3.3. Equipartition of energy

If the energy of the systems in an assembly is made up of terms quadratic in the position and momentum coordinates of the systems then, for each such quadratic term, the contribution to the mean energy will be $\frac{1}{2}kT$ where T is the temperature of the assembly. This fact is illustrated by the following examples.

Consider first a gas molecule of mass m and let its energy due to its motion in the x-direction be quadratic in the momentum p_x i.e. $\epsilon_x = p_x^2/2m$ the mean value of is given by equation 3.4 so that, at temperature T,

$$\bar{\epsilon}_x = \frac{\int_\Gamma p_x^2/2m\, e^{-\epsilon/kT}\, d\Gamma}{\int_\Gamma e^{-\epsilon/kT}\, d\Gamma} \qquad \textbf{3.13}$$

where the energy is the total energy including ϵ_x. Taking the energy in two parts as $\epsilon_x = p_x^2/2m$ and $(\epsilon - p_x^2/2m)$ so that the second term is independent of allows equation 3.13 to be written as

$$\bar{\epsilon}_x = \frac{kT \int_{-\infty}^{\infty} e^{-u^2} u^2\, du}{\int_{-\infty}^{\infty} e^{-u^2}\, du} \qquad \textbf{3.14}$$

Integrating by part gives

$$\bar{\epsilon}_x = \tfrac{1}{2}kT \qquad \textbf{3.15}$$

A similar result *to* that of equation 3.15 would have been obtained had the energy in the x-direction been taken as quadratic in the coordinate x, i.e. $\epsilon_x = \frac{1}{2}\mu x^2$. However, if the energy is composed of more than one term, the energy may be evaluated either by splitting the integrals or in the following manner.

Consider a one-dimensional simple harmonic oscillator which has its energy composed of two quadratic terms, i.e.

$$\epsilon_x = \frac{p_x^2}{2m} + \tfrac{1}{2}\mu x^2 \qquad \textbf{3.16}$$

Where μ is the restoring force per unit displacement of the oscillator. The mean energy of the oscillator at temperature T and is

$$\bar{\epsilon}_x = \frac{\int_\Gamma \{p_x^2/2m + \frac{1}{2}\mu x^2\}\, e^{-\epsilon/kT}\, d\Gamma}{\int_\Gamma e^{-\epsilon/kT}\, d\Gamma} \qquad \textbf{3.17}$$

If the common integral of exp(-(ϵ- p_x^2/2m - $\frac{1}{2}\mu x^2$)/kT)$dydzdp_ydp_z$ taken over all values of y, z, p_y and p_z is cancelled from equation 3.17 the mean energy becomes

$$\bar{\epsilon}_x = \frac{\int_0^{2\pi} d\theta \int_0^{\infty} e^{-r^2/kT}\, r^3\, dr}{\int_0^{2\pi} d\theta \int_0^{\infty} e^{-r^2/kT}\, r\, dr} = kT \tag{3.18}$$

The energy given by equation 3.18 is in agreement with the value given by for each quadratic term. The mean energy of a free structure less molecule will be given, on a similar analysis, by

$$\bar{\epsilon} = \overline{\left\{\frac{p_x^2}{2m}+\frac{p_y^2}{2m}+\frac{p_z^2}{2m}\right\}} = \tfrac{1}{2}kT+\tfrac{1}{2}kT+\tfrac{1}{2}kT = \tfrac{3}{2}kT$$

in agreement with equation 2.42 while the mean energy of a three-dimensional oscillator will be

$$\bar{\epsilon} = \overline{\left\{\frac{p_x^2}{2m}+\tfrac{1}{2}\mu_1 x^2+\frac{p_y^2}{2m}+\tfrac{1}{2}\mu_2 y^2+\frac{p_z^2}{2m}+\tfrac{1}{2}\mu_3 z^2\right\}} = 6\,.\,\tfrac{1}{2}kT = 3kT \tag{3.19}$$

It is usual, and useful, to refer to each independent quadratic term in the energy as a 'degree of freedom' of the system and then an average energy of *½kT is* assigned to each degree of freedom or independent mode of taking energy. As an example consider a gramme atom of a solid element containing N_A atoms, where N_A is Avogadro's number. If each. atom is considered to behave as a three-dimensional harmonic oscillator there will be a total of $6N_A$ degrees of freedom. The energy of the gramme atom of solid at temperature T will be

$$E = 6N_A\cdot\tfrac{1}{2}kT = 3RT \tag{3.19}$$

The specific heat per gramme atom of the solid element will then be

$$C_v = \left\{\frac{\partial E}{\partial T}\right\}_V = 3R \simeq 5{\cdot}94\ \text{cal/°K/gramme atom} \tag{3.20}$$

if the volume of the solid is maintained constant. This is the result which was obtained by Delong and Petit for the specific heat of a metal.

A further discussion of degrees of freedom is given in the following section