

The total number of molecules striking δA in time δt is given by:

$$\tilde{N} = \int_0^\infty v^2 dv \int_0^{\pi/2} d\theta \sin \theta \int_0^{2\pi} d\phi N_V \quad (28)$$

Again, assuming the gas is homogeneous in space:

$$N_V = \delta V n f(\mathbf{v}, t) = \delta A \delta t v \cos \theta n f(\mathbf{v}, t) \quad (29)$$

and the total number is given by:

$$\begin{aligned} \tilde{N} &= \int_0^\infty v^2 dv \int_0^{\pi/2} d\theta \sin \theta \int_0^{2\pi} d\phi \delta A \delta t v \cos \theta n f(\mathbf{v}, t) \\ &= \delta A \delta t n \int_0^\infty v^3 dv \int_0^{\pi/2} d\theta \sin \theta \cos \theta \int_0^{2\pi} d\phi f(\mathbf{v}, t) \end{aligned} \quad (30)$$

If we further assume the system is in thermal equilibrium, then we can use Eq. (23) and evaluate the remaining integrals (see Problem 7.2) to obtain:

$$\tilde{N} = a \delta A \delta t \quad (31)$$

where a , the rate of effusion, is given by:

$$a = n \left(\frac{kT}{2\pi m} \right)^{1/2} \quad (32)$$

and is the number of particles that escape from a hole in a wall enclosing a sample per unit time per unit area.

7.2.2

Mean-Free Path

Having considered collisions between molecules and a wall we now move on to consider binary collisions between molecules. The problem we address was formulated by Clausius [9]. In looking at the kinetics of dilute gases, one finds that disturbances are not communicated across a sample at thermal speeds. If one had thermal ballistic motion, disturbances would travel across a sample with speed $v_0^2 = k_B T/m$. Instead, thermal transport is much slower due to collisions. Collisions lead to a type of random walk of particles across the sample, with steps on the order of the mean-free path – the average distance between collisions. Thus we have diffusion as opposed to ballistic motion. We can estimate this mean-free path using elementary geometrical and probabilistic arguments.

Let us assume that the range of interactions between particles is r_0 and is short compared to the distance between molecules in the gas. To a first approximation we can think of the molecules as spheres of diameter r_0 .

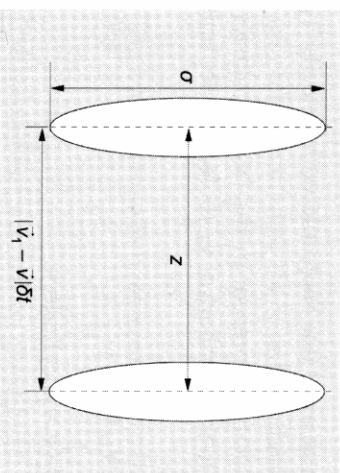


Fig. 7.2 Collision cylinder for particles with velocities \mathbf{v} and \mathbf{v}_1 that collide during a time interval δt .

We carry out this determination of the mean-free path using the idea of a collision cylinder. Suppose a molecule with velocity \mathbf{v} collides with another particle with velocity \mathbf{v}_1 at time t . We describe the collision by choosing a coordinate system (see Fig. 7.2) with its origin at the center of the first molecule, and the z -axis is drawn in the direction of the relative velocity vector $\mathbf{v}_1 - \mathbf{v}$. The molecules collide with each other only if the distance between their centers is smaller than r_0 . This means that the center of the molecule with velocity \mathbf{v}_1 must at time t lie inside the cylinder if a collision is to take place in the succeeding time interval δt . The height of this collision cylinder (see Fig. 7.2) is:

$$h = |\mathbf{v}_1 - \mathbf{v}| \delta t \quad (33)$$

The cross sectional area is simply πr_0^2 , so the volume of the collision cylinder is:

$$V_c = \pi r_0^2 h = \pi r_0^2 |\mathbf{v}_1 - \mathbf{v}| \delta t \quad (34)$$

