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Chapter 8

The Boltzmann Equation

8.1 References

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8.2 Equilibrium, Nonequilibrium and Local Equilibrium

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

$$\varrho_N(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N,\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N)=\frac{1}{N!}\times\begin{cases} Z_N^{-1}\,e^{-\beta\hat{H}_N(\{\boldsymbol{p}_i\},\{\boldsymbol{x}_i\})} & \text{OCE}\\ \Xi^{-1}\,e^{\beta\mu N}\,e^{-\beta\hat{H}_N(\{\boldsymbol{p}_i\},\{\boldsymbol{x}_i\})} & \text{GCE}\end{cases}\quad, \tag{8.1}$$

We assume a Hamiltonian of the form

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

Here $v(\boldsymbol{x})=U_{\text{ext}}(\boldsymbol{x})$ is due to external forces. In the context of transport theory, $v(\hat{\boldsymbol{x}})$ typically will denote the effect of an applied external field, *e.g.* $v(\hat{\boldsymbol{x}})=-q\boldsymbol{E}\cdot\hat{\boldsymbol{x}}$ for a particle of charge q in the presence of a uniform electric field $\boldsymbol{E}$. We write $\hat{\boldsymbol{x}}_i$ and $\hat{\boldsymbol{p}}_i$ for the corresponding phase space variables, the position and momentum vectors for the i^{th} particle, respectively. The quantity

$$\varrho_N^{\text{eq}}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N,\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N)\prod_{j=1}^{N}d\mu_j\quad, \tag{8.3}$$

with $d\mu_j\equiv d^dx_j\,d^dp_j/h^d$, is the probability, under equilibrium conditions, of finding N particles in the system, witparticle #1 lying within d^3x_1 of $\boldsymbol{x}_1$ and having momentum within d^dp_1 of $\boldsymbol{p}_1$, *etc.* The temperature T and chemical potential μ are constants, independent of position. Note that $\varrho_N^{\text{eq}}(\{\boldsymbol{x}_i\},\{\boldsymbol{p}_i\})$ has units of h^{-N}.

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. Rather, it is a time-dependent quantity, $\varrho_N($ 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

$$\begin{aligned} f(\boldsymbol{r},\boldsymbol{p};t)&=\sum_{i=1}^{N}\big\langle\,\delta\big(\boldsymbol{r}-\boldsymbol{x}_i(t)\big)\,\delta\big(\boldsymbol{p}-\boldsymbol{p}_i(t)\big)\,\big\rangle\\ &=Nh^{-d}\!\int\prod_{i=2}^{N}d\mu_i\;\varrho_N(\boldsymbol{r},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N,\boldsymbol{p},\boldsymbol{p}_2,\ldots,\boldsymbol{p}_N,t)\quad. \end{aligned} \tag{8.4}$$

Note that $f(\boldsymbol{r},\boldsymbol{p},t)$ 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. The full k-particle density matrix, which for classical systems we may write in terms of its diagonal matrix elements in the $\big(\{\boldsymbol{x}_i\},\{\boldsymbol{p}_i\}\big)$ basis, is given by

$$\begin{aligned} f_k\big(\{\boldsymbol{x}_i\}\,,\{\boldsymbol{p}_i\}\,,t\big) &= \sum_{\{j_1,\ldots,j_k\}}{}^{\!\prime}\big\langle\delta\big(\boldsymbol{x}_1-\hat{\boldsymbol{x}}_{j_1}(t)\big)\cdots\delta\big(\boldsymbol{x}_k-\hat{\boldsymbol{x}}_{j_k}(t)\big)\,\delta\big(\boldsymbol{p}_1-\hat{\boldsymbol{p}}_{j_1}(t)\big)\cdots\delta\big(\boldsymbol{p}_k-\hat{\boldsymbol{p}}_{j_k}(t)\big)\big\rangle \\ &= \frac{N!\,h^{-kd}}{(N-k)!}\int\prod_{i=k+1}^{N} d\mu_i\;\varrho_N\big(\{\boldsymbol{x}_j\}\,,\,\{\boldsymbol{p}_j\}\,,\,t\big) \quad , \end{aligned} \tag{8.5}$$

where $\{\boldsymbol{x}_j\}$ as an argument of the s-body density matrix f_k denotes the ordered set $\{\boldsymbol{x}_1,\ldots,\boldsymbol{x}_k\}$, where $k\in\{1,\ldots,N\}$ (similarly for $\{\boldsymbol{p}_j\}$). The prime on the sum over the indices $\{j_1,\ldots,j_k\}$ indicates that no two indices take the same value. Note that the normalization of f_k is

$$\int\prod_{i=1}^{k} d^d\!x_i\,d^d\!p_i\;f_k(\{\boldsymbol{x}_j\},\{\boldsymbol{p}_j\},t)=\frac{N!}{(N-k)!} \quad , \tag{8.6}$$

for all t. We write the one-body density matrix $f_1(\boldsymbol{x}_1,\boldsymbol{p}_1,t)\equiv f(\boldsymbol{r},\boldsymbol{p},t)$, where $\boldsymbol{r}=\boldsymbol{x}_1$ and $\boldsymbol{p}=\boldsymbol{p}_1$.

In the GCE, we sum over different particle numbers 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:

$$f^0(\boldsymbol{r},\boldsymbol{p})=n\,(2\pi m k_{\rm B}T)^{-3/2}\,e^{-\boldsymbol{p}^2/2mk_{\rm B}T} \quad , \tag{8.7}$$

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, $\boldsymbol{j}_\varepsilon$:

$$\boldsymbol{j}(\boldsymbol{r},t)=\int\! d^d\!p\;f(\boldsymbol{r},\boldsymbol{p};t)\,\frac{\boldsymbol{p}}{m} \tag{8.8}$$

$$\boldsymbol{j}_\varepsilon(\boldsymbol{r},t)=\int\! d^d\!p\;f(\boldsymbol{r},\boldsymbol{p};t)\;\varepsilon(\boldsymbol{p})\,\frac{\boldsymbol{p}}{m} \quad , \tag{8.9}$$

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

$$đq=T\,ds=d\varepsilon-\mu\,dn \quad , \tag{8.10}$$

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

$$\boldsymbol{j}_q=T\boldsymbol{j}_s=\boldsymbol{j}_\varepsilon-\mu\,\boldsymbol{j} \quad . \tag{8.11}$$

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 $\varGamma=(\boldsymbol{p},\boldsymbol{L})$ for these two variables for the case of diatomic molecules, and $\varGamma = (\boldsymbol{p}, \boldsymbol{L}, \hat{\boldsymbol{n}} \cdot \boldsymbol{L})$ 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,

$$d\varGamma = \begin{cases} d^3\!p & \text{point particles} \\ d^3\!p\, L\, dL\, d\varOmega_{\hat{\boldsymbol{L}}} & \text{diatomic molecules} \\ d^3\!p\, L^2\, dL\, d\varOmega_{\hat{\boldsymbol{L}}}\, d\cos\vartheta & \text{symmetric tops} \quad , \end{cases} \tag{8.12}$$

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

$$n(\boldsymbol{r}, t) = \int d\varGamma\, f(\boldsymbol{r}, \varGamma; t) \quad . \tag{8.13}$$

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 (ii) 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

$$f(\boldsymbol{r}, \boldsymbol{p}, t)\, d^3\!r\, d^3\!p \equiv \begin{cases} \text{\# of particles with positions within } d^3\!r \text{ of} \\ \boldsymbol{r} \text{ and momenta within } d^3\!p \text{ of } \boldsymbol{p} \text{ at time } t. \end{cases} \tag{8.14}$$

Thus, the units of $f(\boldsymbol{r}, \boldsymbol{p}, t)$ are those of inverse action, *i.e.* T/ML^2. 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,

$$\frac{\partial f}{\partial t} + \boldsymbol{\nabla} \cdot (\boldsymbol{u} f) = 0 \quad . \tag{8.15}$$

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:

$$\boldsymbol{u} = (\ \dot{x} \quad , \ \dot{y} \quad , \ \dot{z} \quad , \ \dot{p}_x \quad , \ \dot{p}_y \quad , \ \dot{p}_z \ ) \tag{8.16}$$

$$\boldsymbol{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}, \frac{\partial}{\partial p_x}, \frac{\partial}{\partial p_y}, \frac{\partial}{\partial p_z} \right) \quad . \tag{8.17}$$

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

$$\frac{d\boldsymbol{r}}{dt} = \frac{\partial H}{\partial \boldsymbol{p}} = \boldsymbol{v}(\boldsymbol{p}) \qquad , \qquad \frac{d\boldsymbol{p}}{dt} = -\frac{\partial H}{\partial \boldsymbol{r}} = \boldsymbol{F}_{\text{ext}} \quad , \tag{8.18}$$

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

$$H(\boldsymbol{p},\boldsymbol{r}) = \varepsilon(\boldsymbol{p}) + U_{\text{ext}}(\boldsymbol{r}) \quad . \tag{8.19}$$

For example, under the influence of gravity, $U_{\text{ext}}(\boldsymbol{r}) = m\boldsymbol{g}\cdot\boldsymbol{r}$ 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

$$\frac{\partial f}{\partial t} + \boldsymbol{u}\cdot\boldsymbol{\nabla} f = 0 \quad . \tag{8.20}$$

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

$$\frac{Df}{Dt} = \frac{\partial f}{\partial t} + \dot{\boldsymbol{r}}\cdot\frac{\partial f}{\partial \boldsymbol{r}} + \dot{\boldsymbol{p}}\cdot\frac{\partial f}{\partial \boldsymbol{p}} = \left(\frac{df}{dt}\right)_{\text{coll}} \tag{8.21}$$

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. Suppose we evaluate the time-dependent distribution $f(\boldsymbol{r},\boldsymbol{p},t)$ along a particle trajectory, *i.e.* substituting $\boldsymbol{r}\to\boldsymbol{r}(t)$ and $\boldsymbol{p} = \boldsymbol{p}(t)$. Then

$$\frac{d}{dt} f\big(\boldsymbol{r}(t),\boldsymbol{p}(t),t\big) = \frac{\partial f}{\partial \boldsymbol{r}}\cdot\frac{d\boldsymbol{r}}{dt}\bigg|_{\{\boldsymbol{r}(t),\boldsymbol{p}(t),t\}} + \frac{\partial f}{\partial \boldsymbol{p}}\cdot\frac{d\boldsymbol{p}}{dt}\bigg|_{\{\boldsymbol{r}(t),\boldsymbol{p}(t),t\}} + \frac{\partial f}{\partial t}\bigg|_{\{\boldsymbol{r}(t),\boldsymbol{p}(t),t\}} = \frac{Df}{Dt}\bigg|_{\{\boldsymbol{r}(t),\boldsymbol{p}(t),t\}} \quad . \tag{8.22}$$

Thus, in the absence of collisions, the convective derivative of the distribution $f(\boldsymbol{r},\boldsymbol{p},t)$ vanishes, meaning that the one-body distribution does not vary in time along a particle trajectory.

We can write the Boltzmann equation as

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{\text{str}} + \left(\frac{df}{dt}\right)_{\text{coll}} \quad , \tag{8.23}$$

where

$$\left(\frac{\partial f}{\partial t}\right)_{\text{str}} \equiv -\dot{\boldsymbol{r}}\cdot\frac{\partial f}{\partial \boldsymbol{r}} - \dot{\boldsymbol{p}}\cdot\frac{\partial f}{\partial \boldsymbol{p}} \tag{8.24}$$

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

$$\frac{\partial f}{\partial t} + \frac{\partial \varepsilon}{\partial \boldsymbol{p}}\cdot\frac{\partial f}{\partial \boldsymbol{r}} - \boldsymbol{\nabla} U_{\text{ext}}\cdot\frac{\partial f}{\partial \boldsymbol{p}} = 0 \quad . \tag{8.25}$$

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

$$\frac{\partial f}{\partial t}+\boldsymbol{v}(\boldsymbol{p})\cdot\frac{\partial f}{\partial \boldsymbol{r}}=0 \quad . \tag{8.26}$$

Clearly, then, *any* function of the form

$$f(\boldsymbol{r},\boldsymbol{p},t)=\varphi\big(\boldsymbol{r}-\boldsymbol{v}(\boldsymbol{p})\,t\,,\,\boldsymbol{p}\big) \tag{8.27}$$

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,

$$f(\boldsymbol{r},\boldsymbol{p},t)=C\,e^{\mu/k_{\text{B}}T}e^{-\varepsilon(\boldsymbol{p})/k_{\text{B}}T} \quad , \tag{8.28}$$

which is time-independent[1]. Here, C is a constant with units of $(T/ML^2)^d$. For a ballistic dispersion, $\varepsilon(\boldsymbol{p})=\boldsymbol{p}^2/2m$ and $C=h^{-3}$, in which case $\int d^d\!r\,d^d\!p\,f(\boldsymbol{r},\boldsymbol{p})=V\exp(\mu/k_{\text{B}}T)=\langle\hat{N}\rangle$.

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

$$f(\boldsymbol{r},\boldsymbol{p},t)=C\,e^{-\left(\boldsymbol{r}-\frac{\boldsymbol{p}t}{m}\right)^2/2\sigma^2}\,e^{-\boldsymbol{p}^2/2\kappa^2} \quad . \tag{8.29}$$

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

$$f(x,p,t)=C\,e^{-(\bar{x}-\bar{p}\,\bar{t})^2/2}\,e^{-\bar{p}^2/2} \quad . \tag{8.30}$$

Now consider the level sets of f, where $f(x,p,t)=C\,e^{-\alpha^2/2}$. The equation for these sets is

$$\bar{x}=\bar{p}\,\bar{t}\pm\sqrt{\alpha^2-\bar{p}^2} \quad . \tag{8.31}$$

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

$$f(\boldsymbol{r},\boldsymbol{p},t)=\varphi\bigg(\boldsymbol{r}-\frac{\boldsymbol{p}\,t}{m}-\frac{\boldsymbol{F}_{\text{ext}}t^2}{2m}\,,\,\boldsymbol{p}-\frac{\boldsymbol{F}_{\text{ext}}t}{m}\bigg) \tag{8.32}$$

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.

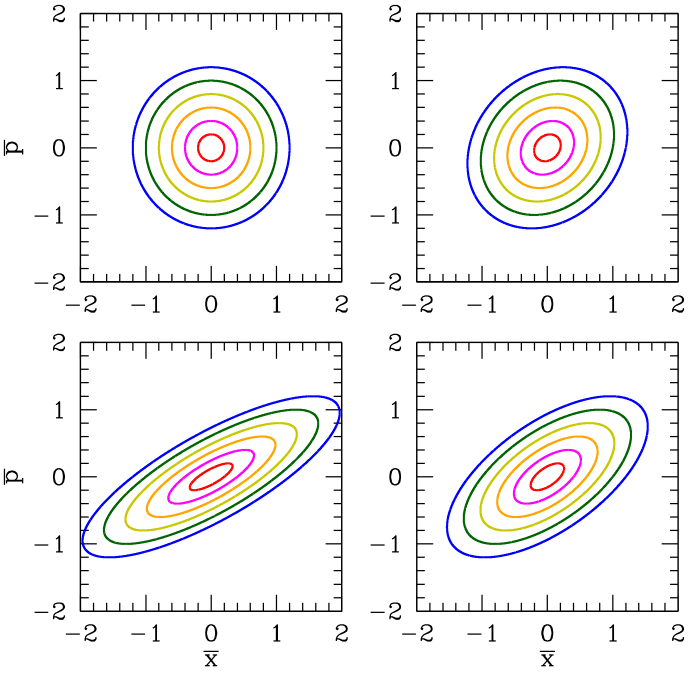

Figure 8.1: Level sets for a sample $f(\bar{x},\bar{p},\bar{t}) = C\,e^{-(\bar{x}-\bar{p}\bar{t})^2/2}e^{-\bar{p}^2/2}$, for values $f = C\,e^{-\alpha^2/2}$ with α in equally spaced intervals from $\alpha = 0.2$ (red) to $\alpha = 1.2$ (blue). The time variable $\bar{t}$ is taken to be $\bar{t} = 0.0$ (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

$$\langle A(t)\rangle = \int d^3\!r\, d^3\!p\, A(\boldsymbol{r},\boldsymbol{p})\, f(\boldsymbol{r},\boldsymbol{p},t) \quad . \tag{8.33}$$

Taking the time derivative,

$$\begin{aligned}\frac{dA}{dt} &= \int d^3\!r \int d^3\!p\, A(\boldsymbol{r},\boldsymbol{p})\,\frac{\partial f}{\partial t} \\ &= \int d^3\!r \int d^3\!p\, A(\boldsymbol{r},\boldsymbol{p}) \left\{ -\frac{\partial}{\partial \boldsymbol{r}}\cdot(\dot{\boldsymbol{r}} f) - \frac{\partial}{\partial \boldsymbol{p}}\cdot(\dot{\boldsymbol{p}} f) + \left(\frac{df}{dt}\right)_{\rm coll} \right\} \\ &= \int d^3\!r \int d^3\!p \left\{ \left(\frac{\partial A}{\partial \boldsymbol{r}}\cdot\frac{d\boldsymbol{r}}{dt} + \frac{\partial A}{\partial \boldsymbol{p}}\cdot\frac{d\boldsymbol{p}}{dt}\right) f + A(\boldsymbol{r},\boldsymbol{p}) \left(\frac{df}{dt}\right)_{\rm coll} \right\} \quad .\end{aligned} \tag{8.34}$$

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

$$\frac{d\langle A(t)\rangle}{dt} = \frac{\partial A}{\partial \boldsymbol{r}}\cdot\frac{d\boldsymbol{r}}{dt} + \frac{\partial A}{\partial \boldsymbol{p}}\cdot\frac{d\boldsymbol{p}}{dt} = 0 \quad . \tag{8.35}$$

---

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

We therefore have that the rate of change of $\langle A(t)\rangle$ is determined wholly by the collision integral

$$\frac{d\langle A(t)\rangle}{dt} = \int \! d^3\!r \int \! d^3\!p \; A(\boldsymbol{r},\boldsymbol{p}) \left(\frac{df}{dt}\right)_{\rm coll} \quad . \tag{8.36}$$

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 $|\varGamma\rangle$ scatters, in the presence of an external potential, to a state $|\varGamma'\rangle$. Recall that $\varGamma$ is an abbreviation for the set of kinematic variables, *e.g.* $\varGamma=(\boldsymbol{p},\boldsymbol{L})$ in the case of a diatomic molecule. For point particles, $\varGamma=(p_x,p_y,p_z)$ and $d\varGamma=d^3\!p$.

Single particle scattering

We now define the function $w\big(\varGamma'\,|\,\varGamma\big)$ such that

$$w\big(\varGamma'\,|\,\varGamma\big)\, f(\varGamma)\, d\varGamma\, d\varGamma' = \text{rate per unit volume to scatter } \big\{|\,\varGamma+d\varGamma\,\rangle\big\} \to \big\{|\,\varGamma'+d\varGamma'\,\rangle\big\} \tag{8.37}$$

at time t. Here we have suppressed the time dependence in the distribution $f(\varGamma,t)$, and typically we will presume $w\big(\varGamma'\,|\,\varGamma\big)$ to be independent of both $\boldsymbol{r}$ and t. By $\big\{|\,\varGamma+d\varGamma\,\rangle\big\}$ we mean states with momenta within $d^3\!p$ of $\boldsymbol{p}$ (more generally, within $d\varGamma = d^3\!p\, d^3\!L$ of $(\boldsymbol{p},\boldsymbol{L})$) and at the same position coordinate $\boldsymbol{r}$. We assume the rate is independent of the position $\boldsymbol{r}$ and the time t. The units of $w\,d\varGamma$ are therefore $1/T$. The *differential scattering cross section* for single particle scattering is then

$$d\sigma = \frac{w\big(\varGamma'\,|\,\varGamma\big)}{n\,|\boldsymbol{v}|}\, d\varGamma' \quad , \tag{8.38}$$

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

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

$$\frac{D}{Dt}\, f(\boldsymbol{r},\varGamma;t) = \int \! d\varGamma' \,\Big\{ w(\varGamma\,|\,\varGamma')\, f(\boldsymbol{r},\varGamma';t) - w(\varGamma'\,|\,\varGamma)\, f(\boldsymbol{r},\varGamma;t)\Big\} = \left(\frac{df}{dt}\right)_{\rm coll} \quad . \tag{8.39}$$

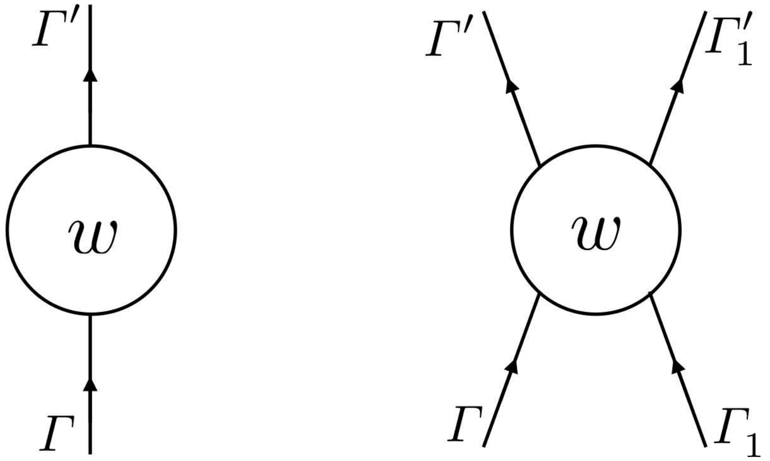

Figure 8.2: Left: single particle scattering process $|\Gamma\rangle \to |\Gamma'\rangle$. Right: two-particle scattering process $|\Gamma,\Gamma_1\rangle \to |\Gamma',\Gamma'_1\rangle$.

