

If each molecule carries with it a property  $\psi_j$ , then the flux of this property is

$$\psi_j f_j(\mathbf{n} \cdot \mathbf{V}_j) d\mathbf{v}_j$$

and the total flux across this surface is

$$\text{total flux} = \int \psi_j f_j(\mathbf{n} \cdot \mathbf{V}_j) d\mathbf{v}_j = \mathbf{n} \cdot \int \psi_j f_j \mathbf{V}_j d\mathbf{v}_j = \mathbf{n} \cdot \boldsymbol{\psi}_j \quad (18-22)$$

The vector  $\boldsymbol{\psi}_j$ ,

$$\boldsymbol{\psi}_j = \int \psi_j f_j \mathbf{V}_j d\mathbf{v}_j \quad (18-23)$$

is called the flux vector associated with the property  $\psi_j$ . The component of this vector in any direction is the transport of the property  $\psi_j$  in that direction. Let us now consider the various examples of  $\psi_j$ .

#### TRANSPORT OF MASS

In this case,  $\psi_j = m_j$ , and

$$\boldsymbol{\psi}_j = m_j \int f_j \mathbf{V}_j d\mathbf{v}_j = \rho_j m_j \overline{\mathbf{V}_j} \equiv \mathbf{j}_j \quad (18-24)$$

#### TRANSPORT OF MOMENTUM

Here  $\psi_j = m_j V_{jx}$ , and

$$\boldsymbol{\psi}_j = m_j \int V_{jx} f_j \mathbf{V}_j d\mathbf{v}_j = \rho_j m_j \overline{V_{jx} \mathbf{V}_j} \quad (18-25)$$

which is the flux of the  $x$ -component of momentum relative to  $\mathbf{v}_0$ . The flux of momentum is a pressure, which has components

$$(p_j)_{xx} = \rho_j m_j \overline{V_{jx} V_{jx}}$$

$$(p_j)_{xy} = \rho_j m_j \overline{V_{jx} V_{jy}}, \text{ etc}$$

or, in general,

$$p_j = \rho_j m_j \overline{\mathbf{V}_j \mathbf{V}_j} \quad (18-26)$$

which is the partial pressure tensor of the  $j$ th species.

#### TRANSPORT OF KINETIC ENERGY

$$\psi_j = \frac{1}{2} m_j V_j^2$$

and

$$\boldsymbol{\psi}_j = \frac{m_j}{2} \int v_j^2 \mathbf{V}_j f_j d\mathbf{v}_j = \frac{1}{2} \rho_j m_j \overline{v_j^2 \mathbf{V}_j} = \mathbf{q}_j \quad (18-27)$$

the heat flux vector of the  $j$ th species.

It should be clear at this point that once we have an expression for  $f_j(\mathbf{r}, \mathbf{v}_j, t)$ , we can calculate all the fluxes and hence all the transport properties of a dilute gas. What we need now is  $f_j$ , or at least an equation that gives  $f_j$  as its solution. The only equation we have up to now is Eq. (18-14) with  $n = 1$ , and it can be seen that this also contains  $f_j^{(2)}$ . As we said earlier, nobody has found a successful way to uncouple this system. In the next section we shall derive an equation for  $f_j$ , the Boltzmann equation, which is the fundamental equation of the rigorous kinetic theory of gases.

### 18-4 THE BOLTZMANN EQUATION

In this section we shall derive the Boltzmann equation for  $f_j$  by a simple, physical argument. The gas is assumed to be dilute enough that only two-body interactions are ever important. The number of  $j$ -molecules in the phase space volume element  $d\mathbf{r} d\mathbf{v}_j$  at the point  $(\mathbf{r}, \mathbf{v}_j)$  is given by  $f_j d\mathbf{r} d\mathbf{v}_j$ . In the absence of collisions in the gas, the molecules at the point  $(\mathbf{r}, \mathbf{v}_j)$  at time  $t$  move according to the equations of motion of the system and arrive at the point  $(\mathbf{r} + \mathbf{v}_j dt, \mathbf{v}_j + (1/m_j)\mathbf{X}_j dt)$  at the time  $(t + dt)$ . The quantity  $\mathbf{X}_j$  is an external force. Because all the points that start out end up at the same point (in the absence of collisions), we have that

$$f_j(\mathbf{r}, \mathbf{v}_j, t) = f_j\left(\mathbf{r} + \mathbf{v}_j dt, \mathbf{v}_j + \frac{\mathbf{X}_j}{m_j} dt, t + dt\right) \quad (\text{no collisions}) \quad (18-28)$$

But since collisions occur in the gas, not all those molecules that start out at the point  $(\mathbf{r}, \mathbf{v}_j)$  at time  $t$  end up at  $(\mathbf{r} + \mathbf{v}_j dt, \mathbf{v}_j + (1/m_j)\mathbf{X}_j dt)$  at the time  $(t + dt)$ . Some molecules leave this stream because of collisions, and furthermore some molecules enter this stream because of collisions. Let the number of  $j$ -molecules lost from the velocity range  $(\mathbf{v}_j, \mathbf{v}_j + d\mathbf{v}_j)$  and the position range  $(\mathbf{r}, \mathbf{r} + d\mathbf{r})$  because of collisions with  $i$ -molecules during the time interval  $(t, t + dt)$  be  $\Gamma_{ji}^{(-)} d\mathbf{r} d\mathbf{v}_j dt$ . Similarly, let the number of  $j$ -molecules that join the group of molecules that starts at  $(\mathbf{r}, \mathbf{v}_j)$  at time  $t$  because of collisions with  $i$ -molecules be  $\Gamma_{ji}^{(+)} d\mathbf{r} d\mathbf{v}_j dt$ . If we now include these collision terms in Eq. (18-28), we can write

$$f_j(\mathbf{r} + \mathbf{v}_j dt, \mathbf{v}_j + m_j^{-1}\mathbf{X}_j dt, t + dt) d\mathbf{r} d\mathbf{v}_j = f_j(\mathbf{r}, \mathbf{v}_j, t) d\mathbf{r} d\mathbf{v}_j + \sum_i (\Gamma_{ji}^{(+)} - \Gamma_{ji}^{(-)}) d\mathbf{r} d\mathbf{v}_j dt \quad (18-29)$$

