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Chapter 8

The Boltzmann Equation

8.1 References

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

8.2 Equilibrium, Nonequilibrium and Local Equilibrium

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

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

We assume a Hamiltonian of the form

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

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

$$\varrho_N(\mathbf{x}_1, \dots, \mathbf{x}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) \prod_{j=1}^N d\mu_j, \quad (8.3)$$

with $d\mu_j \equiv d^d x_j d^d p_j / h^d$, is the probability, under equilibrium conditions, of finding N particles in the system, with particle #1 lying within $d^3 x_1$ of \mathbf{x}_1 and having momentum within $d^d p_1$ of \mathbf{p}_1 , etc. The temperature T and chemical potential μ are constants, independent of position. Note that $\varrho_N(\{\mathbf{x}_i\}, \{\mathbf{p}_i\})$ has units of h^{-dN} .

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

We will mainly be interested in the one-body distribution

$$\begin{aligned} f(\mathbf{x}, \mathbf{p}; t) &= \sum_{i=1}^N \langle \delta(\mathbf{x} - \mathbf{x}_i(t)) \delta(\mathbf{p} - \mathbf{p}_i(t)) \rangle \\ &= N h^{-d} \int \prod_{i=2}^N d\mu_i \varrho_N(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{p}, \mathbf{p}_2, \dots, \mathbf{p}_N, t) \quad . \end{aligned} \quad (8.4)$$

Note that $f(\mathbf{x}, \mathbf{p}, t)$ has dimensions of h^{-d} , and $f(\mathbf{x}, \mathbf{p}, t) d^3\mathbf{x} d^3\mathbf{p}$ is the average number of particles found within $d^3\mathbf{x}$ of \mathbf{x} and $d^3\mathbf{p}$ of \mathbf{p} at time t . The full k -particle density matrix, which for classical systems we may write in terms of its diagonal matrix elements in the $(\{\mathbf{x}_i\}, \{\mathbf{p}_i\})$ basis, is given by

$$\begin{aligned} f_k(\{\mathbf{x}_i\}, \{\mathbf{p}_i\}, t) &= \sum'_{\{j_1, \dots, j_k\}} \langle \delta(\mathbf{x}_1 - \mathbf{x}_{j_1}(t)) \cdots \delta(\mathbf{x}_k - \mathbf{x}_{j_k}(t)) \delta(\mathbf{p}_1 - \mathbf{p}_{j_1}(t)) \cdots \delta(\mathbf{p}_k - \mathbf{p}_{j_k}(t)) \rangle \\ &= \frac{N! h^{-kd}}{(N-k)!} \int \prod_{i=k+1}^N d\mu_i \varrho_N(\mathbf{x}_1, \dots, \mathbf{x}_k, \mathbf{x}_{k+1}, \dots, \mathbf{x}_N; \mathbf{p}_1, \dots, \mathbf{p}_k, \mathbf{p}_{k+1}, \dots, \mathbf{p}_N, t) \quad , \end{aligned} \quad (8.5)$$

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

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

for all t . We write the one-body density matrix $f_1(\mathbf{x}_1, \mathbf{p}_1, t) \equiv f(\mathbf{x}, \mathbf{p}, t)$, where $\mathbf{x} = \mathbf{x}_1$ and $\mathbf{p} = \mathbf{p}_1$. Henceforth we will drop the distinction between boldface Roman symbols $\{\mathbf{x}, \mathbf{p}\}$ and boldface math italic $\{\mathbf{x}, \mathbf{p}\}$, as it will no longer be needed.

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

$$f^0(\mathbf{r}, \mathbf{p}) = n (2\pi m k_B T)^{-3/2} e^{-\mathbf{p}^2/2mk_B T} = h^{-d} z e^{-\mathbf{p}^2/2mk_B T} \quad , \quad (8.7)$$

where $n = N/V$ or $n = n(T, \mu)$ is the particle density in the OCE or GCE, with $z = \exp(\mu/k_B T) = n\lambda_T^d$ the fugacity. From the one-body distribution we can compute things like the particle current, \mathbf{j} , and the energy current, \mathbf{j}_ε :

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

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

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

Thermodynamics says that

$$d\mathbf{q} = T ds = d\varepsilon - \mu dn \quad , \quad (8.10)$$

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

$$\mathbf{j}_q = T \mathbf{j}_s = \mathbf{j}_\varepsilon - \mu \mathbf{j} \quad . \quad (8.11)$$

Thus, in a system with no particle flow, $j = 0$ and the *heat current* j_q is the same as the energy current j_ϵ .

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

$$d\Gamma = \begin{cases} d^3p & \text{point particles} \\ d^3p L dL d\Omega_{\hat{\mathbf{L}}} & \text{diatomic molecules} \\ d^3p L^2 dL d\Omega_{\hat{\mathbf{L}}} d\cos\vartheta & \text{symmetric tops} \end{cases} \quad (8.12)$$

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

$$n(\mathbf{r}, t) = \int d\Gamma f(\mathbf{r}, \Gamma; t) \quad (8.13)$$

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

8.3 Boltzmann Transport Theory

8.3.1 Derivation of the Boltzmann equation

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

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

Thus, the units of $f(\mathbf{r}, \mathbf{p}, t)$ are those of inverse action, *i.e.* T/ML^2 . We now ask how the distribution functions $f(\mathbf{r}, \mathbf{p}, t)$ evolves in time. It is clear that in the absence of collisions, the distribution function must satisfy the continuity equation,

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

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

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

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

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

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

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

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

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

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

$$\frac{\partial f}{\partial t} + \mathbf{u} \cdot \nabla f = 0 \quad . \quad (8.20)$$

The differential operator $D_t \equiv \partial_t + \mathbf{u} \cdot \nabla$ is sometimes called the ‘convective derivative’, because $D_t f$ is the time derivative of f in a comoving frame of reference. To see this, evaluate the time derivative of the time-dependent distribution $f(\mathbf{r}, \mathbf{p}, t)$ along a particle trajectory, *i.e.* substituting $\mathbf{r} \rightarrow \mathbf{r}(t)$ and $\mathbf{p} = \mathbf{p}(t)$. We have

$$\frac{d}{dt} f(\mathbf{r}(t), \mathbf{p}(t), t) = \frac{\partial f}{\partial \mathbf{r}} \cdot \frac{d\mathbf{r}}{dt} \Big|_{\{\mathbf{r}(t), \mathbf{p}(t), t\}} + \frac{\partial f}{\partial \mathbf{p}} \cdot \frac{d\mathbf{p}}{dt} \Big|_{\{\mathbf{r}(t), \mathbf{p}(t), t\}} + \frac{\partial f}{\partial t} \Big|_{\{\mathbf{r}(t), \mathbf{p}(t), t\}} = \frac{Df}{Dt} \Big|_{\{\mathbf{r}(t), \mathbf{p}(t), t\}} \quad . \quad (8.21)$$

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

$$\frac{Df}{Dt} = \frac{\partial f}{\partial t} + \dot{\mathbf{r}} \cdot \frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{p}} \cdot \frac{\partial f}{\partial \mathbf{p}} = \left(\frac{df}{dt} \right)_{\text{coll}} \quad (8.22)$$

where the right side is known as the *collision integral*. The collision integral is in general a *function* of \mathbf{r} , \mathbf{p} , and t and a *functional* of the distribution f . Thus, in the absence of collisions, the convective derivative of the distribution $f(\mathbf{r}, \mathbf{p}, t)$ vanishes, meaning that the one-body distribution does not vary in time along a particle trajectory.