We can use the collision cylinder to compute the number of binary collisions that take place in a small column of gas in time δt between molecules with velocity \mathbf{v} and \mathbf{v}_1 . In a small volume d^3x in the gas, there are $f(\mathbf{x}, \mathbf{v}, t) d^3x d^3v$ molecules with velocity \mathbf{v} located at position \mathbf{x} . To each of these molecules there is attached a collision cylinder appropriate for collisions with molecules of velocity \mathbf{v}_1 within a time interval δt . The number of such collision cylinders is therefore $f(\mathbf{x}, \mathbf{v}, t) d^3x d^3v$. The total volume occupied by the collision cylinder is the number of cylinders times the volume per cylinder:

$$V_c^T = f(\mathbf{x}, \mathbf{v}, t) d^3x d^3v V_c = f(\mathbf{x}, \mathbf{v}, t) d^3x d^3v \pi r_0^2 |\mathbf{v}_1 - \mathbf{v}| \delta t \quad (35)$$

To compute the number of $(\mathbf{v}, \mathbf{v}_1)$ collisions, we must compute the number of molecules with velocity \mathbf{v}_1 that are present in collision cylinders at the beginning of the time interval. Going forward we assume that the gas is sufficiently

dilute that collision cylinders contain at most one molecule with velocity \mathbf{v}_1 and these molecules lead to $(\mathbf{v}, \mathbf{v}_1)$ collisions.

The number of molecules with velocity \mathbf{v}_1 present in the $(\mathbf{v}, \mathbf{v}_1)$ collision cylinders at the instant t , N_T , is equal to the numbers of \mathbf{v}_1 -molecules per unit volume,

$$N(\mathbf{v}_1) = f(\mathbf{x}, \mathbf{v}_1, t) d^3 v_1, \quad (36)$$

multiplied by the total volume, V_c^T , of $(\mathbf{v}, \mathbf{v}_1)$ cylinders:

$$N_T = N(\mathbf{v}_1) V_c^T. \quad (37)$$

In summary the number of collisions occurring within time interval δt between molecules in the velocity range \mathbf{v} to $\mathbf{v} + d\mathbf{v}$ and the molecules in the range \mathbf{v}_1 to $\mathbf{v}_1 + d\mathbf{v}_1$ in volume $d^3 x$ of gas centered about position \mathbf{x} is given by:

$$\begin{aligned} N_T &= f(\mathbf{x}, \mathbf{v}_1, t) d^3 v_1 f(\mathbf{x}, \mathbf{v}, t) d^3 x d^3 v \pi r_0^2 |\mathbf{v}_1 - \mathbf{v}| \delta t \\ &= f(\mathbf{x}, \mathbf{v}, t) f(\mathbf{x}, \mathbf{v}_1, t) \pi r_0^2 |\mathbf{v}_1 - \mathbf{v}| d^3 v d^3 v_1 d^3 x \delta t. \end{aligned} \quad (38)$$

Notice that this expression is symmetric in \mathbf{v} and \mathbf{v}_1 [10].

The total number of collisions suffered by molecules of velocity \mathbf{v} in spatial volume $d^3 x$ in time δt comes from integrating over the velocities of all their collision partners:

$$\begin{aligned} N(\mathbf{x}, \mathbf{v}, t) d^3 v d^3 x \delta t \\ = f(\mathbf{x}, \mathbf{v}, t) \pi r_0^2 d^3 x \delta t \int d^3 v_1 f(\mathbf{x}, \mathbf{v}_1, t) |\mathbf{v}_1 - \mathbf{v}|. \end{aligned} \quad (39)$$

The total number of collisions suffered by molecules of all velocities in spatial volume $d^3 x$ and in time δt is given by:

$$N(\mathbf{x}, t) d^3 x \delta t = d^3 x \delta t \int d^3 v \pi r_0^2 \int d^3 v_1 f(\mathbf{x}, \mathbf{v}_1, t) |\mathbf{v}_1 - \mathbf{v}|. \quad (40)$$