If we expand the left-hand side of the equation, we can get (Problem 18-8)

$$\frac{\partial f_j}{\partial t} + \mathbf{v}_j \cdot \nabla_{\mathbf{r}} f_j + \frac{\mathbf{X}_j}{m_j} \cdot \nabla_{\mathbf{v}_j} f_j = \sum_i (\Gamma_{ji}^{(+)} - \Gamma_{ji}^{(-)}) \quad (18-30)$$

The left-hand side of the equation represents the change in  $f_j$  due to the collisionless motion of the molecules, called streaming, and the right-hand side represents the change in  $f_j$  due to collisions. Notice that this equation looks very similar to the Liouville equation for  $f_j^{(1)}$ .

We now want to find an explicit expression for the collision terms in this equation. Let us look at  $\Gamma_{ji}^{(-)} d\mathbf{r} d\mathbf{v}_j dt$  first. Consider a molecule of type  $j$  located at  $\mathbf{r}$  with velocity  $\mathbf{v}_j$ . The probability that this molecule will collide with an  $i$ -molecule in the time interval  $dt$  and with impact parameter in a range  $db$  about  $b$  is given by the following argument. (See Fig. 18-2). If molecule  $j$  is considered to be fixed, the  $i$ -molecule approaches it with a relative velocity  $(\mathbf{v}_i - \mathbf{v}_j) = \mathbf{g}_{ij}$ . If  $A$  in Fig. 18-2 is the range of the intermolecular potential, any  $i$ -molecule within the cylindrical shell indicated in the figure will collide with the fixed  $j$ -molecule during the time interval  $dt$ . The probable number of  $i$ -molecules within this cylindrical shell is

$$2\pi f_i(\mathbf{r}, \mathbf{v}_i, t) g_{ij} b db dt$$

where  $g_{ij} = |\mathbf{g}_{ij}|$ . The total number of collisions that would occur with this one fixed  $j$ -molecule is

$$2\pi dt \iint f_i(\mathbf{r}, \mathbf{v}_i, t) g_{ij} b db d\mathbf{v}_i$$

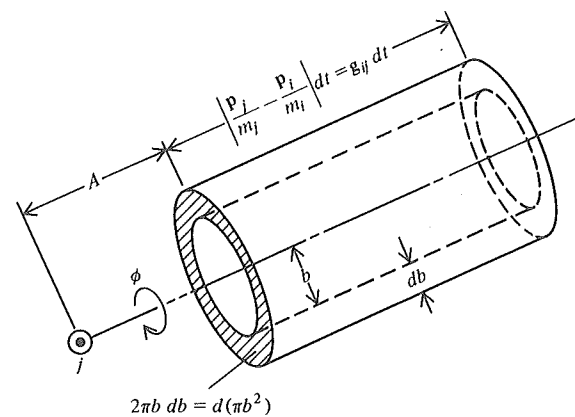


Figure 18-2. Collisions of molecules of type  $i$  with one molecule of type  $j$ . The distance  $A$  is essentially the intermolecular distance at which the potential begins to "take hold." (From J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*. New York: Wiley, 1954.)

The probable number of molecules of type  $j$  located in the volume element  $d\mathbf{r}$  about  $\mathbf{r}$  with velocity between  $\mathbf{v}_j$  and  $\mathbf{v}_j + d\mathbf{v}_j$  is  $f_j(\mathbf{r}, \mathbf{v}_j, t) d\mathbf{r} d\mathbf{v}_j$ . Therefore we write

$$\Gamma_{ji}^{(-)} d\mathbf{r} d\mathbf{v}_j dt = 2\pi d\mathbf{r} d\mathbf{v}_j dt \iint f_j(\mathbf{r}, \mathbf{v}_j, t) f_i(\mathbf{r}, \mathbf{v}_i, t) g_{ij} b db d\mathbf{v}_i$$

and see that

$$\Gamma_{ji}^{(-)} = 2\pi \iint f_j f_i g_{ij} b db d\mathbf{v}_i \quad (18-31)$$

We should notice at this point that we have assumed that the mean number of  $i$ -molecules about the fixed  $j$ -molecule is given by the product of  $f_i$  and  $f_j$ ; i.e., we are assuming that their positions and velocities are uncorrelated. The assumption, known as the molecular chaos assumption or the stosszahlansatz, is not strictly true and is the weakest point in the entire derivation. This turns out to be a very important point, and we shall discuss this later on when we do the critique on the Boltzmann equation.