We can write the Boltzmann equation as

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

where

$$\left(\frac{df}{dt} \right)_{\text{str}} \equiv \dot{\mathbf{r}} \cdot \frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{p}} \cdot \frac{\partial f}{\partial \mathbf{p}} \quad (8.24)$$

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

8.3.2 Collisionless Boltzmann equation

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

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

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

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

Clearly, then, *any* function of the form

$$f(\mathbf{r}, \mathbf{p}, t) = \varphi(\mathbf{r} - \mathbf{v}(\mathbf{p})t, \mathbf{p}) \quad (8.27)$$

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

$$f(\mathbf{r}, \mathbf{p}, t) = C e^{\mu/k_B T} e^{-\varepsilon(\mathbf{p})/k_B T} \quad , \quad (8.28)$$

which is time-independent¹. Here, C is a constant with units of $(T/ML^2)^d$. For a ballistic dispersion, $\varepsilon(\mathbf{p}) = \mathbf{p}^2/2m$ and $C = h^{-3}$, in which case $\int d^d r d^d p f(\mathbf{r}, \mathbf{p}) = V \exp(\mu/k_B T) = \langle \hat{N} \rangle$.

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

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

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

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

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

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

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

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

$$f(\mathbf{r}, \mathbf{p}, t) = \varphi\left(\mathbf{r} - \frac{\mathbf{p}t}{m} - \frac{\mathbf{F}_{\text{ext}}t^2}{2m}, \mathbf{p} - \frac{\mathbf{F}_{\text{ext}}t}{m}\right) \quad (8.32)$$

satisfies the collisionless Boltzmann equation (ballistic dispersion assumed).

¹Indeed, any arbitrary function of \mathbf{p} alone would be a solution. Ultimately, we require some energy exchanging processes, such as collisions, in order for any initial nonequilibrium distribution to converge to the Boltzmann distribution.

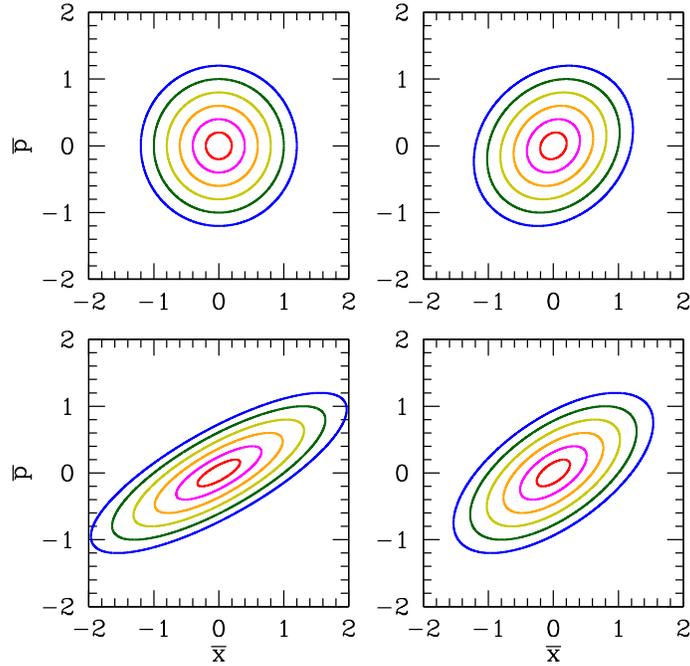


Figure 8.1: Level sets for a sample $f(\bar{x}, \bar{p}, \bar{t}) = C e^{-(\bar{x}-\bar{p}\bar{t})^2/2} e^{-\bar{p}^2/2}$, for values $f = C e^{-\alpha^2/2}$ with α in equally spaced intervals from $\alpha = 0.2$ (red) to $\alpha = 1.2$ (blue). The time variable \bar{t} is taken to be $\bar{t} = 0.0$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

8.3.3 Scattering processes

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

Single particle scattering

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

$$w(\Gamma' | \Gamma) f(\mathbf{r}, \Gamma; t) d\Gamma d\Gamma' = \text{rate per unit volume to scatter } \{|\Gamma + d\Gamma\rangle\} \rightarrow \{|\Gamma' + d\Gamma'\rangle\} \quad (8.33)$$

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

$$d\sigma = \frac{w(\Gamma | \Gamma')}{n_s |\mathbf{v}|} d\Gamma' \quad , \quad (8.34)$$

where $\mathbf{v} = \mathbf{p}/m$ is the particle's velocity and n_s the number density of scatterers.

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

$$\frac{D}{Dt} f(\mathbf{r}, \Gamma; t) = \int d\Gamma' \left\{ w(\Gamma | \Gamma') f(\mathbf{r}, \Gamma'; t) - w(\Gamma' | \Gamma) f(\mathbf{r}, \Gamma; t) \right\} = \left(\frac{df}{dt} \right)_{\text{coll}} . \quad (8.35)$$

Mathematically, in the case of point particles, where $\Gamma = \mathbf{p}$, this is a linear, first-order integro-differential equation in seven variables $\{x, y, z, p_x, p_y, p_z, t\}$. It can be expressed as $\partial_t f = \mathcal{L} f$, where \mathcal{L} is a linear integro-differential operator. With initial conditions $f(\mathbf{r}, \mathbf{p}, t = 0)$ this can in principle be integrated forward in time, and in the autonomous case where all the rates and external forces are time-independent, we have $f(t) = \exp(\mathcal{L}t) f(0)$.

Two particle scattering

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

$$w(\Gamma', \Gamma'_1 | \Gamma, \Gamma_1) f_2(\mathbf{r}, \Gamma; \mathbf{r}, \Gamma_1; t) d\Gamma d\Gamma_1 d\Gamma' d\Gamma'_1 = \left\{ \begin{array}{l} \text{rate per unit volume to scatter two particles} \\ \{|\Gamma + d\Gamma, \Gamma_1 + d\Gamma_1\rangle\} \rightarrow \{|\Gamma + d\Gamma', \Gamma'_1 + d\Gamma'_1\rangle\} \end{array} \right\} \quad (8.36)$$

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

$$d\sigma = \frac{w(\Gamma, \Gamma_1 | \Gamma', \Gamma'_1)}{|\mathbf{v} - \mathbf{v}_1|} d\Gamma' d\Gamma'_1 . \quad (8.37)$$

For two-body scattering, we therefore have

$$\begin{aligned} \frac{D}{Dt} f(\mathbf{r}, \Gamma; t) = \int d\Gamma_1 \int d\Gamma' \int d\Gamma'_1 \left\{ w(\Gamma, \Gamma_1 | \Gamma', \Gamma'_1) f_2(\mathbf{r}, \Gamma'; \mathbf{r}, \Gamma'_1; t) \right. \\ \left. - w(\Gamma', \Gamma'_1 | \Gamma, \Gamma_1) f_2(\mathbf{r}, \Gamma; \mathbf{r}, \Gamma_1; t) \right\} = \left(\frac{df}{dt} \right)_{\text{coll}} . \end{aligned} \quad (8.38)$$

Unlike the one-body scattering case, the kinetic equation for two-body scattering does not close, since the LHS involves the one-body distribution $f \equiv f_1$ and the RHS involves the two-body distribution f_2 . One can then write an equation for f_2 which also does not close – it involves f_3 – and so on. The result is known as the *BBGKY hierarchy*, and is discussed in some detail in the appendix §??.