Assuming the gas is homogeneous in space, where Eq. (19) holds, we have:

$$N(\mathbf{v}, t) = n^2 f(\mathbf{v}, t) \pi r_0^2 \int d^3 v_1 f(\mathbf{v}_1, t) |\mathbf{v}_1 - \mathbf{v}| \quad (41)$$

and the number of collisions per unit volume per unit time is:

$$\begin{aligned} N(t) &= \int d^3 v N(\mathbf{v}, t) \\ &= n^2 \pi r_0^2 \int d^3 v f(\mathbf{v}, t) \int d^3 v_1 f(\mathbf{v}_1, t) |\mathbf{v}_1 - \mathbf{v}|. \end{aligned} \quad (42)$$

The average collision rate $\nu(t)$ is the number of collisions per unit volume per unit time divided by the number of molecules per unit volume,

$$\nu(t) = \frac{N(t)}{n} = n \pi r_0^2 \int d^3 v f(\mathbf{v}, t) \int d^3 v_1 f(\mathbf{v}_1, t) |\mathbf{v}_1 - \mathbf{v}|. \quad (43)$$

The average time between collisions, the mean-free time, is:

$$\tau = 1/\nu. \quad (44)$$

The mean-free path is then given by:

$$\ell = u \tau, \quad (45)$$

where u is the average speed:

$$u = \langle v \rangle = \int d^3 v v f(\mathbf{v}, t). \quad (46)$$

If we further restrict ourselves to thermal equilibrium then $\nu(t)$ is independent of time and $f(v)$ is the Maxwell velocity distribution. In Problem 7.3 we show that the average speed is given by:

$$u = \left(\frac{8kT}{\pi m} \right)^{1/2}. \quad (47)$$

The collision rate in equilibrium can then be evaluated using:

$$\nu = n \pi r_0^2 \left(\frac{m}{2\pi kT} \right)^3 \int d^3 v \int d^3 v_1 e^{-\frac{1}{2} \beta m (v^2 + v_1^2)} |\mathbf{v}_1 - \mathbf{v}|. \quad (48)$$

The remaining integrals are evaluated in Problem 7.4, with the result:

$$\tau^{-1} = \nu = 4n^2 r_0^2 \sqrt{\frac{\pi k_B T}{m}}. \quad (49)$$

The mean-free path is given by:

$$\ell = \frac{u}{\nu} = \frac{1}{\sqrt{2} n \pi r_0^2}. \quad (50)$$

As expected the mean-free path is inversely proportional to density and molecular diameter.

7.2.3

Boltzmann Equation: Kinematics

The elementary ideas developed in the previous sections makes the assumption that we know the singlet distribution function in equilibrium. Here, we

develop some of the ideas we need to determine the singlet distribution under a variety of nonequilibrium conditions. The first step is to look at the equation of motion for the phase-space density. In Chapter 5 we established that:

$$\frac{\partial}{\partial t} \hat{f}(\mathbf{x}, \mathbf{p}, t) = iL\hat{f}(\mathbf{x}, \mathbf{p}, t) \quad (51)$$

where L is the Liouville operator. Going further, we found that:

$$\frac{\partial}{\partial t} \hat{f}(\mathbf{x}, \mathbf{p}, t) = -\frac{\mathbf{p} \cdot \nabla_{\mathbf{x}}}{m} \hat{f}(\mathbf{x}, \mathbf{p}) + \hat{f}_1(\mathbf{x}, \mathbf{p}, t) \quad (52)$$

where, for pair interactions, the nonlinear interaction contribution is given by:

$$\hat{f}_1(\mathbf{x}, \mathbf{p}, t) = -\int d^3x_1 d^3p_1 iL_1(\mathbf{x} - \mathbf{x}_1, \mathbf{p}, \mathbf{p}_1) \hat{f}(\mathbf{x}_1, \mathbf{p}_1) \hat{f}(\mathbf{x}, \mathbf{p}) \quad (53)$$

where we define the interaction part of the two-body Liouville operator,

$$L_1(\mathbf{x} - \mathbf{x}_1, \mathbf{p}, \mathbf{p}_1) = i\nabla_{\mathbf{x}} V(\mathbf{x} - \mathbf{x}_1) \cdot (\nabla_{\mathbf{p}} - \nabla_{\mathbf{p}_1}) \quad (54)$$

