$$

$$\left\langle \eta(t_1) \, \eta(t_2) \, \eta(t_3) \, \eta(t_4) \right\rangle = G(t_1 - t_2) \, G(t_3 - t_4) + G(t_1 - t_3) \, G(t_2 - t_4) \tag{8.356}$$
$$+ \, G(t_1 - t_4) \, G(t_2 - t_3) .$$

The generalization is now easy to prove, and is known as *Wick's theorem*:

$$\left\langle \eta(t_1) \cdots \eta(t_{2n}) \right\rangle = \sum_{\text{contractions}} G(t_{i_1} - t_{i_2}) \cdots G(t_{i_{2n-1}} - t_{i_{2n}}) , \tag{8.357}$$

where the sum is over all distinct *contractions* of the sequence 1-2$\cdots$2n into products of pairs. How many terms are there? Some simple combinatorics answers this question. Choose the index 1. There are $(2n-1)$ other time indices with which it can be contracted. Now choose another index. There are $(2n-3)$ indices with which *that* index can be contracted. And so on. We thus obtain

$$C(n) \equiv \frac{\text{\# of contractions}}{\text{of 1-2-3} \cdots 2n} = (2n-1)(2n-3) \cdots 3 \cdot 1 = \frac{(2n)!}{2^n \, n!} . \tag{8.358}$$

8.13   Appendix III : General Linear Autonomous Inhomogeneous ODEs

We can also solve general autonomous linear inhomogeneous ODEs of the form

$$\frac{d^n x}{dt^n} + a_{n-1} \frac{d^{n-1} x}{dt^{n-1}} + \ldots + a_1 \frac{dx}{dt} + a_0 \, x = \xi(t) . \tag{8.359}$$

We can write this as

$$\mathcal{L}_t \, x(t) = \xi(t) , \tag{8.360}$$

where $\mathcal{L}_t$ is the nth order differential operator

$$\mathcal{L}_t = \frac{d^n}{dt^n} + a_{n-1} \frac{d^{n-1}}{dt^{n-1}} + \ldots + a_1 \frac{d}{dt} + a_0 . \tag{8.361}$$

The general solution to the inhomogeneous equation is given by

$$x(t) = x_{\text{h}}(t) + \int\limits_{-\infty}^{\infty} dt' \, G(t, t') \, \xi(t') , \tag{8.362}$$

where $G(t, t')$ is the Green's function. Note that $\mathcal{L}_t\, x_{\mathrm{h}}(t) = 0$. Thus, in order for eqns. 8.360 and 8.362 to be true, we must have

$$\mathcal{L}_t\, x(t) = \overbrace{\mathcal{L}_t\, x_{\mathrm{h}}(t)}^{\text{this vanishes}} + \int\limits_{-\infty}^{\infty} dt'\, \mathcal{L}_t\, G(t, t')\, \xi(t') = \xi(t)\ , \qquad (8.363)$$

which means that

$$\mathcal{L}_t\, G(t, t') = \delta(t - t')\ , \qquad (8.364)$$

where $\delta(t - t')$ is the Dirac δ-function.

If the differential equation $\mathcal{L}_t\, x(t) = \xi(t)$ is defined over some finite or semi-infinite t interval with prescribed boundary conditions on $x(t)$ at the endpoints, then $G(t, t')$ will depend on t and t' separately. For the case we are now considering, let the interval be the entire real line $t \in (-\infty, \infty)$. Then $G(t, t') = G(t - t')$ is a function of the single variable $t - t'$.

Note that $\mathcal{L}_t = \mathcal{L}\!\left(\frac{d}{dt}\right)$ may be considered a function of the differential operator $\frac{d}{dt}$. If we now Fourier transform the equation $\mathcal{L}_t\, x(t) = \xi(t)$, we obtain

$$\int\limits_{-\infty}^{\infty} dt\, e^{i\omega t}\, \xi(t) = \int\limits_{-\infty}^{\infty} dt\, e^{i\omega t}\, \left\{ \frac{d^n}{dt^n} + a_{n-1}\frac{d^{n-1}}{dt^{n-1}} + \ldots + a_1\frac{d}{dt} + a_0 \right\} x(t)$$

$$= \int\limits_{-\infty}^{\infty} dt\, e^{i\omega t}\, \left\{ (-i\omega)^n + a_{n-1}\,(-i\omega)^{n-1} + \ldots + a_1\,(-i\omega) + a_0 \right\} x(t)\ . \qquad (8.365)$$