In practice, an approximation is made in order to close the equations. The simplest and most common such approximation, known as the *Stosszahlansatz*, or *molecular chaos assumption*, is due to Boltzmann himself. We replace the two-body distribution by a product of one-body distributions, *viz.*

$$f_2(\mathbf{r}, \Gamma; \mathbf{r}_1, \Gamma_1; t) \approx f(\mathbf{r}, \Gamma; t) f(\mathbf{r}_1, \Gamma_1; t) . \quad (8.39)$$

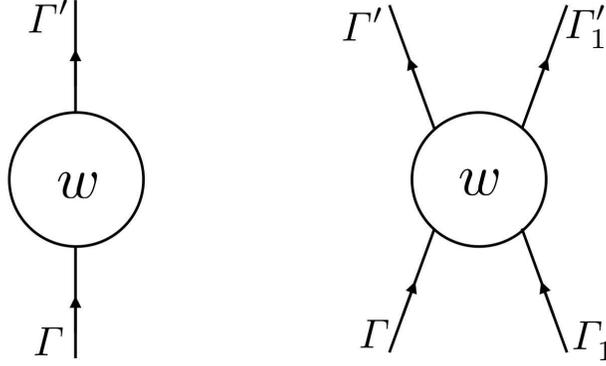


Figure 8.2: Left: single particle scattering process $|\Gamma\rangle \rightarrow |\Gamma'\rangle$. Right: two-particle scattering process $|\Gamma, \Gamma_1\rangle \rightarrow |\Gamma', \Gamma'_1\rangle$.

We then have

$$\begin{aligned} \frac{D}{Dt} f(\mathbf{r}, \Gamma; t) = \int d\Gamma_1 \int d\Gamma' \int d\Gamma'_1 \left\{ w(\Gamma, \Gamma_1 | \Gamma', \Gamma'_1) f(\mathbf{r}, \Gamma'; t) f(\mathbf{r}, \Gamma'_1; t) \right. \\ \left. - w(\Gamma', \Gamma'_1 | \Gamma, \Gamma_1) f(\mathbf{r}, \Gamma; t) f(\mathbf{r}, \Gamma_1; t) \right\} = \left(\frac{df}{dt} \right)_{\text{coll}} . \end{aligned} \quad (8.40)$$

Now we have a closed but *nonlinear* first-order integro-PDE. The nonlinearity adds a new wrinkle, and as we shall see below a further approximation involves *linearizing* the collision integral.

We stress that in both cases (*i.e.* single-particle and two-particle scattering) we assume that all scattering occurs *locally*, *i.e.* the particles attain their asymptotic kinematic states on distance scales small compared to the mean interparticle separation. In this case we can treat each scattering process independently. This assumption is particular to rarefied systems, *i.e.* gases, and is not appropriate for dense liquids. The two types of scattering processes are depicted in fig. 8.2.

Nota bene: All $w(\Gamma' | \Gamma)$ and all $w(\Gamma', \Gamma'_1 | \Gamma, \Gamma_1)$ are non-negative!

8.3.4 Collisional invariants

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

$$\langle A(t) \rangle = \int d^3r d^3p A(\mathbf{r}, \mathbf{p}) f(\mathbf{r}, \mathbf{p}, t) . \quad (8.41)$$

Taking the time derivative,

$$\begin{aligned} \frac{d\langle A(t) \rangle}{dt} &= \int d^3r \int d^3p A(\mathbf{r}, \mathbf{p}) \frac{\partial f}{\partial t} \\ &= \int d^3r \int d^3p A(\mathbf{r}, \mathbf{p}) \left\{ -\frac{\partial}{\partial \mathbf{r}} \cdot (\dot{\mathbf{r}} f) - \frac{\partial}{\partial \mathbf{p}} \cdot (\dot{\mathbf{p}} f) + \left(\frac{df}{dt} \right)_{\text{coll}} \right\} \\ &= \int d^3r \int d^3p \left\{ \left(\frac{\partial A}{\partial \mathbf{r}} \cdot \frac{d\mathbf{r}}{dt} + \frac{\partial A}{\partial \mathbf{p}} \cdot \frac{d\mathbf{p}}{dt} \right) f + A(\mathbf{r}, \mathbf{p}) \left(\frac{df}{dt} \right)_{\text{coll}} \right\} . \end{aligned} \quad (8.42)$$

Hence, if A is preserved by the dynamics between collisions, then²

$$\frac{dA(\mathbf{r}(t), \mathbf{p}(t))}{dt} = \frac{\partial A}{\partial \mathbf{r}} \cdot \frac{d\mathbf{r}}{dt} + \frac{\partial A}{\partial \mathbf{p}} \cdot \frac{d\mathbf{p}}{dt} = 0 \quad . \quad (8.43)$$

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

$$\frac{d\langle A(t) \rangle}{dt} = \int d^3r \int d^3p A(\mathbf{r}, \mathbf{p}) \left(\frac{df}{dt} \right)_{\text{coll}} \quad . \quad (8.44)$$

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

8.3.5 Detailed balance

Classical mechanics places some restrictions on the form of the kernel $w(\Gamma, \Gamma_1 | \Gamma', \Gamma'_1)$. In particular, if $\Gamma^\tau = (-\mathbf{p}, -\mathbf{L})$ denotes the kinematic variables under time reversal (\mathcal{T}), then

$$w(\Gamma', \Gamma'_1 | \Gamma, \Gamma_1) = w(\Gamma^\tau, \Gamma_1^\tau | \Gamma'^\tau, \Gamma_1'^\tau) \quad . \quad (8.45)$$

This is because the time reverse of the process $|\Gamma, \Gamma_1\rangle \rightarrow |\Gamma', \Gamma'_1\rangle$ is $|\Gamma'^\tau, \Gamma_1'^\tau\rangle \rightarrow |\Gamma^\tau, \Gamma_1^\tau\rangle$.