It is left to Problem 7.5 to show that if we have an external force \mathbf{F}_E that occurs in Newton's law in the form:

$$\frac{d\mathbf{p}_i(t)}{dt} = \mathbf{F}_E(\mathbf{r}_i, \mathbf{p}_i, t) - \sum_{j(\neq i)=1}^N \nabla_{\mathbf{r}_i} V(\mathbf{r}_i - \mathbf{r}_j) \quad (55)$$

then the equation of motion for the phase-space density takes the form:

$$\frac{\partial}{\partial t} \hat{f}(\mathbf{x}, \mathbf{p}, t) = -\frac{\mathbf{p} \cdot \nabla_{\mathbf{x}}}{m} \hat{f}(\mathbf{x}, \mathbf{p}, t) - \nabla_{\mathbf{p}} \cdot (\mathbf{F}_E(\mathbf{x}, \mathbf{p}, t) \hat{f}(\mathbf{x}, \mathbf{p}, t)) + \hat{f}_1(\mathbf{x}, \mathbf{p}, t) \quad (56)$$

If we have uniform applied electric and magnetic fields then:

$$\mathbf{F}_E = q\mathbf{E} + \frac{q}{c}(\mathbf{v} \times \mathbf{B}) \quad (57)$$

and because:

$$\nabla_{\mathbf{p}} \cdot (\mathbf{p} \times \mathbf{B}) = 0 \quad (58)$$

then we have the equation of motion:

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{p} \cdot \nabla_{\mathbf{x}}}{m} + \mathbf{F}_E(\mathbf{x}, \mathbf{p}, t) \cdot \nabla_{\mathbf{p}} \right] \hat{f}(\mathbf{x}, \mathbf{p}, t) = \hat{f}_1(\mathbf{x}, \mathbf{p}, t) \quad (59)$$

After taking the average over a nonequilibrium ensemble we have:

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{p} \cdot \nabla_{\mathbf{x}}}{m} + \mathbf{F}_E(\mathbf{x}, \mathbf{p}, t) \cdot \nabla_{\mathbf{p}} \right] f(\mathbf{x}, \mathbf{p}, t) = f_1(\mathbf{x}, \mathbf{p}, t) \quad (60)$$

7.2.4

Boltzmann Collision Integral

Let us turn next to the treatment of collisions in the Boltzmann kinetic equation. The effect of intermolecular collisions is to modify the count of molecules entering and leaving the region in phase space \mathbf{x} to $\mathbf{x} + d\mathbf{x}$ and \mathbf{v} to $\mathbf{v} + d\mathbf{v}$ in time interval δt . The number of particles in this volume is effected by collisions in two ways. Some streaming molecules are kicked out while others are knocked into the volume of interest. We can write the contribution to the kinetic equation in the form:

$$f_1(\mathbf{x}, \mathbf{p}, t) d^3x d^3v \delta t = (I_+ - I_-) d^3x d^3v \delta t \quad (61)$$

This is the net change in the number of particles in $d^3x d^3v \delta t$ due to collisions. In this equation $I_+ d^3x d^3v \delta t$ is the number of particles entering the region of phase space in time δt via collisions, and $I_- d^3x d^3v \delta t$ the number of particles leaving the region of phase space in time δt via collisions.

Before determining I_+ and I_- we need some background on two-body dynamics. We assume we have elastic collisions between two particles of equal mass m as shown schematically in Fig. 7.3. We assume that well before the collision at time t at position \mathbf{x} , the particles have velocities \mathbf{v}_1 and \mathbf{v}_2 . Well after the collision, the particles have the final velocities \mathbf{v}'_1 and \mathbf{v}'_2 . These asymptotic velocities are connected by conservation of momentum and kinetic energy (for short-ranged interactions):

$$\mathbf{v}_1 + \mathbf{v}_2 = \mathbf{v}'_1 + \mathbf{v}'_2 \quad (62)$$

$$v_1^2 + v_2^2 = (v'_1)^2 + (v'_2)^2 \quad (63)$$

If we introduce center of mass (COM) variables:

