2.4. The sharpness of the configuration maximum

The values of the occupation numbers given in equation 2.20 define a stationary point for the weight *W*. The properties of *Win* the neighborhood of this stationary point may be considered most conveniently by expanding the value of log Was a Taylor series about this point. This expansion *will* have the form

$$\log W = \log W_{max} + \sum_s \left\{\frac{\partial \log W}{\partial n_s}\right\}_{max} \Delta n_s + \sum_s \left\{\frac{\partial^2 \log W}{\partial n_s^2}\right\}_{max} \frac{\Delta n_s^2}{2} + \ldots \qquad 2.22$$

where W_{max} is taken as the stationary value and *W* is the weight of the configuration for which the occupation numbers differ by Δn_s etc. from those for W_{max} (There would be additional terms in equation 2.22 of the form

$$\sum_s \sum_t \{\partial^2 \log W/\partial n_s \partial n_t\}_{max} \Delta n_s \Delta n_t$$

besides higher order terms but since $\frac{\partial logw}{\partial ns}$ is a function of n_s only, as shown by equation 2.19, these terms will be identically zero.)

Now, by definition,

$$\sum_s \{\partial \log W/\partial n_s\} \Delta n_s$$

is zero at a stationary point of *W*. It is therefore necessary to evaluate the second order term only. From equation 2.19

$$\frac{\partial^2 \log W}{\partial n_s^2} = -\frac{1}{n_s} \qquad \mathbf{2.23}$$

Writing for the value of at the stationary point, substitution from equation 2.23 into equation 2.22 gives

$$\log W = \log W_{max} - \tfrac{1}{2} \sum_s \frac{\Delta n_s^2}{n_{sm}} \qquad 2.24$$

or

$$W = W_{max} \exp\left(-\tfrac{1}{2} \sum_s \frac{\Delta n_s^2}{n_{sm}}\right) \qquad 2.25$$

That the quantity W_{max} is indeed the maximum value of *W* is seen from equation 2.25 since any deviation Δn_s positive or negative, of n_s from the value will produce a weight *W* less than W_{max}.

To appreciate the sharpness of this maximum let $\Delta n_s/n_{sm} = \delta_s$ so that equation 2.25 becomes

$$W = W_{max} \exp\left(-\tfrac{1}{2} \sum_s n_{sm} \delta_s^2\right) \qquad 2.26$$

Then, if that case is considered in which all the fractional deviations have the same value δ_s equation 2.26 gives

$$W = W_{\max}\exp\left(-\tfrac{1}{2}\delta^2 \sum_s n_{sm}\right) = W_{\max}\exp(-\tfrac{1}{2}N\delta^2) \quad 2.27$$

The average assembly considered will have a total number of systems N greater than 10^{20} so that, even with a fractional deviation δ from the most probable configuration of one part in (i.e. $\delta = 10^{-8}$), the weight of the configuration will have fallen to

$$W \simeq W_{\max}\exp(-\tfrac{1}{2}10^{20} . 10^{-16}) \simeq W_{\max} . 10^{-2150}$$

It is clear from these calculations that the maximum of W is extremely sharp and that only those configurations which are very close to the most probable configuration will have a probability of occurrence appreciably different from zero. It will therefore introduce no detectable error if it is assumed that the most probable configuration of the assembly is the same as its equilibrium configuration and that · the properties calculated for this· most probable configuration will correspond to the average properties of the assembly. (It should be clear, however, that if the number of systems in the assembly is substantially reduced, the sharpness of the configuration - maximum will become less marked and fluctuations from the most probable configuration will become important)

2.5. The multiplier β

There are a number of criteria which can be applied in considering the identity of the multiplier β. Clearly, since the number of systems having an infinite energy must be zero, equation 2.20 predicts that the value of β is negative. Also, the value of β may be determined by substituting in equation 2.20 for the original conditions that $\sum_s n_s = N$ and $\sum_s \epsilon_s n_s = E$. However, before proceeding with these substitutions, it is interesting to consider β from the point of view of thermodynamics and this will now be done in two ways

1- Consider· two assemblies A' and A'' which contain N' and N'' systems respectively. Let these assemblies be placed in thermal contact so that energy, but not systems, may be exchanged between them and let them be otherwise isolated from their surroundings.

By the exchange of energy the two assemblies will eventually attain the same temperature as they come into thermal equilibrium (the zeroth law of thermodynamic). The total energy E of the two assemblies is now a fixed quantity and the conditions

$$dN' = 0, \qquad dN'' = 0 \qquad \text{and} \qquad dE = 0 \qquad 2.28$$

are imposed on the assemblies.

Let the energies in the two assemblies be divided into sheets and let the sheet s have energies ϵ_s' and ϵ_s'' occupation numbers n_s' and n_s'' for the assemblies A' and A'' respectively. Then the total energy will be

$$E = \sum_s n_s'\epsilon_s' + \sum_s n_s''\epsilon_s''$$

and the conditions of equation 2.28 may be written as

$$dN' = \sum_s dn_s' = 0; \qquad dN'' = \sum_s dn_s'' = 0$$

and

$$dE = \sum_s \epsilon_s' \, dn_s' + \sum_s \epsilon_s'' \, dn_s'' = 0 \qquad 2.29$$

If the individual weights of the two assemblies in a particular configuration are W' and W'' respectively then the total weight of the configuration of the two assemblies taken together will be

$$W_T = W'W'' \qquad 2.30$$

each arrangement of A' being taken together with every arrangement of A''. The condition for the most probable configuration of the combined assemblies is given, by analogy with equation 2.13, as

$$d \log W_T + \alpha' \, dN' + \alpha'' dN'' + \beta \, dE = 0 \qquad 2.31$$

where the conditions imposed by equation 2.28 are introduced through the undetermined multipliers α', α'' and β. Now, from equation 2.30, log W = log W' + log W'' and, since W' will depend only on the occupation number n_s'.

$$d \log W' = \sum_s \frac{\partial \log W'}{\partial n_s'} dn_s'$$

and, similarly,

$$d \log W'' = \sum_s \frac{\partial \log W''}{\partial n_s''} dn_s''.$$

Equation 2.31 can therefore be written with the conditions taken from equation 2.29 as

$$\sum_s \left\{ \frac{\partial \log W'}{\partial n_s'} + \alpha' + \beta\epsilon_s' \right\} dn_s' + \sum_s \left\{ \frac{\partial \log W''}{\partial n_s''} + \alpha'' + \beta\epsilon_s'' \right\} dn_s'' = 0 \qquad 2.32$$

Since equation 2.32 is taken as defining a stationary point it must be satisfied for any small values of dn_s' and dn_s'' and the condition for the most probable configuration is then equivalent to the two conditions

$$\frac{\partial \log W'}{\partial n_s'} + \alpha' + \beta\epsilon_s' = 0 \qquad 2.33a$$

and

$$\frac{\partial \log W''}{\partial n_s''} + \alpha'' + \beta\epsilon_s'' = 0 \qquad 2.33b$$

for all values of s. The equations *2.33a* and *2.33b* define the most probable distributions for the two assemblies and it is seen that both of these distributions will depend on the value of the multiplier β. Then, since it is only the temperatures of the two assemblies which necessarily have the same value, it follows that is a function of the temperature alone, i.e.

$$\beta = f(T) \qquad 2.34$$

where T is the thermodynamic temperature of the assemblies. Thus, by consideration of the thermal equilibrium between two assemblies, it is possible to establish that the multiplier depends only on this thermodynamic temperature.