Near-exact formulation of transport theory

14

OUR TREATMENT of transport processes in the preceding chapter left much to be desired. We assumed the existence of a relaxation time τ and had only approximate means of calculating this quantity. More important, we did not treat the effects of collisions in a detailed way. Thus we neglected correlations between molecular velocities before and after a collision, i.e., persistence of velocity effects. We shall now formulate the problem in a more rigorous and satisfactory way *without* using the concept of a relaxation time. The procedure will be to write down an equation for the distribution function $f(\boldsymbol{r},\boldsymbol{v},t)$ directly in terms of the scattering cross section σ for binary collisions between the molecules. The solution of this equation provides, in principle, a solution of the physical problem. Since the equation is quite complicated, the task of solving it is not easy, and approximation methods must again be used. Nevertheless, despite increased complexity, there is an important advantage in formulating the problem in this way. The reason is that the point of departure of the theory is an equation which is fairly rigorous. Hence general theorems can be proved and systematic approximation procedures developed. On the other hand, if one starts from the simpler formulations of the preceding chapter, it is difficult to estimate the errors committed and to know how to correct for certain effects (like persistence of velocities) in a systematic way.

14 · 1 *Description of two-particle collisions*

We begin our discussion by considering in detail collisions between two molecules. Throughout this chapter we shall assume that if the molecules are not monatomic, their states of internal motion (e.g., rotation or vibration) are unaffected by the collisions. Thus the two molecules under consideration can be treated as simple particles with respective masses m_1 and m_2, position vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, and velocities $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$. The interaction between these particles depends then in some way on their relative positions and velocities. (If the particles also have spins, we assume for the sake of simplicity that their interaction does *not* depend on their spins.)

The collision problem can be much simplified by an appropriate change of variables. Conservation of the total momentum implies the relation

$$m_1\boldsymbol{v}_1 + m_2\boldsymbol{v}_2 = \boldsymbol{P} = \text{constant} \tag{14·1·1}$$

Thus the velocities $\boldsymbol{v}_1(t)$ and $\boldsymbol{v}_2(t)$ are not independent, but must always satisfy the relation (14·1·1). The other quantity of physical interest is the relative velocity

$$\boldsymbol{v}_1 - \boldsymbol{v}_2 \equiv \boldsymbol{V} \tag{14·1·2}$$

One can then use (14·1·1) and (14·1·2) to express $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$ in terms of $\boldsymbol{P}$ and $\boldsymbol{V}$. Thus

$$\left.\begin{aligned}(m_1 + m_2)\boldsymbol{v}_1 &= \boldsymbol{P} + m_2\boldsymbol{V}\\ (m_1 + m_2)\boldsymbol{v}_2 &= \boldsymbol{P} - m_1\boldsymbol{V}\end{aligned}\right\}$$

or

$$\left.\begin{aligned}\boldsymbol{v}_1 &= \boldsymbol{c} + \frac{\mu}{m_1}\boldsymbol{V}\\ \boldsymbol{v}_2 &= \boldsymbol{c} - \frac{\mu}{m_2}\boldsymbol{V}\end{aligned}\right\} \tag{14·1·3}$$

where

$$\boldsymbol{c} \equiv \frac{\boldsymbol{P}}{m_1 + m_2} = \frac{m_1\boldsymbol{v}_1 + m_2\boldsymbol{v}_2}{m_1 + m_2} \tag{14·1·4}$$

is the time-independent velocity of the center of mass; i.e.,

$$\boldsymbol{c} = \frac{d\boldsymbol{r}_c}{dt}$$

where

$$\boldsymbol{r}_c \equiv \frac{m_1\boldsymbol{r}_1 + m_2\boldsymbol{r}_2}{m_1 + m_2} \tag{14·1·5}$$

is the position vector of the center of mass. In addition, we have introduced the quantity

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \tag{14·1·6}$$

which is called the "reduced mass" of the particles.

The total kinetic energy K of the particles becomes by (14·1·3)

$$K = \tfrac{1}{2}m_1\boldsymbol{v}_1^2 + \tfrac{1}{2}m_2\boldsymbol{v}_2^2 = \tfrac{1}{2}(m_1 + m_2)\boldsymbol{c}^2 + \tfrac{1}{2}\mu\boldsymbol{V}^2 \tag{14·1·7}$$

Consider now a collision process. Denote the velocities of the two particles *before* they interact with each other in the collision process by $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$; denote their respective velocities *after* the collision by $\boldsymbol{v}_1'$ and $\boldsymbol{v}_2'$. In terms of the new variables the situation is described in a particularly simple way. The center-of-mass velocity $\boldsymbol{c}$ remains unchanged as a consequence of conservation of momentum. The relative velocity changes from the value $\boldsymbol{V}$ before the collision to the value $\boldsymbol{V}'$ after the collision. We assume the collisions to be elastic so that the internal energies of the molecules remain unchanged. Then the kinetic energy K remains unchanged in a collision, and it follows, by (14·1·7), that $\boldsymbol{V}^2$ also remains unchanged so that $|\boldsymbol{V}'| = |\boldsymbol{V}|$. Hence the only

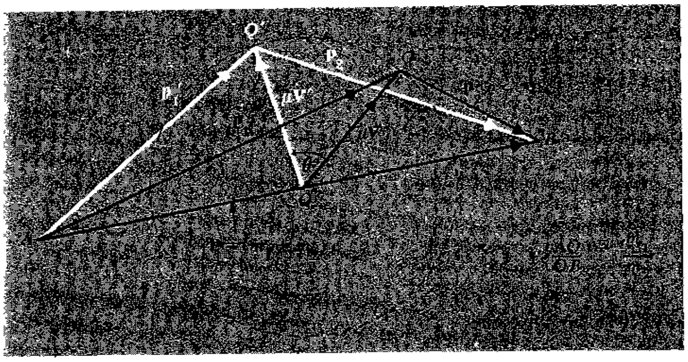


Fig. 14·1·1 Geometrical construction based on (14·1·8) and illustrating an elastic collision process. Consider the original momenta $p_1 = m_1v$ and $p_2 = m_2v_2$ represented by the vectors $\overrightarrow{AQ}$ and $\overrightarrow{QB}$, respectively. Their vector sum yields the total momentum $P = (m_1 + m_2)c = \overrightarrow{AB}$, which remains unchanged in time. Divide this vector $\overrightarrow{AB}$ in the ratio $m_1 : m_2$ to locate the point O; then $\overrightarrow{AO} = m_1c$ and $\overrightarrow{OB} = m_2c$. Hence the vector $\overrightarrow{OQ}$ represents μV. Draw a sphere about O of radius OQ. Then the final relative velocity must be such that the vector $\mu V' = \overrightarrow{OQ'}$ terminates somewhere on this same sphere (although not necessarily in the same plane ABQ). The final momenta p_1' and p_2' are simply given by the vectors $\overrightarrow{AQ'}$ and $\overrightarrow{Q'B}$. Their directions with respect to the original vectors p_1 and p_2 are then immediately apparent from the diagram.

effect of a collision is that $\boldsymbol{V}$ changes its direction without changing its magnitude. The collision process can thus be described by merely specifying the polar angle θ' and azimuthal angle φ' of the final relative velocity $\boldsymbol{V}'$ with respect to the relative velocity $\boldsymbol{V}$ before the collision.

It is simplest to visualize the relationship between the velocities before and after the collision by considering the corresponding molecular momenta $\boldsymbol{p}_1$, $\boldsymbol{p}_2$ before and $\boldsymbol{p}_1'$, $\boldsymbol{p}_2'$ after the collision. By (14·1·3) one has at all times

$$\left.\begin{aligned} \boldsymbol{p}_1 &= m_1\boldsymbol{c} + \mu\boldsymbol{V} \\ \boldsymbol{p}_2 &= m_2\boldsymbol{c} - \mu\boldsymbol{V} \end{aligned}\right\} \tag{14·1·8}$$

The geometrical relationships are illustrated in Fig. 14·1·1.

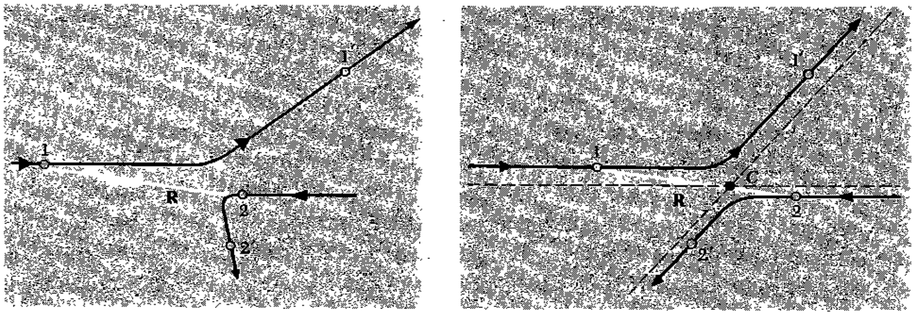
One can correspondingly visualize (classically) the positions of the particles at all times. In addition to the center-of-mass position vector $\boldsymbol{r}_c$ of (14·1·5) we introduce, corresponding to (14·1·2), the relative position vector

$$\boldsymbol{r}_1 - \boldsymbol{r}_2 \equiv \boldsymbol{R} \tag{14·1·9}$$

Then, analogously to (14·1·3), one has

$$\left.\begin{aligned} \boldsymbol{r}_1^* &\equiv \boldsymbol{r}_1 - \boldsymbol{r}_c = \frac{\mu}{m_1}\boldsymbol{R} \\ \boldsymbol{r}_2^* &\equiv \boldsymbol{r}_2 - \boldsymbol{r}_c = -\frac{\mu}{m_2}\boldsymbol{R} \end{aligned}\right\} \tag{14·1·10}$$

Thus the position $\boldsymbol{r}_c$ of the center of mass moves with the constant velocity $\boldsymbol{c}$ of



Laboratory system *Center-of-mass system*

***Fig. 14·1·2** Classical trajectories for two colliding particles illustrated in the laboratory system and in the reference frame moving with their center of mass C.*

(14·1·4). In the frame of reference which moves with the center of mass, the collision process is described very simply: The position vectors $\mathbf{r}_1^*$ and $\mathbf{r}_2^*$ of the particles relative to the center of mass are, by (14·1·10), at all times oppositely directed, and their magnitudes have a fixed ratio so that

$$m_1\mathbf{r}_1^* = -m_2\mathbf{r}_2^*$$

The vector $\mathbf{R}$ joining the particles passes always through their center of mass. If the force exerted on molecule 1 by molecule 2 is denoted by $\mathbf{F}_{12}$, it follows by (14·1·8) that

$$\frac{d\mathbf{p}_1}{dt} = \mu\frac{d^2\mathbf{R}}{dt^2} = \mathbf{F}_{12} \tag{14·1·11}$$

Hence the motion $\mathbf{R}(t)$ of molecule 1 relative to molecule 2 is the same as if it had a mass μ and were acted on by the force $\mathbf{F}_{12}$. The discussion of the two-particle problem is thus reduced to the solution of a simple one-particle problem. With respect to particle 2 the scattering process appears as shown in Fig. 14·1·3.

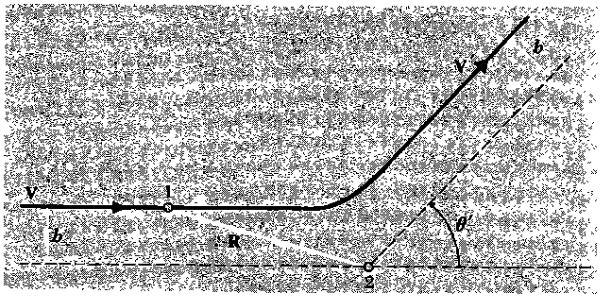


***Fig. 14·1·3** Scattering process relative to molecule 2 regarded as fixed. The polar scattering angle is denoted by θ'. Classically, various scattering angles θ' correspond to different values of the impact parameter b, the distance of closest approach of the molecules if there were no interaction between them.*

14 · 2 *Scattering cross sections and symmetry properties*

Molecules having initially velocities $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$ can get scattered in their relative motion through various angles θ' and φ' (depending classically on the value of the initial impact parameter b). If the only information available are these initial velocities $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$ (and quantum mechanically this is *all* the information one can possibly have, since simultaneous determination of the impact parameter b would be impossible in principle), then the outcome of the scattering process must be described in statistical terms. This can be done in terms of the quantity σ' defined so that

$$\left.\begin{array}{l}\sigma'(\boldsymbol{v}_1,\boldsymbol{v}_2 \to \boldsymbol{v}_1',\boldsymbol{v}_2')\, d^3\boldsymbol{v}_1'\, d^3\boldsymbol{v}_2' \equiv \text{the number of molecules per} \\ \text{unit time (per unit flux of type 1 molecules incident with} \\ \text{relative velocity } \boldsymbol{V} \text{ upon a type 2 molecule) emerging after} \\ \text{scattering with respective final velocities between } \boldsymbol{v}_1' \text{ and} \\ \boldsymbol{v}_1' + d\boldsymbol{v}_1' \text{ and between } \boldsymbol{v}_2' \text{ and } \boldsymbol{v}_2' + d\boldsymbol{v}_2'.\end{array}\right\} \qquad (14\cdot 2\cdot 1)$$

Analogously to (14·1·3), one has

$$\boldsymbol{v}_1' = \boldsymbol{c}' + \frac{\mu}{m_1}\boldsymbol{V}' \qquad \text{and} \qquad \boldsymbol{v}_2' = \boldsymbol{c}' - \frac{\mu}{m_2}\boldsymbol{V}' \qquad (14\cdot 2\cdot 2)$$

where, by virtue of conservation of momentum and energy, $\boldsymbol{c}' = \boldsymbol{c}$ and $|\boldsymbol{V}'| = |\boldsymbol{V}|$. Thus σ' must vanish unless $\boldsymbol{v}_1'$ and $\boldsymbol{v}_2'$ are such that these conditions are satisfied. Indeed, in terms of the variables $\boldsymbol{c}$ and $\boldsymbol{V}$, the scattering process is completely described in terms of the equivalent one-body problem of relative motion of Fig. 14·1·3, where $\boldsymbol{V}'$ is specified completely in terms of the polar and azimuthal angles θ' and φ' with respect to $\boldsymbol{V}$. Hence one can define a simpler but less symmetrical quantity, the differential scattering cross section σ already introduced in (12·2·1), by the statement that

$$\left.\begin{array}{l}\sigma(\boldsymbol{V}')\, d\Omega' \equiv \text{the number of molecules per unit time (per unit} \\ \text{flux of type 1 molecules incident with relative velocity } \boldsymbol{V} \\ \text{upon a type 2 molecule) emerging after scattering with final} \\ \text{relative velocity } \boldsymbol{V}' \text{ with a direction in the solid-angle range} \\ d\Omega' \text{ about the angles } \theta' \text{ and } \varphi'.\end{array}\right. \qquad (14\cdot 2\cdot 3)$$

Here σ depends in general on the relative speed $|\boldsymbol{V}| = |\boldsymbol{V}'|$ and on the angles θ' and φ'; i.e., it depends on the magnitude and direction of $\boldsymbol{V}'$. By the definitions (14·2·3) and (14·2·2), σ is related to σ' by

$$\sigma(\boldsymbol{V}')\, d\Omega' = \int_{\boldsymbol{c}'} \int_{V'} \sigma'(\boldsymbol{v}_1,\boldsymbol{v}_2 \to \boldsymbol{v}_1',\boldsymbol{v}_2')\, d^3\boldsymbol{v}_1'\, d^3\boldsymbol{v}_2' \qquad (14\cdot 2\cdot 4)$$

where the integration is over all values of $\boldsymbol{c}'$ and of $|\boldsymbol{V}'|$. (The integration is, of course, trivial, since $\sigma' = 0$ unless $\boldsymbol{c}' = \boldsymbol{c}$ and $|\boldsymbol{V}'| = |\boldsymbol{V}|$.)

