243(4): Derivation of the Boltzmann Distribution: Mean Square Energy

As explained in note 243(3) the Boltzmann distribution needs to be evaluated for the square of energy in order to extend the Einstein theory of specific heats. Consider an oscillator of angular frequency ω which possesses quantized energy levels:

$$0, \hbar\omega, 2\hbar\omega, \ldots, n\hbar\omega.$$

The energy of the oscillator in the quantum state n is E_n. Let the probability that it is in that state be p_n. Then the average energy is:

$$\langle E \rangle = \sum_n p_n E_n \quad -(1)$$

At thermal equilibrium at a temperature T the Boltzmann distribution defines p_n:

$$p_n = \frac{\exp\left(-\frac{E_n}{kT}\right)}{\sum_n \exp\left(-\frac{E_n}{kT}\right)} \quad -(2)$$

It is necessary to find $\langle E^2 \rangle$, so the origin of the distribution (2) must be known in detail.

Derivation of the Boltzmann Distribution

The total energy is:

$$E = \sum_{i=0}^{\infty} n_i \epsilon_i = \text{constant} \quad -(3)$$

The number of particles is constant:

$$N = \sum_{i=0}^{\infty} n_i \quad -(4)$$

2) The number of states is:

$$W = \frac{N!}{n_0! n_1! n_2! \ldots} \quad -(5)$$

Approximately:

$$\log_e N! = N \log_e N - N, \quad -(6)$$

so

$$\log_e \overline{W} = N \log_e N - \sum_i n_i \log_e n_i \quad -(7)$$

and

$$\frac{d(\log_e \overline{W})}{d n_i} = - \sum_i (1 + \log_e n_i) \quad -(8)$$

$$= - \sum_i \log_e n_i$$

because:

$$dN = \sum_i dn_i = 0 \quad -(9)$$

Note that:

$$dE = \sum_i \epsilon_i \, dn_i = 0 \quad -(10)$$

$$dN = \sum_i dn_i = 0 \quad -(11)$$

so

$$d(\log_e \overline{W}) = - \sum_i \log_e n_i \, dn_i - \alpha \sum_i dn_i - \beta \sum_i \epsilon_i \, dn_i \quad -(12)$$

At the maximum $\overline{W}$:

$$d(\log_e \overline{W}) = 0 \quad -(13)$$

so:

3)
$$-\sum_i \left(\alpha + \beta\epsilon_i + \log_e n_i\right) dn_i = 0 \quad -(14)$$

i.e. $$\alpha + \beta\epsilon_i + \log_e n_i = 0 \quad -(15)$$

or $$\log_e n_i = -\alpha - \beta\epsilon_i \quad -(16)$$

$$n_i = e^{-\alpha} e^{-\beta\epsilon_i} \quad -(17)$$

At maximum W:

$$N = \sum_i n_i = \sum e^{-\alpha} e^{-\beta\epsilon_i} \quad -(18)$$

$$= e^{-\alpha} \sum_i e^{-\beta\epsilon_i}$$

i.e $$e^{-\alpha} = \frac{N}{\sum_i e^{-\beta\epsilon_i}} \quad -(19)$$

and $$\frac{n_i}{N} = \frac{e^{-\beta\epsilon_i}}{\sum_i e^{-\beta\epsilon_i}} \quad -(20)$$

In order to transform eq. (20) into eq. (2) the zeroth law of thermodynamics is used to define

$$\beta := \frac{1}{RT} \quad -(21)$$

This derivation must now be repeated

-) to find $\langle E^2 \rangle$.

The total energy is defined by eq. (3):

$$E = \sum_{i=0}^{\infty} n_i \epsilon_i \quad - (22)$$

$$= n_0 \epsilon_0 + n_1 \epsilon_1 + \ldots +$$

$$= \text{constant}$$

so

$$E^2 = \left(\sum_{i=0}^{\infty} n_i \epsilon_i \right)^2 = \text{constant} \quad - (23)$$

and eqs. (10), (14) and (15) modified.

In eq. (2), P_n is the probability that the system is in a state with energy E_n. However, a state ~~is~~ with energy E_n has squared energy E_n^2 so it follows ~~that~~:

$$\langle E^2 \rangle = \sum_n P_n E_n^2 \quad - (24)$$

with P_n given by eq. (2). So:

$$\boxed{\langle E^2 \rangle = \frac{\sum_n E_n^2 \exp\left(-\frac{E_n}{kT}\right)}{\sum_n \exp\left(-\frac{E_n}{kT}\right)} \quad - (25)}$$