Thus, if we define

$$\hat{\mathcal{L}}(\omega) = \sum_{k=0}^{n} a_k\,(-i\omega)^k\ , \qquad (8.366)$$

then we have

$$\hat{\mathcal{L}}(\omega)\, \hat{x}(\omega) = \hat{\xi}(\omega)\ , \qquad (8.367)$$

where $a_n \equiv 1$. According to the Fundamental Theorem of Algebra, the nth degree polynomial $\hat{\mathcal{L}}(\omega)$ may be uniquely factored over the complex ω plane into a product over n roots:

$$\hat{\mathcal{L}}(\omega) = (-i)^n\,(\omega - \omega_1)(\omega - \omega_2)\cdots(\omega - \omega_n)\ . \qquad (8.368)$$

If the $\{a_k\}$ are all real, then $\left[\hat{\mathcal{L}}(\omega)\right]^* = \hat{\mathcal{L}}(-\omega^*)$, hence if Ω is a root then so is $-\Omega^*$. Thus, the roots appear in pairs which are symmetric about the imaginary axis. *I.e.* if $\Omega = a + ib$ is a root, then so is $-\Omega^* = -a + ib$.

The general solution to the homogeneous equation is

$$x_{\mathrm{h}}(t) = \sum_{\sigma=1}^{n} A_\sigma\, e^{-i\omega_\sigma t}\ , \qquad (8.369)$$

which involves n arbitrary complex constants A_i. The susceptibility, or Green's function in Fourier space, $\hat{G}(\omega)$ is then

$$\hat{G}(\omega) = \frac{1}{\hat{\mathcal{L}}(\omega)} = \frac{i^n}{(\omega - \omega_1)(\omega - \omega_2)\cdots(\omega - \omega_n)}\ , \qquad (8.370)$$

Note that $\left[\hat{G}(\omega)\right]^* = \hat{G}(-\omega)$, which is equivalent to the statement that $G(t - t')$ is a real function of its argument. The general solution to the inhomogeneous equation is then

$$x(t) = x_{\mathrm{h}}(t) + \int\limits_{-\infty}^{\infty} dt'\, G(t - t')\, \xi(t')\ , \qquad (8.371)$$

where $x_{\mathrm{h}}(t)$ is the solution to the homogeneous equation, *i.e.* with zero forcing, and where

$$
\begin{aligned}
G(t - t') &= \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, e^{-i\omega(t-t')}\, \hat{G}(\omega) \\
&= i^n \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \frac{e^{-i\omega(t-t')}}{(\omega - \omega_1)(\omega - \omega_2)\cdots(\omega - \omega_n)} \\
&= \sum_{\sigma=1}^{n} \frac{e^{-i\omega_\sigma(t-t')}}{i\, \mathcal{L}'(\omega_\sigma)}\, \Theta(t - t') \,,
\end{aligned}
\tag{8.372}
$$

where we assume that $\operatorname{Im}\omega_\sigma < 0$ for all σ. This guarantees *causality* – the *response* $x(t)$ to the *influence* $\xi(t')$ is nonzero only for $t > t'$.

As an example, consider the familiar case

$$
\begin{aligned}
\hat{\mathcal{L}}(\omega) &= -\omega^2 - i\gamma\omega + \omega_0^2 \\
&= -(\omega - \omega_+)\,(\omega - \omega_-)\,,
\end{aligned}
\tag{8.373}
$$

with $\omega_\pm = -\frac{i}{2}\gamma \pm \beta$, and $\beta = \sqrt{\omega_0^2 - \frac{1}{4}\gamma^2}$. This yields

$$
\mathcal{L}'(\omega_\pm) = \mp(\omega_+ - \omega_-) = \mp 2\beta\,.
\tag{8.374}
$$

Then according to equation 8.372,

$$
\begin{aligned}
G(s) &= \left\{ \frac{e^{-i\omega_+ s}}{i\mathcal{L}'(\omega_+)} + \frac{e^{-i\omega_- s}}{i\mathcal{L}'(\omega_-)} \right\} \Theta(s) \\
&= \left\{ \frac{e^{-\gamma s/2}\, e^{-i\beta s}}{-2i\beta} + \frac{e^{-\gamma s/2}\, e^{i\beta s}}{2i\beta} \right\} \Theta(s) \\
&= \beta^{-1}\, e^{-\gamma s/2}\, \sin(\beta s)\, \Theta(s)\,.
\end{aligned}
\tag{8.375}
$$