Remark It is useful to express the velocity range $d^3\mathbf{v}_1\, d^3\mathbf{v}_2$ in terms of the variables $\mathbf{c}$ and $\mathbf{V}$. One has

$$d^3\mathbf{v}_1\, d^3\mathbf{v}_2 = |J'|\, d^3\mathbf{c}\, d^3\mathbf{V} \tag{14·2·5}$$

where J' is the Jacobian of the transformation (14·1·3). But

$$dv_{1x}\, dv_{2x} = \frac{\partial(v_{1x},v_{2x})}{\partial(c_x,V_x)}\, dc_x\, dV_x = \begin{vmatrix} 1 & \dfrac{\mu}{m_1} \\ 1 & -\dfrac{\mu}{m_2} \end{vmatrix} dc_x\, dV_x$$

$$= -\mu\left(\frac{1}{m_2} + \frac{1}{m_1}\right) dc_x\, dV_x = -dc_x\, dV_x$$

where we have used (14·1·6). The transformation (14·2·5) is just the absolute value of a product of three such terms, corresponding to x, y, and z components. Hence one gets simply

$$d^3\mathbf{v}_1\, d^3\mathbf{v}_2 = d^3\mathbf{c}\, d^3\mathbf{V} \tag{14·2·6}$$

Similarly, one has

$$d^3\mathbf{v}_1'\, d^3\mathbf{v}_2' = d^3\mathbf{c}'\, d^3\mathbf{V}' \tag{14·2·7}$$

Now $\mathbf{c}' = \mathbf{c}$; furthermore $\mathbf{V}'$ and $\mathbf{V}$ differ only in direction but not in magnitude, and since volume elements remain unchanged under simple rotations of coordinates, $d^3\mathbf{V}' = d^3\mathbf{V}$. Hence (14·2·6) and (14·2·7) also imply

$$d^3\mathbf{v}_1'\, d^3\mathbf{v}_2' = d^3\mathbf{v}_1\, d^3\mathbf{v}_2 \tag{14·2·8}$$

The probability σ' has various useful symmetry properties which imply connections between a given collision process and related processes. The interactions between the molecules are basically electromagnetic in origin. The equations of motion must therefore have the following very general properties:

1. The equations of motion must be invariant under reversal of the sign of the time from $t \to -t$. Under such a time reversal, which implies of course a corresponding reversal of all the velocities, one obtains the "reverse" collision in which the particles simply retrace their paths in time. Thus one must have the following relation between scattering probabilities

$$\sigma'(\mathbf{v}_1,\mathbf{v}_2 \to \mathbf{v}_1',\mathbf{v}_2')\, d^3\mathbf{v}_1'\, d^3\mathbf{v}_2' = \sigma'(-\mathbf{v}_1',-\mathbf{v}_2' \to -\mathbf{v}_1,-\mathbf{v}_2)\, d^3\mathbf{v}_1\, d^3\mathbf{v}_2$$

or by (14·2·8)

$$\sigma'(\mathbf{v}_1,\mathbf{v}_2 \to \mathbf{v}_1',\mathbf{v}_2') = \sigma'(-\mathbf{v}_1',-\mathbf{v}_2' \to -\mathbf{v}_1,-\mathbf{v}_2) \tag{14·2·9}$$

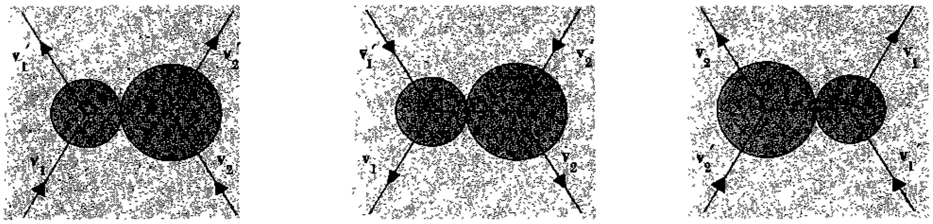
Remark If the particles had spin and the interaction between them were spin-dependent, then time reversal would also necessitate simultaneous reversal of all spins. Equation (14·2·9) would therefore not be valid as it stands, but would still hold if averaged over all possible directions of the initial and final spins.

2. The equations of motion must be invariant under the transformation which reverses the sign of all spatial coordinates so that $\boldsymbol{r} \to -\boldsymbol{r}$. Under such a "space inversion," the signs of all velocities also change, but the time order does not. Thus one must have

$$\sigma'(\boldsymbol{v}_1,\boldsymbol{v}_2 \to \boldsymbol{v}_1',\boldsymbol{v}_2') = \sigma'(-\boldsymbol{v}_1,-\boldsymbol{v}_2 \to -\boldsymbol{v}_1',-\boldsymbol{v}_2') \qquad (14\cdot2\cdot10)$$

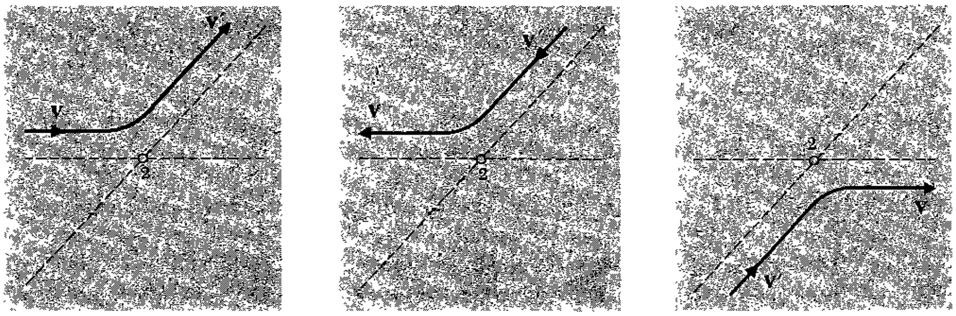
It is of particular interest to consider the so-called "inverse" collision which, by definition, is obtained from the original collision by interchanging the initial and final states. Whereas in the original collision the particles collide with velocities $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$ and emerge with velocities $\boldsymbol{v}_1'$ and $\boldsymbol{v}_2'$, in the inverse collision precisely the opposite takes place; i.e., the particles collide with velocities $\boldsymbol{v}_1'$ and $\boldsymbol{v}_2'$ and emerge with velocities $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$ (see Figs. 14·2·1 and 14·2·2). The inverse collision can be obtained from the original collision by considering the operation of time reversal followed by the operation of space inversion which changes the sign of all spatial coordinates. Successive application of (14·2·9) and (14·2·10) shows that the collision probabilities for the original and inverse collisions are also equal; i.e., by applying the operation of space inversion to the right side of (14·2·9), one obtains by (14·2·10)

$$\sigma'(\boldsymbol{v}_1,\boldsymbol{v}_2 \to \boldsymbol{v}_1',\boldsymbol{v}_2') = \sigma'(\boldsymbol{v}_1',\boldsymbol{v}_2' \to \boldsymbol{v}_1,\boldsymbol{v}_2) \qquad (14\cdot2\cdot11)$$



Original collision *Reverse collision* *Inverse collision*

Fig. 14·2·1 Figure illustrating related collisions between hard spheres. The scattering cross sections are the same for all these collisions.



Original collision *Reverse collision* *Inverse collision*

Fig. 14·2·2 Figure illustrating classical relative orbits for related collisions.

14 · 3 *Derivation of the Boltzmann equation*

We are now in a position to make use of our knowledge of molecular collisions to derive an explicit expression for D_Cf in the Boltzmann equation (13·6·1),

$$Df = D_Cf \tag{14·3·1}$$

In order to calculate D_Cf, the rate of change of f caused by collisions, we shall make the following assumptions:

a. The gas is sufficiently dilute that only two-particle collisions need be taken into account.

b. Any possible effects of the external force $\boldsymbol{F}$ on the magnitude of the collision cross section can be ignored.

c. The distribution function $f(\boldsymbol{r},\boldsymbol{v},t)$ does not vary appreciably during a time interval of the order of the duration of a molecular collision, nor does it vary appreciably over a spatial distance of the order of the range of intermolecular forces.

d. When considering a collision between two molecules one can neglect possible correlations between their initial velocities prior to the collision. This fundamental approximation in the theory is called the assumption of "molecular chaos." It is justified when the gas density is sufficiently low. Then the mean free path l is much greater than the range of intermolecular forces, and two molecules originate before their encounter at a relative separation which is of the order of l and thus sufficiently large that a correlation between their initial velocities is unlikely.

Focus attention on molecules located in the volume element $d^3\boldsymbol{r}$ located between $\boldsymbol{r}$ and $\boldsymbol{r} + d\boldsymbol{r}$, and consider the collisions which occur there in the time between t and $t + dt$. (Here $d\boldsymbol{r}$ is taken to be large compared to the range of intermolecular forces and dt to be large compared to the duration of a collision. Nevertheless, they can be considered infinitesimally small with respect to variations in f by virtue of the assumption (*c*).) We are interested in calculating how collisions cause a net change $D_Cf(\boldsymbol{r},\boldsymbol{v},t)\, d^3\boldsymbol{r}\, d^3\boldsymbol{v}\, dt$ in the number of such molecules with velocity between $\boldsymbol{v}$ and $\boldsymbol{v} + d\boldsymbol{v}$. First, the molecules in $d^3\boldsymbol{r}$ can be thrown *out* of this velocity range by virtue of collisions with other molecules; we denote the resulting *decrease* in time dt of the number of such molecules by $D_C^{(-)}f(\boldsymbol{r},\boldsymbol{v},t)\, d^3\boldsymbol{r}\, d^3\boldsymbol{v}\, dt$. Second, molecules in $d^3\boldsymbol{r}$ whose velocity is originally not in the range between $\boldsymbol{v}$ and $\boldsymbol{v} + d\boldsymbol{v}$ can be thrown *into* this velocity range by virtue of collisions with other molecules; we denote the resulting *increase* in time dt of the number of molecules thus scattered into this velocity range by $D_C^{(+)}f(\boldsymbol{r},\boldsymbol{v},t)\, d^3\boldsymbol{r}\, d^3\boldsymbol{v}\, dt$. Hence one can write

$$D_Cf = -D_C^{(-)}f + D_C^{(+)}f \tag{14·3·2}$$

To calculate $D_C^{(-)}f$, we consider in the volume element $d^3\boldsymbol{r}$ molecules with velocity near $\boldsymbol{v}$ (call these A molecules) which are scattered out of this velocity range by virtue of collisions with other molecules (call them A_1 molecules) which are in the same volume element $d^3\boldsymbol{r}$ and which have some velocity $\boldsymbol{v}_1$.

The probability of occurrence of such a collision where an A molecule changes its velocity from $\mathbf{v}$ to one near $\mathbf{v}'$, while an A_1 molecules changes its velocity from $\mathbf{v}_1$ to one near $\mathbf{v}_1'$ is by (14·2·1) described in terms of the scattering probability $\sigma'(\mathbf{v},\mathbf{v}_1 \to \mathbf{v}',\mathbf{v}_1')\, d^3\mathbf{v}'\, d^3\mathbf{v}_1'$. To obtain the *total* collision-induced decrease $D_C^{(-)}f\, d^3\mathbf{r}\, d^3\mathbf{v}\, dt$ in time dt of the number of molecules located in $d^3\mathbf{r}$ with velocity between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$ one must first multiply $\sigma'\, d^3\mathbf{v}'\, d^3\mathbf{v}_1'$ by the relative flux $|\mathbf{v} - \mathbf{v}_1| f(\mathbf{r},\mathbf{v},t)\, d^3\mathbf{v}$ of A molecules incident upon an A_1 molecule and must then multiply this by the number of A_1 molecules $f(\mathbf{r},\mathbf{v}_1,t)\, d^3\mathbf{r}\, d^3\mathbf{v}_1$ which can do such scattering. Then one has to sum the result over all possible initial velocities $\mathbf{v}_1$ of the A_1 molecules with which A can collide and over all possible final velocities $\mathbf{v}'$ and $\mathbf{v}_1'$ of the scattered A and A_1 molecules. Thus one obtains:

$$D_C^{(-)}f(\mathbf{r},\mathbf{v},t)\, d^3\mathbf{r}\, d^3\mathbf{v}\, dt = \int_{\mathbf{v}_1'}\int_{\mathbf{v}'}\int_{\mathbf{v}_1} [|\mathbf{v} - \mathbf{v}_1| f(\mathbf{r},\mathbf{v},t)\, d^3\mathbf{v}][f(\mathbf{r},\mathbf{v}_1,t)\, d^3\mathbf{r}\, d^3\mathbf{v}_1][\sigma'(\mathbf{v},\mathbf{v}_1 \to \mathbf{v}',\mathbf{v}_1')\, d^3\mathbf{v}'\, d^3\mathbf{v}_1'] \qquad (14·3·3)$$

Here we have used the fundamental assumption (d) of molecular chaos in writing for the probability of simultaneous presence in $d^3\mathbf{r}$ of molecules with respective velocities near $\mathbf{v}$ and $\mathbf{v}_1$ an expression proportional to the simple product

$$f(\mathbf{r},\mathbf{v},t)\, d^3\mathbf{v} \cdot f(\mathbf{r},\mathbf{v}_1,t)\, d^3\mathbf{v}_1$$

which assumes the absence of any correlations between the initial velocities $\mathbf{v}$ and $\mathbf{v}_1$, so that these are statistically independent.

