8
Irreversible processes: kinetic theory

In this chapter we shall discuss a microscopic theory of transport phenomena, namely kinetic theory. The central idea of kinetic theory is to explain the behaviour of out-of-equilibrium systems as the consequence of collisions among the particles forming the system. These collisions are described using the concept of cross section which will be introduced in Section 8.1 where we shall also demonstrate an elementary, but not rigorous, first calculation of transport coefficients. Then, in the following section, we introduce the Boltzmann–Lorentz model which describes collisions of molecules with fixed randomly distributed scattering centres. This model gives a good description of transport properties in several physically important systems such as the transport of electrons and holes in a semiconductor. In Section 8.3 we shall give a general discussion of the Boltzmann equation, with two important results: the derivation of hydrodynamics and that of the H-theorem, which gives an explicit proof of irreversibility. Finally, in the last section, we shall address the rigorous calculation of the transport coefficients, viscosity and thermal conductivity, in a dilute mono-atomic gas.

8.1 Generalities, elementary theory of transport coefficients

8.1.1 Distribution function

We adopt straight away the classical description where a point in phase space is given by its position, \( \vec{r} \), and momentum, \( \vec{p} \). The basic tool of kinetic theory is the distribution function \( f(\vec{r}, \vec{p}, t) \), which is the density of particles in phase space: the number of particles at time \( t \) in the volume \( d^3r d^3p \) at the phase space point \( (\vec{r}, \vec{p}) \) is, by definition, given by \( f(\vec{r}, \vec{p}, t)d^3r d^3p \). The goal of kinetic theory is to calculate spatio-temporal dynamics of the distribution function. The particle
density in position space, \( n(\vec{r}, t) \), is the momentum integral of \( f(\vec{r}, \vec{p}, t) \)

\[
\begin{align*}
n(\vec{r}, t) &= \int d^3p \, f(\vec{r}, \vec{p}, t) \quad (8.1)
\end{align*}
\]

Let \( A(\vec{r}, \vec{p}) \) be a classical dynamical variable. We define its average value, \( A(\vec{r}, t) \), at point \( \vec{r} \) by

\[
A(\vec{r}, t) = \frac{1}{n(\vec{r}, t)} \int d^3p \, A(\vec{r}, \vec{p}) f(\vec{r}, \vec{p}, t) \quad (8.2)
\]

Rather than using the momentum, it is clearly equivalent to use the velocity \( \vec{v} = \vec{p} / m \), where \( m \) is the particle mass. The distribution function \( f_v(\vec{r}, \vec{v}, t) \) is related to \( f \) by a simple proportionality

\[
f_v(\vec{r}, \vec{v}, t) = m^3 f(\vec{r}, \vec{p}, t) \quad (8.3)
\]

### 8.1.2 Cross section, collision time, mean free path

The central concept in the description of collisions is that of cross section. We start with a simple case. Consider a flux of particles of density \( n \) and momentum \( \vec{p} \), incident on a target of fixed scattering centres with density \( n_d \) (Figure 8.1). The target is thin enough to ignore multiple collisions.\(^1\) The momentum after a collision is \( \vec{p}' \), its direction given by \( \Omega' = (\theta', \varphi') \), where \( \theta' \) and \( \varphi' \) are respectively the polar and azimuthal angles when the \( Oz \) axis is chosen parallel to \( \vec{p} \). Let \( dN / dt \, dV \)

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\(^1\) In other words we assume that the mean free path, defined in (8.10), is large compared to the thickness of the target.
be the number of collisions per unit time and unit target volume for collisions where particles are scattered within the solid angle $d\Omega'$ in the direction of $\vec{p}'$. This number is proportional to

(i) the incident flux $F = n v$, (ii) the solid angle $d\Omega'$, which defines the cone into which the particles are scattered, (iii) the density $n_d$ of target particles as long as we ignore multiple collisions.

We can then write

$$\frac{dN}{dt \, dV} = F n_d \sigma(v, \Omega') \, d\Omega'$$

(8.4)

The coefficient of proportionality $\sigma(v, \Omega')$ in (8.4) is called the *differential scattering cross section*.\(^2\) We often use (8.4) in the form

$\nu \sigma(v, \Omega') \, d\Omega'$ is the number of collisions per unit time and unit target volume for unit densities of target and incident particles where the scattered particle is in $d\Omega'$ around $\vec{p}'$.

Dimensional analysis shows that $\sigma$ has dimensions of area and is therefore measured in $m^2$.

An important concept is that of *collision time*\(^3\) which is the elapsed time between two successive collisions of the same particle. Consider a particle in flight between the target particles (Figure 8.1(b)): to obtain the collision time from (8.4), we first divide by $n$ and integrate over $\Omega'$. This gives the average number of collisions per second suffered by an incident particle which is just the inverse of the collision time $\tau^*(p)$

$$\frac{1}{\tau^*(p)} = n_d v \int d\Omega' \sigma(v, \Omega') = n_d v \sigma_{\text{tot}}(v)$$

(8.5)

The *total cross section* $\sigma_{\text{tot}}(v)$ is obtained by integrating the differential cross section over $\Omega'$.

We now consider the general case. The incident particles, characterized by their density $n_2$ and velocity $\vec{v}_2 = \vec{p}_2/m_2$, are moving toward the target particles which in turn are characterized by their density $n_1$ and velocity $\vec{v}_1 = \vec{p}_1/m_1$. Clearly, in a gas containing only one kind of atom, the incident and target particles are identical but it is convenient to distinguish them at least to begin with. We may regain the previous situation by applying a Galilean transformation of velocity $\vec{v}_1$.

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\(^2\) We assume that collisions are rotation invariant by not considering cases where the target or incident particles are polarized.

\(^3\) The reader should not confuse ‘collision time’ with ‘duration of collision’. To avoid confusion, we may use *time of flight* instead of collision time.
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\[ \vec{p}'_1 = -\vec{p}'_2 \]

Figure 8.2 Centre-of-mass reference frame.

to place ourselves in the rest frame of the target particles i.e. the target frame.\(^4\) In this frame, the incident particles have a velocity \((\vec{v}_2 - \vec{v}_1)\) and the incident particle flux, \(\mathcal{F}_2\), i.e. the number of incident particles crossing a unit area perpendicular to \((\vec{v}_2 - \vec{v}_1)\) per unit time, is given by

\[ \mathcal{F}_2 = n_2 |\vec{v}_2 - \vec{v}_1| \quad (8.6) \]

In place of the target frame, it is often convenient to use the centre-of-mass reference frame, where the total momentum is zero. In this frame, two colliding particles have equal and opposite momenta (Figure 8.2) \(\vec{p}'_1 = -\vec{p}'_2\) and, if the masses are the same, \(\vec{v}'_1 = -\vec{v}'_2\). After the collision, particles (1) and (2) propagate respectively with momenta \(\vec{p}'_3\) and \(\vec{p}'_4 = -\vec{p}'_3\) (\(|\vec{p}'_1| = |\vec{p}'_3|\) if the collision is elastic) and \(\Omega' = (\theta', \varphi')\) are the polar and azimuthal angles taken with respect to \(\vec{p}'_1\), which defines the \(Oz\) axis. It is important to remember that by convention \(\Omega'\) will always be measured in the centre-of-mass frame so that there is no limitation on the range of the polar angle \(\theta'\), \(0 \leq \theta' < \pi\). Let \(dN/dt dV\) be the number of collisions per unit time and unit target volume when particle \(\vec{p}'_1\) is scattered into the solid angle \(d\Omega'\) around the direction \(\vec{p}'_3\). A straightforward generalization of (8.4) gives this quantity as

\[ \frac{dN}{dt dV} = \mathcal{F}_2 n_1 \sigma(\vec{v}_2, \vec{v}_1, \Omega') d\Omega' \quad (8.7) \]

The coefficient of proportionality \(\sigma(\vec{v}_2, \vec{v}_1, \Omega')\) in (8.7) is the differential cross section. Since all the terms in (8.7) are Galilean invariants, the differential cross section itself is also a Galilean invariant and consequently depends on \((\vec{v}_2 - \vec{v}_1)\), not on \(\vec{v}_1\) or \(\vec{v}_2\) separately. In addition, due to rotation invariance, the cross section depends only on the modulus of the velocity difference, \((|\vec{v}_2 - \vec{v}_1|)\). Therefore, the total cross section, obtained by integrating over the solid angle, also depends only

\(^4\) In the previous case where the target was at rest, the target frame was the same as the laboratory frame.
As before, \( (|\vec{v}_2 - \vec{v}_1|) \sigma_{\text{tot}}(|\vec{v}_2 - \vec{v}_1|) \) is the number of collisions per unit time and unit target volume for unit densities of target and incident particles.

The concept of collision time, previously defined for fixed targets, extends to the general case: in a gas, the collision time \( \tau^* \) is the average time between two successive collisions of the same particle. It is given by the generalization of Equation (8.5)

\[
\tau^* \sim \frac{1}{n \langle v \rangle \sigma_{\text{tot}}}
\]

(8.9)

where \( \langle v \rangle \) is an average velocity of the particle whose definition is intentionally left imprecise. The mean free path \( \ell \) is the average distance between two successive collisions: \( \ell \sim \tau^* \langle v \rangle \)

\[
\ell \sim \frac{1}{n \sigma_{\text{tot}}}
\]

(8.10)

A more precise determination of the collision time is given in Exercise 8.4.4, where we find for the Maxwell velocity distribution and a cross section independent of energy

\[
\tau^* = \frac{1}{\sqrt{2} n \langle v \rangle \sigma_{\text{tot}}} \quad \ell = \frac{1}{\sqrt{2} n \sigma_{\text{tot}}}
\]

(8.11)

\( \langle v \rangle \) being the average velocity of the Maxwell distribution (3.54b)

\[
\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}
\]

Let us illustrate the concept of cross section with the simple example of hard spheres, radius \( a \) and velocity \( \vec{v}_2 \), incident on a target of fixed point particles. During a time \( dt \) a sphere sweeps a volume \( \pi a^2 v_2 dt \), which contains \( n_1 \pi a^2 v_2 dt \) target particles. The total number of collisions per unit time and unit target volume is therefore given by \( n_1 n_2 \pi a^2 v_2 \), which, when combined with the definition (8.5), yields \( \sigma_{\text{tot}} = \pi a^2 \).

Now consider spheres of radius \( a_1 \) incident on target spheres of radius \( a_2 \) (Figure 8.3). A collision takes place if the two centres pass each other at a distance \( b \leq (a_1 + a_2) \). The distance \( b \) is called the impact parameter of the collision. This situation is equivalent to the case of a sphere of radius \( (a_1 + a_2) \) scattering off a
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Figure 8.3 Collision of two spheres.

point particle. The total cross section is then

$$\sigma_{\text{tot}} = \pi (a_1 + a_2)^2$$

(8.12)

We can show, in classical mechanics, that the differential cross section for a collision of two hard spheres depends neither on $\Omega'$ nor on the relative velocity and is therefore given by $\sigma(\Omega') = \sigma_{\text{tot}}/(4\pi)$. In general, the determination of the cross section should be done within the framework of quantum mechanics and taking into account the interaction potential $U(\vec{r})$ between the two particles. If we are given an interaction potential $U(\vec{r})$, there are standard quantum mechanical methods to calculate the cross section. Quantum mechanics shows up only during the calculation of the cross section; once this quantity is known, kinetic theory becomes a theory of classical particles.

Having defined the key ideas for describing collisions, we are now in a position to state the assumptions behind kinetic theory:

(i) The collision time $\tau^*$ is very long compared to the duration of the collision $\delta \tau$, which is the time an incident particle spends in the field of influence of a target particle: $\tau^* \gg \delta \tau$. To leading approximation, we can assume that collisions take place instantaneously and that, for the most part, the particles are free and independent. The potential energy and interactions are taken into account effectively by the collisions.

(ii) The probability of having three particles in close proximity is very small. Consequently, the probability of three or more particles colliding is negligible: it is sufficient to consider only binary collisions.
The classical gas approximation holds, in other words the thermal wavelength is very small compared to the average distance between particles, $\lambda \ll d$. This assumption may be relaxed and the theory extended to the quantum case, see Problems 8.6.2 and 8.6.7.

These conditions are satisfied by a dilute classical gas. Let us consider some orders of magnitude: For a gas such as nitrogen, under standard temperature and pressure, the density is about $2.7 \times 10^{25}$ molecules/m$^3$ and the distance between molecules is $d \sim n^{-1/3} \sim 3 \times 10^{-9}$ m. Taking a cross section$^5$ of $4 \times 10^{-19}$ m$^2$, which corresponds to a hard sphere radius $a \simeq 1.8 \times 10^{-10}$ m, we find a collision time $\tau^* \simeq 2 \times 10^{-10}$ s, and a mean free path $\ell \simeq 10^{-7}$ m. With a typical value for the average velocity $\langle v \rangle \simeq 500$ m/s, the duration of a collision is approximately $\delta \tau \sim a/\langle v \rangle = 3 \times 10^{-13}$ s. We then see a clear separation of the three length scales

$$a \ll d \ll \ell \quad (8.13)$$

and the two time scales $\delta \tau \ll \tau^*$. However, when a gas is so dilute that the mean free path is of the order of the dimension of the system, we enter a regime, called the Knudsen regime, where local equilibrium no longer exists.

### 8.1.3 Transport coefficients in the mean free path approximation

We shall calculate the transport coefficients in a dilute medium in the so called mean free path approximation. This elementary calculation is physically very instructive but not rigorous; for example we shall keep vague the definition of the average velocity that appears in the final equations. This calculation will allow us to identify the dependence of the transport coefficients on the relevant physical parameters, although the numerical values will be off by a factor of 2 to 3. The value of this calculation lies in the fact that a rigorous evaluation based on the Boltzmann equation is considerably more complicated as will be seen in Section 8.4.

#### Thermal conductivity or energy transport

Consider a stationary fluid with a temperature gradient $dT/dz$ in the $Oz$ direction. Let $Q$ be the heat flux, i.e. the amount of heat crossing the plane at $z$ per unit area and unit time. Recall the definition (6.18) of the coefficient of thermal conductivity $\kappa$

$$Q = j^E_z = -\kappa \frac{dT}{dz} \quad (8.14)$$

$^5$ The cross section is estimated from viscosity measurements and theoretical estimates based on the Boltzmann equation.
because $Q$ is also the $z$ component of the energy current $\vec{j}_E$ which, in this case, is simply a heat current. Since we ignore interactions, the average energy $\varepsilon$ of a molecule\textsuperscript{6} is purely kinetic and therefore depends on the height $z$ because of the temperature dependence on $z$.

We shall define the average velocity $\langle v \rangle$ by the following approximation. For an arbitrary function $g(\cos \theta)$, where $\theta$ is the angle between the velocity $\vec{v}$ of a molecule and the $Oz$ axis, we have\textsuperscript{7}

$$\int d^3p \, v_z f(\vec{p}) g(\cos \theta) \rightarrow \frac{n}{2} \langle v \rangle \int d(\cos \theta) \cos \theta \, g(\cos \theta) \quad (8.15)$$

Now consider molecules whose velocity makes an angle $\theta$ with the $Oz$ axis, $0 \leq \theta \leq \pi$. Such a molecule crossing the plane at $z$ has travelled, on average, a distance $\ell$ and therefore its last collision took place at an altitude $z - \ell \cos \theta$. Its energy is $\varepsilon(z - \ell \cos \theta)$. The heat flux crossing the plane at $z$ and coming from molecules whose velocities make an angle $\theta$ with the vertical is then

$$dQ(\cos \theta) = \frac{n}{2} d(\cos \theta) \langle v \rangle \cos \theta \varepsilon(z - \ell \cos \theta)$$

$$\approx \frac{n}{2} d(\cos \theta) \langle v \rangle \cos \theta \left[ \varepsilon(z) - \ell \cos \theta \frac{d\varepsilon(z)}{dz} \right]$$

We have made a Taylor expansion, to first order in $\ell$, of the term $\varepsilon(z - \ell \cos \theta)$. The integral over $d(\cos \theta)$ from $-1$ to $+1$ in the first term of the bracket vanishes. Using

$$\int_{-1}^{+1} d(\cos \theta) \cos^2 \theta = \frac{2}{3} \quad (8.16)$$

we obtain for the heat flux

$$Q = \int_{-1}^{1} dQ(\cos \theta) = -\frac{1}{3} n \langle v \rangle \ell \frac{d\varepsilon(z)}{dz}$$

$$= -\frac{1}{3} n \langle v \rangle \ell \frac{dT}{dz} = -\frac{1}{3} n \langle v \rangle \ell c \frac{dT}{dz}$$

where $c$ is the specific heat per molecule, which is equal to $3k/2$ for mono-atomic gases, $5k/2$, etc. for poly-atomic gases (Section 3.2.4). Comparing with (8.14)

\textsuperscript{6} Since we are now discussing gases, we talk about molecules rather than particles.

\textsuperscript{7} The factor $n/2$ gives the correct normalization (8.2) since $\int_{-1}^{+1} d(\cos \theta) = 2$. Put $v_z = g = 1$ to find that both integrals give $n$. We have suppressed the labels $\vec{r}$ and $t$ in $f$. 

gives the coefficient of thermal conductivity
\[ \kappa = \frac{1}{3} n \langle v \rangle \ell c \] (8.17)

**Viscosity or momentum transport**
Let us now consider the fluid flow described in Section 6.3.1, Figure 6.6, and recall Equation (6.71) for the component \( P_{xz} \) of the pressure tensor for this situation
\[ P_{xz} = -\eta \frac{d u_x(z)}{d z} \] (8.18)
The fluid flows in the \( Ox \) direction with horizontal velocity \( u_x(z) \) (a function of \( z \)), \( \eta \) is the shear viscosity and \( -P_{xz} \) is the \( x \) component of the force per unit area at \( z \) applied by the fluid above \( z \) on the fluid below it. From the fundamental law of dynamics, this is also the moment transfer per second from the fluid above \( z \) to the fluid below it. Therefore, \( P_{xz} \) is the momentum flux across the plane at height \( z \) with the normal to the plane pointing upward. Since the fluid is assumed to be dilute, we can ignore interactions among the molecules and the momentum flux is therefore purely convective
\[ P_{xz} = \int d^3 p \, p_x v_z f(\bar{p}) \] (8.19)
We repeat the above reasoning by considering molecules whose velocities make an angle \( \theta \) with the vertical, \( 0 \leq \theta \leq \pi \). As before, a molecule crossing the plane at \( z \) has travelled, on average, a distance \( \ell \) and therefore its last collision took place at an altitude \( z - \ell \cos \theta \), and the \( x \) component of its momentum is \( m u_x(z - \ell \cos \theta) \). Clearly, in this calculation we only consider the flow velocity \( \bar{u} \) of the fluid and not the thermal velocity, also present, which averages to zero since its direction is random. Using the approximation (8.15), the momentum flux due to these molecules is
\[ dP_{xz}(\cos \theta) = \frac{n}{2} d(\cos \theta) \langle v \rangle \cos \theta m u_x(z - \ell \cos \theta) \]
\[ \approx \frac{n}{2} d(\cos \theta) \langle v \rangle \cos \theta m \left[ u_x(z) - \ell \cos \theta \frac{d u_x(z)}{d z} \right] \]
We have performed a Taylor expansion of the term \( u_x(z - \ell \cos \theta) \) to first order in \( \ell \). The integral from \(-1\) to \(+1\) over \( d(\cos \theta) \) of the first term in the bracket vanishes, and using (8.16) we obtain
\[ P_{xz} = \int_{-1}^{+1} dP_{xz}(\cos \theta) = -\frac{1}{3} n m \langle v \rangle \ell \frac{d u_x(z)}{d z} \] (8.20)
which becomes, upon comparing with (8.18),

\[
\eta = \frac{1}{3} \frac{nm\langle v \rangle \ell}{\sigma_{\text{tot}}} = \frac{1}{3} \frac{m\langle v \rangle}{\sigma_{\text{tot}}}
\]  

(8.21)

We remark that the product \( n\ell = 1/\sigma_{\text{tot}} \) is constant and that, at constant temperature, the viscosity is independent of the density and the pressure. If the density is doubled, the number of molecules participating in the transport is also doubled, but the mean free path is halved and the two effects cancel out leaving the viscosity constant. In fact, the second equation in (8.21) shows that the viscosity is a function of \( T \) only through the dependence of \( \langle v \rangle \) on the temperature, and that it increases with \( T \) as \( \langle v \rangle \propto T^{1/2} \). This should be contrasted with the case of liquids where the viscosity decreases with increasing temperature.

