The total number of molecules striking \( \delta A \) in time \( \delta t \) is given by:

\[
\tilde{N} = \int_0^\infty v^2 dv \int_0^{\pi/2} \sin \theta \int_0^{2\pi} d\phi \, N_V .
\]  
(28)

Again, assuming the gas is homogeneous in space:

\[
N_V = \delta V n f(v, t) = \delta A \delta t \, v \cos \theta \, n f(v, t)
\]
(29)

and the total number is given by:

\[
\tilde{N} = \int_0^\infty v^2 dv \int_0^{\pi/2} \sin \theta \int_0^{2\pi} d\phi \, \delta A \delta t \, v \cos \theta \, n f(v, t)
= \delta A \delta t \, n \int_0^\infty v^2 dv \int_0^{\pi/2} \sin \theta \cos \theta \int_0^{2\pi} d\phi \, f(v, t) .
\]  
(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:

\[
\tilde{N} = a \delta A \delta t ,
\]
(31)

where \( a \), the rate of effusion, is given by:

\[
a = n \left( \frac{kT}{2\pi m} \right)^{1/2} ,
\]
(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

\textbf{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 \( r_0 \).

We carry out this determination of the mean-free path using the idea of a collision cylinder. Suppose a molecule with velocity \( v \) collides with another particle with velocity \( v_1 \) 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 \( v_1 - v \). 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 \( v_1 \) must at time \( t \) lie inside the cylinder if a collision is to take place in the succeeding time interval \( \delta t \). The height of this collision cylinder (see Fig. 7.2) is:

\[
h = |v_1 - v| \delta t .
\]
(33)

The cross sectional area is simply \( \pi r_0^2 \), so the volume of the collision cylinder is:

\[
V_c = \pi r_0^2 h = \pi r_0^2 |v_1 - v| \delta t .
\]
(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 \( \delta t \) between molecules with velocity \( v \) and \( v_1 \). In a small volume \( d^3x \) in the gas, there are \( f(x, v, t) d^3x \, d^3v \) molecules with velocity \( v \) located at position \( x \). To each of these molecules there is attached a collision cylinder appropriate for collisions with molecules of velocity \( v_1 \) within a time interval \( \delta t \). The number of such collision cylinders is therefore \( f(x, v, t) d^3x \, d^3v \). The total volume occupied by the collision cylinder is the number of cylinders times the volume per cylinder:

\[
V_c^T = f(x, v, t) d^3x \, d^3v \, V_c = f(x, v, t) d^3x \, d^3v \, \pi r_0^2 |v_1 - v| \delta t .
\]
(35)

To compute the number of \((v, v_1)\) collisions, we must compute the number of molecules with velocity \( v_1 \) that are present in collision cylinders at the beginning of the time interval. Going forward we assume that the gas is sufficiently
The equation for the average distribution of the particles is derived from the Boltzmann equation. Here, we assume that we know the single-particle distribution function in equilibrium. For simplicity, we use the mean-field approximation in the previous sections, making the assumption that the average number of particles is constant.

**Boltzmann Equation:**

\[ \frac{\partial f}{\partial t} = - \nabla \cdot ( \mathbf{v} f ) - f \mathbf{v} \cdot \nabla \mathbf{v} \]

where \( f = f(t, \mathbf{v}) \) is the distribution function, \( \mathbf{v} \) is the velocity, and \( \nabla \mathbf{v} \) is the velocity gradient.

### Molecular Dynamics

For a simple system of interacting particles, the Boltzmann equation can be written as:

\[ \frac{\partial f_i}{\partial t} + \mathbf{v}_i \cdot \nabla f_i = \sum_{j \neq i} C_{ij} f_i f_j \]

where \( C_{ij} \) is the collision term.

### The Mean Free Path

The mean free path \( \lambda \) is the average distance a particle travels between collisions. It is given by:

\[ \lambda = \int_0^a \frac{\text{d}r}{\langle \sigma \rangle} \]

where \( \langle \sigma \rangle \) is the mean cross-sectional area.

### Collision Rate

The collision rate \( n \) is given by:

\[ n = \int \frac{\text{d}v}{\mathcal{V}} \lambda \]

where \( \mathcal{V} \) is the volume.

### Volume of collisions

The volume of collisions is given by:

\[ V = \frac{1}{(i')N} \int (i') \int \mathcal{V} \int \frac{\text{d}v}{\mathcal{V}} = \frac{1}{(i')N} \]

where \( i' \) is the number of collisions and \( N \) is the total number of particles.

### Conclusion

In summary, the number of collisions occurring within a given volume is given by the collision rate, multiplied by the total volume. The mean molecular velocity \( \mathbf{v} \) can be calculated by dividing the total momentum of all molecules by the total volume.
The Boltzmann equation is defined as:

\[ \frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_x f - \mathbf{v} \cdot \nabla_v f = S \]

where \( f(\mathbf{x}, \mathbf{v}, t) \) is the distribution function, \( \mathbf{v} \) is the velocity, \( S \) is the source term, and \( \mathbf{v} \cdot \nabla_x f \) and \( \mathbf{v} \cdot \nabla_v f \) are the velocity and energy flux terms, respectively.

For a gas of classical particles, the collision term is given by:

\[ S = \frac{1}{2} \sum_{i \neq j} \mathbf{v}_i \cdot (\mathbf{v}_i - \mathbf{v}_j) f_i f_j \]

where the sum is over all pairs of particles and \( f_i \) and \( f_j \) are the distribution functions of the two particles, respectively.

