The kinetic theory of the classical perfect gas (largely due to Maxwell and Boltzmann) was the first statistical theory to be introduced into physics. The equilibrium results of kinetic theory can now all be obtained as special cases of the general results of statistical mechanics obtained in chapter 7 but the detailed nature of the kinetic theory can give added insight into processes such as the pressure exerted by a gas on the wall of a container. The kinetic theory approach can also be extended to non-equilibrium situations and, as shown in the next chapter, may be used to calculate the transport coefficients (thermal conductivity, coefficient of viscosity, etc.) of a perfect gas. The kinetic theory of the perfect gas is of great importance in applied physics because the results are directly relevant to real gases at low pressure as in vacuum systems, the upper atmosphere and space research.

The model of a gas on which the kinetic theory is based is that of a set of molecules moving rapidly at random throughout the whole volume of the containing vessel. The energy of a monatomic gas is set equal to the sum of the kinetic energies of the molecules. In the simplest model the molecules are treated as elastic spheres (this assumption is discussed in more detail in chapter 9) which on average travel a distance (the mean free path) which is large compared to their diameter, before making a collision. The total volume occupied by the molecules is assumed to be much less than the volume of the containing vessel. The kinetic theory will be seen in chapter 9 to be internally consistent in that the mean free path in a gas at N.T.P. calculated using the measured and predicted transport coefficients is indeed much greater than the molecular diameter.

The statistical nature of the kinetic theory should be clear from the discussion of chapter 7. An individual molecule will change its velocity after each collision. Only the probability of the molecule being found to have a given velocity (or small range of velocities) can be specified, but for a gas in thermal equilibrium the fraction of the molecules within the given range of velocities remains constant. The equilibrium results of kinetic theory will be discussed in this chapter and the transport theory in chapter 9.
8.1 DISTRIBUTION FUNCTIONS

A number of distribution functions are sometimes useful in kinetic theory calculations although they do not contain any information that cannot be found from the partition function. The distribution function for some property \( x \) is defined either by the relation

\[ f(x)dx = \text{probability of } x \text{ lying in the range } x \text{ to } x + dx \]

or alternatively

\[ F(x)dx = \text{number of molecules with } x \text{ in the range } x \text{ to } x + dx \]

In the first case the integral of the distribution function over all values of \( x \) is equal to unity and in the second case is equal to the total number of molecules \( (N) \). The two distribution functions are simply related

\[ F(x) = N f(x) \]

It is usual in kinetic theory however to write simply \( f(x) \) for either distribution function. The parameter \( x \) may be either a vector (for example momentum, velocity) or a scalar (for example energy, speed) quantity.

The fundamental distribution function may be derived directly from the classical partition function of a single particle

\[
\begin{align*}
    f(p, r) d^3p \ d^3r &= \frac{e^{-\beta e} d^3p \ d^3r}{\int e^{-\beta e} d^3p \ d^3r} \\
    &= \text{probability that a molecule has momentum in the range } p \text{ to } p + dp \text{ and position in the range } r \text{ to } r + dr
\end{align*}
\]

The limits of the integrals are taken to be plus and minus infinity for the momentum and the whole of the volume of the container for the position coordinates. The extension to plus and minus infinity of the momentum variable is not of course consistent with the theory of relativity but this is of no practical importance since the exponential term is negligible at such high energies. When the momentum of a particle is independent of its position the left-hand side of equation 8.1 may be factorised

\[
f(p, r) d^3p \ d^3r = f(p) d^3p f(r) d^3r
\]

and when gravitational effects are neglected the energy of a particle is independent of its position so equation 8.1 becomes

\[
f(p) d^3p = \frac{e^{-\beta e} d^3p}{\int e^{-\beta e} d^3p} \quad (8.2)
\]