By comparing (8.17) and (8.21), we predict that the ratio \( \kappa/\eta \) is equal to \( c/m \). Experimentally we have

\[
1.3 \lesssim \frac{\kappa}{\eta} \frac{m}{c} \lesssim 2.5
\]  

(8.22)

which confirms the validity of our calculation to within a factor of 2 to 3. We can understand qualitatively the origin of this factor. In the above calculation, all the molecules have the same velocity and they all travel the same distance, the mean free path, between successive collisions. However, faster molecules have a higher flux across the horizontal plane and while they transport the same horizontal momentum as the average, they transport more kinetic energy. Therefore, the ratio \( \kappa/\eta \) is underestimated in our simple calculation.

**Diffusion or particle transport**

As a last example, we study diffusion. Let \( n(z) \) be the \( z \) dependent density of solute in a solvent. The diffusion current \( \vec{j}_N \) is governed by Fick’s law (6.26), which becomes in the present case

\[
\vec{j}_N = -D \frac{dn}{dz}
\]  

(8.23)

By using, once again, the same reasoning as above, we have

\[
d\vec{j}_N (\cos \theta) = \frac{1}{2} d(\cos \theta)\langle v \rangle \cos \theta n(z - \ell \cos \theta)
\]

The Taylor expansion and integration over \( \theta \) yield

\[
\vec{j}_N = -\frac{1}{3} \langle v \rangle \ell \frac{dn}{dz}
\]
which allows the identification of the diffusion coefficient

$$D = \frac{1}{3} \langle v \rangle \ell$$ (8.24)

8.2 Boltzmann–Lorentz model

8.2.1 Spatio-temporal evolution of the distribution function

The starting point will be a spatio-temporal evolution equation for the distribution function \(f(\vec{r}, \vec{p}, t)\) in phase space. Consider first a collection of non-interacting particles moving under the influence of external forces. When \(t \rightarrow t + dt\), a particle which at time \(t\) was at point \(\vec{r}(t)\) and had a momentum \(\vec{p}(t)\) will at time \(t + dt\) find itself at \(\vec{r}(t + dt)\) with momentum \(\vec{p}(t + dt)\). Since the number of particles in a volume element in phase space is constant, we have

$$f[\vec{r}(t + dt), \vec{p}(t + dt), t + dt]d^3 r' d^3 p' = f[\vec{r}(t), \vec{p}(t), t]d^3 r d^3 p$$ (8.25)

where \(d^3 r' d^3 p'\) is the phase space volume at \(t + dt\) (Figure 8.4): motion in phase space takes a point in \(d^3 r d^3 p\) to a point in \(d^3 r' d^3 p'\).

Liouville’s theorem (2.34) \(d^3 r' d^3 p' = d^3 r d^3 p\) means that the two functions in (8.25) are equal. Expanding to first order in \(dt\) gives

$$\frac{\partial f}{\partial t} + \frac{d\vec{r}}{dt} \cdot \nabla_{\vec{r}} f + \frac{d\vec{p}}{dt} \cdot \nabla_{\vec{p}} f = \frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_{\vec{r}} f + \vec{F} \cdot \nabla_{\vec{p}} f = 0$$ (8.26)

Figure 8.4 Motion in phase space.
In the presence of a magnetic field, the passage from the first to the second of equations (8.26) is not obvious (see Problem 8.5.5). Comparing with (6.65), we see that the operator

\[ D = \frac{\partial}{\partial t} + \frac{d\vec{r}}{dt} \cdot \vec{\nabla}_{\vec{r}} + \frac{d\vec{p}}{dt} \cdot \vec{\nabla}_{\vec{p}} = \frac{\partial}{\partial t} + \sum_{\alpha} v_{\alpha} \partial_{\alpha} + \sum_{\alpha} \dot{p}_{\alpha} \partial_{p_{\alpha}} \]  

(8.27)

is simply the material derivative in phase space (also see Exercise 2.7.3). Equation (8.26) expresses the fact that the distribution function is constant along a trajectory in phase space.

Equation (8.26) is valid only in the absence of interactions. We now include interactions in the form of collisions among the particles. Recall that one of the assumptions of kinetic theory stipulates that the duration of collisions is very short compared with the collision time. We shall, therefore, assume instantaneous collisions. The effect of collisions is to replace the zero on the right hand side of Equation (8.26) by a collision term, \( C[f] \), which is a functional of the distribution function \( f \). Equation (8.26) then becomes

\[ \frac{\partial f}{\partial t} + \vec{v} \cdot \vec{\nabla}_{\vec{r}} f + \vec{F} \cdot \vec{\nabla}_{\vec{p}} f = C[f] \]  

(8.28)

The left hand side of Equation (8.28) is called the drift term. The collision term is in fact a balance term, and to establish its form we need to keep track of the number of particles which enter or exit the phase space volume \( d^3r \, d^3p \). We note that the units of \( C[f] \) are inverse phase space volume per second. Equation (8.28) does not in any way specify the form of the collision term. As a result, Equation (8.28) is equally valid for the Boltzmann–Lorentz model with fixed scattering centres, as well as for the Boltzmann model where both incident and target particles are in motion. It is important to keep in mind that, strictly speaking, we cannot take time and space intervals to zero in Equation (8.28). For example, the derivative \( \partial f/\partial t \) should be understood as \( \Delta f/\Delta t \) with

\[ \delta \tau \ll \Delta t \ll \tau^* \]  

(8.29)

Similarly, the phase space volumes we consider should be small but not microscopic; they should contain a sufficiently large number of particles. The fact that \( \Delta t \) has to remain finite shows that (8.28) cannot be considered an exact equation.

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9 In the presence of a magnetic field \( \vec{B} \), the canonically conjugate momentum \( \vec{p} \) is not the same as the momentum \( m\vec{v} \): \( \vec{p} = m\vec{v} + q\vec{A} \) where \( q \) is the electric charge and \( \vec{A} \) is the vector potential, \( \vec{B} = \vec{\nabla} \times \vec{A} \).

10 We keep the notations of Chapter 6 for space derivatives \( (\vec{\nabla}_{\vec{r}} = (\partial_{x}, \partial_{y}, \partial_{z})) \) and introduce the following notation for derivatives in momentum space: \( \vec{\nabla}_{\vec{p}} = (\partial_{p_{x}}, \partial_{p_{y}}, \partial_{p_{z}}) \).

11 We do not follow the motion of each particle during infinitesimally small time intervals.
The discretization of time (8.29) cannot guarantee the reversibility of the equations of motion, and the observation of irreversible behaviour will not contradict micro-reversibility.

### 8.2.2 Basic equations of the Boltzmann–Lorentz model

The Boltzmann–Lorentz model is a model of collisions between light incident particles and randomly distributed fixed scattering centres. The gas of incident particles is assumed to be dilute enough to ignore collisions among these incident particles. For example, this model is used to describe

- electrons and holes in semiconductors,
- diffusion of impurities in a solid,
- diffusion of light solute molecules in a solvent whose molecules are heavy,
- neutron diffusion in a moderator.

This model may also be used to describe electrons in a metal if one makes the necessary changes to accommodate Fermi–Dirac statistics (Problem 8.6.2). In what follows we shall concentrate on a gas of classical particles. In order to justify the approximation of fixed scattering centres, consider a gas made of a mixture of light particles of mass $m$ and heavy particles of mass $\mu$. The two types of particles have kinetic energies of the order of $kT$, but the ratio of their momenta is $\sqrt{m/\mu}$ with the consequence that the contribution of the light particles to momentum conservation is negligible. The heavy particles can, therefore, absorb and supply momentum during collisions with the light ones, and thus they may be considered infinitely heavy and stationary. Since we assume elastic collisions, the energy of the light particles is conserved but not their momentum. As in Section 6.2.1, there will be only two conservation laws: conservation of particle number and energy along with the associated densities, $n$ and $\epsilon$, and their currents $\vec{j}_N$ and $\vec{j}_E$ (however, see Footnote 12).

In the absence of external forces, we can write Equation (8.28) for the distribution function $f(\vec{r}, \vec{p}, t)$ of the light particles

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \vec{\nabla}_r f = C[f]$$  \hspace{1cm} (8.30)

To evaluate $C[f]$, we shall account for the particles which enter and leave the phase space element $d^3r \, d^3p$. First consider particles leaving this element. We assume this volume to be small enough so that any particle initially in it will be ejected after a collision. Before the collision the particle has momentum $\vec{p}$, after the collision its momentum is $\vec{p}'$, which is no longer in $d^3r \, d^3p$ around $\vec{p}$ (Figure 8.5).
Irreversible processes: kinetic theory

The collision term will be calculated in terms of the cross sections defined in (8.4). However, rather than using the variable $\Omega'$ of (8.4), it will be more convenient, for the purpose of identifying the symmetries of the problem, to use the variable $\vec{p}'$. This is possible because we may include in the cross section a $\delta$-function that ensures the conservation of energy, which is purely kinetic in the present case: for a particle of momentum $\vec{p}$, the energy is $\varepsilon(\vec{p}) = \vec{p}^2 / (2m)$. We note that

$$d^3 p' \delta(\varepsilon - \varepsilon') = p'^2 d p' d\Omega' \frac{m}{p} \delta(p - p') \rightarrow m^2 v d\Omega'$$

and we introduce the quantity $W(p, \Omega')$

$$W(p, \Omega') d^3 p' = \frac{n_d}{m^2} \sigma(v, \Omega') d^3 p' \delta(\varepsilon - \varepsilon') \rightarrow n_d v \sigma(v, \Omega') d\Omega'$$  \hspace{1cm} (8.32)

$W(p, \Omega') d^3 p'$ is the number of particles scattered in $d^3 p'$ per second and per unit target volume for unit incident particle density. The number of collisions per second in $d^3 r d^3 p$ with a final momentum in $d^3 p'$ is then

$$\frac{dN}{dt} = [d^3 r d^3 p] f(\vec{r}, \vec{p}, t) W(p, \Omega') d^3 p'$$

By integrating over $d^3 p'$, we obtain from the above equation the contribution to $C[f]$ of the particles leaving the volume element

$$C_-[f] = f(\vec{r}, \vec{p}, t) \int d^3 p' W(p, \Omega') \left( = \frac{1}{\tau^*(p)} f(\vec{r}, \vec{p}, t) \right)$$  \hspace{1cm} (8.33)
Conversely, collisions with $\vec{p}' \rightarrow \vec{p}$ will populate the volume element $d^3r \, d^3p$ (Figure 8.5(b)). The number of these collisions is given by

$$[d^3r \, d^3p] \int d^3p' \, f(\vec{r}, \vec{p}', t)W(p', \Omega) = [d^3r \, d^3p]C_+[f]$$

The total collision term is the difference between entering and exiting contributions

$$C[f] = C_+[f] - C_-[f]$$

The expression for $C[f]$ simplifies if we note that the collision angle is the same for the collisions $\vec{p} \rightarrow \vec{p}'$ and $\vec{p}' \rightarrow \vec{p}$ and that $p = p'$ due to energy conservation

$$W(p, \Omega') = W(p', \Omega)$$

and therefore

$$C[f] = \int d^3p' \left[ f(\vec{r}, \vec{p}', t) - f(\vec{r}, \vec{p}, t) \right] W(p, \Omega')$$  (8.34)

By using (8.32) and introducing the shorthand notation $f = f(\vec{r}, \vec{p}, t)$ and $f' = f(\vec{r}, \vec{p}', t)$, we write (8.34) as

$$C[f] = \int d^3p' \left[ f' - f \right] W(p, \Omega') = vn_d \int d\Omega' \left[ f' - f \right] \sigma(v, \Omega')$$  (8.35)

### 8.2.3 Conservation laws and continuity equations

We should be able to show that the model satisfies number and energy conservation equations. We shall obtain these equations from the following preliminary results. Let $\chi(\vec{p})$ (or $\chi(\vec{r}, \vec{p})$) be an arbitrary function, and define the functional, $I[\chi]$, of $\chi$ by

$$I[\chi] = \int d^3p \, \chi(\vec{p})C[f]$$  (8.36)

First we show that $I[\chi] = 0$ if $\chi$ depends only on the modulus $p$ of $\vec{p}$. The demonstration is simple. From the definition of $I[\chi]$ and using (8.35) we may write

$$I[\chi] = \int d^3p \, d^3p' \, \chi(\vec{p}) W(p, \Omega') [f' - f]$$

12 The physical interpretation of this result is as follows. The collision term is a balance term in the phase space volume element $d^3r \, d^3p$. Like all quantities dependent only on $p$, which are conserved in the collisions, its integral over $d^3p$ should vanish. Therefore, this model has an infinite number of conservation laws. A realistic model should take into account the inelasticity of collisions that is necessary for reaching thermal equilibrium.
Exchanging the integration variables $p$ and $p'$ gives

$$I[\chi] = - \int d^3 p \, d^3 p' \, \chi(p') W(p', \Omega)[f' - f]$$

Using $W(p, \Omega') = W(p', \Omega)$ the above two equations yield

$$I[\chi] = \frac{1}{2} \int d^3 p \, d^3 p' \, \left[ \chi(p) - \chi(p') \right] W(p, \Omega')[f' - f]$$

Therefore, $I[\chi] = 0$ if $\chi$ depends only on the modulus of $\bar{p}$ since $p = p'$. In the special cases $\chi = 1$ and $\chi = \varepsilon(\bar{p}) = p^2/(2m)$ we obtain

$$\int d^3 p \, C[f] = 0 \quad \int d^3 p \, \varepsilon(\bar{p}) C[f] = 0 \quad (8.37)$$

Integrating Equation (8.28) over $d^3 p$ and using (8.37) we have

$$\frac{\partial n}{\partial t} + \nabla \cdot \int d^3 p \, \bar{v} f = 0 \quad (8.38)$$

We thus identify the particle current and the corresponding continuity equation

$$\vec{j}_N = \int d^3 p \, \bar{v} f \quad \frac{\partial n}{\partial t} + \nabla \cdot \vec{j}_N = 0 \quad (8.39)$$

Multiplying Equation (8.28) by $\varepsilon(\bar{p})$, integrating over $d^3 p$ and using (8.37) leads to

$$\frac{\partial \varepsilon}{\partial t} + \nabla \cdot \int d^3 p \, \varepsilon(\bar{p}) \bar{v} f = 0 \quad (8.40)$$

where $\varepsilon$ is the energy density, which is given by

$$\varepsilon = \int d^3 p \, \varepsilon(\bar{p}) f = \int d^3 p \, \frac{\vec{p}^2}{2m} f \quad (8.41)$$

We define, with the help of (8.40), the energy current $\vec{j}_E$

$$\vec{j}_E = \int d^3 p \, \varepsilon(\bar{p}) \bar{v} f = \int d^3 p \, \frac{\vec{p}^2}{2m} \bar{v} f \quad \frac{\partial \varepsilon}{\partial t} + \nabla \cdot \vec{j}_E = 0 \quad (8.42)$$

### 8.2.4 Linearization: Chapman–Enskog approximation

The collision term $C[f]$ vanishes for any distribution function which is isotropic in $\bar{p}$, $f(\bar{r}, p, t)$, since in such a case $f' = f$. In particular, it vanishes for any local
equilibrium distribution \( f_0, C[f_0] = 0 \), where (cf. (3.141))

\[
f_0(\vec{r}, \vec{p}, t) = \frac{1}{h^3} \exp \left( \alpha(\vec{r}, t) - \beta(\vec{r}, t) \frac{\vec{p}^2}{2m} \right) \equiv f_0(\vec{r}, p, t) \tag{8.43}
\]

In this equation, \( \beta(\vec{r}, t) \) and \( \alpha(\vec{r}, t) \) are related to the local temperature \( T(\vec{r}, t) \) and chemical potential \( \mu(\vec{r}, t) \) by

\[
\beta(\vec{r}, t) = \frac{1}{kT(\vec{r}, t)} \quad \alpha(\vec{r}, t) = \frac{\mu(\vec{r}, t)}{kT(\vec{r}, t)} \tag{8.44}
\]

If in Equation (8.35), the difference \( [f' - f] \) is not small, the collision term will be of the order of \( f/\tau^*(p) \) where \( \tau^*(p) \) is a microscopic time of the order of \( 10^{-10} \) to \( 10^{-14} \) s. Then the collision term leads to a rapid exponential decrease, \( \exp(-t/\tau^*) \), in the distribution function. This rapid decrease evolves the distribution function toward an almost local equilibrium distribution in a time \( t \gtrsim \tau^* \). The collision term of the Boltzmann equation is solely responsible for this evolution, which takes place spatially over a distance of the order of the mean free path. Subsequently, the collision term becomes small since it vanishes for a local equilibrium distribution. The subsequent evolution is hydrodynamic, and this is what we shall now examine by linearizing Equation (8.35) near a local equilibrium distribution. We write the distribution function at \( t = 0 \) in the form \( f = f_0 + \bar{f} \). The local equilibrium distribution \( f_0 \) must obey

\[
n(\vec{r}, t = 0) = \int d^3p \ f_0(\vec{r}, p, t = 0) \tag{8.45}
\]

\[
\epsilon(\vec{r}, t = 0) = \int d^3p \ \frac{p^2}{2m} \ f_0(\vec{r}, p, t = 0) \tag{8.46}
\]

where \( n(\vec{r}, t = 0) \) and \( \epsilon(\vec{r}, t = 0) \) are the initial particle and energy densities. These densities determine the local temperature and chemical potential or, equivalently, the local parameters \( \alpha \) and \( \beta \) given by

\[
n(\vec{r}) = \frac{1}{h^3} e^{\alpha(\vec{r})} \left( \frac{2\pi m}{\beta(\vec{r})} \right)^{3/2} \quad \epsilon(\vec{r}) = \frac{3}{2\beta(\vec{r})} n(\vec{r}) \tag{8.47}
\]

where we have suppressed the time dependence. By construction, the deviation from local equilibrium, \( \bar{f} \), satisfies

\[
\int d^3p \ \bar{f} = \int d^3p \ \frac{p^2}{2m} \bar{f} = 0 \tag{8.48}
\]
Since the equilibrium distribution function $f_0$ is isotropic, it does not contribute to
the currents which are given solely by $\tilde{f}$

$$
\tilde{j}_N = \int d^3 p \, \tilde{v} \tilde{f} \quad \tilde{j}_E = \int d^3 p \, \tilde{v} \frac{p^2}{2m} \tilde{f}
$$

The currents vanish to first order in $f_0$ and, from the continuity equations, the time
derivatives of $n$ and $\epsilon$ (or equivalently $\alpha$ and $\beta$) also vanish as does $(\partial f_0/\partial t)$. We
also have $C[f_0] = 0$ but $\tilde{\nabla} f_0 \neq 0$ (unless $f_0$ is a global equilibrium solution in
which case the problem is not interesting) and so $f_0$ is not a solution of (8.28). Therefore, (8.28) becomes

$$
(\tilde{v} \cdot \tilde{\nabla}) f_0 = C[\tilde{f}] \quad \text{(8.50)}
$$

In orders of magnitude, we have $C[\tilde{f}] \sim \tilde{f}/\tau^*$, and $\tilde{f} \sim \tau^* (\tilde{v} \cdot \tilde{\nabla}) f_0$. It is possible to iterate the solution by calculating the currents from $\tilde{f}$, which allows us to
calculate the time derivatives of $n$ and $\epsilon$, which in turn yields $\partial f_0/\partial t$, but instead we stay with the approximation (8.50). We therefore work at an order of approximation where the drift $(\tilde{v} \cdot \tilde{\nabla}) f_0$ balances the collision term $C[\tilde{f}]$. The expansion
parameter is $\tau^*/\tau \ll 1$ where $\tau$ is a characteristic time of macroscopic (or hydro-
dynamic) evolution.

We now calculate the collision term $C[\tilde{f}]$. At point $\tilde{r}$, $\tilde{\nabla} f_0$ is oriented in a di-
rection that we define as the $Oz$ axis

$$
\tilde{\nabla} f_0 = \hat{z} \frac{\partial f_0}{\partial z}
$$

Let $\gamma$ be the angle between $\tilde{v}$ and $Oz$

$$
(\tilde{v} \cdot \tilde{\nabla}) f_0 = v \cos \gamma \frac{\partial f_0}{\partial z} \quad \text{(8.51)}
$$

Also, we take $\gamma'$ as the angle between $\tilde{p}'$ and $Oz$, $\theta'$ the angle between $\tilde{p}$ and $\tilde{p}'$ and $\varphi'$ the azimuthal angle in the plane perpendicular to $\tilde{p}$ (Figure 8.6). The collision term is given by (8.35)

$$
C[\tilde{f}] = vn_d \int d\Omega' \sigma(v, \Omega')[\tilde{f}(\tilde{r}, \tilde{p}') - \tilde{f}(\tilde{r}, \tilde{p})] \quad \text{(8.52)}
$$

We assume the solution of (8.50) takes the form

$$
\tilde{f}(\tilde{r}, \tilde{p}) = g(z, p) \cos \gamma \quad \text{(8.53)}
$$

Then, using

$$
\cos \gamma' = \cos \theta' \cos \gamma + \sin \theta' \sin \gamma \cos \varphi' \quad d\Omega' = d(\cos \theta') \, d\varphi'
$$
and the fact that \( \sigma(v, \Omega') = \sigma(v, \theta') \),\(^{14}\) Equation (8.52) becomes

\[
C[\tilde{f}] = vn_d g(z, p) \\
\times \int d(\cos \theta') \, d\varphi' \left[ \cos \theta' \cos \gamma + \sin \theta' \sin \gamma \cos \varphi' - \cos \gamma \right] \sigma(v, \Omega') \\
= -vn_d g(z, p) \cos \gamma \int d\Omega' (1 - \cos \theta') \sigma(v, \Omega')
\]

We define the transport cross section \( \sigma_{tr} \) by\(^ {15}\)

\[
\sigma_{tr}(v) = \int d\Omega' (1 - \cos \theta') \sigma(v, \Omega')
\]

which when combined with (8.50) and (8.51) gives for the collision term

\[
C[\tilde{f}] = -vn_d g(z, p) \cos \gamma \sigma_{tr}(v) = v \cos \gamma \frac{\partial f_0}{\partial z}
\]

\(^{14}\) By rotation invariance, \( \sigma \) cannot depend on \( \varphi' \) unless the particles are polarized.