Two particle scattering

The second class is that of two-particle scattering processes, *i.e.* $|\,\{\boldsymbol{r},\Gamma\},\{\boldsymbol{r},\Gamma_1\}\,\rangle \to |\,\{\boldsymbol{r},\Gamma'\},\{\boldsymbol{r},\Gamma'_1\}\,\rangle$. We define the scattering function $w\big(\Gamma',\Gamma'_1\,|\,\Gamma,\Gamma_1\big)$ by

$$w\big(\Gamma',\Gamma'_1\,|\,\Gamma,\Gamma_1\big)\,f(\Gamma)\,f(\Gamma_1)\,d\Gamma\,d\Gamma_1\,d\Gamma'\,d\Gamma'_1 = \begin{cases}\text{rate per unit volume to scatter two particles}\\ \big\{|\,\Gamma+d\Gamma,\Gamma_1+d\Gamma_1\,\rangle\big\} \to \big\{|\,\Gamma+d\Gamma',\Gamma'_1+d\Gamma'_1\,\rangle\big\}\end{cases} \tag{8.40}$$

at time t. We assume that $w\big(\Gamma',\Gamma'_1\,|\,\Gamma,\Gamma_1\big)$ is independent of $\boldsymbol{r}$ and t. Thus the units of $w\,d\Gamma\,d\Gamma_1$ are again $1/T$, and the differential scattering cross section is

$$d\sigma = \frac{w\big(\Gamma,\Gamma_1\,|\,\Gamma',\Gamma'_1\big)}{|\boldsymbol{v}-\boldsymbol{v}_1|}\,d\Gamma'\,d\Gamma'_1 \quad . \tag{8.41}$$

For two-body scattering, we therefore have

$$\begin{aligned}\frac{D}{Dt}\,f(\boldsymbol{r},\Gamma;t) = \int\! d\Gamma_1\!\int\! d\Gamma'\!\int\! d\Gamma'_1\,\Big\{&w\big(\Gamma,\Gamma_1\,|\,\Gamma',\Gamma'_1\big)\,f_2(\boldsymbol{r},\Gamma';\boldsymbol{r},\Gamma'_1;t)\\ &- w\big(\Gamma',\Gamma'_1\,|\,\Gamma,\Gamma_1\big)\,f_2(\boldsymbol{r},\Gamma;\boldsymbol{r},\Gamma_1;t)\Big\} = \bigg(\frac{df}{dt}\bigg)_{\!\text{coll}} \quad .\end{aligned} \tag{8.42}$$

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*

$$f_2(\boldsymbol{r},\Gamma;\tilde{\boldsymbol{r}},\tilde{\Gamma};t) \approx f(\boldsymbol{r},\Gamma;t)\,f(\tilde{\boldsymbol{r}},\tilde{\Gamma};t) \quad . \tag{8.43}$$

We then have

$$\begin{aligned}\frac{D}{Dt}\,f(\boldsymbol{r},\varGamma;t)=\int\! d\varGamma_1\!\int\! d\varGamma'\!\int\! d\varGamma_1'\,\Big\{&w\big(\varGamma,\varGamma_1\,\big|\,\varGamma',\varGamma_1'\big)\,f(\boldsymbol{r},\varGamma';t)\,f(\boldsymbol{r},\varGamma_1';t)\\ &-w\big(\varGamma',\varGamma_1'\,\big|\,\varGamma,\varGamma_1\big)\,f(\boldsymbol{r},\varGamma;t)\,f(\boldsymbol{r},\varGamma_1;t)\Big\}=\bigg(\frac{df}{dt}\bigg)_{\!\rm coll}\quad.\end{aligned}\tag{8.44}$$

We stress that in both cases we assume 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.

8.3.5 Detailed balance

Classical mechanics places some restrictions on the form of the kernel $w\big(\varGamma,\varGamma_1\,\big|\,\varGamma',\varGamma_1'\big)$. In particular, if $\varGamma^\mathcal{T}=(-\boldsymbol{p},-\boldsymbol{L})$ denotes the kinematic variables under time reversal ($\mathcal{T}$), then

$$w\big(\varGamma',\varGamma_1'\,\big|\,\varGamma,\varGamma_1\big)=w\big(\varGamma^\mathcal{T},\varGamma_1^\mathcal{T}\,\big|\,\varGamma'^\mathcal{T},\varGamma_1'^\mathcal{T}\big)\quad.\tag{8.45}$$

This is because the time reverse of the process $|\varGamma,\varGamma_1\rangle\to|\varGamma',\varGamma_1'\rangle$ is $|\varGamma'^\mathcal{T},\varGamma_1'^\mathcal{T}\rangle\to|\varGamma^\mathcal{T},\varGamma_1^\mathcal{T}\rangle$.

In equilibrium, we must have

$$w\big(\varGamma',\varGamma_1'\,\big|\,\varGamma,\varGamma_1\big)\;f^0(\varGamma)\,f^0(\varGamma_1)\,d^4\!\varGamma=w\big(\varGamma^\mathcal{T},\varGamma_1^\mathcal{T}\,\big|\,\varGamma'^\mathcal{T},\varGamma_1'^\mathcal{T}\big)\;f^0(\varGamma'^\mathcal{T})\,f^0(\varGamma_1'^\mathcal{T})\,d^4\!\varGamma^\mathcal{T}\tag{8.46}$$

where

$$d^4\!\varGamma\equiv d\varGamma\,d\varGamma_1\,d\varGamma'd\varGamma_1'\qquad,\qquad d^4\!\varGamma^\mathcal{T}\equiv d\varGamma^\mathcal{T}\,d\varGamma_1^\mathcal{T}\,d\varGamma'^\mathcal{T}d\varGamma_1'^\mathcal{T}\quad.\tag{8.47}$$

Since $d\varGamma=d\varGamma^\mathcal{T}$ *etc.*, we may cancel the differentials above, and after invoking eqn. 8.45 and suppressing the common $\boldsymbol{r}$ label, we find

$$f^0(\varGamma)\,f^0(\varGamma_1)=f^0(\varGamma'^\mathcal{T})\,f^0(\varGamma_1'^\mathcal{T})\quad.\tag{8.48}$$

This is the condition of *detailed balance*. For the Boltzmann distribution, we have $f^0(\varGamma)=A\,e^{-\varepsilon/k_{\rm B}T}$, where A is a constant and where $\varepsilon=\varepsilon(\varGamma)$ is the kinetic energy, *e.g.* $\varepsilon(\varGamma)=\boldsymbol{p}^2/2m$ in the case of point particles. Note that $\varepsilon(\varGamma^\mathcal{T})=\varepsilon(\varGamma)$. Detailed balance is satisfied because the kinematics of the collision requires energy conservation:

$$\varepsilon+\varepsilon_1=\varepsilon'+\varepsilon_1'\quad.\tag{8.49}$$

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

$$\boldsymbol{p}+\boldsymbol{p}_1=\boldsymbol{p}'+\boldsymbol{p}_1'\quad,\tag{8.50}$$

any distribution of the form

$$f^0(\varGamma)=A\,\exp\!\bigg(-\,\frac{\varepsilon(\varGamma)-\boldsymbol{V}\cdot\boldsymbol{p}}{k_{\rm B}T}\bigg)\tag{8.51}$$

also satisfies detailed balance, for any velocity parameter $\boldsymbol{V}$. This distribution is appropriate for gases which are flowing with average particle $\boldsymbol{V}$. Note that

$$\frac{\partial}{\partial \boldsymbol{p}}\big(\varepsilon - \boldsymbol{V}\cdot\boldsymbol{p}\big) = \boldsymbol{v} - \boldsymbol{V} \quad , \tag{8.52}$$

which is the velocity relative to the local flow.

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

$$w\big(\varGamma', \varGamma_1' \,|\, \varGamma, \varGamma_1\big) = w\big(\varGamma^{c}, \varGamma_1^{c} \,|\, \varGamma'^{c}, \varGamma_1'^{c}\big) \quad . \tag{8.53}$$

For point particles, invariance under T and P then means

$$w(\boldsymbol{p}', \boldsymbol{p}_1' \,|\, \boldsymbol{p}, \boldsymbol{p}_1) = w(\boldsymbol{p}, \boldsymbol{p}_1 \,|\, \boldsymbol{p}', \boldsymbol{p}_1') \quad , \tag{8.54}$$

and therefore the collision integral takes the simplified form,

$$\frac{Df(\boldsymbol{p})}{Dt} = \int\! d^3\!p_1 \!\int\! d^3\!p' \!\int\! d^3\!p_1' \; w(\boldsymbol{p}', \boldsymbol{p}_1' \,|\, \boldsymbol{p}, \boldsymbol{p}_1) \Big\{ f(\boldsymbol{p}')\, f(\boldsymbol{p}_1') - f(\boldsymbol{p})\, f(\boldsymbol{p}_1) \Big\} = \bigg(\frac{df}{dt}\bigg)_{\!\rm coll} \quad , \tag{8.55}$$

where we have suppressed both $\boldsymbol{r}$ and t variables.

The most general statement of detailed balance is

$$\frac{f^0(\varGamma')\, f^0(\varGamma_1')}{f^0(\varGamma)\, f^0(\varGamma_1)} = \frac{w\big(\varGamma', \varGamma_1' \,|\, \varGamma, \varGamma_1\big)}{w\big(\varGamma, \varGamma_1 \,|\, \varGamma', \varGamma_1'\big)} \quad . \tag{8.56}$$

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. 8.55 in the form

$$\frac{Df(\boldsymbol{p})}{Dt} = \int\! d^3\!p_1 \!\int\! d\varOmega \, |\boldsymbol{v} - \boldsymbol{v}_1| \, \frac{d\sigma}{d\varOmega} \Big\{ f(\boldsymbol{p}')\, f(\boldsymbol{p}_1') - f(\boldsymbol{p})\, f(\boldsymbol{p}_1) \Big\} \quad , \tag{8.57}$$

where $\frac{d\sigma}{d\varOmega}$ is the *differential scattering cross section*. Recall the definition from scattering theory in classical mechanics,

$$d\sigma = \frac{\text{\# of particles scattered into solid angle } d\varOmega \text{ per unit time}}{\text{incident flux}} \quad . \tag{8.58}$$

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 $\boldsymbol{p}' - \boldsymbol{p}_1' = |\boldsymbol{p} - \boldsymbol{p}_1|\,\hat{\boldsymbol{\varOmega}}$, where $\hat{\boldsymbol{\varOmega}}$ is a unit vector. Then $\boldsymbol{p}'$ and $\boldsymbol{p}_1'$ are determined to be

$$\begin{aligned} \boldsymbol{p}' &= \tfrac{1}{2}\big(\boldsymbol{p} + \boldsymbol{p}_1 + |\boldsymbol{p} - \boldsymbol{p}_1|\,\hat{\boldsymbol{\varOmega}}\big) \\ \boldsymbol{p}_1' &= \tfrac{1}{2}\big(\boldsymbol{p} + \boldsymbol{p}_1 - |\boldsymbol{p} - \boldsymbol{p}_1|\,\hat{\boldsymbol{\varOmega}}\big) \quad . \end{aligned} \tag{8.59}$$

Recall that for the scattering of classical hard spheres of radius a, the differential scattering cross section is $\frac{d\sigma}{d\varOmega} = a^2$. Thus, the total scattering cross section is $\sigma_{\textsf{tot}} = 4\pi a^2 = \pi d^2$, where $d = 2a$ is the sphere diameter. For Coulomb scattering of two point particles of charge q, one has

$$\frac{d\sigma}{d\varOmega} = \bigg(\frac{me^2}{|\boldsymbol{p}_1 - \boldsymbol{p}_2|^2 \, \sin^2(\frac{1}{2}\vartheta)}\bigg)^2 \quad , \tag{8.60}$$

where $\hat{\boldsymbol{p}}_1 \cdot \hat{\boldsymbol{p}}_2 = \cos\vartheta$. The total cross section for Coulomb scattering diverges since the differential cross section behaves as ϑ^{-4} as $\vartheta \to 0$.

8.3.7 $\mathcal{H}$-theorem

To peek ahead, we are about to prove the following. Let

$$\begin{aligned} h(\boldsymbol{r},t) &= \int\! d^3\!p\, f(\boldsymbol{r},\boldsymbol{p},t)\, \ln\!\big[f(\boldsymbol{r},\boldsymbol{p},t)/f^0\big] \\ j(\boldsymbol{r},t) &= \int\! d^3\!p\, f(\boldsymbol{r},\boldsymbol{p},t)\, \ln\!\big[f(\boldsymbol{r},\boldsymbol{p},t)/f^0\big]\, \frac{d\boldsymbol{r}}{dt} \quad . \end{aligned} \tag{8.61}$$

Here f^0 can be any constant which has the appropriate dimensions of A^{-3}, where A stands for action. Then if $f(\boldsymbol{r},\boldsymbol{p},t)$ evolves according to the Boltzmann equation, it is necessarily the case that

$$\frac{\partial h(\boldsymbol{r},t)}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j}(\boldsymbol{r},t) \le 0 \quad , \tag{8.62}$$

Where $\boldsymbol{\nabla} \equiv \partial/\partial\boldsymbol{r}$. If we integrate over all space, and we adopt boundary conditions where $\boldsymbol{j} \to 0$ at spatial infinity,

$$\mathcal{H}(t) = \int\! d^3\!r\; h(\boldsymbol{r},t) \quad \Rightarrow \quad \frac{d\mathcal{H}}{dt} \le 0 \quad . \tag{8.63}$$

Thus, Boltzmann dynamics recognizes an arrow of time. Time increases in the direction that $h(\boldsymbol{r},t)$ decreases.

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

$$\rho_\varphi(\boldsymbol{r},t) \equiv \int\! d^3\!p\, f(\boldsymbol{r},\boldsymbol{p},t)\, \varphi\big(f(\boldsymbol{r},\boldsymbol{p},t)\big) \quad , \tag{8.64}$$

where $f = f(\boldsymbol{r},\boldsymbol{p},t)$ and $\varphi(f)$ is arbitrary. At this point, $\varphi(\boldsymbol{p},f)$ is arbitrary. We now compute

$$\begin{aligned}\frac{\partial\rho_\varphi}{\partial t} &= \int\! d^3\!p\, \frac{\partial(f\varphi)}{\partial t} = \int\! d\Gamma\, \frac{\partial(f\varphi)}{\partial f}\,\frac{\partial f}{\partial t}\\ &= \int\! d^3\!p\, \frac{\partial(f\varphi)}{\partial f}\left\{ -\dot{\boldsymbol{r}}\cdot\frac{\partial f}{\partial \boldsymbol{r}} - \dot{\boldsymbol{p}}\cdot\frac{\partial f}{\partial \boldsymbol{p}} + \left(\frac{df}{dt}\right)_{\rm coll}\right\}\\ &= \int\! d^3\!p \left\{ -\dot{\boldsymbol{r}}\cdot\frac{\partial (f\varphi)}{\partial \boldsymbol{r}} - \dot{\boldsymbol{p}}\cdot\frac{\partial (f\varphi)}{\partial \boldsymbol{p}} + \frac{\partial(f\varphi)}{\partial f}\left(\frac{df}{dt}\right)_{\rm coll}\right\}\end{aligned} \tag{8.65}$$

We may integrate the second term in the brackets by parts on $\boldsymbol{p}$. Assuming $f = 0$ for infinite values of the kinematic variables, which is the only physical possibility, we then have

$$\begin{aligned}\frac{\partial\rho_\varphi}{\partial t} &= \int\! d^3\!p \left\{ -\dot{\boldsymbol{r}}\cdot\frac{\partial (f\varphi)}{\partial \boldsymbol{r}} - \frac{\partial \dot{\boldsymbol{r}}}{\partial \boldsymbol{r}}\,(f\varphi) + \frac{\partial(f\varphi)}{\partial f}\left(\frac{df}{dt}\right)_{\rm coll}\right\}\\ &= -\frac{\partial}{\partial \boldsymbol{r}}\int\! d^3\!p\; f\varphi\,\dot{\boldsymbol{r}} + \int\! d^3\!p\,\frac{\partial(f\varphi)}{\partial f}\left(\frac{df}{dt}\right)_{\rm coll} \quad .\end{aligned} \tag{8.66}$$

Thus,

$$\frac{\partial\rho_\varphi(\boldsymbol{r},t)}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j}_\varphi(\boldsymbol{r},t) = \sigma_\varphi(\boldsymbol{r},t) \quad , \tag{8.67}$$

where

$$\begin{aligned}\boldsymbol{j}_\varphi(\boldsymbol{r},t) &= \int\! d^3\!p\; f(\boldsymbol{r},\boldsymbol{p},t)\,\varphi\big(f(\boldsymbol{r},\boldsymbol{p},t)\big)\;\boldsymbol{v}(\boldsymbol{p})\\ \sigma_\varphi(\boldsymbol{r},t) &= \int\! d^3\!p\,\frac{\partial(f\varphi)}{\partial f}\bigg|_{f(\boldsymbol{r},\boldsymbol{p},t)}\left(\frac{df}{dt}\right)_{\rm coll}\end{aligned} \tag{8.68}$$

and $\dot{\boldsymbol{r}} = \boldsymbol{v}(\boldsymbol{p}) = \partial H_0/\partial\boldsymbol{p}$ is the velocity.

Thus, we arrive at eqn. 8.67, which is a continuity equation with a source term $\sigma_\varphi(\boldsymbol{r},t)$. The source term is nonzero only in the presence of collisions. We now evaluate σ_φ under the assumption that f satisfies the Boltzmann equation with two particle scattering. Thus,

$$\begin{aligned}\sigma_\varphi(\boldsymbol{r},t) &= \int\! d^3\!p\!\int\! d^3\!p_1\!\int\! d^3\!p'\!\int\! d^3\!p'_1\,\Big\{ w\big(\boldsymbol{p}',\boldsymbol{p}'_1\,|\,\boldsymbol{p},\boldsymbol{p}_1\big)\,f(\boldsymbol{p})f(\boldsymbol{p}_1)\,\chi(\boldsymbol{p}) - w\big(\boldsymbol{p},\boldsymbol{p}_1\,|\,\boldsymbol{p}',\boldsymbol{p}'_1\big)\,f(\boldsymbol{p}')f(\boldsymbol{p}'_1)\,\chi(\boldsymbol{p}')\Big\}\\ &= \int\! d^3\!p\!\int\! d^3\!p_1\!\int\! d^3\!p'\!\int\! d^3\!p'_1\; w\big(\boldsymbol{p}',\boldsymbol{p}'_1\,|\,\boldsymbol{p},\boldsymbol{p}_1\big)\,f(\boldsymbol{p})f(\boldsymbol{p}_1)\,\big(\chi(\boldsymbol{p}) - \chi'(\boldsymbol{p})\big) \quad ,\end{aligned} \tag{8.69}$$

where

$$\chi = \frac{\partial(f\varphi)}{\partial f} = \varphi + f\,\frac{\partial\varphi}{\partial f} \quad , \tag{8.70}$$

and where we have suppressed the $\boldsymbol{r}$ and t dependences. We now invoke the symmetry

$$w\big(\boldsymbol{p}',\boldsymbol{p}'_1\,|\,\boldsymbol{p},\boldsymbol{p}_1\big) = w\big(\boldsymbol{p}'_1,\boldsymbol{p}'\,|\,\boldsymbol{p}_1,\boldsymbol{p}\big) \quad , \tag{8.71}$$

which allows us to write

$$\sigma = \tfrac{1}{2}\int\! d^3\!p\int\! d^3\!p_1\int\! d^3\!p'\int\! d^3\!p_1'\; w\big(\boldsymbol{p}',\boldsymbol{p}_1'\,|\,\boldsymbol{p},\boldsymbol{p}_1\big)\; f(\boldsymbol{p})f(\boldsymbol{p}_1)\,\big(\chi(\boldsymbol{p})+\chi(\boldsymbol{p}_1)-\chi(\boldsymbol{p}')-\chi(\boldsymbol{p}_1')\big) \quad , \tag{8.72}$$

This shows that $\sigma_\varphi = 0$ if $\chi(\boldsymbol{p})$ is a collisional invariant.

