Notes on Statistical Mechanics*

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Classical MB distribution

Key features

- Particles are identical and distinguishable.
- They are of classical nature. So no spin consideration.
- Heisenberg's uncertainty relation is not applicable. As a result there is no multiplicity in energy states.
- Particles don't obey Pauli's exclusion principle. So there is no restriction for the number of accomodations in any energy state.
- For an isolated system, the total number of particles (N) is constant. If N_i is the number of particles having energy E_i in the i th state, then $N = \sum\limits_i N_i = constant$ and

$$\delta \sum_i N_i = 0 \tag{1}$$

- For non-interacting particles, The total energy $U = \sum\limits_i N_i E_i = constant$. Therefore,

$$\delta U = 0 \tag{2}$$

Equations (1) and (2) serve as the conditions for the evolution of the system.

Thermodynamic probability

Let g_i be the degeneracy for the energy state E_i. The number of ways the groups of N_1, N_2, ... particles are chosen from N particles is

$$\Omega_1 = \frac{N!}{N_1!N_2!....} = \frac{N!}{\prod\limits_i N_i!} \tag{3}$$

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Again the number of ways in which N_i particles are accomodated in g_i states is

$$\Omega_2 = g_1^{N_1} \times g_2^{N_2} \times ..... = \prod_i g_i^{N_i} \tag{4}$$

Thus the thermodynamic probability or the number of ways in which N particles are accommodated in the states is

$$\Omega = \Omega_1 \Omega_2 = \frac{N!}{\prod_i N_i!} \prod_i g_i^{N_i} \tag{5}$$

The distribution function

let us consider eqn (5).

$$\begin{aligned} \ln \Omega &= \ln N! + \sum_i N_i \ln g_i - \sum_i \ln N_i! \\ &= N \ln N + \sum_i N_i \ln g_i - \sum_i N_i \ln N_i \end{aligned} \tag{6}$$

For equilibrium,

$$\delta S = 0 \quad \text{or} \quad \delta \ln \Omega = 0$$

and Ω should be maximum for which we get using eqn (6)

$$\delta \ln \Omega = \sum_i (\ln g_i - \ln N_i) \, \delta N_i = 0 \tag{7}$$

Now, let us apply the method of Lagrange's undetermined multipliers to eqns (1), (2) and (7)

$$\sum_i (\ln g_i - \ln N_i - \alpha - \beta E_i) \, \delta N_i = 0 \tag{8}$$

where α and β are the coefficients to be determined.
For any arbitrary δN_i,

$$\ln g_i - \ln N_i - \alpha - \beta E_i = 0 \tag{9}$$

Eqn (9) gives

$$N_i = g_i e^{-(\alpha + \beta E_i)} \tag{10}$$

from which we have the **Distribution function** $f(E_i)$

$$f(E_i) = \frac{N_i}{g_i} = e^{-(\alpha + \beta E_i)} \tag{11}$$

The quantity $f(E_i)$ in eqn (11) represents the average number of particles per state of the system.

Enumeration of $e^{-\alpha}$

It's observed that

$$N = \sum_i N_i = e^{-\alpha} \sum_i g_i e^{-\beta E_i} = e^{-\alpha} Z \tag{12}$$

Here $Z = \sum_i g_i e^{-\beta E_i}$ is the partition function of the system. From eqn (12)

$$e^{-\alpha} = \frac{N}{Z} \tag{13}$$

and

$$f(E_i) = \frac{N_i}{g_i} = \frac{N}{Z} e^{-\beta E_i} \tag{14}$$

Enumeration of β

From eqn (6) and (14)

$$\ln \Omega = N \ln Z + \beta U \tag{15}$$

which yields

$$S = k \ln \Omega = kN \ln Z + k\beta U \tag{16}$$

Now from the relation

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \tag{17}$$

and from eqn (16), we have

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{Nk}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_V \left(\frac{\partial \beta}{\partial U}\right)_V + k\beta + kU\left(\frac{\partial \beta}{\partial U}\right)_V \tag{18}$$

From the definition of Z

$$\left(\frac{\partial Z}{\partial \beta}\right)_V = -\frac{UZ}{N}$$

and from eqn (18)

$$\left(\frac{\partial S}{\partial U}\right)_V = k\beta$$

$$\implies \beta = \frac{1}{kT} \tag{19}$$

Final form

Thus with all the coefficients the M-B distribution function asumes the final form

$$f(E_i) = \frac{N}{Z} e^{-\frac{E_i}{kT}} \tag{20}$$