We now turn to the calculation of $D_C^{(+)}f$. Considering again the same volume element $d^3\mathbf{r}$, we ask how many molecules will end up after collisions with a velocity in the range between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$. But this involves precisely a consideration of what we called "inverse collisions" in Sec. 14·2. Namely, we should like to consider all molecules in $d^3\mathbf{r}$ with arbitrary initial velocities $\mathbf{v}'$ and $\mathbf{v}_1'$ which are such that, after collision, one molecule acquires a velocity in the range of interest between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$, while the other acquires some velocity between $\mathbf{v}_1$ and $\mathbf{v}_1 + d\mathbf{v}_1$. This scattering process is described by the scattering probability $\sigma'(\mathbf{v}',\mathbf{v}_1' \to \mathbf{v},\mathbf{v}_1)$. The relative flux of molecules with initial velocity near $\mathbf{v}'$ is $|\mathbf{v}' - \mathbf{v}_1'| f(\mathbf{r},\mathbf{v}',t)\, d^3\mathbf{v}'$, and these molecules get scattered by the $f(\mathbf{r},\mathbf{v}_1',t)\, d^3\mathbf{r}\, d^3\mathbf{v}_1'$ molecules with velocity near $\mathbf{v}_1'$. Hence one can write for the total increase in time dt of the number of molecules located in $d^3\mathbf{r}$ with velocity between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$ the expression

$$D_C^{(+)}f(\mathbf{r},\mathbf{v},t)\, d^3\mathbf{r}\, d^3\mathbf{v}\, dt = \int_{\mathbf{v}_1}\int_{\mathbf{v}_1'}\int_{\mathbf{v}'} [|\mathbf{v}' - \mathbf{v}_1'| f(\mathbf{r},\mathbf{v}',t)\, d^3\mathbf{v}'][f(\mathbf{r},\mathbf{v}_1',t)\, d^3\mathbf{r}\, d^3\mathbf{v}_1'][\sigma'(\mathbf{v}',\mathbf{v}_1' \to \mathbf{v},\mathbf{v}_1)\, d^3\mathbf{v}\, d^3\mathbf{v}_1] \qquad (14·3·4)$$

where the integrations are over all the possible initial velocities $\mathbf{v}'$ and $\mathbf{v}_1'$ of the molecules, and over all possible final velocities $\mathbf{v}_1$ of the other molecule whose velocity does not end up in the range of interest near $\mathbf{v}$.

By (14·3·2), D_Cf is then obtained by subtracting (14·3·3) from (14·3·4). Note the following simplifying features. By (14·2·11) the probabilities for inverse collisions are equal so that

$$\sigma'(\mathbf{v}',\mathbf{v}_1' \to \mathbf{v},\mathbf{v}_1) = \sigma'(\mathbf{v},\mathbf{v}_1 \to \mathbf{v}',\mathbf{v}_1')$$

Furthermore, we can introduce the relative velocities

$$\mathbf{V} \equiv \mathbf{v} - \mathbf{v}_1, \qquad \mathbf{V}' \equiv \mathbf{v}' - \mathbf{v}_1' \tag{14·3·5}$$

Then the conservation of energy for elastic collisions implies that

$$|\mathbf{V}'| = |\mathbf{V}| \equiv V$$

In order to save writing, it is also convenient to introduce the abbreviations

$$\begin{aligned} f &\equiv f(\mathbf{r},\mathbf{v},t), & f_1 &\equiv f(\mathbf{r},\mathbf{v}_1,t) \\ f' &\equiv f(\mathbf{r},\mathbf{v}',t), & f_1' &\equiv f(\mathbf{r},\mathbf{v}_1',t) \end{aligned} \tag{14·3·6}$$

Then (14·3·2) becomes

$$D_C f = \int_{\mathbf{v}_1} \int_{\mathbf{v}_1'} \int_{\mathbf{v}'} (f'f_1' - ff_1) V\sigma'(\mathbf{v},\mathbf{v}_1 \to \mathbf{v}',\mathbf{v}_1')\, d^3\mathbf{v}_1\, d^3\mathbf{v}'\, d\mathbf{v}_1' \tag{14·3·7}$$

One can use (14·2·4) to express this result in terms of $\mathbf{V}'$ and the solid-angle range $d\Omega'$ about this vector. Using (13·2·8), the Boltzmann equation (14·3·1) for $f(\mathbf{r},\mathbf{v},t)$ can then be written in the explicit form

▶ $$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial f}{\partial \mathbf{v}} = \int_{\mathbf{v}_1} \int_{\Omega'} (f'f_1' - ff_1) V\sigma\, d\Omega'\, d^3\mathbf{v}_1 \tag{14·3·8}$$

where $\sigma = \sigma(\mathbf{V}')$.

14 · 4 *Equation of change for mean values*

Consider any function $\chi(\mathbf{r},\mathbf{v},t)$ which describes a property of a molecule that has a position $\mathbf{r}$ and a velocity $\mathbf{v}$ at time t. As in (13·1·4), the mean value of χ is defined by

$$\langle \chi(\mathbf{r},t) \rangle \equiv \frac{1}{n(\mathbf{r},t)} \int d^3\mathbf{v}\, f(\mathbf{r},\mathbf{v},t)\chi(\mathbf{r},\mathbf{v},t) \tag{14·4·1}$$

where $n(\mathbf{r},t)$ is the mean number of molecules per unit volume. We should like to derive an equation which describes how $\langle \chi \rangle$ varies as a function of t and $\mathbf{r}$. This can be done in two ways, either by analyzing the situation directly from the beginning, or by starting from the Boltzmann equation (14·3·8). Since both approaches are instructive, we shall illustrate them in turn.

Direct analysis Consider the fixed volume element $d^3\mathbf{r}$, located between $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$, which contains $n(\mathbf{r},t)\, d^3\mathbf{r}$ molecules. In a time interval between t and $t + dt$ the total mean value $\langle n\, d^3\mathbf{r}\, \chi \rangle$ of the quantity χ for all molecules in $d^3\mathbf{r}$ increases by an amount

$$\frac{\partial}{\partial t} \langle n\chi \rangle\, d^3\mathbf{r}\, dt = A_{\text{int}} + A_{\text{flux}} + A_{\text{col}} \tag{14·4·2}$$

Note that n can always be taken outside the averaging brackets, since it does not depend on $\mathbf{v}$. The quantities A represent various contributions to be described presently.

1. There is an intrinsic increase A_{int} in the total mean value of χ due to the fact that the quantity $\chi(\boldsymbol{r},\boldsymbol{v},t)$ for each molecule in $d^3\boldsymbol{r}$ changes. In time dt, each molecule changes position by $d\boldsymbol{r} = \boldsymbol{v}\,dt$ and velocity by $d\boldsymbol{v} = (\boldsymbol{F}/m)\,dt$; hence the corresponding change in χ is given by

$$\frac{\partial\chi}{\partial t}\,dt + \frac{\partial\chi}{\partial x_\alpha}\,v_\alpha\,dt + \frac{\partial\chi}{\partial v_\alpha}\frac{F_\alpha}{m}\,dt$$

Here x_α and v_α denote the respective cartesian components of the vectors $\boldsymbol{r}$ and $\boldsymbol{v}$, and we have adopted the "summation convention" that a summation from 1 to 3 is implied whenever a Greek subscript occurs twice. Hence the intrinsic increase in the mean value of χ in $d^3\boldsymbol{r}$ is given by

$$A_{\text{int}} = \langle n\,d^3\boldsymbol{r}\;D\chi\;dt\rangle = n\,d^3\boldsymbol{r}\;dt\,\langle D\chi\rangle \tag{14·4·3}$$

where
$$D\chi \equiv \frac{\partial\chi}{\partial t} + v_\alpha\frac{\partial\chi}{\partial x_\alpha} + \frac{F_\alpha}{m}\frac{\partial\chi}{\partial v_\alpha} = \frac{\partial\chi}{\partial t} + \boldsymbol{v}\cdot\frac{\partial\chi}{\partial\boldsymbol{r}} + \frac{\boldsymbol{F}}{m}\cdot\frac{\partial\chi}{\partial\boldsymbol{v}} \tag{14·4·4}$$

2. There is an increase A_{flux} in the total mean value of χ in $d^3\boldsymbol{r}$ due to the net flux of molecules which enter the volume element $d^3\boldsymbol{r}$ in time dt. By an argument similar to that in Sec. 13·2, the increase in the mean value of χ caused by molecules entering the element of volume in time dt through the face x_1 is the mean value contained in the volume $v_1\,dt\,dx_2\,dx_3$, i.e., $\langle n\chi[v_1\,dt\,dx_2\,dx_3]\rangle$. The decrease in the mean value of χ caused by molecules leaving through the face $x_1 + dx_1$ is correspondingly given by

$$\langle n\chi v_1\,dt\,dx_2\,dx_3\rangle + \frac{\partial}{\partial x_1}\langle n\chi v_1\,dt\,dx_2\,dx_3\rangle\,dx_1$$

By subtracting these two expressions one obtains for the net increase in the mean value of χ due to molecules entering and leaving through these two faces the contribution

$$-\frac{\partial}{\partial x_1}\langle n\chi v_1\,dt\,d^3\boldsymbol{r}\rangle$$

Adding contributions from all other faces one gets thus

$$A_{\text{flux}} = -\frac{\partial}{\partial x_\alpha}\langle n v_\alpha \chi\rangle\,dt\,d^3\boldsymbol{r} \tag{14·4·5}$$

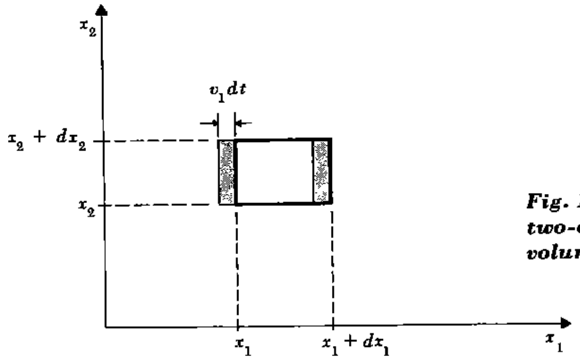


Fig. 14·4·1 Figure illustrating a two-dimensional projection of the volume element $d^3\boldsymbol{r}$.

3. Finally, there is an increase A_{col} in the total mean value of χ in $d^3\boldsymbol{r}$ because of collisions between molecules in this volume element. In such a collision where a molecule with velocity $\boldsymbol{v}$ collides with another one of velocity $\boldsymbol{v}_1$, and the molecules then emerge with respective final velocities $\boldsymbol{v}'$ and $\boldsymbol{v}_1'$, the change in χ is equal to

$$\Delta\chi = \chi' + \chi_1' - \chi - \chi_1 \tag{14·4·6}$$

where

$$\begin{aligned} \chi &\equiv \chi(\boldsymbol{r},\boldsymbol{v},t), \qquad & \chi_1 &\equiv \chi(\boldsymbol{r},\boldsymbol{v}_1,t) \\ \chi' &\equiv \chi(\boldsymbol{r},\boldsymbol{v}',t), \qquad & \chi_1' &\equiv \chi(\boldsymbol{r},\boldsymbol{v}_1',t) \end{aligned} \tag{14·4·7}$$

The number of such collisions is again given by

$$[|\boldsymbol{v} - \boldsymbol{v}_1| f(\boldsymbol{r},\boldsymbol{v},t)\, d^3\boldsymbol{v}][\sigma'\, d^3\boldsymbol{v}'\, d^3\boldsymbol{v}_1'][f(\boldsymbol{r},\boldsymbol{v}_1,t)\, d^3\boldsymbol{r}\, d^3\boldsymbol{v}_1]$$

where we have used the assumption of molecular chaos. Thus A_{col} is obtained by multiplying this number by $\Delta\chi$ and summing over all possible initial velocities $\boldsymbol{v}$ and $\boldsymbol{v}_1$ of the molecules and over all their possible final velocities. This result must then be divided by 2, since in the above sums over molecular velocities each colliding pair of molecules is counted twice. Thus one has

$$A_{\text{col}} = \tfrac{1}{2}\, d^3\boldsymbol{r}\, dt \iiiint d^3\boldsymbol{v}\, d^3\boldsymbol{v}_1\, d^3\boldsymbol{v}'\, d^3\boldsymbol{v}_1' f f_1 V \sigma'\, \Delta\chi \tag{14·4·8}$$

By (14·4·3), (14·4·5) and (14·4·8), Eq. (14·4·2) then becomes

▶
$$\frac{\partial}{\partial t}\langle n\chi\rangle = n\langle D\chi\rangle - \frac{\partial}{\partial x_\alpha}\langle n v_\alpha \chi\rangle + \mathcal{C}(\chi) \tag{14·4·9}$$

where $\mathcal{C}(\chi)$ denotes the rate of change of χ per unit volume due to collisions; by (14·4·8) and (14·2·4) it can be written

▶
$$\mathcal{C}(\chi) = \frac{A_{\text{col}}}{d^3\boldsymbol{r}\, dt} = \frac{1}{2} \iiint d^3\boldsymbol{v}\, d^3\boldsymbol{v}_1\, d\Omega' f f_1 V \sigma\, \Delta\chi \tag{14·4·10}$$

Note again that n can always be taken outside the averaging angular brackets since it does not depend on $\boldsymbol{v}$. Equation (14·4·9) is sometimes called "Enskog's equation of change."

