## 2.2. *Weights of configurations*

Because the possible configurations of an assembly are not equally probable it is necessary to define a weight, *W,* for each configuration. This weight is taken as the number of distinct arrangements of the systems which all correspond to the particular configuration The probability that an assembly is in the given configuration will then be proportional to the weight of that configuration.

If the systems in the assembly are distributed so that there are $n_s$ systems in the sheet *s,* as discussed in the previous section, the weight of this configuration will be found from the number of ways of producing the configuration with the *N* systems of the assembly. Taking the sheets in order, the number of ways of choosing the *n1* systems of the first energy sheet from a total of *N* systems is simply

$$_NC_{n_1} = \frac{N!}{n_1!\,(N-n_1)!} \qquad 2.1$$

The $n_2$ systems of the second sheet may then be chosen from the remaining $(N - n_1)$ systems in

$$_{(N-n_1)}C_{n_2} = \frac{(N-n_1)!}{n_2!\,(N-n_1-n_2)!} \qquad 2.2$$

ways. The total number of ways of choosing the systems for the first and second sheets is then the product of the numbers in equations 2.1 and 2.2, i.e.

$$\frac{N!}{n_1!\,(N-n_1)!}\times\frac{(N-n_1)!}{n_2!\,(N-n_1-n_2)!} = \frac{N!}{n_1!\,n_2!\,(N-n_1-n_2)!} \qquad 2.3$$

If there were only three sheets the number of systems in the third sheet would be

$$n_3 = (N-n_1-n_2)$$

and, since the choosing of the $n_1$ and $n_2$ systems will necessarily choose also the $n_3$ systems in the third sheet, the total number of ways of choosing the configuration with the numbers $n_1$, $n_2$ and $n_3$ is, from equation 2.3,

$$\frac{N!}{n_1!\,n_2!\,n_3!} \qquad 2.4$$

An extension of this argument to the case of *r* sheets· gives the number of ways of choosing the systems for the various sheets as

$$\frac{N!}{n_1!\, n_2!\, n_3! \ldots n_s! \ldots n_r!} \qquad 2.5$$

Now, in the energy sheet $s$ there are $g_s$ energy states. Thus, without altering the configuration, each of the $n_s$ systems in this sheet may be placed in $g_s$ ways and there will be a total of $g_s^{ns}$ ways of arranging the $n_s$ systems within the sheet. The total number of arrangements of the systems in the given configuration, the weight of the configuration, is thus

$$W = \frac{N!}{n_1!\, n_2! \ldots n_s! \ldots n_r!} g_1^{n_1} g_2^{n_2} \ldots g_s^{n_s} \ldots g_r^{n_r} \qquad 2.6$$

Using the product symbolism

$$\prod_s \{g_s^{n_s}/n_s!\}$$

to denote the product of the quantities $g_s^{ns}/n_s!$ for all values of s from 1 to r this result becomes, more concisely,

$$W = N! \prod_s \left\{\frac{g_s^{n_s}}{n_s!}\right\} \qquad 2.7$$

The type of distribution of the systems considered here has apparently ignored any possible variation of the positions of-the systems over the volume of the assembly. While the effect of this positional variation will be discussed later, particularly with reference to interacting systems, it is sufficient to note here that new arrangements formed by changing the positions of non-interacting systems are allowed for in the values of the weights of the sheets $g_s$

### *2.3. The most probable configuration*

From the form of equation 2.7 it should be clear that there will be some particular values of the occupation numbers for which the weight of the corresponding configuration will be a maximum. Then, since the probability that the assembly is in a given configuration is directly proportional to the weight *W*, it follows that this configuration with the maximum weight will be the most probable configuration for the assembly.

It will be shown below that, because the assemblies under consideration are composed of very large numbers of systems, the peak of the weight *W* in the neighborhood of its maximum value, $W_{max}$, is extremely sharp. It follows that the assembly will spend by far the greater proportion of its time in configurations very close to the most probable one and that the average properties of the assembly will therefore correspond very closely to its properties when it is in this most probable configuration.

To find the occupation numbers which correspond to the most probable configuration it is necessary to 'maximize' the weight $W$ by the condition

$$dW = \sum_s \frac{\partial W}{\partial n_s} dn_s = 0 \qquad 2.8$$

where the partial differentials are taken to indicate that, in each differentiation, all but one of the occupation numbers is considered constant. The solution of equation 2.8 must take into account the limitations imposed on the values of and by the conditions that the total energy $E$, and the total number of systems, $N$., ar.e fixed. Let the condition for a constant number of systems be expressed by the equation

$$\sum_s n_s = N = \text{constant} \qquad 2.9a$$

or

$$\sum_s dn_s = dN = 0 \qquad 2.9b$$

and the condition for a constant total energy by

$$\sum_s n_s \epsilon_s = E = \text{constant} \qquad 2.10a$$

or

$$\sum_s \epsilon_s \, dn_s = dE = 0 \qquad 2.10b$$

where the summations are taken over the values $s$ = to $s= r$.