\(^{15}\) This definition is specific to the process we are studying here. In other cases, the term \((1 - \cos \theta')\) may be replaced by a function \( f(\cos \theta') \) satisfying \( f(\pm 1) = 0 \), and \( \sigma_{tr} \) may be different from \( \sigma_{tot} \) even for an isotropic differential cross section: see Section 8.4.3 where the transport cross section is defined with a \((1 - \cos^2 \theta)\) factor.
This in turn leads to the following expression for the function $g(z, p)$ defined in (8.53)

$$g(z, p) = -\frac{1}{n_d \sigma_{tr}(v)} \frac{\partial f_0}{\partial z}$$  \hspace{1cm} (8.55)

and therefore

$$\bar{f} = -\frac{1}{n_d \sigma_{tr}(v)} \cos \gamma \frac{\partial f_0}{\partial z}$$

which can be written as

$$\bar{f} = -\frac{1}{n_d v \sigma_{tr}(v)} (\vec{v} \cdot \vec{v}) f_0 = -\tau_{tr}^*(p) (\vec{v} \cdot \vec{v}) f_0$$  \hspace{1cm} (8.56)

We have defined the characteristic time $\tau_{tr}^*(p)$ by

$$\tau_{tr}^*(p) = \frac{1}{n_d v \sigma_{tr}}$$  \hspace{1cm} (8.57)

We see that the transport process is controlled by the cross section $\sigma_{tr}$ and not the total cross section and by $\tau_{tr}^*(p)$ and not the collision time $\tau^*(p)$. When the cross section is isotropic (independent of $\Omega'$) we have $\sigma_{tr}(v) = \sigma_{tot}(v)$ and $\tau_{tr}^*(p) = \tau^*(p)$. Since we usually consider such isotropic cases, we will take $\tau_{tr}^*(p) = \tau^*(p)$ but keep in mind that these two time scales can be very different when the cross section is strongly anisotropic as in the case of Coulomb interactions.

### 8.2.5 Currents and transport coefficients

Equations (8.49) for the currents and (8.56) for $\bar{f}$ allow us to express the currents in the following form

$$\vec{j}_N = -\int d^3 p \ \tau^*(p) \ (\vec{v} \cdot \vec{v}) f_0$$  \hspace{1cm} (8.58)

$$\vec{j}_E = -\int d^3 p \ \tau^*(p) \ \epsilon(p) (\vec{v} \cdot \vec{v}) f_0$$  \hspace{1cm} (8.59)

Using the result (A.34) for a function $g(|\vec{p}|)$ (see also Exercise 8.4.2)

$$\int d^3 p \ v_{\alpha} v_{\beta} g(p) = \frac{4\pi}{3} \delta_{\alpha\beta} \int dp \ p^2 v^2 g(p) = \frac{1}{3} \delta_{\alpha\beta} \int d^3 p \ v^2 g(p)$$  \hspace{1cm} (8.60)
the equations for the currents may be written as

\[ \vec{j}_N = -\frac{1}{3} \int d^3 p \ v^2 \tau^*(p) \vec{\nabla} f_0 \] (8.61)

\[ \vec{j}_E = -\frac{1}{3} \int d^3 p \ v^2 \tau^*(p) \varepsilon (p) \vec{\nabla} f_0 \] (8.62)

From the form of \( f_0 \) (8.43) we have

\[ \vec{\nabla} f_0 = \left( \vec{\nabla} \alpha - \varepsilon (p) \vec{\nabla} \beta \right) f_0 \]

which leads to the final form for the currents

\[ \vec{j}_N = \frac{1}{3k} \int d^3 p \ v^2 \tau^*(p) \left[ \vec{\nabla} \left( -\frac{\mu}{T} \right) + \varepsilon (p) \vec{\nabla} \left( \frac{1}{T} \right) \right] f_0 \] (8.63)

\[ \vec{j}_E = \frac{1}{3k} \int d^3 p \ v^2 \tau^*(p) \varepsilon (p) \left[ \vec{\nabla} \left( -\frac{\mu}{T} \right) + \varepsilon (p) \vec{\nabla} \left( \frac{1}{T} \right) \right] f_0 \] (8.64)

By comparing with Equations (6.48) and (6.49) we deduce the transport coefficients

\[ L_{NN} = \frac{1}{3k} \int d^3 p \ v^2 \tau^*(p) f_0 \] (8.65)

\[ L_{EN} = \frac{1}{3k} \int d^3 p \ v^2 \tau^*(p) \varepsilon (p) f_0 = L_{NE} \] (8.66)

\[ L_{EE} = \frac{1}{3k} \int d^3 p \ v^2 \tau^*(p) \varepsilon^2 (p) f_0 \] (8.67)

The Onsager reciprocity relation \( L_{EN} = L_{NE} \) is explicitly satisfied. It is also easy to verify the positivity condition (Exercise 8.4.3)

\[ L_{EE} L_{NN} - L_{EN}^2 \geq 0 \] (8.68)

In order to calculate explicitly these coefficients, we need \( \tau^*(p) \). In the simple case where the mean free path \( \ell \) is independent of \( p \), we have \( \tau^*(p) = m\ell / p = \ell / v \) and by defining \( \tau^* = (8/3\pi)\ell / \langle v \rangle \) (Problem 8.6.2) we find

\[ L_{NN} = \frac{\tau^*}{m} nT \quad L_{EN} = \frac{2\tau^*}{m} nkT^2 \quad L_{EE} = \frac{6\tau^*}{m} nk^2T^3 \] (8.69)

Combining this with (6.27) (for a classical ideal gas), (6.50) and (6.57), we obtain the diffusion coefficient \( D \) and the electric and thermal conductivities \( \sigma_{el} \) and \( \kappa \)

\[ D = \frac{\tau^*}{m} kT \quad \sigma_{el} = q^2 \frac{\tau^*}{m} n \quad \kappa = 2 \frac{\tau^*}{m} nk^2T \] (8.70)
which give the Franz–Wiedeman law

$$\frac{\kappa}{\sigma_{\text{el}}} = 2 \frac{k^2}{q^2} T \simeq 1.5 \times 10^{-8} T$$  \hspace{1cm} (8.71)

In this equation, $q$ is the electron charge and the units are MKSA. The Franz–Wiedeman law predicts that the ratio $\kappa/\sigma_{\text{el}}$ is independent of the material and depends linearly on the temperature. Experimentally, this is well satisfied by semiconductors, but for metals we need to take into account the Fermi–Dirac statistics. The local equilibrium distribution $f_0$ then becomes

$$f_0(\vec{r}, \vec{p}, t) = \frac{2}{\hbar^3} \frac{1}{\exp \left[ -\alpha(\vec{r}, t) + \beta(\vec{r}, t)p^2/2m \right] + 1}$$  \hspace{1cm} (8.72)

where the factor 2 comes from the spin degree of freedom. Then the Franz–Wiedeman law becomes (Problem 8.5.2)

$$\frac{\kappa}{\sigma_{\text{el}}} = \frac{\pi^2}{3} \frac{k^2}{q^2} T \simeq 2.5 \times 10^{-8} T$$  \hspace{1cm} (8.73)

which is also very well satisfied experimentally.

8.3 Boltzmann equation

8.3.1 Collision term

The Boltzmann equation governs the spatio-temporal evolution of the distribution function for a dilute gas. To the general assumptions of kinetic theory, which were discussed in Section 8.1.2, we must also add the condition of ‘molecular chaos’, which is crucial for writing the collision term.\textsuperscript{17} This condition stipulates that the two-particle distribution function $f^{(2)}$, which contains the correlations, can be written as a product of one-particle distribution functions

$$f^{(2)}(\vec{r}_1, \vec{p}_1; \vec{r}_2, \vec{p}_2; t) = f(\vec{r}_1, \vec{p}_1, t)f(\vec{r}_2, \vec{p}_2, t)$$  \hspace{1cm} (8.74)

In other words, the joint distribution is a product of the individual distributions: we ignore two-particle correlations (and \textit{a fortiori} those of higher order). However, it is important to place this molecular chaos hypothesis in the general framework of

\textsuperscript{16} The reader will correctly object that, due to the uncertainty principle, we cannot give simultaneously sharp values to the position and the momentum in a situation where quantum effects are important. However, it can be shown that (8.172) is valid provided the typical scales on which $\vec{r}$ and $t$ vary are large enough. See Problem 8.6.7.

\textsuperscript{17} We must also assume that the dilute gas is mono-atomic, so that the collisions are always elastic. There cannot be any transfer of kinetic energy toward the internal degrees of freedom.
the approach of Chapter 2. Among all possible dynamic variables, we focus only on the specific variable $A(\vec{r}, \vec{p}, t)$

$$A(\vec{r}, \vec{p}, t) = \sum_{j=1}^{N} \delta(\vec{r} - \vec{r}_j(t))\delta(\vec{p} - \vec{p}_j(t))$$ (8.75)

The sum is over the total number of particles $N$ and $\vec{r}_j(t)$ and $\vec{p}_j(t)$ are respectively the position and momentum of particle $j$. The average of $A$ is, in fact, the distribution function $f$, which is given by an ensemble average18 (Exercise 6.4.1) which generalizes (3.75)

$$f(\vec{r}, \vec{p}, t) = \langle A(\vec{r}, \vec{p}, t) \rangle = \left\langle \sum_{j=1}^{N} \delta(\vec{r} - \vec{r}_j(t))\delta(\vec{p} - \vec{p}_j(t)) \right\rangle$$ (8.76)

Knowing the distribution function is equivalent to knowing the average values of a number of dynamic variables, in fact an infinite number. The index $i$ used in Chapter 2 to label these variables corresponds here to $(\vec{r}, \vec{p})$. As in Chapter 2, the ensemble average of the variable $A(\vec{r}, \vec{p}, t)$ will be constrained to take the value $f(\vec{r}, \vec{p}, t)$ at every instant. The other dynamic variables, i.e. the correlations, are not constrained.

We start with Equation (8.28) for the function $f(\vec{r}, \vec{p}_1, t) \equiv f_1$

$$\frac{\partial f_1}{\partial t} + \vec{v}_1 \cdot \vec{\nabla}_r f_1 + \vec{F}(\vec{r}) \cdot \vec{\nabla}_p f_1 = \mathcal{C}[f_1]$$ (8.77)

The collision term $\mathcal{C}[f_1]$ is evaluated from the collision cross section. Let us examine, in the centre-of-mass frame, an elastic collision between two particles of equal mass, which in the laboratory frame is written as $\vec{p}_1 + \vec{p}_2 \rightarrow \vec{p}_3 + \vec{p}_4$, and let $\vec{P}$ be the total momentum. Momenta in the centre-of-mass frame will have a ‘prime’. We have

$$\vec{P} = \vec{p}_1 + \vec{p}_2 = \vec{p}_3 + \vec{p}_4$$

$$\vec{p}_3' = \vec{p}_3 - \frac{1}{2} \vec{P} = \frac{1}{2}(\vec{p}_3 - \vec{p}_4)$$

$$\vec{p}_4' = \vec{p}_4 - \frac{1}{2} \vec{P} = -\frac{1}{2}(\vec{p}_3 - \vec{p}_4) = -\vec{p}_3'$$

18 Ensemble averaging is effected by taking many copies of the same physical system with the same macroscopic characteristics (in this case the same distribution function) but with different microscopic configurations. The ensemble average in (8.75) takes the place of the average with respect to the Boltzmann weight in (3.75).
and similar relations for \( \vec{p}'_1 \) and \( \vec{p}'_2 \). The energies are given in terms of the momenta by

\[
\varepsilon_3 = \frac{\vec{p}'_3^2}{2m} = \frac{1}{2m} \left( \vec{p}'_3 + \frac{1}{2} \vec{P} \right)^2 = \frac{1}{2m} (\vec{p}'_3)^2 + \frac{1}{2m} \vec{p}'_3 \cdot \vec{P} + \frac{1}{8m} \vec{P}^2
\]

\[
\varepsilon_4 = \frac{\vec{p}'_4^2}{2m} = \frac{1}{2m} \left( -\vec{p}'_3 + \frac{1}{2} \vec{P} \right)^2 = \frac{1}{2m} (\vec{p}'_3)^2 - \frac{1}{2m} \vec{p}'_3 \cdot \vec{P} + \frac{1}{8m} \vec{P}^2
\]

Energy conservation is ensured by the \( \delta \) function

\[
\delta(\varepsilon_1 + \varepsilon_2 - \varepsilon_3 - \varepsilon_4) = \delta \left( \frac{(\vec{p}'_1)^2}{m} - \frac{(\vec{p}'_3)^2}{m} \right)
\]

(8.78)

As in the Boltzmann–Lorentz model, it will be convenient to define a quantity \( \overline{W} \) that is related to the cross section by

\[
\overline{W}(\vec{p}_1, \vec{p}_2; \vec{p}_3, \vec{p}_4) = \frac{4}{m^2} \sigma(|\vec{v}_1 - \vec{v}_2|, \Omega')
\]

(8.79)

Let us calculate the integral

\[
\frac{dN}{dt} = \int d^3 p_3 \, d^3 p_4 \, \overline{W} \delta(\vec{p}_1 + \vec{p}_2 - \vec{p}_3 - \vec{p}_4) \delta(\varepsilon_1 + \varepsilon_2 - \varepsilon_3 - \varepsilon_4)
\]

\[
= \int d^3 p'_3 \, \overline{W} \, \delta \left( \frac{(\vec{p}'_1)^2}{m} - \frac{(\vec{p}'_3)^2}{m} \right)
\]

\[
= \int d p'_3 (p'_3)^2 \, d\Omega' \, \overline{W} \, \delta \left( \frac{(\vec{p}'_1)^2}{m} - \frac{(\vec{p}'_3)^2}{m} \right)
\]

\[
= \frac{m}{2} \, p'_1 \int d\Omega' \, \overline{W} = \frac{2p'_1}{m} \int d\Omega' \sigma(|\vec{v}_1 - \vec{v}_2|, \Omega')
\]

But \( 2p'_1/m \) is just the absolute value of the relative velocity

\[
|\vec{v}_1 - \vec{v}_2| = \frac{|\vec{p}_1 - \vec{p}_2|}{m} = 2 \frac{p'_1}{m}
\]

Consequently we have

\[
\frac{dN}{dt} = |\vec{v}_1 - \vec{v}_2| \int d\Omega' \sigma(|\vec{v}_1 - \vec{v}_2|, \Omega') = |\vec{v}_1 - \vec{v}_2| \sigma_{\text{tot}}(|\vec{v}_1 - \vec{v}_2|)
\]

(8.80)

Recall that from (8.7) \( dN/dt \) is the number of collisions per second for unit densities of target and incident particles. In other words the quantity \( Wd^3p_3 \, d^3p_4 \),
defined by
\[
W(\tilde{p}_1, \tilde{p}_2 \to \tilde{p}_3, \tilde{p}_4) \, d^3 p_3 \, d^3 p_4 = \overline{W} \delta(\tilde{p}_1 + \tilde{p}_2 - \tilde{p}_3 - \tilde{p}_4) \delta(\varepsilon_1 + \varepsilon_2 - \varepsilon_3 - \varepsilon_4) \, d^3 p_3 \, d^3 p_4 \quad (8.81)
\]
is the number of collisions per second with final momenta in \(d^3 p_3 \, d^3 p_4\) for unit densities of target and incident particles. Under these conditions, the term \(d^3 r \, d^3 p_1 C_-[f_1]\), which counts the number of particles leaving the volume \(d^3 r \, d^3 p_1\), is obtained by multiplying \(W d^3 p_3 \, d^3 p_4\) by the number of particles in \(d^3 r \, d^3 p_1\), namely \(f(\tilde{r}, \tilde{p}_1, t) d^3 r \, d^3 p_1\), and then integrating over the distribution of incident particles and over all the final configurations of \(\tilde{p}_3\) and \(\tilde{p}_4\)
\[
C_-[f_1] \, d^3 r \, d^3 p_1 = f(\tilde{r}, \tilde{p}_1, t) \, d^3 r \, d^3 p_1 \times \int d^3 p_2 \, d^3 p_3 \, d^3 p_4 \, \frac{1}{2} W(\tilde{p}_1, \tilde{p}_2 \to \tilde{p}_3, \tilde{p}_4) \quad (8.82)
\]
In the same way, the number of particles entering \(d^3 r \, d^3 p_1\) is
\[
C_+[f_1] \, d^3 r \, d^3 p_1 = d^3 r \, d^3 p_1 \int d^3 p_2 \, d^3 p_3 \, d^3 p_4 \, f(\tilde{r}, \tilde{p}_3, t) \times f(\tilde{r}, \tilde{p}_4, t) W(\tilde{p}_3, \tilde{p}_4 \to \tilde{p}_1, \tilde{p}_2) \quad (8.83)
\]
We note that the molecular chaos hypothesis (8.74) was used in the two cases to decouple incident and target particles.
Before adding these two terms we are going to exploit some symmetry properties of the function \(W\). The interactions which intervene in the collisions are electromagnetic and are known to be invariant under rotation \((R)\), space inversion or parity \((P)\) and time reversal \((T)\). These invariances lead to the following symmetries of \(W\) (see Figure 8.7):

(i) rotation: \(W(R \tilde{p}_1, R \tilde{p}_2 \to R \tilde{p}_3, R \tilde{p}_4) = W(\tilde{p}_1, \tilde{p}_2 \to \tilde{p}_3, \tilde{p}_4)\),
(ii) parity: \(W(-\tilde{p}_1, -\tilde{p}_2 \to -\tilde{p}_3, -\tilde{p}_4) = W(\tilde{p}_1, \tilde{p}_2 \to \tilde{p}_3, \tilde{p}_4)\),
(iii) time reversal: \(W(-\tilde{p}_3, -\tilde{p}_4 \to -\tilde{p}_1, -\tilde{p}_2) = W(\tilde{p}_1, \tilde{p}_2 \to \tilde{p}_3, \tilde{p}_4)\).