Now let us evaluate the two-point correlation function $\langle x(t)\,x(t')\rangle$, assuming the noise is correlated according to $\langle \xi(s)\,\xi(s')\rangle = \phi(s - s')$. We assume $t, t' \to \infty$ so the transient contribution x_{h} is negligible. We then have

$$
\begin{aligned}
\langle x(t)\,x(t')\rangle &= \int\limits_{-\infty}^{\infty} ds \int\limits_{-\infty}^{\infty} ds'\, G(t - s)\, G(t' - s')\, \langle \xi(s)\,\xi(s')\rangle \\
&= \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \hat{\phi}(\omega)\, \big|\hat{G}(\omega)\big|^2\, e^{i\omega(t-t')}\,.
\end{aligned}
\tag{8.376}
$$

Higher order ODEs

Note that any n^{th} order ODE, of the general form

$$
\frac{d^n x}{dt^n} = F\!\left(x\,, \frac{dx}{dt}\,, \ldots\,, \frac{d^{n-1}x}{dt^{n-1}} \right),
\tag{8.377}
$$

may be represented by the first order system $\dot{\boldsymbol{\varphi}} = \boldsymbol{V}(\boldsymbol{\varphi})$. To see this, define $\varphi_k = d^{k-1}x/dt^{k-1}$, with $k = 1, \ldots, n$. Thus, for $k < n$ we have $\dot{\varphi}_k = \varphi_{k+1}$, and $\dot{\varphi}_n = F$. In other words,

$$
\frac{d}{dt}\overbrace{\begin{pmatrix} \varphi_1 \\ \vdots \\ \varphi_{n-1} \\ \varphi_n \end{pmatrix}}^{\dot{\boldsymbol{\varphi}}} = \overbrace{\begin{pmatrix} \varphi_2 \\ \vdots \\ \varphi_n \\ F(\varphi_1, \ldots, \varphi_p) \end{pmatrix}}^{\boldsymbol{V}(\boldsymbol{\varphi})}. \tag{8.378}
$$

An inhomogeneous linear n^{th} order ODE,

$$
\frac{d^n x}{dt^n} + a_{n-1}\frac{d^{n-1}x}{dt^{n-1}} + \ldots + a_1\frac{dx}{dt} + a_0\, x = \xi(t) \tag{8.379}
$$

may be written in matrix form, as

$$
\frac{d}{dt}\begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \vdots \\ \varphi_n \end{pmatrix} = \overbrace{\begin{pmatrix} 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ -a_0 & -a_1 & -a_2 & \cdots & -a_{n-1} \end{pmatrix}}^{Q}\begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \vdots \\ \varphi_n \end{pmatrix} + \overbrace{\begin{pmatrix} 0 \\ 0 \\ \vdots \\ \xi(t) \end{pmatrix}}^{\boldsymbol{\xi}}. \tag{8.380}
$$

Thus,

$$
\dot{\boldsymbol{\varphi}} = Q\,\boldsymbol{\varphi} + \boldsymbol{\xi}, \tag{8.381}
$$

and if the coefficients c_k are time-independent, *i.e.* the ODE is *autonomous*.

For the homogeneous case where $\xi(t) = 0$, the solution is obtained by exponentiating the constant matrix Qt:

$$
\boldsymbol{\varphi}(t) = \exp(Qt)\,\boldsymbol{\varphi}(0) ; \tag{8.382}
$$

the exponential of a matrix may be given meaning by its Taylor series expansion. If the ODE is not autonomous, then $Q = Q(t)$ is time-dependent, and the solution is given by the path-ordered exponential,

$$
\boldsymbol{\varphi}(t) = \mathsf{P}\exp\left\{\int\limits_0^t dt'\, Q(t')\right\}\boldsymbol{\varphi}(0), \tag{8.383}
$$

where P is the *path ordering operator* which places earlier times to the right. As defined, the equation $\dot{\boldsymbol{\varphi}} = \boldsymbol{V}(\boldsymbol{\varphi})$ is autonomous, since the t-advance mapping g_t depends only on t and on no other time variable. However, by extending the phase space $\mathbb{M} \ni \boldsymbol{\varphi}$ from $\mathbb{M} \to \mathbb{M} \times \mathbb{R}$, which is of dimension $n + 1$, one can describe arbitrary time-dependent ODEs.