We can apply the very same argument that we used to derive Eq. (18-31) to the inverse collisions, i.e., those that scatter particles into the point  $(\mathbf{r} + \mathbf{v}_j dt, \mathbf{v}_j + (1/m_j)\mathbf{X}_j dt)$ . We can immediately write

$$\Gamma_{ji}^{(+)} d\mathbf{r} d\mathbf{v}_j dt = 2\pi d\mathbf{r} d\mathbf{v}_j' dt \iint f_i(\mathbf{r}, \mathbf{v}_i', t) f_j(\mathbf{r}, \mathbf{v}_j', t) g_{ij}' b' db' d\mathbf{v}_i' \quad (18-32)$$

where we use primes to indicate those quantities before the collision which will go over into  $b$ ,  $\mathbf{v}_i$ , and  $\mathbf{v}_j$  after the collision. They can be computed from  $b$ ,  $\mathbf{v}_i$ , and  $\mathbf{v}_j$  by solving the collisional equations of motion. Liouville's theorem says that

$$d\mathbf{r} d\mathbf{v}_i d\mathbf{v}_j g_{ij} dt b db = d\mathbf{r} d\mathbf{v}_i' d\mathbf{v}_j' g_{ij}' dt b' db' \quad (18-33)$$

Using this, we can rewrite Eq. (18-32) in the form

$$\Gamma_{ji}^{(+)} = 2\pi \iint f_i(\mathbf{r}, \mathbf{v}_i', t) f_j(\mathbf{r}, \mathbf{v}_j', t) g_{ij} b db d\mathbf{v}_i \quad (18-34)$$

$$= 2\pi \iint f_i' f_j' g_{ij} b db d\mathbf{v}_i \quad (18-35)$$

where the primes on the  $f_i$  and  $f_j$  indicate that the velocity arguments of these functions are primed.

Substituting Eqs. (18-31) and (18-35) into Eq. (18-30) finally gives the Boltzmann equation:

$$\frac{\partial f_j}{\partial t} + \mathbf{v}_j \cdot \nabla_{\mathbf{r}} f_j + \frac{1}{m_j} \mathbf{X}_j \cdot \nabla_{\mathbf{v}_j} f_j = 2\pi \sum_j \iint \{f_i' f_j' - f_i f_j\} g_{ij} b db d\mathbf{v}_i \quad (18-36)$$

This is an integrodifferential equation for  $f_j^{(1)}$ . We have one such equation for each component of the gas. Notice that the equations of motion, and hence the intermolecular potential, enter this equation implicitly in the integrand on the right-hand side. The functions  $f_i'$  and  $f_j'$  depend upon the postcollisional velocities  $\mathbf{v}_i'$  and  $\mathbf{v}_j'$ , which depend upon the precollisional velocities  $\mathbf{v}_i$  and  $\mathbf{v}_j$  through the equations of motion governing the collision. Notice also that once the right-hand side is integrated over  $b$  and  $\mathbf{v}_i$ , the only variables left are  $\mathbf{r}$ ,  $\mathbf{v}_j$ , and  $t$ , exactly those variables on which the left-hand side depends.

For several reasons which we shall discuss, the Boltzmann equation is a remarkable equation. The derivation we have presented here is the standard derivation and has the advantage of being simple and physical.

The Boltzmann equation is not only an integrodifferential equation, but a nonlinear one as well. Solving such an equation is not simple, but it turns out that there exists a very elegant and straightforward approximate scheme due to Hilbert, Chapman, and Enskog, which we shall present in the next chapter. Before doing this, however, we can extract some very interesting consequences from the Boltzmann equation without a great deal of work.

#### 18-5 SOME GENERAL CONSEQUENCES OF THE BOLTZMANN EQUATION

First, we shall discuss the equations of change. The fundamental equations of continuum mechanics that we derived in Chapter 17 may be obtained from the Boltzmann equation without determining the form of  $f$ . If we multiply the Boltzmann equation for  $f_i$  by  $\psi_i$  and integrate over  $\mathbf{v}_i$ , we obtain

$$\int \psi_i \left\{ \frac{\partial f_i}{\partial t} + \mathbf{v}_i \cdot \nabla_{\mathbf{r}} f_i + \frac{1}{m_i} \mathbf{X}_i \cdot \nabla_{\mathbf{v}_i} f_i \right\} d\mathbf{v}_i = 2\pi \sum_j \iint \psi_i (f_i' f_j' - f_i f_j) g_{ij} b db d\mathbf{v}_i d\mathbf{v}_j \quad (18-37)$$

Each of the three terms on the left-hand side of Eq. (18-37) can be transformed into more convenient forms:

$$\begin{aligned} \int \psi_i \frac{\partial f_i}{\partial t} d\mathbf{v}_i &= \frac{\partial}{\partial t} \int \psi_i f_i d\mathbf{v}_i - \int f_i \frac{\partial \psi_i}{\partial t} d\mathbf{v}_i \\ &= \frac{\partial}{\partial t} (\rho_i \bar{\psi}_i) - \rho_i \frac{\partial \bar{\psi}_i}{\partial t} \end{aligned} \quad (18-38)$$

$$\begin{aligned} \int \psi_i v_{ix} \frac{\partial f_i}{\partial x} d\mathbf{v}_i &= \frac{\partial}{\partial x} \int \psi_i v_{ix} f_i d\mathbf{v}_i - \int f_i v_{ix} \frac{\partial \psi_i}{\partial x} d\mathbf{v}_i \\ &= \frac{\partial}{\partial x} (\rho_i \overline{\psi_i v_{ix}}) - \rho_i v_{ix} \frac{\partial \bar{\psi}_i}{\partial x} \end{aligned} \quad (18-39)$$

$$\begin{aligned} \int \psi_i \frac{\partial f_i}{\partial v_{ix}} d\mathbf{v}_i &= \iint |\psi_i f_i|_{-\infty}^{\infty} dv_{iy} dv_{iz} - \int f_i \frac{\partial \psi_i}{\partial v_{ix}} d\mathbf{v}_i \\ &= -\rho_i \frac{\partial \bar{\psi}_i}{\partial v_{ix}} \end{aligned} \quad (18-40)$$

