2- The multiplier β may also be considered from the point of view of its association with the change in the energy, *dE*.

Let an amount of heat *dQ* be supplied to an assembly and let the assembly expand by an amount *dV*. The assembly will then do an amount of work *pdV* where *p* is the pressure exerted on the assembly by its surroundings. The increase in the energy of the assembly is then given by the first law of thermodynamics as

$$dE = dQ - p\,dV \qquad 2.35$$

This change of energy will also be given by

$$dE = d\sum_s n_s \epsilon_s$$
$$= \sum_s \epsilon_s\,dn_s + \sum_s n_s\,d\epsilon_s \qquad 2.36$$

The two terms in this expression arise from the two forms of energy in equation 2.35. The change $d\epsilon_s$ of the energy level ϵ_s will$\sum_s n_s d\epsilon_s$ be caused by a change *dV* in the volume of the assembly and hence the term will be related to the work done by the assembly. The rearrangement of the systems among the energy sheets, which leads to the term $\sum_s \epsilon_s dn_s$ must therefore be related to the heat supplied to the assembly. A comparison between equations 2.35 and 2.36 shows therefore that the respective terms can be identified as

$$\sum_s n_s\,d\epsilon_s = -pdV \qquad 2.37$$

and

$$\sum_s \epsilon_s\,dn_s = dQ \qquad 2.38$$

(The difference between these two expressions may be considered as the difference between the 'ordered' energy or work and the 'disordered' energy or heat.) If the result of equation 2.38 is used together with equation 2.13 for that case where there is no change in the volume of the assembly, then the equilibrium condition of the assembly becomes

$$d\log W + \alpha\,dN + \beta\,dQ = 0 \qquad 2.39$$

since any increment of energy must here be due to a supply of heat *dQ*. In the case where heat *dQ* is supplied to an assembly with a constant number of systems (i.e. *dN* = 0) there will be a change in the weight of the assembly given by

$$d\log W = -\beta dQ \qquad 2.40$$

In this expression the term *d* log *W* is a perfect differential and therefore the term *dQ* must be a perfect differential also. Now, it is well known in thermodynamics that the multiplier 1/T converts the quantity *dQ* irito the perfect differential

$$dS = dQ/T$$

where S is the entropy of the assembly and T is the temperature on the Kelvin scale. It therefore follows that, in place of the gen. era! relation given by equation 2.34, it is now possible to write

$$\beta = -\frac{1}{kT} \qquad 2.41$$

where k is a constant and use is here made of the fact that β must be negative. That k is well known **Boltzmann constant** which occurs in elementary kinetic theory will now be shown by considering the mean energy of the systems in the assembly.

3- Finally, in this discussion of β, the conditions imposed ·on the distribution by the total energy and the number of systems in the assembly are used to determine the mean energy ϵ of the systems. From elementary kinetic theory it is well known that this mean energy has a value derived from the ideal. gas equation as

$$\epsilon = \frac{3}{2} KT \qquad \mathbf{2.42}$$

where $k = R/N_A$ is the Boltzmann constant, R being the universal gas constant and N_A is **Avogadro's number**. Taking the energy of the assembly as $E = \sum_s \epsilon_s n_s$ and the number of systems as $N = \sum_s n_s$ gives, on substitution for n_s from equation 2.20,

$$E = \sum_s \epsilon_s g_s e^{\alpha+\beta\epsilon_s} \qquad 2.43a$$

and

$$N = \sum_s g_s e^{\alpha+\beta\epsilon_s} \qquad 2.43b$$

The factor e^{α} may be eliminated between these two equations to give the mean energy per system as

$$\bar{\epsilon} = \frac{E}{N} = \frac{\sum_s \epsilon_s g_s e^{\beta\epsilon_s}}{\sum_s g_s e^{\beta\epsilon_s}} \qquad 2.44$$

Before this expression can be evaluated it is necessary to express g_s as a function of ϵ_s, the energy of the sheet, and of $d\epsilon_s$ the range of energies included in the sheet. For this purpose it is assumed that equal volumes of phase space contain equal numbers of allowed states. Let there be B states per unit volume of phase space so that an element $d\Gamma$ of phase space will contain $Bd\Gamma$ states. The weight of the sheet s will then be

$$g_s = B(\Delta\Gamma)_s \qquad 2.45$$

Where $(\Delta\Gamma)_s$ is that volume of the six-dimensional phase space lying in the energy range ϵ_s to $\epsilon_s + d\epsilon_s$ and within the volume V of the assembly.
It is shown that

$$(\Delta\Gamma)_s \equiv 2\pi(2m)^{\frac{3}{2}}\epsilon_s^{\frac{1}{2}}\, d\epsilon_s \,.\, V \qquad 2.46$$

where m is the mass of a component system of the assembly. (This volume of phase space is obtained by integrating the element $d\Gamma = dxdydzdp_xdp_ydp_z$ over all values of x, y and z and over all directions of the momenta since the energy ϵ_s is taken to be independent of both the position of the system and its direction of motion.) Substituting from equation 2.46 in equation 2.45 gives

$$g_s \equiv BV.\, 2\pi(2m)^{\frac{3}{2}}\epsilon_s^{\frac{1}{2}}\, d\epsilon_s \qquad 2.47$$