In general, path ordered exponentials are difficult to compute analytically. We will henceforth consider the autonomous case where Q is a constant matrix in time. We will assume the matrix Q is real, but other than that it has no helpful symmetries. We can however decompose it into left and right eigenvectors:

$$
Q_{ij} = \sum_{\sigma=1}^n \nu_\sigma\, R_{\sigma,i}\, L_{\sigma,j}. \tag{8.384}
$$

Or, in bra-ket notation, $Q = \sum_\sigma \nu_\sigma\, |R_\sigma\rangle\langle L_\sigma|$. The normalization condition we use is

$$
\langle\, L_\sigma \,|\, R_{\sigma'} \,\rangle = \delta_{\sigma\sigma'}, \tag{8.385}
$$

where $\{\nu_\sigma\}$ are the eigenvalues of Q. The eigenvalues may be real or imaginary. Since the characteristic polynomial $P(\nu) = \det(\nu\,\mathbb{I} - Q)$ has real coefficients, we know that the eigenvalues of Q are either real or come in complex conjugate pairs.

Consider, for example, the $n = 2$ system we studied earlier. Then

$$Q = \begin{pmatrix} 0 & 1 \\ -\omega_0^2 & -\gamma \end{pmatrix}. \tag{8.386}$$

The eigenvalues are as before: $\nu_\pm = -\frac{1}{2}\gamma \pm \sqrt{\frac{1}{4}\gamma^2 - \omega_0^2}$. The left and right eigenvectors are

$$L_\pm = \frac{\pm 1}{\nu_+ - \nu_-}\begin{pmatrix} -\nu_\mp & 1 \end{pmatrix} \quad , \qquad R_\pm = \begin{pmatrix} 1 \\ \nu_\pm \end{pmatrix}. \tag{8.387}$$

The utility of working in a left-right eigenbasis is apparent once we reflect upon the result

$$f(Q) = \sum_{\sigma=1}^n f(\nu_\sigma)\,\big|\,R_\sigma\,\big\rangle\big\langle\,L_\sigma\,\big| \tag{8.388}$$

for any function f. Thus, the solution to the general autonomous homogeneous case is

$$\big|\,\boldsymbol{\varphi}(t)\,\big\rangle = \sum_{\sigma=1}^n e^{\nu_\sigma t}\,\big|\,R_\sigma\,\big\rangle\big\langle\,L_\sigma\,\big|\,\boldsymbol{\varphi}(0)\,\big\rangle \tag{8.389}$$

$$\varphi_i(t) = \sum_{\sigma=1}^n e^{\nu_\sigma t}\,R_{\sigma,i}\sum_{j=1}^n L_{\sigma,j}\,\varphi_j(0)\,. \tag{8.390}$$

If $\mathrm{Re}\,(\nu_\sigma) \leq 0$ for all σ, then the initial conditions $\boldsymbol{\varphi}(0)$ are forgotten on time scales $\tau_\sigma = \nu_\sigma^{-1}$. Physicality demands that this is the case.

Now let's consider the inhomogeneous case where $\xi(t) \neq 0$. We begin by recasting eqn. 8.381 in the form

$$\frac{d}{dt}\big(e^{-Qt}\,\boldsymbol{\varphi}\big) = e^{-Qt}\,\boldsymbol{\xi}(t)\,. \tag{8.391}$$

We can integrate this directly:

$$\boldsymbol{\varphi}(t) = e^{Qt}\,\boldsymbol{\varphi}(0) + \int_0^t ds\,e^{Q(t-s)}\,\boldsymbol{\xi}(s)\,. \tag{8.392}$$

In component notation,

$$\varphi_i(t) = \sum_{\sigma=1}^n e^{\nu_\sigma t}\,R_{\sigma,i}\,\big\langle\,L_\sigma\,\big|\,\boldsymbol{\varphi}(0)\,\big\rangle + \sum_{\sigma=1}^n R_{\sigma,i}\int_0^t ds\,e^{\nu_\sigma(t-s)}\,\big\langle\,L_\sigma\,\big|\,\boldsymbol{\xi}(s)\,\big\rangle. \tag{8.393}$$

Note that the first term on the RHS is the solution to the homogeneous equation, as must be the case when $\boldsymbol{\xi}(s) = 0$.