The Boltzmann collision integral is defined as:

\[ J = \int \mathbf{v} f(\mathbf{x}, \mathbf{v}, t) \mathbf{v}' \cdot \nabla_v f(\mathbf{x}', \mathbf{v}', t) \, d\mathbf{v}' \]

where the integral is over the phase space.

For hard sphere particles, the collision integral can be approximated by:

\[ J \approx \frac{1}{4} \int \mathbf{v} f(\mathbf{x}, \mathbf{v}, t) \mathbf{v}' \cdot \nabla_v f(\mathbf{x}', \mathbf{v}', t) \, d\mathbf{v}' \]

This integral represents the contribution of collisions to the change in the distribution function over time.
The number of collisions with velocity \( \mathbf{v} \) in the collision cylinder from \( \mathbf{v} \) is:

\[
1_{c} p(t; \mathbf{v}, \mathbf{x}) f
\]

and the total volume of collision cylinders for the collision cylinder is:

\[
\varphi \mathcal{V} x \mathcal{V} p(1; \mathbf{v}, \mathbf{x}) f
\]

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

\[
\mathcal{V} x \mathcal{V} p(1; \mathbf{v}, \mathbf{x}) f
\]

where \( \mathcal{V} x \mathcal{V} \) is the total number of molecules moving with velocity \( \mathbf{v} \) in the region of the collision cylinder.

The difference is the base we use for the collision cylinder. The problem here is very similar to the one described, but the problem is moved in \( \Phi \)'s coordinate system. Notice that the problem is moved inside the collision cylinder. The center of the two molecules are located inside the collision cylinder. The plane in which the collision is assumed to be conducted to the face of the molecule is assumed to be conducting the plane of the cylinder. The azimuthal angle of the collision is assumed to be conducting to the face of the molecule is assumed to be conducting to the face of the molecule is assumed to be conducting to the face of the molecule is assumed to be conducting to the face of the molecule.

Therefore, the number of molecules that leave the volume is:

\[
\cos \theta = \mathbf{a} \cdot \mathbf{v}
\]

where \( \theta = \mathbf{a} \cdot \mathbf{v} \). We also have in the impact parameter:\n
\[
\phi = \varphi = \angle \mathbf{a} \cdot \mathbf{v}
\]

Figure 21.1. Collision efficiency for two-particle collisions in terms of impact parameters.

Since we have two elastic collisions, the total collision efficiency is:

\[
\frac{\mathbf{v}_2}{\mathbf{v}_1} = \frac{\mathbf{v}_3}{\mathbf{v}_2} = \frac{\mathbf{v}_4}{\mathbf{v}_3} = \frac{\mathbf{v}_1}{\mathbf{v}_4}
\]

where \( \mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3, \mathbf{v}_4 \) are the velocities of the particles.

Then, the total collision efficiency is:

\[
\frac{\mathbf{v}_1}{\mathbf{v}_4} = \frac{\mathbf{v}_2}{\mathbf{v}_3} = \frac{\mathbf{v}_3}{\mathbf{v}_2} = \frac{\mathbf{v}_4}{\mathbf{v}_1}
\]

where \( \mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3, \mathbf{v}_4 \) are the velocities of the particles.

![Collision efficiency for two-particle collisions in terms of impact parameters.](image)
We see that the integrand is same as before the exchange except W

\[ \lambda \alpha \beta \int (\alpha \lambda \beta \alpha \beta \int = (\lambda \lambda \alpha \beta \int \] 

(86) \( (\int \int - \int \int ) |1A - 1A| (U |1A - 1A| \alpha \beta \int = (\lambda \lambda \alpha \beta \int \) 

If we exchange \( \lambda \) and \( \beta \) in the integrand we have:

\[ (1A - 1A) (U |1A - 1A| \alpha \beta \int = (\lambda \lambda \alpha \beta \int \) 

(87) \( (\int \int - \int \int ) |1A - 1A| (U |1A - 1A| \alpha \beta \int = (\lambda \lambda \alpha \beta \int \) 

It is important to consider momentum integrals of the collision integral.

**Collision Integrals**

(88) \( (\int \int - \int \int ) |1A - 1A| (U |1A - 1A| \alpha \beta \int = (\lambda \lambda \alpha \beta \int \) 

We have the Boltzmann collision integral that is usual differential form in a special coordinates. Then we have:

\[ \frac{\partial f}{\partial \mathbf{r}} = \nabla f \] 

(89) \( (\int \int - \int \int ) \alpha \beta \int = (\lambda \lambda \alpha \beta \int \) 

Where

\[ \cdots (U |1A - 1A| \alpha \beta \int = \cdots \phi \beta \alpha \beta \int \] 

Weights average over the scattering angles.

We flip the order of the integrals.

(90) \( (\int \int - \int \int ) \alpha \beta \int = (\lambda \lambda \alpha \beta \int \) 

We show in Problem 7.6 that:

(91) \( (\int \int - \int \int ) \alpha \beta \int = (\lambda \lambda \alpha \beta \int \) 

We denote the number of particles flowing from \( \alpha \) to \( \beta \) in the volume \( (\lambda \lambda \alpha \beta \int ) \) and we satisfy the number equation in form of conservation of momentum. The Boltzmann equation is then given by:

\[ \frac{\partial f}{\partial t} + \hat{\nabla} \cdot \mathbf{F} = \frac{4\pi}{f0} \int (\int \int - \int \int ) \alpha \beta \int \] 

where we have used the convolution of the collision integral.

(92) \( (\int \int - \int \int ) \alpha \beta \int = (\lambda \lambda \alpha \beta \int \) 

The molecular flux \( f \) comes from integrating over all velocities \( \mathbf{v} \).