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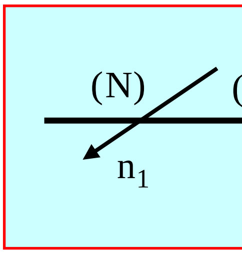
1. Prove the following relation for the occupation number n_i due to Boltzmann distribution $n_i = \sum_i \frac{N}{Z} e^{-\beta\varepsilon}$

---------------------------------- **Solution** ---------------------------------

Let the number of allowed states associated with the energy ε_i be g_i. Let us first calculate the number of ways of putting n_1 particles of N particles in one box, then n_2 out of $N - n_1$ in second, and so on until we have exhausted all of the particles. The number of ways of choosing n_1 particles out of N particles is given by



$$W_1 = \frac{N!}{(N - n_1)!\, n_1!} \qquad (1)$$

and the number of choosing n_2 out of $N - n_1$ is:

$$W_2 = \frac{(N - n_1)!}{(N - n_1 - n_2)!\, n_2!} \qquad (٢)$$

and the number of ways of achieving this arrangement is

$$W = W_1 \cdot W_2 \ \cdots$$

$$= \frac{N!}{(N-n_1)!\ n_1!} \cdot \frac{(N-n_1)!}{(N-n_1-n_2)!\ n_2!} \ \cdots$$

$$= \frac{N!}{n_1!\ n_2! \quad \cdots \quad n_i!}$$

$$W = N! \prod_i \frac{g_i^{n_i}}{n_i} \qquad (٣)$$

$$\ln W = \ln N! + \sum_i (n \ln g_i - n \ln n_i!)$$

$$= N \ln N + \sum_i (n \ln g_i - n \ln n_i)$$

To obtain the most probable distribution, we maximize Eq. (3) with $dN = 0$:

$$\delta \ln W = \sum_i (\ln g_i - n \ln n_i - \frac{n_i}{n_i})\delta n_i = 0$$

$$\delta \ln W = \sum_i (\ln g_i - n \ln n_i - 1)\delta n_i = 0$$

but

$$\delta N = \sum_i \delta n_i = 0 \qquad (4)$$

$$\delta U = \sum_i \varepsilon_i \delta n_i = 0 \qquad (5)$$

multiply Eq. (4) by $\alpha + 1$ and Eq. (5) bt $-B$ and add the resulting equations to each other:

$$\sum_{i}(\ln g_i - n\ln n_i + \alpha - \beta\varepsilon_i)\delta n_i = 0 \qquad (6)$$

Since n_i is vary independent,

$$\ln g_i - n\ln n_i + \alpha - \beta\varepsilon_i = 0$$

or

$$\ln\frac{g_i}{n_i} + \alpha - \beta\varepsilon_i = 0 \qquad (7)$$

Solving Eq. (7) for n_i gives

$$n_i = \frac{N}{Z} g_i e^{-\beta\varepsilon_i}$$

2. Find the relation between the partition function Z and thermodynamic functions U, and S.

------------------------------- **Solution** --------------------------------

(a) Relation between Z and U

Since

$$Z = \sum_i g_i e^{\varepsilon_i / KT}$$

differentiate Z with respect to T, holding V constant,

$$\left(\frac{\partial Z}{\partial T}\right)_V = \sum_i g_i \left(\frac{\varepsilon_i}{KT^2}\right) e^{\varepsilon_i / KT}$$

$$= \frac{1}{KT^2} \sum_i \varepsilon_i g_i \; e^{\varepsilon_i / KT}$$

$$= \frac{1}{KT^2} \frac{\sum_i n_i \varepsilon_i}{\sum_i n_i} g_i \; e^{\varepsilon_i / KT}$$

$$= \frac{ZU}{NKT^2}$$

It follow that

$$U = NKT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V \quad (8)$$

and U may be calculated once lnZ is known as a function of T and V.

(b) Relation between Z and S

The entropy S is related to the order or distribution of the particles, through the relation:

$$S = K\ln W$$

but

$$\ln W = -\sum_i n_i \ln\frac{n_i}{g_i} + N\ln N$$

Hence

$$S = K\ln W = K\left[-\sum_i n_i \ln\frac{n_i}{g_i} + N\ln N\right]$$

By using the relation

$$n_i = \frac{N}{Z} g_i e^{-\varepsilon_i / KT}$$

we have

$$\frac{n_i}{g_i} = \frac{N}{Z} e^{-\varepsilon_i / KT}$$

then

$$\begin{aligned} S = K\ln W &= K\left[-N\ln N + N\ln Z + \frac{U}{KT} + N\ln N\right] \\ &= NKT\ln Z + \frac{U}{T} \end{aligned} \qquad (9)$$

and S may be calculated once lnZ is known as a function of T and V.

3. Discus in details the partition function of a harmonic oscillator**.**

-------------------- Solution ----------------------------

4. Find the relation between Z and U, S for an ideal monatomic gas.

Taking into account that, the partition function for this system is given by

$$Z = V\left(\frac{2\pi mKT}{h^2}\right)^{3/2}$$

---------------------------------- **Solution** --------------------------------------

(a) Relation between Z and U

Since

$$U = NKT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V$$

So

$$\ln Z = \ln V + \tfrac{3}{2}\ln T + \tfrac{3}{2}\ln\left(\frac{2\pi mK}{h^2}\right)$$

$$\left(\frac{\partial \ln Z}{\partial T}\right)_V = \frac{3}{2T}$$

So the internal energy has already been established as:

$$U = \tfrac{3}{2}NKT$$

(b) Relation between Z and S

Since

$$S = K\ln W = NK\left[\ln N + T\frac{\partial \ln Z}{\partial T}\right]$$

Since

$$\ln Z = \ln V + \tfrac{3}{2}\ln T + \tfrac{3}{2}\ln\left(\frac{2\pi mK}{h^2}\right)$$

So

$$\left(\frac{\partial \ln Z}{\partial T}\right)_V = \frac{3}{2T}$$

By substituting we have:

$$S = NK\left[\ln V + \frac{3}{2}\ln T + \frac{3}{2}\ln\left(\frac{2\pi mK}{h^2}\right) + \frac{3}{2}\right]$$