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

-------------------------------- **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

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

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

$$W_2 = \frac{(N - n_1)!}{(N - n_1 - n_2)! \, n_2!} \tag{2}$$

and the number of ways of achieving this arrangement is

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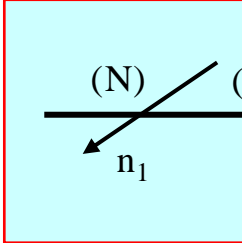
$$W = W_1 \cdot W_2 \cdots$$

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

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

$$W = N! \prod_i \frac{g_i^{n_i}}{n_i} \tag{3}$$

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

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

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

$$\delta N = \sum_i \delta n_i = 0 \tag{4}$$

$$\delta U = \sum_i \varepsilon_i \delta n_i = 0 \tag{5}$$

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

equations to each other:

$$\sum_i (\ln g_i - n \ln n_i + \alpha - \beta \varepsilon_i) \delta n_i = 0 \tag{6}$$

Since n_i is vary independent,

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

or

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

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

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

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

$$S = K \ln W = K\left[-N \ln N + N \ln Z + \frac{U}{KT} + N \ln N\right]$$
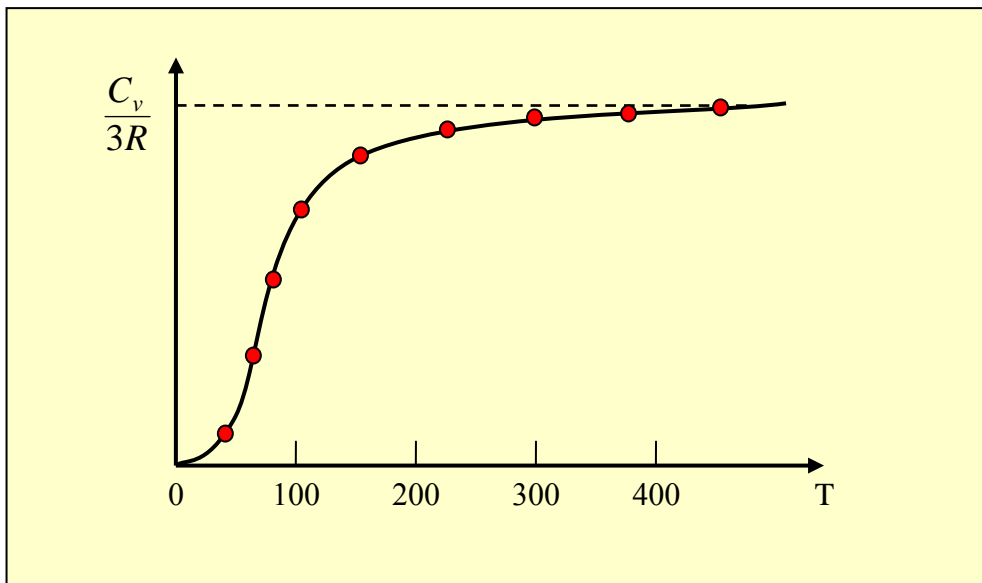
$$= NKT \ln Z + \frac{U}{T}$$

(9)

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

3. Debye treated with crystal as a continuous elastic medium and his expression of C_V is a good approximation to the Duling-Petit law.

Discuss the previous paragraph.

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

The specific heat depends on the temperature as in the figure. At high temperature the value of C_v is close to 3R