The solution in eqn. 8.393 holds for general Q and $\boldsymbol{\xi}(s)$. For the particular form of Q and $\xi(s)$ in eqn. 8.380, we can proceed further. For starters, $\langle L_\sigma | \boldsymbol{\xi}(s)\rangle = L_{\sigma,n}\,\xi(s)$. We can further exploit a special feature of the Q matrix to analytically determine all its left and right eigenvectors. Applying Q to the right eigenvector $|R_\sigma\rangle$, we obtain

$$R_{\sigma,j} = \nu_\sigma\,R_{\sigma,j-1} \qquad (j > 1)\,. \tag{8.394}$$

We are free to choose $R_{\sigma,1} = 1$ for all σ and defer the issue of normalization to the derivation of the left eigenvectors. Thus, we obtain the pleasingly simple result,

$$R_{\sigma,k} = \nu_\sigma^{k-1} \ . \tag{8.395}$$

Applying Q to the left eigenvector $\langle L_\sigma |$, we obtain

$$-a_0 \, L_{\sigma,n} = \nu_\sigma \, L_{\sigma,1} \tag{8.396}$$

$$L_{\sigma,j-1} - a_{j-1} \, L_{\sigma,n} = \nu_\sigma \, L_{\sigma,j} \qquad (j > 1) \ . \tag{8.397}$$

From these equations we may derive

$$L_{\sigma,k} = -\frac{L_{\sigma,n}}{\nu_\sigma} \sum_{j=0}^{k-1} a_j \, \nu_\sigma^{j-k-1} = \frac{L_{\sigma,n}}{\nu_\sigma} \sum_{j=k}^{n} a_j \, \nu_\sigma^{j-k-1} \ . \tag{8.398}$$

The equality in the above equation is derived using the result $P(\nu_\sigma) = \sum_{j=0}^{n} a_j \, \nu_\sigma^j = 0$. Recall also that $a_n \equiv 1$. We now impose the normalization condition,

$$\sum_{k=1}^{n} L_{\sigma,k} \, R_{\sigma,k} = 1 \ . \tag{8.399}$$

This condition determines our last remaining unknown quantity (for a given σ), $L_{\sigma,p}$:

$$\langle \, L_\sigma \, | \, R_\sigma \, \rangle = L_{\sigma,n} \sum_{k=1}^{n} k \, a_k \, \nu_\sigma^{k-1} = P'(\nu_\sigma) \, L_{\sigma,n} \ , \tag{8.400}$$

where $P'(\nu)$ is the first derivative of the characteristic polynomial. Thus, we obtain another neat result,

$$L_{\sigma,n} = \frac{1}{P'(\nu_\sigma)} \ . \tag{8.401}$$

Now let us evaluate the general two-point correlation function,

$$C_{jj'}(t,t') \equiv \langle \varphi_j(t) \, \varphi_{j'}(t') \rangle - \langle \varphi_j(t) \rangle \langle \varphi_{j'}(t') \rangle \ . \tag{8.402}$$

We write

$$\langle \xi(s) \, \xi(s') \rangle = \phi(s - s') = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \hat{\phi}(\omega) \, e^{-i\omega(s-s')} \ . \tag{8.403}$$

When $\hat{\phi}(\omega)$ is constant, we have $\langle \xi(s) \, \xi(s') \rangle = \hat{\phi}(t) \, \delta(s - s')$. This is the case of so-called *white noise*, when all frequencies contribute equally. The more general case when $\hat{\phi}(\omega)$ is frequency-dependent is known as *colored noise*. Appealing to eqn. 8.393, we have

$$C_{jj'}(t,t') = \sum_{\sigma,\sigma'} \frac{\nu_\sigma^{j-1}}{P'(\nu_\sigma)} \frac{\nu_{\sigma'}^{j'-1}}{P'(\nu_{\sigma'})} \int_0^t ds \, e^{\nu_\sigma(t-s)} \int_0^{t'} ds' \, e^{\nu_{\sigma'}(t'-s')} \, \phi(s - s') \tag{8.404}$$

$$= \sum_{\sigma,\sigma'} \frac{\nu_\sigma^{j-1}}{P'(\nu_\sigma)} \frac{\nu_{\sigma'}^{j'-1}}{P'(\nu_{\sigma'})} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \frac{\hat{\phi}(\omega) \, (e^{-i\omega t} - e^{\nu_\sigma t})(e^{i\omega t'} - e^{\nu_{\sigma'} t'})}{(\omega - i\nu_\sigma)(\omega + i\nu_{\sigma'})} \ . \tag{8.405}$$

