6. Weakly Coupled Systems

The discussion in section 2.3 showed that thermodynamic concepts such as temperature are not required for the discussion of the behaviour of a single particle in a conservative system, since the energy of the particle is constant. When the isolated system consists of a number of particles (such as molecules of a gas) however, the individual particle energies change after each collision in such a way that the energy of the entire system \(E\) is conserved.

\[ E = \epsilon_1 + \epsilon_2 + \cdots + \epsilon_N \]

In general it is no longer possible (or indeed interesting) to discuss the exact behaviour of each molecule. In thermal equilibrium the macroscopic properties of the system become independent of time and at the molecular level it is postulated that the fraction of the molecules with a given range of energies is also independent of time. An individual molecule will leave the chosen energy range after a collision but elsewhere in the gas another molecule will on average also make a collision such that it enters the energy range.

The concept of a distribution function to describe the equilibrium properties of a classical perfect gas was first introduced by Maxwell and was later extended by Boltzmann. The distribution function \(f_0 (\mathbf{v}, \mathbf{r})\) is defined such that: \(f_0 (\mathbf{v}, \mathbf{r}) \, d^3 \mathbf{v} \, d^3 \mathbf{r}\) is the number of molecules of the gas in the velocity range \(\mathbf{v}\) to \(\mathbf{v} + d\mathbf{v}\) and with position between \(\mathbf{r}\) and \(\mathbf{r} + d\mathbf{r}\) when the gas is in the thermal equilibrium.

Velocity is a vector quantity involving both magnitude (speed) and direction. In many books however no distinction is made in the text between speed and velocity and it is then necessary to consider whether the vector or scalar quantity is under consideration. The symbols \(d^3 \mathbf{v}\), \(d^3 \mathbf{r}\) are used to mean a three-dimensional volume element such as \(dv_x \, dv_y \, dv_z\) in cartesian coordinates or \(v^2 \, dv\sin \theta \, d\theta \, d\phi\) in polar coordinates as convenient.

The general distribution function can often be simplified. When gravitational effects are neglected the energy of a molecule of a perfect gas is independent of position. The integral of \(f_0 (\mathbf{v}, \mathbf{r})\) over all velocities and over the allowed volume of the gas (which is simply equal to \(N\), the total number of molecules) is then
separable
\[ \int \int f_0 (v, r) \, d^3 v \, d^3 r = \int \int f_0 (v) \, d^3 v \cdot \int d^3 r = N \]

Therefore
\[ \int f_0 (v) \, d^3 v = \frac{N}{V} \]

The correct form for the velocity distribution function \( f_0 (v) \) was first given by Maxwell by an ingenious but inadequate argument (exercise 6.1) and first derived rigorously by Boltzmann for the case of binary collisions of gas molecules
\[ f_0 (v) \, d^3 v = \frac{N}{V} \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} \, d^3 v \quad (6.1) \]

This equation will be derived as a special case of the general results of statistical mechanics in section 8.1. In equation 6.1, \( m \) is the mass of the molecule, \( k \) is the Boltzmann constant and \( T \) the absolute temperature.

An alternative interpretation of equation 6.1 is that the probability of a given molecule having velocity in the range \( v \) to \( v + dv \) is given by
\[ \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} \, d^3 v \quad (6.2) \]

The transition between the properties of a single molecule (which can only be described statistically by equation 6.2) and the whole system of \( N \) particles is only possible because in a perfect gas the molecules are on average well separated and weakly interacting. This separation would not be possible in a liquid, where the properties of the system as a whole must always be considered.

The fundamental concept of thermodynamics was found to be the entropy function. The fundamental concept of classical statistical mechanics is the distribution function. The relationship between these two quantities was first established by Boltzmann who defined a function \( H \) such that
\[ H = \int f (v, r, t) \ln f (v, r, t) \, d^3 v \, d^3 r \quad (6.3) \]

Boltzmann showed that as a result of binary collisions in the gas an arbitrary function \( f (v, r, t) \) always changed in time until it came into the Maxwell form given by equation 6.1. The function \( H \) always decreased with time to a minimum value which was associated with thermal equilibrium. A connection is therefore suggested with the (negative) of the entropy of the system since the entropy cannot decrease for a system within adiabatic walls. The form
\[ S_B = -kVH_0 \quad (6.4) \]