Now let us fix $\varphi(f) = \ln(f/f^0)$ and evaluate the source term $\sigma \equiv \sigma_{\varphi=\ln(f/f^0)}$. We have

$$\sigma = -\tfrac{1}{2}\int\! d^3\!p\int\! d^3\!p_1\int\! d^3\!p'\int\! d^3\!p_1'\; w\big(\boldsymbol{p}',\boldsymbol{p}_1'\,|\,\boldsymbol{p},\boldsymbol{p}_1\big)\; f(\boldsymbol{p}')f(\boldsymbol{p}_1')\cdot x(\boldsymbol{p},\boldsymbol{p}_1\,|\,\boldsymbol{p}',\boldsymbol{p}_1')\ln x(\boldsymbol{p},\boldsymbol{p}_1\,|\,\boldsymbol{p}',\boldsymbol{p}_1') \quad , \tag{8.73}$$

where $x(\boldsymbol{p},\boldsymbol{p}_1,\boldsymbol{p}',\boldsymbol{p}_1') \equiv f(\boldsymbol{p})f(\boldsymbol{p}_1)/f(\boldsymbol{p}')f(\boldsymbol{p}_1')$. We next invoke the result

$$\int\! d^3\!p'\int\! d^3\!p_1'\; w\big(\boldsymbol{p}',\boldsymbol{p}_1'\,|\,\boldsymbol{p},\boldsymbol{p}_1\big) = \int\! d^3\!p'\int\! d^3\!p_1'\; w\big(\boldsymbol{p},\boldsymbol{p}_1\,|\,\boldsymbol{p}',\boldsymbol{p}_1'\big) \tag{8.74}$$

which is a statement of unitarity of the scattering matrix[3]. Multiplying both sides by $f(\boldsymbol{p})\,f(\boldsymbol{p}_1)$, then integrating over $\boldsymbol{p}$ and $\boldsymbol{p}_1$, and finally changing variables $(\boldsymbol{p},\boldsymbol{p}_1)\leftrightarrow(\boldsymbol{p}',\boldsymbol{p}_1')$, we find

$$\begin{aligned} 0 &= \int\! d^3\!p\int\! d^3\!p_1\int\! d^3\!p'\int\! d^3\!p_1'\; w\big(\boldsymbol{p}',\boldsymbol{p}_1'\,|\,\boldsymbol{p},\boldsymbol{p}_1\big)\,\Big(f(\boldsymbol{p})f(\boldsymbol{p}_1)-f(\boldsymbol{p}')f(\boldsymbol{p}_1')\Big) \\ &= \int\! d^3\!p\int\! d^3\!p_1\int\! d^3\!p'\int\! d^3\!p_1'\; w\big(\boldsymbol{p}',\boldsymbol{p}_1'\,|\,\boldsymbol{p},\boldsymbol{p}_1\big)\; f(\boldsymbol{p}')f(\boldsymbol{p}_1')\,\Big\{x(\boldsymbol{p},\boldsymbol{p}_1\,|\,\boldsymbol{p}',\boldsymbol{p}_1')-1\Big\} \quad . \end{aligned} \tag{8.75}$$

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

$$\sigma = -\tfrac{1}{2}\int\! d^3\!p\int\! d^3\!p_1\int\! d^3\!p'\int\! d^3\!p_1'\; w\big(\boldsymbol{p}',\boldsymbol{p}_1'\,|\,\boldsymbol{p},\boldsymbol{p}_1\big)\; f(\boldsymbol{p}')f(\boldsymbol{p}_1')\;\,(x\ln x - x + 1) \quad , \tag{8.76}$$

where $x \equiv x(\boldsymbol{p},\boldsymbol{p}_1,\boldsymbol{p}',\boldsymbol{p}_1') = f(\boldsymbol{p})f(\boldsymbol{p}_1)/f(\boldsymbol{p}')f(\boldsymbol{p}_1')$. It is now 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

$$\frac{\partial h(\boldsymbol{r},t)}{\partial t} + \boldsymbol{\nabla}\cdot j(\boldsymbol{r},t) = \sigma(\boldsymbol{r},t) \le 0 \quad . \tag{8.77}$$

Boltzmann's $\mathcal{H}$ function is the space integral of the local density $h(\boldsymbol{r})$: $\mathcal{H} = \int\! d^3\!r\; h(\boldsymbol{r})$.

Thus, everywhere in space, the source term $\sigma(\boldsymbol{r},t)$ is nonpositive. In equilibrium, $\dot{h} = 0$ everywhere, which requires $x = 1$, *i.e.*

$$f^0(\boldsymbol{p})\,f^0(\boldsymbol{p}_1) = f^0(\boldsymbol{p}')\,f^0(\boldsymbol{p}_1') \quad , \tag{8.78}$$

or, taking the logarithm,

$$\ln f^0(\boldsymbol{p}) + \ln f^0(\boldsymbol{p}_1) = \ln f^0(\boldsymbol{p}') + \ln f^0(\boldsymbol{p}_1') \quad . \tag{8.79}$$

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,

$$-\ln f^0 = \frac{\varepsilon(\boldsymbol{p}) - \boldsymbol{V}\cdot\boldsymbol{p} - \mu}{k_{\mathrm{B}}T} \quad , \tag{8.80}$$

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 Boltzmann equation is written

$$\bigg(\frac{\partial}{\partial t} + \frac{\boldsymbol{p}}{m}\cdot\frac{\partial}{\partial \boldsymbol{r}} + \boldsymbol{F}\cdot\frac{\partial}{\partial \boldsymbol{p}}\bigg)(f^0+\delta f) = \bigg(\frac{df}{dt}\bigg)_{\rm coll} \quad . \tag{8.81}$$

The RHS of this equation must be of order δf because the local equilibrium distribution f^0 is annihilated by the collision integral.

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

$$f^0(\boldsymbol{r},\varGamma) = C \exp\bigg(\frac{\mu - \varepsilon(\varGamma) + \boldsymbol{V}\cdot\boldsymbol{p}}{k_{\rm B}T}\bigg) \quad , \tag{8.82}$$

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

$$\begin{aligned} df^0 &= \bigg(d\mu + \boldsymbol{p}\cdot d\boldsymbol{V} + (\varepsilon - \boldsymbol{V}\cdot\boldsymbol{p} - \mu)\,\frac{dT}{T} - d\varepsilon\bigg)\bigg(-\frac{\partial f^0}{\partial\varepsilon}\bigg) \\ &= \bigg(\frac{1}{n}\,dp + \boldsymbol{p}\cdot d\boldsymbol{V} + (\varepsilon - h)\,\frac{dT}{T} - d\varepsilon\bigg)\bigg(-\frac{\partial f^0}{\partial\varepsilon}\bigg) \quad , \end{aligned} \tag{8.83}$$

where $h = \mu + Ts$ is the enthalpy per particle, and where we drop the term proportional to $\boldsymbol{V}\cdot\boldsymbol{p}\,dT$, which on the assumption that $\boldsymbol{V} = 0$ on average is second order in smallness. We have also invoked local thermodynamics in the form

$$d\mu = \bigg(\frac{\partial\mu}{\partial T}\bigg)_{\!p} dT + \bigg(\frac{\partial\mu}{\partial p}\bigg)_{\!T} dp = -s\,dT + \frac{1}{n}\,dp \quad , \tag{8.84}$$

where s is the entropy per particle and n is the number density. We also have

$$-\frac{\partial f^0}{\partial\varepsilon} = \frac{f^0}{k_{\rm B}T} \quad , \tag{8.85}$$

which we shall invoke further on below. When f^0 is the Maxwell-Boltzmann distribution, we have

$$f^0(\boldsymbol{p}) = n\,(2\pi m k_{\rm B}T)^{-3/2}\,e^{-\boldsymbol{p}^2/2mk_{\rm B}T} \tag{8.86}$$

is normalized so that $\int\! d^3\!r \int\! d^3\!p\; f^0(\boldsymbol{p}) = N$.

We wish to evaluate one of the contributions to the LHS of eqn. 8.81:

$$\begin{aligned} \frac{\partial f^0}{\partial t} + \frac{\boldsymbol{p}}{m}\cdot\frac{\partial f^0}{\partial\boldsymbol{r}} + \boldsymbol{F}\cdot\frac{\partial f^0}{\partial\boldsymbol{p}} = \bigg(-\frac{\partial f^0}{\partial\varepsilon}\bigg)\bigg\{&\frac{1}{n}\frac{\partial p}{\partial t} + \frac{\varepsilon - h}{T}\frac{\partial T}{\partial t} + m\boldsymbol{v}\cdot\Big[(\boldsymbol{v}\cdot\boldsymbol{\nabla})\,\boldsymbol{V}\Big] \\ &+ \boldsymbol{v}\cdot\bigg(m\,\frac{\partial\boldsymbol{V}}{\partial t} + \frac{1}{n}\,\boldsymbol{\nabla}p\bigg) + \frac{\varepsilon - h}{T}\,\boldsymbol{v}\cdot\boldsymbol{\nabla}T - \boldsymbol{F}\cdot\boldsymbol{v}\bigg\} \quad . \end{aligned} \tag{8.87}$$

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,

$$\frac{\partial \ln n}{\partial t} = \frac{\partial \ln p}{\partial t} - \frac{\partial \ln T}{\partial t} = -\boldsymbol{\nabla}\cdot\boldsymbol{V} \quad , \tag{8.88}$$

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

$$\frac{\partial(ns)}{\partial t} + \boldsymbol{\nabla}\cdot(ns\boldsymbol{V}) = n\bigg(\frac{\partial s}{\partial t} + \boldsymbol{V}\cdot\boldsymbol{\nabla} s\bigg) + s\bigg(\frac{\partial n}{\partial t} + \boldsymbol{\nabla}\cdot(n\boldsymbol{V})\bigg) = 0 \quad . \tag{8.89}$$

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

$$ds = \bigg(\frac{\partial s}{\partial T}\bigg)_{\!p} dT + \bigg(\frac{\partial s}{\partial p}\bigg)_{\!T} dp = \frac{c_p}{T}\, dT - \frac{k_{\mathrm{B}}}{p}\, dp \quad , \tag{8.90}$$

since $c_p = T\big(\partial s/\partial T\big)_p$ and $\big(\partial s/\partial p\big)_T = \big(\partial v/\partial T\big)_p$, where $v = V/N$. Here, c_p is the heat capacity per particle at constant pressure[5]. Thus,

$$\frac{c_p}{k_{\mathrm{B}}}\,\frac{\partial \ln T}{\partial t} - \frac{\partial \ln p}{\partial t} = 0 \quad . \tag{8.91}$$

We now have in eqns. 8.88 and 8.91 two equations in the two unknowns $\partial \ln T/\partial t$ and $\partial \ln p/\partial t$, yielding

$$\frac{\partial \ln T}{\partial t} = -\frac{k_{\mathrm{B}}}{c_V}\,\boldsymbol{\nabla}\cdot\boldsymbol{V} \quad , \quad \frac{\partial \ln p}{\partial t} = -\frac{c_p}{c_V}\,\boldsymbol{\nabla}\cdot\boldsymbol{V} \quad . \tag{8.92}$$

Thus eqn. 8.87 becomes

$$\frac{\partial f^0}{\partial t} + \frac{\boldsymbol{p}}{m}\cdot\frac{\partial f^0}{\partial \boldsymbol{r}} + \boldsymbol{F}\cdot\frac{\partial f^0}{\partial \boldsymbol{p}} = \bigg(-\frac{\partial f^0}{\partial \varepsilon}\bigg)\bigg\{\frac{\varepsilon - h}{T}\,\boldsymbol{v}\cdot\boldsymbol{\nabla} T + m\,v_\alpha v_\beta\,\mathcal{Q}_{\alpha\beta} + \frac{h - Tc_p - \varepsilon}{c_V/k_{\mathrm{B}}}\,\boldsymbol{\nabla}\cdot\boldsymbol{V} - \boldsymbol{F}\cdot\boldsymbol{v}\bigg\} \quad , \tag{8.93}$$

where $\varepsilon = \varepsilon(\varGamma)$ and

$$\mathcal{Q}_{\alpha\beta} = \frac{1}{2}\bigg(\frac{\partial V_\alpha}{\partial x_\beta} + \frac{\partial V_\beta}{\partial x_\alpha}\bigg) \quad . \tag{8.94}$$

Therefore, the Boltzmann equation takes the form

$$\frac{\partial\,\delta f}{\partial t} + \bigg\{\frac{\varepsilon(\varGamma) - h}{T}\,\boldsymbol{v}\cdot\boldsymbol{\nabla} T + m\,v_\alpha v_\beta\,\mathcal{Q}_{\alpha\beta} - \frac{\varepsilon(\varGamma) - h + Tc_p}{c_V/k_{\mathrm{B}}}\,\boldsymbol{\nabla}\cdot\boldsymbol{V} - \boldsymbol{F}\cdot\boldsymbol{v}\bigg\}\frac{f^0}{k_{\mathrm{B}}T} = \bigg(\frac{df}{dt}\bigg)_{\mathrm{coll}} \quad . \tag{8.95}$$

---

[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.

Notice we have dropped the terms $\boldsymbol{v}\cdot\partial\,\delta f/\partial\boldsymbol{r}$ and $\boldsymbol{F}\cdot\partial\,\delta f/\partial\boldsymbol{p}$, since δf must already be first order in smallness, and both the $\partial/\partial\boldsymbol{r}$ operator as well as $\boldsymbol{F}$ add a second order of smallness, which is negligible. Typically $\partial\,\delta f/\partial t$ 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, $h=c_pT$.

8.5 Relaxation Time Approximation

8.5.1 Approximation of collision integral

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

$$\left(\frac{df}{dt}\right)_{\rm coll}=-\,\frac{f-f^0}{\tau}=-\frac{\delta f}{\tau}\quad . \tag{8.96}$$

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

$$\frac{\partial\,\delta f}{\partial t}=-\frac{\delta f}{\tau}\qquad\Longrightarrow\qquad \delta f(\boldsymbol{r},\boldsymbol{p},t)=\delta f(\boldsymbol{r},\boldsymbol{p},0)\,e^{-t/\tau}\quad . \tag{8.97}$$

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 II, 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

$$\langle\,|\boldsymbol{v}-\boldsymbol{v}'|\,\rangle=\int\! d^3\!v\int\! d^3\!v'\;P(\boldsymbol{v})\,P(\boldsymbol{v}')\,|\boldsymbol{v}-\boldsymbol{v}'|\quad , \tag{8.98}$$

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

$$P(\boldsymbol{v})=\left(\frac{m}{2\pi k_{\rm B}T}\right)^{3/2}\exp\left(-\frac{m\boldsymbol{v}^2}{2k_{\rm B}T}\right)\quad , \tag{8.99}$$

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

$$\bar{v}_{\rm rel}\equiv\langle\,|\boldsymbol{v}-\boldsymbol{v}'|\,\rangle=\frac{4}{\sqrt{\pi}}\left(\frac{k_{\rm B}T}{m}\right)^{1/2}\quad . \tag{8.100}$$

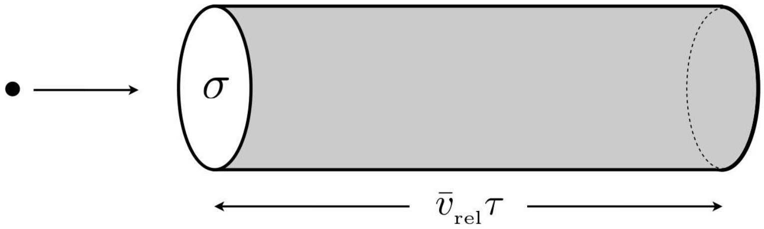

Figure 8.3: Graphic representation of the equation $n\,\sigma\,\bar{v}_{\rm rel}\,\tau = 1$, which yields the scattering time τ in terms of the number density n, average particle pair relative velocity $\bar{v}_{\rm rel}$, and two-particle total scattering cross section σ. The equation says that on average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

Note that $\bar{v}_{\rm rel} = \sqrt{2}\,\bar{v}$, 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

$$\frac{1}{\tau} = n\,\bar{v}_{\rm rel}\,\sigma \quad . \tag{8.101}$$

The particle *mean free path* is then

$$\ell = \bar{v}\,\tau = \frac{1}{\sqrt{2}\,n\,\sigma} \quad . \tag{8.102}$$

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

$$\tau(T) = \frac{1}{n\,\bar{v}_{\rm rel}\,\sigma} = \frac{\sqrt{\pi}}{4n\sigma}\left(\frac{m}{k_{\rm B}T}\right)^{1/2} \quad . \tag{8.103}$$

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. 8.95, and using the relaxation time approximation for the collision integral, we have

$$\delta f = -\frac{\tau(\varepsilon - c_p\,T)}{k_{\rm B}T^2}\,(\boldsymbol{v}\cdot\boldsymbol{\nabla} T)\,f^0 \quad . \tag{8.104}$$

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:

$$\rho_A(\boldsymbol{r},t) = \int\! d^3\!p\, A(\boldsymbol{r},\boldsymbol{p})\,f(\boldsymbol{r},\boldsymbol{p},t) \quad , \tag{8.105}$$

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

$$j^\alpha_\varepsilon(\boldsymbol{r}) = \int\! d^3\!p\, \varepsilon\, v^\alpha\, \delta f = -\frac{n\tau}{k_\mathrm{B}T^2}\,\langle\, v^\alpha v^\beta\, \varepsilon\,(\varepsilon - c_p\, T)\,\rangle\, \frac{\partial T}{\partial x^\beta} \quad , \tag{8.106}$$

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

$$\langle\, \phi(\boldsymbol{p})\,\rangle = \int\! d^3\!p\; \phi(\boldsymbol{p})\, f^0(\boldsymbol{p}) \bigg/ \!\! \int\! d^3\!p\, f^0(\boldsymbol{p}) = \!\int\! d^3\!v\; P(\boldsymbol{v})\, \phi(m\boldsymbol{v}) \quad . \tag{8.107}$$

In this context, it is useful to invoke the identity $d^3\!p\, f^0(\boldsymbol{p}) = n\, d^3\!v\; P(\boldsymbol{v})$, where

$$P(\boldsymbol{v}) = \bigg(\frac{m}{2\pi k_\mathrm{B}T}\bigg)^{3/2}\, e^{-m(\boldsymbol{v}-\boldsymbol{V})^2/2k_\mathrm{B}T} \tag{8.108}$$

is the Maxwell velocity distribution.

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

$$d^3\!p\, f^0(\boldsymbol{p}) = n\, d^3\!v\; P(\boldsymbol{v}) = n\, \mathcal{P}(\varepsilon)\, d\varepsilon \quad , \tag{8.109}$$

where

$$\mathcal{P}(\varepsilon) = \frac{2}{\sqrt{\pi}}\,(k_\mathrm{B}T)^{-3/2}\, \varepsilon^{1/2}\, e^{-\varepsilon/k_\mathrm{B}T} \quad , \tag{8.110}$$

is the Maxwellian distribution expressed in terms of ε, and is normalized according to $\int\limits_0^\infty\! d\varepsilon\, \mathcal{P}(\varepsilon) = 1$.[6] Averages with respect to this distribution are given by

$$\langle\, \phi(\varepsilon)\,\rangle = \int\limits_0^\infty\! d\varepsilon\; \phi(\varepsilon)\, \mathcal{P}(\varepsilon) = \frac{2}{\sqrt{\pi}}\,(k_\mathrm{B}T)^{-3/2}\!\int\limits_0^\infty\! d\varepsilon\; \varepsilon^{1/2}\, \phi(\varepsilon)\, e^{-\varepsilon/k_\mathrm{B}T} \quad . \tag{8.111}$$

For homogeneous $\phi(s) = \varepsilon^s$ we have

$$\langle\, \varepsilon^s\,\rangle = \frac{2}{\sqrt{\pi}}\,\Gamma\big(s+\tfrac{3}{2}\big)\,(k_\mathrm{B}T)^s \quad . \tag{8.112}$$

Due to spatial isotropy, it is clear that we can replace $v^\alpha\, v^\beta$ by $\frac{1}{3}\,\boldsymbol{v}^2\,\delta_{\alpha\beta}$ and then $\varepsilon = \frac{1}{2}m\boldsymbol{v}^2$ in eqn. 8.106.. We then have $\boldsymbol{j}_\varepsilon = -\kappa\, \boldsymbol{\nabla} T$, with

$$\kappa = \frac{2n\tau}{3mk_\mathrm{B}T^2}\,\langle\, \varepsilon^2\big(\varepsilon - c_p\, T\big)\,\rangle = \frac{5n\tau k_\mathrm{B}^2 T}{2m} = \frac{\pi}{8} n\ell\bar{v}\, c_p \quad , \tag{8.113}$$

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

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[6] $\mathcal{P}(\varepsilon)$ can also be recognized as the normalized product of the Boltzmann energy distribution $\exp(-\varepsilon/k_\mathrm{B}T)$ and the density of states $g(\varepsilon)$. In $d = 3$ we have $g(\varepsilon) \propto \varepsilon^{1/2}$.

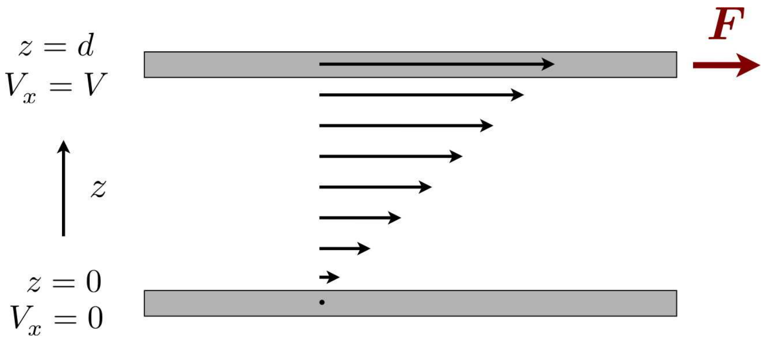

Figure 8.4: *Gedankenexperiment* to measure shear viscosity η in a fluid. The lower plate is fixed. The viscous drag force per unit area on the upper plate is $F_{\text{drag}}/A = -\eta V/d$. This must be balanced by an applied force F.