Analysis based on the Boltzmann equation To find the equation satisfied by $\langle\chi\rangle$ defined in (14·4·1), we multiply both sides of the Boltzmann equation (14·3·8) by χ and then integrate over all velocities $\boldsymbol{v}$. Thus we get

$$\int d^3\boldsymbol{v}\, Df\, \chi = \int d^3\boldsymbol{v}\, D_c f\, \chi \tag{14·4·11}$$

where
$$\int d^3\boldsymbol{v}\, Df\,\chi \equiv \int d^3\boldsymbol{v}\, \frac{\partial f}{\partial t}\chi + \int d^3\boldsymbol{v}\, \boldsymbol{v}\cdot\frac{\partial f}{\partial \boldsymbol{r}}\chi + \int d^3\boldsymbol{v}\, \frac{\boldsymbol{F}}{m}\cdot\frac{\partial f}{\partial \boldsymbol{v}}\chi \tag{14·4·12}$$

and where
$$\mathcal{C}(\chi) \equiv \int d^3\boldsymbol{v}\, D_c f\, \chi = \iiint d^3\boldsymbol{v}\, d^3\boldsymbol{v}_1\, d\Omega'\, (f' f_1' - f f_1) V \sigma \chi \tag{14·4·13}$$

Let us now transform the integrals in (14·4·12) into quantities which are averages, i.e., into integrals which involve f itself rather than its derivatives. Thus we have

$$\int d^3\boldsymbol{v}\, \frac{\partial f}{\partial t}\chi = \int d^3\boldsymbol{v} \left[\frac{\partial}{\partial t}(f\chi) - f\frac{\partial \chi}{\partial t}\right] = \frac{\partial}{\partial t}\int d^3\boldsymbol{v}\, f\chi - \int d^3\boldsymbol{v}\, f\frac{\partial\chi}{\partial t}$$

since the order of differentiation with respect to t and integration over $\boldsymbol{v}$ can be interchanged. Hence

$$\int d^3\boldsymbol{v}\,\frac{\partial f}{\partial t}\,\chi = \frac{\partial}{\partial t}\,(n\langle\chi\rangle) - n\left\langle\frac{\partial\chi}{\partial t}\right\rangle \qquad (14\cdot4\cdot14)$$

The second integral in (14·4·12) can be similarly rewritten. To avoid confusion, we express the vector quantities in terms of their cartesian components denoted by Greek subscripts and again use the summation convention. Keeping in mind that $\boldsymbol{r}$, $\boldsymbol{v}$, t are to be considered as *independent* variables, one has

$$\begin{aligned}\int d^3\boldsymbol{v}\,\boldsymbol{v}\cdot\frac{\partial f}{\partial \boldsymbol{r}}\,\chi &= \int d^3\boldsymbol{v}\,v_\alpha\,\frac{\partial f}{\partial x_\alpha}\,\chi\\ &= \int d^3\boldsymbol{v}\left[\frac{\partial}{\partial x_\alpha}\,(v_\alpha f\chi) - v_\alpha f\,\frac{\partial\chi}{\partial x_\alpha}\right]\\ &= \frac{\partial}{\partial x_\alpha}\int d^3\boldsymbol{v}\,fv_\alpha\chi - \int d^3\boldsymbol{v}\,fv_\alpha\,\frac{\partial\chi}{\partial x_\alpha}\end{aligned}$$

or

$$\int d^3\boldsymbol{v}\,\boldsymbol{v}\cdot\frac{\partial f}{\partial \boldsymbol{r}}\,\chi = \frac{\partial}{\partial x_\alpha}\,(n\langle v_\alpha\chi\rangle) - n\left\langle v_\alpha\,\frac{\partial\chi}{\partial x_\alpha}\right\rangle \qquad (14\cdot4\cdot15)$$

Finally, since we assumed the force $\boldsymbol{F}$ to be independent of velocity, one gets

$$\begin{aligned}\int d^3\boldsymbol{v}\,\frac{\boldsymbol{F}}{m}\cdot\frac{\partial f}{\partial \boldsymbol{v}}\,\chi &= \int d^3\boldsymbol{v}\,\frac{F_\alpha}{m}\,\frac{\partial f}{\partial v_\alpha}\,\chi\\ &= \int d^3\boldsymbol{v}\left[\frac{\partial}{\partial v_\alpha}\left(\frac{F_\alpha}{m}f\chi\right) - \frac{F_\alpha}{m}f\,\frac{\partial\chi}{\partial v_\alpha}\right]\\ &= \left[\frac{F_\alpha}{m}f\chi\right]_{v_\alpha=-\infty}^{v_\alpha=+\infty} - \int d^3\boldsymbol{v}\,\frac{F_\alpha}{m}f\,\frac{\partial\chi}{\partial v_\alpha}\end{aligned}$$

Since $f \to 0$ as $|v_\alpha| \to \infty$, this becomes simply

$$\int d^3\boldsymbol{v}\,\frac{\boldsymbol{F}}{m}\cdot\frac{\partial f}{\partial \boldsymbol{v}}\,\chi = -\frac{F_\alpha}{m}\,n\left\langle\frac{\partial\chi}{\partial v_\alpha}\right\rangle \qquad (14\cdot4\cdot16)$$

Hence (14·4·12) is obtained by adding the expressions (14·4·14) through (14·4·16). The result is

▶
$$\int d^3\boldsymbol{v}\,Df\,\chi = \frac{\partial}{\partial t}\,(n\langle\chi\rangle) + \frac{\partial}{\partial x_\alpha}\,(n\langle v_\alpha\chi\rangle) - n\langle D\chi\rangle \qquad (14\cdot4\cdot17)$$

where $D\chi$ is defined in (14·4·4).

We now turn to the evaluation of the collision term (14·4·13). This is by (14·2·4) most symmetrically written in the form

$$\mathfrak{C}(\chi) = \iiiint d^3\boldsymbol{v}\,d^3\boldsymbol{v}_1\,d^3\boldsymbol{v}'\,d^3\boldsymbol{v}_1'\,(f'f_1' - ff_1)V\sigma'(\boldsymbol{v},\boldsymbol{v}_1 \to \boldsymbol{v}',\boldsymbol{v}_1')\chi(\boldsymbol{r},\boldsymbol{v},t) \qquad (14\cdot4\cdot18)$$

The high symmetry of this expression can be exploited by interchanging $\boldsymbol{v}$ and $\boldsymbol{v}_1$ as well as $\boldsymbol{v}'$ and $\boldsymbol{v}_1'$. This leaves σ' unchanged so that one obtains

$$\mathfrak{C}(\chi) = \iiiint d^3\boldsymbol{v}\,d^3\boldsymbol{v}_1\,d^3\boldsymbol{v}'\,d^3\boldsymbol{v}_1'\,(f'f_1' - ff_1)V\sigma'\chi(\boldsymbol{r},\boldsymbol{v}_1,t) \qquad (14\cdot4\cdot19)$$

Adding (14·4·18) and (14·4·19) then yields

$$\mathcal{C}(\chi) = \tfrac{1}{2}\iiiint d^3\boldsymbol{v}\, d^3\boldsymbol{v}_1\, d^3\boldsymbol{v}'\, d^3\boldsymbol{v}_1'\, (f'f_1' - ff_1)V\sigma'[\chi + \chi_1] \tag{14·4·20}$$

with χ and χ_1 defined in (14·4·7).

But one can exploit a further symmetry by interchanging $\boldsymbol{v}$ and $\boldsymbol{v}'$, as well as $\boldsymbol{v}_1$ and $\boldsymbol{v}_1'$. This leads to the inverse collision which leaves σ' also unchanged. Thus one can write

$$\begin{aligned}\iiiint d^3\boldsymbol{v}\, d^3\boldsymbol{v}_1\, d^3\boldsymbol{v}'\, d^3\boldsymbol{v}_1'\, f'f_1'V\sigma\,[\chi + \chi_1]& \\ = \iiiint d^3\boldsymbol{v}\, d^3\boldsymbol{v}_1\, d^3\boldsymbol{v}'\, d^3\boldsymbol{v}_1'\, ff_1V\sigma'[\chi' + \chi_1']&\end{aligned} \tag{14·4·21}$$

where χ' and χ_1' are defined in (14·4·7).

Substituting (14·4·21) in (14·4·20) then yields

$$\mathcal{C}(\chi) = \tfrac{1}{2}\iiiint d^3\boldsymbol{v}\, d^3\boldsymbol{v}_1\, d^3\boldsymbol{v}'\, d^3\boldsymbol{v}_1'\, ff_1V\sigma'\,\Delta\chi$$

or

▶
$$\mathcal{C}(\chi) = \tfrac{1}{2}\iiint d^3\boldsymbol{v}\, d^3\boldsymbol{v}_1\, d\Omega'\, ff_1V\sigma\,\Delta\chi \tag{14·4·22}$$

where $\Delta\chi \equiv \chi' + \chi_1' - \chi - \chi_1$ is the total change in the quantity χ in the collision between two molecules. Substitution of (14·4·17) and (14·4·22) into (14·4·11) leads then again to Eq. (14·4·9).

14·5 *Conservation equations and hydrodynamics*

The equation of change (14·4·9) becomes particularly simple if χ refers to a quantity which is conserved in collisions between molecules so that $\Delta\chi = 0$. Then $\mathcal{C}(\chi) = 0$ and Eq. (14·4·9) reduces simply to*

$$\frac{\partial}{\partial t}\langle n\chi\rangle + \frac{\partial}{\partial x_\alpha}\langle nv_\alpha\chi\rangle = n\langle D\chi\rangle \tag{14·5·1}$$

The fundamental quantities which are conserved in a collision are, first, any constant, in particular the mass m of a molecule. Furthermore, each component of the total momentum of the colliding molecules is conserved. Finally, assuming the internal energies of all molecules to remain unchanged in collisions, the total kinetic energy of the colliding molecules is also conserved. These conservation laws lead then to five corresponding cases where $\Delta\chi = 0$ in (14·4·6). These are

conservation of mass $\quad \chi = m \quad$ (14·5·2)
conservation of momentum $\quad \chi = mv_\gamma, \quad \gamma = 1, 2, 3 \quad$ (14·5·3)
conservation of energy $\quad \chi = \tfrac{1}{2}mv^2 \quad$ (14·5·4)

One then obtains by (14·5·1) five corresponding conservation laws satisfied by the gas.

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* This equation and all subsequent considerations of this section are very general. They depend only on the conservation laws, not on the assumption of molecular chaos and the consequent special form (14.4.10) of $\mathcal{C}(\chi)$ involving ff_1 as a simple product.

Conservation of mass Putting $\chi = m$, Eq. (14·5·1) leads immediately to

$$\frac{\partial}{\partial t}(nm) + \frac{\partial}{\partial x_\alpha}\langle nmv_\alpha\rangle = 0 \qquad (14\cdot5\cdot5)$$

Here n is independent of $\boldsymbol{v}$ and can be taken outside the angular averaging brackets. Also by (13·1·5), $\langle \boldsymbol{v}\rangle = \boldsymbol{u}$, the mean velocity of the gas. Furthermore, the mass density of the gas, i.e., its mass per unit volume, is given by

$$\rho(\boldsymbol{r},t) = mn(\boldsymbol{r},t) \qquad (14\cdot5\cdot6)$$

Hence (14·5·5) becomes simply

▶
$$\frac{\partial\rho}{\partial t} + \frac{\partial}{\partial x_\alpha}(\rho u_\alpha) = 0 \qquad (14\cdot5\cdot7)$$

or using the vector notation of the divergence,

$$\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\boldsymbol{u}) = 0 \qquad (14\cdot5\cdot8)$$

This is the so-called "equation of continuity" of hydrodynamics. It expresses the macroscopic condition necessary to guarantee the conservation of mass.

Conservation of momentum By (14·5·3) we put $\chi = mv_\gamma$ so that Eq. (14·5·1) becomes

$$\frac{\partial}{\partial t}\langle nmv_\gamma\rangle + \frac{\partial}{\partial x_\alpha}\langle nmv_\alpha v_\gamma\rangle = n\langle m\, Dv_\gamma\rangle \qquad (14\cdot5\cdot9)$$

By the definition (14·4·4),

$$Dv_\gamma = \frac{F_\alpha}{m}\frac{\partial v_\gamma}{\partial v_\alpha} = \frac{F_\alpha}{m}\delta_{\gamma\alpha} = \frac{F_\gamma}{m}$$

Hence (14·5·9) becomes, using (14·5·7),

$$\frac{\partial}{\partial t}(\rho u_\gamma) + \frac{\partial}{\partial x_\alpha}(\rho\langle v_\alpha v_\gamma\rangle) = \rho F_\gamma' \qquad (14\cdot5\cdot10)$$

where
$$\boldsymbol{F}' \equiv \frac{\boldsymbol{F}}{m} \qquad (14\cdot5\cdot11)$$

is the force per unit mass of the fluid.

