$$= \frac{1}{\beta}\left(\frac{\partial}{\partial V}\right)_T .$$

4.5 The Entropy:

From Maxwell-Boltzmann distribution, the number of particles in the i-th energy level is

$$N_i = \frac{N e^{-\beta E_i}}{Z_1}$$

$$\therefore \ln N_i = \ln N - \beta E_i - \ln Z_1$$

The entropy:

$$S = k_B \ln \Omega = k_B \ln \frac{N!}{N_1! N_2! \cdots N_M!}$$

$$= k_B \left[\ln N! - \sum_i \ln N_i!\right]$$

$$= k_B \left[N \ln N - N - \sum_i N_i \ln N_i + \sum_i N_i\right]$$

$$\therefore S' = k_B \left[N \ln N - \sum_i N_i [\ln N - \beta E_i - \ln Z_1] \right]$$

$$= k_B \left[N \ln N - \ln N \sum_i N_i + \beta \sum_i N_i E_i + \ln Z_1 \sum_i N_i \right]$$

$$\therefore S = k_B [N \ln Z_1 + \beta U]$$

4.6 The coefficient β:

From the first law of thermodynamics:

$$dU = T\,dS' - p\,dV.$$

At constant volume:

$$\left(\frac{dS}{dU} \right)_V = \frac{1}{T}.$$

The entropy $S' = k_B [N \ln Z_1 + \beta U]$

$$\therefore \left(\frac{\partial S}{\partial U} \right)_V = k_B \left[N \frac{d \ln Z_1}{d\beta} \left(\frac{\partial \beta}{\partial U} \right) + \beta + U \left(\frac{\partial \beta}{\partial U} \right)_V \right]$$

But $N \dfrac{d \ln Z_1}{d\beta} = -U$

$$\therefore \left(\frac{\partial S'}{\partial U} \right)_V = k_B \beta = \frac{1}{T}$$

$$\therefore \beta = \frac{1}{k_B T}.$$

4.7 The Helmholtz Free Energy:

$$F = U - TS$$
$$= U - k_B T N \ln Z_1 - k_B T \beta U$$
$$= -N k_B T \ln Z_1 .$$

* Example 2. An atom has two energy levels 0 and ε. Calculate the internal energy for a system consisting of N atoms, using Maxwell-Boltzmann distribution. Then calculate the specific heat.

solution

The partition function for a single particle:

$$Z_1 = 1 + e^{-\beta E}$$

The internal energy:

$$U = -N \frac{\partial \ln Z_1}{\partial \beta}$$

$$\therefore U = \frac{N \varepsilon e^{-\beta \varepsilon}}{1 + e^{-\beta \varepsilon}}$$

$$\therefore U = \frac{N \varepsilon e^{-\frac{\varepsilon}{kT}}}{1 + e^{-\frac{\varepsilon}{kT}}}$$

The specific heat:

$$c = \frac{dU}{dT}$$

$$= \frac{\varepsilon^2 N}{kT^2} \frac{(1+e^{-\frac{\varepsilon}{kT}})e^{\frac{-\varepsilon}{kT}} - e^{\frac{-\varepsilon}{kT}} e^{\frac{-\varepsilon}{kT}}}{(1+e^{-\frac{\varepsilon}{kT}})^2}$$

$$= \frac{\varepsilon^2 N}{kT^2} \frac{e^{-\varepsilon/kT}}{(1+e^{\frac{-\varepsilon}{kT}})^2}$$

* Example 3. Consider a system consisting of N distinguishable particles. Each particle can be in one of two microstates with single-particle energy 0 and ε. The system is in equilibrium at temprature T. Find the thermodynamic properties of the system.

Solution

* The single-particle partition function:

$$z_1 = \sum_{i=1}^{2} e^{-\beta E_i} = 1 + e^{-\beta\varepsilon}.$$

* The average energy:

$$\langle E \rangle = -\frac{\partial \ln z_1}{\partial \beta}.$$

$$\therefore \langle E \rangle = \frac{-1}{1+e^{-\beta\varepsilon}} \left(-\varepsilon e^{-\beta\varepsilon}\right)$$

$$= \frac{\varepsilon e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}.$$

* The internal energy:

$$U = N \langle E \rangle$$

$$= \frac{N\varepsilon e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}.$$

* The free energy:

$$F = -NkT \ln Z_1$$

$$= -NkT \ln\left(1+e^{-\beta\varepsilon}\right)$$

$$= -NkT \ln\left(1+e^{-\frac{\varepsilon}{kT}}\right)$$

* The entropy:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$= Nk\left[\frac{T}{1+e^{-\frac{\varepsilon}{kT}}}\left(\frac{\varepsilon}{kT^2}\right)e^{\frac{-\varepsilon}{kT}} + \ln\left(1+e^{\frac{-\varepsilon}{kT}}\right)\right]$$

$$= \frac{N\varepsilon e^{\frac{-\varepsilon}{kT}}}{T\left(1+e^{\frac{-\varepsilon}{kT}}\right)} + Nk\ln\left(1+e^{\frac{-\varepsilon}{kT}}\right).$$