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 $F_{\text{drag}}/A = -\eta V/d$, 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.* $F + F_{\text{drag}} = 0$. Clearly in the steady state the net momentum density of the fluid does not change, and is given by $\frac{1}{2}\rho V \hat{\boldsymbol{x}}$, 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 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: $\Pi_{xz} = -\eta \, \partial V_x/\partial z$. 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 $\boldsymbol{V}$, we have

$$\begin{aligned} \Pi_{\alpha\beta} &= nm \, \langle \, (V_\alpha + v'_\alpha)(V_\beta + v'_\beta) \, \rangle \\ &= nm \, V_\alpha V_\beta + nm \, \langle \, v'_\alpha v'_\beta \, \rangle \\ &= nm \, V_\alpha V_\beta + \tfrac{1}{3} nm \, \langle \, \boldsymbol{v}'^2 \, \rangle \, \delta_{\alpha\beta} = \rho \, V_\alpha V_\beta + p \, \delta_{\alpha\beta} \quad , \end{aligned} \tag{8.114}$$

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

When $\boldsymbol{V}$ is spatially varying,

$$\Pi_{\alpha\beta} = p \, \delta_{\alpha\beta} + \rho \, V_\alpha V_\beta - \tilde{\sigma}_{\alpha\beta} \quad , \tag{8.115}$$

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 $\boldsymbol{V}$, there is a unique two-parameter decomposition:

$$\begin{aligned}\tilde{\sigma}_{\alpha\beta} &= \eta\bigg(\frac{\partial V_\alpha}{\partial x_\beta} + \frac{\partial V_\beta}{\partial x_\alpha} - \tfrac{2}{3}\,\boldsymbol{\nabla}\!\cdot\!\boldsymbol{V}\,\delta_{\alpha\beta}\bigg) + \zeta\,\boldsymbol{\nabla}\!\cdot\!\boldsymbol{V}\,\delta_{\alpha\beta} \\ &= 2\eta\,\Big(\mathcal{Q}_{\alpha\beta} - \tfrac{1}{3}\,\mathsf{Tr}\,(\mathcal{Q})\,\delta_{\alpha\beta}\Big) + \zeta\;\mathsf{Tr}\,(\mathcal{Q})\,\delta_{\alpha\beta} \quad .\end{aligned} \tag{8.116}$$

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:

$$\sigma_{\alpha\beta} = -p\,\delta_{\alpha\beta} + \tilde{\sigma}_{\alpha\beta} \quad . \tag{8.117}$$

The differential force dF_α that a fluid exerts on on a surface element $\hat{\boldsymbol{n}}\,dA$ is $dF_\alpha = -\sigma_{\alpha\beta}\,n_\beta\,dA$, 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. 8.95, with $\boldsymbol{F} = 0$ and $h = c_p T$, we find

$$\delta f = -\frac{\tau}{k_{\rm B}T}\bigg\{ m\,v_\alpha v_\beta\,\mathcal{Q}_{\alpha\beta} + \frac{\varepsilon - c_p\,T}{T}\,\boldsymbol{v}\cdot\boldsymbol{\nabla}T - \frac{\varepsilon}{c_V/k_{\rm B}}\,\boldsymbol{\nabla}\cdot\boldsymbol{V}\bigg\}\,f^0 \quad . \tag{8.118}$$

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

$$\begin{aligned}\Pi_{xz} &= n\!\int\! d^3\!p\;p_x v_z\,\delta f = -\frac{nm^2\tau}{k_{\rm B}T}\,\mathcal{Q}_{\alpha\beta}\,\langle\, v_x\,v_z\,v_\alpha\,v_\beta\,\rangle \\ &= -\frac{n\tau}{k_{\rm B}T}\bigg(\frac{\partial V_x}{\partial z} + \frac{\partial V_z}{\partial x}\bigg)\,\langle\, mv_x^2\cdot mv_z^2\,\rangle = -n\tau k_{\rm B}T\bigg(\frac{\partial V_z}{\partial x} + \frac{\partial V_x}{\partial z}\bigg) \quad .\end{aligned} \tag{8.119}$$

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

$$\Pi_{xz} = -n\tau k_{\rm B}T\,\frac{\partial V_x}{\partial z} \tag{8.120}$$

from which we read off the viscosity,

$$\eta = nk_{\rm B}T\tau = \frac{\pi}{8}nm\ell\bar{v} \quad . \tag{8.121}$$

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 $d\ln\kappa/d\ln T$ is approximately 0.65 and $d\ln\eta/d\ln T$ 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 $\boldsymbol{\nabla}T$ as well as the momentum current which flows in response to $\partial V_x/\partial z$

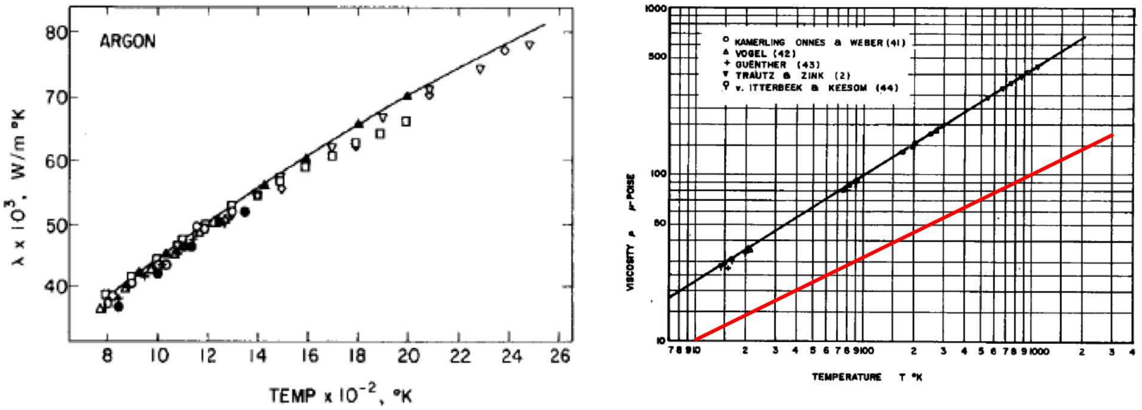

Figure 8.5: Left: thermal conductivity (λ in figure) of Ar between $T = 800\,\mathrm{K}$ and $T = 2600\,\mathrm{K}$. The best fit to a single power law $\lambda = aT^b$ results in $b = 0.651$. Source: G. S. Springer and E. W. Wingeier, *J. Chem Phys.* **59**, 1747 (1972). Right: log-log plot of shear viscosity (μ in figure) of He between $T \approx 15\,\mathrm{K}$ and $T \approx 1000\,\mathrm{K}$. 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).

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 $\boldsymbol{\nabla} T = 0$. The Boltzmann equation is then written

$$\frac{\partial f}{\partial t} + \frac{\boldsymbol{p}}{m} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \boldsymbol{F} e^{-i\omega t} \cdot \frac{\partial f}{\partial \boldsymbol{p}} = -\frac{f - f^0}{\tau} \quad . \tag{8.122}$$

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

$$\frac{\partial\, \delta f}{\partial t} + \boldsymbol{F} e^{-i\omega t} \cdot \boldsymbol{v}\, \frac{\partial f^0}{\partial \varepsilon} = -\frac{\delta f}{\tau} \quad . \tag{8.123}$$

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

$$\delta f(t) = -\frac{\tau\, e^{-i\omega t}}{1 - i\omega\tau}\, \frac{\partial f^0}{\partial \varepsilon}\, \boldsymbol{F} \cdot \boldsymbol{v} \quad . \tag{8.124}$$

We now compute the particle current:

$$\begin{aligned} j_\alpha(\boldsymbol{r},t) &= \int d^3\!p\, \boldsymbol{v}\, \delta f = \frac{\tau\, e^{-i\omega t}}{1-i\omega\tau} \cdot \frac{F_\beta}{k_{\rm B}T} \int d^3\!p\, f^0(\boldsymbol{p})\, v_\alpha\, v_\beta \\ &= \frac{\tau\, e^{-i\omega t}}{1-i\omega\tau} \cdot \frac{nF_\alpha}{3k_{\rm B}T} \int d^3\!v\, P(\boldsymbol{v})\, \boldsymbol{v}^2 = \frac{n\tau}{m} \cdot \frac{F_\alpha\, e^{-i\omega t}}{1-i\omega\tau} \quad . \end{aligned} \tag{8.125}$$

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

$$j^{\rm (elec)}_\alpha(t) = \frac{ne^2\tau}{m} \cdot \frac{E_\alpha\, e^{-i\omega t}}{1-i\omega\tau} \equiv \sigma_{\alpha\beta}(\omega)\, E_\beta\, e^{-i\omega t} \quad , \tag{8.126}$$

where

$$\sigma_{\alpha\beta}(\omega) = \frac{ne^2\tau}{m} \cdot \frac{1}{1-i\omega\tau}\, \delta_{\alpha\beta} \tag{8.127}$$

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 calculation of transport coefficiencs

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

$$\begin{aligned} \boldsymbol{j}_\phi &= n\hat{\boldsymbol{z}} \int\limits_{v_z>0} d^3\!v\, P(\boldsymbol{v})\, v_z\, \phi(z-\ell\cos\theta) + n\hat{\boldsymbol{z}} \int\limits_{v_z<0} d^3\!v\, P(\boldsymbol{v})\, v_z\, \phi(z+\ell\cos\theta) \\ &= -n\ell\, \frac{\partial\phi}{\partial z}\hat{\boldsymbol{z}} \int d^3\!v\, P(\boldsymbol{v})\, \frac{v_z^2}{v} = -\tfrac{1}{3} n\bar{v}\ell\, \frac{\partial\phi}{\partial z}\, \hat{\boldsymbol{z}} \quad , \end{aligned} \tag{8.128}$$

where $\bar{v} = (8k_{\rm B}T/\pi m)^{1/2}$ 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

$$\boldsymbol{j}_\phi = -\tfrac{1}{3}\, n\ell\bar{v}\, \frac{\partial\phi}{\partial T}\, \boldsymbol{\nabla} T \equiv -K\, \boldsymbol{\nabla} T \quad , \tag{8.129}$$

where

$$K = \tfrac{1}{3} n\ell\bar{v}\, \frac{\partial\phi}{\partial T} \tag{8.130}$$

is the transport coefficient. If $\phi = \langle \varepsilon \rangle$, then $\partial\phi/\partial T = c_p$, 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 $\kappa = \frac{1}{3} n \ell \bar{v}\, c_p$. Our Boltzmann equation calculation yielded the same result (eqn. 8.113), 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

$$j^z_{p_x} = \Pi_{xz} = -\tfrac{1}{3} n m \ell \bar{v}\, \frac{\partial V_x}{\partial z} \quad , \tag{8.131}$$

from which we identify the viscosity, $\eta = \frac{1}{3} n m \ell \bar{v}$. 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 $K_{\text{QDC}}/K_{\text{BRT}} = \frac{8}{3\pi} = 0.849$ in both cases[7].

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

$$n c_p\, \frac{\partial T}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_q = 0 \quad . \tag{8.132}$$

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,

$$\frac{\partial T}{\partial t} = \frac{\kappa}{n c_p}\, \nabla^2 T \quad . \tag{8.133}$$

The combination $a \equiv \kappa/nc_p$ is known as the *thermal diffusivity*. Our Boltzmann equation calculation in the relaxation time approximation yielded the result $\kappa = n k_{\text{B}} T \tau c_p/m$. 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 $\eta = n k_{\text{B}} T \tau$ 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,

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

Gas	$\eta\,(\mu\mathrm{Pa}\cdot\mathrm{s})$	$\kappa\,(\mathrm{mW/m}\cdot\mathrm{K})$	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 $T = 293\,\mathrm{K}$ and $p = 1\,\mathrm{atm}$. (Source: Table 1.1 of Smith and Jensen, with data for triatomic gases added.)

let $f(\boldsymbol{r},\boldsymbol{v},t)$ be the distribution function, here written in terms of $(\boldsymbol{r},\boldsymbol{v},t)$ rather than $(\boldsymbol{r},\boldsymbol{p},t)$ as before[8]. In the absence of external forces, the Boltzmann equation in the relaxation time approximation is

$$\frac{\partial f}{\partial t} + \boldsymbol{v}\cdot\frac{\partial f}{\partial \boldsymbol{r}} = -\frac{f-f^0}{\tau} \quad . \tag{8.134}$$

We can solve this equation by first defining $\delta f(\boldsymbol{r},\boldsymbol{v},t) \equiv f(\boldsymbol{r},\boldsymbol{v},t) - f^0(\boldsymbol{v})$, and then taking the Laplace transform in time and the Fourier transform in space,

$$\delta\hat{f}(\boldsymbol{k},\boldsymbol{v},s) = \int\limits_0^\infty \! dt\, e^{-st} \!\int\! d^3\!r\; e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\; \delta f(\boldsymbol{r},\boldsymbol{v},t) \quad , \tag{8.135}$$

resulting in

$$\big(s + i\boldsymbol{v}\cdot\boldsymbol{k} + \tau^{-1}\big)\,\delta\hat{f}(\boldsymbol{k},\boldsymbol{v},s) = \delta f(\boldsymbol{k},\boldsymbol{v},t=0) \quad\Rightarrow\quad \delta\hat{f}(\boldsymbol{k},\boldsymbol{v},s) = \frac{\delta f(\boldsymbol{k},\boldsymbol{v},t=0)}{s + i\boldsymbol{v}\cdot\boldsymbol{k} + \tau^{-1}} \quad . \tag{8.136}$$

Taking the inverse transforms,

$$\begin{aligned}
\delta f(\boldsymbol{r},\boldsymbol{v},t) &= \int\!\frac{d^d\!k}{(2\pi)^3}\int\limits_{\mathcal{C}}\frac{ds}{2\pi i}\;\delta\hat{f}(\boldsymbol{k},\boldsymbol{v},s)\,e^{st} \\
&= \int\!\frac{d^d\!k}{(2\pi)^3}\;\delta f(\boldsymbol{k},\boldsymbol{v},t=0)\,e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\int\limits_{\mathcal{C}}\frac{ds}{2\pi i}\;\frac{e^{st}}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}} \\
&= \int\!\frac{d^d\!k}{(2\pi)^3}\;\delta f(\boldsymbol{k},\boldsymbol{v},t=0)\,e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{v}t)}\;e^{-t/\tau} = \delta f(\boldsymbol{r}-\boldsymbol{v}t,\boldsymbol{v},0)\,e^{-t/\tau} \quad ,
\end{aligned} \tag{8.137}$$

where $\mathcal{C}$ is an integration contour from $c - i\infty$ to $c + i\infty$ where c is chosen so that $\mathcal{C}$ lies to the right of all singularities of the integrand. Thus, choosing an initial distribution is localized at $\boldsymbol{r} = 0$ and $\boldsymbol{v} = \boldsymbol{v}_0$, we

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

find it evolves according to

$$\delta f(\boldsymbol{r},\boldsymbol{v},0)=N\,\delta(\boldsymbol{r})\,\delta(\boldsymbol{v}-\boldsymbol{v}_0)\quad\Rightarrow\quad\delta f(\boldsymbol{r},\boldsymbol{v},t)=N\,\delta(\boldsymbol{r}-\boldsymbol{v}_0t)\,\delta(\boldsymbol{v}-\boldsymbol{v}_0)\,e^{-t/\tau}\quad. \tag{8.138}$$

This result is profoundly unphysical – it says that particle number is not conserved. Not only that, but the spatial distribution remains instantaneously localized about $\boldsymbol{r}=\boldsymbol{v}t$, whereas we expect that in a model of random impurity elastic scattering the particle velocity distribution should become isotropic.

8.6.2 Modified Boltzmann equation and its solution

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

$$\frac{\partial f}{\partial t}+\boldsymbol{v}\cdot\frac{\partial f}{\partial\boldsymbol{r}}=\frac{1}{\tau}\bigg[-f+\int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\,f\bigg]\equiv\frac{1}{\tau}\big(\mathbb{P}-1\big)f\quad, \tag{8.139}$$

where $\mathbb{P}$ is a projector onto a space of isotropic functions of $\boldsymbol{v}$: $\mathbb{P}F=\int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\,F(\boldsymbol{v})=\int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\,F(v\,\hat{\boldsymbol{v}})$ for any function $F(\boldsymbol{v})$. Note that $\mathbb{P}F$ is a function of the speed $v=|\boldsymbol{v}|$. Since the equilibrium distribution $f^0(\boldsymbol{v})=f^0(v)$ is the Maxwell distribution, it is isotropic in velocity space, *i.e.* $f^0(\boldsymbol{v})=f^0(v)$, we have that $(\mathbb{P}-1)f^0(\boldsymbol{v})=0$, and thus the above modified Boltzmann equation holds for f as well as for δf. Note that the number density $n(\boldsymbol{r},t)=\int\!d^3v\,f(\boldsymbol{r},\boldsymbol{v},t)$ and number current density $\boldsymbol{j}(\boldsymbol{r},t)=\int\!d^3v\,f(\boldsymbol{r},\boldsymbol{v},t)\,\boldsymbol{v}$ satisfy the continuity equation

$$\frac{\partial n(\boldsymbol{r},t)}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{j}(\boldsymbol{r},t)=0\quad, \tag{8.140}$$

since integrating over $\hat{\boldsymbol{v}}$ annihilates the RHS of eqn. 8.139 for all $(\boldsymbol{r},v)$. Thus, total particle number is conserved, which is not the case in the naïve relaxation time approximation.

The model in eqn. 8.139 is known as the *Lorentz model*[9]. To solve it, we again begin with the double Laplace-Fourier transform,

$$\hat{f}(\boldsymbol{k},\boldsymbol{v},s)=\int\limits_0^\infty\!dt\,e^{-st}\!\int\!d^3\!r\;e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\;f(\boldsymbol{r},\boldsymbol{v},t)\quad. \tag{8.141}$$

Applying this transform to eqn. 8.139, we obtain

$$\big(s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}\big)\,\hat{f}(\boldsymbol{k},\boldsymbol{v},s)=\tau^{-1}\,\mathbb{P}\hat{f}(\boldsymbol{k},\boldsymbol{v},s)+f(\boldsymbol{k},\boldsymbol{v},t=0)\quad. \tag{8.142}$$

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

$$\hat{f}(\boldsymbol{k},\boldsymbol{v},s)=\frac{\tau^{-1}}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\;\mathbb{P}\hat{f}(\boldsymbol{k},\boldsymbol{v},s)+\frac{f(\boldsymbol{k},\boldsymbol{v},t=0)}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\quad, \tag{8.143}$$

which entails

$$\mathbb{P}\hat{f}(\boldsymbol{k},\boldsymbol{v},s)=\bigg[\int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\,\frac{\tau^{-1}}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\bigg]\,\mathbb{P}\hat{f}(\boldsymbol{k},\boldsymbol{v},\boldsymbol{s})+\int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\,\frac{f(\boldsymbol{k},\boldsymbol{v},t=0)}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\quad. \tag{8.144}$$

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

Now we have

$$\int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\,\frac{\tau^{-1}}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}=\int\limits_{-1}^{1}\!dx\,\frac{\tau^{-1}}{s+ivkx+\tau^{-1}}=\frac{1}{vk}\tan^{-1}\!\bigg(\frac{vk\tau}{1+\tau s}\bigg)\quad . \tag{8.145}$$

Thus,

$$\mathbb{P}f(\boldsymbol{k},\boldsymbol{v},s)=\Bigg[1-\frac{1}{vk\tau}\tan^{-1}\!\bigg(\frac{vk\tau}{1+\tau s}\bigg)\Bigg]^{-1}\!\int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\,\frac{f(\boldsymbol{k},\boldsymbol{v},t=0)}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\quad . \tag{8.146}$$

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

$$\hat{f}(\boldsymbol{k},\boldsymbol{v},s)=\frac{\tau^{-1}}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\Bigg[1-\frac{1}{vk\tau}\tan^{-1}\!\bigg(\frac{vk\tau}{1+\tau s}\bigg)\Bigg]^{-1}\!\int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\,\frac{f(\boldsymbol{k},\boldsymbol{v},t=0)}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}+\frac{f(\boldsymbol{k},\boldsymbol{v},t=0)}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\quad . \tag{8.147}$$

Thus,

$$\begin{aligned}f(\boldsymbol{r},\boldsymbol{v},t)=\int\!\frac{d^3\!k}{(d\pi)^3}\,e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\!\int\limits_{\mathcal{C}}\!\frac{ds}{2\pi i}\,e^{st}\Bigg\{\frac{\tau^{-1}}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\Bigg[1-\frac{1}{vk\tau}\tan^{-1}\!\bigg(\frac{vk\tau}{1+\tau s}\bigg)\Bigg]^{-1}\!\int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\,\frac{f(\boldsymbol{k},\boldsymbol{v},t=0)}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\Bigg\}\\ +f(\boldsymbol{r}-\boldsymbol{v}t\,\boldsymbol{v},0)\,e^{-t/\tau}\quad .\end{aligned} \tag{8.148}$$

Note that the last term $f(\boldsymbol{r}-\boldsymbol{v}t,\boldsymbol{v},0)\,\exp(-t/\tau)$ vanishes as $t\to\infty$. However, we have already seen that the full expression must satisfy the continuity equation for $n(\boldsymbol{r},t)$. We will now show that in the long time limit, when the exponentially decaying transient may be neglected, the remaining result is an expanding cloud describing isotropic particle diffusion.