We have assumed that the external force  $\mathbf{X}_i$  appearing in Eq. (18-37) is independent of  $\mathbf{v}_i$ . Putting these results together, we can write Eq. (18-37) as

$$\begin{aligned} & \frac{\partial(\rho_i \bar{\psi}_i)}{\partial t} + \nabla_{\mathbf{r}} \cdot \rho_i \bar{\psi}_i \mathbf{v}_i - \rho_i \left\{ \frac{\partial \bar{\psi}_i}{\partial t} + \mathbf{v}_i \cdot \nabla_{\mathbf{r}} \bar{\psi}_i + \frac{\mathbf{X}_i}{m_i} \cdot \nabla_{\mathbf{v}_i} \bar{\psi}_i \right\} \\ & = 2\pi \sum_j \iiint \psi_i (f_i' f_j' - f_i f_j) g_{ij} b \, db \, d\mathbf{v}_i \, d\mathbf{v}_j \end{aligned} \quad (18-41)$$

This is known as Enskog's general equation of change for the property  $\psi_i$ . We shall now show that if  $\psi_i$  is any of the collisional invariants, i.e.,  $m_i$ ,  $m_i \mathbf{v}_i$ , or  $\frac{1}{2} m_i v_i^2$ , the right-hand side of Eq. (18-41) vanishes when summed over  $i$ . To prove this, first notice that the integral

$$\iiint \psi_i (f_i' f_j' - f_i f_j) g_{ij} b \, db \, d\mathbf{v}_i \, d\mathbf{v}_j \quad (18-42)$$

is equal to the integral

$$\iiint \psi_i' (f_i f_j - f_i' f_j') g_{ij}' b' \, db' \, d\mathbf{v}_i' \, d\mathbf{v}_j' \quad (18-43)$$

which is written in terms in inverse collisions (Problem 18-9). This is so because an integral over a collision in one direction must be the same as an integral over a collision in the opposite direction. This can be seen from Fig. 16-3. Furthermore, from Liouville's theorem and from the dynamics of molecular collisions, we know that

$$g_{ij} = g_{ij}', \quad b = b', \quad d\mathbf{v}_i \, d\mathbf{v}_j = d\mathbf{v}_i' \, d\mathbf{v}_j' \quad (18-44)$$

and so Eq. (18-43) may be written as

$$-\iiint \psi_i' (f_i' f_j' - f_i f_j) g_{ij} b \, db \, d\mathbf{v}_i \, d\mathbf{v}_j \quad (18-45)$$

Since the integrals of Eqs. (18-42) and (18-45) are equal to each other, they must also each be equal to one-half the sum of the two. This gives us that (Problem 18-10)

$$\begin{aligned} & \iiint \psi_i (f_i' f_j' - f_i f_j) g_{ij} b \, db \, d\mathbf{v}_i \, d\mathbf{v}_j \\ & = \frac{1}{2} \iiint (\psi_i - \psi_i') (f_i' f_j' - f_i f_j) g_{ij} b \, db \, d\mathbf{v}_i \, d\mathbf{v}_j \end{aligned} \quad (18-46)$$

Note that if  $\psi_i = m_i$ , then the integrand equals zero. This is simply because the mass of the  $i$ th species is conserved in an elastic collision.

Now if we sum Eq. (18-46) over both  $i$  and  $j$  and then interchange the dummy indices  $i$  and  $j$ , we get

$$\begin{aligned} & \frac{1}{2} \sum_{i,j} \iiint (\psi_i - \psi_i') (f_i' f_j' - f_i f_j) g_{ij} b \, db \, d\mathbf{v}_i \, d\mathbf{v}_j \\ & = \frac{1}{2} \sum_{i,j} \iiint (\psi_j - \psi_j') (f_i' f_j' - f_i f_j) g_{ij} b \, db \, d\mathbf{v}_i \, d\mathbf{v}_j \end{aligned} \quad (18-47)$$

Since these two integrals are equal to each other, each equals one-half of the sum of the two, and so we can finally write (Problem 18-11)

$$\begin{aligned} & \sum_{i,j} \iiint \psi_i (f_i' f_j' - f_i f_j) g_{ij} b \, db \, d\mathbf{v}_i \, d\mathbf{v}_j \\ & = \frac{1}{4} \sum_{i,j} \iiint (\psi_i + \psi_j - \psi_i' - \psi_j') (f_i' f_j' - f_i f_j) g_{ij} b \, db \, d\mathbf{v}_i \, d\mathbf{v}_j \end{aligned} \quad (18-48)$$

Now  $\psi_i + \psi_j - \psi_i' - \psi_j'$  vanishes when  $\psi_i = m_i$ ,  $m_i \mathbf{v}_i$ , or  $\frac{1}{2} m_i v_i^2$ , and so we have shown that the sum of the right-hand side of Eq. (18-41) over  $i$  equals zero. This leaves, then,

$$\frac{\partial}{\partial t} \sum_i (\rho_i \bar{\psi}_i) + \nabla_{\mathbf{r}} \cdot \sum_i (\rho_i \bar{\psi}_i \mathbf{v}_i) - \sum_i \rho_i \left\{ \frac{\partial \bar{\psi}_i}{\partial t} + \mathbf{v}_i \cdot \nabla_{\mathbf{r}} \bar{\psi}_i + \frac{\mathbf{X}_i}{m_i} \cdot \nabla_{\mathbf{v}_i} \bar{\psi}_i \right\} = 0 \quad (18-49)$$

as the general equation of change.