In the Debye model, the frequency of the lattice vibration covrs a wide range of values. The lowest frequency in the Debye model is $\nu = 0$ and the highest allowed is ν_D such that the integral of $g(\nu)d\nu$ from 0 to ν_D equals 3N, see Fig. (2)
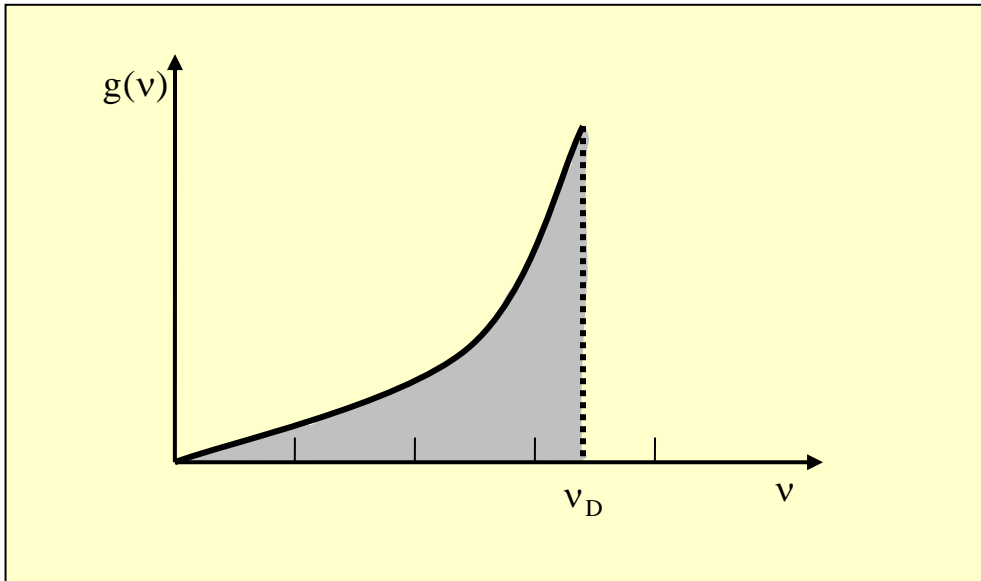
Thus

$$\int_0^{v_D} g(v)\,dv = 3N$$

By using the equation

$$g(v) = \frac{3V}{2\pi^2 c^3} v^2$$

We get

$$\frac{3V}{2\pi^2 c^3} \int_0^{v_D} v^2\,dv = 3N$$

$$\frac{3V}{2\pi^2 c^3} \frac{v_d^3}{3} = 3N$$

$$v_d^3 = \frac{6\pi^2 N c^3}{V}$$

Where v_D is called Debye frequency. In terms of v_D the function $g(v)$ is obtained as

$$g(v) = \frac{9N}{v_D^3} v^2 \qquad\qquad 0 \le v \le v_D$$

This summarizes the Debye theory of crystals.

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4. Discus in details the internal energy and specific heat for harmonic oscillator

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

Let us calculate U and C_V from the quantum partition function for monatomic crystal when lattice points free to move in one dimension only

$$Z = \frac{e^{-\Theta/2T}}{1 - e^{-\Theta/T}}$$

From which

$$\ln Z = \frac{\Theta}{2T} - \ln\left(1 - e^{-\Theta/T}\right)$$

So the energy U of N simple harmonic vibrators is:

$$U = NKT^2 \frac{\partial \ln Z}{\partial T} = NKT^2 \frac{\partial}{\partial T}\left[-\frac{\Theta}{2T} - \ln\left(1 - e^{-\Theta/T}\right)\right]$$

$$= NKT^2\left[\frac{\Theta}{2T^2} + \frac{e^{-\Theta/T}\frac{\Theta}{T^2}}{e^{\Theta/T} - 1}\right] = NK\Theta\left[\frac{1}{2} + \frac{e^{-\Theta/T}}{1 - e^{-\Theta/T}}\right]$$

$$= NK\Theta\left[\frac{1}{2} + \frac{1}{e^{\Theta/T} - 1}\right]$$

Therefore, the average energy per vibrator is

$$\langle \varepsilon \rangle = \frac{U}{N} = K\Theta\left[\frac{1}{2} + \frac{1}{e^{\Theta/T} - 1}\right]$$

Thus for a given oscillator the internal energy is a function of temperature only. The heat capacity C_V is

$$C_V = \left(\frac{\partial U}{\partial N}\right)_V = NK\left(\frac{\Theta}{T}\right)^2\left[\frac{e^{\Theta/T}}{e^{\Theta/T} - 1}\right]^2$$

The following curves are graphs of the internal energy U and of the heat capacity C_V divided by NK as functions of T/Θ

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