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

$$f(\boldsymbol{r},\boldsymbol{v},t=0)=N\,\delta(\boldsymbol{r})\,\delta(\boldsymbol{v}-\boldsymbol{v}_0)\quad . \tag{8.149}$$

For these initial conditions, we find

$$\int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\,\frac{f(\boldsymbol{k},\boldsymbol{v},t=0)}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}=\frac{1}{s+i\boldsymbol{v}_0\cdot\boldsymbol{k}+\tau^{-1}}\cdot\frac{N\,\delta(v-v_0)}{4\pi v_0^2}\quad . \tag{8.150}$$

We are interested in the long time limit of $f(\boldsymbol{r},v,t)$, where $t\gg\tau$. Long times are dominated in the Laplace transform by $s\sim t^{-1}$. We also assume the distribution in space becomes smooth, as we shall show, and expand in the regime where $s\tau\ll 1$ and $vk\tau\ll 1$. We then have

$$1-\frac{1}{vk\tau}\tan^{-1}\!\bigg(\frac{vk\tau}{1+\tau s}\bigg)=s\tau+\tfrac{1}{3}k^2v^2\tau^2+\ldots\quad , \tag{8.151}$$

and therefore

$$\begin{aligned}\hat{f}(\boldsymbol{k},\boldsymbol{v},s)&=\frac{\tau^{-1}}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\cdot\frac{\tau^{-1}}{s+i\boldsymbol{v}_0\cdot\boldsymbol{k}+\tau^{-1}}\cdot\frac{1}{s+\frac{1}{3}v_0^2\,k^2\,\tau+\ldots}\cdot\frac{N\,\delta(v-v_0)}{4\pi v_0^2}+\frac{N\,\delta(\boldsymbol{v}-\boldsymbol{v}_0)}{s+i\boldsymbol{v}_0\cdot\boldsymbol{k}+\tau^{-1}}\\ &\approx\frac{1}{s+\frac{1}{3}v_0^2\,k^2\,\tau}\cdot\frac{N\,\delta(v-v_0)}{4\pi v_0^2}+\frac{N\,\delta(\boldsymbol{v}-\boldsymbol{v}_0)}{s+i\boldsymbol{v}_0\cdot\boldsymbol{k}+\tau^{-1}}\quad ,\end{aligned} \tag{8.152}$$

since τ^{-1} is dominant over s and $i\boldsymbol{v}\cdot\boldsymbol{k}$ in the denominators of the the first two multiplicative factors on the RHS of the top equation. We then have

$$\hat{f}(\boldsymbol{k},\boldsymbol{v},s) \approx \frac{1}{s+\frac{1}{3}v_0^2\,k^2\,\tau}\cdot\frac{N\,\delta(v-v_0)}{4\pi v_0^2} + \frac{N\,\delta(\boldsymbol{v}-\boldsymbol{v}_0)}{s+i\boldsymbol{v}_0\cdot\boldsymbol{k}+\tau^{-1}} \quad . \tag{8.153}$$

Performing the inverse Laplace and Fourier transforms, and dropping the transient term for $t \gg \tau$, we obtain our final result,

$$f(\boldsymbol{r},\boldsymbol{v},t\gg\tau) = (4\pi Dt)^{-3/2}\,e^{-r^2/4Dt}\cdot\frac{N\,\delta(v-v_0)}{4\pi v_0^2} \quad , \tag{8.154}$$

where the *diffusion constant* is $D=\frac{1}{3}v_0^2\,\tau$. The units are $[D]=L^2/T$. Integrating over velocities, we have the density

$$n(\boldsymbol{r},t\gg\tau) = \int\! d^3\!v\; f(\boldsymbol{r},\boldsymbol{v},t\gg\tau) = N\,(4\pi Dt)^{-3/2}\,e^{-r^2/4Dt} \quad . \tag{8.155}$$

Note that $\int\! d^3\!r\; n(\boldsymbol{r},t\gg\tau)=N$ at all times in this limit. In addition to particle number being conserved, we see that the late time distribution $f(\boldsymbol{r},\boldsymbol{v},t\gg\tau)$ is isotropic in both $\boldsymbol{r}$ as well as $\boldsymbol{v}$.

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

$$\bigg(\frac{df}{dt}\bigg)_{\!\rm coll} = \int\! d^3\!p_1\!\int\! d^3\!p'\!\int\! d^3\!p_1'\; w(\boldsymbol{p}',\boldsymbol{p}_1'\,|\,\boldsymbol{p},\boldsymbol{p}_1)\,\Big\{f(\boldsymbol{p}')\,f(\boldsymbol{p}_1') - f(\boldsymbol{p})\,f(\boldsymbol{p}_1)\Big\} \quad . \tag{8.156}$$

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

$$f(\boldsymbol{p}) = f^0(\boldsymbol{p}) + f^0(\boldsymbol{p})\,\psi(\boldsymbol{p}) \quad , \tag{8.157}$$

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

$$\bigg(\frac{df}{dt}\bigg)_{\!\rm coll} = f^0(\boldsymbol{p})\,\hat{L}\psi + \mathcal{O}(\psi^2) \quad , \tag{8.158}$$

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

$$\begin{aligned}\hat{L}\psi &= \int\! d^3\!p_1\!\int\! d^3\!p'\!\int\! d^3\!p_1'\; w(\boldsymbol{p}',\boldsymbol{p}_1'\,|\,\boldsymbol{p},\boldsymbol{p}_1)\,f^0(\boldsymbol{p}_1)\,\Big\{\psi(\boldsymbol{p}')+\psi(\boldsymbol{p}_1')-\psi(\boldsymbol{p})-\psi(\boldsymbol{p}_1)\Big\}\\ &= \int\! d^3\!p_1\!\int\! d\Omega\,|\boldsymbol{v}-\boldsymbol{v}_1|\,\frac{d\sigma}{d\Omega}\,f^0(\boldsymbol{p}_1)\,\Big\{\psi(\boldsymbol{p}')+\psi(\boldsymbol{p}_1')-\psi(\boldsymbol{p})-\psi(\boldsymbol{p}_1)\Big\} \quad ,\end{aligned} \tag{8.159}$$

where we have invoked eqn. 8.57 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,

$$f^0(\boldsymbol{p})\, f^0(\boldsymbol{p}_1) = f^0(\boldsymbol{p}')\, f^0(\boldsymbol{p}_1') \quad . \tag{8.160}$$

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

From eqn. 8.95, we then have the linearized equation

$$\bigg(\hat{L} - \frac{\partial}{\partial t}\bigg)\psi = Y, \tag{8.161}$$

where, for point particles,

$$Y = \frac{1}{k_{\rm B}T}\Bigg\{\frac{\varepsilon(\boldsymbol{p}) - c_p T}{T}\,\boldsymbol{v}\cdot\boldsymbol{\nabla} T + m\, v_\alpha v_\beta\, \mathcal{Q}_{\alpha\beta} - \frac{k_{\rm B}\,\varepsilon(\boldsymbol{p})}{c_V}\,\boldsymbol{\nabla}\cdot\boldsymbol{V} - \boldsymbol{F}\cdot\boldsymbol{v}\Bigg\} \quad . \tag{8.162}$$

Eqn. 8.161 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*[10],

$$\langle\, \psi_1 \,|\, \psi_2 \,\rangle \equiv \int\! d^3\!p\, f^0(\boldsymbol{p})\, \psi_1(\boldsymbol{p})\, \psi_2(\boldsymbol{p}) \quad . \tag{8.163}$$

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*: $\langle\, \psi_1 \,|\, \hat{L}\psi_2 \,\rangle = \langle\, \hat{L}\psi_1 \,|\, \psi_2 \,\rangle$.

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,

$$\hat{L}\,\phi_n = -\lambda_n\,\phi_n \quad , \tag{8.164}$$

and may be chosen to be orthonormal, *i.e.* $\langle\, \phi_m \,|\, \phi_n \,\rangle = \delta_{mn}$. 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

$$\phi_n(\boldsymbol{p}) = \frac{1}{\sqrt{n}} \quad , \quad \phi_{p_\alpha}(\boldsymbol{p}) = \frac{p_\alpha}{\sqrt{nmk_{\rm B}T}} \quad , \quad \phi_\varepsilon(\boldsymbol{p}) = \sqrt{\frac{2}{3n}}\left(\frac{\varepsilon(\boldsymbol{p})}{k_{\rm B}T} - \frac{3}{2}\right) \quad . \tag{8.165}$$

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

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

$$\frac{\partial\psi}{\partial t} = \hat{L}\psi \quad . \tag{8.166}$$

We can therefore write the most general solution in the form

$$\psi(\boldsymbol{p},t) = \sum_n{}' C_n\,\phi_n(\boldsymbol{p})\,e^{-\lambda_n t} \quad , \tag{8.167}$$

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,

$$\begin{aligned}
\boldsymbol{j} &= \int\! d^3\!p\;\boldsymbol{v}\,f(\boldsymbol{p}) = \int\! d^3\!p\;f^0(\boldsymbol{p})\,\boldsymbol{v}\,\psi(\boldsymbol{p}) = \langle\,\boldsymbol{v}\,|\,\psi\,\rangle \\
\boldsymbol{j}_\varepsilon &= \int\! d^3\!p\;\boldsymbol{v}\,\varepsilon\,f(\boldsymbol{p}) = \int\! d^3\!p\;f^0(\boldsymbol{p})\,\boldsymbol{v}\,\varepsilon\,\psi(\boldsymbol{p}) = \langle\,\boldsymbol{v}\,\varepsilon\,|\,\psi\,\rangle \\
\boldsymbol{j}_q &= \int\! d^3\!p\;\boldsymbol{v}\,(\varepsilon-\mu)\,f(\boldsymbol{p}) = \int\! d^3\!p\;f^0(\boldsymbol{p})\,\boldsymbol{v}\,(\varepsilon-\mu)\,\psi(\boldsymbol{p}) = \langle\,\boldsymbol{v}\,(\varepsilon-\mu)\,|\,\psi\,\rangle \quad .
\end{aligned} \tag{8.168}$$

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 $\hat{L}\psi = Y$. 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

$$C_j = -\frac{1}{\lambda_j}\,\langle\,\phi_j\,|\,Y\,\rangle \quad . \tag{8.169}$$

Thus, the formal solution to the linearized Boltzmann equation is

$$\psi(\boldsymbol{p}) = -\sum_n \frac{1}{\lambda_n}\,\langle\,\phi_n\,|\,Y\,\rangle\,\phi_n(\boldsymbol{p}) \quad . \tag{8.170}$$

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

$$Y = \frac{1}{k_{\rm B}T^2}\,\frac{\partial T}{\partial x}\cdot X_\kappa \quad , \tag{8.171}$$

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

$$\langle\, X_\kappa \,|\, \psi \,\rangle = -\kappa\, \frac{\partial T}{\partial x} \quad . \tag{8.172}$$

Viscosity

For the viscosity, we take

$$Y = \frac{m}{k_\mathrm{B} T}\, \frac{\partial V_x}{\partial y} \cdot X_\eta \quad , \tag{8.173}$$

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

$$\Pi_{xy} = \langle\, m\, v_x\, v_y \,|\, \psi \,\rangle = -\eta\, \frac{\partial V_x}{\partial y} \quad . \tag{8.174}$$

Thus,

$$\langle\, X_\eta \,|\, \psi \,\rangle = -\frac{\eta}{m}\, \frac{\partial V_x}{\partial y} \quad . \tag{8.175}$$

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,

$$\langle\, \psi \,|\, \hat{H} \,|\, \psi \,\rangle \cdot \langle\, \phi \,|\, \hat{H} \,|\, \phi \,\rangle \geq \langle\, \phi \,|\, \hat{H} \,|\, \psi \,\rangle^2 \quad , \tag{8.176}$$

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

$$\hat{H}\psi = -\frac{1}{k_\mathrm{B} T^2}\, \frac{\partial T}{\partial x}\, X_\kappa \tag{8.177}$$

and therefore

$$\kappa = \frac{k_\mathrm{B} T^2}{(\partial T/\partial x)^2}\, \langle\, \psi \,|\, \hat{H} \,|\, \psi \,\rangle \geq \frac{1}{k_\mathrm{B} T^2}\, \frac{\langle\, \phi \,|\, X_\kappa \,\rangle^2}{\langle\, \phi \,|\, \hat{H} \,|\, \phi \,\rangle} \quad . \tag{8.178}$$

Similarly, for the viscosity, we have

$$\hat{H}\psi = -\frac{m}{k_\mathrm{B} T}\, \frac{\partial V_x}{\partial y}\, X_\eta \quad , \tag{8.179}$$

from which we derive

$$\eta = \frac{k_\mathrm{B} T}{(\partial V_x/\partial y)^2}\, \langle\, \psi \,|\, \hat{H} \,|\, \psi \,\rangle \geq \frac{m^2}{k_\mathrm{B} T}\, \frac{\langle\, \phi \,|\, X_\eta \,\rangle^2}{\langle\, \phi \,|\, \hat{H} \,|\, \phi \,\rangle} \quad . \tag{8.180}$$

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

$$\eta \geq \frac{m^2}{k_{\rm B}T} \, \frac{\langle \, v_x v_y \, | \, v_x v_y \, \rangle^2}{\langle \, v_x v_y \, | \, \hat{H} \, | \, v_x v_y \, \rangle} \quad . \tag{8.181}$$

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

$$\langle \, \phi \, | \, \hat{L} \, | \, \psi \, \rangle = \int \! d^3\!p \; g^0(\boldsymbol{p}) \, \phi(\boldsymbol{p}) \! \int \! d^3\!p_1 \! \int \! d\Omega \, \frac{d\sigma}{d\Omega} \, |\boldsymbol{v}-\boldsymbol{v}_1| \, f^0(\boldsymbol{p}_1) \, \Big\{ \psi(\boldsymbol{p}) + \psi(\boldsymbol{p}_1) - \psi(\boldsymbol{p}') - \psi(\boldsymbol{p}_1') \Big\} \quad . \tag{8.182}$$

Here the kinematics of the collision guarantee total energy and momentum conservation, so $\boldsymbol{p}'$ and $\boldsymbol{p}_1'$ are determined as in eqn. 8.59.

We have $d\Omega = \sin\chi \, d\chi \, d\varphi$, 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

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

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

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

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

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

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

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

$$\begin{aligned} \boldsymbol{v} &= \boldsymbol{V} + \tfrac{1}{2}\boldsymbol{u} & \qquad \boldsymbol{v}' &= \boldsymbol{V} + \tfrac{1}{2}\boldsymbol{u}' \\ \boldsymbol{v}_1 &= \boldsymbol{V} - \tfrac{1}{2}\boldsymbol{u} & \qquad \boldsymbol{v}_1' &= \boldsymbol{V} - \tfrac{1}{2}\boldsymbol{u}' \quad , \end{aligned} \tag{8.186}$$

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

$$\Delta(\psi) \equiv \psi(\boldsymbol{p}) + \psi(\boldsymbol{p}_1) - \psi(\boldsymbol{p}') - \psi(\boldsymbol{p}_1') = \tfrac{1}{2}\big(u_x u_y - u_x' u_y'\big) \quad . \tag{8.187}$$

We may write

$$\boldsymbol{u}' = u \Big(\sin\chi \cos\varphi \, \hat{\mathbf{e}}_1 + \sin\chi \sin\varphi \, \hat{\mathbf{e}}_2 + \cos\chi \, \hat{\mathbf{e}}_3 \Big) \quad , \tag{8.188}$$

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

$$\int\limits_0^{2\pi} \! d\varphi \; \tfrac{1}{2}\big(u_\alpha u_\beta - u_\alpha' u_\beta'\big) = -\pi \sin^2\!\chi \, \big(u^2 \, \delta_{\alpha\beta} - 3u_\alpha u_\beta\big) \quad . \tag{8.189}$$

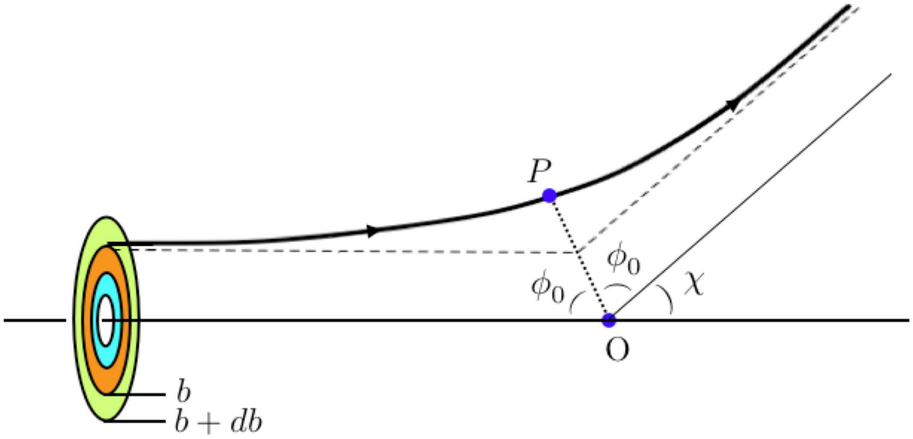

Figure 8.6: Scattering in the CM frame. O is the force center and P is the point of periapsis. The impact parameter is b, and χ is the scattering angle. ϕ_0 is the angle through which the relative coordinate moves between periapsis and infinity.

Note that we have used here the relation

$$e_{1\alpha}\, e_{1\beta} + e_{2\alpha}\, e_{2\beta} + e_{3\alpha}\, e_{3\beta} = \delta_{\alpha\beta} \quad , \tag{8.190}$$

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

It is convenient to define the following integral:

$$R(u) \equiv \int\limits_0^\infty db\, b\, \sin^2\!\chi(b,u) \quad . \tag{8.191}$$

Since the Jacobian satisfies

$$\left| \det \frac{(\partial \boldsymbol{v}, \partial \boldsymbol{v}_1)}{(\partial \boldsymbol{V}, \partial \boldsymbol{u})} \right| = 1 \quad , \tag{8.192}$$

we have

$$\langle\, v_x v_y \,|\, \hat{L} \,|\, v_x v_y \,\rangle = n^2 \bigg(\frac{m}{2\pi k_{\rm B} T}\bigg)^{3} \int\! d^3V \!\int\! d^3u\; e^{-m\boldsymbol{V}^2/k_{\rm B}T}\, e^{-m\boldsymbol{u}^2/4k_{\rm B}T} \cdot u \cdot \tfrac{3\pi}{2} u_x u_y \cdot R(u) \cdot v_x v_y \quad . \tag{8.193}$$

This yields

$$\langle\, v_x v_y \,|\, \hat{L} \,|\, v_x v_y \,\rangle = \tfrac{\pi}{40}\, n^2 \, \big\langle u^5 \, R(u) \big\rangle \quad , \tag{8.194}$$

where

$$\big\langle F(u) \big\rangle \equiv \int\limits_0^\infty du\, u^2\, e^{-mu^2/4k_{\rm B}T}\, F(u) \bigg/ \int\limits_0^\infty du\, u^2\, e^{-mu^2/4k_{\rm B}T} \quad . \tag{8.195}$$

It is easy to compute the term in the numerator of eqn. 8.181:

$$\langle\, v_x v_y \,|\, v_x v_y \,\rangle = n \left(\frac{m}{2\pi k_{\rm B} T}\right)^{3/2} \int\! d^3v\; e^{-m\boldsymbol{v}^2/2k_{\rm B}T}\, v_x^2\, v_y^2 = n \bigg(\frac{k_{\rm B}T}{m}\bigg)^2 \quad . \tag{8.196}$$

Putting it all together, we find

$$\eta \geq \frac{40\,(k_{\rm B}T)^3}{\pi\, m^2} \bigg/ \big\langle u^5\, R(u)\big\rangle \quad . \tag{8.197}$$

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

$$\Delta(\psi) = \frac{1}{2} m \Big[(\boldsymbol{V}\cdot\boldsymbol{u})\, u_x - (\boldsymbol{V}\cdot\boldsymbol{u}')\, u'_x \Big] \quad . \tag{8.198}$$

Ultimately, one obtains the lower bound

$$\kappa \geq \frac{150\, k_{\rm B}\, (k_{\rm B}T)^3}{\pi\, m^3} \bigg/ \big\langle u^5\, R(u)\big\rangle \quad . \tag{8.199}$$

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

$$\text{Pr} = \frac{\nu}{a} = \frac{\eta\, c_p}{m\, \kappa} = \frac{2}{3} \quad , \tag{8.200}$$

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 $b = d \sin\phi_0 = d\cos(\frac{1}{2}\chi)$, where d is the hard sphere diameter. Thus, the impact parameter b is independent of the relative speed u, and one finds $R(u) = \frac{1}{3} d^3$. Then

$$\big\langle u^5\, R(u)\big\rangle = \frac{1}{3} d^3 \big\langle u^5 \big\rangle = \frac{128}{\sqrt{\pi}} \bigg(\frac{k_{\rm B}T}{m}\bigg)^{5/2} d^2 \tag{8.201}$$

and one finds

$$\eta \geq \frac{5\,(m k_{\rm B} T)^{1/2}}{16\sqrt{\pi}\, d^2} \qquad , \qquad \kappa \geq \frac{75\, k_{\rm B}}{64\sqrt{\pi}\, d^2} \bigg(\frac{k_{\rm B}T}{m}\bigg)^{1/2} \quad . \tag{8.202}$$

8.8 The Equations of Hydrodynamics

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

$$\frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}\cdot(\rho\, \boldsymbol{V}) = 0 \tag{8.203}$$

$$\frac{\partial(\rho\, V_\alpha)}{\partial t} + \frac{\partial \Pi_{\alpha\beta}}{\partial x^\beta} = 0 \quad , \tag{8.204}$$

where

$$\Pi_{\alpha\beta} = \rho\, V_\alpha V_\beta + p\, \delta_{\alpha\beta} - \overbrace{\left\{ \eta\bigg(\frac{\partial V_\alpha}{\partial x_\beta} + \frac{\partial V_\beta}{\partial x_\alpha} - \frac{2}{3}\, \boldsymbol{\nabla}\!\cdot\!\boldsymbol{V}\, \delta_{\alpha\beta}\bigg) + \zeta\, \boldsymbol{\nabla}\!\cdot\!\boldsymbol{V}\, \delta_{\alpha\beta} \right\}}^{\tilde\sigma_{\alpha\beta}} \quad . \tag{8.205}$$

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

$$\rho\,\frac{\partial \boldsymbol{V}}{\partial t} + \rho\,(\boldsymbol{V}\cdot\boldsymbol{\nabla})\boldsymbol{V} = -\boldsymbol{\nabla} p + \eta\,\nabla^2\boldsymbol{V} + (\zeta + \tfrac{1}{3}\eta)\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\boldsymbol{V}) \quad , \tag{8.206}$$

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

$$T\,\frac{\partial s}{\partial T} + T\,\boldsymbol{\nabla}\cdot(s\boldsymbol{V}) = \tilde{\sigma}_{\alpha\beta}\,\frac{\partial V_\alpha}{\partial x^\beta} + \boldsymbol{\nabla}\cdot(\kappa\boldsymbol{\nabla}T) \quad , \tag{8.207}$$

where $\tilde{\sigma}_{\alpha\beta}$ is the viscosity stress tensor of eqn. 8.116 (also identified in eqn. 8.205 above). Note that the LHS of eqn. 8.206 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.