If we let  $\psi_i = m_i$ , Eq. (18-41) becomes

$$\frac{\partial \rho_i}{\partial t} + \nabla_{\mathbf{r}} \cdot (\rho_i \mathbf{v}_i) = 0 \quad (18-50)$$

This is the continuity equation for the  $i$ th species. If we sum this over  $i$  and use Eq. (18-18), we get the continuity equation for the entire system:

$$\frac{\partial \rho}{\partial t} + \nabla_{\mathbf{r}} \cdot (\rho \mathbf{v}_0) = 0 \quad (18-51)$$

If we let  $\psi_i = m_i \mathbf{v}_i$  and sum over  $i$ , Eq. (18-49) becomes (Problem 18-12)

$$\rho_m \frac{D\mathbf{v}_0}{Dt} = \sum_j \rho_j \mathbf{X}_j - \nabla \cdot \mathbf{p} \quad (18-52)$$

where  $\mathbf{p}$  is the pressure tensor defined in Eq. (18-26). Similarly, if we let  $\psi_i = \frac{1}{2} m_i v_i^2$ , for example, we get the energy balance equation, Eq. (17-31). (See Problem 18-13.) It is reassuring, although not surprising, that these equations should come out of the Boltzmann equation. The next general consequence we shall derive is not particularly obvious and, in fact, is a rather profound result.

Next we discuss the so-called Boltzmann  $H$ -theorem and the equilibrium solution to the Boltzmann equation. Consider a one-component system. The Boltzmann  $H$ -function is defined by

$$H(t) = \iint f(\mathbf{r}, \mathbf{v}, t) \ln f(\mathbf{r}, \mathbf{v}, t) \, d\mathbf{r} \, d\mathbf{v} \quad (18-53)$$

Differentiate  $H(t)$  with respect to  $t$ :

$$\frac{dH}{dt} = \iint \frac{\partial f}{\partial t} \ln f \, d\mathbf{r} \, d\mathbf{v} + \iint \frac{\partial f}{\partial t} \, d\mathbf{r} \, d\mathbf{v} \quad (18-54)$$

The second term here vanishes since

$$\iint \frac{\partial f}{\partial t} \, d\mathbf{r} \, d\mathbf{v} = \frac{d}{dt} \iint f \, d\mathbf{r} \, d\mathbf{v} = \frac{dN}{dt} = 0$$

if the number of particles in the system is conserved. Equation (18-54) becomes then

$$\frac{dH}{dt} = \iint \frac{\partial f}{\partial t} \ln f \, d\mathbf{r} \, d\mathbf{v} \quad (18-55)$$

To evaluate this integral, multiply the Boltzmann equation by  $\ln f$  and integrate over  $d\mathbf{r}$  and  $d\mathbf{v}$ . This gives

$$\begin{aligned} \iint \frac{\partial f}{\partial t} \ln f \, d\mathbf{r} \, d\mathbf{v} & = - \iint (\ln f) \mathbf{v} \cdot \nabla_{\mathbf{r}} f \, d\mathbf{r} \, d\mathbf{v} - \iint (\ln f) \frac{\mathbf{X}}{m} \cdot \nabla_{\mathbf{v}} f \, d\mathbf{r} \, d\mathbf{v} \\ & \quad + 2\pi \iiint \ln f \{f' f_1' - f f_1\} g b \, d\mathbf{v} \, d\mathbf{v}_1 \end{aligned} \quad (18-56)$$

The subscript 1 in the collision integral here is to distinguish the two colliding molecules. The first two integrals on the right vanish since we assume as always that  $f$  vanishes at the walls of the container and as  $\mathbf{v} \rightarrow \pm\infty$  (Problem 18-14). This leaves

$$\frac{dH}{dt} = 2\pi \iiint \ln f \{f'f_1' - ff_1\} gb \, d\mathbf{v} \, d\mathbf{v}_1 \quad (18-57)$$

This integral may be symmetrized by the same method we used to derive Eq. (18-48) to give (Problem 18-15)

$$\frac{dH}{dt} = \frac{2\pi}{4} \iiint \ln \left( \frac{ff_1}{f'f_1'} \right) \{f'f_1' - ff_1\} gb \, d\mathbf{v} \, d\mathbf{v}_1 \quad (18-58)$$

Now this integrand is of the form  $-(x-y)\ln(x/y)$ . If  $x > y$ , this function is negative; if  $x < y$ , it is also negative; and if  $x = y$ , it is equal to zero. Therefore, we get the result that

$$\frac{dH}{dt} \leq 0 \quad (18-59)$$

The definition of  $H(t)$  shows that it is bounded, and hence  $H(t)$  must approach a limit as  $t \rightarrow \infty$ . In this limit,  $dH/dt = 0$ , and so we have an equilibrium or steady-state situation with

$$f'f_1' = ff_1 \quad (18-60)$$

or

$$\ln f' + \ln f_1' = \ln f + \ln f_1 \quad (18-61)$$

This tells us that  $\ln f$  is a summational invariant. However, we know that the only summational invariants of bimolecular collisions of spherically symmetric molecules are the mass, the momentum, and the kinetic energy. Therefore,  $\ln f$  must be a linear combination of these three quantities, or

$$\ln f = \alpha m + \boldsymbol{\beta} \cdot (m\mathbf{v}) - \gamma \frac{mv^2}{2} = \alpha m + \frac{m \boldsymbol{\beta} \cdot \boldsymbol{\beta}}{2} - \frac{m\gamma}{2} \left( \mathbf{v} - \frac{\boldsymbol{\beta}}{\gamma} \right)^2 \quad (18-62)$$