Substitution for g_s in equation 2.44 now allows the summations over s to be replaced by an integration over all the possible energies so that, on cancelling the constant terms in g_s from numerator and denominator and dropping the subscript s,

$$\bar{\epsilon} = \frac{\int_0^\infty \epsilon^{\frac{3}{2}} e^{\beta\epsilon}\, d\epsilon}{\int_0^\infty \epsilon^{\frac{1}{2}} e^{\beta\epsilon}\, d\epsilon} \qquad 2.48$$

If it is remembered that β is a negative quantity, partial integration of the numerator of equation 2.48 gives

$$\int_0^\infty \epsilon^{\frac{3}{2}} e^{\beta\epsilon}\, d\epsilon = -\frac{3}{2\beta}\int_0^\infty \epsilon^{\frac{1}{2}} e^{\beta\epsilon}\, d\epsilon$$

Equation 2.48 thus reduces to

$$\bar{\epsilon} = -\frac{3}{2\beta} \qquad 2.49$$

and comparison with equation 2.42 leads to the identity

$$\beta = -\frac{1}{kT}$$

as in equation 2.41

2.6. The multiplier α

In determining the multiplier α it is convenient to make the substitution

$$A = e^{\alpha}$$

The distribution of equation 2.20 then becomes **2.50**

$$n_s = A g_s e^{\beta \epsilon_s} \quad 2.51$$

so that the total number of systems is

$$N = A \sum_s g_s e^{\beta \epsilon_s} \quad 2.52$$

and

$$A = \frac{N}{\sum_s g_s e^{\beta \epsilon_s}} \quad 2.53$$

Taking the value of g_s as given by equation 2.47 gives

$$A = \frac{N}{2\pi(2m)^{\frac{3}{2}} B V \int_0^\infty \epsilon^{\frac{1}{2}} e^{\beta\epsilon}\, d\epsilon} \quad 2.54$$

then

$$A = \frac{N}{BV(2\pi mkT)^{\frac{3}{2}}} \quad 2.55$$

The multiplier α taken from equation 2.50 is then

$$\alpha = \log A = \log\left[\frac{N}{BV(2\pi mkT)^{\frac{3}{2}}}\right] \quad 2.56$$

2.7. *The Maxwell-Boltzmann Distribution*

Once β and α are known in terms of the parameters of the assembly it is also possible to write the distribution over energies, as given by equation 2.20, in terms of these parameters. However, for this distribution to be useful, it must be expressed as a differential distribution. For example, if *dn* is taken as the number of systems having their coordinates in a volume dΓ of phase space then this differential distribution may be written by replacing the number of states g_s in equation 2.20 by $Bd\Gamma$ to give

$$dn = e^{\alpha + \beta\epsilon} B\, d\Gamma \quad 2.57$$

Alternatively, if $g(\epsilon)d\epsilon$ is the number of states with energies in the range ϵ to $\epsilon + d\epsilon$ equation 2.20 gives

$$n(\epsilon)\, d\epsilon = e^{\alpha + \beta\epsilon} g(\epsilon)\, d\epsilon \quad 2.58$$

for the number of systems having energies in the range ϵ to $\epsilon + d\epsilon$ The value of $g(\epsilon)d\epsilon$ will be simply that given for the weight g_s by equation 2.47 with ϵ_s replaced by ϵ. Thus, on substituting for α and β from equations 2.56 and 2.41 respectively, equation 2.58 becomes

$$n(\epsilon)\,d\epsilon = \frac{2\pi N}{(\pi kT)^{\frac{3}{2}}} e^{-\epsilon/kT} \epsilon^{\frac{1}{2}}\, d\epsilon \qquad 2.59$$

This is the Maxwell-Boltzmann distribution in differential form. It is of interest to note here that the distribution in equation 2.59 is independent of the constant *B*. From this it may be concluded that, in the completely classical limit where the separation of energy levels disappears, the same distribution will be obtained.

Problem

From equation 2.59 find the total energy of the assembly?