If the fluid is incompressible, then $\boldsymbol{\nabla}\cdot\boldsymbol{V} = 0$, and with the kinematic viscosity $\nu \equiv \eta/\rho$ we have the inviscid Navier-Stokes equations,

$$\frac{\partial \boldsymbol{V}}{\partial t} + (\boldsymbol{V}\cdot\boldsymbol{\nabla})\boldsymbol{V} = -\frac{1}{\rho}\,\boldsymbol{\nabla} p + \nu\,\nabla^2\boldsymbol{V} \quad . \tag{8.208}$$

Since $[\eta] = M/LT$ and $[\rho] = M/L^3$, we have $[\eta] = L^2/T$. At $T = 20°\mathrm{C}$,

$$\nu_{\mathrm{H_2O}} = 10^{-2}\,\mathrm{cm^2/sec} \quad , \quad \nu_{\mathrm{air}} = 0.15\,\mathrm{cm^2/sec} \quad , \quad \nu_{\mathrm{glycerine}} = 6.8\,\mathrm{cm^2/sec} \quad . \tag{8.209}$$

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,

$$f^0(\boldsymbol{r},\boldsymbol{k},t) = \left\{ \exp\left(\frac{\varepsilon(\boldsymbol{k}) - \mu(\boldsymbol{r},t)}{k_{\mathrm{B}}T(\boldsymbol{r},t)}\right) \mp 1 \right\}^{-1} \quad , \tag{8.210}$$

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

$$\left(\frac{df}{dt}\right)_{\!\mathrm{coll}} = \int\!\frac{d^3\!k_1}{(2\pi)^3}\!\int\!\frac{d^3\!k'}{(2\pi)^3}\!\int\!\frac{d^3\!k'_1}{(2\pi)^3}\, w\,\Big\{ f' f'_1\,(1 \pm f)\,(1 \pm f_1) - f f_1\,(1 \pm f')\,(1 \pm f'_1) \Big\} \tag{8.211}$$

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

$$\frac{f}{1\pm f}\cdot\frac{f_1}{1\pm f_1} = \frac{f'}{1\pm f'}\cdot\frac{f_1'}{1\pm f_1'} \quad , \tag{8.212}$$

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

$$f = \frac{1}{e^{\beta(\varepsilon-\mu)}\mp 1} \qquad \Rightarrow \qquad \frac{f}{1\pm f} = e^{\beta(\mu-\varepsilon)} \quad , \tag{8.213}$$

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

$$\begin{aligned} df^0 &= k_\mathrm{B}T\,\frac{\partial f^0}{\partial\varepsilon}\,d\bigg(\frac{\varepsilon-\mu}{k_\mathrm{B}T}\bigg) \\ &= k_\mathrm{B}T\,\frac{\partial f^0}{\partial\varepsilon}\left\{-\frac{d\mu}{k_\mathrm{B}T} - \frac{(\varepsilon-\mu)\,dT}{k_\mathrm{B}T^2} + \frac{d\varepsilon}{k_\mathrm{B}T}\right\} \\ &= -\frac{\partial f^0}{\partial\varepsilon}\left\{\frac{\partial\mu}{\partial\boldsymbol{r}}\cdot d\boldsymbol{r} + \frac{\varepsilon-\mu}{T}\,\frac{\partial T}{\partial\boldsymbol{r}}\cdot d\boldsymbol{r} - \frac{\partial\varepsilon}{\partial\boldsymbol{k}}\cdot d\boldsymbol{k}\right\} \quad , \end{aligned} \tag{8.214}$$

from which we read off

$$\begin{aligned} \frac{\partial f^0}{\partial\boldsymbol{r}} &= -\frac{\partial f^0}{\partial\varepsilon}\left\{\frac{\partial\mu}{\partial\boldsymbol{r}} + \frac{\varepsilon-\mu}{T}\,\frac{\partial T}{\partial\boldsymbol{r}}\right\} \\ \frac{\partial f^0}{\partial\boldsymbol{k}} &= \hbar\boldsymbol{v}\,\frac{\partial f^0}{\partial\varepsilon} \quad . \end{aligned} \tag{8.215}$$

Here we have assumed $\boldsymbol{V} = 0$ for the unforced flow velocity of the electron fluid. 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:

$$\begin{aligned} \bigg(\frac{\partial f(\boldsymbol{k})}{\partial t}\bigg)'_\mathrm{coll} &= \frac{2\pi}{\hbar}\sum_{\boldsymbol{k}'\in\hat\Omega} |\langle\,\boldsymbol{k}'\,|\,U\,|\,\boldsymbol{k}\,\rangle|^2\,\big(f(\boldsymbol{k}')-f(\boldsymbol{k})\big)\,\delta\big(\varepsilon(\boldsymbol{k})-\varepsilon(\boldsymbol{k}')\big) \\ &= \frac{2\pi}{\hbar V}\int\limits_{\hat\Omega}\frac{d^3\!k}{(2\pi)^3}\,|\,\hat U(\boldsymbol{k}-\boldsymbol{k}')|^2\,\big(f(\boldsymbol{k}')-f(\boldsymbol{k})\big)\,\delta\big(\varepsilon(\boldsymbol{k})-\varepsilon(\boldsymbol{k}')\big) \quad . \end{aligned} \tag{8.216}$$

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[11]. Note that $f = f^0$ satisfies detailed balance with respect to one-body collisions as well[12].

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

[12] 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. 8.216.

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

$$\frac{\partial\,\delta f}{\partial t} - \frac{e}{\hbar c}\,\boldsymbol{v}\times\boldsymbol{B}\cdot\frac{\partial\,\delta f}{\partial \boldsymbol{k}} - \boldsymbol{v}\cdot\bigg[e\,\boldsymbol{\mathcal{E}} + \frac{\varepsilon-\mu}{T}\,\boldsymbol{\nabla}T\bigg]\frac{\partial f^0}{\partial\varepsilon} = -\frac{\delta f}{\tau} \quad , \tag{8.217}$$

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 $\boldsymbol{v}\cdot\partial\,\delta f/\partial\boldsymbol{r}$ (higher order in spatial derivatives) and $\boldsymbol{E}\cdot\partial\,\delta f/\partial\boldsymbol{k}$ (both $\boldsymbol{E}$ and δf are assumed small). Typically τ is energy-dependent, *i.e.* $\tau = \tau\big(\varepsilon(\boldsymbol{k})\big)$.

We can use eqn. 8.217 to compute the electrical current $\boldsymbol{j}$ and the thermal current $\boldsymbol{j}_q$,

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

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

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

We now consider both the electrical current[13] $\boldsymbol{j}$ as well as the thermal current density $\boldsymbol{j}_q$. One readily obtains

$$\begin{aligned}\boldsymbol{j} &= -2e\int\limits_{\hat\Omega}\frac{d^3\!k}{(2\pi)^3}\;\boldsymbol{v}\,\delta f \equiv L_{11}\,\boldsymbol{\mathcal{E}} - L_{12}\,\boldsymbol{\nabla}T \\ \boldsymbol{j}_q &= 2\int\limits_{\hat\Omega}\frac{d^3\!k}{(2\pi)^3}\;(\varepsilon-\mu)\,\boldsymbol{v}\,\delta f \equiv L_{21}\,\boldsymbol{\mathcal{E}} - L_{22}\,\boldsymbol{\nabla}T\end{aligned} \tag{8.220}$$

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

$$\begin{aligned}L^{\alpha\beta}_{11} &= \frac{e^2}{4\pi^3\hbar}\int\! d\varepsilon\,\tau(\varepsilon)\left(-\frac{\partial f^0}{\partial\varepsilon}\right)\int\! dS_\varepsilon\,\frac{v^\alpha\,v^\beta}{|\boldsymbol{v}|} \\ L^{\alpha\beta}_{21} = T L^{\alpha\beta}_{12} &= -\frac{e}{4\pi^3\hbar}\int\! d\varepsilon\,\tau(\varepsilon)\,(\varepsilon-\mu)\left(-\frac{\partial f^0}{\partial\varepsilon}\right)\int\! dS_\varepsilon\,\frac{v^\alpha\,v^\beta}{|\boldsymbol{v}|} \\ L^{\alpha\beta}_{22} &= \frac{1}{4\pi^3\hbar T}\int\! d\varepsilon\,\tau(\varepsilon)\,(\varepsilon-\mu)^2\left(-\frac{\partial f^0}{\partial\varepsilon}\right)\int\! dS_\varepsilon\,\frac{v^\alpha\,v^\beta}{|\boldsymbol{v}|} \quad ,\end{aligned} \tag{8.221}$$

where dS_ε is a differential surface element in $\boldsymbol{k}$-space at fixed energy $\varepsilon(\boldsymbol{k}) = \varepsilon$, and

$$d^3\!k = \frac{d\varepsilon\,dS_\varepsilon}{|\partial\varepsilon/\partial\boldsymbol{k}|} = \frac{d\varepsilon\,dS_\varepsilon}{\hbar|\boldsymbol{v}|} \quad . \tag{8.222}$$

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

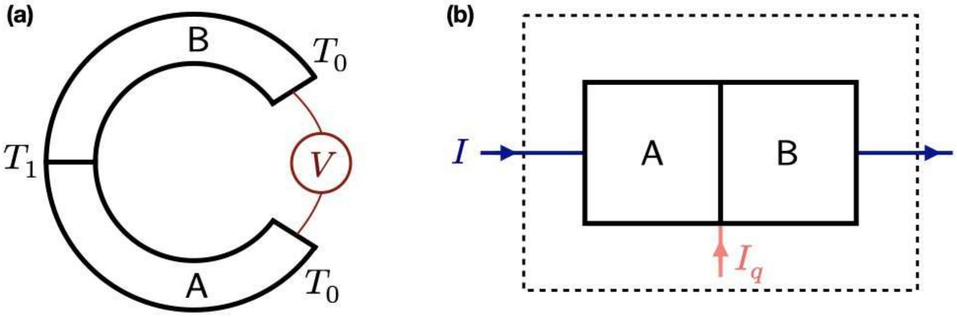

Figure 8.7: (a) A thermocouple is a junction formed of two dissimilar metals. With no electrical current passing, an electric field is generated in the presence of a temperature gradient, resulting in a voltage $V = V_\mathrm{A} - V_\mathrm{B} = (Q_\mathsf{B} - Q_\mathsf{A})(T_1 - T_0)$. (b) A sketch 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 $\sqcap_\mathsf{B} > \sqcap_\mathsf{A}$, in order to maintain a heat current balance at the junction, according to $I_q = (\sqcap_\mathsf{B} - \sqcap_\mathsf{A})I$.

If we define the hierarchy of integral expressions

$$\mathcal{J}_n^{\alpha\beta} \equiv \frac{1}{4\pi^3\hbar}\int d\varepsilon\,\tau(\varepsilon)\,(\varepsilon-\mu)^n\left(-\frac{\partial f^0}{\partial\varepsilon}\right)\int dS_\varepsilon\,\frac{v^\alpha\,v^\beta}{|\boldsymbol{v}|} \tag{8.223}$$

then we may write

$$L_{11}^{\alpha\beta} = e^2\mathcal{J}_0^{\alpha\beta} \quad , \quad L_{21}^{\alpha\beta} = T L_{12}^{\alpha\beta} = -e\,\mathcal{J}_1^{\alpha\beta} \quad , \quad L_{22}^{\alpha\beta} = \frac{1}{T}\,\mathcal{J}_2^{\alpha\beta} \quad . \tag{8.224}$$

The linear relations in eqn. (8.220) may be recast in the following form:

$$\begin{aligned} \boldsymbol{\mathcal{E}} &= \rho\,\boldsymbol{j} + Q\,\boldsymbol{\nabla}\,T \\ \boldsymbol{j}_q &= \sqcap\,\boldsymbol{j} - \kappa\,\boldsymbol{\nabla}\,T \quad , \end{aligned} \tag{8.225}$$

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

$$\rho = L_{11}^{-1} \quad , \quad Q = L_{11}^{-1}\,L_{12} \quad , \quad \sqcap = L_{21}\,L_{11}^{-1} \quad , \quad \kappa = L_{22} - L_{21}\,L_{11}^{-1}\,L_{12} \quad , \tag{8.226}$$

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

$$\rho = \frac{1}{e^2}\,\mathcal{J}_0^{-1} \quad , \quad Q = -\frac{1}{e\,T}\,\mathcal{J}_0^{-1}\,\mathcal{J}_1 \quad , \quad \sqcap = -\frac{1}{e}\,\mathcal{J}_1\,\mathcal{J}_0^{-1} \quad , \quad \kappa = \frac{1}{T}\Big(\mathcal{J}_2 - \mathcal{J}_1\,\mathcal{J}_0^{-1}\,\mathcal{J}_1\Big) \quad , \tag{8.227}$$

These equations describe a wealth of transport phenomena:

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

- Thermal conduction ($\boldsymbol{j} = \boldsymbol{B} = 0$)
  A temperature gradient $\boldsymbol{\nabla} T$ gives rise to a heat current $\boldsymbol{j}_q = -\kappa \boldsymbol{\nabla} T$, where κ is the thermal conductivity.
- Seebeck effect ($\boldsymbol{j} = \boldsymbol{B} = 0$)
  A temperature gradient $\boldsymbol{\nabla} T$ gives rise to an electric field $\boldsymbol{\mathcal{E}} = Q \boldsymbol{\nabla} T$, 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

$$V_{\mathrm{A}} - V_{\mathrm{B}} = -\int\limits_{\mathrm{A}}^{\mathrm{B}} \boldsymbol{\mathcal{E}} \cdot d\boldsymbol{l} = (Q_{\mathrm{B}} - Q_{\mathrm{A}})(T_1 - T_0) \quad . \tag{8.228}$$

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*.

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 $W = (\sqcap_{\mathrm{A}} - \sqcap_{\mathrm{B}})\, I$. 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. [14]

8.9.2 The Heat Equation

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

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j} = 0 \qquad , \qquad \frac{\partial \varepsilon}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_\varepsilon = \boldsymbol{j} \cdot \boldsymbol{E} \quad , \tag{8.229}$$

where $\boldsymbol{E}$ is the electric field[15]. Now we invoke local thermodynamic equilibrium and write

$$\frac{\partial \varepsilon}{\partial t} = \frac{\partial \varepsilon}{\partial n} \frac{\partial n}{\partial t} + \frac{\partial \varepsilon}{\partial T} \frac{\partial T}{\partial t} = -\frac{\mu}{e} \frac{\partial \rho}{\partial t} + c_V \frac{\partial T}{\partial t} \quad , \tag{8.230}$$

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

$$\begin{aligned} c_V \frac{\partial T}{\partial t} &= \frac{\partial \varepsilon}{\partial t} + \frac{\mu}{e} \frac{\partial \rho}{\partial t} \\ &= \boldsymbol{j} \cdot \boldsymbol{E} - \boldsymbol{\nabla} \cdot \boldsymbol{j}_\varepsilon - \frac{\mu}{e} \boldsymbol{\nabla} \cdot \boldsymbol{j} = \boldsymbol{j} \cdot \boldsymbol{\mathcal{E}} - \boldsymbol{\nabla} \cdot \boldsymbol{j}_q \quad . \end{aligned} \tag{8.231}$$

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

[15] 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.

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*

$$c_V \, \frac{\partial T}{\partial t} = \kappa_{\alpha\beta} \, \frac{\partial^2 T}{\partial x^\alpha \, \partial x^\beta} \quad . \tag{8.232}$$

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

$$\mathcal{J}_n = \frac{1}{12\pi^3 \hbar} \int \! d\varepsilon \, \tau(\varepsilon) \, (\varepsilon - \mu)^n \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int \! dS_\varepsilon \, |\boldsymbol{v}| \quad . \tag{8.233}$$

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

$$\mathcal{I} \equiv \int\limits_{-\infty}^{\infty} \! d\varepsilon \, H(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) = \pi \mathcal{D} \csc(\pi \mathcal{D}) \, H(\varepsilon) \Big|_{\varepsilon=\mu} = H(\mu) + \frac{\pi^2}{6} (k_\mathrm{B} T)^2 \, H''(\mu) + \ldots \quad , \tag{8.234}$$

where $\mathcal{D} \equiv k_\mathrm{B} T \, \frac{\partial}{\partial \varepsilon}$ is a dimensionless differential operator[16].

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

$$\mathcal{J}_n = \frac{\sigma_0}{e^2} \, \varepsilon_\mathrm{F}^{-3/2} \, \pi \mathcal{D} \csc \pi \mathcal{D} \, \varepsilon^{3/2} \, (\varepsilon - \mu)^n \Big|_{\varepsilon=\mu} \quad , \tag{8.235}$$

where $\sigma_0 = n e^2 \tau / m^*$. Note that

$$n = \frac{1}{3\pi^2} \left(\frac{2 m^* \varepsilon_\mathrm{F}}{\hbar^2} \right)^{3/2} \tag{8.236}$$

and that ε_F and μ are related by

$$\varepsilon_\mathrm{F}^{3/2} = \pi \mathcal{D} \csc \pi \mathcal{D} \, \varepsilon^{3/2} \Big|_{\varepsilon=\mu} \quad . \tag{8.237}$$

Thus,

$$\mathcal{J}_0 = \frac{\sigma_0}{e^2} \quad , \quad \mathcal{J}_1 = \frac{\sigma_0}{e^2} \, \frac{\pi^2}{2} \, \frac{(k_\mathrm{B} T)^2}{\mu} + \ldots \quad , \quad \mathcal{J}_2 = \frac{\sigma_0}{e^2} \, \frac{\pi^2}{3} (k_\mathrm{B} T)^2 + \ldots \quad , \tag{8.238}$$

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[16] 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 $\rho = \sigma_0^{-1}$,

$$Q = -\frac{\pi^2}{2}\,\frac{k_{\rm B}^2 T}{e\,\varepsilon_{\rm F}} \qquad , \qquad \kappa = \frac{\pi^2}{3}\,\frac{n\tau}{m^*}\,k_{\rm B}^2 T \quad , \tag{8.239}$$

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

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3}\,(k_{\rm B}/e)^2 = 2.45 \times 10^{-8}\,{\rm V}^2\,{\rm K}^{-2} \quad , \tag{8.240}$$

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,

$$J_i = L_{ik}\,F_k \quad , \tag{8.241}$$

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

$$\dot{S} = \sum_i F_i\,J_i \quad \Longrightarrow \quad F_i = \frac{\partial \dot{S}}{\partial J_i} \quad . \tag{8.242}$$

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

$$L_{ik}(\boldsymbol{B}) = \eta_i\,\eta_k\,L_{ki}(-\boldsymbol{B}) \quad , \tag{8.243}$$

where η_i describes the parity of J_i under time reversal:

$$J_i^T = \eta_i\,J_i \quad , \tag{8.244}$$

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,

$$\rho_{\alpha\beta}(\boldsymbol{B}) = \rho_{\beta\alpha}(-\boldsymbol{B}) \qquad , \qquad \kappa_{\alpha\beta}(\boldsymbol{B}) = \kappa_{\beta\alpha}(-\boldsymbol{B}) \qquad , \qquad \sqcap_{\alpha\beta}(\boldsymbol{B}) = T\,Q_{\beta\alpha}(-\boldsymbol{B}) \quad . \tag{8.245}$$

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

$$\begin{aligned}
\rho_{\alpha\beta}(\boldsymbol{B}) &= \rho\,\delta_{\alpha\beta} + \nu\,\epsilon_{\alpha\beta\gamma}\,B^\gamma \\
\kappa_{\alpha\beta}(\boldsymbol{B}) &= \kappa\,\delta_{\alpha\beta} + \varpi\,\epsilon_{\alpha\beta\gamma}\,B^\gamma \\
Q_{\alpha\beta}(\boldsymbol{B}) &= Q\,\delta_{\alpha\beta} + \zeta\,\epsilon_{\alpha\beta\gamma}\,B^\gamma \\
\sqcap_{\alpha\beta}(\boldsymbol{B}) &= \sqcap\,\delta_{\alpha\beta} + \theta\,\epsilon_{\alpha\beta\gamma} B^\gamma \quad .
\end{aligned} \tag{8.246}$$

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

$$\begin{aligned}
\boldsymbol{\mathcal{E}} &= \rho\,\boldsymbol{j} + \nu\,\boldsymbol{j}\times\boldsymbol{B} + Q\,\boldsymbol{\nabla} T + \zeta\,\boldsymbol{\nabla} T\times\boldsymbol{B} \\
\boldsymbol{j}_q &= \sqcap\,\boldsymbol{j} + \theta\,\boldsymbol{j}\times\boldsymbol{B} - \kappa\,\boldsymbol{\nabla} T - \varpi\,\boldsymbol{\nabla} T\times\boldsymbol{B} \quad .
\end{aligned} \tag{8.247}$$

There are several new phenomena lurking:

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

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

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

- Righi-Leduc effect ($j_x = j_y = \mathcal{E}_y = 0$)
  A temperature gradient $\boldsymbol{\nabla} T = \frac{\partial T}{\partial x}\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield an orthogonal 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 Appendix I : The BBGKY Hierarchy and the Boltzmann Equation

The procedure by which the Boltzmann equation for a gas is obtained from N-particle Hamiltonian dynamics of its constituent particles is known as the *Boltzmann-Grad limit*. An excellent source, which we follow here, is Kardar (Particles), §3.3. The formal derivation of the Boltzmann equation from reversible hard sphere dynamics in the low-density limit is generally credited to R. Lanford, "Time Evolution of Large Classical Systems" in *Dynamical Systems, Theory and Applications* (Springer Lecture Notes in Physics, 1975).