$$\mathbf{V} = \frac{1}{2}(\mathbf{v}_1 + \mathbf{v}_2) \quad (64)$$

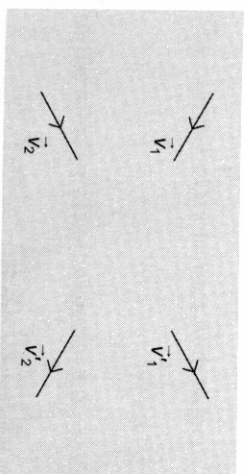


Fig. 7.3 Before and after collision kinematics for two particles with velocities \mathbf{v}_1 and \mathbf{v}_2 before the collision and \mathbf{v}'_1 and \mathbf{v}'_2 after the collision.

$$\mathbf{v} = \mathbf{v}_1 - \mathbf{v}_2, \quad (65)$$

then clearly:

$$\mathbf{V} = \mathbf{V}' . \quad (66)$$

Since we have the inverse relations:

$$\mathbf{v}_1 = \mathbf{V} + \frac{\mathbf{v}}{2} \quad (67)$$

$$\mathbf{v}_2 = \mathbf{V} - \frac{\mathbf{v}}{2}, \quad (68)$$

we have for conservation of kinetic energy:

$$v_1^2 + v_2^2 = 2V^2 + \frac{1}{2}v^2 = 2(V')^2 + \frac{1}{2}(v')^2 . \quad (69)$$

Since $V^2 = (V')^2$ we have that the relative speed is unchanged by the collision: $v^2 = (v')^2$. The angle between \mathbf{v} and \mathbf{v}' is defined by:

$$\mathbf{v} \cdot \mathbf{v}' = v^2 \cos \theta . \quad (70)$$

If we limit ourselves at first to the case of hard spheres, then we have the collision diagram shown in Fig. 7.4. We can then connect the before and after velocities in the COM using:

$$\mathbf{v}' = \mathbf{v} - 2\hat{\rho}(\hat{\rho} \cdot \mathbf{v}), \quad (71)$$

where $\hat{\rho}$ is the unit vector connecting the centers of the two colliding particles at contact. The scattering angle θ is related to the angle between $\hat{\rho}$ and \mathbf{v} ,

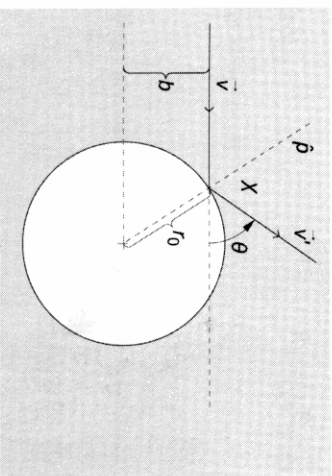


Fig. 7.4 Scattering kinematics for particles with initial relative velocity \mathbf{v} , final velocity \mathbf{v}' , impact parameter b , r_0 is the hard-sphere diameter and $\hat{\rho}$ is the unit vector connecting the centers of the particles at contact.

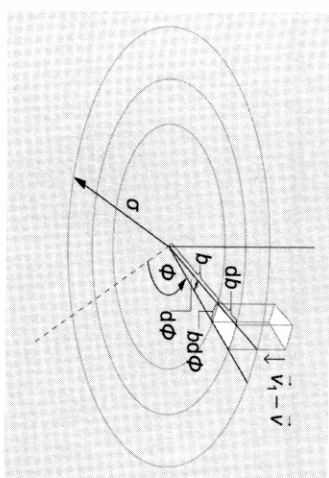


Fig. 7.5 Kinematics for two-particle collisions in terms of a collision cylinder.

$\cos \chi = \hat{\rho} \cdot \mathbf{v}$ by $2\chi + \theta = \pi$. We also have $\sin \chi = b/r_0$ where b is the impact parameter.