The second term in (14·5·10) is usefully expressed in terms of $\boldsymbol{u}$ and the peculiar velocity $\boldsymbol{U}$. By (13·1·6),

$$\boldsymbol{v} = \boldsymbol{u} + \boldsymbol{U}$$

and $\langle v_\alpha v_\gamma\rangle = \langle(u_\alpha + U_\alpha)(u_\gamma + U_\gamma)\rangle = \langle u_\alpha u_\gamma + U_\alpha U_\gamma + u_\alpha U_\gamma + U_\alpha u_\gamma\rangle$

or
$$\langle v_\alpha v_\gamma\rangle = u_\alpha u_\gamma + \langle U_\alpha U_\gamma\rangle \qquad (14\cdot5\cdot12)$$

since
$$\langle u_\alpha U_\gamma\rangle = u_\alpha\langle U_\gamma\rangle = 0$$

Furthermore, we define the "pressure tensor" $P_{\alpha\gamma}$ by

$$P_{\alpha\gamma} \equiv \rho\langle U_\alpha U_\gamma\rangle, \qquad P_{\gamma\alpha} = P_{\alpha\gamma} \qquad (14\cdot5\cdot13)$$

This definition agrees with that of (13·1·7). By (14·5·12) and (14·5·13), Eq. (14·5·10) then becomes

$$\frac{\partial}{\partial t}(\rho u_\gamma) + \frac{\partial}{\partial x_\alpha}(\rho u_\alpha u_\gamma) = -\frac{\partial P_{\alpha\gamma}}{\partial x_\alpha} + \rho F_\gamma{}' \tag{14·5·14}$$

This is the Euler equation of motion of macroscopic hydrodynamics. It can be put into more transparent form by rewriting the left side of (14·5·14) as

$$\begin{aligned} u_\gamma \frac{\partial \rho}{\partial t} + \rho \frac{\partial u_\gamma}{\partial t} + u_\gamma \frac{\partial}{\partial x_\alpha}(\rho u_\alpha) + \rho u_\alpha \frac{\partial u_\gamma}{\partial x_\alpha} \\ = u_\gamma \left[\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_\alpha}(\rho u_\alpha)\right] + \rho\left[\frac{\partial u_\gamma}{\partial t} + u_\alpha \frac{\partial u_\gamma}{\partial x_\alpha}\right] = 0 + \rho \frac{du_\gamma}{dt} \end{aligned}$$

Here the first square bracket vanishes by the equation of continuity (14·5·7); furthermore, we have defined the "substantial derivative" of any function $\phi(\mathbf{r},t)$ by

$$\frac{d\phi}{dt} \equiv \frac{\partial \phi}{\partial t} + u_\alpha \frac{\partial \phi}{\partial x_\alpha} \tag{14·5·15}$$

This measures the rate of change of the function ϕ if one considers oneself moving along with the mean velocity $\mathbf{u}$ of the fluid. Hence (14·5·14) becomes

▶
$$\rho \frac{du_\gamma}{dt} = -\frac{\partial P_{\alpha\gamma}}{\partial x_\alpha} + \rho F_\gamma{}' \tag{14·5·16}$$

This expresses physically the fact that the rate of change of mean momentum of any element of fluid is due to the stress forces (including the ordinary pressure) of the surrounding fluid, as well as to the external forces acting on the fluid.

We could, similarly, go on to use (14·5·4) to derive the hydrodynamic equation for energy conservation, but we shall not do this here.

The conservation equations (14·5·7) and (14·5·16) are rigorous consequences of the Boltzmann equation (14·3·8). Nevertheless it is clear that, in order to obtain from them practical hydrodynamic equations, one must find explicit expressions for quantities such as the pressure tensor $P_{\alpha\gamma}$. Of course, (14·5·13) provides a prescription for calculating this quantity in terms of molecular quantities, but this requires finding the actual distribution function f which is a solution of the Boltzmann equation (14·3·8). Hydrodynamic equations can thus be obtained to various orders of approximation. Details are discussed in the references.

14·6 *Example: simple discussion of electrical conductivity*

Before turning to detailed applications of the theory of this chapter to the solution of problems of physical interest, we shall show how the present formulation of the theory can also be useful in discussing situations in less rigorous terms. As an example, we shall give a semiquantitative treatment of electrical conductivity which, although almost as simple as the elementary arguments of Chapter 12, will bring out several new features of physical significance.

Consider the case of ions of mass m and charge e which move in a neutral gas consisting of molecules of mass m_1. Let the number of ions per unit volume be n, the number of neutral molecules per unit volume be n_1. The temperature is T, and a small uniform electric field $\mathcal{E}$ is applied in the z direction. We should like to find the electrical conductivity σ_{el} of the ions.

This situation was already discussed in Secs. 12·6, 13·4, and 13·8. Here we shall consider the collision processes in somewhat greater detail. We are interested in finding the electrical current density of the ions

$$j_z = enu_z \tag{14·6·1}$$

Since $\mathcal{E}$ depends on neither $\mathbf{r}$ nor t, it follows that neither n nor the mean ion velocity $\mathbf{u}$ depends on position $\mathbf{r}$ or on the time t once a steady-state situation has been reached. One can immediately write the equation for the mean momentum balance for the ions contained in a unit volume by using the equation of change (14·4·9). The direct physical argument is that the [rate of change of mean momentum of these ions] must be equal to [the mean external force exerted on these ions by the electric field] plus [the mean rate of momentum gain of these ions due to collisions]. In symbols

$$nm\frac{\partial u_z}{\partial t} = ne\mathcal{E} + \mathcal{C}(mv_z)$$

In the steady state $\partial u_z/\partial t = 0$ so that this condition becomes simply

$$ne\mathcal{E} + \mathcal{C}(mv_z) = 0 \tag{14·6·2}$$

To calculate the mean rate of ion-momentum gain caused by collisions, we note first that, when two ions collide, their total momentum is conserved. Hence there is *no* mean change of ion momentum caused by collisions between ions. Thus $\mathcal{C}(mv_z)$ is due entirely to momentum changes suffered by ions in collisions with neutral molecules.

The mean number of such ion-molecule collisions per unit time is approximately given by

$$\tau^{-1} = \bar{V}\sigma_{im}n_1 \tag{14·6·3}$$

where $\bar{V}$ is the mean relative speed between an ion and a molecule and σ_{im} is the total scattering cross section for scattering of an ion by a molecule. Here one can put approximately, as in (12·2·11),

$$\bar{V}^2 \approx \overline{V^2} = \overline{v^2} + \overline{v_1^2} = 3kT\left(\frac{1}{m} + \frac{1}{m_1}\right) = \frac{3kT}{\mu} \tag{14·6·4}$$

where we have used the equipartition theorem and introduced the reduced mass

$$\mu \equiv \frac{mm_1}{m + m_1} \tag{14·6·5}$$

We calculate next the mean momentum gain $\langle \boldsymbol{p} \rangle$ of an ion in an ion-molecule collision. By (14·1·3) we can write the ion velocity $\boldsymbol{v}$ in terms of the velocity $\boldsymbol{V}$ of an ion relative to the molecule with which it collides and the velocity $\boldsymbol{c}$ of their center of mass. Thus $\boldsymbol{p} = m\boldsymbol{v} = m\boldsymbol{c} + \mu\boldsymbol{V}$. The momentum change of the ion in this collision is then

$$\Delta \boldsymbol{p} = m(\boldsymbol{v}' - \boldsymbol{v}) = \mu(\boldsymbol{V}' - \boldsymbol{V}) = \mu[(\cos\theta' - 1)\boldsymbol{V} + \boldsymbol{V}_\perp'] \qquad (14\cdot6\cdot6)$$

Here we have resolved $\boldsymbol{V}'$ into components parallel and perpendicular to $\boldsymbol{V}$. The relative velocity $\boldsymbol{V}'$ after collision is such that $|\boldsymbol{V}'| = |\boldsymbol{V}|$ and that it makes an angle θ' with respect to $\boldsymbol{V}$. On the average, $\boldsymbol{V}'$ will have no components perpendicular to $\boldsymbol{V}$ so that $\langle \boldsymbol{V}_\perp' \rangle = 0$. Furthermore, if the collision is like that between hard spheres, all scattering angles θ' are equally probable so that $\cos\theta' = 0$ on the average. (See Problem 12.4.) Hence on the average (14·6·6) gives, for the mean momentum gain of an ion per collision,

$$\begin{aligned} &\langle \Delta \boldsymbol{p} \rangle = -\mu\langle \boldsymbol{V} \rangle = -\mu\langle \boldsymbol{v} - \boldsymbol{v}_1 \rangle \\ \text{or} \qquad &\langle \Delta \boldsymbol{p} \rangle = -\mu\boldsymbol{u} \qquad (14\cdot6\cdot7) \end{aligned}$$

if we assume that the neutral molecules are at rest with respect to the container walls so that their mean velocity $\boldsymbol{u}_1 = 0$.

It is of interest to compare $\langle \Delta \boldsymbol{p} \rangle$ with the mean momentum $m\boldsymbol{u}$ of the ions. (In the present problem, $\boldsymbol{u}$ has, of course, only a nonvanishing component in the z direction.) Then (14·6·7) can be written

$$\langle \Delta \boldsymbol{p} \rangle \equiv -\xi m\boldsymbol{u}, \qquad \xi \equiv \frac{\mu}{m} = \frac{m_1}{m + m_1} \qquad (14\cdot6\cdot8)$$

where ξ denotes the fractional mean momentum loss of an ion per collision. This shows that if $m \ll m_1$, then $\xi \approx 1$; the ion loses then, on the average, practically all its forward momentum in each collision with the much heavier molecule. On the other hand, if $m \gg m_1$, then $\xi \approx m_1/m$; the ion loses then, on the average, only a relatively small fraction m_1/m of its forward momentum in each collision with the much lighter molecule. In the latter case, collisions with molecules are, of course, not very effective in reducing the electrical conductivity of the ions. The factor ξ of (14·6·8) shows that an ion after a collision may have a velocity which depends strongly on its velocity before the collision, particularly if $m \gg m_1$. Hence this factor takes into account the persistence of velocity effects which we ignored in the preceding two chapters.

The mean rate of collision-induced momentum gain of an ion can then be computed by multiplying the mean number τ^{-1} of ion-molecule collisions per unit time by the mean momentum gain $\langle \Delta \boldsymbol{p} \rangle$ per collision. By (14·6·8) the momentum balance (14·6·2) becomes simply

$$e\mathcal{E} - \tau^{-1}(\xi m u_z) = 0 \qquad (14\cdot6\cdot9)$$

Hence

$$u_z = \frac{e}{m}\frac{\tau}{\xi}\mathcal{E}$$

By (14·6·1) the electrical conductivity is then

$$\sigma_{\text{el}} \equiv \frac{j_z}{\mathcal{E}} = \frac{ne^2}{m}\frac{\tau}{\xi}] \qquad (14\cdot 6\cdot 10)$$

This differs from the previous expressions (12·6·8) or (13·4·10) by the factor ξ which takes into account the persistence-of-velocity effects. Using (14·6·3) and (14·6·8) one gets explicitly

$$\sigma_{\text{el}} = \frac{ne^2}{m}\left[\sqrt{\frac{3kT}{\mu}}\,\sigma_{\text{im}}n_1\right]^{-1}\left(\frac{m}{\mu}\right)$$

or

$$\sigma_{\text{el}} = \frac{ne^2}{n_1\sigma_{\text{im}}}\frac{1}{\sqrt{3\mu kT}} \qquad (14\cdot 6\cdot 11)$$

Note that this depends only on the *reduced* mass of the ion and molecule. If $m \ll m_1$ so that persistence-of-velocity effects are negligible, then $\mu = m$ and (14·6·11) reduces essentially to (12·6·9). But in the opposite limit, where $m \gg m_1$, one gets $\mu = m_1$, and σ_{el} becomes independent of the mass of the ion.

The relation (14·6·11) exhibits the correct dependence on the various parameters of the problem. In particular, it takes into account persistence-of-velocity effects and shows properly that ion-ion collisions have no appreciable effect on the electrical conductivity. A more careful evaluation of the momentum-balance equation would lead to numerically more accurate results. We leave this as an exercise in one of the problems at the end of the chapter.

14 · 7 *Approximation methods for solving the Boltzmann equation*

To apply the transport theory developed in this chapter to a quantitative discussion of situations of physical interest, it is necessary to find approximate solutions of the Boltzmann equation

$$Df = D_cf \qquad (14\cdot 7\cdot 1)$$

written out explicitly in (14·3·8). Our aim will not be to find the most exact solutions accessible by means of elaborate approximation procedures, but to show how results of good accuracy can be obtained by relatively simple methods.

To find the distribution function $f(\mathbf{r},\mathbf{v},t)$ which satisfies (14·7·1), we assume again that we are dealing with a physical situation which is not too far removed from equilibrium conditions. Then one expects that $f(\mathbf{r},\mathbf{v},t)$ does not differ too much from a Maxwell distribution $f^{(0)}(\mathbf{r},\mathbf{v},t)$, which describes *local* equilibrium conditions near a particular place and time; i.e.,

$$f^{(0)}(\mathbf{r},\mathbf{v},t) = n\left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} e^{-\frac{1}{2}\beta m(\mathbf{v}-\mathbf{u})^2} \qquad (14\cdot 7\cdot 2)$$

where n, β, and $\mathbf{u}$ may all be slowly varying functions of $\mathbf{r}$ and t, but do not depend on $\mathbf{v}$. Since the dependence of $f^{(0)}$ on $\mathbf{v}$ is thus the same as that for a genuine equilibrium distribution, and since the collision term in the Boltzmann equation involves only integrations over velocities, it follows that $f^{(0)}$ has the same property as a genuine equilibrium distribution of remaining unchanged under the influence of collisions; i.e.,

$$D_C f^{(0)} = 0 \tag{14·7·3}$$

Remark This can be readily verified by showing that, for any $\mathbf{r}$ and t,

$$f^{(0)}(\mathbf{v})f^{(0)}(\mathbf{v}_1) = f^{(0)}(\mathbf{v}')f^{(0)}(\mathbf{v}_1') \tag{14·7·4}$$

so that the integrand on the right side of (14·3·8) vanishes. Equivalently, it is necessary to show that

$$\ln f^{(0)}(\mathbf{v}) + \ln f^{(0)}(\mathbf{v}_1) = \ln f^{(0)}(\mathbf{v}') + \ln f^{(0)}(\mathbf{v}_1')$$

or by (14·7·2) that

$$\tfrac{1}{2}m(\mathbf{v} - \mathbf{u})^2 + \tfrac{1}{2}m(\mathbf{v}_1 - \mathbf{u})^2 = \tfrac{1}{2}m(\mathbf{v}' - \mathbf{u})^2 + \tfrac{1}{2}m(\mathbf{v}_1' - \mathbf{u})^2 \tag{14·7·5}$$

But the left side of (14·7·5) can be written simply as

$$(\tfrac{1}{2}mv^2 + \tfrac{1}{2}mv_1^2) - (m\mathbf{v} + m\mathbf{v}_1)\cdot\mathbf{u} + mu^2$$

which involves, besides constants, only the total kinetic energy and the total momentum of the particles before collision. Since the right side of (14·7·5) is of the same form, except for referring to velocities after the collision, the conditions of conservation of total kinetic energy and of total momentum in a collision imply immediately the validity of (14·7·5) and hence of (14·7·3).