8.10.1 BBGKY hierarchy

We start with the time-dependent distribution function, $\varrho_N(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N, \boldsymbol{p}_1, \ldots, \boldsymbol{p}_N, t)$, on N-particle phase space, which is assumed normalized according to

$$\int \prod_{j=1}^{N} d\mu_j \; \varrho_N(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N, \boldsymbol{p}_1, \ldots, \boldsymbol{p}_N, t) = 1 \quad , \tag{8.248}$$

where $d\mu_j \equiv d^d\!x_j \, d^d\!p_j$ (we assume $d = 3$). We define the s-particle distribution function,

$$f_s\big(\{\boldsymbol{x}_i\}, \{\boldsymbol{p}_i\}, t\big) = \frac{N!}{(N-s)!} \int \prod_{i=s+1}^{N} d\mu_i \; \varrho_N\big(\{\boldsymbol{x}_j\}, \{\boldsymbol{p}_j\}, t\big) \equiv \frac{N!}{(N-s)!} \, \varrho_s\big(\{\boldsymbol{x}_i\}, \{\boldsymbol{p}_i\}, t\big) \quad . \tag{8.249}$$

We adopt the notation that $\{\boldsymbol{x}_j\} \equiv \{\boldsymbol{x}_1, \ldots, \boldsymbol{x}_s\}$ when it appears as an argument of a function f_s or ϱ_s, and similarly for $\{\boldsymbol{p}_j\}$. The dynamics of ϱ_N are given by Liouville's equation, $\partial_t \, \varrho_N + \{\varrho_N, H_N\} = 0$, where

$$H_N\big(\{\boldsymbol{x}_j\}, \{\boldsymbol{p}_j\}\big) = \sum_{j=1}^{N} \left[\frac{\boldsymbol{p}_j^2}{2m} + v(\boldsymbol{x}_j) \right] + \sum_{i<j}^{N} u(\boldsymbol{x}_i - \boldsymbol{x}_n) \quad , \tag{8.250}$$

where $v(\boldsymbol{x})$ is an external potential. We may write, for any $s \in \{1, \ldots, N\}$,

$$H_N = H_s + \bar{H}_s + H_s' \quad , \tag{8.251}$$

where

$$\begin{aligned} H_s &= \sum_{j=1}^{s} \left[\frac{\boldsymbol{p}_j^2}{2m} + v(\boldsymbol{x}_j) \right] + \sum_{0<i<j}^{s} u(\boldsymbol{x}_i - \boldsymbol{x}_n) \\ \bar{H}_s &= \sum_{j=s+1}^{N} \left[\frac{\boldsymbol{p}_j^2}{2m} + v(\boldsymbol{x}_j) \right] + \sum_{s<i<j}^{N} u(\boldsymbol{x}_i - \boldsymbol{x}_n) \\ H_s' &= \sum_{i=1}^{s} \sum_{j=s+1}^{N} u(\boldsymbol{x}_i - \boldsymbol{x}_j) \quad . \end{aligned} \tag{8.252}$$

We further assume that $u(\boldsymbol{x}_i - \boldsymbol{x}_j) = u(\boldsymbol{x}_i - \boldsymbol{x}_j)$ is a central potential.

The dynamics of ϱ_s is then given by

$$\frac{\partial \varrho_s}{\partial t} = \int \prod_{j=s+1}^{N} d\mu_j \, \frac{\partial \varrho_N}{\partial t} = -\int \prod_{j=s+1}^{N} d\mu_j \; \{\varrho_N, H_s + \bar{H}_s + H_s'\} \quad . \tag{8.253}$$

We now evaluate each of the three contributions to the Poisson bracket.

The first contribution is easy:

$$\left[\frac{\partial \varrho_s}{\partial t}\right]_{(1)} = -\int \prod_{j=s+1}^{N} d\mu_j \; \{\varrho_N, H_s\} = -\{\varrho_s, H_s\} \quad . \tag{8.254}$$

The second contribution is

$$\begin{aligned}\left[\frac{\partial \varrho_s}{\partial t}\right]_{(2)} &= -\int \prod_{j=s+1}^{N} d\mu_j \{\varrho_N, \bar{H}_s\} \\ &= \int \prod_{j=s+1}^{N} d\mu_j \sum_{k=s+1}^{N} \left[\frac{\partial \varrho_N}{\partial \boldsymbol{p}_k} \cdot \frac{\partial \bar{H}_s}{\partial \boldsymbol{x}_k} - \frac{\partial \varrho_N}{\partial \boldsymbol{x}_k} \cdot \frac{\partial \bar{H}_s}{\partial \boldsymbol{p}_k}\right] \\ &= \int \prod_{j=s+1}^{N} d\mu_j \sum_{k=s+1}^{N} \left[\frac{\partial \varrho_N}{\partial \boldsymbol{p}_k} \cdot \overbrace{\left(\frac{\partial v(\boldsymbol{x}_k)}{\partial \boldsymbol{x}_k} + \frac{1}{2} \sum_{\ell=s+1}^{N} \frac{\partial u(\boldsymbol{x}_k - \boldsymbol{x}_\ell)}{\partial \boldsymbol{x}_k}\right)}^{\text{independent of } \boldsymbol{p}_k} - \frac{\partial \varrho_N}{\partial \boldsymbol{x}_k} \cdot \frac{\boldsymbol{p}_k}{m}\right] = 0 \quad .\end{aligned} \tag{8.255}$$

Here we integrate by parts on both terms inside the square brackets. The term in rounded brackets is independent of $\boldsymbol{p}_k$, while $\boldsymbol{p}_k/m$ is independent of $\boldsymbol{x}_k$. Thus, the second contribution vanishes.

The third contribution is

$$\begin{aligned}\left[\frac{\partial \varrho_s}{\partial t}\right]_{(3)} &= -\int \prod_{j=s+1}^{N} d\mu_j \, \{\varrho_N, H_s'\} \\ &= \int \prod_{j=s+1}^{N} d\mu_j \sum_{k=1}^{s} \sum_{\ell=s+1}^{N} \left(\frac{\partial \rho_N}{\partial \boldsymbol{p}_k} \cdot \frac{\partial u(\boldsymbol{x}_k - \boldsymbol{x}_\ell)}{\partial \boldsymbol{x}_k} - \frac{\partial \rho_N}{\partial \boldsymbol{p}_\ell} \cdot \frac{\partial u(\boldsymbol{x}_k - \boldsymbol{x}_\ell)}{\partial \boldsymbol{x}_\ell}\right) \\ &= (N-s) \int d\mu_{s+1} \sum_{k=1}^{s} \frac{\partial u(\boldsymbol{x}_k - \boldsymbol{x}_{s+1})}{\partial \boldsymbol{x}_k} \cdot \frac{\partial}{\partial \boldsymbol{p}_k} \left(\int \prod_{\ell=s+2}^{N} d\mu_\ell \, \varrho_N\right)\end{aligned} \tag{8.256}$$

Thus, we arrive at

$$\frac{\partial \varrho_s}{\partial t} + \{\rho_s, H_s\} = (N-s) \int d\mu_{s+1} \sum_{k=1}^{s} \frac{\partial u(\boldsymbol{x}_k - \boldsymbol{x}_{s+1})}{\partial \boldsymbol{x}_k} \cdot \frac{\partial \varrho_{s+1}}{\partial \boldsymbol{p}_k} \quad , \tag{8.257}$$

or

$$\frac{\partial f_s}{\partial t} + \{f_s, H_s\} = \int d\mu_{s+1} \sum_{k=1}^{s} \frac{\partial u(\boldsymbol{x}_k - \boldsymbol{x}_{s+1})}{\partial \boldsymbol{x}_k} \cdot \frac{\partial f_{s+1}}{\partial \boldsymbol{p}_k} \quad . \tag{8.258}$$

This is the BBGKY hierarchy.

8.10.2 Boltzmann equation

At each level of the hierarchy, we may identify three types of terms, each of which is associated with its own time scale. The size of each type is roughly inversely proportional to its characteristic time scale[17]. The first type of term arises from the noninteracting terms in H_s, *i.e.* the one-body terms, which do not involve the interaction potential $u(\boldsymbol{x}_i - \boldsymbol{x}_j)$. The time scale associated with these terms behaves as

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[17] See Kardar §3.3 for a more detailed discussion.

$\tau_v \sim L/V$, where V is a characteristic velocity and L the linear system size. This extrinsic scale becomes arbitrarily large as $L \to \infty$. The second type of term are those on the LHS of the equation for ϱ_s. Assuming $u(\boldsymbol{x})$ is short-ranged, such as a van der Waals or Lennard-Jones potential, the typical distance scale is $d \sim 1$ Å, which entails a collision time $\tau_c \sim 10^{-12}$ s. Finally, the third type at each level are terms on the RHS which are proportional to the interaction potential u. Because the distribution function f_{s+1} enters, these terms require an additional particle be present, and the time constant is longer than τ by a factor $nd^3 \sim 10^4$. One concludes that the terms proportional to nd^3/τ_c that appear on the RHS at each level may be dropped, because they are dominated by the terms proportional to $1/\tau_c$ on the LHS at any given level. This means that each level of the hierarchy provides a closed equation for f_s, with the sole exception of $s = 1$, where there is no interaction term on the LHS.

At level $s = 2$, the equation for f_2 is

$$\left\{ \frac{\partial}{\partial t} + \frac{\boldsymbol{p}_1}{m} \cdot \frac{\partial}{\partial \boldsymbol{x}_1} + \frac{\boldsymbol{p}_2}{m} \cdot \frac{\partial}{\partial \boldsymbol{x}_2} - \frac{\partial u(\boldsymbol{x}_2 - \boldsymbol{x}_1)}{\partial \boldsymbol{x}_1} \cdot \frac{\partial}{\partial \boldsymbol{p}_1} - \frac{\partial u(\boldsymbol{x}_2 - \boldsymbol{x}_1)}{\partial \boldsymbol{x}_2} \cdot \frac{\partial}{\partial \boldsymbol{p}_2} \right\} f_2(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{p}_1, \boldsymbol{p}_2, t) = 0 \quad . \tag{8.259}$$

On time scales long compared with τ_c, the distribution f_2 reaches a steady state value. In the presence of slowly time-varying parameters such as the temperature $T(\boldsymbol{r}, t)$ or chemical potential $\mu(\boldsymbol{r}, t)$, or in the presence of a time-dependent external force $\boldsymbol{F}(\boldsymbol{r}, t)$, the distribution f_2 will evolve, but on a longer time scale associated with these respective variations. Therefore we can fix the time t and freeze these slow changes and ask about the steady state distribution $f_2^{\text{ss}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{p}_1, \boldsymbol{p}_2, t)$. In discussing the 'instantaneous steady state' – a seemingly nonsensical collocation which however has meaning given the aforementioned separation of time scales – we suppress for the moment the t label and we define $\phi(\boldsymbol{X}, \boldsymbol{x}, \boldsymbol{p}_1, \boldsymbol{p}_2) \equiv f_2(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{p}_2, \boldsymbol{p}_2)$, where $\boldsymbol{X} \equiv \frac{1}{2}(\boldsymbol{x}_2 + \boldsymbol{x}_2)$ is the center-of-mass coordinate and $\boldsymbol{x} \equiv \boldsymbol{x}_2 - \boldsymbol{x}_1$ is the relative coordinate. We then have

$$\left\{ \left(\frac{\boldsymbol{p}_1 + \boldsymbol{p}_2}{2m} \right) \cdot \frac{\partial}{\partial \boldsymbol{X}} + \left(\frac{\boldsymbol{p}_1 - \boldsymbol{p}_2}{m} \right) \cdot \frac{\partial}{\partial \boldsymbol{x}} + \boldsymbol{\nabla} u(\boldsymbol{x}) \cdot \left(\frac{\partial}{\partial \boldsymbol{p}_1} - \frac{\partial}{\partial \boldsymbol{p}_2} \right) \right\} \phi(\boldsymbol{X}, \boldsymbol{x}, \boldsymbol{p}_1, \boldsymbol{p}_2) = 0 \quad . \tag{8.260}$$

We recognize this as a linear partial differential equation in the 12 variables $\{\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{p}_1, \boldsymbol{p}_2\}$, which, in principle, may be solved by the method of characteristics. This entails introducing a scalar variable τ and solving the coupled ODEs

$$\frac{d\boldsymbol{X}}{d\tau} = \frac{\boldsymbol{p}_1 + \boldsymbol{p}_2}{2m} \quad , \quad \frac{d\boldsymbol{x}}{d\tau} = \frac{\boldsymbol{p}_2 - \boldsymbol{p}_1}{m} \quad , \quad \frac{d\boldsymbol{p}_1}{d\tau} = \boldsymbol{\nabla} u(\boldsymbol{x}) \quad , \quad \frac{d\boldsymbol{p}_2}{d\tau} = -\boldsymbol{\nabla} u(\boldsymbol{x}) \quad . \tag{8.261}$$

This defines a path in the 12-dimensional space. Along such a path,

$$\frac{d\phi\big(\boldsymbol{X}(\tau), \boldsymbol{x}(\tau), \boldsymbol{p}_1(\tau), \boldsymbol{p}_2(\tau)\big)}{d\tau} = \frac{\partial \phi}{\partial \boldsymbol{X}} \cdot \frac{d\boldsymbol{X}}{d\tau} + \frac{\partial \phi}{\partial \boldsymbol{x}} \cdot \frac{d\boldsymbol{x}}{d\tau} + \frac{\partial \phi}{\partial \boldsymbol{p}_1} \cdot \frac{d\boldsymbol{p}_1}{d\tau} + \frac{\partial \phi}{\partial \boldsymbol{p}_2} \cdot \frac{d\boldsymbol{p}_2}{d\tau} = 0 \quad . \tag{8.262}$$

The $N = 12$ variable PDE of eqn. 8.259 thus has been converted into a system of $N + 1 = 13$ coupled ODEs of eqns. 8.261 and 8.262. We see that τ functions as a time variable, and the coupled ODEs of eqn. 8.261 are simply Hamilton's equations of motion. Note that $\boldsymbol{P} \equiv \boldsymbol{p}_1 + \boldsymbol{p}_2$ satisfies $d\boldsymbol{P}/dt = 0$ and we have the familiar CM motion $\boldsymbol{X}(\tau) = \boldsymbol{P}\tau/M$, with $M = 2m$ the total mass. Initial conditions for the N variables $\boldsymbol{w} = \{w_1, \ldots, w_N\}$ at $\tau = 0$ are specified by fixing a hypersurface parameterized by $N - 1$ variables $\boldsymbol{\zeta} = \{\zeta_1, \ldots, \zeta_{N-1}\}$, where

$$w_j(\tau = 0) = h_j(\zeta_1, \ldots, \zeta_{N-1}) \qquad , \qquad \phi(\tau = 0) = F(\zeta_1, \ldots, \zeta_{N-1}) \quad , \tag{8.263}$$

and where the $\{h_j(\boldsymbol{\zeta})\}$ define the hypersurface. A simple way to think of this is to define the hypersurface by the relation $w_N = 0$, and take $w_j(\tau = 0) = \zeta_j$ for $j \in \{1, \ldots, N-1\}$, *i.e.* $h_j(\boldsymbol{\zeta}) = \zeta_j$. Each characteristic is labeled by an $(N-1)$-tuple $\boldsymbol{\zeta}$, and the solution along a characteristic is $\phi(\boldsymbol{w}) = \phi(\tau; \boldsymbol{\zeta})$[18].

Now we turn to level $s = 1$ of the hierarchy, where we have

$$\frac{\partial f}{\partial t} + \frac{\boldsymbol{p}_1}{m} \cdot \frac{\partial f}{\partial \boldsymbol{x}_1} - \boldsymbol{\nabla} v(\boldsymbol{x}_1) \cdot \frac{\partial f}{\partial \boldsymbol{p}_1} = \int \! d\mu_2 \, \frac{\partial u(\boldsymbol{x}_2 - \boldsymbol{x}_1)}{\partial \boldsymbol{x}_1} \cdot \left(\frac{\partial f_2}{\partial \boldsymbol{p}_1} - \frac{\partial f_2}{\partial \boldsymbol{p}_2} \right) \tag{8.264}$$

We now invoke the relation

$$-\boldsymbol{\nabla} u(\boldsymbol{x}) \cdot \left(\frac{\partial f_2}{\partial \boldsymbol{p}_1} - \frac{\partial f_2}{\partial \boldsymbol{p}_2} \right) = \left(\frac{\boldsymbol{p}_1 + \boldsymbol{p}_2}{2m} \right) \cdot \frac{\partial f_2}{\partial \boldsymbol{X}} + \left(\frac{\boldsymbol{p}_1 - \boldsymbol{p}_2}{m} \right) \cdot \frac{\partial f_2}{\partial \boldsymbol{x}} \quad , \tag{8.265}$$

leading us to

$$\frac{\partial f}{\partial t} + \frac{\boldsymbol{p}_1}{m} \cdot \frac{\partial f}{\partial \boldsymbol{x}_1} - \boldsymbol{\nabla} v(\boldsymbol{x}_1) \cdot \frac{\partial f}{\partial \boldsymbol{p}_1} = \int \! d^3\!p_2 \! \int \! d^3\!x \left(\frac{\boldsymbol{p}_1 - \boldsymbol{p}_2}{m} \right) \cdot \frac{\partial f_2(\boldsymbol{x}_1, \boldsymbol{x}_1 + \boldsymbol{x}, \boldsymbol{p}_1, \boldsymbol{p}_2, t)}{\partial \boldsymbol{x}} \quad , \tag{8.266}$$

where we have restored the time label t. In arriving at this last equation, note that we have dropped terms proportional fo $\partial f_2 / \partial \boldsymbol{X}$. This is justified by the presumption that the center-of-mass dynamics are relatively slow. Note also that on the RHS we are expressing the spatial coordinates in terms of $\boldsymbol{x}_1$ and $\boldsymbol{x}$, hence we have substituted $\boldsymbol{x}_2 = \boldsymbol{x}_1 + \boldsymbol{x}$ in the second vector argument of f_2.