In equilibrium, we must have

$$w(\Gamma', \Gamma'_1 | \Gamma, \Gamma_1) f^0(\Gamma) f^0(\Gamma_1) d^4\Gamma = w(\Gamma^\tau, \Gamma_1^\tau | \Gamma'^\tau, \Gamma_1'^\tau) f^0(\Gamma'^\tau) f^0(\Gamma_1'^\tau) d^4\Gamma^\tau \quad (8.46)$$

where

$$d^4\Gamma \equiv d\Gamma d\Gamma_1 d\Gamma' d\Gamma'_1 \quad , \quad d^4\Gamma^\tau \equiv d\Gamma^\tau d\Gamma_1^\tau d\Gamma'^\tau d\Gamma_1'^\tau \quad . \quad (8.47)$$

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

$$f^0(\Gamma) f^0(\Gamma_1) = f^0(\Gamma'^\tau) f^0(\Gamma_1'^\tau) \quad . \quad (8.48)$$

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

$$\varepsilon + \varepsilon_1 = \varepsilon' + \varepsilon'_1 \quad . \quad (8.49)$$

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

$$\mathbf{p} + \mathbf{p}_1 = \mathbf{p}' + \mathbf{p}'_1 \quad , \quad (8.50)$$

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

any distribution of the form

$$f^0(\Gamma) = A \exp\left(-\frac{\varepsilon(\Gamma) - \mathbf{V} \cdot \mathbf{p}}{k_B T}\right) \quad (8.51)$$

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

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

which is the velocity relative to the local flow.

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

$$w(\Gamma', \Gamma'_1 | \Gamma, \Gamma_1) = w(\Gamma^{\mathcal{C}}, \Gamma_1^{\mathcal{C}} | \Gamma'^{\mathcal{C}}, \Gamma_1'^{\mathcal{C}}) \quad . \quad (8.53)$$

For point particles, invariance under T and P then means

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

and therefore the collision integral takes the simplified form,

$$\frac{Df(\mathbf{r}, \mathbf{p}, t)}{Dt} = \int d^3p_1 \int d^3p'_1 \int d^3p'_1 w(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1) \left\{ f(\mathbf{r}, \mathbf{p}', t) f(\mathbf{r}, \mathbf{p}'_1, t) - f(\mathbf{r}, \mathbf{p}, t) f(\mathbf{r}, \mathbf{p}_1, t) \right\} = \left(\frac{df}{dt} \right)_{\text{coll}} \quad . \quad (8.55)$$

The most general statement of detailed balance is

$$\frac{f^0(\Gamma') f^0(\Gamma'_1)}{f^0(\Gamma) f^0(\Gamma_1)} = \frac{w(\Gamma', \Gamma'_1 | \Gamma, \Gamma_1)}{w(\Gamma, \Gamma_1 | \Gamma', \Gamma'_1)} \quad . \quad (8.56)$$

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

Detailed balance and single particle scattering

For single particle scattering, similar considerations lead to

$$f^0(\Gamma) = f^0(\Gamma'^{\tau}) \quad , \quad \frac{f^0(\Gamma')}{f^0(\Gamma)} = \frac{w(\Gamma' | \Gamma)}{w(\Gamma | \Gamma')} \quad . \quad (8.57)$$

In the first of these equations, the time reversal operation also acts on the external potential off which the particles scatter. In general, detailed balance pertains when the static equilibrium distribution $f^0(\Gamma)$ is such that the integrand of the collision term vanishes for all Γ , hence $(df^0(\Gamma)/dt)_{\text{coll}} = 0$.

8.3.6 Kinematics and cross section

We can rewrite eqn. 8.55 in the form

$$\frac{Df(\mathbf{r}, \mathbf{p}, t)}{Dt} = \int d^3p_1 \int d\Omega |\mathbf{v} - \mathbf{v}_1| \frac{d\sigma}{d\Omega} \left\{ f(\mathbf{r}, \mathbf{p}', t) f(\mathbf{r}, \mathbf{p}_1', t) - f(\mathbf{r}, \mathbf{p}, t) f(\mathbf{r}, \mathbf{p}_1, t) \right\} , \quad (8.58)$$

where $d\sigma/d\Omega$ is the *differential scattering cross section*. Recall the definition from scattering theory in classical mechanics,

$$d\sigma = \frac{\text{\# of particles scattered into solid angle } d\Omega \text{ per unit time}}{\text{incident flux}} . \quad (8.59)$$

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

$$\begin{aligned} \mathbf{p}' &= \frac{1}{2}(\mathbf{p} + \mathbf{p}_1 + |\mathbf{p} - \mathbf{p}_1| \hat{\Omega}) \\ \mathbf{p}_1' &= \frac{1}{2}(\mathbf{p} + \mathbf{p}_1 - |\mathbf{p} - \mathbf{p}_1| \hat{\Omega}) . \end{aligned} \quad (8.60)$$

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

$$\frac{d\sigma}{d\Omega} = \left(\frac{me^2}{|\mathbf{p}_1 - \mathbf{p}_2|^2 \sin^2(\frac{1}{2}\vartheta)} \right)^2 , \quad (8.61)$$

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

8.3.7 \mathcal{H} -theorem

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

$$\begin{aligned} h(\mathbf{r}, t) &= \int d^3p f(\mathbf{r}, \mathbf{p}, t) \log [f(\mathbf{r}, \mathbf{p}, t) a^3] \\ \mathbf{j}(\mathbf{r}, t) &= \int d^3p f(\mathbf{r}, \mathbf{p}, t) \log [f(\mathbf{r}, \mathbf{p}, t) a^3] \frac{d\mathbf{r}}{dt} . \end{aligned} \quad (8.62)$$

Here a can be any constant which has the appropriate dimensions of action. Then if $f(\mathbf{r}, \mathbf{p}, t)$ evolves according to the Boltzmann equation, it is necessarily the case that

$$\frac{\partial h(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}, t) \leq 0 , \quad (8.63)$$

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

$$\mathcal{H}(t) = \int d^3r h(\mathbf{r}, t) \Rightarrow \frac{d\mathcal{H}}{dt} \leq 0 \quad . \quad (8.64)$$

Thus, Boltzmann dynamics recognizes an arrow of time. Time increases in the direction that \mathcal{H} decreases.

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

$$\rho_\varphi(\mathbf{r}, t) \equiv \int d^3p f(\mathbf{r}, \mathbf{p}, t) \varphi(f(\mathbf{r}, \mathbf{p}, t)) \quad , \quad (8.65)$$

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

$$\begin{aligned} \frac{\partial \rho_\varphi}{\partial t} &= \int d^3p \frac{\partial(f\varphi)}{\partial t} = \int d\Gamma \frac{\partial(f\varphi)}{\partial f} \frac{\partial f}{\partial t} \\ &= \int d^3p \frac{\partial(f\varphi)}{\partial f} \left\{ -\dot{\mathbf{r}} \cdot \frac{\partial f}{\partial \mathbf{r}} - \dot{\mathbf{p}} \cdot \frac{\partial f}{\partial \mathbf{p}} + \left(\frac{df}{dt} \right)_{\text{coll}} \right\} \\ &= \int d^3p \left\{ -\dot{\mathbf{r}} \cdot \frac{\partial(f\varphi)}{\partial \mathbf{r}} - \dot{\mathbf{p}} \cdot \frac{\partial(f\varphi)}{\partial \mathbf{p}} + \frac{\partial(f\varphi)}{\partial f} \left(\frac{df}{dt} \right)_{\text{coll}} \right\} \end{aligned} \quad (8.66)$$