In the limit $t, t' \to \infty$, assuming $\mathrm{Re}\,(\nu_\sigma) < 0$ for all σ (*i.e.* no diffusion), the exponentials $e^{\nu_\sigma t}$ and $e^{\nu_{\sigma'} t'}$ may be neglected, and we then have

$$C_{jj'}(t,t') = \sum_{\sigma,\sigma'} \frac{\nu_\sigma^{j-1}}{P'(\nu_\sigma)} \frac{\nu_{\sigma'}^{j'-1}}{P'(\nu_{\sigma'})} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \frac{\hat{\phi}(\omega) \, e^{-i\omega(t-t')}}{(\omega - i\nu_\sigma)(\omega + i\nu_{\sigma'})} \ . \tag{8.406}$$

8.14   Appendix IV : Correlations in the Langevin formalism

As shown above, integrating the Langevin equation $\dot{p} + \gamma p = F + \eta(t)$ yields

$$p(t) = p(0)\, e^{-\gamma t} + \frac{F}{\gamma}\left(1 - e^{-\gamma t}\right) + \int_0^t ds\, \eta(s)\, e^{\gamma(s-t)} \,. \tag{8.407}$$

. Thus, the momentum autocorrelator is

$$\langle p(t)\, p(t')\rangle - \langle p(t)\rangle\langle p(t')\rangle = \int_0^t ds \int_0^{t'} ds'\, e^{\gamma(s-t)}\, e^{\gamma(s'-t')}\, \langle \eta(s)\, \eta(s')\rangle$$

$$= \Gamma\, e^{-\gamma(t+t')} \int_0^{t_{\min}} ds\, e^{2\gamma s} = Mk_{\mathrm{B}}T\left(e^{-\gamma|t-t'|} - e^{-\gamma(t+t')}\right) , \tag{8.408}$$

where

$$t_{\min} = \min(t, t') = \begin{cases} t & \text{if } t < t' \\ t' & \text{if } t' < t \end{cases} \tag{8.409}$$

is the lesser of t and t'. Here we have used the result

$$\int_0^t ds \int_0^{t'} ds'\, e^{\gamma(s+s')}\, \delta(s - s') = \int_0^{t_{\min}} ds \int_0^{t_{\min}} ds'\, e^{\gamma(s+s')}\, \delta(s - s')$$

$$= \int_0^{t_{\min}} ds\, e^{2\gamma s} = \frac{1}{2\gamma}\left(e^{2\gamma t_{\min}} - 1\right) . \tag{8.410}$$

One way to intuitively understand this result is as follows. The double integral over s and s' is over a rectangle of dimensions $t \times t'$. Since the δ-function can only be satisfied when $s = s'$, there can be no contribution to the integral from regions where $s > t'$ or $s' > t$. Thus, the only contributions can arise from integration over the square of dimensions $t_{\min} \times t_{\min}$. Note also

$$t + t' - 2\min(t, t') = |t - t'| \,. \tag{8.411}$$

Let's now compute the position $x(t)$. We have

$$x(t) = x(0) + \frac{1}{M} \int_0^t ds\, p(s)$$

$$= x(0) + \int_0^t ds \left[\left(v(0) - \frac{F}{\gamma M}\right) e^{-\gamma s} + \frac{F}{\gamma M}\right] + \frac{1}{M} \int_0^t ds \int_0^s ds_1\, \eta(s_1)\, e^{\gamma(s_1-s)} \tag{8.412}$$

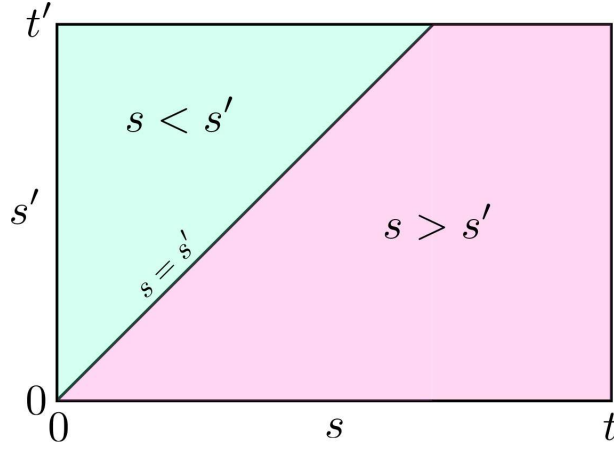$$= \langle x(t)\rangle + \frac{1}{M} \int_0^t ds \int_0^s ds_1\, \eta(s_1)\, e^{\gamma(s_1-s)} \,,$$