Of course, $f^{(0)}$ does *not* in general reduce the left side of the Boltzmann equation (14·7·1) to zero. That is, $Df^{(0)} \neq 0$, unless n, β, and $\mathbf{u}$ are independent of $\mathbf{r}$ and t. Only then would $f^{(0)}$ be a genuine, rather than merely a local, equilibrium distribution function satisfying the Boltzmann equation (14·7·1).

To exploit the assumption that the situation is not far removed from equilibrium, one can write f in the form

$$f = f^{(0)}(1 + \Phi), \qquad \text{where } \Phi \ll 1 \tag{14·7·6}$$

In the Boltzmann equation (14·7·1), the contribution of the correction term $f^{(0)}\Phi$ to the left side can then be neglected compared to the contribution of $f^{(0)}$. Thus

$$Df \approx Df^{(0)} \tag{14·7·7}$$

The right side of (14·7·1) is given by (14·3·8) as

$$D_C f = \iint d^3\mathbf{v}_1\, d\Omega'\, (f'f_1' - ff_1)V\sigma \tag{14·7·8}$$

Using (14·7·6), one has

$$ff_1 = f^{(0)}f_1^{(0)}(1 + \Phi + \Phi_1)$$

where we have neglected the small quadratic term $\Phi\Phi_1$. Similarly, one has

$$f'f_1' = f^{(0)}f_1^{(0)}(1 + \Phi' + \Phi_1')$$

where we have used (14·7·4) to put $f^{(0)\prime}f_1^{(0)\prime} = f^{(0)}f_1^{(0)}$.

Substituting these relations into (14·7·8), and using the fact that terms involving only $f^{(0)}$'s lead to a vanishing contribution to the integral (since

$D_C f^{(0)} = 0$ by (14·7·3)), one obtains

$$D_C f = \mathfrak{L}\Phi \tag{14·7·9}$$

where

▶ $$\mathfrak{L}\Phi \equiv \iint d^3\mathbf{v}\, d\Omega'\, f^{(0)} f_1^{(0)} V\sigma\, \Delta\Phi \tag{14·7·10}$$

with

$$\Delta\Phi = \Phi' + \Phi_1' - \Phi - \Phi_1 \tag{14·7·11}$$

In terms of these abbreviations the Boltzmann equation (14·7·1) is then, by (14·7·7) and (14·7·9), reduced to the approximate form

▶ $$Df^{(0)} = \mathfrak{L}\Phi \tag{14·7·12}$$

The functional form of $f^{(0)}$ is known by (14·7·2); hence the left side of (14·7·12) is a known function. The unknown function Φ appears in (14·7·12) only in the *integrand* of the right side. Finding the functional form of Φ which satisfies the integral equation (14·7·12) is still not a trivial task. On the other hand, this equation is linear in Φ and very much simpler than the original Boltzmann equation (14·7·1).

Remark We can impose one physical requirement which helps to place some restriction on the possible form of Φ. Let us require that the actual function $f(\mathbf{r},\mathbf{v},t)$ be such that the quantities $n(\mathbf{r},t)$, $\mathbf{u}(\mathbf{r},t)$, and $\beta(\mathbf{r},t) \equiv (kT)^{-1}$ in (14·7·2) preserve their usual meaning of denoting respectively the mean number of particles per unit volume, their mean velocity, and their mean thermal kinetic energy. In more mathematical terms this means that we require the following relations, true in the equilibrium situation when n, $\mathbf{u}$, and T are independent of $\mathbf{r}$ and t, to remain valid even if these parameters do depend on $\mathbf{r}$ and t:

$$\left.\begin{aligned} \int d^3\mathbf{v}\, f &= n(\mathbf{r},t) \\ \frac{1}{n}\int d^3\mathbf{v}\, f\mathbf{v} &= \mathbf{u}\,(\mathbf{r},t) \\ \frac{1}{n}\int d^3\mathbf{v}\, f\left[\frac{1}{2}m(\mathbf{v}-\mathbf{u})^2\right] &= kT(\mathbf{r},t) \end{aligned}\right\} \tag{14·7·13}$$

By (14·7·6), the first term $f^{(0)}$ by itself satisfies all these relations. Hence it follows that, to satisfy (14·7·13), the function Φ must be such that

$$\left.\begin{aligned} \int d^3\mathbf{v}\, f^{(0)}\Phi &= 0 \\ \int d^3\mathbf{v}\, f^{(0)}\Phi\mathbf{v} &= 0 \\ \int d^3\mathbf{v}\, f^{(0)}\Phi(\mathbf{v}-\mathbf{u})^2 &= 0 \end{aligned}\right\} \tag{14·7·14}$$

To determine the function Φ which satisfies (14·7·12), one can assume that it has some reasonable functional form which depends on q parameters $A_1, A_2, A_3, \ldots, A_q$. For example, one could assume that Φ is a function of $\mathbf{U} \equiv \mathbf{v} - \mathbf{u}$ of the form

$$\Phi = \sum_{\lambda=1}^{3} a_\lambda U_\lambda + \sum_{\lambda,\mu=1}^{3} a_{\lambda\mu} U_\lambda U_\mu + \cdots \tag{14·7·15}$$

where the coefficients a_λ and $a_{\lambda\mu}$ are parameters. If one takes this assumed form of Φ and substitutes it into (14·7·12), one will in general find that $\mathfrak{L}\Phi$ is not the same function of $\boldsymbol{v}$ as the left-hand side $Df^{(0)}$. Hence no choice of the parameters $A_1, \ldots, A_q$ will really fulfill the requirement that (14·7·12) be satisfied for all values of $\boldsymbol{v}$. Nevertheless, one's guess as to the functional form of Φ may not be too bad, provided that one makes an optimum choice of the parameters $A_1, \ldots, A_q$. One systematic way of making this choice is to replace the task of satisfying Eq. (14·7·12) by the weaker requirement of satisfying it only in an average sort of way. For example, if $\Psi(\boldsymbol{v})$ is any function of $\boldsymbol{v}$, then it follows by (14·7·12) that

$$\int d^3\boldsymbol{v}\,\Psi\,Df^{(0)} = \int d^3\boldsymbol{v}\,\Psi\,\mathfrak{L}\Phi \qquad (14\cdot 7\cdot 16)$$

Since one has integrated over $\boldsymbol{v}$, both sides of this equation are independent of $\boldsymbol{v}$. Although (14·7·12) implies (14·7·16), the converse is, of course, *not* true; i.e., if Φ satisfies (14·7·16) for a given choice of the function Ψ, it does *not* necessarily satisfy the original equation (14·7·12). Only if (14·7·16) were satisfied for *all* possible functions Ψ, could one conclude that (14·7·16) is equivalent to (14·7·12). Nevertheless, if one chooses some set of q functions $\Psi_1, \ldots, \Psi_q$ and tries to satisfy the resulting q equations (14·7·16) for all of these, then one obtains q simple *algebraic* equations for the q unknown parameters $A_1 \ldots A_q$. One would then expect that this choice of the A's would give a reasonably good solution of (14·7·12). Of course, the larger the number q of parameters at one's disposal (and the corresponding number of Ψ's used to obtain independent algebraic equations (14·7·16)), the better can one expect the solution to approximate the real solution of (14·7·12). If one assumes the functional form (14·7·15) for Φ, then the various "test functions" Ψ are most conveniently chosen to be functions of the form U_λ, $U_\lambda U_\mu$, ... The method just described is then called the "method of moments."

Note that (14·7·16) is equivalent to (14·4·11); thus the condition (14·7·16) implies physically the requirement that the *mean* value $\langle\Psi\rangle$ satisfies the correct equation of change (14·4·9).

Solution by use of a variational principle A particularly powerful method of solving (14·7·12) is provided by the use of a suitable variational principle. Note that the integral in (14·7·12) is linear in Φ; i.e., for any two functions Φ and Ψ

$$\mathfrak{L}(\Phi + \Psi) = \mathfrak{L}\Phi + \mathfrak{L}\Psi \qquad (14\cdot 7\cdot 17)$$

Note also that the integral in (14·7·16) has a lovely degree of symmetry. Using (14·7·10) and (14·2·4) it can be written in the symmetric form

$$\int d^3\boldsymbol{v}\,\Psi\,\mathfrak{L}\Phi = \iiiint d^3\boldsymbol{v}\,d^3\boldsymbol{v}_1\,d^3\boldsymbol{v}'\,d^3\boldsymbol{v}_1'\,f^{(0)}f_1^{(0)}V\sigma'(\boldsymbol{v},\boldsymbol{v}_1 \rightarrow \boldsymbol{v}',\boldsymbol{v}_1')\Psi\,\Delta\Phi \qquad (14\cdot 7\cdot 18)$$

One can now proceed as we did in transforming the expression (14·4·18) into (14·4·22). First interchange $\boldsymbol{v}$ and $\boldsymbol{v}_1$, as well as $\boldsymbol{v}'$ and $\boldsymbol{v}_1'$. Then σ' as well as $\Delta\Phi$ are unchanged. Thus (14·7·8) becomes (we omit the volume elements in the integrals for the sake of brevity)

$$\int \Psi\,\mathfrak{L}\Phi = \iiiint f^{(0)}f_1^{(0)}V\sigma'\Psi_1\,\Delta\Phi$$

Adding this to (14·7·18) then gives

$$\int \Psi\,\mathfrak{L}\Phi = \tfrac{1}{2}\iiiint f^{(0)}f_1^{(0)}V\sigma'[\Psi + \Psi_1]\,\Delta\Phi \tag{14·7·19}$$

Interchanging $\mathbf{v}$ and $\mathbf{v}'$ as well as $\mathbf{v}_1$ and $\mathbf{v}_1'$ (i.e., passing to the inverse collision) leaves σ' unchanged and changes the sign of $\Delta\Phi$. Also by (14·7·4), $f^{(0)\prime}f_1^{(0)\prime} = f^{(0)}f_1^{(0)}$. Hence (14·7·19) becomes

$$\int \Psi\,\mathfrak{L}\Phi = -\tfrac{1}{2}\iiiint f^{(0)}f_1^{(0)}V\sigma'[\Psi' + \Psi_1']\,\Delta\Phi$$

Adding this to (14·7·19) yields the symmetrical form

$$\int \Psi\,\mathfrak{L}\Phi = -\tfrac{1}{4}\iiiint f^{(0)}f_1^{(0)}V\sigma'\,\Delta\Psi\,\Delta\Phi \tag{14·7·20}$$

where $\Delta\Psi = \Psi' + \Psi_1' - \Psi - \Psi_1$.

The result (14·7·20) implies two important properties. First it yields the symmetry relation

$$\blacktriangleright \qquad \int \Psi\,\mathfrak{L}\Phi = \int \Phi\,\mathfrak{L}\Psi \tag{14·7·21}$$

Second, if $\Psi = \Phi$, then the integrand in (14·7·20) is positive so that

$$\blacktriangleright \qquad \int \Phi\,\mathfrak{L}\Phi \le 0 \tag{14·7·22}$$

Let us now compare the actual solution Φ of (14·7·12) with *any* other function $\Phi' = \Phi + \delta\Phi$. If we multiply both sides of (14·7·12) by Φ, we obtain the expressions $\int \Phi\,\mathfrak{L}\Phi$ and $\int \Phi\,Df^{(0)}$. Using instead the function Φ' and exploiting (14·7·21), these expressions become, respectively,

$$\int \Phi'\,\mathfrak{L}\Phi' = \int (\Phi + \delta\Phi)\,\mathfrak{L}(\Phi + \delta\Phi) = \int \Phi\,\mathfrak{L}\Phi + 2\int \delta\Phi\,\mathfrak{L}\Phi + \int \delta\Phi\,\mathfrak{L}\,\delta\Phi \tag{14·7·23}$$

and

$$\int \Phi'\,Df^{(0)} = \int (\Phi + \delta\Phi)\,Df^{(0)} = \int \Phi\,Df^{(0)} + \int \delta\Phi\,Df^{(0)} \tag{14·7·24}$$

Hence, if one considers the expression

$$\blacktriangleright \qquad M \equiv \int d^3v\,\Phi\,\mathfrak{L}\Phi - 2\int d^3v\,\Phi\,Df^{(0)} = \int d^3v\,\Phi(\mathfrak{L}\Phi - 2\,Df^{(0)}) \tag{14·7·25}$$

and the corresponding expression M' calculated with the function Φ', one finds by (14·7·23) and (14·7·24) that

$$M' - M = \int \delta\Phi\,\mathfrak{L}\,\delta\Phi \le 0 \tag{14·7·26}$$

where we have deliberately defined M so that, by virtue of (14·7·12), terms linear in $\delta\Phi$ vanish in (14·7·26). Hence M does not change for small changes $\delta\Phi$ in the function Φ, but is always negative for larger values of $\delta\Phi$. Thus we arrive at the "variational principle":

> The expression M assumes its maximum value for that particular function Φ which is a solution of the Boltzmann equation (14·7·12).

This provides one with a *very* powerful method of finding approximate solutions of the Boltzmann equation (14·7·12). If one assumes a functional form for Φ which contains several parameters, then the optimum choice of these parameters which provides one with the best solution to (14·7·12) is that which makes the expression M a maximum. One can also quite systematically find increasingly better approximations to the real solution of (14·7·12) by successively modifying one's first guess of the function Φ in such a way as to make M greater and greater.

As the simplest example, assume that Φ is of the form $\Phi = A\phi$, where ϕ is some function of $\mathbf{v}$ and A is a parameter. Then (14·7·25) gives

$$M = A^2 \int \phi\, \mathcal{L}\phi - 2A \int \phi\, Df^{(0)}$$

The optimum choice of A is obtained by maximizing M, i.e., by putting

$$\frac{\partial M}{\partial A} = 0 = 2A \int \phi\, \mathcal{L}\phi - 2 \int \phi\, Df^{(0)}$$

so that

$$A = \frac{\int \phi\, Df^{(0)}}{\int \phi\, \mathcal{L}\phi} \tag{14·7·27}$$

14 · 8 *Example: calculation of the coefficient of viscosity*

Consider again the physical situation illustrated in Fig. 12·3·2 where the gas has a mean velocity $u_x(z)$ in the x direction and a gradient $\partial u_x/\partial z \neq 0$. We are interested in calculating the shearing stress P_{zx}.