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

$$\begin{aligned} \frac{\partial \rho_\varphi}{\partial t} &= \int d^3p \left\{ -\dot{\mathbf{r}} \cdot \frac{\partial(f\varphi)}{\partial \mathbf{r}} - \frac{\partial \dot{\mathbf{r}}}{\partial \mathbf{r}} (f\varphi) + \frac{\partial(f\varphi)}{\partial f} \left(\frac{df}{dt} \right)_{\text{coll}} \right\} \\ &= -\frac{\partial}{\partial \mathbf{r}} \int d^3p f \varphi \dot{\mathbf{r}} + \int d^3p \frac{\partial(f\varphi)}{\partial f} \left(\frac{df}{dt} \right)_{\text{coll}} \quad . \end{aligned} \quad (8.67)$$

Thus,

$$\frac{\partial \rho_\varphi(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j}_\varphi(\mathbf{r}, t) = \sigma_\varphi(\mathbf{r}, t) \quad , \quad (8.68)$$

where

$$\begin{aligned} \mathbf{j}_\varphi(\mathbf{r}, t) &= \int d^3p f(\mathbf{r}, \mathbf{p}, t) \varphi(f(\mathbf{r}, \mathbf{p}, t)) \mathbf{v}(\mathbf{p}) \\ \sigma_\varphi(\mathbf{r}, t) &= \int d^3p \frac{\partial(f\varphi)}{\partial f} \Big|_{f(\mathbf{r}, \mathbf{p}, t)} \left(\frac{df}{dt} \right)_{\text{coll}} \end{aligned} \quad (8.69)$$

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

Thus, we arrive at eqn. 8.68, which is a continuity equation with a source term $\sigma_\varphi(\mathbf{r}, t)$. The source term is nonzero only in the presence of collisions. We now evaluate σ_φ under the assumption that f satisfies the Boltzmann equation with two particle scattering. Thus,

$$\begin{aligned} \sigma_\varphi(\mathbf{r}, t) &= \int d^3p \int d^3p_1 \int d^3p' \int d^3p'_1 \left\{ w(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1) f(\mathbf{p}) f(\mathbf{p}_1) \chi(\mathbf{p}) - w(\mathbf{p}, \mathbf{p}_1 | \mathbf{p}', \mathbf{p}'_1) f(\mathbf{p}') f(\mathbf{p}'_1) \chi(\mathbf{p}') \right\} \\ &= \int d^3p \int d^3p_1 \int d^3p' \int d^3p'_1 w(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1) f(\mathbf{p}) f(\mathbf{p}_1) (\chi(\mathbf{p}) - \chi'(\mathbf{p})) \quad , \end{aligned} \quad (8.70)$$

where

$$\chi = \frac{\partial(f\varphi)}{\partial f} = \varphi + f \frac{\partial\varphi}{\partial f} \quad , \quad (8.71)$$

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

$$w(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1) = w(\mathbf{p}'_1, \mathbf{p}' | \mathbf{p}_1, \mathbf{p}) \quad , \quad (8.72)$$

which allows us to write

$$\sigma = \frac{1}{2} \int d^3p \int d^3p_1 \int d^3p' \int d^3p'_1 w(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1) f(\mathbf{p}) f(\mathbf{p}_1) (\chi(\mathbf{p}) + \chi(\mathbf{p}_1) - \chi(\mathbf{p}') - \chi(\mathbf{p}'_1)) \quad , \quad (8.73)$$

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

Now let us fix $\varphi(f) = \log(f a^3)$ and evaluate the source term $\sigma \equiv \sigma_{\varphi=\log(f a^3)}$. We have

$$\sigma = -\frac{1}{2} \int d^3p \int d^3p_1 \int d^3p' \int d^3p'_1 w(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1) f(\mathbf{p}') f(\mathbf{p}'_1) \cdot x(\mathbf{p}, \mathbf{p}_1 | \mathbf{p}', \mathbf{p}'_1) \log x(\mathbf{p}, \mathbf{p}_1 | \mathbf{p}', \mathbf{p}'_1) \quad , \quad (8.74)$$

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

$$\int d^3p' \int d^3p'_1 w(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1) = \int d^3p' \int d^3p'_1 w(\mathbf{p}, \mathbf{p}_1 | \mathbf{p}', \mathbf{p}'_1) \quad (8.75)$$

which is a statement of unitarity of the scattering matrix³. Multiplying both sides by $f(\mathbf{p}) f(\mathbf{p}_1)$, then integrating over \mathbf{p} and \mathbf{p}_1 , and finally changing variables $(\mathbf{p}, \mathbf{p}_1) \leftrightarrow (\mathbf{p}', \mathbf{p}'_1)$, we find

$$\begin{aligned} 0 &= \int d^3p \int d^3p_1 \int d^3p' \int d^3p'_1 w(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1) \left(f(\mathbf{p}) f(\mathbf{p}_1) - f(\mathbf{p}') f(\mathbf{p}'_1) \right) \\ &= \int d^3p \int d^3p_1 \int d^3p' \int d^3p'_1 w(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1) f(\mathbf{p}') f(\mathbf{p}'_1) \left\{ x(\mathbf{p}, \mathbf{p}_1 | \mathbf{p}', \mathbf{p}'_1) - 1 \right\} \quad . \end{aligned} \quad (8.76)$$

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

$$\sigma = -\frac{1}{2} \int d^3p \int d^3p_1 \int d^3p' \int d^3p'_1 w(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1) f(\mathbf{p}') f(\mathbf{p}'_1) (x \log x - x + 1) \quad , \quad (8.77)$$

where $x \equiv x(\mathbf{p}, \mathbf{p}_1, \mathbf{p}', \mathbf{p}'_1) = f(\mathbf{p}) f(\mathbf{p}_1) / f(\mathbf{p}') f(\mathbf{p}'_1)$. It is now easy to prove that the function $g(x) = x \log x - x + 1$ is nonnegative for all positive x values⁴, which therefore entails the important result

$$\frac{\partial h(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = \sigma(\mathbf{r}, t) \leq 0 \quad . \quad (8.78)$$

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

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

⁴The function $g(x) = x \log x - x + 1$ satisfies $g'(x) = \log x$, hence $g'(x) < 0$ on the interval $x \in [0, 1)$ and $g'(x) > 0$ on $x \in (1, \infty]$. Thus, $g(x)$ monotonically decreases from $g(0) = 1$ to $g(1) = 0$, and then monotonically increases to $g(\infty) = \infty$, never becoming negative.