Let us determine J_- , the number of molecules that leave the volume $d^3x d^3v$ in time δt via collisions. Consider collisions between molecules with velocity \mathbf{v} in volume d^3x centered at position \mathbf{x} and molecules that move with a different velocity \mathbf{v}_1 such that the impact parameter of the $(\mathbf{v}, \mathbf{v}_1)$ collision falls in the range of impact parameter b to $b + db$, as shown in Fig. 7.5. The azimuthal angle of the collision is assumed to be confined to the range ϕ to $\phi + d\phi$ about a plane fixed in space and containing the relative velocity $\mathbf{v}_1 - \mathbf{v}$. A collision takes place if the centers of the two molecules are located inside the collision cylinder shown in Fig. 7.5. Notice that the problem here is very similar to the determination of the collision cylinder in determining the mean collision rate. The difference is the base we use for the collision cylinder. In Fig. 7.5 the base is the full collisional cross sectional area πr_0^2 . In the current case, for reasons that become clear when we treat J_+ , the base is $db b d\phi$ as shown in Fig. 7.5.

The number of molecules moving with velocity \mathbf{v} in the region d^3x is $f(\mathbf{x}, \mathbf{v}, t) d^3x d^3v$ and the total volume of collision cylinders for the $(\mathbf{v}, \mathbf{v}_1)$ collision is:

$$f(\mathbf{x}, \mathbf{v}, t) d^3x d^3v db d\phi |\mathbf{v}_1 - \mathbf{v}| \delta t . \quad (72)$$

The number of molecules with velocity \mathbf{v}_1 in the collision cylinder is:

$$f(\mathbf{x}, \mathbf{v}_1, t) d^3v_1 \quad (73)$$

so the number of collisions under consideration is:

$$\mathcal{N}(\mathbf{v}, \mathbf{v}_1) = f(\mathbf{x}, \mathbf{v}_1, t) d^3v_1 f(\mathbf{x}, \mathbf{v}, t) d^3x d^3v db d\phi |\mathbf{v}_1 - \mathbf{v}| \delta t . \quad (74)$$

The molecular flux J_- comes from integrating over all velocities \mathbf{v}_1 , impact parameters b and azimuthal angles ϕ :

$$J_- d^3x d^3v \delta t = \left[\int d^3v_1 \int_0^{r_0} db \int_0^{2\pi} d\phi |\mathbf{v}_1 - \mathbf{v}| f(\mathbf{x}, \mathbf{v}, t) f(\mathbf{x}, \mathbf{v}_1, t) \right] \times d^3x d^3v \delta t, \quad (75)$$

where r_0 denotes the range of forces. In this case, in contrast with our treatment of J_+ below, we can do the integral over b and ϕ to find that $J_- = N(\mathbf{x}, \mathbf{v}, t)$ where $N(\mathbf{x}, \mathbf{v}, t)$ is given in the treatment of the mean collision rate by Eq. (39).

Next we need to evaluate J_+ , the number of particles scattered into the phase-space volume $d^3v d^3x$ in time δt . This is the process where two particles with velocities \mathbf{v}' and \mathbf{v}'_1 are scattered into \mathbf{v} and \mathbf{v}_1 . We easily have that the number of particles going from $(\mathbf{v}', \mathbf{v}'_1)$ into $(\mathbf{v}, \mathbf{v}_1)$ in the volume $d^3v' d^3v'_1 d^3x \delta t$, is, in complete analogy with Eq. (74),

$$N(\mathbf{v}', \mathbf{v}'_1) = f(\mathbf{x}, \mathbf{v}'_1, t) d^3v'_1 f(\mathbf{x}, \mathbf{v}', t) d^3x d^3v' b db d\phi |\mathbf{v}'_1 - \mathbf{v}'| \delta t. \quad (76)$$

We show in Problem 7.6 that:

$$d^3v' d^3v'_1 = d^3v d^3v_1, \quad (77)$$

and we know that:

$$|\mathbf{v}'_1 - \mathbf{v}'| = |\mathbf{v}_1 - \mathbf{v}|, \quad (78)$$

since the magnitude of the relative velocity is preserved in an elastic collision. We have then:

$$N(\mathbf{v}', \mathbf{v}'_1) = f(\mathbf{x}, \mathbf{v}'_1, t) f(\mathbf{x}, \mathbf{v}', t) b db d\phi |\mathbf{v}_1 - \mathbf{v}| d^3v d^3v_1 d^3x \delta t. \quad (79)$$

