Statistical mechanics B

Ex. 1.7 Pathria Ultra-relativistic particles

Consider relativistic particle

$$\varepsilon^2 = \bar{p}^2 c^2 + m^2 c^4$$

In ultrarelativistic limit $m^2c^4 \to 0$, so we get

$$\varepsilon^2 = \bar{p}^2 c^2 = c^2 (p_x^2 + p_y^2 + p_z^2)$$

We can quantize this

$$\varepsilon^2 \psi = c^2\hbar^2 (\partial_x^2 + \partial_y^2 + \partial_z^2)\psi$$

We can get the solution in a cubic box $V = L^3$

$$\varepsilon = c\hbar (k_x^2 + k_y^2 + k_z^2)^{1/2} \quad \text{when } k_i = \frac{\pi n_i}{L}, \quad n_i = 1, 2, \dots$$

$$\varepsilon = \pi c\hbar \left(\frac{n_x^2}{L^2} + \frac{n_y^2}{L^2} + \frac{n_z^2}{L^2}\right)^{1/2}$$

If we consider $L \gg 1$ then we can treat $\{k_x, k_y, k_z\}$ as continuous variables. ~~To calculate the sum~~ The number of microstates will be just the following integral

$$\Omega_1(\varepsilon) = \int_0^L dx \int_0^L dy \int_0^L dz \, \frac{1}{8} \int dk_x \int dk_y \int dk_z \Big|_{k_x^2 + k_y^2 + k_z^2 = \frac{\varepsilon}{\pi c\hbar}} = V \int d\theta \int d\varphi \sin\theta \int dk\, k^2 \Big|_{k = \varepsilon^*} =$$

$$= \frac{1}{2}\pi V \int_0^\infty dk\, k^2 \, \delta(k - \varepsilon^*) = \frac{1}{2}\pi V \varepsilon^{*2}$$

This was ~~for~~ one particle. Consider now N such particles with condition for total energy

$$\sum_{i=1}^N \varepsilon_i = \pi c\hbar \sum_{i=1}^N |\vec{k}| = E, \qquad E^* = \frac{E}{\pi\hbar c}$$

$$\Omega_N(E) = \left(\int_0^L dx \int_0^L dy \int_0^L dz\right)^N \int_0^{+\infty} dk_{1x} \int_0^{+\infty} dk_{1y} \int_0^{+\infty} dk_{1z} \dots \int dk_{Nx} \int dk_{Ny} \int dk_{Nz} \, \delta\left(E^* - \sum_{i=1}^N |\vec{k}_i|\right) =$$

For every particles momenta we use spherical coordinates separately.

$$\Omega_N(E) = V^N \left(\frac{1}{8} \int d\varphi_i \int d\theta_i \sin\theta_i \int_0^\infty dk_i\, k_i^2\right)^N \delta\left(E^* - \sum_{i=1}^N k_i\right) =$$

$$= V^N \left(\frac{\pi}{2}\right)^N \int_0^{+\infty} dk_1\, k_1^2 \int_0^{+\infty} dk_2\, k_2^2 \dots \int_0^{+\infty} dk_N\, k_N^2\, \delta\left(E^* - \sum_{i=1}^{N-1} k_i - k_N\right) =$$

$$= \left(\frac{\pi V}{2}\right)^N \int_0^{+\infty} dk_1\, k_1^2 \int_0^{+\infty} dk_2\, k_2^2 \dots \int_0^{+\infty} dk_{N-1}\, k_{N-1}^2 \left(E^* - \sum_{i=1}^{N-2} k_i - k_{N-1}\right)^2 \theta\left(E^* - \sum_{i=1}^{N-1} k_i\right) =$$

Comment

// We get Heaviside theta function, because k_N is positive, so $E^* - \sum_{i=1}^{N-1} k_i$ also has to be "≥ 0". //

$$= \left(\frac{\pi V}{2}\right)^N \int_0^{E^*} dk_1\, k_1^2 \int_0^{E^* - k_1} dk_2\, k_2^2 \dots \int_0^{E^* - \sum_i^{N-2} k_i} dk_{N-1}\, k_{N-1}^2 \left(E^* - \sum_{i=1}^{N-2} k_i - k_{N-1}\right)^2$$

Let's calculate the following integral:

$$J_m(A) = \int_0^A dx\, x^2 (A-x)^m = \left\{\begin{matrix}\text{integrate} \\ \text{by parts}\end{matrix}\right\} = \frac{-1}{m+1} x^2 (A-x)^{m+1}\Big|_0^A +$$

$$+ \frac{2}{m+1} \int_0^A dx\, x (A-x)^{m+1} = \frac{2}{m+1} \int_0^A dx\, x (A-x)^{m+1} = \left\{\begin{matrix}\text{integrate by parts} \\ \text{one more time}\end{matrix}\right\} =$$

$$= \frac{-2}{(m+1)(m+2)} x (A-x)^{m+2}\Big|_0^A + \frac{2}{(m+1)(m+2)} \int_0^A dx\, (A-x)^{m+2} =$$

$$= \frac{2}{(m+1)(m+2)(m+3)} A^{m+3}$$

One can easily check for $m=0$ $\quad J_{m=0}(A) = \int_0^A dx\, x^2 = \frac{1}{3} x^3 \Big|_0^A = \frac{1}{3} A^3$

Come back to our integral. We will get a sequence of the integrals with different $A = E^* - \sum_{i=1}^{N-l-1} k_i$. We (N-1) integrals

Then: $$\Omega_N(E) = \left(\frac{\pi V}{2}\right)^N \frac{2^{N-1}}{(3N-1)!} E^{*\,3N-1} = \underbrace{\frac{(\pi V)^N}{(3N)!} (E^*)^{3N}}_{V_N(E)} \frac{3N}{2E^*}$$

$V_N(E)$ is just the volume ~~of the~~ occupied by particles with energy smaller than E. The last term will be not important in $N \gg 1$

~~As~~ We got the formula for number of microstates

$$\Gamma'_{\omega}(N,E,V) \approx \cancel{V_N}\,\Omega_N(E) \approx V_N(E) = \frac{(\pi V)^N}{(3N)!}\left(E\right)^{3N}$$

As in the classical gas example we should take into account ~~indistinguis~~ the fact the particles are indistinguishable.

true value:
$$\Gamma(N,E,V) = \frac{1}{N!}\Gamma'(N,E,V) = \frac{(\pi V)^N}{(3N)!\,N!}\left(\frac{E}{\pi\hbar c}\right)^{3N}$$

$$S = k\log\Gamma \approx k\left(3N\log\left(\frac{V^{1/3}E}{\pi^{2/3}\hbar c}\right) - 3N\log(3N) + 3N - N\log(N) + N\right) =$$
$$= 3Nk\log\left(\frac{V^{1/3}E}{\pi^{2/3}\hbar c}\right) - 3Nk\log\left(3N^{4/3}\right) + 4Nk =$$
$$= 3Nk\log\left(\frac{3}{\pi^{2/3}}\cdot\frac{V^{1/3}E}{\hbar c N^{4/3}}\right) + 4Nk$$

As we see the quantity in the logarithm is both dimensionless and intensive.

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T} = \frac{3Nk}{E} \quad\rightarrow\quad E = 3NkT$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{p}{T} = \frac{Nk}{V} \quad\rightarrow\quad pV = NkT$$