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

$$f^0(\mathbf{p}) f^0(\mathbf{p}_1) = f^0(\mathbf{p}') f^0(\mathbf{p}'_1) \quad , \quad (8.79)$$

or, taking the logarithm,

$$\log f^0(\mathbf{p}) + \log f^0(\mathbf{p}_1) = \log f^0(\mathbf{p}') + \log f^0(\mathbf{p}'_1) \quad . \quad (8.80)$$

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

$$-\log f^0 = \frac{\varepsilon(\mathbf{p}) - \mathbf{V} \cdot \mathbf{p} - \mu}{k_B T} \quad , \quad (8.81)$$

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

8.4 Weakly Inhomogeneous Gas

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

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \frac{\partial}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial}{\partial \mathbf{p}} \right) (f^0 + \delta f) = \left(\frac{df}{dt} \right)_{\text{coll}} \quad . \quad (8.82)$$

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

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

$$f^0(\mathbf{r}, \Gamma) = C \exp\left(\frac{\mu - \varepsilon(\Gamma) + \mathbf{V} \cdot \mathbf{p}}{k_B T} \right) \quad , \quad (8.83)$$

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

$$\begin{aligned} df^0 &= \left(d\mu + \mathbf{p} \cdot d\mathbf{V} + (\varepsilon - \mathbf{V} \cdot \mathbf{p} - \mu) \frac{dT}{T} - d\varepsilon \right) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \\ &= \left(\frac{1}{n} dp + \mathbf{p} \cdot d\mathbf{V} + (\varepsilon - h) \frac{dT}{T} - d\varepsilon \right) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \quad , \end{aligned} \quad (8.84)$$

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

$$d\mu = \left(\frac{\partial \mu}{\partial T} \right)_p dT + \left(\frac{\partial \mu}{\partial p} \right)_T dp = -s dT + \frac{1}{n} dp \quad , \quad (8.85)$$

where s is the entropy per particle and n is the number density. Note as well that

$$-\frac{\partial f^0}{\partial \varepsilon} = \frac{f^0}{k_B T} \quad , \quad (8.86)$$

which we shall invoke further on below.

We wish to evaluate one of the contributions to the LHS of eqn. 8.82:

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

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

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

$$\frac{\partial \log n}{\partial t} = \frac{\partial \log p}{\partial t} - \frac{\partial \log T}{\partial t} = -\nabla \cdot \mathbf{V} \quad , \quad (8.88)$$

where we have invoked the ideal gas law $n = p/k_B T$ above.

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

$$\frac{\partial (ns)}{\partial t} + \nabla \cdot (ns\mathbf{V}) = n \left(\frac{\partial s}{\partial t} + \mathbf{V} \cdot \nabla s \right) + s \left(\frac{\partial n}{\partial t} + \nabla \cdot (n\mathbf{V}) \right) = 0 \quad . \quad (8.89)$$

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

$$ds = \left(\frac{\partial s}{\partial T} \right)_p dT + \left(\frac{\partial s}{\partial p} \right)_T dp = \frac{c_p}{T} dT - \frac{k_B}{p} dp \quad , \quad (8.90)$$

since $c_p = T(\partial s/\partial T)_p$ and $(\partial s/\partial p)_T = (\partial v/\partial T)_p$, where $v = V/N$. Here, c_p is the heat capacity per particle at constant pressure⁵. Thus,

$$\frac{c_p}{k_B} \frac{\partial \log T}{\partial t} - \frac{\partial \log p}{\partial t} = 0 \quad . \quad (8.91)$$

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

$$\frac{\partial \log T}{\partial t} = -\frac{k_B}{c_V} \nabla \cdot \mathbf{V} \quad , \quad \frac{\partial \log p}{\partial t} = -\frac{c_p}{c_V} \nabla \cdot \mathbf{V} \quad . \quad (8.92)$$

⁵In the chapter on thermodynamics, we adopted a slightly different definition of c_p as the heat capacity per mole. In this chapter c_p is the heat capacity per particle.

Thus eqn. 8.87 becomes

$$\frac{\partial f^0}{\partial t} + \frac{\mathbf{p}}{m} \cdot \frac{\partial f^0}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial f^0}{\partial \mathbf{p}} = \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \left\{ \frac{\varepsilon - h}{T} \mathbf{v} \cdot \nabla T + m v_\alpha v_\beta \mathcal{Q}_{\alpha\beta} + \frac{h - T c_p - \varepsilon}{c_V/k_B} \nabla \cdot \mathbf{V} - \mathbf{F} \cdot \mathbf{v} \right\}, \quad (8.93)$$

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

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

Therefore, the Boltzmann equation takes the form

$$\frac{\partial \delta f}{\partial t} + \left\{ \frac{\varepsilon(\Gamma) - h}{T} \mathbf{v} \cdot \nabla T + m v_\alpha v_\beta \mathcal{Q}_{\alpha\beta} - \frac{\varepsilon(\Gamma) - h + T c_p}{c_V/k_B} \nabla \cdot \mathbf{V} - \mathbf{F} \cdot \mathbf{v} \right\} \frac{f^0}{k_B T} = \left(\frac{df}{dt} \right)_{\text{coll}}. \quad (8.95)$$

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

8.5 Relaxation Time Approximation

8.5.1 Approximation of collision integral

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

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

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

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

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

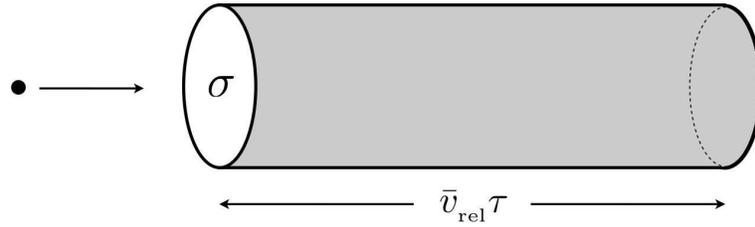


Figure 8.3: Graphic representation of the equation $n \sigma \bar{v}_{\text{rel}} \tau = 1$, which yields the scattering time τ in terms of the number density n , average particle pair relative velocity \bar{v}_{rel} , and two-particle total scattering cross section σ . The equation says that on average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

8.5.2 Computation of the scattering time

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

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

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

$$P(\mathbf{v}) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{m\mathbf{v}^2}{2k_B T} \right) \quad , \quad (8.99)$$

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

$$\bar{v}_{\text{rel}} \equiv \langle |\mathbf{v} - \mathbf{v}'| \rangle = \frac{4}{\sqrt{\pi}} \left(\frac{k_B T}{m} \right)^{1/2} \quad . \quad (8.100)$$

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

$$\frac{1}{\tau} = n \bar{v}_{\text{rel}} \sigma \quad . \quad (8.101)$$

The particle *mean free path* is then

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

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

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

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

8.5.3 Thermal conductivity

We consider a system with a temperature gradient ∇T and seek a steady state (*i.e.* time-independent) solution to the Boltzmann equation. We assume $F_\alpha = Q_{\alpha\beta} = 0$. Appealing to eqn. 8.95, and using the relaxation time approximation for the collision integral, we have

$$\delta f = -\frac{\tau(\varepsilon - c_p T)}{k_B T^2} (\mathbf{v} \cdot \nabla T) f^0 \quad . \quad (8.104)$$

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

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

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

$$j_\varepsilon^\alpha(\mathbf{r}) = \int d^3p \varepsilon v^\alpha \delta f = -\frac{n\tau}{k_B T^2} \langle v^\alpha v^\beta \varepsilon (\varepsilon - c_p T) \rangle \frac{\partial T}{\partial x^\beta} \quad , \quad (8.106)$$

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

$$\langle \phi(\mathbf{p}) \rangle = \int d^3p \phi(\mathbf{p}) f^0(\mathbf{p}) / \int d^3p f^0(\mathbf{p}) = \int d^3v P(\mathbf{v}) \phi(m\mathbf{v}) \quad . \quad (8.107)$$

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

$$P(\mathbf{v}) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-m(\mathbf{v}-\mathbf{V})^2/2k_B T} \quad (8.108)$$

is the Maxwell velocity distribution.