This situation is time-independent and only u_x depends on z. Hence the *local* equilibrium distribution is simply that already used in (13·8·6); i.e.,

$$f^{(0)}(\mathbf{r},\mathbf{v},t) = n\left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} e^{-\frac{1}{2}\beta m\{[v_x - u_x(z)]^2 + v_y^2 + v_z^2\}}$$

where β and n are just constants. More compactly one can write this in the form

$$f^{(0)}(\mathbf{r},\mathbf{v},t) = g(U) \tag{14·8·1}$$

where

$$U_x(z) \equiv v_x - u_x(z), \qquad U_y = v_y, \qquad U_z = v_z \tag{14·8·2}$$

and

$$g(U) = n\left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} e^{-\frac{1}{2}\beta m U^2} \tag{14·8·3}$$

Since there are no external forces so that $\mathbf{F} = 0$, one has simply

$$Df^{(0)} = v_z \frac{\partial f^{(0)}}{\partial z} = v_z \frac{\partial g}{\partial U_x}\left(-\frac{\partial u_x}{\partial z}\right) = \beta m g(U) U_z U_x \frac{\partial u_x}{\partial z}$$

where we have put $v_z = U_z$ by (14·8·2). Hence the Boltzmann equation (14·7·12) becomes, using (14·8·3),

$$\left(\beta m \frac{\partial u_x}{\partial z}\right) g(U) U_z U_x = \iint d^3U_1\, d\Omega'\, g(U) g(U_1) V\sigma\, \Delta\Phi \tag{14·8·4}$$

It remains to determine how Φ depends on $\boldsymbol{v}$, or equivalently on $\boldsymbol{U}$, so that it yields upon integration the left side of (14·8·4). This left side transforms under rotation of coordinate axes like the product of the vector components $U_z U_x$. The right side must, therefore, behave similarly. Thus we are led to expect that Φ has the form

$$\Phi = A U_z U_x \tag{14·8·5}$$

where A, in general, might be some function of $|\boldsymbol{U}|$. We shall, however, assume that to a first approximation A is simply independent of $|\boldsymbol{U}|$. To determine the value of this one parameter A which gives the best solution, we proceed by the method of (14·7·16). We shall multiply both sides of (14·8·4) by the test function $U_z U_x$, integrate over $\boldsymbol{v}$ (or equivalently $\boldsymbol{U}$), and try to satisfy the resulting equation by proper choice of A. This means that we are trying to satisfy, instead of (14·8·4), the equation

$$\beta m \frac{\partial u_x}{\partial z} \int d^3\boldsymbol{U}\, g(U) U_z^2 U_x^2 = A \iiint d^3\boldsymbol{U}\, d^3\boldsymbol{U}_1\, d\Omega'\, g(U) g(U_1) V\sigma U_z U_x\, \Delta(U_z U_x) \tag{14·8·6}$$

(Note that this choice of A is exactly equivalent to that given by the variational principle in (14·7·27).)

The integral on the left is by (14·8·6) simply

$$\int d^3\boldsymbol{U}\, g(U) U_z^2 U_x^2$$
$$= n\left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m U_y^2}\, dU_y \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m U_z^2}\, U_z^2\, dU_z \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m U_x^2}\, U_x^2\, dU_x$$

or

$$\int d^3\boldsymbol{U}\, g(U) U_z^2 U_x^2 = n\overline{U_z^2}\,\overline{U_x^2} = n\left(\frac{kT}{m}\right)^2 \tag{14·8·7}$$

where the bars denote equilibrium values calculated with the equilibrium function g; these can therefore be obtained by the equipartition theorem without need of explicit calculation.

In the integral on the right side of (14·8·6) we shall first integrate over all angles of scattering, i.e., over all $d\Omega'$, and then integrate over $\boldsymbol{U}$ and $\boldsymbol{U}_1$. Thus we write this integral in the form

$$I \equiv \iint d^3\boldsymbol{U}\, d^3\boldsymbol{U}_1\, g(U) g(U_1) U_z U_x\, J(\boldsymbol{U},\boldsymbol{U}_1) \tag{14·8·8}$$

where

$$J(\boldsymbol{U},\boldsymbol{U}_1) \equiv \int d\Omega'\, V\sigma\, \Delta(U_z U_x) \tag{14·8·9}$$

Using (14·8·7), Eq. (14·8·6) then becomes simply

▶
$$n\left(\frac{kT}{m}\right)\frac{\partial u_x}{\partial z} = AI \tag{14·8·10}$$

Before evaluating I, note that the function Φ of (14·8·5) satisfies, by symmetry, the conditions (14·7·14). Note also that the pressure tensor P_{zx} can be immediately calculated from (14·8·5). By (13·1·17)

$$P_{zx} = m\int d^3\boldsymbol{v}\, f U_z U_x = m\int d^3\boldsymbol{U}\, g(U)(1 + \Phi) U_z U_x$$
$$= 0 + m\int d^3\boldsymbol{U}\, g\Phi U_z U_x = Am\int d^3\boldsymbol{U}\, g U_z^2 U_x^2$$

where we have used the fact that the integral involving $g(U)$ alone vanishes by symmetry. Since the last integral is just that of (14·8·7), one obtains

▶
$$P_{zx} = nm\left(\frac{kT}{m}\right)^2 A \tag{14·8·11}$$

Thus the calculation is completed once the integral I is evaluated, since A is then known by (14·8·10).

Evaluation of the collision integral I We first evaluate the integral J of (14·8·9). Since the integrand involves V directly as well as in the cross section $\sigma(V)$, we express $\mathbf{U}$ in terms of the relative velocity $\mathbf{V}$ and the center-of-mass velocity $\mathbf{c}$. Thus

$$\mathbf{V} = \mathbf{v} - \mathbf{v}_1 = \mathbf{U} - \mathbf{U}_1 \tag{14·8·12}$$

Also, since all molecules have the same mass m,

$$\mathbf{c} = \frac{m\mathbf{v} + m\mathbf{v}_1}{2m} = \frac{1}{2}(\mathbf{v} + \mathbf{v}_1)$$

or

$$\mathbf{C} \equiv \mathbf{c} - \mathbf{u} = \tfrac{1}{2}(\mathbf{U} + \mathbf{U}_1) \tag{14·8·13}$$

where $\mathbf{C}$ is the center-of-mass velocity measured relative to the mean velocity $\mathbf{u}$ of the gas. By (14·8·12) and (14·8·13) one finds, analogously to (14·1·3),

$$\mathbf{U} = \mathbf{C} + \tfrac{1}{2}\mathbf{V}, \qquad \mathbf{U}_1 = \mathbf{C} - \tfrac{1}{2}\mathbf{V} \tag{14·8·14}$$

After the collision one has similarly

$$\mathbf{U}' = \mathbf{C} + \tfrac{1}{2}\mathbf{V}', \qquad \mathbf{U}_1 = \mathbf{C} - \tfrac{1}{2}\mathbf{V}' \tag{14·8·15}$$

since $\mathbf{C}$ remains constant. Now, by (14·7·11),

$$\Delta(U_zU_x) = U_z'U_x' + U_{1z}'U_{1x}' - U_zU_x - U_{1z}U_{1x}$$

Using (14·8·14), one obtains

$$\begin{aligned} U_zU_x + U_{1z}U_{1x} &= (C_z + \tfrac{1}{2}V_z)(C_x + \tfrac{1}{2}V_x) + (C_z - \tfrac{1}{2}V_z)(C_x - \tfrac{1}{2}V_x) \\ &= 2C_zC_x + \tfrac{1}{2}V_zV_x \end{aligned}$$

Hence

$$\Delta(U_zU_x) = \tfrac{1}{2}(V_z'V_x' - V_zV_x) \tag{14·8·16}$$

Thus (14·8·9) becomes

$$J = \tfrac{1}{2}\int_0^\pi \int_0^{2\pi} \sin\theta'\, d\theta'\, d\varphi'\, V\sigma[V_z'V_x' - V_zV_x] \tag{14·8·17}$$

where θ' and φ' are the polar and azimuthal angles of $\mathbf{V}'$ measured with respect to $\mathbf{V}$ as polar axis. This vector $\mathbf{V}$ is, of course, fixed in the integration (14·8·17) which is over the various directions of $\mathbf{V}'$. Imagine that $\mathbf{V}$ is taken to be along the ζ axis of a cartesian coordinate system ξ, η, ζ. Without loss of generality one can then choose the ξ axis, from which the angle φ' is measured, to lie in the $(\mathbf{V},\hat{\mathbf{z}})$ plane. Here $\hat{\boldsymbol{\xi}}$, $\hat{\boldsymbol{\eta}}$, $\hat{\boldsymbol{\zeta}}$ denote unit vectors directed along the ξ, η, ζ axes; similarly $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ denote unit vectors directed along the labora-

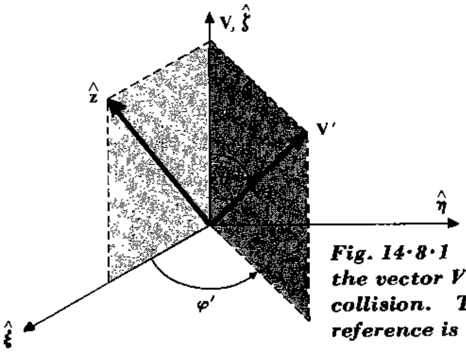

Fig. 14·8·1 Geometrical relationships between the vector V before and the vector V′ after a collision. The $\hat{\mathbf z}$ axis of the laboratory frame of reference is also shown.

tory x, y, z axes. The geometrical relationships are illustrated in Fig. 14·8·1. Since $|\mathbf{V}'| = |\mathbf{V}|$, one can write

$$\mathbf{V}' = V\cos\theta'\hat{\boldsymbol\zeta} + V\sin\theta'\cos\varphi'\hat{\boldsymbol\xi} + V\sin\theta'\sin\varphi'\hat{\boldsymbol\eta}$$

Remembering that $V\hat{\boldsymbol\zeta} = \mathbf{V}$ and that $\hat{\boldsymbol\eta} \perp \hat{\mathbf z}$, one then gets

$$\begin{aligned} V_z' &= \mathbf{V}'\cdot\hat{\mathbf z} = V_z\cos\theta' + V\sin\theta'\cos\varphi'\,\hat{\boldsymbol\xi}\cdot\hat{\mathbf z} \\ V_x' &= \mathbf{V}'\cdot\hat{\mathbf x} = V_x\cos\theta' + V\sin\theta'\cos\varphi'\,\hat{\boldsymbol\xi}\cdot\hat{\mathbf x} + V\sin\theta'\cos\varphi'\,\hat{\boldsymbol\xi}\cdot\hat{\boldsymbol\eta} \end{aligned} \qquad (14\cdot 8\cdot 18)$$

We shall assume that the forces between molecules depend only on the relative distance between them. Then the differential scattering cross section σ is independent of the azimuthal angle φ'; i.e., $\sigma = \sigma(V;\theta')$. The integral (14·8·17) is then much simplified. Consider first the integration over φ' from 0 to 2π. Since $\int\sin\varphi'\,d\varphi' = \int\cos\varphi'\,d\varphi' = \int\sin\varphi'\cos\varphi'\,d\varphi' = 0$, while $\int\cos^2\varphi'\,d\varphi' = \int\sin^2\varphi'\,d\varphi' = \pi$, use of (14·8·18) in (14·8·17) shows that all cross terms cancel. Thus (14·8·18) yields

$$\int_0^{2\pi} d\varphi'\,(V_z'V_x' - V_zV_x) = 2\pi V_zV_x\cos^2\theta' + \pi V^2\sin^2\theta'(\hat{\boldsymbol\xi}\cdot\hat{\mathbf z})(\hat{\boldsymbol\xi}\cdot\hat{\mathbf x}) - 2\pi V_zV_x \qquad (14\cdot 8\cdot 19)$$

To eliminate the vector $\hat{\boldsymbol\xi}$, we note that the condition $\hat{\mathbf z} \perp \hat{\mathbf x}$ can be expressed in terms of ξ, η, ζ components (i.e., in terms of direction cosines) as

$$\hat{\mathbf z}\cdot\hat{\mathbf x} = 0 = (\hat{\boldsymbol\xi}\cdot\hat{\mathbf z})(\hat{\boldsymbol\xi}\cdot\hat{\mathbf x}) + (\hat{\boldsymbol\eta}\cdot\hat{\mathbf z})(\hat{\boldsymbol\eta}\cdot\hat{\mathbf x}) + (\hat{\boldsymbol\zeta}\cdot\hat{\mathbf z})(\hat{\boldsymbol\zeta}\cdot\hat{\mathbf x})$$

Since $\hat{\boldsymbol\eta} \perp \hat{\mathbf z}$, this implies that

$$V^2(\hat{\boldsymbol\xi}\cdot\hat{\mathbf z})(\hat{\boldsymbol\xi}\cdot\hat{\mathbf x}) = -V^2(\hat{\boldsymbol\zeta}\cdot\hat{\mathbf z})(\hat{\boldsymbol\zeta}\cdot\hat{\mathbf x}) = -V_zV_x$$

Hence (14·8·19) becomes

$$\int_0^{2\pi} d\varphi'\,(V_z'V_x' - V_zV_x) = \pi V_zV_x(2\cos^2\theta' - \sin^2\theta' - 2) = -3\pi V_zV_x\sin^2\theta'$$

and (14·8·17) can be written in the form

▶ $$J = -\tfrac{3}{4}V_zV_xV\sigma_\eta(V) \qquad (14\cdot 8\cdot 20)$$

where

▶
$$\sigma_\eta(V) \equiv 2\pi \int_0^\pi \sigma(V,\theta') \sin^3\theta'\, d\theta' \tag{14·8·21}$$

can be interpreted as the total effective scattering cross section which enters the viscosity calculation.