In the above, \(R \tilde{p}\) is the result of rotating \(\tilde{p}\) by \(R\) and the effect of time reversal is to change the sign of the momenta. Combining properties (ii) and (iii) yields
\[
W(\tilde{p}_3, \tilde{p}_4 \to \tilde{p}_1, \tilde{p}_2) = W(\tilde{p}_1, \tilde{p}_2 \to \tilde{p}_3, \tilde{p}_4) \quad (8.84)
\]
The collision \(\tilde{p}_3 + \tilde{p}_4 \to \tilde{p}_1 + \tilde{p}_2\) is called the inverse collision of \(\tilde{p}_1 + \tilde{p}_2 \to \tilde{p}_3 + \tilde{p}_4\). By using the symmetry relation (8.84), which relates a collision to its inverse, we can combine \(C_-[f_1]\) and \(C_+[f_1]\) to obtain \(C[f_1] = C_+[f_1] - C_-[f_1]\) in
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Figure 8.7 The effects of rotation, space inversion and time reversal symmetries on collisions.

the form

$$C[f_1] = \int \prod_{i=2}^{4} d^3 p_i \ W(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4)[f_3 f_4 - f_1 f_2]$$  \hspace{1cm} (8.85)

with the notation $f_i = f(\vec{r}, \vec{p}_i, t)$. The Boltzmann equation then takes on its final form

$$\frac{\partial f_1}{\partial t} + \vec{v}_1 \cdot \vec{\nabla}_r f_1 + \vec{F}(\vec{r}) \cdot \vec{\nabla}_{\vec{p}_1} f_1 = \int \prod_{i=2}^{4} d^3 p_i \ W(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4)[f_3 f_4 - f_1 f_2]$$

$$= \int d\Omega' \int d^3 p_2 \sigma(|\vec{v}_1 - \vec{v}_2|, \Omega')[\vec{v}_1 - \vec{v}_2][f_3 f_4 - f_1 f_2]$$ \hspace{1cm} (8.86)

One should be careful to integrate over only half the phase space to take into account the fact that the particles are identical. To make the connection with the Boltzmann–Lorentz model, it is sufficient to take $f_2 = f_4 = n_d \delta(\vec{p})$. The Boltzmann equation explicitly breaks time reversal invariance: $f(\vec{r}, -\vec{p}, -t)$ does not obey the Boltzmann equation since the drift term changes sign while the collision term does not.
8.3 Boltzmann equation

8.3.2 Conservation laws

We have a priori five conservation laws: particle number (or mass), energy and the three components of momentum. These laws, in the form of continuity equations for the densities and currents, are the result of the conservation of mass, energy and momentum in each collision \( \vec{p}_1 + \vec{p}_2 \rightarrow \vec{p}_3 + \vec{p}_4 \). The argument is a simple generalization of the one given for the Boltzmann–Lorentz model. Let \( \chi(\vec{p}) \) be a conserved quantity in the collision \( \vec{p}_1 + \vec{p}_2 \rightarrow \vec{p}_3 + \vec{p}_4 \)

\[
\chi_1 + \chi_2 = \chi_3 + \chi_4 \tag{8.87}
\]

where we use the notation \( \chi_i = \chi(\vec{p}_i) \). We shall demonstrate the following preliminary result

\[
I[\chi] = \int d^3 p_1 \chi(\vec{p}_1)C[f_1] = 0 \tag{8.88}
\]

Taking into account Equation (8.85) for the collision term,\(^{19}\) we have

\[
I[\chi] = \int \prod_{i=1}^{4} d^3 p_i \chi_1 W(12 \rightarrow 34)[f_3 f_4 - f_1 f_2]
\]

Since the particles 1 and 2 are identical, we have \( W(12 \rightarrow 34) = W(21 \rightarrow 34) \), and changing variables \( \vec{p}_1 \leftrightarrow \vec{p}_2 \), we obtain a second expression for \( I[\chi] \)

\[
I[\chi] = \int \prod_{i=1}^{4} d^3 p_i \chi_2 W(12 \rightarrow 34)[f_3 f_4 - f_1 f_2]
\]

A third expression is obtained by exchanging (12) and (34) and by using the property of the inverse collision \( W(34 \rightarrow 12) = W(12 \rightarrow 34) \)

\[
I[\chi] = -\int \prod_{i=1}^{4} d^3 p_i \chi_3 W(12 \rightarrow 34)[f_3 f_4 - f_1 f_2]
\]

and a fourth by exchanging particles 3 and 4. Finally we obtain

\[
I[\chi] = \frac{1}{4} \int \prod_{i=1}^{4} d^3 p_i [\chi_1 + \chi_2 - \chi_3 - \chi_4] W(12 \rightarrow 34)[f_3 f_4 - f_1 f_2] \tag{8.89}
\]

Consequently, from (8.87), \( I[\chi] = 0 \) if the quantity \( \chi \) is conserved in the collision (see Footnote 12 for the physical interpretation of this result). This demonstration is unchanged if \( \chi \) also depends on \( \vec{r} \). We multiply the Boltzmann equation (8.86) by the conserved quantity \( \chi(\vec{r}, \vec{p}_1) \), change notation \( \vec{p}_1 \rightarrow \vec{p} \) and integrate over \( \vec{p} \).

\(^{19}\) We use the notation \( W(12 \rightarrow 34) = W(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) \).
We obtain
\[
\int d^3 p \, \chi(\vec{r}, \vec{p}) \left( \frac{\partial f}{\partial t} + \vec{v} \cdot \vec{\nabla}_f f + \vec{F}(\vec{r}) \cdot \vec{\nabla}_p f \right) = 0 \quad (8.90)
\]
This may be explicitly expressed in terms of physical quantities. To do this we use
\[
\int d^3 p \, \chi v_\alpha \partial_\alpha f = \partial_\alpha \int d^3 p \, (\chi v_\alpha f) - \int d^3 p \, f v_\alpha \partial_\alpha \chi \quad (8.91)
\]
and
\[
\int d^3 p \, \chi F_\alpha \partial_p \partial_\alpha f = \int d^3 p \, \partial_p \chi (\partial_\alpha F_\alpha f) - \int d^3 p \, (\partial_\alpha \chi) F_\alpha f = - \int d^3 p \, (\partial_\alpha \chi) F_\alpha f \quad (8.92)
\]
The second line in (8.92) is obtained by noting that the first term in the first line is the integral of a divergence that can be written as a surface integral which vanishes since \( f \to 0 \) rapidly for \(|\vec{p}| \to \infty\). In addition we assume, for simplicity, that the force does not depend on the velocity, which eliminates the third term.

From (8.2) the average value of \( \chi \) is
\[
n\langle \chi \rangle = \int d^3 p \, \chi f \quad (8.93)
\]
and the current is given by a simple convection term since we neglect interactions
\[
\vec{j}_\chi = \int d^3 p \, \vec{v} \chi f = n\langle \vec{v} \chi \rangle \quad (8.94)
\]
The above results allow us to put (8.90) in the final form
\[
\frac{\partial}{\partial t} (n\langle \chi \rangle) + \partial_\alpha (n\langle v_\alpha \chi \rangle) = n \langle v_\alpha \partial_\alpha \chi \rangle + n \langle F_\alpha \partial_p \partial_\alpha \chi \rangle \quad (8.95)
\]
In the absence of an external source, Equation (8.95) has the form of a continuity equation \( \partial_t \rho \chi + \vec{\nabla} \cdot \vec{j}_\chi = 0 \).

The velocity \( \vec{v} \) may be decomposed into two components \( \vec{v} = \vec{u} + \vec{w} \). The first component is an average velocity \( \vec{u} = \langle \vec{v} \rangle \), which is nothing more than the flow velocity of the fluid introduced in Section 6.3.1. The second component, \( \vec{w} \), which has zero average, \( \langle \vec{w} \rangle = 0 \), is the velocity measured in the fluid rest frame and is, therefore, the velocity due to thermal fluctuations. By taking \( \chi = m \), we obtain a

\[20\] Repeated indexes are summed.
continuity equation for the mass (see Table 6.1)
\[
\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{g} = 0
\] (8.96)

with \( \rho = nm \) and \( \vec{g} = \rho \langle \vec{v} \rangle = \rho \vec{u} \). The momentum continuity equation is obtained by taking \( \chi = mv_\beta \), \( \partial_{\rho_\alpha} \chi = \delta_{\alpha \beta} \)
\[
\frac{\partial}{\partial t} (\rho \langle v_\beta \rangle) + \partial_{\alpha} (\rho \langle v_\alpha v_\beta \rangle) = nF_\beta
\] (8.97)

where \( nF_\beta = f_\beta \) is the force density. This equation allows us to obtain the momentum current \( T_{\alpha \beta} \) (compare with (6.69) and (6.74))
\[
T_{\alpha \beta} = \rho \langle v_\alpha v_\beta \rangle
\] (8.98)

By writing \( \vec{v} = \vec{u} + \vec{w} \), we obtain
\[
T_{\alpha \beta} = \rho u_\alpha u_\beta + \rho \langle w_\alpha w_\beta \rangle
\]

and thus the pressure tensor \( P_{\alpha \beta} \) (see Table 6.1) is
\[
P_{\alpha \beta} = \rho \langle w_\alpha w_\beta \rangle
\] (8.99)

We note that the trace of the pressure tensor has the remarkable value
\[
P_{\alpha \alpha} = nm \langle \vec{w}^2 \rangle = \rho \langle \vec{w}^2 \rangle
\] (8.100)

Finally, let us take \( \chi \) as the energy in the absence of external forces: \( \chi = m\vec{v}^2/2 \). The energy density is
\[
\epsilon = \frac{1}{2} \rho \langle \vec{v}^2 \rangle
\] (8.101)

and the associated current is
\[
\vec{j}_E = \frac{1}{2} \rho \langle \vec{v}^2 \vec{v} \rangle
\] (8.102)

Equation (8.95) ensures the conservation of energy in the absence of external forces
\[
\frac{\partial \epsilon}{\partial t} + \nabla \cdot \vec{j}_E = 0
\] (8.103)

It is possible to relate the energy current to the heat current \( \vec{j}_E' = \vec{j}_Q \), which is the current measured in the fluid rest frame. Using \( \vec{v} = \vec{u} + \vec{w} \), it is easy to show that (Exercise 8.4.5)
\[
j^E_\alpha = \epsilon u_\alpha + \sum_\beta u_\beta P_{\alpha \beta} + j^E'_\alpha
\]
which is just Equation (6.83). The local temperature is defined in the fluid rest frame by

\[
\frac{1}{2} m \langle \mathbf{w}^2 \rangle = \frac{3}{2} kT(\mathbf{r}, t)
\]

which gives

\[
\rho \langle \mathbf{w}^2 \rangle = 3nkT = 3\mathcal{P}
\]

and by comparing with (8.100) we have

\[
\sum_\alpha \mathcal{P}_{\alpha\alpha} - 3\mathcal{P} = 0 \tag{8.105}
\]

This property of the trace of the pressure tensor allows us to show, when used in (6.88), that the bulk viscosity \( \zeta \) vanishes for an ideal mono-atomic gas.

### 8.3.3 H-theorem

We end our discussion of this section with a demonstration of the increase of the Boltzmann entropy. We adopt the framework defined in Chapter 2 by considering a set of dynamic variables \( A_i \) whose average values \( A_i \) are fixed.\(^{21}\) This allows us to construct the corresponding Boltzmann (or relevant) entropy. In the present case, the dynamic variables are the one-particle distributions (8.75) whose average values are the distribution functions \( f(\mathbf{r}, \mathbf{p}, t) \). The index \( i \) in Chapter 2 here represents the variables \( (\mathbf{r}, \mathbf{p}) \) which label the dynamic variables. The Lagrange multipliers \( \lambda_i \) become \( \lambda(\mathbf{r}, \mathbf{p}) \) with the corresponding notation\(^{22}\)

\[
i \rightarrow (\mathbf{r}, \mathbf{p}) \quad \lambda_i \rightarrow \lambda(\mathbf{r}, \mathbf{p}) \quad \sum_i \rightarrow \int d^3r \ d^3p
\]

\[
\sum_i \lambda_i A_i \rightarrow \int d^3r \ d^3p \lambda(\mathbf{r}, \mathbf{p}) \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j) \delta(\mathbf{p} - \mathbf{p}_j) = \sum_{j=1}^N \lambda(\mathbf{r}_j, \mathbf{p}_j)
\]

Recall the semi-classical expression (3.42) for the trace, which we generalize to the grand canonical ensemble

\[
\text{Tr} = \sum_N \frac{1}{N!} \int \prod_{j=1}^N \frac{d^3r_j d^3p_j}{h^3} \tag{8.106}
\]

\(^{21}\) Since our discussion is classical, we use the notation \( A \) for a dynamic variable and not \( \mathcal{A} \).

\(^{22}\) We have taken in (8.75) \( t = 0 \) and \( \mathbf{r}_i(t = 0) = \mathbf{r}_i, \mathbf{p}_i(t = 0) = \mathbf{p}_i \).
The grand partition function is

\[
Q = \sum_N \frac{1}{N!} \prod_{j=1}^{N} \left( \frac{d^3r_j \, d^3p_j}{\hbar^3} \exp[\lambda(\vec{r}_j, \vec{p}_j)] \right)
\]

which yields

\[
\ln Q = \frac{1}{\hbar^3} \int d^3r' \, d^3p' \, e^{\lambda(\vec{r}', \vec{p}')} \tag{8.107}
\]

The distribution function is given by the functional derivative of \(\ln Q\) (see Appendix A.6)

\[
f(\vec{r}, \vec{p}) = \frac{\delta \ln Q}{\delta \lambda(\vec{r}, \vec{p})} = \frac{1}{\hbar^3} \exp[\lambda(\vec{r}, \vec{p})] \tag{8.108}
\]

which allows us to identify the Lagrange multiplier \(\lambda(\vec{r}, \vec{p})\)

\[
\lambda(\vec{r}, \vec{p}) = \ln(h^3 f(\vec{r}, \vec{p})) \tag{8.109}
\]

We finally arrive at the Boltzmann entropy by using (2.65)

\[
S_B = k \left( \ln Q - \sum_i \lambda_i A_i \right)
\]

which gives in the present case

\[
S_B = k \int d^3r \, d^3p \, f(\vec{r}, \vec{p}) \left[ 1 - \ln(h^3 f(\vec{r}, \vec{p})) \right] \tag{8.110}
\]

Equation (8.110) permits the determination of the entropy density, \(s_B\), and current, \(\vec{j}_S\), by using once more the fact that this current is purely convective within kinetic theory

\[
s_B = k \int d^3p \, f(\vec{r}, \vec{p}) \left[ 1 - \ln(h^3 f(\vec{r}, \vec{p})) \right] \tag{8.111}
\]

\[
\vec{j}_S = k \int d^3p \, \vec{v} \, f(\vec{r}, \vec{p}) \left[ 1 - \ln(h^3 f(\vec{r}, \vec{p})) \right] \tag{8.112}
\]

We note that we are working with the classical approximation where \(h^3 f \ll 1\). Therefore, the 1 in the brackets in (8.111) and (8.112) may be dropped.

This form of the Boltzmann entropy (8.110) may be obtained with a more intuitive argument by writing the density in phase space (see Section 2.2.2) as a product
of one-particle distribution functions

\[ D_N(\mathbf{r}_1, \mathbf{p}_1; \ldots; \mathbf{r}_N, \mathbf{p}_N) \propto \prod_{i=1}^{N} f(\mathbf{r}_i, \mathbf{p}_i) \]

which is equivalent to ignoring correlations. We thus obtain Equation (8.110) for

the entropy up to factors of 1 and \( h \). Boltzmann called this expression \( -H \)

\[ H(t) = k \int d^3r \ d^3p \ f(\mathbf{r}, \mathbf{p}, t) \ln f(\mathbf{r}, \mathbf{p}, t) \]

hence the name ‘H-theorem’ for Equation (8.113) below.

Having expressed the entropy in terms of \( f \), we use the Boltzmann equation

(8.86) to write the entropy continuity equation. To this end, we multiply the two

sides of (8.86) by \(-k \ln(h^3 f_1)\) and integrate over \( \mathbf{p}_1 \). Using

\[ df \left( f \left[ 1 - \ln(h^3 f(\mathbf{r}, \mathbf{p})) \right] \right) = -\ln[h^3 f(\mathbf{r}, \mathbf{p})]df \]

we obtain

\[ \frac{\partial S_B}{\partial t} + \mathbf{\nabla} \cdot \mathbf{j}_S = -k \int \prod_{i=1}^{4} d^3p_i \ln(h^3 f_1)[f_3 f_4 - f_1 f_2]W(\mathbf{p}_1, \mathbf{p}_2 \rightarrow \mathbf{p}_3, \mathbf{p}_4) \]

\[ = \frac{k}{4} \int \prod_{i=1}^{4} d^3p_i \ln \frac{f_1 f_2}{f_3 f_4} [f_1 f_2 - f_3 f_4]W(\mathbf{p}_1, \mathbf{p}_2 \rightarrow \mathbf{p}_3, \mathbf{p}_4) \]

\[ = \frac{k}{4} \int \prod_{i=1}^{4} d^3p_i \ln \frac{f_1 f_2}{f_3 f_4} \left[ \frac{f_1 f_2}{f_3 f_4} - 1 \right] f_3 f_4 W(\mathbf{p}_1, \mathbf{p}_2 \rightarrow \mathbf{p}_3, \mathbf{p}_4) \geq 0 \]

(8.113)

To obtain the second line of (8.113) we have used the same symmetry properties

used to obtain (8.89). The last inequality comes from the fact that \((x - 1) \ln x \geq 0\)

for all \( x \). Therefore, there is an entropy source on the right hand side of this con-

tinuity equation. This means that the total entropy increases: \(23 \) \( dS_B / dt \geq 0 \). The

above calculation shows that the origin of the source term in the continuity equa-

tion is the collisions suffered by the particles. It is, therefore, these collisions that

lead to the entropy increase.

That entropy increases becomes clear if we reason in terms of the relevant en-

tropy. The available information is contained in the one-particle distribution func-

tions. Collisions create correlations, but information about these correlations is lost

in the picture using one-particle functions: there is a leak of information toward

correlations.

\[23\] This statement is valid on the average. One may observe fluctuations during which \( S_B(t) \) decreases for a short

period of time. Such fluctuations are found in molecular dynamics simulations.
Let \( f_0 \) be a local equilibrium distribution corresponding to local temperature \( T(\vec{r}, t) \), local chemical potential \( \mu(\vec{r}, t) \) and local fluid velocity \( \vec{u}(\vec{r}, t) \),

\[
f_0(\vec{r}, \vec{p}, t) = \frac{1}{h^3} \exp \left( \alpha(\vec{r}, t) - \beta(\vec{r}, t) \frac{(\vec{p} - m\vec{u}(\vec{r}, t))^2}{2m} \right) \tag{8.114}
\]

with \( \alpha = \mu / kT \) and \( \beta = 1 / kT \). As implied by Equation (8.118), the collision term vanishes, \( C[f_0] = 0 \), and \( dS_{\text{tot}}/dt = 0 \). Conversely, one can show (Exercise 8.5.6) that \( f(\vec{r}, \vec{p}, t) \) may be written in the form (8.114) if the collision term vanishes. A fortiori the entropy is constant for a global equilibrium distribution.

In order to avoid confusion, we revisit some key points in the preceding discussion. The first observation is that the increase in the Boltzmann entropy \( dS_B / dt \geq 0 \) rests on the assumption that there are no correlations between molecules prior to collision. Of course, two molecules are correlated after suffering a collision. It is for this reason that there is an asymmetry in the temporal evolution: times ‘before’ and ‘after’ a collision are not equivalent. However, because the gas is dilute, two such molecules have negligible probability of colliding again, rather, they will collide with other molecules with which they are not correlated and the molecular chaos hypothesis continues to hold beyond the initial time. However, by waiting long enough, one would observe ‘long time tails’, namely a power law, and not exponential, dependence of the time-correlation functions, which behave as \( t^{-3/2} \) for \( t \gg \tau^* \). These long time tails are due to the long lived hydrodynamic modes of the fluid (see [108], Chapter 11). The second remark concerns the comparison between the Boltzmann and thermodynamic entropies. The quantity \( S_B \) is indeed the Boltzmann (or relevant) entropy in the sense of the construction in Chapter 2, but the density \( s_B \) in (8.111) should not be identified with a thermodynamic entropy density at local equilibrium. In fact, the distribution \( f(\vec{r}, \vec{p}) \) is a priori not a Maxwell distribution and does not allow the definition of a temperature: the kinetic description is more detailed than the thermodynamic one and cannot, in general, be reduced to it. After a time of the order of the collision time, a local equilibrium of the type (8.114) is established. A straightforward calculation allows one to check that the density of Boltzmann entropy defined in (8.111) coincides with the local thermodynamic entropy (3.17). Under these conditions the collision term vanishes. Thus, the entropy increases following the mechanisms described in Chapter 6, which are governed by the viscosity and thermal conductivity transport coefficients. The ‘H-theorem’ is then not related to the increase of thermodynamic entropy, which is defined only at local equilibrium. Finally, the assumption of dilute gas is crucial: the Boltzmann equation breaks down if the potential energy becomes important. In such a case, the equation satisfied by \( f(\vec{r}, \vec{p}, t) \) exhibits memory effects and is no longer an autonomous equation like the Boltzmann
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The entropy (8.110) is still defined but it loses its utility since the property of entropy increase (8.113) is no longer automatically valid except at $t = 0$.

8.4 Transport coefficients from the Boltzmann equation

In this last section, we show how the transport coefficients may be computed from the Boltzmann equation. We shall limit ourselves to the computation of the shear viscosity, which is slightly simpler than that of the thermal conductivity, for which we refer to Problem 8.6.8.