4.8 Maxwell-Boltzmann Distribution for Degenerate States:

Consider that the state i is degenerate, and its degree of degeneracy is g_i. Then the partition function becomes,

$$Z = \sum_i g_i e^{-\beta E_i}.$$

The Maxwell-Boltzmann distribution becomes,

$$N_i = N g_i \frac{e^{-\beta E_i}}{Z}.$$

* Example 4. A system consists of two distinguishable particles, and has two energy levels 0 and ε. The degrees of degeneracy $g_1 = 2$ and $g_2 = 1$. Calculate the total number of microstates.

solution

<table>
<tr><th>Energy</th><th colspan="18">Microstates</th></tr>
<tr><td>ε</td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td><td colspan="2">○</td><td colspan="2">●</td><td colspan="2">●</td><td colspan="2">○</td><td colspan="2">○●</td></tr>
<tr><td>0</td><td>●○</td><td></td><td></td><td>●○</td><td>○</td><td>●</td><td>●</td><td>○</td><td>●</td><td></td><td>○</td><td></td><td></td><td>○</td><td></td><td>●</td><td></td><td></td></tr>
<tr><td>E</td><td colspan="2">0</td><td colspan="2">0</td><td colspan="2">0</td><td colspan="2">0</td><td colspan="2">ε</td><td colspan="2">ε</td><td colspan="2">ε</td><td colspan="2">ε</td><td colspan="2">2ε</td></tr>
</table>

The total number of microstates:

$$\Omega = 9.$$

* Example 5. A system consisting of three energy levels $E_1 = 0$, $E_2 = 100\,k_B$ and $E_3 = 200\,k_B$. The degrees of degeneracy are $g_1 = 1$, $g_2 = 3$ and $g_3 = 5$. Using the Maxwell-Boltzmann distribution, Calculate the partition function, and the average energy at $T = 100\,°K$.

Solution

For a single particle,

$$Z_1 = \sum_i g_i\, e^{-\beta E_i}$$

$$= 1 + 3\, e^{\frac{-100\,k_B}{100\,k_B}} + 5\, e^{\frac{-200\,k_B}{100\,k_B}}$$

$$= 1 + \frac{3}{e} + \frac{5}{e^2} = 2.78$$

The probability of finding a particle at the i-th energy level:

$$P_i = g_i\, \frac{e^{-\beta E_i}}{Z_1}$$

$$\therefore P_1 = \frac{1}{Z} = 0.36$$

$$P_2 = \frac{3}{Ze} = 0.397$$

$$P_3 = \frac{5}{Ze^2} = 0.243$$

The average energy:

$$\langle E \rangle = \sum_i P_i E_i = 88.3 k_B .$$

* Example 6. A system consists of 4000 distinguishable particles, and has three degenerate energy levels $\varepsilon_i = i\varepsilon$ J, $i = 0, 1, 2$. The degree of degeneracy is g for all levels. Find the number of particles in each level for the most probable distribution, such that $U = 2300\,\varepsilon$ J.

Solution

In Maxwell - Boltzmann distribution:

$$N_i = Ng \, \frac{e^{-\beta E_i}}{Z} , \quad i = 1, 2, 3$$

$$\therefore N_1 = \frac{Ng}{Z} , \quad N_2 = \frac{Ng}{Z} e^{-\beta \varepsilon} = N_1 x$$

$$N_3 = \frac{Ng}{Z} e^{-2\beta\varepsilon} = N_1 x^2,$$

where $x = e^{-\beta\varepsilon}$.

The total number of particles:

$$N_1 + N_2 + N_3 = 4000$$

$$\therefore N_1(1 + x + x^2) = 4000 \qquad \text{--- (1)}$$

The Internal energy:

$$U = N_1 x \varepsilon + N_1 x^2 (2\varepsilon) = 2300\varepsilon$$

$$\therefore N_1(x + 2x^2) = 2300 \qquad \text{--- (2)}$$

Dividing Eq.(1) by Eq.(2):

$$\frac{1 + x + x^2}{x + 2x^2} = \frac{4000}{2300}$$

$$\therefore 57x^2 + 17x - 23 = 0$$

$$\therefore x = 0.503 \quad \text{or} \quad x = -0.802$$

$$\therefore N_1 = \frac{2300}{x + 2x^2} \simeq 2277.$$

$$N_2 = N_1 x = 1146$$

$$N_3 = N_1 x^2 = 577.$$