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

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

where

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

is the Maxwellian distribution expressed in terms of ε , and is normalized according to $\int_0^\infty d\varepsilon \mathcal{P}(\varepsilon) = 1$.⁶

Averages with respect to this distribution are given by

$$\langle \phi(\varepsilon) \rangle = \int_0^\infty d\varepsilon \phi(\varepsilon) \mathcal{P}(\varepsilon) = \frac{2}{\sqrt{\pi}} (k_B T)^{-3/2} \int_0^\infty d\varepsilon \varepsilon^{1/2} \phi(\varepsilon) e^{-\varepsilon/k_B T} \quad . \quad (8.111)$$

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

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

$$\langle \varepsilon^s \rangle = \frac{2}{\sqrt{\pi}} \Gamma\left(s + \frac{3}{2}\right) (k_B T)^s \quad . \quad (8.112)$$

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

$$\kappa = \frac{2n\tau}{3mk_B T^2} \langle \varepsilon^2 (\varepsilon - c_p T) \rangle = \frac{5n\tau k_B^2 T}{2m} = \frac{\pi}{8} n \ell \bar{v} c_p \quad , \quad (8.113)$$

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

8.5.4 Viscosity

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

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

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

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

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

When \mathbf{V} is spatially varying,

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

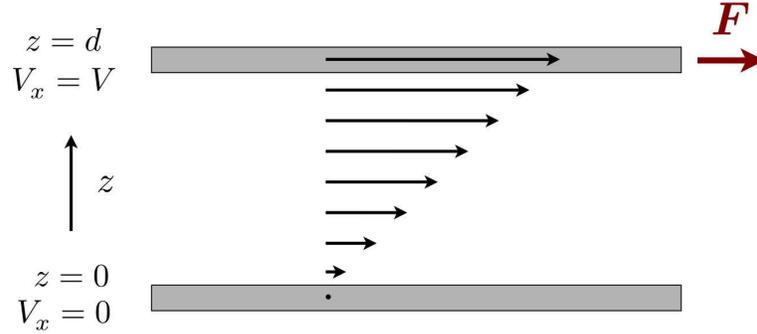


Figure 8.4: *Gedankenexperiment* to measure shear viscosity η in a fluid. The lower plate is fixed. The viscous drag force per unit area on the upper plate is $F_{\text{drag}}/A = -\eta V/d$. This must be balanced by an applied force F .

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

$$\begin{aligned}\tilde{\sigma}_{\alpha\beta} &= \eta \left(\frac{\partial V_\alpha}{\partial x_\beta} + \frac{\partial V_\beta}{\partial x_\alpha} - \frac{2}{3} \nabla \cdot \mathbf{V} \delta_{\alpha\beta} \right) + \zeta \nabla \cdot \mathbf{V} \delta_{\alpha\beta} \\ &= 2\eta \left(\mathcal{Q}_{\alpha\beta} - \frac{1}{3} \text{Tr}(\mathcal{Q}) \delta_{\alpha\beta} \right) + \zeta \text{Tr}(\mathcal{Q}) \delta_{\alpha\beta} \quad ,\end{aligned}\tag{8.116}$$

where $\mathcal{Q}_{\alpha\beta}$ is defined in eqn. 8.94. The coefficient of the traceless component is η , known as the *shear viscosity*. The coefficient of the component proportional to the identity is ζ , known as the *bulk viscosity*. The full stress tensor $\sigma_{\alpha\beta}$ contains a contribution from the pressure:

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

The differential force dF_α that a fluid exerts on a surface element $\hat{\mathbf{n}} dA$ is $dF_\alpha = -\sigma_{\alpha\beta} n_\beta dA$, where we are using the Einstein summation convention and summing over the repeated index β . We will now compute the shear viscosity η using the Boltzmann equation in the relaxation time approximation.

Appealing again to eqn. 8.95, with $\mathbf{F} = 0$ and $h = c_p T$, we find

$$\delta f = -\frac{\tau}{k_B T} \left\{ m v_\alpha v_\beta \mathcal{Q}_{\alpha\beta} + \frac{\varepsilon - c_p T}{T} \mathbf{v} \cdot \nabla T - \frac{\varepsilon}{c_V/k_B} \nabla \cdot \mathbf{V} \right\} f^0 \quad .\tag{8.118}$$

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

$$\begin{aligned}\Pi_{xz} &= n \int d^3p p_x v_z \delta f = -\frac{nm^2\tau}{k_B T} \mathcal{Q}_{\alpha\beta} \langle v_x v_z v_\alpha v_\beta \rangle \\ &= -\frac{n\tau}{k_B T} \left(\frac{\partial V_x}{\partial z} + \frac{\partial V_z}{\partial x} \right) \langle m v_x^2 \cdot m v_z^2 \rangle = -n\tau k_B T \left(\frac{\partial V_z}{\partial x} + \frac{\partial V_x}{\partial z} \right) \quad .\end{aligned}\tag{8.119}$$

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

$$\Pi_{xz} = -n\tau k_B T \frac{\partial V_x}{\partial z}\tag{8.120}$$

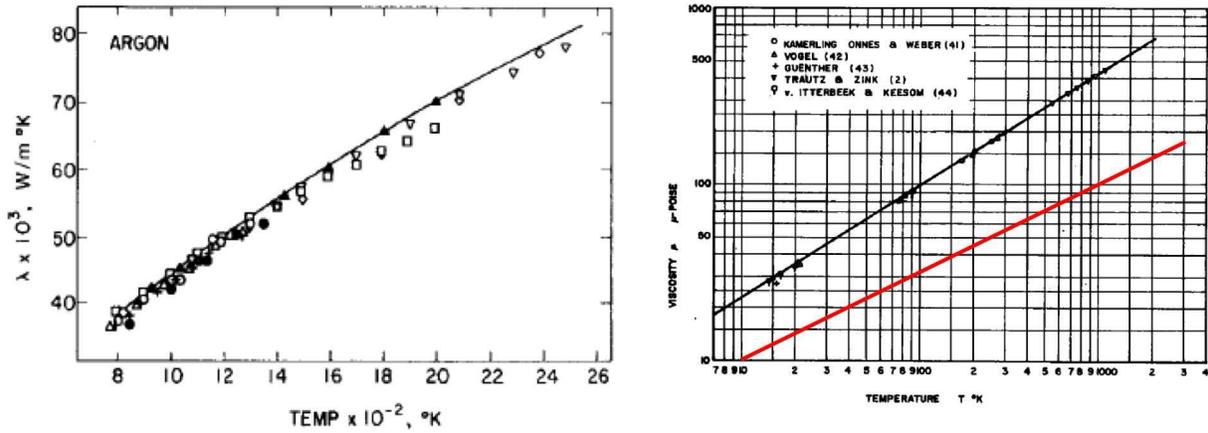


Figure 8.5: Left: thermal conductivity (λ in figure) of Ar between $T = 800$ K and $T = 2600$ K. The best fit to a single power law $\lambda = aT^b$ results in $b = 0.651$. Source: G. S. Springer and E. W. Wingeier, *J. Chem Phys.* **59**, 1747 (1972). Right: log-log plot of shear viscosity (μ in figure)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