8.4.1 Linearization of the Boltzmann equation

As in the case of the Boltzmann–Lorentz model, we follow the Chapman–Enskog method by linearizing the Boltzmann equation in the vicinity of a local equilibrium distribution of the form (8.114), which we rewrite by introducing the local density $n(\vec{r}, t)$

$$f_0(\vec{r}, \vec{p}, t) = n(\vec{r}, t) \left( \frac{\beta(\vec{r}, t)}{2\pi m} \right)^{3/2} \exp \left[ -\frac{1}{2} m \beta(\vec{r}, t)(\vec{v} - \vec{u}(\vec{r}, t))^2 \right]$$ (8.115)

The local density, the local inverse temperature $\beta(\vec{r}, t)$ and the local fluid velocity $\vec{u}(\vec{r}, t)$ are defined from $f_0$ following (8.45)–(8.46) and (8.104)

$$n(\vec{r}, t) = \int d^3p \, f_0(\vec{r}, \vec{p}, t)$$

$$\vec{u}(\vec{r}, t) = \frac{1}{n(\vec{r}, t)} \int d^3p \, \vec{v} f_0(\vec{r}, \vec{p}, t)$$ (8.116)

$$kT(\vec{r}, t) = \frac{1}{\beta(\vec{r}, t)} = \frac{m}{3n(\vec{r}, t)} \int d^3p \, f_0(\vec{r}, \vec{p}, t)(\vec{v} - \vec{u}(\vec{r}, t))^2$$

The collision term vanishes if computed with the local equilibrium distribution (8.115): $C[f_0] = 0$. Indeed, because of the conservation laws in the two-body elastic collisions

$$\vec{p}_1 + \vec{p}_2 = \vec{p}_3 + \vec{p}_4 \quad \text{and} \quad \vec{p}_1^2 + \vec{p}_2^2 = \vec{p}_3^2 + \vec{p}_4^2$$ (8.117)

one verifies at once the identity

$$\ln f_{01} + \ln f_{02} = \ln f_{03} + \ln f_{04}$$

so that

$$f_{01}f_{02} = f_{03}f_{04}$$ (8.118)
However \( f_0 \) is not a solution of the Boltzmann equation, as the drift term does not vanish, except in the trivial case where the local equilibrium reduces to a global one

\[
Df_0 = \left( \frac{\partial}{\partial t} + \vec{v} \cdot \vec{\nabla} \right) f_0 \neq 0
\]

(8.119)

In the previous equation, and in all that follows, we have assumed that there are no external forces. As in the Boltzmann–Lorentz model we write the distribution \( f \) in terms of a small deviation \( \bar{f} \) from the local equilibrium distribution \( f_0 \)

\[
f = f_0 + \bar{f}
\]

Because of (8.116), \( \bar{f} \) must obey the following three conditions, which are the analogues of (8.48) in the Boltzmann–Lorentz model

\[
\int d^3 p \, \bar{f} = \int d^3 p \, \vec{p} \cdot \bar{f} = \int d^3 p \, \epsilon \bar{f} = 0
\]

(8.120)

We now follow the reasoning of Section 8.2.4: collisions bring the gas to local equilibrium after a time of the order of the collision time \( \tau^* \), and one observes afterwards a slow relaxation toward global equilibrium during which a time-independent drift term \( Df = \vec{v} \cdot \vec{\nabla} f \) is balanced by the collision term as in (8.50). It will be convenient to write \( f \) as

\[
f = f_0 \left( 1 - \Phi \right) \quad \bar{f} = -f_0 \Phi, \quad |\Phi| \ll 1
\]

(8.121)

so that, with the notation \( \Phi_i = \Phi(\vec{p}_i) \) and keeping only terms linear in \( \Phi_i \)

\[
f_i f_j \simeq f_{0i} f_{0j} (1 - \Phi_i - \Phi_j)
\]

Taking into account (8.118), the collision term becomes

\[
C[f] = \int \prod_{i=2}^{4} d^3 p_i \, W f_{01} f_{02} \left[ \Phi_1 + \Phi_2 - \Phi_3 - \Phi_4 \right]
\]

and the linearized Boltzmann equation reads

\[
Df_{01} = \frac{\beta}{m} f_{01} L \left[ \Phi \right]
\]

\[
L \left[ \Phi \right] = \frac{m}{\beta} \int \prod_{i=2}^{4} d^3 p_i \, W f_{02} \Delta \Phi
\]

\[
\Delta \Phi = \Phi_1 + \Phi_2 - \Phi_3 - \Phi_4
\]

(8.122)

where the factor \( m/\beta \) has been introduced for later purposes. The functional \( L \left[ \Phi \right] \) may be considered as a linear operator acting on a space of functions \( \Phi(\vec{p}) \). Let
\( \bar{\Psi}(\vec{p}) \) be an arbitrary function, let us multiply both sides of (8.122) by \( \bar{\Psi}(\vec{p}) \) and integrate over \( \vec{p}_1 \)

\[
\int d^3 p_1 \bar{\Psi}_1 Df_{01} = \frac{\beta}{m} \int d^3 p_1 \bar{\Psi}_1 f_{01} L[\bar{\Phi}] \\
= \frac{1}{4} \int \prod_{i=1}^{4} d^3 p_i \Delta \bar{\Psi} Wf_{01}f_{02} \Delta \bar{\Phi} \tag{8.123}
\]

where we have used the symmetry properties of the collision term, as in the derivation of (8.89). The right hand side of (8.123) defines a scalar product \( (\bar{\Psi}, \bar{\Phi}) \), which will turn out to be most useful in the derivation of a variational method, as explained in Section 8.4.2

\[
(\bar{\Psi}, \bar{\Phi}) = \frac{1}{4} \int \prod_{i=1}^{4} d^3 p_i \Delta \bar{\Psi} Wf_{01}f_{02} \Delta \bar{\Phi} \tag{8.124}
\]

which is positive semi-definite

\[
||\bar{\Phi}||^2 = (\bar{\Phi}, \bar{\Phi}) = \frac{1}{4} \int \prod_{i=1}^{4} d^3 p_i Wf_{01}f_{02}(\Delta \bar{\Phi})^2 \geq 0
\]

because \( W \) and \( f_0 \) are positive functions. More precisely, the left hand side of the previous equation will be strictly positive unless \( \bar{\Phi}(\vec{p}) \) is one of the five conserved densities, also called ‘zero modes’ of the linearized Boltzmann equation, which obey \( L[\bar{\Phi}] = 0 \)

\[
\bar{\Phi}^{(1)}(\vec{p}) = 1 \quad \bar{\Phi}^{(2)}(\vec{p}) = p_x \quad \bar{\Phi}^{(3)}(\vec{p}) = p_y \quad \bar{\Phi}^{(4)}(\vec{p}) = p_z \quad \bar{\Phi}^{(5)}(\vec{p}) = p^2
\]

Otherwise we shall have \( ||\bar{\Phi}||^2 = 0 \iff \bar{\Phi} = 0. \)

\[8.4.2 \text{ Variational method}\]

We now specialize our analysis to the calculation of the shear viscosity coefficient \( \eta \), by using a particular form of the local equilibrium distribution \( f_0 \) in (8.115). We assume the temperature to be uniform, while the fluid velocity is directed along the \( x \)-axis and depends on the \( z \) coordinate (see Figure 6.6)

\[
\vec{u} = (u_x(z), 0, 0) \tag{8.125}
\]
The time-independent drift term becomes

\[
Df \simeq Df_0 = n \left( \frac{\beta}{2\pi m} \right)^{3/2} v_z \frac{\partial}{\partial z} \exp \left( -\frac{1}{2} \frac{\beta m}{\sigma} \left[ (v_x - u_x(z))^2 + v_y^2 + v_z^2 \right] \right)
\]

\[
= \beta m f_0(\vec{r}, \vec{p}) v_z (v_x - u_x(z)) \frac{\partial u_x(z)}{\partial z}
\]

\[
= \beta m f_0(\vec{r}, \vec{p}) w_z w_x \frac{\partial u_x(z)}{\partial z}
\]

(8.126)

with \( \vec{w} = \vec{v} - \vec{u} \). The linearized Boltzmann equation (8.122) becomes

\[
\beta m w_{1x} w_{1z} \frac{\partial u_x(z)}{\partial z} = \int \prod_{i=2}^{4} d^3 p_i W f_{02} \Delta \Phi
\]

We consider a fixed point \( \vec{r} \) in ordinary space and use the Galilean frame where the fluid is locally at rest, \( u_x(z) = 0 \) (but \( \partial u_x/\partial z \neq 0 \)) so that \( f_0(\vec{r}, \vec{p}) \to f_0(p) \) and \( \vec{w} = \vec{v} \). Instead of \( \Phi \) in (8.121), it is more convenient to use \( \Phi \) defined by

\[
f(\vec{p}) = f_0(p) \left( 1 - \Phi(\vec{p}) \right) = f_0 \left( 1 - \Phi(\vec{p}) \frac{\partial u_x}{\partial z} \right)
\]

(8.127)

which corresponds to an expansion to first order in \( \partial u_x/\partial z \). With this definition the linearized Boltzmann equation now reads

\[
\boxed{\rho_{1x} \rho_{1z} = \frac{m}{\beta} \int \prod_{i=2}^{4} d^3 p_i W f_{02} \Delta \Phi = L[\Phi]}
\]

(8.128)

The left hand side of (8.128) is a second rank tensor \( T_{xz} \), and since \( \vec{p} \) is the only vector at our disposal, \( \Phi \) must be proportional to \( p_x p_z \) and its most general form is

\[
\Phi(\vec{p}) = A(p) p_x p_z
\]

(8.129)

so that \( \Delta \Phi \) reads

\[
\Delta \Phi = A(p_1) \rho_{1x} \rho_{1z} + A(p_2) \rho_{2x} \rho_{2z} - A(p_3) \rho_{3x} \rho_{3z} - A(p_4) \rho_{4x} \rho_{4z}
\]

It is important to remark that the three conditions (8.120) are verified by our choice (8.129) for \( \Phi \). The pressure tensor \( \rho_{xz} \) is given from (8.19) by

\[
\rho_{xz} = \int d^3 p p_x v_z f = - \int d^3 p p_x v_z f_0 \Phi \frac{\partial u_x}{\partial z}
\]

\[
= - \frac{1}{m} \frac{\partial u_x}{\partial z} \int d^3 p A(p) f_0(p) p_x^2 p_z^2 = -\eta \frac{\partial u_x}{\partial z}
\]
and we get the following expression for $\eta$

$$\eta = \frac{1}{m} \int d^3p \ A(p) f_0(p) p_x^2 p_z^2$$  \hspace{1cm} (8.130)

We now rewrite the linearized Boltzmann equation (8.128) by using a Dirac notation in a (real) Hilbert space where a function $F(\vec{p})$ is represented by a vector $|F\rangle$ and the scalar product of two functions $F(\vec{p})$ and $G(\vec{p})$ is defined by

$$\langle F|G \rangle = \frac{1}{m} \int d^3p \ F(\vec{p}) f_0(p) G(\vec{p})$$  \hspace{1cm} (8.131)

This scalar product is obviously positive definite: $\langle F|F \rangle \geq 0$ and $\langle F|F \rangle = 0 \iff F = 0$. We represent the function $p_x p_z$ in (8.128) by a vector $|X\rangle$. Note that because $f_0(p)$ decreases exponentially with $p^2$ at infinity, the norm $\langle X|X \rangle$ is finite and $|X\rangle$ belongs to our Hilbert space. With these notations, the linearized Boltzmann equation reads in operator form

$$p_{1x} p_{1z} = |X\rangle = L|\Phi\rangle$$  \hspace{1cm} (8.132)

and the viscosity is given from (8.16) by

$$\eta = \langle \Phi|X \rangle = \langle \Phi|L|\Phi \rangle = \frac{\langle \Phi|X \rangle^2}{\langle \Phi|L|\Phi \rangle}$$  \hspace{1cm} (8.133)

This formula will serve as the starting point for a variational method. Indeed, $\Phi$ is an unknown function of $\vec{p}$, or, in other words, we do not know the functional form of $A(p)$, and an exact solution for $A(p)$ would require rather complicated methods. An efficient way to proceed is to use a variational method by introducing a trial function $\Psi(\vec{p})$, where we must restrict our choice to functions orthogonal to the zero modes. We define a $\Psi$-dependent viscosity coefficient $\eta[\Psi]$ as a functional of $\Psi$ by

$$\eta[\Psi]\overset{\Delta}{=} \frac{|\langle X|\Psi \rangle|^2}{\langle \Psi|L|\Psi \rangle} = \frac{|\langle \Phi|L|\Phi \rangle|^2}{\langle \Phi|L|\Phi \rangle}$$  \hspace{1cm} (8.134)

The choice $\Psi = \Phi$ gives the exact value of the viscosity: $\eta \equiv \eta[\Phi]$. The quantity $\langle \Psi|L|\Phi \rangle$ can be rewritten by using the (positive definite) scalar product already introduced in (8.124)\(^{24}\)

$$\langle \Psi|L|\Phi \rangle = (\Psi, \Phi) = \frac{1}{4\beta} \int \prod_{i=1}^{4} d^3p_i \ \Delta \Psi W f_{01} f_{02} \Delta \Phi$$  \hspace{1cm} (8.135)

\(^{24}\) Within a $1/\beta$ multiplicative factor.
The Schwartz inequality leads to an inequality on $\eta[\Psi]$

$$\eta[\Psi] = \frac{|(\Psi, \Phi)|^2}{(\Psi, \Psi)} \leq \frac{(\Psi, \Psi)(\Phi, \Phi)}{(\Psi, \Psi)} = \langle \Phi|L|\Phi \rangle = \eta[\Phi]$$

We have thus derived an inequality typical of a variational method

$$\eta[\Psi] \leq \eta_{\text{exact}} = \eta[\Phi] \quad (8.136)$$

### 8.4.3 Calculation of the viscosity

One possible choice for a trial function would be

$$\Psi_\alpha = Ap^\alpha p_x p_z$$

and the best choice for $\alpha$ would be obtained by minimizing $\eta[\Psi_\alpha]$ with respect to the parameter $\alpha$. We shall limit ourselves to the simple case $\alpha = 0$, which already gives results that do not differ from those of an exact calculation by more than a few percent. The computation of $\langle X|\Psi \rangle$ is then straightforward, with $f_0(p)$ given by

$$f_0(p) = n \left( \frac{\beta}{2\pi m} \right)^{3/2} \exp \left( -\frac{\beta p^2}{2m} \right) \quad (8.137)$$

One obtains

$$\langle X|\Psi \rangle = \frac{1}{m} \int d^3 p \; p_x p_z f_0(p) Ap_x p_z$$

$$= \frac{4\pi}{15} A \int_0^\infty dp \; p^6 f_0(p)$$

where we have computed the angular average from (A.36)\(^{25}\)

$$\langle p_x p_z p_x p_z \rangle_{\text{ang}} = \frac{1}{15} p^4$$

The $p$-integration is completed thanks to the Gaussian integration (A.37) in the form

$$\int_0^\infty dp \; p^n e^{-\alpha p^2} = \frac{1}{2} \Gamma \left( \frac{n+1}{2} \right) \alpha^{-(n+1)/2}$$

\(^{25}\) In this elementary case, one can also use

$$\int \frac{d\Omega}{4\pi} p_x^2 p_z^2 = \frac{p^4}{4\pi} \int_{-1}^1 d(\cos \alpha) \sin^2 \alpha \cos^2 \alpha \int_0^{2\pi} d\phi \cos^2 \phi = \frac{1}{15}$$
with the result

\[ \langle X | \Psi \rangle = \frac{nA m}{\beta^2} \]  
(8.138)

The calculation of \( \langle \Psi | L | \Psi \rangle \) is slightly more involved

\[ \langle \Psi | L | \Psi \rangle = \frac{1}{4\beta} \int \prod_{i=1}^{4} d^3 p_i \, f_{01} f_{02} W(\Delta \Psi)^2 \]  
(8.139)

Using the centre-of-mass kinematics we get

\[ \begin{align*}
\vec{p}_1 &= \vec{p} + \frac{1}{2} \vec{P} \\
\vec{p}_2 &= -\vec{p} + \frac{1}{2} \vec{P} \\
\vec{p}_3 &= \vec{p}' + \frac{1}{2} \vec{P} \\
\vec{p}_4 &= -\vec{p}' + \frac{1}{2} \vec{P}
\end{align*} \]

where \( \vec{P} \) is the centre-of-mass momentum; we recall the expression of the relative velocity, \( v_{\text{rel}} = 2p/m \). These equations give

\[ \begin{align*}
p_{1x} p_{1z} + p_{2x} p_{2z} &= 2p_x p_z + \frac{1}{4} P_x P_z \\
p_{3x} p_{3z} + p_{4x} p_{4z} &= 2p'_x p'_z + \frac{1}{4} P_x P_z
\end{align*} \]

so that

\[ \Delta \Psi = 2A(p_x p_z - p'_x p'_z) \]

The differential cross section \( \sigma(\Omega, p) \) in the Boltzmann equation depends on the angle \( \theta \) between \( \vec{p} \) and \( \vec{p}' \). The integration in (8.139) leads to an angular average at fixed \( (\Omega, p) \), which is again computed thanks to (A.36)

\[ \langle (\Delta \Psi)^2 \rangle_{\text{ang}} = 4A^2 \left[ p_x^2 p_z^2 + p'_x^2 p'_z^2 - 2p_x p'_x p_z p'_z \right]_{\text{ang}} \]

\[ = 4A^2 p^4 \left[ \frac{2}{15} - \frac{1}{15} (-1 + 3 \cos^2 \theta) \right] \]

\[ = \frac{4}{5} A^2 p^4 (1 - \cos^2 \theta) \]

Inserting this result in (8.138) and using the relation between \( W \) and \( \sigma(\Omega, p) \) (see (8.86))

\[ \int d^3 p_3 d^3 p_4 W \rightarrow \frac{2p}{m} \int d\Omega \sigma(\Omega, p) \]
8.4 Transport coefficients from the Boltzmann equation

\[ \langle \Psi | L | \Psi \rangle = \frac{2A^2}{5\beta m} \int d^3 p_1 \int d^3 p_2 \int d\Omega \ f_{01} f_{02} \ p^5 (1 - \cos^2 \theta) \sigma(\Omega, \ p) \]  

(8.140)

The result features the transport cross section \( \sigma_{tr}(p) \), and not the total cross section \( \sigma_{tot}(p) \)

\[ \sigma_{tr}(p) = \int d\Omega (1 - \cos^2 \theta) \sigma(\Omega, \ p) \]  

(8.141)

The physical reason behind the occurrence of the transport cross section is that forward scattering is very inefficient in transferring momentum, hence the suppression factor \( (1 - \cos \theta) \) (and \( (1 + \cos \theta) \) for the backward scattering). We also need to write the product \( f_{01} f_{02} \) in terms of the centre-of-mass variables \( p \) and \( P \)

\[ f_{01} f_{02} = n^2 \left( \frac{\beta}{2\pi m} \right)^3 \exp \left( -\frac{\beta p^2}{m} \right) \exp \left( -\frac{\beta P^2}{4m} \right) \]

It remains to use the change of variables with unit Jacobian

\[ d^3 p_1 \int d^3 p_2 = d^3 P \int d^3 p \]

and the Gaussian integration (A.37) to compute

\[ \int d^3 p_1 \int d^3 p_2 \ f_{01} f_{02} \ p^5 \sigma_{tr}(p) \]

\[ = 4\pi n^2 2^{3/2} \left( \frac{\beta}{2\pi m} \right)^{3/2} \int_0^\infty dp \ p^7 \exp \left( -\frac{\beta p^2}{m} \right) \sigma_{tr}(p) = \frac{12}{\sqrt{\pi}} n^2 \left( \frac{m}{\beta} \right)^{5/2} \sigma_{tr} \]

where, in the last line of the previous equation, we have assumed \( \sigma_{tr} \) to be independent of \( p \). If this is not the case, the integral in the first line may be used to define an effective \( T \)-dependent transport cross section \( \sigma_{tr}^{eff}(T) \) which should be used instead of a \( T \)-independent \( \sigma_{tr} \). We thus get

\[ \langle \Psi | L | \Psi \rangle = \frac{24A^2}{5\sqrt{\pi}} n^2 m^{3/2} \beta^{-7/2} \sigma_{tr} \]  

(8.142)

Gathering (8.134), (8.138) and (8.142) we obtain the following result for \( \eta \)

\[ \eta = \frac{5\sqrt{\pi}}{24} \frac{\sqrt{mkT}}{\sigma_{tr}} \]  

(8.143)
In the case of a hard sphere gas, the transport cross section is \( \frac{2}{3} \) of the total cross section \( \sigma_{\text{tot}} \)

\[
\sigma_{\text{tot}} = 4\pi R^2 \quad \sigma_{\text{tr}} = \frac{8\pi}{3} R^2 = \frac{2}{3} \sigma_{\text{tot}}
\]

where \( R \) is the radius of the spheres, and one may rewrite (8.143)

\[
\eta = \frac{5\sqrt{\pi}}{16} \frac{\sqrt{mkT}}{\sigma_{\text{tot}}} \simeq 0.553 \frac{\sqrt{mkT}}{\sigma_{\text{tot}}}
\]

(8.144)

This result is to be compared with the qualitative estimate (8.21), which may be written

\[
\eta = 0.377 \frac{\sqrt{mkT}}{\sigma_{\text{tot}}}
\]

(8.145)

where we have used the mean free path (8.11) of the Maxwell distribution and the corresponding mean value of the velocity

\[
\ell = \frac{1}{\sqrt{2} n \sigma_{\text{tot}}} \quad v = \sqrt{\frac{8kT}{\pi m}}
\]

An analogous calculation (Problem 8.6.8) gives for the coefficient of thermal conductivity, assuming a \( p \)-independent transport cross section

\[
\kappa = \frac{25\sqrt{\pi}}{32\sigma_{\text{tr}}} k \sqrt{\frac{kT}{m}}
\]

(8.146)

and the ratio \( \kappa/\eta \) is

\[
\frac{\kappa}{\eta} = \frac{15}{4} \frac{k}{m} = \frac{5}{2} \frac{c}{m}
\]

(8.147)

instead of the qualitative estimate \( \kappa/\eta = c/m \) derived in Section 8.1.3. The factor \( 5/2 \) in (8.147) is in excellent quantitative agreement with the experimental results on mono-atomic gases.