If we let  $\alpha m + m\boldsymbol{\beta} \cdot \boldsymbol{\beta}/2\gamma$  be  $\ln c$ , then

$$\ln f = \ln c - \frac{m\gamma}{2} \left( \mathbf{v} - \frac{\boldsymbol{\beta}}{\gamma} \right)^2$$

or

$$f(\mathbf{r}, \mathbf{v}) = c \exp \left[ -\frac{m\gamma}{2} \left( \mathbf{v} - \frac{\boldsymbol{\beta}}{\gamma} \right)^2 \right] \quad (18-63)$$

Notice how closely this resembles a Maxwellian distribution. We can determine our unknown parameters  $c$ ,  $\boldsymbol{\beta}$ , and  $\gamma$  from the following conditions. First, we have

$$\rho(\mathbf{r}, t) = \int f \, d\mathbf{v} = c \int \exp \left[ -\frac{m\gamma}{2} \left( \mathbf{v} - \frac{\boldsymbol{\beta}}{\gamma} \right)^2 \right] d\mathbf{v} \quad (18-64)$$

Evaluating the integral in Eq. (18-64) gives (Problem 18-16)

$$\rho(\mathbf{r}, t) = c \left( \frac{2\pi}{m\gamma} \right)^{3/2} \quad (18-65)$$

Similarly, we have (Problem 18-16)

$$\mathbf{v}_0 = \bar{\mathbf{v}} = \frac{1}{\rho} \int \mathbf{v} f \, d\mathbf{v} = \frac{\boldsymbol{\beta}}{\gamma} \quad (18-66)$$

Lastly, we define temperature by the usual relation

$$\frac{3}{2}kT = \frac{m}{2} \overline{(\mathbf{v} - \mathbf{v}_0)^2}$$

which gives (Problem 18-16)

$$\frac{3}{2}kT = \frac{3}{2}\gamma^{-1} \quad (18-67)$$

Equations (18-65), (18-66), and (18-67) then give

$$f(\mathbf{r}, \mathbf{v}) = \rho \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-m\mathbf{v}^2/2kT} \quad (18-68)$$

which is the classical expression for the Maxwellian distribution of velocities. Since  $\rho$  and  $T$  can be functions of position here, this is more generally a local Maxwellian distribution. This might be the distribution in a steady state rather than at equilibrium. We see then that the equilibrium solution to the Boltzmann equation is indeed the Maxwellian distribution, another reassuring, but nevertheless necessary, result.

The really interesting consequence of the Boltzmann equation is the  $H$ -theorem, whose significance we have glossed over. The  $H$ -theorem attributes a direction in time to the Boltzmann equation since it states that if we start out with some arbitrary distribution function, it will relax to the equilibrium (or steady-state) Maxwellian distribution. Of course, one can say that this is a necessary feature of any equation we derive to describe a gas since we know from the second law of thermodynamics that systems tend toward their equilibrium states. But the fact that it comes out of the Boltzmann equation was at first severely attacked for the following reasons.

The equations of motion of classical mechanics,

$$m \frac{d^2 \mathbf{r}_j}{dt^2} = -\text{grad}_j U(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad 1 \leq j \leq N \quad (18-69)$$

are symmetrical in time. If we let  $t \rightarrow -t$  in Eq. (18-69), one gets the same equations back again. This means that classical mechanical systems have no preferred direction in time; motion in one direction is no more preferred than motion in the opposite direction. On the other hand, the  $H$ -theorem shows that the Boltzmann equation does have a preferred direction. From a purely mechanical point of view, if all the molecules move in such a way to make  $H$  decrease, there is at least a possible mechanical motion where everything is reversed, and if everything is reversed,  $H$  must increase. This is part of the more general question of how the irreversible processes that we observe in nature can be reconciled with the basic reversibility of the underlying mechanical equations of motion. The  $H$ -theorem is a particular expression of this situation. This objection was first raised by Loschmidt. Boltzmann tried to answer this by claiming that Eqs. (18-31) and (18-35) should be interpreted as the probability of a collision rather than the actual number of collisions, and this means that  $H(t)$  does, indeed, not always decrease, but that the probability that it decrease is far greater than it increase. The further the system is from equilibrium, the more likely  $H(t)$  is to decrease. Boltzmann's arguments were not convincing to all of his critics, and it was left to

the Ehrenfests and Smoluchowski some years later to clearly explain the statistical nature of the Boltzmann equation. They were able to show that on the average, the  $H$ -function decreases with time to its equilibrium value, but that fluctuations can and will always occur. Furthermore,  $H$  will almost always remain near its equilibrium value once it gets there. We have encountered a somewhat similar situation when we discussed entropy in Chapter 2. Notice, in fact, that the equilibrium value of the  $H$ -function is equal to  $-S/k$  for an ideal gas. A decreasing  $H$ -function is in some sense an increasing entropy. The  $H$ -function can actually be computed as a function of time by molecular dynamics. In fact, one of the most powerful and interesting applications of molecular dynamics calculations is to nonequilibrium systems. Figure 18-3 shows  $H(t)$  calculated by Alder and Wainwright in their pioneering review article (in "Additional Reading").