Consider the integral on the RHS of eqn. 8.266 over the relative coordinate $\boldsymbol{x}$. Following Kardar, at fixed $\boldsymbol{x}_1$, $\boldsymbol{p}_1$, and $\boldsymbol{p}_2$, we choose a coordinate system for $\boldsymbol{x}$ where one axis is parallel to $\hat{\boldsymbol{n}} = (\boldsymbol{p}_1 - \boldsymbol{p}_2)/|\boldsymbol{p}_1 - \boldsymbol{p}_2|$ and write

$$\boldsymbol{x} = x_\parallel \, \hat{\boldsymbol{n}} + \boldsymbol{b} \quad , \tag{8.267}$$

where $\hat{\boldsymbol{n}} \cdot \boldsymbol{b} = 0$. The vector $\boldsymbol{b}$ is known as the *impact parameter vector*. We then have

$$\left(\frac{df}{dt} \right)_{\text{coll}} = \int \! d^3\!p_2 \! \int \! d^2\!b \left| \frac{\boldsymbol{p}_1 - \boldsymbol{p}_2}{m} \right| \Big\{ \tilde{f}_2^+(\boldsymbol{x}_1, \boldsymbol{b}, \boldsymbol{p}_1, \boldsymbol{p}_2, t) - \tilde{f}_2^-(\boldsymbol{x}_1, \boldsymbol{b}, \boldsymbol{p}_1, \boldsymbol{p}_2, t) \Big\} \quad , \tag{8.268}$$

where

$$\tilde{f}_2^\pm(\boldsymbol{x}_1, \boldsymbol{b}, \boldsymbol{p}_1, \boldsymbol{p}_2, t) \equiv f_2(\boldsymbol{x}_1, \boldsymbol{x}_1 + x_\perp^+ \, \hat{\boldsymbol{n}} + \boldsymbol{b}, \boldsymbol{p}_1, \boldsymbol{p}_2, t) \quad , \tag{8.269}$$

and where $x_\parallel^\pm$ is the value of $\hat{\boldsymbol{n}} \cdot \boldsymbol{x}$ after $(+)$ or before $(-)$ the collision. We assume the potential $u(\boldsymbol{x})$ is sufficiently short-ranged that $x_\parallel^\pm$ may be evaluated a short distance from the collision center $\boldsymbol{x} = 0$. In a scattering process, the momenta $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ prior to the scattering event evolve into $\boldsymbol{p}_1'$ and $\boldsymbol{p}_2'$ after the event. The relation between the incoming and outgoing momenta is given by eqn. 8.59, *i.e.*

$$\begin{aligned} \boldsymbol{p}_1' &= \tfrac{1}{2} \big(\boldsymbol{p}_1 + \boldsymbol{p}_2 + |\boldsymbol{p}_1 - \boldsymbol{p}_2| \, \hat{\boldsymbol{\Omega}} \big) \\ \boldsymbol{p}_2' &= \tfrac{1}{2} \big(\boldsymbol{p}_1 + \boldsymbol{p}_2 - |\boldsymbol{p}_1 - \boldsymbol{p}_2| \, \hat{\boldsymbol{\Omega}} \big) \quad , \end{aligned} \tag{8.270}$$

where $\hat{\boldsymbol{\Omega}} = \hat{\boldsymbol{\Omega}}(\boldsymbol{b})$ is a unit vector which is determined by the impact parameter vector $\boldsymbol{b}$. Assuming the system is time-reversal invariant, we may relate $\tilde{f}_2^+$ and $\tilde{f}_2^-$ by

$$\tilde{f}_2^+(\boldsymbol{x}_1, \boldsymbol{b}, \boldsymbol{p}_1, \boldsymbol{p}_2, t) = \tilde{f}_2^-(\boldsymbol{x}_1, \boldsymbol{b}, \boldsymbol{p}_1', \boldsymbol{p}_2', t) \quad . \tag{8.271}$$

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[18] If two characteristics cross, a shock has occurred.

This suggests that we could write the collision integral in either of two ways:

$$\begin{aligned}\left(\frac{df}{dt}\right)_{\text{coll},-} &= \int\! d^3\!p_2 \int\! d\Omega\, \frac{d\sigma}{d\Omega}\, |\boldsymbol{v}_1-\boldsymbol{v}_2| \left\{ \tilde{f}_2^-(\boldsymbol{x}_1,\boldsymbol{b},\boldsymbol{p}_1',\boldsymbol{p}_2',t) - \tilde{f}_2^-(\boldsymbol{x}_1,\boldsymbol{b},\boldsymbol{p}_1,\boldsymbol{p}_2,t)\right\} \\ \left(\frac{df}{dt}\right)_{\text{coll},+} &= \int\! d^3\!p_2 \int\! d\Omega\, \frac{d\sigma}{d\Omega}\, |\boldsymbol{v}_1-\boldsymbol{v}_2| \left\{ \tilde{f}_2^+(\boldsymbol{x}_1,\boldsymbol{b},\boldsymbol{p}_1,\boldsymbol{p}_2,t) - \tilde{f}_2^+(\boldsymbol{x}_1,\boldsymbol{b},\boldsymbol{p}_1',\boldsymbol{p}_2',t)\right\} \quad .\end{aligned} \tag{8.272}$$

Here we have also written

$$d^2b = \frac{d\sigma}{d\Omega}\,d\Omega \quad , \tag{8.273}$$

where $d\Omega$ is the differential solid angle of the scattering process. The expression $d\sigma/d\Omega$, which should be familiar from both classical mechanics and quantum mechanics, is the *differential scattering cross-section*. We assume there is a unique relationship between the scattering direction $\hat{\boldsymbol{\Omega}}(\boldsymbol{b})$ and the impact parameter vector $\boldsymbol{b}$, which is to say that the $\boldsymbol{b}$ plane can be mapped to the unit sphere $\hat{\boldsymbol{\Omega}}(\boldsymbol{b})$ in a one-to-one fashion. In general, $d\sigma/d\Omega \to 0$ for $|\boldsymbol{b}| \gg r_\text{c}$, where r_c is the length scale over which the scattering occurs, which is presumed to be microscopic. At long last, we make the assumption,

$$\tilde{f}_2^\pm(\boldsymbol{x}_1,\boldsymbol{b},\boldsymbol{p}_1,\boldsymbol{p}_2,t) \approx f_1(\boldsymbol{x}_1,\boldsymbol{p}_1,t) \times f_1(\boldsymbol{x}_2,\boldsymbol{p}_2,t) \quad . \tag{8.274}$$

This is known as the *Stosszahlanzatz* or the *hypothesis of molecular chaos*, and amounts to assuming that the velocities of colliding particles are uncorrelated. But are they uncorrelated before ($-$) or after ($+$) the collision? The answer makes a huge difference! It determines which of the candidate collision integrals in eqn. 8.272 is correct.

Our Boltzmann equation for the one-body distribution $f(\boldsymbol{r},\boldsymbol{p},t)$ is now given by

$$\begin{aligned}\left(\frac{df}{dt}\right)_{\text{coll}} &= \pm\!\int\! d^3\!p_1\!\int\! d\Omega\,\frac{d\sigma}{d\Omega}\left|\frac{\boldsymbol{p}-\boldsymbol{p}_1}{m}\right| \left\{ f(\boldsymbol{r},\boldsymbol{p},t)f(\boldsymbol{r},\boldsymbol{p}_1,t) - f(\boldsymbol{r},\boldsymbol{p}',t)f(\boldsymbol{r},\boldsymbol{p}_1',t)\right\} \\ &= \pm\!\int\! d^3\!p_1\!\int\! d^3\!p'\!\int\! d^3\!p_1'\; w(\boldsymbol{p},\boldsymbol{p}_1\,|\,\boldsymbol{p}',\boldsymbol{p}_1') \left\{ f(\boldsymbol{r},\boldsymbol{p},t)f(\boldsymbol{r},\boldsymbol{p}_1,t) - f(\boldsymbol{r},\boldsymbol{p}',t)f(\boldsymbol{r},\boldsymbol{p}_1',t)\right\}\end{aligned} \tag{8.275}$$

where we have used eqn. 8.41 in the last line. According to the results of §8.3.7, we see that choosing $\tilde{f}_2^+$ in eqn. 8.274 results in a generically *positive* source for Boltzmann's $\mathcal{H}$ density, h, which is to say $\partial_t h + \boldsymbol{\nabla}\cdot\boldsymbol{j} \ge 0$, so for this choice we have an "anti $\mathcal{H}$-theorem". Thermodynamically, this means that entropy of an isolated system *decreases* (since $S = -k_\text{B}\mathcal{H}$), which is the exact opposite of what the second law of thermodynamics requires. Thus, the correct choice is to take $\tilde{f}_2^-$ in eqn. 8.274, in which case our Boltzmann equation takes the final form[19]

$$\frac{\partial f}{\partial t} + \frac{\boldsymbol{p}}{m}\cdot\frac{\partial f}{\partial \boldsymbol{r}} - \frac{\partial v}{\partial \boldsymbol{r}}\cdot\frac{\partial f}{\partial \boldsymbol{p}} = \int\! d^3\!p_1\!\int\! d^3\!p'\!\int\! d^3\!p_1'\; w(\boldsymbol{p},\boldsymbol{p}_1\,|\,\boldsymbol{p}',\boldsymbol{p}_1') \left\{ f(\boldsymbol{r},\boldsymbol{p}',t)f(\boldsymbol{r},\boldsymbol{p}_1',t) - f(\boldsymbol{r},\boldsymbol{p},t)f(\boldsymbol{r},\boldsymbol{p}_1,t)\right\} \quad . \tag{8.276}$$

Why is it necessary to invoke the *Stosszahlansatz* for particles which are just about to collide, but *not* for particles which have just collided? This is a deep question, and the essence of Loschmidt's objection

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[19] Note also that if we were to impose the *Stosszahlansatz* on each term inside the curly brackets on the RHS of eqn. 8.268, the collision integral would vanish!

to the Boltzmann equation and the $\mathcal{H}$-theorem it entails (also called *Lohschmidt's paradox*) – how can irreversibility result from microscopic dynamics which are invariant under time-reversal? As Lanford (1975) stresses, "the BBGKY hierarchy is time-reversal invariant but the Boltzmann equation is not." The answer appears to be quite subtle and still somewhat contentious. Bodineau *et al.*[20] claim that the BBGKY dynamics for dilute hard spheres in d dimensions[21] converges to the solution of the Boltzmann equation, *i.e.* one must specify pre-collisional data.

8.11 Appendix II : Boltzmann Equation and Collisional Invariants

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

$$\begin{aligned}\mathcal{L}\psi = -\gamma\,\psi(\boldsymbol{v},t) + \gamma\bigg(\frac{m}{2\pi k_\text{B}T}\bigg)^{3/2}&\int\! d^3\!u\, \exp\bigg(-\frac{m\boldsymbol{u}^2}{2k_\text{B}T}\bigg)\\ &\times\bigg\{1+\frac{m}{k_\text{B}T}\,\boldsymbol{u}\cdot\boldsymbol{v} + \frac{2}{3}\bigg(\frac{m\boldsymbol{u}^2}{2k_\text{B}T}-\frac{3}{2}\bigg)\bigg(\frac{m\boldsymbol{v}^2}{2k_\text{B}T}-\frac{3}{2}\bigg)\bigg\}\,\psi(\boldsymbol{u},t)\quad .\end{aligned} \tag{8.277}$$

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,

$$\psi(\boldsymbol{v},t) = \sum_{r\ell m} a_{r\ell m}(t)\, S^r_{\ell+\frac{1}{2}}(x)\, x^{\ell/2}\, Y_{\ell,m}(\hat{\boldsymbol{n}}), \tag{8.278}$$

with $x = mv^2/2k_\text{B}T$, 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

$$S^n_\alpha(x) = \sum_{m=0}^{n} \frac{\Gamma(\alpha+n+1)\,(-x)^m}{\Gamma(\alpha+m+1)\,(n-m)!\,m!}\quad , \tag{8.279}$$

and satisfy the generalized orthogonality relation

$$\int\limits_0^\infty\! dx\, e^{-x}\, x^\alpha\, S^n_\alpha(x)\, S^{n'}_\alpha(x) = \frac{\Gamma(\alpha+n+1)}{n!}\,\delta_{n,n'}\quad . \tag{8.280}$$

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.

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[20] See T. Bodineau, I. Gallagher, L. Saint-Raymond, and S. Simonella, "One-sided convergence in the Boltzmann-Grad limit," *Annales de la Faculté des Sciences de Tolouse*, vol. XXVIII, no. 5, p. 985 (2018).

[21] The Boltzmann-Grad limit is defined by N hard spheres each of diameter δ in a box of volume V, with $n\delta^{d-1}\ell \sim 1$, where $n = N/V \to \infty$ is the number density of spheres and ℓ is the finite mean free path. Thus $\delta \sim n^{-1/(d-1)} \to 0$.

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

$$\begin{aligned}\mathcal{L}\psi = -\gamma \sum_{r\ell m} a_{r\ell m}(t)\, S^r_{\ell+\frac{1}{2}}(x)\, x^{\ell/2}\, Y_{\ell,m}(\hat{\boldsymbol{n}}) \;+\; \frac{\gamma}{2\pi^{3/2}} \sum_{r\ell m} a_{r\ell m}(t) \int\limits_0^\infty dx_1\, x_1^{1/2}\, e^{-x_1} \\ \times \int d\hat{\boldsymbol{n}}_1 \Big[1 + 2\,x^{1/2} x_1^{1/2}\, \hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{n}}_1 + \tfrac{2}{3}\big(x-\tfrac{3}{2}\big)\big(x_1-\tfrac{3}{2}\big)\Big]\, S^r_{\ell+\frac{1}{2}}(x_1)\, x_1^{\ell/2}\, Y_{\ell,m}(\hat{\boldsymbol{n}}_1) \quad ,\end{aligned} \tag{8.281}$$

where we've used

$$u = \sqrt{\frac{2k_{\rm B}T}{m}}\, x_1^{1/2} \qquad , \qquad du = \sqrt{\frac{k_{\rm B}T}{2m}}\, x_1^{-1/2}\, dx_1 \quad . \tag{8.282}$$

Now recall $Y_{0,0}(\hat{\boldsymbol{n}}) = \frac{1}{\sqrt{4\pi}}$ and

$$\begin{aligned} &Y_{1,1}(\hat{\boldsymbol{n}}) = -\sqrt{\frac{3}{8\pi}}\, \sin\theta\, e^{i\varphi} \qquad && Y_{1,0}(\hat{\boldsymbol{n}}) = \sqrt{\frac{3}{4\pi}}\, \cos\theta \qquad && Y_{1,-1}(\hat{\boldsymbol{n}}) = +\sqrt{\frac{3}{8\pi}}\, \sin\theta\, e^{-i\varphi} \\ &S^0_{1/2}(x) = 1 && S^0_{3/2}(x) = 1 && S^1_{1/2}(x) = \tfrac{3}{2} - x \quad , \end{aligned} \tag{8.283}$$

which allows us to write

$$\begin{aligned} 1 &= 4\pi\, Y_{0,0}(\hat{\boldsymbol{n}})\, Y^*_{0,0}(\hat{\boldsymbol{n}}_1) \\ \hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{n}}_1 &= \frac{4\pi}{3}\Big[\, Y_{1,0}(\hat{\boldsymbol{n}})\, Y^*_{1,0}(\hat{\boldsymbol{n}}_1) + Y_{1,1}(\hat{\boldsymbol{n}})\, Y^*_{1,1}(\hat{\boldsymbol{n}}_1) + Y_{1,-1}(\hat{\boldsymbol{n}})\, Y^*_{1,-1}(\hat{\boldsymbol{n}}_1) \Big] \quad . \end{aligned} \tag{8.284}$$

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

$$\begin{aligned} \int d\hat{\boldsymbol{n}}\, Y_{\ell,m}(\hat{\boldsymbol{n}})\, Y^*_{l',m'}(\hat{\boldsymbol{n}}) &= \delta_{l,l'}\, \delta_{m,m'} \\ \int\limits_0^\infty dx\, e^{-x}\, x^\alpha\, S^n_\alpha(x)\, S^{n'}_\alpha(x) &= \frac{\Gamma(n+\alpha+1)}{\Gamma(n+1)}\, \delta_{n,n'} \quad . \end{aligned} \tag{8.285}$$

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

$$\begin{aligned} \mathcal{L}\psi = -\gamma \sum_{r\ell m} a_{r\ell m}(t)\, S^r_{\ell+\frac{1}{2}}(x)\, x^{\ell/2}\, Y_{\ell,m}(\hat{\boldsymbol{n}}) \\ + \frac{2\gamma}{\sqrt{\pi}} \sum_{r\ell m} a_{r\ell m}(t) \int\limits_0^\infty dx_1\, x_1^{1/2}\, e^{-x_1} \int d\hat{\boldsymbol{n}}_1\, \Big[Y_{0,0}(\hat{\boldsymbol{n}})\, Y^*_{0,0}(\hat{\boldsymbol{n}}_1)\, S^0_{1/2}(x)\, S^0_{1/2}(x_1) \\ + \tfrac{2}{3}\, x^{1/2} x_1^{1/2} \sum_{m'=-1}^{1} Y_{1,m'}(\hat{\boldsymbol{n}})\, Y^*_{1,m'}(\hat{\boldsymbol{n}}_1)\, S^0_{3/2}(x)\, S^0_{3/2}(x_1) \\ + \tfrac{2}{3}\, Y_{0,0}(\hat{\boldsymbol{n}})\, Y^*_{0,0}(\hat{\boldsymbol{n}}_1)\, S^1_{1/2}(x)\, S^1_{1/2}(x_1) \Big]\, S^r_{\ell+\frac{1}{2}}(x_1)\, x_1^{\ell/2}\, Y_{\ell,m}(\hat{\boldsymbol{n}}_1) \quad , \end{aligned} \tag{8.286}$$

we obtain the intermediate result

$$\begin{aligned}\mathcal{L}\psi = -\gamma \sum_{r\ell m} a_{r\ell m}(t)\, S^r_{\ell+\frac{1}{2}}(x)\, x^{\ell/2}\, Y_{\ell,m}(\hat{\boldsymbol{n}}) \\ + \frac{2\gamma}{\sqrt{\pi}} \sum_{r\ell m} a_{r\ell m}(t) \int\limits_0^\infty \! dx_1\, x_1^{1/2}\, e^{-x_1} \Big[Y_{0,0}(\hat{\boldsymbol{n}})\, \delta_{l,0}\, \delta_{m,0}\, S^0_{1/2}(x)\, S^0_{1/2}(x_1) \\ + \tfrac{2}{3}\, x^{1/2} x_1^{1/2} \sum_{m'=-1}^{1} Y_{1,m'}(\hat{\boldsymbol{n}})\, \delta_{l,1}\, \delta_{m,m'}\, S^0_{3/2}(x)\, S^0_{3/2}(x_1) \\ + \tfrac{2}{3}\, Y_{0,0}(\hat{\boldsymbol{n}})\, \delta_{l,0}\, \delta_{m,0}\, S^1_{1/2}(x)\, S^1_{1/2}(x_1) \Big]\, S^r_{\ell+\frac{1}{2}}(x_1)\, x_1^{1/2} .\end{aligned} \tag{8.287}$$

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

$$\Gamma(\tfrac{1}{2}) = \sqrt{\pi} \quad , \quad \Gamma(1) = 1 \quad , \quad \Gamma(z+1) = z\,\Gamma(z) \quad , \tag{8.288}$$

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

$$\mathcal{L}\psi = -\gamma {\sum_{r\ell m}}' a_{r\ell m}(t)\, S^r_{\ell+\frac{1}{2}}(x)\, x^{\ell/2}\, Y_{\ell,m}(\hat{\boldsymbol{n}}) \tag{8.289}$$

where the prime on the sum indicates that the set

$$\text{CI} = \Big\{ (0,0,0) \quad , \quad (1,0,0) \quad , \quad (0,1,1) \quad , \quad (0,1,0) \quad , \quad (0,1,-1) \Big\} \tag{8.290}$$

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

$$\psi_{r\ell m}(\boldsymbol{v}) = \mathcal{N}_{r\ell m}\, S^r_{\ell+\frac{1}{2}}(x)\, x^{\ell/2}\, Y_{\ell,m}(\hat{\boldsymbol{n}}), \tag{8.291}$$

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

$$(\mathcal{L}a)_{r\ell m} = \begin{cases} -\gamma\, a_{r\ell m} & \text{if } (r,\ell,m) \notin \text{CI} \\ = 0 & \text{if } (r,\ell,m) \in \text{CI} \end{cases} \tag{8.292}$$

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

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

$$\begin{aligned}\langle\, \phi \,|\, \mathcal{L}\psi \,\rangle = \langle\, \mathcal{L}\phi \,|\, \psi \,\rangle &\equiv \int\! d^3\!v\; f^0(\boldsymbol{v})\, \phi(\boldsymbol{v})\, \mathcal{L}[\psi(\boldsymbol{v})] \\ &= -\gamma\, n \left(\frac{m}{2\pi k_{\rm B} T}\right)^{3/2} \int\! d^3\!v\; \exp\left(-\,\frac{m\boldsymbol{v}^2}{2k_{\rm B}T}\right) \phi(\boldsymbol{v})\, \psi(\boldsymbol{v}) \\ &\qquad + \gamma\, n \left(\frac{m}{2\pi k_{\rm B} T}\right)^{3} \int\! d^3\!v \!\int\! d^3\!u\; \exp\left(-\,\frac{m\boldsymbol{u}^2}{2k_{\rm B}T}\right) \exp\left(-\,\frac{m\boldsymbol{v}^2}{2k_{\rm B}T}\right) \\ &\qquad\qquad \times\, \phi(\boldsymbol{v}) \left[1 + \frac{m}{k_{\rm B}T}\, \boldsymbol{u}\cdot\boldsymbol{v} + \frac{2}{3}\left(\frac{m\boldsymbol{u}^2}{2k_{\rm B}T} - \frac{3}{2}\right)\left(\frac{m\boldsymbol{v}^2}{2k_{\rm B}T} - \frac{3}{2}\right)\right] \psi(\boldsymbol{u}) \quad ,\end{aligned} \tag{8.293}$$

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