8.5 Exercises

8.5.1 Time distribution of collisions

We consider the collisions of a labelled molecule starting at the initial time \( t = 0 \). An excellent approximation consists of considering the collisions as independent: the collision process is without memory. Let \( \lambda \) be the average number of collisions per unit time suffered by a molecule. What is the probability \( P(n, t) \) that
the molecule undergoes \( n \) collisions in the time interval \([0, t]\)? What is the survival probability \( P(t) \), i.e. the probability that the molecule has not suffered any collisions in the interval \([0, t]\)? What is the probability \( \mathcal{P}(t) \, dt \) that the molecule will suffer its first collision in the interval \([t, t + dt]\)? Use these results to find an expression for the collision time \( \tau^* \) defined as the average time from \( t = 0 \) for the molecule to undergo its first collision. Since the process is Markovian (without memory), \( \tau^* \) is also the average time between collisions as well as the time elapsed since the last collision.

8.5.2 Symmetries of an integral

Show that if \( \bar{a} \) is a fixed vector and \( g(p) \) a function of \(|\vec{p}| = p\), then

\[
\vec{I} = \int d^3p \, (\vec{p} \cdot \bar{a}) \vec{p} \, g(p) = \frac{1}{3} \bar{a} \int d^3p \, p^2 g(p)
\]

or that equivalently

\[
I_{\alpha\beta} = \int d^3p \, p_\alpha p_\beta g(p) = \frac{1}{3} \delta_{\alpha\beta} \int d^3p \, p^2 g(p)
\]

Use this to obtain relation (8.60).

8.5.3 Positivity conditions

Demonstrate the positivity condition (8.68) for the transport coefficients.

\[
L_{EE}L_{NN} - L_{EN}^2 \geq 0
\]

8.5.4 Calculation of the collision time

1. Show that the collision time \( \tau^* \) of a molecule in a gas is given by

\[
\frac{1}{\tau^*} = \frac{1}{n} \int d^3p_1 \, d^3p_2 \, f(\vec{p}_1) f(\vec{p}_2) |\vec{v}_2 - \vec{v}_1| \sigma_{\text{tot}}(|\vec{v}_2 - \vec{v}_1|)
\]

Hint: First calculate the collision time of a particle with momentum \( \vec{p}_1 \).

2. A simple calculation of the collision time is obtained in the case where all the molecules have the same absolute value \( v_0 \) for the velocity and therefore momentum \( p_0 \). The distribution function then is

\[
f(\vec{p}) = \frac{n}{4\pi p_0^2} \delta(p - p_0)
\]
Verify that the distribution is correctly normalized. Assuming that the total cross section is independent of the velocity, show that the collision time is
\[ \tau^* = \frac{3}{4 n v_0 \sigma_{\text{tot}}} \] (8.152)
and calculate the mean free path \( \ell \).

3. We now assume we have a Maxwell distribution for the momenta
\[ f(\vec{p}) = n \left( \frac{1}{2\pi m k T} \right)^{3/2} \exp \left( -\frac{\vec{p}^2}{2 m k T} \right) \] (8.153)
Again assuming that the total cross section is independent of velocity, show that the collision time is given by (8.11).

**8.5.5 Derivation of the energy current**

Demonstrate the expression (6.83) for the energy current starting with the Boltzmann equation.

**8.5.6 Equilibrium distribution from the Boltzmann equation**

1. We first assume a situation with no external forces. Show that the Boltzmann entropy \( S_B(t) \) (8.110) must tend to a constant when \( t \to \infty \)
\[ \lim_{t \to \infty} S_B(t) = \text{const} \]
In this limit, show that one must have
\[ \ln f_1 + \ln f_2 = \ln f_3 + \ln f_4 \]
2. From this condition, deduce that \( \ln f \) must be of the form
\[ \ln f = \chi^{(1)}(\vec{p}) + \chi^{(2)}(\vec{p}) + \cdots \]
where the \( \chi^{(i)} \)s are conserved quantities in the collisions
\[ \chi^{(i)}(\vec{p}_1) + \chi^{(i)}(\vec{p}_2) = \chi^{(i)}(\vec{p}_3) + \chi^{(i)}(\vec{p}_4) \]
From this, deduce that \( f(\vec{p}) \) can be written as
\[ f(\vec{p}) = -A (\vec{p} - \vec{p}_0)^2 + B \]
where \( A, B \) and \( \vec{p}_0 \) are constants. Compute the density, the flow velocity and the temperature as functions of \( A, B \) and \( \vec{p}_0 \) and show that \( f(\vec{p}) \) must be a Maxwell distribution centred at \( \vec{p}_0 \).
3. In the presence of external forces
\[ \vec{F}(\vec{r}) = -\vec{\nabla} \Phi(\vec{r}) \]
show that the previous result is multiplied by
\[ \exp \left( -\frac{\Phi(\vec{r})}{kT} \right) \]

8.6 Problems

8.6.1 Thermal diffusion in the Boltzmann–Lorentz model

The Boltzmann–Lorentz model is particularly well suited to describe the scattering of light solute molecules (density \( n \)) on the heavy molecules of a solvent (density \( n_d \)). We consider a stationary situation, and we assume that the solution is not subject to any external force (\( \vec{F} = \vec{0} \)). The equilibrium distribution of the solute is that of a non-relativistic classical ideal gas
\[ f_0(\vec{r}, \vec{p}) = \frac{1}{\hbar^3} \exp \left[ \beta(\vec{r}) \mu(\vec{r}) - \beta(\vec{r}) \frac{\vec{p}^2}{2m} \right] = \frac{n(\vec{r})}{[2\pi mkT(\vec{r})]^{3/2}} \exp \left[ -\beta(\vec{r}) \frac{\vec{p}^2}{2m} \right] \] (8.154)

1. The density and temperature vary with space but the solution is maintained at constant and uniform pressure
\[ \mathcal{P} = \tilde{n}(\vec{r}) kT(\vec{r}) \]
where \( \tilde{n} = n + n_d \) is the total particle density. In this situation, we define two response coefficients: the diffusion coefficient \( D \) and the thermodiffusion coefficient \( \lambda \). These coefficients appear in the phenomenological expression for the particle current
\[ \vec{j}_N = -\tilde{n} D \vec{\nabla} c - \frac{\tilde{n} c}{T} \lambda \vec{\nabla} T \] (8.155)
where \( c \) is the concentration of light particles \( c = n/\tilde{n} \). Calculate the particle current \( \vec{j}_N \) in the framework of the Chapman–Enskog approximation and establish the microscopic expressions for \( D \) and \( \lambda \)
\[ D = \frac{1}{3} \frac{1}{n_d} \left\langle \frac{v}{\sigma_{\text{tot}}(v)} \right\rangle = \frac{1}{3} \left\langle v^2 \tau \right\rangle \]
\[ \lambda = \frac{1}{3} \frac{T^2}{n_d} \frac{\partial}{\partial T} \left[ \frac{1}{T} \left\langle \frac{v}{\sigma_{\text{tot}}(v)} \right\rangle \right] \] (8.156)
Irreversible processes: kinetic theory

\[ \langle \bullet \rangle = \frac{1}{n(\vec{r})} \int d^3 p \langle \bullet \rangle f_0(\vec{r}, \vec{p}) = \frac{1}{\left[ 2\pi m kT(\vec{r}) \right]^{3/2}} \int d^3 p \langle \bullet \rangle \exp \left[ -\beta(\vec{r}) \frac{\vec{p}^2}{2m} \right] \]

2. We now take the solute molecules to be spheres of diameter \( a \), which have only elastic collisions with the solvent molecules assumed to be point particles. This is the hard sphere model with \( \sigma_{\text{tot}} = \pi a^2 \). Verify that in this framework we have

\[ D = \frac{1}{3\pi a^2 n_d} \sqrt{\frac{8kT}{\pi m}} \]

\[ \lambda = -\frac{1}{6\pi a^2 n_d} \sqrt{\frac{8kT}{\pi m}} \]  

(8.157)

When the diffusion and thermodiffusion currents equilibrate, i.e. when the particle current vanishes, what region of the gas will contain the highest concentration of solute molecules?

3. We are now interested in the energy current. We introduce the two phenomenological coefficients, \( \kappa \), coefficient of thermal conductivity, and \( \gamma \), the Dufour coefficient

\[ \vec{j}_E = -\vec{n} \gamma \vec{\nabla} c - \kappa \vec{\nabla} T \]  

(8.158)

Establish the microscopic expression for \( \vec{j}_E \) and show that

\[ \kappa = \frac{1}{6} mcT \frac{\partial}{\partial T} \left[ \frac{1}{T} \left\langle \frac{v^3}{\sigma_{\text{tot}}(v)} \right\rangle \right] \]

\[ \gamma = \frac{1}{6} mkT \frac{\partial}{\partial \rho} \left\langle \frac{v^3}{\sigma_{\text{tot}}(v)} \right\rangle \]  

(8.159)

where it should be recalled that in the Boltzmann–Lorentz model we have \( n \ll n_d \).

4. Do the response coefficients in (8.155) and (8.158) obey an Onsager relation? If not, why?

8.6.2 Electron gas in the Boltzmann–Lorentz model

A Introduction

We consider a non-relativistic ideal gas of electrons, mass \( m \) and charge \( q (q < 0) \), obeying the Boltzmann–Lorentz equation (8.28). When the differential cross section \( \sigma(v, \Omega) \) is independent of \( \Omega \), \( \sigma(v, \Omega) = \sigma(v)/(4\pi) \) where \( \sigma(v) \) is the
total cross section and \( v = p/m \), we can solve this equation using the Chapman–Enskog method by following a simpler procedure than that in Section 8.2.4. We write \( f = f_0 + \bar{f} \) where \( f_0 \) is a local equilibrium distribution and we seek a solution in the stationary regime satisfying

\[
\int d\Omega' \bar{f}(\vec{r}, \vec{p}') = 0
\]

Show that the collision term (8.35) becomes

\[
\mathcal{C}[\bar{f}] = -\frac{1}{\tau^*(p)} \bar{f}
\]

Use this to obtain \( f_0 \). In what follows we will assume that the differential cross section \( \sigma(v, \Omega) \) is independent of velocity

\[
\sigma(v, \Omega) = \frac{\sigma}{4\pi}
\]

Show that in the absence of external forces, we can write the particle and energy densities in the form

\[
\vec{j}_N = -\frac{\ell}{3} \int d^3 p \, v \vec{\nabla} f_0 \quad \vec{j}_E = -\frac{\ell}{3} \int d^3 p \, \varepsilon v \vec{\nabla} f_0
\]

where \( \varepsilon = p^2/(2m) \). What is the physical interpretation of \( \ell \)?

**B Classical ideal gas**

We assume that the electrons form a classical ideal gas, which is a good approximation for semiconductors. The local equilibrium distribution is then

\[
f_0(\vec{r}, \vec{p}) = \frac{2}{\hbar^3} \exp\left(\alpha(\vec{r}) - \beta(\vec{r}) \frac{p^2}{2m}\right) \quad \alpha(\vec{r}) = \frac{\mu(\vec{r})}{kT(\vec{r})} \quad \beta(\vec{r}) = \frac{1}{kT(\vec{r})}
\]

where \( \mu(\vec{r}) \) and \( T(\vec{r}) \) are the local chemical potential and temperature and \( k \) the Boltzmann constant.

1. Express the four transport coefficients \( L_{ij}: (i, j) = (E, N) \) in the form

\[
L_{ij} = \frac{8\pi}{3} \frac{\ell m}{k} \int_0^\infty d\varepsilon \, \varepsilon^\nu \, f_0
\]
\( \nu \) is an integer whose value, which depends on the transport coefficient, is to be determined for the four cases. We give the integral

\[
I = \frac{8\pi}{3} \ell \frac{m}{k} \int_0^\infty \text{d} \varepsilon \varepsilon^\nu f_0 = \frac{\tau^* \nu!}{m} nk^{\nu-1} T^\nu
\]

where the collision time \( \tau^* \) is defined in terms of the average electron velocity \( \langle v \rangle = \sqrt{\frac{8kT}{\pi m}} \) by \( \tau^* = \frac{8}{3\pi} \ell \langle v \rangle \). Express the \( L_{ij} \) in terms of \( n, T, m \) and \( \tau^* \).

2. Show that the diffusion coefficient \( D \) and the thermal conductivity coefficient \( \kappa \) defined by

\[
\vec{j}_N = -D \vec{\nabla} n \ (T \text{ constant}) \quad \vec{j}_E = -\kappa \vec{\nabla} T \ (\vec{j}_N = 0)
\]
can be expressed in terms of the \( L_{ij} \). Give their explicit expressions in terms of \( n, T, m \) and \( \tau^* \).

3. We now subject the electrons to an electric potential \( \Phi(z) \) which is time independent but varies slowly with space along the \( z \) direction. We assume the system is still at equilibrium: the total particle current vanishes and \( T \) is uniform. How does the density \( n \) vary with \( z \)? Establish a relation between the diffusion coefficient and the electrical conductivity \( \sigma_{el} \) defined in terms of the electric current by

\[
\vec{j}_{el} = \sigma_{el} \vec{E} = -\sigma_{el} \vec{\nabla} \Phi
\]

and show that

\[
\sigma_{el} = \frac{q^2 n \tau^*}{m}
\]

Obtain this expression using an elementary argument and calculate \( \kappa / \sigma_{el} \).

4. We now introduce an external force \( \vec{F} = -\vec{\nabla}_r V(\vec{r}) \). The Boltzmann–Lorentz equation then becomes

\[
\frac{\partial f}{\partial t} + \vec{v} \cdot \vec{\nabla}_r f - \vec{\nabla}_r V \cdot \vec{\nabla}_{\vec{p}} f = \mathcal{C}[f]
\]

The local equilibrium distribution takes the form

\[
f_0(\vec{r}, \vec{p}) = \frac{2}{h^3} \exp \left( \alpha(\vec{r}) - \beta(\vec{r}) \left[ \frac{p^2}{2m} + V(\vec{r}) \right] \right)
\]

Give the expression for \( \bar{f} \) in terms of \( f_0, \alpha, V \) and their gradients. Indicating the response coefficients in the absence of an external force with primes, demonstrate
the following transformation laws

\[
L_{NN} = L'_{NN} \\
L_{NE} = L'_{EE} + V L'_{NN} \\
L_{EE} = L'_{EE} + 2 V L'_{NE} + V^2 L'_{NN}
\]

5. We can calculate the electric conductivity without using \( L_{NN} \). Consider a stationary situation with uniform density where the electrons are subjected to a constant uniform electric field \( \vec{E} \). With the results of Part A and the Chapman–Enskog approximation, the Boltzmann–Lorentz equation then becomes

\[
q \vec{E} \cdot \vec{\nabla} \bar{\rho} f_0 = -\frac{v}{\ell} \bar{f}
\]

Show that the electric current may be written as

\[
\vec{j}_{el} = -q^2 \ell \frac{E}{3m} \int d^3 p \, p \frac{df_0}{d\varepsilon}
\]

and find \( \sigma_{el} \).

C  Ideal Fermi gas

We now assume that the electrons form an ideal Fermi gas whose temperature is low compared to the Fermi temperature \( T \ll T_F \), which is an excellent approximation for electrons in a metal.

1. Derive the relation between \( n \) and \( \mu \) for \( T = 0 \).

2. Show that, due to the Pauli principle, the distribution function \( f(\vec{r}, \vec{p}) \) in the collision term needs to be replaced by

\[
f(\vec{r}, \vec{p}) \left( 1 - \frac{h^3}{2} f(\vec{r}, \vec{p}') \right)
\]

Hint: What is the number of microscopic states in the phase space volume element \( d^3 r \, d^3 p' \)? What is the occupation probability of such a state? How should we modify the term \( f(\vec{r}, \vec{p}') \) in \( C[f] \)? Show that the two modifications cancel out and we regain the initial \( C[f] \). What would be the corresponding reasoning for a boson gas?

3. The local equilibrium distribution now is

\[
f_0 = \frac{2}{h^3} \frac{1}{\exp[-\alpha(\vec{r}) + \beta(\vec{r}) p^2/(2m)] + 1}
\]
We assume that the local temperature \( T(\vec{r}) \) is small enough compared to \( T_F \) to justify the use of the Sommerfeld approximation (5.29). Show that
\[
\vec{\nabla} f_0 = -c_1 \left[ \vec{\nabla} \left( -\frac{\mu}{T} \right) + \epsilon \vec{\nabla} \left( \frac{1}{T} \right) \right] \left[ \delta(\epsilon - \mu) + c_2 \delta''(\epsilon - \mu) \right]
\]
and determine the coefficients \( c_1 \) and \( c_2 \). Show that the coefficients \( L_{ij} \) may be put in the form
\[
L_{ij} = \frac{16\pi}{3} \frac{m\ell T}{h^3} \int_0^\infty d\epsilon \epsilon^v \left( \delta(\epsilon - \mu) + c_2 \delta''(\epsilon - \mu) \right)
\]
and determine the integer \( v \) for all values of \((i, j)\).

4. Show that the term \( \delta'' \) does not contribute to \( L_{NN} \) and that
\[
L_{NN} = \frac{\tau_F}{m} nT \quad \tau_F = \frac{\ell}{v_F}
\]
Why are the electrons with velocities \( v \simeq v_F = p_F/m \) the only ones that contribute to the transport coefficients?

5. The expressions for the diffusion coefficient \( D \) and electrical conductivity \( \sigma_{el} \) established in Part B for a classical ideal gas are \textit{a priori} no longer valid for a Fermi ideal gas. Give the new expression for \( D \) in terms of the \( L_{ij} \) and show that the expression for \( \sigma_{el} \) does not change. Express \( D \) and \( \sigma_{el} \) in terms of \( n, T, m, \tau_F \).

6. Calculate the numerical value of the collision time \( \tau_F \) in copper with mass density \( 8.9 \times 10^3 \text{ kg m}^{-3} \), atomic number \( A = 63.5 \) and conductivity \( \sigma_{el} = 5 \times 10^7 \Omega^{-1} \text{ m}^{-1} \). Copper has one conduction electron per atom.

7. Calculate the other transport coefficients and the ratio \( \kappa/\sigma_{el} \) (Franz–Wiedemann law)
\[
\frac{\kappa}{\sigma_{el}} = \frac{\pi^2}{3} \frac{k^2}{q^2} T
\]
Compare this expression with that previously obtained in B.3. Calculate the electrical conductivity using the method of Question B.5.

### 8.6.3 Photon diffusion and energy transport in the Sun

In this problem we study the transfer of heat from the centre of the Sun (or more generally a star) to its surface. This is what allows energy to be radiated into space. The main contribution to this heat transfer (and the only mechanism we consider) is the scattering of photons by electrons in the Sun.
Solar data

Radius \( R_\odot = 7 \times 10^8 \text{ m} \)
Mass \( M_\odot = 2 \times 10^{30} \text{ kg} \)
Mean specific mass \( \rho = 1.4 \times 10^3 \text{ kg m}^{-3} \)
Specific mass at the centre \( \rho_c = 10^5 \text{ kg m}^{-3} \)
Surface temperature \( T_s = 6000 \text{ K} \)
Temperature at the centre \( T_c = 1.5 \times 10^7 \text{ K} \)

A Preliminaries

1. Consider a photon gas in equilibrium at temperature \( T \). The photon momentum is \( \vec{p} \), energy \( \varepsilon = pc \) and velocity \( \vec{v} = c \vec{p}/p = c \hat{p} \). The equilibrium distribution is given by (5.38)

\[
f_{eq}(\vec{p}) = \frac{2}{\hbar^3} \frac{1}{e^{\beta \varepsilon} - 1}
\]

which satisfies

\[
\int d^3p f_{eq}(\vec{p}) = \frac{N}{V} = n
\]

Show that the number of photons per unit volume \( n \) and the energy density \( \epsilon \) are of the form

\[
n = \lambda' T^3 \quad \epsilon = \lambda T^4
\]

Determine \( \lambda \) and \( \lambda' \) in terms of \( \hbar, k \) and \( c \). Calculate the numerical values of \( n \) and \( \epsilon \) at the centre of the Sun as well as the pressure of the photon gas. We give \( k^4/(\hbar^3 c^3) = 1.16 \times 10^{-15} \text{ MKSA} \).