Figure 8.11: Regions for some of the double integrals encountered in the text.

with $v = p/M$. Since $\langle \eta(t) \rangle = 0$, we have

$$
\begin{aligned}
\langle x(t) \rangle &= x(0) + \int_0^t ds \left[\left(v(0) - \frac{F}{\gamma M} \right) e^{-\gamma s} + \frac{F}{\gamma M} \right] \\
&= x(0) + \frac{Ft}{\gamma M} + \frac{1}{\gamma} \left(v(0) - \frac{F}{\gamma M} \right) \left(1 - e^{-\gamma t} \right) .
\end{aligned}
\tag{8.413}
$$

Note that for $\gamma t \ll 1$ we have $\langle x(t) \rangle = x(0) + v(0)\, t + \frac{1}{2} M^{-1} F t^2 + \mathcal{O}(t^3)$, as is appropriate for ballistic particles moving under the influence of a constant force. This long time limit of course agrees with our earlier evaluation for the terminal velocity, $v_\infty = \langle p(\infty) \rangle / M = F/\gamma M$.

We next compute the position autocorrelation:

$$
\begin{aligned}
\langle x(t)\, x(t') \rangle - \langle x(t) \rangle \langle x(t') \rangle &= \frac{1}{M^2} \int_0^t ds \int_0^{t'} ds'\, e^{-\gamma(s+s')} \int_0^s ds_1 \int_0^{s'} ds_1'\, e^{\gamma(s_1+s_2)} \langle \eta(s_1)\, \eta(s_2) \rangle \\
&= \frac{\Gamma}{2\gamma M^2} \int_0^t ds \int_0^{t'} ds' \left(e^{-\gamma|s-s'|} - e^{-\gamma(s+s')} \right)
\end{aligned}
\tag{8.414}
$$

We have to be careful in computing the double integral of the first term in brackets on the RHS. We can assume, without loss of generality, that $t \geq t'$. Then

$$
\begin{aligned}
\int_0^t ds \int_0^{t'} ds'\, e^{-\gamma|s-s'|} &= \int_0^{t'} ds'\, e^{\gamma s'} \int_{s'}^t ds\, e^{-\gamma s} + \int_0^{t'} ds'\, e^{-\gamma s'} \int_0^{s'} ds\, e^{\gamma s} \\
&= 2\gamma^{-1} t' + \gamma^{-2} \left(e^{-\gamma t} + e^{-\gamma t'} - 1 - e^{-\gamma(t-t')} \right) .
\end{aligned}
\tag{8.415}
$$

We then find, for $t > t'$,

$$
\langle x(t)\, x(t') \rangle - \langle x(t) \rangle \langle x(t') \rangle = \frac{2k_{\mathrm{B}}T}{\gamma M}\, t' + \frac{k_{\mathrm{B}}T}{\gamma^2 M} \left(2e^{-\gamma t} + 2e^{-\gamma t'} - 2 - e^{-\gamma(t-t')} - e^{-\gamma(t+t')} \right) .
\tag{8.416}
$$

In particular, the equal time autocorrelator is

$$\left\langle x^2(t) \right\rangle - \left\langle x(t) \right\rangle^2 = \frac{2k_{\mathrm{B}}T}{\gamma M}\, t + \frac{k_{\mathrm{B}}T}{\gamma^2 M}\left(4e^{-\gamma t} - 3 - e^{-2\gamma t}\right). \tag{8.417}$$

We see that for long times

$$\left\langle x^2(t) \right\rangle - \left\langle x(t) \right\rangle^2 \sim 2Dt \,, \tag{8.418}$$

where $D = k_{\mathrm{B}}T/\gamma M$ is the diffusion constant.