One can now return to the integral (14·8·8), which becomes

$$I = -\tfrac{3}{4}\iint d^3\boldsymbol{U}\, d^3\boldsymbol{U}_1\, g(U)g(U_1)U_zU_xV_zV_xV\sigma_\eta(V)$$

or by (14·8·3)

$$I = -\frac{3}{4}n^2\left(\frac{m\beta}{2\pi}\right)^3 \iint_{-\infty}^{\infty} d^3\boldsymbol{U}\, d^3\boldsymbol{U}_1\, e^{-\frac{1}{2}\beta m(U^2+U_1^2)}U_zU_xV_zV_xV\sigma_\eta(V) \tag{14·8·22}$$

This integral depends again on the relative velocity $\boldsymbol{V}$. Hence we again make the transformation (14·8·14) to the variables $\boldsymbol{V}$ and $\boldsymbol{C}$. Analogously to (14·2·6), one has $d^3\boldsymbol{U}\, d^3\boldsymbol{U}_1 = d^3\boldsymbol{C}\, d^3\boldsymbol{V}$. Then (14·8·22) becomes

$$\begin{aligned} I &= -\frac{3}{4}n^2\left(\frac{m\beta}{2\pi}\right)^3 \iint_{-\infty}^{\infty} d^3\boldsymbol{C}\, d^3\boldsymbol{V}\, e^{-\beta m(C^2+\frac{1}{4}V^2)} \\ &\qquad\qquad \left(C_zC_x + \frac{1}{4}V_zV_x + \frac{1}{2}C_zV_x + \frac{1}{2}C_xV_z\right)V_zV_xV\sigma_\eta \\ &= -\frac{3}{4}n^2\left(\frac{m\beta}{2\pi}\right)^3 \int_{-\infty}^{\infty} d^3\boldsymbol{C}\, e^{-\beta mC^2} \int_{-\infty}^{\infty} d^3\boldsymbol{V}\, e^{-\frac{1}{4}\beta mV^2}\left(C_zC_xV_zV_x + \frac{1}{4}V_z^2V_x^2\right. \\ &\qquad\qquad \left. + \frac{1}{2}C_zV_zV_x^2 + \frac{1}{2}C_xV_z^2V_x\right)V\sigma_\eta(V) \end{aligned}$$

By symmetry it is clear that three of the terms in the parentheses are odd functions of V_z or V_x and lead therefore, by symmetry, to a vanishing result upon integration over $\boldsymbol{V}$. Thus one is left with

$$I = -\frac{3}{16}n^2\left(\frac{m\beta}{2\pi}\right)^3 \int_{-\infty}^{\infty} d^3\boldsymbol{C}\, e^{-\beta mC^2} \int_{-\infty}^{\infty} d^3\boldsymbol{V}\, e^{-\frac{1}{4}\beta mV^2}V_z^2V_x^2V\sigma_\eta(V) \tag{14·8·23}$$

By Appendix A·4 one has simply

$$\int_{-\infty}^{\infty} d^3\boldsymbol{C}\, e^{-\beta mC^2} = 4\pi \int_0^\infty e^{-\beta mC^2}\, C^2\, dC = \left(\frac{\pi}{m\beta}\right)^{\frac{3}{2}} \tag{14·8·24}$$

Expressing $\boldsymbol{V}$ in terms of spherical coordinates with $\hat{\boldsymbol{z}}$ as polar axis, one has $V_z = V\cos\theta$, $V_x = V\sin\theta\cos\varphi$, and $d^3\boldsymbol{V} = V^2\, dV \sin\theta\, d\theta\, d\varphi$. Thus one gets

$$\begin{aligned} \int d^3\boldsymbol{V}\, e^{-\frac{1}{4}\beta mV^2}V_z^2V_x^2\sigma_\eta(V) &= \int_0^\infty dV\, e^{-\frac{1}{4}\beta mV^2}V^7\sigma_\eta(V) \int_0^\pi d\theta \sin^3\theta\cos^2\theta \\ &\qquad \int_0^{2\pi} d\varphi \cos^2\varphi \\ &= \left[\left(\frac{2}{\sqrt{m\beta}}\right)^8 \int_0^\infty ds\, e^{-s^2}s^7\sigma_\eta\left(\frac{2s}{\sqrt{m\beta}}\right)\right]\left[\frac{4}{15}\right][\pi] \end{aligned} \tag{14·8·25}$$

where we have introduced the dimensionless variable

$$s = \frac{1}{2}\sqrt{m\beta}\, V = \frac{1}{\sqrt{2}}\frac{V}{\tilde{v}}$$

which physically expresses the relative speed V in terms of the most probable speed $\tilde{v}$ of the gas in equilibrium. If σ_η did not depend on the relative speed of the molecules, then the integral in (14 · 8 · 25) would, by Appendix A · 4, be equal to $3\sigma_\eta$. More generally, let us define a mean effective cross section by

▶ $$\bar{\sigma}_\eta(T) \equiv \frac{1}{3}\int_0^\infty ds\, e^{-s^2}\sigma_\eta\left(\frac{2s}{\sqrt{m\beta}}\right) \tag{14·8·26}$$

Then (14 · 8 · 25) becomes

$$\int d^3V\, e^{-\frac{1}{4}\beta m V^2} V_z{}^2 V_x{}^2 V \sigma_\eta(V) = \frac{1024\pi}{5}\frac{\bar{\sigma}_\eta}{(m\beta)^4} \tag{14·8·27}$$

Substituting (14 · 8 · 27) and (14 · 8 · 24) into (14 · 8 · 23) yields then

▶ $$I = -\frac{24}{5\sqrt{\pi}}\, n^2 \left(\frac{kT}{m}\right)^{\frac{3}{2}} \bar{\sigma}_\eta \tag{14·8·28}$$

Evaluation of the coefficient of viscosity Using (14 · 8 · 28), the parameter A is now given by (14 · 8 · 10) as

$$A = -\frac{5\sqrt{\pi}}{24}\frac{1}{n\bar{\sigma}_\eta}\left(\frac{m}{kT}\right)^{\frac{3}{2}}\frac{\partial u_x}{\partial z} \tag{14·8·29}$$

Then one obtains by (14 · 8 · 11)

$$P_{zx} = -\eta\frac{\partial u_x}{\partial z}$$

where

▶ $$\eta = \frac{5\sqrt{\pi}}{24}\frac{\sqrt{mkT}}{\bar{\sigma}_\eta} \tag{14·8·30}$$

This completes the calculation. It is, of course, apparent by (14 · 8 · 30) that η depends only on the temperature, but not on the pressure.

Note that it is the cross section σ_η of (14 · 8 · 21), rather than the total cross section $\sigma_0 = 2\pi \int_0^{2\pi} \sigma \sin\theta'\, d\theta'$, which enters this viscosity calculation. The extra $\sin^2\theta'$ factor in the integrand implies that scattering angles near 90° are weighted most heavily. The physical reason is clear; scattering through such angles is most effective in cutting down the rate of momentum transfer responsible for the viscosity.

Example Let us evaluate (14 · 8 · 30) for the special case where the molecules can be considered hard spheres of radius a. Then the total scattering cross section is

$$\sigma_0 = \pi(2a)^2 = 4\pi a^2 \tag{14·8·31}$$

The differential scattering cross section for hard spheres does not depend on the scattering angle θ' (see Problem 12.4). Thus

$$\sigma = \frac{\sigma_0}{4\pi} = a^2$$

Then one finds, by (14·8·21),

$$\sigma_\eta = 2\pi \left(\frac{\sigma_0}{4\pi}\right) \int_0^\pi \sin^3 \theta' \, d\theta' = \frac{1}{2}\sigma_0 \left(\frac{4}{3}\right) = \frac{2}{3}\sigma_0$$

Since this is independent of V, (14·8·26) gives simply

$$\bar{\sigma}_\eta = \sigma_\eta = \tfrac{2}{3}\sigma_0 \qquad (14\cdot 8\cdot 32)$$

Thus (14·8·30) becomes

$$\eta = \frac{5\sqrt{\pi}}{16} \frac{\sqrt{mkT}}{\sigma_0} = 0.553 \frac{\sqrt{mkT}}{\sigma_0} \qquad (14\cdot 8\cdot 33)$$

This is actually a very good value for the hard-sphere model. More refined approximations would only increase this result by 1.6 percent.

It is of interest to note that (14·8·33) is larger than the result of the most elementary mean-free-path calculation (12·3·19) by a factor of 1.47.

SUGGESTIONS FOR SUPPLEMENTARY READING

Relatively elementary discussions

R. D. Present: "Kinetic Theory of Gases," chaps. 8 and 11, McGraw-Hill Book Company, New York, 1958.

E. A. Guggenheim: "Elements of the Kinetic Theory of Gases," Pergamon Press, New York, 1960.

A. Sommerfeld: "Thermodynamics and Statistical Mechanics," chap. 5, Academic Press, New York, 1956.

E. M. Kennard: "Kinetic Theory of Gases," chap. 4, McGraw-Hill Book Company, New York, 1938.

More advanced books

K. Huang: "Statistical Mechanics," chaps. 3, 5, and 6, John Wiley & Sons, Inc., New York, 1963.

K. M. Watson, J. W. Bond, and J. A. Welch: "Atomic Theory of Gas Dynamics," Addison-Wesley Publishing Company, Reading, Mass., 1965.

S. Chapman and T. G. Cowling: "The Mathematical Theory of Non-uniform Gases," 2d ed., Cambridge University Press, Cambridge, 1952.

J. O. Hirschfelder, C. F. Curtiss, and R. B. Byrd, "Molecular Theory of Gases and Liquids," chaps. 7 and 8, John Wiley & Sons, Inc., New York, 1954.

PROBLEMS

14.1 Consider the physical situation envisaged in Sec. 14·6 where there are n ions per unit volume, each having charge e and mass m. These ions are free to the sake of simplicity, that the scattering of an ion by a molecule can be approximated by the scattering of hard spheres of total cross section σ_{im}. The neutral gas has zero drift velocity, since it is at rest with respect to the container. By carrying out the momentum balance argument of Sec. 14·6 exactly, derive an expression for the electrical conductivity of the ions in this gas.

14.2 Consider again the physical situation described in Problem 13.6 where a monatomic dilute gas at temperature T is enclosed in a container and is maintained in the presence of a small temperature gradient in the z direction. The molecular mass is m, and the differential scattering cross section describing collisions between molecules is $\sigma(V,\theta')$.

(*a*) Obtain an approximate form of the molecular distribution function. Refer to the suggestion in Problem 13·6 and note again that the physical situation of no mass motion requires that $\bar{v}_z = 0$.

(*b*) Find an approximate solution of the Boltzmann equation and use this result to find the coefficient of thermal conductivity of this gas. Express your answer in terms of T, m, and the effective total cross section $\bar{\sigma}_\eta(T)$ defined in (14·8·26).

(*c*) If the molecules can be considered hard spheres of total scattering cross section σ_0, calculate the thermal conductivity of this gas in terms of σ_0.

14.3 By comparing the general expressions derived in the case of a monatomic dilute gas for its thermal conductivity κ in Problem 14.2 and for its viscosity coefficient η in (14·8·30), show that the ratio κ/η is a constant independent of the nature of the interactions between the molecules.

(*a*) Find the numerical value of this ratio.

(*b*) Compare this value with the value which would be computed on the basis of the simplest mean-free-path arguments.

(*c*) Compare the value of this ratio predicted by the exact theory with experimental values obtained for several monatomic gases. Appended are a few values of atomic weights μ, viscosity η (in gm cm^{-1} sec^{-1}), and thermal conductivity κ (in ergs cm^{-1} sec^{-1} deg^{-1}) at $T = 373°$K

Gas	μ	η	κ
Neon	20.18	3.65×10^{-4}	5.67×10^3
Argon	39.95	2.70×10^{-4}	2.12×10^3
Xenon	131.3	2.81×10^{-4}	0.702×10^3

14.4 The general expression (6·6·24) for the entropy of a system suggests that the quantity H defined in terms of the distribution function $f(\mathbf{r},\mathbf{v},t)$ by

$$H \equiv \int d^3\mathbf{v}\, f \ln f$$

is related to the entropy of the gas. By using for f the equilibrium Maxwell velocity distribution verify that $H = -S/k$, where S is the entropy per unit volume of a monatomic ideal gas.

14.5 Use the definition

$$H \equiv \int d^3\mathbf{v}\, f \ln f$$

to obtain a general expression for the time derivative dH/dt. Make use of the Boltzmann equation satisfied by f, and exploit the symmetry of the resulting expression in a manner similar to that employed in evaluating the collision term at the end of Sec. 14·4.

(*a*) In this manner show that

$$\frac{dH}{dt} = -\frac{1}{4}\iiint d^3v\, d^3v_1\, d\Omega'\, V\sigma(\ln f'f_1' - \ln ff_1)(f'f_1' - ff_1)$$

(*b*) Since for any y and x,

$$(\ln y - \ln x)(y - x) \geq 0$$

(the equal sign being valid only when $y = x$), show that $dH/dt \leq 0$ and that the equals sign holds if, and only if, $f'f_1' = ff_1$. This is the so-called "Boltzmann H theorem," which proves that the quantity H always tends to decrease (i.e., the generalized entropy defined as $-H/k$ tends to increase).

(*c*) Since in equilibrium it must be true that $dH/dt = 0$, show that when equilibrium has been reached $f'f_1' = ff_1$.

14.6 The equilibrium condition $f'f_1' = ff_1$ is equivalent to

$$\ln f' + \ln f_1' = \ln f + \ln f_1$$

i.e., the sum of quantities before a collision must be equal to the sum of the corresponding quantities after the collision. The only quantities thus conserved are, besides a constant, the three momentum components of a molecule and its kinetic energy. Thus the equilibrium condition can only be satisfied by an expression of the form

$$\ln f = A + B_x mv_x + B_y mv_y + B_z mv_z + C(\tfrac{1}{2}mv^2)$$

where the coefficients A, B_x, B_y, B_z, and C are constants. Show that this implies that f must, therefore, be the Maxwellian velocity distribution (for a gas whose mean velocity does not necessarily vanish).