Appendix HH

Derivation of the Distribution Laws

The distribution laws are derived by maximizing the statistical weight for a perfect gas with respect to the occupation numbers n_r. In the following, we shall find it more convenient to require that the natural log of the weight be a maximum rather than the weight itself. Since the natural logarithm of the weight $\ln W$ increases monotonically with W, the weight will have a maximum when the logarithm of the weight has its maximum. We thus require that the following condition be satisfied

$$\delta \ln W = 0, \tag{HH.1}$$

for small variations of the occupation numbers consistent with the equations

$$N = \sum_r n_r \tag{HH.2}$$

and

$$E = \sum_r n_r \epsilon_r. \tag{HH.3}$$

The condition (HH.1) for changes in the occupation numbers consistent with Eqs. (HH.2) and (HH.3) may be shown to be equivalent to the condition

$$\delta \left[\ln W - \alpha \sum_{r=1}^{\infty} n_r - \beta \sum_{r=1}^{\infty} \epsilon_r n_r \right] = 0, \tag{HH.4}$$

for all changes in the occupation numbers. This variational condition may be written

$$\delta \ln W - \alpha \sum_{r=1}^{\infty} \delta n_r - \beta \sum_{r=1}^{\infty} \epsilon_r \delta n_r = 0. \tag{HH.5}$$

This equation may be used to derive the distribution laws for classical and quantum statistics. Since the expression for the weight W depends upon the particular form of statistics, we must consider each kind of statistics separately.

MAXWELL-BOLTZMANN STATISTICS

For a perfect classical gas, the statistical weight is given by Eq. (7.6). Using the explicit form of this equation with the product notation, the natural logarithm of $W(n_1, n_2, \ldots, n_r, \ldots)$ may be written

$$\ln W = \ln N! + \sum_{r=1}^{\infty} (n_r \ln g_r - \ln n_r!). \tag{HH.6}$$

For a macroscopic sample, the occupation numbers n_r are very large and the natural logarithm of the factorial $\ln n_r!$ may be approximated by Sterling's formula

$$\ln n! = n(\ln n - 1), \quad \text{for large } n. \tag{HH.7}$$

Eq. (HH.6) then becomes

$$\ln W = \ln N! + \sum_{r=1}^{\infty}(n_r \ln g_r - n_r \ln n_r + n_r). \tag{HH.8}$$

Using Eq. (HH.8), the change in $\ln W$ due to changes in the occupation numbers δn_r may be written

$$\delta \ln W = \sum_{r=1}^{\infty}(\ln g_r - \ln n_r)\delta n_r. \tag{HH.9}$$

Substituting the above equation into the variational condition (HH.5), we obtain the condition,

$$\sum_{r=1}^{\infty}(\ln g_r - \ln n_r - \alpha - \beta\epsilon_r)\delta n_r = 0,$$

which can be true for all variations δn_r only if the factors appearing within parentheses are equal to zero. We thus have

$$\ln g_r - \ln n_r - \alpha - \beta\epsilon_r = 0.$$

The above condition can be written

$$\ln \frac{n_r}{g_r} = -\alpha - \beta\epsilon_r. \tag{HH.10}$$

Taking the exponent of each side of Eq. (HH.10), we obtain finally

$$\frac{n_r}{g_r} = \mathrm{e}^{-\alpha-\beta\epsilon_r}. \tag{HH.11}$$

The distribution law (HH.11) may be cast into a more convenient form by expressing the constant α in terms of another constant Z by the equation

$$\mathrm{e}^{-\alpha} = \frac{N}{Z}. \tag{HH.12}$$

We then have

$$\frac{n_r}{g_r} = \frac{N}{Z}\mathrm{e}^{-\beta\epsilon_r}. \tag{HH.13}$$

As shown in the book by McGervey, which is cited in Chapter 7, the constant β is equal to kT with the constant k being called the Boltzmann constant. We thus obtain

$$\frac{n_r}{g_r} = \frac{N}{Z}\mathrm{e}^{\epsilon_r/kT}. \tag{HH.14}$$

The above equation is known as the *Maxwell-Boltzmann distribution law*.