The simplest method of introducing these conditions into equation 2.8 is by means of Lagrange undetermined multipliers by which the equation for a maximum in $W$ becomes

$$dW + a\, dN + b\, dE = 0 \qquad 2.11$$

where $a$ and $b$ are multipliers which are to be determined later. Substituting from equations 2.8, *2.9b* and *2.10b* in equation 2.11 gives

$$\sum_s \frac{\partial W}{\partial n_s} dn_s + a \sum_s dn_s + b \sum_s \epsilon_s \, dn_s = 0 \qquad 2.12$$

Because of the form given for $W$ by equation 2.7 it is found to be convenient to maximize log $W$ rather than $W$ and to rewrite the equations 2.11 and 2.12 in the form

$$d \log W + \alpha \, dN + \beta \, dE = 0 \qquad 2.13$$

and

$$\sum_s \frac{\partial \log W}{\partial n_s} dn_s + \alpha \sum_s dn_s + \beta \sum_s \epsilon_s \, dn_s = 0 \qquad 2.14$$

where the terms α and β replace the multipliers a and *b* of equations 2.11 and 2.12. The equation 2.14 may be rewritten with the summation taken over all three terms so that

$$\sum_s \left\{ \frac{\partial \log W}{\partial n_s} + \alpha + \beta \epsilon_s \right\} dn_s = 0 \qquad 2.15$$

If *W*, and therefore log *W*, is to be a maximum (or possibly a minimum), equation 2.15 must hold irrespective of the magnitudes of the individual increments $dn_s$ . Therefore, for all values of s, the bracketed term in equation 2.15 must be zero and

$$\frac{\partial \log W}{\partial n_s} + \alpha + \beta \epsilon_s = 0 \qquad 2.16$$

The differential of above equation may be evaluated with the aid of Sterling's approximation for the factorials of large numbers. The form of this approximation is discussed in Appendix 2 where it is shown that, for large numbers,

$$\log N! \simeq N \log N - N \qquad 2.17$$

Because the systems are considered to be distributed over energy sheets rather than individual energy states, the occupation numbers $n_s$ may be assumed to be sufficiently large for the approximation of equation 2.17 to apply to the case $n_s!$ of for all values of s.

From the value of *W* given by equation 2. 7 we derive

$$\begin{aligned} \log W &= \log N! + \log \left[ \prod_s \left\{ \frac{g_s^{n_s}}{n_s!} \right\} \right] \\ &= \log N! + \sum_s \log \left\{ \frac{g_s^{n_s}}{n_s!} \right\} \\ &\simeq N \log N - N \\ &\quad + \sum_s (n_s \log g_s - n_s \log n_s + n_s) \qquad 2.18 \end{aligned}$$

Partial differentiation then gives

$$\begin{aligned} \frac{\partial \log W}{\partial n_s} &= \log g_s - \log n_s \\ &= \log \frac{g_s}{n_s} \qquad 2.19 \end{aligned}$$

On substituting from equation 2.19, equation 2.16 becomes

$$\log \frac{g_s}{n_s} + \alpha + \beta\epsilon_s = 0$$

from which is obtained

$$n_s = g_s e^{\alpha + \beta\epsilon_s} \qquad 2.20$$

The result obtained in equation 2.20 gives the distribution of the systems over the various energy sheets for the most probable configuration and is known as the *Maxwell-Boltzmann distribution.*
The term

$$e^{\beta\epsilon_s}$$

which occurs in this distribution is often referred to as the *Boltzmann factor.*

If, instead of energy sheets, only the individual energy states are considered then a mean occupation number $n_i$ may be defined for the state i of energy $\epsilon_I$ . Since such a state has a weight of unity, equation 2.20 predicts a value for this mean occupation number of

$$\bar{n}_i = e^{\alpha + \beta\epsilon_i} \qquad 2.21$$

which may, of course, be fractional. _

Before the distribution given by equation 2.20 is fully defined it is obviously necessary to determine the multipliers α and β. It is also necessary to show that equation 2.20 does define a maximum of *W* and that the sharpness of this maximum is sufficient to justify taking this distribution as representing the average distribution for the assembly. This question of the maximum of *W* will be considered first.