2. What is, in terms of \( \epsilon \), the energy emitted per second per unit area by a black body? Assuming the solar surface is a black body, calculate in terms of \( \lambda, c, R_\odot \) and \( T_s \) the power (energy per second) \( L_\odot \) emitted by the Sun. This quantity is called the luminosity.

3. We assume that the Sun contains only protons and electrons that behave as ideal gases. We may ignore \( m_e \) compared to \( m_p \). Calculate the Fermi momentum and energy at the centre of the Sun in terms of \( \rho_c, h, m_e \) and \( m_p \). Evaluate numerically the Fermi energy in eV and the Fermi temperature in K. Conclude that the electron gas is neither degenerate nor relativistic.

Show that the pressure at the centre of the Sun is given by

\[
P_c = 2\frac{\rho_c}{m_p} kT_c
\]

and compare this expression with that for a photon gas.
B Scattering equation

Our hypothesis is that photons are scattered only by electrons and that this scattering is elastic. The photons are described by the Boltzmann–Lorentz equation with the electrons playing the rôle of the randomly distributed heavy scattering centres. The transport cross section is equal to the total cross section $\sigma$ and is independent of the photon energy. It is given by

$$\sigma = \frac{8\pi}{3} \left( \frac{e^2}{4\pi \varepsilon_0 m_e c^2} \right)^2 \approx 6.6 \times 10^{-29} \text{ m}^2$$

where $-e$ is the electron charge and $\varepsilon_0$ the vacuum permittivity. We solve the Boltzmann–Lorentz equation by writing the photon distribution in the stationary regime

$$f(\vec{r}, \vec{p}) = f_0(\vec{r}, \vec{p}) + \bar{f}(\vec{r}, \vec{p})$$

where $f_0(\vec{r}, \vec{p}) = f_0(\vec{r}, p)$ is a local equilibrium distribution

$$f_0(\vec{r}, \vec{p}) = \frac{2}{\hbar^3} \exp(\beta(\vec{r})\epsilon - 1)^{-1}$$

1. Express the collision time $\tau^*(\vec{r})$ in terms of $m_p, \sigma, c$ and the specific mass $\rho(\vec{r})$ at point $\vec{r}$.

2. Calculate the photon and energy currents, $\vec{j}_N$ and $\vec{j}_E$, in terms of $f_0$ and show that they may be put in the form

$$\vec{j}_N(\vec{r}) = -D'(\vec{r}) \vec{\nabla}n(\vec{r}) \quad \vec{j}_E(\vec{r}) = -D(\vec{r}) \vec{\nabla}\epsilon(\vec{r})$$

Give the expressions for $D$ and $D'$ in terms of $c$ and $\tau^*(\vec{r})$.

3. Assume that the specific mass is uniform $\rho(\vec{r}) \equiv \rho$. Show that in a situation non-stationary but still at local equilibrium, $n(\vec{r}, t)$ satisfies a diffusion equation. If a photon is created at the centre of the Sun at $t = 0$, estimate the time it needs to leave the Sun.

C Model for the Sun

We are now back to a stationary situation and we assume that the problem has spherical symmetry with the origin of coordinates at the centre of the Sun. We call $q(r)$ the energy produced by the thermonuclear reactions per unit time per unit volume, and $Q(r)$ the energy produced per unit time in a sphere $S(r)$ of radius $r$

$$Q(r) = 4\pi \int_0^r dr' q(r') r'^2$$
1. Relate $Q(r)$ to the flux of $\vec{j}_E$ across $S(r)$. Deduce the equation

$$-\frac{4\pi}{3} A \frac{r^2}{\rho(r)} \frac{d}{dr} T^4(r) = Q(r)$$

(8.160)

where $A$ is a constant to be expressed in terms of $\lambda$, $c$, $m_p$ and $\sigma$. In what follows we assume:

(i) the energy is produced uniformly in a sphere of radius $R_c = 0.1 R_\odot$ (the solar core),
(ii) the specific mass is uniform: $\rho(r) \equiv \rho$.

2. Calculate $T^4(r)$ in the regions $0 \leq r \leq R_c$ and $R_c \leq r \leq R_\odot$. Determine the integration constants for the differential equation (8.160) by examining the values $r = R_\odot$ and $r = R_c$.

3. It is useful to express the temperature $T_c$ at the centre of the Sun in terms of its luminosity $L_\odot$. Show that

$$T_c^4 = T_s^4 + \frac{3L_\odot \rho}{4\pi A R_\odot} \left( \frac{3R_\odot}{2R_c} - 1 \right)$$

Use the expression for $L_\odot$ in terms of $T_s$ to calculate the numerical value of $T_c$.

8.6.4 Momentum transfer in a shear flow

We consider a fluid in a stationary state flowing between two infinite parallel plates separated by a distance $L$ in the $z$ direction (see Figure 6.6). One of the plates is held fixed while the other moves at a constant speed $u_0$ in the increasing $x$ direction always staying parallel to the first plate. The fluid is dragged by the moving plate. After enough time has elapsed since the motion started, a stationary situation is reached characterized by a linear dependence of the fluid speed ranging from 0 at one plate to $u_0$ at the other. Each layer of fluid between $z$ and $z + dz$ has a velocity $u_x(z)$. The flow thus established is called ‘simple shear flow’ or ‘plane Couette flow’. The balance of the relative motion of the different layers of width $dz$ leads to the appearance of a friction force that opposes the motion of the plate and tries to re-establish an equilibrium where the fluid moves uniformly. When the velocity gradients are small, we expect a linear relation between the velocity gradient and the force. Let $P_{\alpha\beta}$ be the $\alpha$ component of the force applied on a unit surface perpendicular to $\beta$. $P_{\alpha\beta}$ is given in terms of the shear viscosity $\eta$ by

$$P_{\alpha\beta} = -\eta \partial_\beta u_\alpha$$

The symmetries and invariances of the problem considered here are such that only $P_{xz} = -\eta \partial_z u_x$ is relevant.
We only treat the simple case where the fluid may be considered as a classical ideal gas made of particles of mass $m$. The temperature $T$ and density $n$ of the fluid are uniform. We assume that the total scattering cross section $\sigma_0$ is constant and we limit our attention to the case where the pulling speed $u_0$ is very small compared to the average thermal velocity.

### A Viscosity and momentum diffusion

1. Consider the balance of forces applied on a volume element between two plane parallel faces of unit area and located at $z$ and $z + dz$. Show that the $x$ component of the momentum, $p_x = mu_x$, satisfies the diffusion equation

$$\frac{\partial p_x}{\partial t} - \frac{\eta}{nm} \frac{\partial^2 p_x}{\partial z^2} = 0 \quad (8.161)$$

2. Justify qualitatively the relation between the viscosity and momentum transport.

### B Coefficient of viscosity

1. Starting with (8.21), we easily show that

$$\eta = A\sqrt{T} \quad (8.162)$$

where $A$ is a constant. Measurement of the coefficient of viscosity for air yielded Table 8.1. Does the temperature dependence of $\eta$ given by (8.162) agree with experiments?

2. Relation (8.162) predicts that $\eta$ does not depend on the density of the gas (or its pressure). Although non-intuitive, this has been established experimentally over a rather wide range of density values. Give a qualitative interpretation of this result.

3. Expression (8.21) for the coefficient of viscosity neglects collisions of more than two particles. It is therefore valid only for small density, i.e. $\ell \gg \sqrt{\sigma_{\text{tot}}}$. However, the density cannot be too small. What phenomenon, so far ignored, must be taken into account if $\ell \simeq L$?

---

Table 8.1  Experimental values of the coefficient of viscosity for air

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>911</th>
<th>1023</th>
<th>1083</th>
<th>1196</th>
<th>1307</th>
<th>1407</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$ ($\times 10^{-7}$ poise)</td>
<td>401.4</td>
<td>426.3</td>
<td>441.9</td>
<td>464.3</td>
<td>490.6</td>
<td>520.6</td>
</tr>
</tbody>
</table>
8.6 Problems

C Coefficient of viscosity in the relaxation time approximation

1. In the reference frame that follows the motion of the fluid layer between \(z\) and \(z + dz\) (the fluid rest frame) we have at equilibrium a Maxwell–Boltzmann distribution in the velocity \(\vec{w} = \vec{v} - \vec{u}_f\)

\[
f'_0(\vec{w}) = n \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m\vec{w}^2}{2kT}\right)
\]

Write down the equilibrium velocity distribution \(f_0(\vec{v})\) in the laboratory frame.

2. Like the Boltzmann–Lorentz equation, the Boltzmann equation may be linearized around a local equilibrium solution. This leads to the following expression for the velocity distribution law in the fluid

\[
f \simeq f_0 - \tau^* \vec{v} \cdot \vec{\nabla} f_0 \quad (8.163)
\]

\(\tau^*\) is the characteristic time to return to equilibrium, which is of the order of the time of flight between two collisions. Show that (8.163) allows us to write

\[
\mathcal{P}_{xz} = m \frac{d u_x}{d z} \int d^3 w \tau^* w_x w_z^2 \frac{\partial f'_0}{\partial w_x} \quad (8.164)
\]

3. The relaxation time depends \textit{a priori} on \(v\). To calculate (8.164) explicitly, we need assumptions on the behaviour of \(\tau^*\). To begin with we assume it to be constant. Verify that this assumption leads to results in disagreement with experiments which show that the viscosity coefficient depends linearly on the temperature.

If the cross section is almost independent of the velocity, a physically more reasonable assumption is to take the mean free path \(\ell = \tau^*|\vec{v} - \vec{u}_f|\) to be constant. Show that

\[
\mathcal{P}_{xz} = -\frac{1}{15} m^2 \ell \frac{d u_x}{d z} \int d^3 w w^3 f'_0 \quad (8.165)
\]

and verify that the viscosity coefficient can be written as

\[
\eta = \frac{4}{15} nm \langle v \rangle \ell \quad (8.166)
\]

8.6.5 Electrical conductivity in a magnetic field and quantum Hall effect

We consider a non-relativistic ideal gas of electrons, mass \(m\) and charge \(q\) \((q < 0)\) obeying the Boltzmann–Lorentz equation in the presence of an external force \(\vec{F}(\vec{r})\). We assume here that the densities are independent of space and time

\[
f(\vec{r}, \vec{p}, t) = f(\vec{p}) \quad n(\vec{r}, t) = n
\]
Therefore, the first two terms in (8.28) vanish. In addition we assume that the local equilibrium distribution $f_0$ is a function only of energy $\varepsilon$: $f_0(\vec{p}) = f_0(p^2 / 2m = \varepsilon)$.

**A Electric conductivity in the presence of a magnetic field**

We consider the problem of conduction in a metal where the conduction electrons form a highly degenerate ideal Fermi gas. We subject the metal to an electric field $\vec{E}$ and a magnetic field $\vec{B}$. The force in Equation (8.28) is therefore the Lorentz force

$$\vec{F} = q \left( \vec{E} + \vec{v} \times \vec{B} \right)$$  (8.167)

1. First we take $\vec{B} = 0$. Calculate $\bar{f} = f - f_0$ and show that the electric current density $\vec{j}_{\text{el}}$ is given by

$$\vec{j}_{\text{el}} = -q^2 \int d^3 p \frac{\tau^*(p) \vec{v} \cdot (\vec{E} + \vec{v} \times \vec{B})}{\varepsilon} \frac{\partial f_0}{\partial \varepsilon}$$

If $f_0$ is the Fermi distribution at $T = 0$

$$f_0(\varepsilon) = \frac{2}{h^3} \theta(\varepsilon_F - \varepsilon)$$  (8.168)

where $\varepsilon_F$ is the Fermi energy, show that the electrical conductivity $\sigma_{\text{el}}$, defined by $\vec{j}_{\text{el}} = \sigma_{\text{el}} \vec{E}$, is given by

$$\sigma_{\text{el}} = \frac{nq^2}{m} \tau_F$$

where we took $\tau_F = \tau^*(p_F)$.

2. Now we take $\vec{B} \neq 0$. How is the conductivity modified if the applied $\vec{B}$ field is parallel to $\vec{E}$? Consider the case where the $\vec{E}$ field is in the $xOy$ plane, $\vec{E} = (E_x, E_y, 0)$, and the $\vec{B}$ field parallel to the $z$-axis, $\vec{B} = (0, 0, B)$, $B > 0$. Show that (8.28) becomes

$$q \vec{v} \cdot \vec{E} \frac{\partial f_0}{\partial \varepsilon} + q(\vec{v} \times \vec{B}) \cdot \nabla_{\vec{p}} f = -\frac{\bar{f}}{\tau^*(p)}$$  (8.169)

We seek a solution of the form

$$\bar{f} = -\vec{v} \cdot \vec{C} \frac{\partial f_0}{\partial \varepsilon}$$

where $\vec{C}$ is an unknown vector to be determined that is a function of $\vec{E}$ and $\vec{B}$ but independent of $\vec{v}$. What should $\vec{C}$ be when $\vec{B} = 0$? $\vec{E} = 0$? In this last case, first estimate the average magnetic force.
3. Show that \( \vec{C} \) satisfies

\[
q \vec{E} + \vec{\omega} \times \vec{C} = \frac{\vec{C}}{\tau^*(p)}
\]

with \( \vec{\omega} = (0, 0, \omega) \), where \( \omega = |q|B/m \) is the Larmor frequency. Justify that \( \vec{C} \) is necessarily of the form

\[
\vec{C} = \alpha \vec{E} + \delta \vec{B} + \gamma (\vec{B} \times \vec{E})
\]

where \( \alpha, \delta, \gamma \) are real numbers. Find the expression for \( \vec{C} \) and show that

\[
\vec{f} = -\frac{q \tau^*}{1 + \omega^2 \tau^*^2} \left( \vec{E} + \tau^*(\vec{\omega} \times \vec{E}) \right) \cdot \vec{v} \frac{\partial f_0}{\partial \varepsilon}
\]

4. Calculate the electric current and the components \( \sigma_{\alpha\beta} \) of the conductivity tensor

\[
\begin{align*}
  j^\text{el}_x &= \sigma_{xx} E_x + \sigma_{xy} E_y \\
  j^\text{el}_y &= \sigma_{yx} E_x + \sigma_{yy} E_y
\end{align*}
\]

Verify that

\[
\sigma_{xy} = -\sigma_{yx}
\]

and comment on this relation in terms of the Onsager relation.

**B Simplified model and the Hall effect**

1. To represent the effect of collisions in a simple way, we write an average equation of motion for the electrons (the Drude model)

\[
\frac{d \langle \vec{v} \rangle}{dt} = -\frac{\langle \vec{v} \rangle}{\tau^*} + \frac{q}{m} \left( \vec{E} + \langle \vec{v} \rangle \times \vec{B} \right)
\]

Give a physical interpretation for this equation. Verify that in the stationary regime we have

\[
\langle v_x \rangle = \frac{q \tau^*}{m} E_x - \omega \tau^* \langle v_y \rangle
\]

\[
\langle v_y \rangle = \frac{q \tau^*}{m} E_y + \omega \tau^* \langle v_x \rangle
\]

Show that if we take \( \tau^* = \tau_F \), this model gives the same expressions for \( \sigma_{\alpha\beta} \) found above.

2. Calculate in terms of \( E_x \) the value \( E^\text{H}_y \) of \( E_y \) which cancels \( j^\text{el}_y \). Verify that the transport of electrons in this situation is the same as in the case \( \vec{B} = 0 \), in other
words

\[ j_x = \sigma E_x \]

The field \( E_H \) is called the ‘Hall field’ and we define the ‘Hall resistance’ by

\[ R_H = \frac{V_H}{I} \]

where \( V_H \) is the ‘Hall voltage’, \( V_H/l = E_H \), and \( I \) the total current in the material (Figure 8.8). Show that \( R_H \) is given by

\[ R_H = \frac{B}{ndq} \]

By noting that \( R_H \) is independent of the relaxation time, find its expression using an elementary argument.

C Quantum Hall effect

Experiments of the type represented schematically in Figure 8.8 where electric (\( \vec{E} = (E_x, 0, 0) \)) and magnetic (\( \vec{B} = (0, 0, B) \)) fields are applied, have shown that, after transient effects have dissipated, a Hall field is established. However, in intense magnetic fields (> 1 T) and at very low temperatures, the Hall resistance is not linear in \( B \) as predicted by the Drude model. Experiments where the electrons are confined in two-dimensional geometries of area \( S \) and negligible thickness,
exhibit a plateau structure for the Hall resistance as a function of magnetic field (see Figure 8.9). This suggests that the Hall resistance is quantized.

1. Calculate the energy level density $\rho(\varepsilon)$ of an electron gas in two dimensions without assuming spin degeneracy since this is lifted by the magnetic field.

2. In the presence of a magnetic field perpendicular to the surface, the energy levels (Landau levels) are labeled by an integer $j$: $j = 0, 1, 2, \ldots$ and have the form (see Problem 5.7.2)

$$\varepsilon_j = \hbar \omega \left( j + \frac{1}{2} \right)$$

(8.174)

where $\omega$ is the Larmor frequency. Calculate the degeneracy $g$ of each level. This is equal to the number of levels, in zero field, present between $\varepsilon = \varepsilon_j$ and $\varepsilon = \varepsilon_{j+1}$. 

Figure 8.9 The Hall resistance as a function of the magnetic field for a heterojunction of InGaAs–InP, *Images de la Physique*, (1984).
3. Take $T = 0$. Choose $B$ so that $\nu$ Landau levels are occupied, in other words the Fermi level should be just above the $\nu$th Landau level. Show that the surface electron density is $n_S = \nu |q| B / h$. Show that the Hall resistance is $R_H = -h / (\nu q^2)$.

8.6.6 Specific heat and two-fluid model for helium II

Below the temperature $T_\lambda \simeq 2.18$ K, helium-4 becomes superfluid at atmospheric pressure. This superfluid phase of helium-4 is called helium II. At $T = 0$, helium II is described by the wave function of the ground state. When $T \neq 0$, phonons appear in the helium with a dispersion relation (energy $\varepsilon(\vec{p})$ as a function of momentum $\vec{p}$) given by

$$\varepsilon(\vec{p}) = c |\vec{p}|$$

where $c$ is the speed of sound ($c \simeq 240$ m s$^{-1}$). The sound waves are longitudinal (compression) since shear waves do not exist in a fluid. The phonons in helium II have only one polarization.

A  Specific heat

1. Specific heat due to phonons. Calculate the internal energy and the specific heat due to the phonons. Assume the temperature is much lower than the Debye temperature $T_D \simeq 30$ K. Show that the specific heat per unit volume is given by

$$C_V^{\text{phonon}} = \frac{2\pi^2 k^4}{15\hbar^3 c^3} T^3$$

2. Specific heat due to rotons. In fact, the dispersion law for the phonons (which are called ‘elementary excitations’) is more complicated than Equation (8.175) and is given in Figure 8.10. The region around $p = p_0$ is called the ‘roton’ region. In the neighbourhood of $p = p_0$, we have the following approximate expression for $\varepsilon(p)$

$$\varepsilon(p) = \Delta + \frac{(p - p_0)^2}{2\mu}$$

with $\Delta / k \simeq 8.5$ K, $k_0 = p_0 / \hbar \simeq 1.9$ Å$^{-1}$ and $\mu \simeq 10^{-27}$ kg.

Show that for $T \lesssim 1$ K, we may replace the Bose distribution $n(p)$ by a Boltzmann distribution

$$n(p) \simeq e^{-\beta\varepsilon(p)}$$
Write the expression giving the contribution of the rotons to the internal energy. Compare $\frac{p_0^2}{k_B T}$ and $\Delta$ and $k_B T$. Use this to simplify the integral. Hint: Change variables $x = \sqrt{\frac{\beta}{2\mu}}(p - p_0)$. Then express the roton contribution to the specific heat $C_{V}^{\text{roton}}$. Compare $C_{V}^{\text{phonon}}$ and $C_{V}^{\text{roton}}$ for $T \to 0$ and their numerical values for $T = 1$ K.

### B The two-fluid model

1. **Flow of helium II.** We consider a fluid of mass $M$ containing $N$ particles of mass $m$. The $i$th particle is characterized by its position $\vec{r}_i$ and momentum $\vec{q}_i$ with the total momentum $\vec{P} = \sum \vec{q}_i$. The fluid is assumed to be non-viscous and flows without friction in a tube. Consider this flow of the superfluid helium of mass $M$ in two Galilean reference frames: in the frame $R$ where the helium is at rest and the walls have a velocity $\vec{v}$, and the frame $R'$ where the walls are at rest and the helium flows with velocity $-\vec{v}$. This description is possible because in the absence of viscosity the velocity of the helium does not vanish at the walls of the tube (in $R'$). In frame $R$ the Hamiltonian is

$$H = \sum_{i=1}^{N} \frac{\vec{q}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} U(\vec{r}_i - \vec{r}_j)$$

(8.177)

Give the expression for the Hamiltonian $H'$ in $R'$.