If the objection by Loschmidt were not enough, there was also another paradox pointed out by Zermelo. This one was at the time more awkward than the time-reversal paradox. There is a general theorem in classical mechanics that says that any mechanical system enclosed in a finite volume will return arbitrarily close to its original state. This theorem is called the Poincaré recursion theorem, and the time it takes to essentially return to its original state is called the recurrence time. Such a cycle is called a Poincaré cycle. Zermelo vehemently pointed out that the  $H$ -theorem is at odds with the Poincaré recursion theorem, since how could  $H$  evolve toward an equilibrium value and remain there when classical mechanics dictates that the system must eventually retrace itself. Boltzmann was able to meet this objection as well by pointing out that for physically interesting systems, the recurrence times are ridiculously large. For example, Boltzmann estimated that a system consisting of  $10^{18}$  atoms per cubic centimeter with an average velocity of  $5 \times 10^4$  cm/sec would reproduce all of its

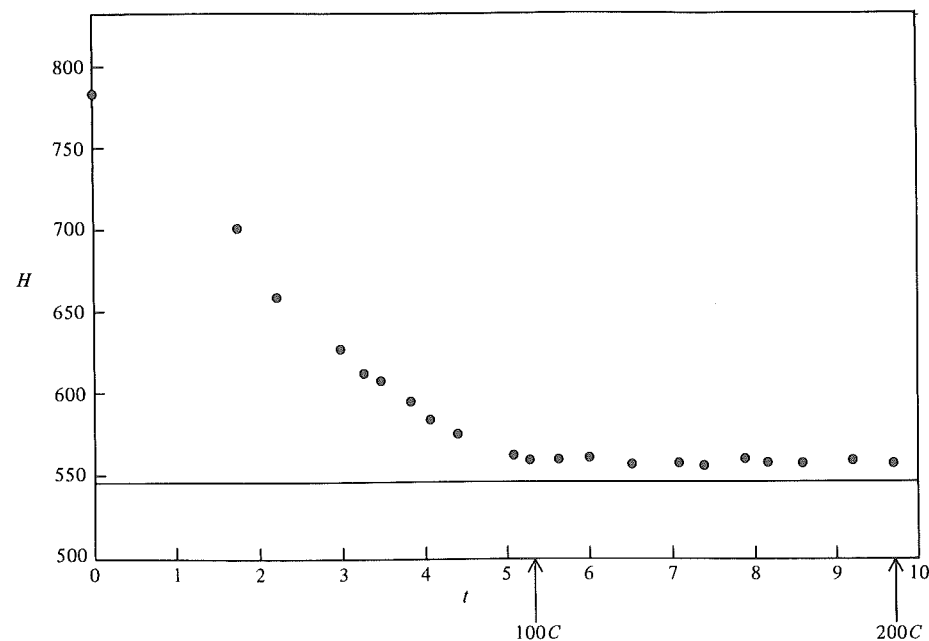


Figure 18-3. A molecular dynamics calculation of the Boltzmann  $H$ -function for a hard-sphere system of 100 particles at a density  $v/v_0 = 14.14$ . The  $H$ -function is plotted versus the collision number  $C$ . (From B. J. Alder and T. Wainwright, in *Transport Processes in Statistical Mechanics*, I. Prigogine, ed., New York: Interscience, 1958.)

coordinates within  $10^{-7}$  cm and all of its velocities to within 100 cm/sec in a time of the order of  $10^{10^{19}}$  years!

The scientific atmosphere of the time, however, was such that Boltzmann was not able to convince all of his critics, and it was finally Smoluchowski who clearly stated that the very concept of irreversibility is intimately involved with the length of the recurrence time. If one is initially in a state with a very long recurrence time, the process will appear to be irreversible. On the other hand, if the recurrence time is short, one does not speak about irreversibility. For any sensible physical system, the Poincaré recurrence times are extremely long.

The above results lead to the following picture of phase space. The overwhelming majority of phase space describes an equilibrium situation. Scattered throughout phase space are small regions that describe certain nonequilibrium configurations. Almost all of these nonequilibrium regions are completely surrounded by equilibrium regions, so that if we do happen to observe a system in a nonequilibrium state, it is almost always headed toward an equilibrium state. Once it reaches equilibrium, it will travel through various equilibrium states, only occasionally, rarely passing through other little regions of nonequilibrium. Such events are what we observe as fluctuations. This is so regardless of whether the phase point travels in a forward or backward direction, and so this picture is consistent with the classical mechanical requirement of time reversibility. Furthermore, the phase point must make its complete circuit through phase space before passing near its original position (since trajectories in phase space never cross). This length of time is the recurrence time. This would simply be observed as another fluctuation from equilibrium.

These little nonequilibrium regions in phase space vary in extent. The smaller the region, the less time the system spends away from equilibrium. It is conceivable, however, that some nonequilibrium region of phase space is such that a phase point can be trapped there. For example, consider a gas prepared such that the velocities of all of its molecules are parallel to each other and perpendicular to the walls of the container. If we assume that the walls are perfectly smooth, the molecules would then travel back and forth between the walls, remain parallel to each other, and hence never collide and come to equilibrium. The phase point describing this gas would be confined to some peculiar region of phase space and get hung up there. Clearly the  $H$ -theorem and the Boltzmann equation itself would not be applicable to such a pathological system. The Boltzmann equation tacitly requires that the system be sufficiently chaotic. This leaves open the question of how to decide when a system can be described by the Boltzmann equation (or statistical mechanics for that matter). All that can be safely said is that such a difficulty never seems to arise in practice. In our pathological system above, for example, any slight imperfection or roughness in the walls of the container would send the molecules off their parallel paths, and the system would become sufficiently chaotic in just a few series of collisions.