from which we read off the viscosity,

$$\eta = nk_B T \tau = \frac{\pi}{8} n m \ell \bar{v} \quad . \quad (8.121)$$

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

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

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

8.5.5 Oscillating external force

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

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

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

$$\frac{\partial \delta f}{\partial t} + \mathbf{F} e^{-i\omega t} \cdot \mathbf{v} \frac{\partial f^0}{\partial \varepsilon} = -\frac{\delta f}{\tau} \quad (8.123)$$

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

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

We now compute the particle current:

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

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

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

where

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

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

8.5.6 Quick and dirty calculation of transport coefficients

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

respect to \hat{z} , *i.e.* $\cos \theta = v_z/v$. We perform the same analysis for particles moving in the $-\hat{z}$ direction, for which $\phi = \phi(z + \ell \cos \theta)$. The current of ϕ through this surface is then

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

where $\bar{v} = (8k_B T/\pi m)^{1/2}$ is the average particle speed. If the z -dependence of ϕ comes through the dependence of ϕ on the local temperature T , then we have

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

where

$$K = \frac{1}{3}n\ell\bar{v} \frac{\partial \phi}{\partial T} \quad (8.130)$$

is the transport coefficient. If $\phi = \langle \varepsilon \rangle$, then $\partial \phi / \partial T = c_p$, where c_p is the heat capacity per particle at constant pressure. We then find $\mathbf{j}_\varepsilon = -\kappa \nabla T$ with thermal conductivity $\kappa = \frac{1}{3}n\ell\bar{v}c_p$. Our Boltzmann equation calculation yielded the same result (eqn. 8.113), but with a prefactor of $\frac{\pi}{8}$ instead of $\frac{1}{3}$.

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

$$j_{p_x}^z = \Pi_{xz} = -\frac{1}{3}nm\ell\bar{v} \frac{\partial V_x}{\partial z} \quad , \quad (8.131)$$

from which we identify the viscosity, $\eta = \frac{1}{3}nm\ell\bar{v}$. Once again, this agrees in its functional dependences with the Boltzmann equation calculation in the relaxation time approximation. Only the coefficients differ. The ratio of the coefficients is $K_{\text{QDC}}/K_{\text{BRT}} = \frac{8}{3\pi} = 0.849$ in both cases⁷.

8.5.7 Thermal diffusivity, kinematic viscosity, and Prandtl number

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

$$nc_p \frac{\partial T}{\partial t} + \nabla \cdot \mathbf{j}_q = 0 \quad . \quad (8.132)$$

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

$$\frac{\partial T}{\partial t} = \frac{\kappa}{nc_p} \nabla^2 T \quad . \quad (8.133)$$

⁷Here we abbreviate QDC for ‘quick and dirty calculation’ and BRT for ‘Boltzmann equation in the relaxation time approximation’.

Gas	η ($\mu\text{Pa} \cdot \text{s}$)	κ ($\text{mW}/\text{m} \cdot \text{K}$)	c_p/k_B	Pr
He	19.5	149	2.50	0.682
Ar	22.3	17.4	2.50	0.666
Xe	22.7	5.46	2.50	0.659
H ₂	8.67	179	3.47	0.693
N ₂	17.6	25.5	3.53	0.721
O ₂	20.3	26.0	3.50	0.711
CH ₄	11.2	33.5	4.29	0.74
CO ₂	14.8	18.1	4.47	0.71
NH ₃	10.1	24.6	4.50	0.90

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

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

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

8.6 The Equations of Hydrodynamics

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

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0 \quad (8.134)$$

$$\frac{\partial(\rho V_\alpha)}{\partial t} + \frac{\partial \Pi_{\alpha\beta}}{\partial x^\beta} = 0 \quad , \quad (8.135)$$

where

$$\Pi_{\alpha\beta} = \rho V_\alpha V_\beta + p \delta_{\alpha\beta} - \overbrace{\left\{ \eta \left(\frac{\partial V_\alpha}{\partial x_\beta} + \frac{\partial V_\beta}{\partial x_\alpha} - \frac{2}{3} \nabla \cdot \mathbf{V} \delta_{\alpha\beta} \right) + \zeta \nabla \cdot \mathbf{V} \delta_{\alpha\beta} \right\}}^{\tilde{\sigma}_{\alpha\beta}} \quad . \quad (8.136)$$

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

$$\rho \frac{\partial \mathbf{V}}{\partial t} + \rho (\mathbf{V} \cdot \nabla) \mathbf{V} = -\nabla p + \eta \nabla^2 \mathbf{V} + (\zeta + \frac{1}{3}\eta) \nabla(\nabla \cdot \mathbf{V}) \quad , \quad (8.137)$$

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

$$T \frac{\partial s}{\partial T} + T \nabla \cdot (s \mathbf{V}) = \tilde{\sigma}_{\alpha\beta} \frac{\partial V_\alpha}{\partial x^\beta} + \nabla \cdot (\kappa \nabla T) \quad , \quad (8.138)$$

where $\tilde{\sigma}_{\alpha\beta}$ is the viscosity stress tensor of eqn. 8.116 (also identified in eqn. 8.136 above). Note that the LHS of eqn. 8.137 is $\rho D\mathbf{V}/Dt$, where D/Dt is the convective derivative. Multiplying by a differential volume, this gives the mass times the acceleration of a differential local fluid element. The RHS, multiplied by the same differential volume, gives the differential force on this fluid element in a frame instantaneously moving with constant velocity \mathbf{V} . Thus, this is Newton's Second Law for the fluid.

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

$$\frac{\partial \mathbf{V}}{\partial t} + (\mathbf{V} \cdot \nabla) \mathbf{V} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{V} \quad . \quad (8.139)$$

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

$$\nu_{\text{H}_2\text{O}} = 10^{-2} \text{ cm}^2/\text{sec} \quad , \quad \nu_{\text{air}} = 0.15 \text{ cm}^2/\text{sec} \quad , \quad \nu_{\text{glycerine}} = 6.8 \text{ cm}^2/\text{sec} \quad . \quad (8.140)$$