8.15   Appendix V : Kramers-Krönig Relations

Suppose $\hat{\chi}(\omega) \equiv \hat{G}(\omega)$ is analytic in the UHP[19]. Then for all ν, we must have

$$\int\limits_{-\infty}^{\infty} \frac{d\nu}{2\pi}\, \frac{\hat{\chi}(\nu)}{\nu - \omega + i\epsilon} = 0 \,, \tag{8.419}$$

where ϵ is a positive infinitesimal. The reason is simple: just close the contour in the UHP, assuming $\hat{\chi}(\omega)$ vanishes sufficiently rapidly that Jordan's lemma can be applied. Clearly this is an extremely weak restriction on $\hat{\chi}(\omega)$, given the fact that the denominator already causes the integrand to vanish as $|\omega|^{-1}$.

Let us examine the function

$$\frac{1}{\nu - \omega + i\epsilon} = \frac{\nu - \omega}{(\nu - \omega)^2 + \epsilon^2} - \frac{i\epsilon}{(\nu - \omega)^2 + \epsilon^2}\,. \tag{8.420}$$

which we have separated into real and imaginary parts. Under an integral sign, the first term, in the limit $\epsilon \to 0$, is equivalent to taking a *principal part* of the integral. That is, for any function $F(\nu)$ which is regular at $\nu = \omega$,

$$\lim_{\epsilon \to 0} \int\limits_{-\infty}^{\infty} \frac{d\nu}{2\pi}\, \frac{\nu - \omega}{(\nu - \omega)^2 + \epsilon^2}\, F(\nu) \equiv \wp \int\limits_{-\infty}^{\infty} \frac{d\nu}{2\pi}\, \frac{F(\nu)}{\nu - \omega}\,. \tag{8.421}$$

The *principal part* symbol $\wp$ means that the singularity at $\nu = \omega$ is elided, either by smoothing out the function $1/(\nu - \epsilon)$ as above, or by simply cutting out a region of integration of width ϵ on either side of $\nu = \omega$.

The imaginary part is more interesting. Let us write

$$h(u) \equiv \frac{\epsilon}{u^2 + \epsilon^2}\,. \tag{8.422}$$

For $|u| \gg \epsilon$, $h(u) \simeq \epsilon/u^2$, which vanishes as $\epsilon \to 0$. For $u = 0$, $h(0) = 1/\epsilon$ which diverges as $\epsilon \to 0$. Thus, $h(u)$ has a huge peak at $u = 0$ and rapidly decays to 0 as one moves off the peak in either direction a distance greater that ϵ. Finally, note that

$$\int\limits_{-\infty}^{\infty} du\, h(u) = \pi \,, \tag{8.423}$$

a result which itself is easy to show using contour integration. Putting it all together, this tells us that

$$\lim_{\epsilon \to 0} \frac{\epsilon}{u^2 + \epsilon^2} = \pi\delta(u) \,. \tag{8.424}$$

---

[19]In this section, we use the notation $\hat{\chi}(\omega)$ for the susceptibility, rather than $\hat{G}(\omega)$

Thus, for positive infinitesimal ϵ,

$$\frac{1}{u \pm i\epsilon} = \frac{\wp}{u} \mp i\pi\delta(u) \,, \tag{8.425}$$

a most useful result.

We now return to our initial result 8.419, and we separate $\hat{\chi}(\omega)$ into real and imaginary parts:

$$\hat{\chi}(\omega) = \hat{\chi}'(\omega) + i\hat{\chi}''(\omega) \,. \tag{8.426}$$

(In this equation, the primes do not indicate differentiation with respect to argument.) We therefore have, for every real value of ω,

$$0 = \int\limits_{-\infty}^{\infty} \frac{d\nu}{2\pi} \left[\chi'(\nu) + i\chi''(\nu) \right] \left[\frac{\wp}{\nu - \omega} - i\pi\delta(\nu - \omega) \right] \,. \tag{8.427}$$

Taking the real and imaginary parts of this equation, we derive the *Kramers-Krönig relations*:

$$\chi'(\omega) \;\; = \;\; +\wp \int\limits_{-\infty}^{\infty} \frac{d\nu}{\pi} \frac{\hat{\chi}''(\nu)}{\nu - \omega} \tag{8.428}$$

$$\chi''(\omega) \;\; = \;\; -\wp \int\limits_{-\infty}^{\infty} \frac{d\nu}{\pi} \frac{\hat{\chi}'(\nu)}{\nu - \omega} \,. \tag{8.429}$$