In the Landau two-fluid model, we assume that helium II is made of a superfluid with zero viscosity, and a normal viscous fluid that is identified with the phonon gas (or more generally with the gas of elementary excitations). We ignore interactions among elementary excitations and also between the normal fluid and superfluid components. The superfluid flows without friction whereas the elementary excitations are in equilibrium with the walls of the tube. The dispersion law
Irreversible processes: kinetic theory

Figure 8.11 The flow of a mass $M$ of superfluid helium in two reference frames.

$\varepsilon(\vec{p})$ of the elementary excitations is given in the frame $R$ where the superfluid has zero velocity: the momentum $\vec{p}$ of the elementary excitations is measured in *this reference frame*.

We consider the flow of helium II in a tube in the two Galilean frames $R$ and $R'$ (Figure 8.11). By examining in $R$ the creation of an elementary excitation of momentum $\vec{p}$ and energy $\varepsilon(\vec{p})$, show that in $R'$ where the tube is at rest, the energy of this excitation is

$$\varepsilon'(\vec{p}) = \varepsilon(\vec{p}) - \vec{p} \cdot \vec{v}$$  \hspace{1cm} (8.178)

2. *Momentum density.* The gas of elementary excitations is in equilibrium with the walls at temperature $T$ and has a bulk velocity $\vec{v}$ in the frame $R$. What is the distribution $\tilde{n}(\vec{p}, \vec{v})$ of the elementary excitations in terms of the Bose distribution $n(\varepsilon) = 1/(e^{\beta \varepsilon} - 1)$? Show that in the frame $R$ the momentum density $\vec{g}$ is given to first order in $v$ by

$$\vec{g} = -\frac{1}{3} \int \frac{d^3 p}{(2\pi \hbar)^3} \frac{p^2}{\varepsilon} \frac{dn}{d\varepsilon} \vec{v}$$  \hspace{1cm} (8.179)

The relation $\vec{g} = \rho_n \vec{v}$ *defines* the density $\rho_n$ of the normal fluid. Note: In what follows it is recommended not to use the explicit expression for $n(\varepsilon)$. By integration by parts, relate $\rho_n$ to the energy density $\varepsilon$ of a phonon gas where the dispersion law is $\varepsilon = c\vec{p}$. What is the pressure $P$ of the phonon gas?

3. *Energy current and momentum density.* Show that for a phonon gas, the energy current $\vec{j}_E$ calculated in the frame $R$ is related to the momentum density by

$$\vec{j}_E = c^2 \vec{g}$$
4. Second sound. Use the continuity equations and Euler’s equation (6.70) to show that in the absence of dissipation and for sufficiently low velocities, we have

\[ \frac{\partial \epsilon}{\partial t} = -c^2 \nabla \cdot (\rho n \vec{v}) \]
\[ \frac{\partial (\rho n \vec{v})}{\partial t} = -\frac{1}{3} \nabla \epsilon \]

Show that \( \epsilon \) obeys a wave equation and verify that the propagation velocity is \( c/\sqrt{3} \). How do you interpret this wave of the so-called ‘second sound’? What happens when helium II is heated locally? What is the sound velocity in a dilute ultra-relativistic gas?

### 8.6.7 Landau theory of Fermi liquids

Our goal in this problem is to go beyond the ideal gas approximation of the Fermi gas in the case of neutral particles, one example being liquid helium-3. We denote the dispersion law of the interacting Fermi liquid\(^{26}\) by \( \epsilon(p) \): more precisely, \( \epsilon(p) \) is the extra energy due to adding one particle of momentum \( \vec{p} \) to the system at equilibrium. In the ideal case, \( \epsilon(p) = p^2/(2m) \), but we want to consider more general dispersion laws. For simplicity, we neglect spin effects: these may be easily taken into account if one is interested, for example, in Pauli paramagnetism. Landau’s first assumption is the existence of a sharp Fermi surface at zero temperature. The Fermi distribution is then the following functional of \( \epsilon(p) \) (\( \mu \) was denoted by \( \epsilon_0 \) in Section 5.2.3)

\[ f_0[\epsilon(p)] = \theta(\mu - \epsilon(p)) \]
\[ \frac{\delta f_0[\epsilon(p)]}{\delta \epsilon(p)} = -\delta(\epsilon(p) - \mu) \]

This distribution is the equilibrium distribution of the interacting Fermi liquid at zero temperature. The Fermi momentum \( p_F \) is still given by (5.17), but \( \mu \neq \frac{p_F^2}{2m} = \epsilon_F \).

### A Static properties

1. One adds (removes) a particle of energy \( \epsilon(p) \) to (from) the Fermi sea, thus creating a quasiparticle (quasihole). Show that

\[ \epsilon(p) \bigg|_{p=p_F} = \mu \]

\(^{26}\) We assume an isotropic Fermi gas, which is the case for helium-3. However, electrons in metals do not obey this assumption due to the loss of rotational invariance arising from the crystal lattice.
Irreversible processes: kinetic theory

Figure 8.12 Perturbation of the equilibrium distribution. $\delta f(\vec{p})$ is non-zero only in the vicinity of the Fermi surface. The negative part of $\delta f$ corresponds to the hole distribution, the positive part to that of particles.

2. One now assumes that many quasiparticles or quasiholes are added to the Fermi sea. This does not necessarily mean that the total number of particles varies, but the particle distribution is modified with respect to the equilibrium distribution

$$\delta f(\vec{p}) = f(\vec{p}) - f_0(\vec{p})$$

The quantity $\delta f(\vec{p})$ is a measure of the deviation of the particle distribution from the equilibrium distribution, or, in other words, it measures the ‘degree of excitation’ in the neighbourhood of the Fermi surface. Because it relies in fact on an expansion in powers of $\delta f$, Landau’s theory will only be valid at low temperatures, and $\delta f$ will differ from zero only in a neighbourhood $\xi$ of the Fermi sea (Figure 8.12)

$$|\varepsilon(p) - \mu| \lesssim \xi \ll \mu$$

Landau’s second assumption is that one may write the energy of a quasiparticle in the environment of other quasiparticles as

$$\tilde{\varepsilon}(\vec{p}) = \varepsilon(p) + \frac{2V}{\hbar^3} \int d^3p' \lambda(\vec{p}, \vec{p}') \delta f(\vec{p}')$$

Therefore, as already mentioned, $\tilde{\varepsilon}(\vec{p}) = \varepsilon(p)$ if one adds a single particle to the system. Note that, contrary to $\varepsilon(p)$, $\tilde{\varepsilon}(\vec{p})$ is not in general an isotropic function, since $\delta f(\vec{p})$ is not isotropic. The function $\lambda(\vec{p}, \vec{p}')$ is defined in the vicinity of the
Fermi surface \((p = p' = p_F)\) and is expanded in Legendre polynomials

\[
\lambda(p, p') = \sum_{\ell=0}^{\infty} \alpha_\ell P_\ell(\cos \theta)
\]

where \(\theta\) is the angle between \(p\) and \(p'\) and the \(\alpha_\ell\)s are real coefficients. Show that the order of magnitude of \(\lambda(p, p')\) is \(a^3/V\), where \(a\) is the range of the interaction between particles. Show that, exactly as \(|\varepsilon(p) - \mu|\), the second term in the equation for \(\tilde{\varepsilon}(p)\) is of the order of \(\xi\), and may not be neglected. However, a term \(\propto (\delta f(p))^2\) in the expansion of \(\tilde{\varepsilon}(p)\) would be negligible. Show that if \(\delta f(p)\) is isotropic, then

\[
\tilde{\varepsilon}(p) = \varepsilon(p) + \alpha_0 \delta N
\]

where \(\delta N\) is the total number of quasiparticles.

3. Instead of \(\delta f(p)\), it is useful to define

\[
\delta \tilde{f}(p) = f(p) - f_0(\tilde{\varepsilon}(p))
\]

Show that

\[
\delta \tilde{f}(p) = \delta f(p) + \delta(\varepsilon - \mu) \frac{2V}{h^3} \int d^3 p' \lambda(p, p') \delta f(p')
\]

4. Let \(f_0(p, T)\) be the equilibrium distribution of quasiparticles at temperature \(T\), \(kT \ll \mu\)

\[
f_0(p, T) = \frac{1}{1 + \exp[(\tilde{\varepsilon}(p) - \mu)/kT]}
\]

and define the ‘thermal excitation’ \(\delta f(p, T)\) by

\[
\delta f(p, T) = f_0(p, T) - f_0[\varepsilon(p)]
\]

Using the Sommerfeld formula (5.29), show that

\[
\int d^3 p \delta f(p, T) \propto (kT)^2 \rho'(\mu)
\]

where \(\rho(\varepsilon)\) is the density of states. Deduce from this result that

\[
\int p^2 dp \delta f(p, T) \propto T^2
\]

for any direction of \(p\), and that one can set \(\tilde{\varepsilon}(p) = \varepsilon(p)\) to leading order in \(T\). Thus one can adapt the formulae of the non-interacting Fermi gas by simply replacing
the free particle dispersion law by \( \varepsilon(p) \). Obtain the specific heat

\[
C_V = \frac{\pi^2 k^2 T}{3} \rho(\mu) = \frac{V k^2 T}{3\hbar^2} m^* p_F
\]

where the effective mass \( m^* \) is defined by

\[
\frac{d\varepsilon}{dp} \bigg|_{p=p_F} = \frac{p_F}{m^*}
\]

**In the rest of the problem, we shall revert to the \( T = 0 \) case.**

**5.** Compute \( \delta \tilde{f}(\vec{p}) \) when the chemical potential varies from \( \mu \) to \( \mu + d\mu \). Taking into account the isotropy of \( \delta f(\vec{p}) \) in this case, show that

\[
\frac{\partial N}{\partial \mu} = \frac{\rho(\mu)}{1 + \Lambda_0}
\]

\( \Lambda_0 = \alpha_0 \rho(\mu) \) is a dimensionless parameter independent of \( V \). Show that the expression for the \( T = 0 \) compressibility is now given by

\[
\kappa = \frac{1}{n^2} \frac{m^* p_F}{\pi^2 \hbar^3 (1 + \Lambda_0)}
\]

For helium-3 at atmospheric pressure, \( m^*/m \approx 3 \) and \( \Lambda_0 \approx 10 \). Is the compressibility over or underestimated when it is computed in the ideal gas model?

**B Boltzmann equation**

**1.** In a local equilibrium situation, the quasiparticle energy, \( \tilde{\varepsilon}(\vec{p}, \vec{r}) \), is a function of \( \vec{p} \) and \( \vec{r} \). In order to describe transport phenomena in a Fermi liquid, Landau assumed that independent quasiparticles are described by a classical Hamiltonian \( \tilde{\varepsilon} \). A kinetic theory of the ideal gas is then possible.\(^{27}\) Taking into account

\[
\frac{d\vec{r}}{dt} = \vec{v} = \nabla_{\vec{p}} \tilde{\varepsilon} \quad \frac{d\vec{p}}{dt} = \vec{F} = -\nabla_{\vec{r}} \tilde{\varepsilon}
\]

the Boltzmann equation for the distribution \( f(\vec{r}, \vec{p}, t) \) of quasiparticles in the absence of collisions reads

\[
\frac{\partial f}{\partial t} + \nabla_{\vec{p}} \tilde{\varepsilon} \cdot \nabla_{\vec{r}} f - (\nabla_{\vec{r}} \tilde{\varepsilon}) \cdot \nabla_{\vec{p}} f = 0
\]

**2.** One writes for the local deviation from equilibrium

\[
f(\vec{r}, \vec{p}, t) = f_0[\varepsilon(p)] + \delta f(\vec{r}, \vec{p}, t)
\]

\(^{27}\) Strictly speaking, the assumption of a one-particle distribution \( f(\vec{r}, \vec{p}, t) \) is incompatible with the uncertainty principle. One can show that the theory is valid provided the characteristic space and time scales \( \ell \) and \( \tau \) of \( f \) obey \( \hbar \nu_{\ell} / \ell \ll \mu \) and \( \hbar / \tau \ll \mu \).
where $f_0$ is the equilibrium distribution. The density $n(\vec{r}, t)$ is given by

$$n(\vec{r}, t) = \frac{2}{h^3} \int d^3p f(\vec{r}, \vec{p}, t)$$

The local $\tilde{\varepsilon}$ is then

$$\tilde{\varepsilon}(\vec{p}, \vec{r}, t) = \varepsilon(p) + \frac{2V}{h^3} \int d^3p' \lambda(\vec{p}, \vec{p}') \delta f(\vec{r}, \vec{p}', t)$$

Show that $\vec{\nabla}_r \tilde{\varepsilon}$ is first order in $\delta f$. Check that

$$\vec{\nabla}_p f_0 = -\frac{\vec{p}}{m^*} \delta(\varepsilon(p) - \mu) = -\vec{v} \delta(\varepsilon(p) - \mu)$$

where $\vec{v}$ is the group velocity. Show that to leading order in $\delta f$, the Boltzmann equation is given by (note that the equation features the time-derivative of $\delta f$ and the space-derivative of $\delta f$!)

$$\frac{\partial \delta f}{\partial t} + \vec{v} \cdot \vec{\nabla}_r \delta f = C[\delta f]$$

Do not try to give the explicit expression for the collision term $C[\delta f]$.  

3. The density excess of quasiparticles is given by

$$\delta n(\vec{r}, t) = \frac{2}{h^3} \int d^3p \delta f(\vec{r}, \vec{p}, t)$$

and the associated current $\vec{j}$ must obey the continuity equation

$$\frac{\partial \delta n}{\partial t} + \vec{\nabla}_r \cdot \vec{j} = 0$$

Using the Boltzmann equation and the property of the collision term

$$\int d^3p C[\delta f] = 0$$

show that the current

$$\vec{j} = \frac{2}{h^3} \int d^3p \vec{v} \delta f$$

obeys the continuity equation. One could have guessed the following form of the current

$$\vec{j}' = \frac{2}{h^3} \int d^3p \vec{v} \delta f$$

Why is it incorrect?
4. One can nevertheless write a correct expression for the current featuring $\delta f$

$$\vec{j} = \frac{2}{\hbar^3} \int d^3 p \vec{j}_p \delta f$$

with

$$\vec{j}_p = \vec{v} + \frac{2V}{\hbar^3} \int d^3 p' \frac{\vec{p}'}{m^*} \lambda(p', \vec{p}') \delta(\varepsilon(p') - \mu) = \vec{v} \left(1 + \frac{1}{3} \alpha_1 \rho(\mu)\right)$$

which one identifies with the current associated with a single localized quasiparticle. For a translation invariant system, Galilean invariance implies $\vec{j}_p = \vec{p}/m$. Use this property to derive a relation between the effective mass and the mass of the free particle

$$\frac{1}{m} = \frac{1}{m^*} \left(1 + \frac{1}{3} \Lambda_1\right) \quad \Lambda_1 = \alpha_1 \rho(\mu)$$

8.6.8 Calculation of the coefficient of thermal conductivity

1. We assume the gas to be at rest, with a temperature gradient along the $z$ direction: the temperature $T(z)$ is a function of $z$. The pressure $P$ must be uniform, otherwise a pressure gradient would set the gas in motion. Show that the local equilibrium distribution $f_0(z)$ is given by ($\beta(z) = 1/(kT(z))$

$$f_0(z) = P \left[\beta(z)\right]^{5/2} (\frac{2\pi m}{2m})^{3/2} \exp\left(-\frac{\beta(z)p^2}{2m}\right)$$

One writes, following (8.127)

$$f = f_0 \left(1 - \Phi \frac{\partial T}{\partial z}\right)$$

Show that the drift term of the Boltzmann equation is

$$Df = \frac{\beta}{T} \left(\frac{5}{2} k - \varepsilon(p)\right) f_0 \frac{\partial T}{\partial z} \quad \varepsilon(p) = \frac{p^2}{2m}$$

If the gas is not mono-atomic, one can show that

$$\Phi = \frac{\beta}{T} (c_P - \varepsilon(p))$$

where $c_P$ is the specific heat per particle at constant pressure, $c_P = 5k/2$ for a mono-atomic gas.

2. Following (8.128), one writes the linearized Boltzmann equation in the form

$$(\varepsilon(p) - c_P T)p_z = \frac{mT}{\beta} \int \prod_{i=2}^4 d^3 p_i W f_{02} \Delta \Phi = L[\Phi]$$
From the symmetry of the problem, the function $\Phi(\vec{p})$ must be proportional to $p_z$

$$\Phi(\vec{p}) = A(p)p_z$$

One must also choose $\Phi(\vec{p})$ in such a way that (8.120) is obeyed. Show that

$$\int d^3p \varepsilon(p)p_z f_0(p) \Phi(\vec{p}) = \frac{Tm}{4\beta} \int \prod_{i=1}^4 d^3p_i \ W f_{01} f_{02} (\Delta \Phi)^2$$

3. Derive the following expression for the coefficient of thermal conductivity $\kappa$

$$\kappa = \frac{1}{m} \int d^3p \varepsilon(p)p_z f_0(p) \Phi(\vec{p})$$

and using the scalar product defined in (8.131), show that

$$\kappa = \langle \Phi | X \rangle = \langle \Phi | L | \Phi \rangle$$

where $|X\rangle$ is the Hilbert space vector representing the function $\varepsilon(p)p_z$. From these results, devise a variational method for computing $\kappa$.

4. The simplest choice one can think of as a trial function is $\Psi = Ap_z$ with a constant $A$. However, with this choice, the second equation in (8.120) is not satisfied. Show that the trial function

$$\Psi(\vec{p}) = A(1 - \gamma p^2)p_z$$

has all the required properties if $\gamma = \beta/(5m)$.

5. Show that

$$\langle X | \Psi \rangle = -\frac{An}{\beta^2}$$

where $n$ is the density, and that

$$\langle \Psi | L | \Psi \rangle = \frac{32}{25\sqrt{\pi}} \ A^2 T n^2 \frac{m}{\beta^3} \left( \frac{\beta}{m} \right)^{1/2} \sigma_{tr}$$

Hint: Going to centre-of-mass variables $\vec{P}$, $\vec{p}$ and $\vec{p}'$, you will have to integrate an expression of the form

$$\int d^3p \ d^3P \left[ (\vec{P} \cdot \vec{p})p_z - (\vec{P} \cdot \vec{p}')p_z' \right]^2 \cdots \rightarrow \frac{2}{9} \int d^3p \ d^3P \ P^2 \ p^4 (1 - \cos^2 \theta)$$

First show that the angular average over the direction of $\vec{P}$ gives a factor 1/3.

6. From these results, derive a variational estimate for $\kappa$, assuming a $p$-independent transport cross section

$$\kappa = \frac{25\sqrt{\pi}}{32} \frac{k}{m} \frac{\sqrt{mkT}}{\sigma_{tr}}$$
Compute the ratio $\kappa/\eta$ and compare with the elementary estimate derived in Section 8.1.3.

### 8.7 Further reading

The classical calculation of cross sections is done in Goldstein [48] (Chapter III), Landau and Lifshitz [69] (Chapter IV) and the quantum calculation in Messiah [89] (Chapter X) and Cohen-Tannoudji et al. [30] (Chapter VIII). An elementary treatment of kinetic theory is in Reif [109] (Chapter 12) and Baierlein [4] (Chapter 15). At a more advanced level, the reference in the subject is the book by Lifshitz and Pitaevskii [81]. The Boltzmann–Lorentz model is treated in Balian [5] (Chapter 15) and Lifshitz and Pitaevskii [81] (Section 11). As further reading on the Boltzmann equation, we recommend Reif [109] (Chapters 13 and 14), Balian [5] (Chapter 15), Kreuzer [67] (Chapter 8), Kubo [68] (Chapter 6), McQuarrie [88] (Chapters 16 to 19) and Lifshitz and Pitaevskii [81] (Sections 1 to 10). One finds in these references a complete calculation of transport coefficients. An example of the increase of the H-function is given by Jaynes [60], but the argument is incomplete. The extension of the Boltzmann equation to the quantum case (the Landau–Uhlenbeck equation) can be found in Balian [5] (Chapter 11), Pines and Nozières [102] (Chapter 1), Baym and Pethick [15] and Lifshitz and Pitaevskii [81] (Chapter VIII).

The following references may be helpful for problems. The integer quantum Hall effect is described in the Nobel lectures by Laughlin [71] and Stormer [116]. For the fractional Hall effect see the reviews by Jain [59], Heiblum and Stern [55] and the Nobel lectures by Laughlin [71] and Stormer [116]. The two-fluid model for helium-4 is discussed in Landau and Lifshitz [70] (Volume 2), Chapter III, Goodstein [49] (Chapter 5) and Nozières and Pines [96] (Chapter 6). Landau’s theory of Fermi liquids is examined in Lifshitz and Pitaevskii [81] (Section 74) to 76. See also Baym and Pethick [15] and Pines and Nozières [102] (Chapter 1).