BOSE-EINSTEIN STATISTICS

The statistical weight for Bose-Einstein statistics is given by Eq. (7.54). Using this formula, the natural logarithm of $W(n_1, n_2, \ldots, n_r, \ldots)$ may be written

$$\ln W = \sum_{r=1}^{\infty}\left[\ln(n_r + g_r - 1)! - \ln n_r! - \ln(g_r - 1)!\right]. \tag{HH.15}$$

Sterling's formula (HH.7) may again be used to evaluate the first two natural logarithms, and we obtain

$$\ln W = \sum_{r=1}^{\infty}\left[(n_r + g_r - 1)\ln(n_r + g_r - 1) \ - n_r \ln n_r - (g_r - 1) - \ln(g_r - 1)!\right]. \tag{HH.16}$$

Using Eq. (HH.16), the change in $\ln W$ due to changes in the occupation numbers δn_r may be written

$$\delta \ln W = \sum_{r=1}^{\infty}\left[\ln(n_r + g_r - 1) - \ln n_r\right]\delta n_r. \tag{HH.17}$$

Since n_r is much larger than one, the number, -1, in the first term may be omitted and the above equation becomes

$$\delta \ln W = \sum_{r=1}^{\infty} \left[\ln(n_r + g_r) - \ln n_r \right] \delta n_r. \tag{HH.18}$$

Substituting Eq. (HH.18) into the variational condition (HH.5), we obtain

$$\sum_{r=1}^{\infty} \left[\ln(n_r + g_r) - \ln n_r - \alpha - \beta\epsilon_r \right] \delta n_r = 0. \tag{HH.19}$$

Again, setting the factor multiplying δn_r equal to zero, we get

$$\ln(n_r + g_r) - \ln n_r - \alpha - \beta\epsilon_r = 0. \tag{HH.20}$$

The above equation can be written

$$\ln \frac{n_r}{n_r + g_r} = -\alpha - \beta\epsilon_r. \tag{HH.21}$$

Taking the exponent of each side of Eq. (HH.21) and collecting together the terms depending upon n_r, we obtain

$$n_r \left(1 - \mathrm{e}^{-\alpha-\beta\epsilon_r}\right) = g_r \mathrm{e}^{-\alpha-\beta\epsilon_r}. \tag{HH.22}$$

We may again take $\beta = kT$, and this equation may be written

$$n_r = g_r \frac{1}{\mathrm{e}^{\alpha}\mathrm{e}^{\epsilon_r/kT} - 1}. \tag{HH.23}$$

Equation (HH.23) is known as the *Bose-Einstein distribution law*.

FERMI-DIRAC STATISTICS

The statistical weight for Fermi-Dirac statistics is given by Eq. (7.55). Using this formula, the natural logarithm of $W(n_1, n_2, \ldots, n_r, \ldots)$ may be written

$$\ln W = \sum_{r=1}^{\infty} \left[\ln g_r! - \ln n_r! - \ln(g_r - n_r)! \right]. \tag{HH.24}$$

Again using Sterling's formula (HH.7) to evaluate the first two terms in the summation, we obtain

$$\ln W = \sum_{r=1}^{\infty} \left[\ln g_r! - n_r \ln n_r - (g_r - n_r) \ln(g_r - n_r) + g_r \right]. \tag{HH.25}$$

Using Eq. (HH.25), the change in $\ln W$ due to changes in the occupation numbers δn_r may be written

$$\delta \ln W = \sum_{r=1}^{\infty} \left[\ln(g_r - n_r) - \ln n_r \right] \delta n_r. \tag{HH.26}$$

As before, we substitute Eq. (HH.26) into the variational condition (HH.5) to obtain

$$\sum_{r=1}^{\infty} \left[\ln(g_r - n_r) - \ln n_r - \alpha - \beta\epsilon_r \right] \delta n_r = 0. \tag{HH.27}$$

The factor multiplying δn_r may again be set equal to zero to give the following equation

$$\ln \frac{n_r}{g_r - n_r} = -\alpha - \beta\epsilon_r. \tag{HH.28}$$

Taking the exponent of each side of Eq. (HH.28) and collecting together the terms depending upon n_r, we obtain

$$n_r \left(1 + \mathrm{e}^{-\alpha-\beta\epsilon_r}\right) = g_r \mathrm{e}^{-\alpha-\beta\epsilon_r} \tag{HH.29}$$

Again setting $\beta = kT$, this equation may be written

$$n_r = g_r \frac{1}{\mathrm{e}^{\alpha}\mathrm{e}^{\epsilon_r/kT} + 1}, \tag{HH.30}$$

which is known as the *Fermi-Dirac distribution law*.