Then after integrating over \mathbf{v}_1 , b and ϕ we arrive at the expression for J_+ :

$$J_+ d^3x d^3v \delta t = \left[\int d^3v_1 \int_0^{r_0} b db \int_0^{2\pi} d\phi |\mathbf{v}_1 - \mathbf{v}| f(\mathbf{x}, \mathbf{v}', t) f(\mathbf{x}, \mathbf{v}'_1, t) \right] \times d^3x d^3v \delta t. \quad (80)$$

Since \mathbf{v}' and \mathbf{v}'_1 depend on \mathbf{v} , \mathbf{v}_1 and b we can not carry out the integral over b . Putting together the results for J_- and J_+ in Eq. (61) we have the famous expression for the Boltzmann collision integral:

$$f_1(\mathbf{x}, \mathbf{v}, t) = \int d^3v_1 \int_0^{r_0} b db \int_0^{2\pi} d\phi |\mathbf{v}_1 - \mathbf{v}| (f' f'_1 - f f_1), \quad (81)$$

where we have used the convenient notation $f = f(\mathbf{x}, \mathbf{v}, t)$, $f_1 = f(\mathbf{x}, \mathbf{v}_1, t)$, $f' = f(\mathbf{x}, \mathbf{v}', t)$ and $f'_1 = f(\mathbf{x}, \mathbf{v}'_1, t)$. Putting Eq. (81) back into Eq. (60) the Boltzmann equation [11] is then given by:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \vec{\nabla} f = f_1, \quad (82)$$

where, here, we assume there is zero external force acting.

It is conventional to write the collisional contribution to the Boltzmann equation in term of the differential cross section σ . We show in Problem 7.7 that we can replace the integral over the impact parameter with a properly weighted average over the scattering angles:

$$\int b db d\phi \dots = \int d\Omega \sigma(|\mathbf{v}_1 - \mathbf{v}|, \Omega) \dots, \quad (83)$$

where:

$$d\Omega = \sin \theta d\theta d\phi \quad (84)$$

is the usual differential for the solid angle in spherical coordinates. Then we have for the Boltzmann collision integral:

$$f_1(\mathbf{x}, \mathbf{v}, t) = \int d^3v_1 \int d\Omega \sigma(|\mathbf{v}_1 - \mathbf{v}|, \Omega) |\mathbf{v}_1 - \mathbf{v}| (f' f'_1 - f f_1). \quad (85)$$

7.2.5

Collisional Invariants

It is important to consider momentum integrals of the collision integral defined by:

$$\begin{aligned} M_{\chi}(\mathbf{x}, t) &\equiv \int d^3v \chi(\mathbf{v}) f_1(\mathbf{x}, \mathbf{v}, t) \\ &= \int d^3v \chi(\mathbf{v}) \int d^3v_1 \int d\Omega \sigma(|\mathbf{v}_1 - \mathbf{v}|, \Omega) |\mathbf{v}_1 - \mathbf{v}| (f' f'_1 - f f_1). \end{aligned} \quad (86)$$

If we exchange \mathbf{v} and \mathbf{v}_1 in the integral we have:

$$\begin{aligned} M_{\chi}(\mathbf{x}, t) &= \int d^3v_1 \chi(\mathbf{v}_1) \int d^3v \\ &\times \int d\Omega \sigma(|\mathbf{v} - \mathbf{v}_1|, \Omega) |\mathbf{v} - \mathbf{v}_1| (f'_1 f' - f f_1). \end{aligned} \quad (87)$$

We see that the integrand is the same as before the exchange except $\chi(\mathbf{v}) \rightarrow \chi(\mathbf{v}_1)$. Next we make the change of variables $\mathbf{v} \rightarrow \mathbf{v}'$ and $\mathbf{v}_1 \rightarrow \mathbf{v}'_1$ in Eq. (86):

$$M_{\chi}(\mathbf{x}, t) = \int d^3v' \chi(\mathbf{v}') \int d^3v'_1$$