There are many long discussions about irreversibility, classical or quantum mechanics, and statistical mechanics in the literature, and the reader is referred to Tolman, Mazo, Huang, Uhlenbeck and Ford, and ter Haar for further discussions. (See "Additional Reading.")

It is interesting to note that Boltzmann (1844-1906) did his pioneering work at a time when atomic theories were not generally accepted. There were essentially two schools of scientific philosophy at that time: the atomists, led by Boltzmann himself, and the school of energeticists, led by Mach, Ostwald, Duhem, and others. Remember that this was a prequantum mechanical time, and the inadequacies of classical

mechanics were becoming increasingly evident. For example, Boltzmann was never to understand why the internal degrees of freedom of molecules could not be successfully treated by classical mechanics. The extent of the controversy can be well summarized in Boltzmann's foreword to Part II of his great work, *Lectures on Gas Theory*. He says, "As the first part of *Gas Theory* was being printed, I had already almost completed the present second and last part, in which the more difficult parts of the subject were to have been treated. It was just at this time that attacks on the theory of gases began to increase. I am convinced that these attacks are merely based on a misunderstanding, and that the role of gas theory in science has not yet been played out. . . .

"In my opinion it would be a great tragedy for science if the theory of gases were temporarily thrown into oblivion because of a momentary hostile attitude toward it, as was for example the wave theory because of Newton's authority.

"I am conscious of being only an individual struggling weakly against the stream of time. But it still remains in my power to contribute in such a way that, when the theory of gases is again revived, not too much will have to be rediscovered. Thus in this book [this Part] I will now include the parts that are the most difficult and most subject to misunderstanding and give (at least in outline) the most easily understood exposition of them. . . ." Boltzmann was clearly pessimistic about the future of the kinetic theory. This led to severe fits of depression, ending with his suicide in 1906.

The Boltzmann equation is accepted today as giving a completely adequate description of the behavior of dilute gases. In the next chapter we shall study some of the numerical results of the Boltzmann equation.

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#### PROBLEMS

- 18-1. Why is the operator  $\exp(-iLt)$  called the time displacement operator?
- 18-2. Derive Eq. (18-13).
- 18-3. Derive the BBGKY hierarchy for the reduced distribution function  $f^{(n)}$ .

18-4. Derive the Born-Green-Yvon-Kirkwood hierarchy for the equilibrium  $n$ -particle correlation function  $g^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$ , Eq. (13-39), from the BBGKY hierarchy for  $f^{(n)}(\mathbf{p}_1, \dots, \mathbf{p}_n, \mathbf{r}_1, \dots, \mathbf{r}_n)$ , Eq. (18-14).

18-5. Why is the average of the peculiar velocity called the diffusion velocity [cf. Eq. (18-20)]?

18-6. Prove that

$$\sum_j \rho_j m_j \bar{\mathbf{v}}_j = 0$$

18-7. Calculate both  $\mathbf{p}$  and  $\mathbf{q}$  given that  $f(\mathbf{r}, \mathbf{v}, t)$  is a local Maxwell distribution

$$f = \rho(\mathbf{r}, t) \left[ \frac{m}{2\pi kT(\mathbf{r}, t)} \right]^{3/2} \exp \left\{ -\frac{m[\mathbf{v} - \mathbf{v}_0(\mathbf{r}, t)]^2}{2kT(\mathbf{r}, t)} \right\}$$

18-8. Derive Eq. (18-30).

18-9. Show that Eq. (18-42) is equal to Eq. (18-43).

18-10. Prove Eq. (18-46).

18-11. Prove Eq. (18-48).

18-12. Derive the momentum balance equation, Eq. (18-52), from Eq. (18-49).

18-13. Derive the energy balance equation from Eq. (18-49).

18-14. Show that the first two integrals on the right-hand side of Eq. (18-56) vanish.

18-15. Derive Eq. (18-58).

18-16. Prove that the Boltzmann  $H$ -theorem implies that the steady-state solution to the Boltzmann equation is a local Maxwellian distribution, i.e., prove Eqs. (18-65), (18-66), and (18-67).

18-17. Show that if a local Maxwellian distribution is used to calculate the averages in the equations of change, Eqs. (18-51) and (18-52), one gets the ideal hydrodynamic equations.

18-18. The collision term in the Boltzmann equation is often written approximately as

$$\left( \frac{\partial f}{\partial t} \right)_{\text{collisions}} \approx -\frac{(f-f_0)}{\tau}$$

where  $f_0$  is a local Maxwellian distribution. Show that this implies that the difference of the distribution function from equilibrium decays as a simple exponential due to collisions. Interpret  $\tau$ . Give an estimate of its magnitude. Should  $\tau$  depend upon the velocity  $\mathbf{v}$ ?

The standard method of solution to the Boltzmann equation, called the Chapman-Enskog method, is fairly long and involved. It is possible, however, to present an illuminating preview of the method by solving a simplified form of the Boltzmann equation in which the collision term is approximated by  $-(f-f_0)/\tau$ . This will be discussed in Problems 18-19 through 18-21.

18-19. We start with the approximate form of the Boltzmann equation (cf. Problem 18-18)

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} f = -\frac{f-f_0}{\tau}$$

where the relaxation time  $\tau$  may depend upon  $\mathbf{v}$  and  $f_0$  is a local Maxwellian distribution. We assume that the deviation of  $f$  from  $f_0$  is linear in the velocity gradient and the temperature gradient. Show that under this assumption we can replace  $f$  by  $f_0$  in the left-hand side of the equation to get

$$\frac{\partial f_0}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} f_0 = -\frac{f-f_0}{\tau}$$