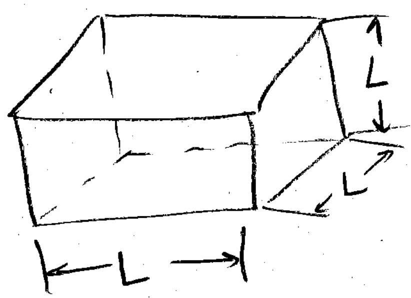
LECTURE

PERFECT GAS , part II

The particles in the gas are inclosed in a volume V (a cube of length L) and undergo a translational motion



The $\boxed{\text{1-particle}}$ energy spectrum and states are

$$\epsilon_{1\text{-particle}} = \frac{h^2}{8mL^2}\left(j_1^2 + j_2^2 + j_3^2\right)$$

with

$$j_1 = 1, 2, 3, \ldots$$
$$j_2 = 1, 2, 3, \ldots$$
$$j_3 = 1, 2, 3, \ldots$$

These states were obtained from the following Schroedinger equation

$$\nabla^2 \phi(x,y,z) + k^2 \phi(x,y,z) = 0$$

with boundary conditions $\phi(x,y,z) = 0$ on all faces of the cube

In the thermodynamic limit, which is

$\#$ of particles $N \to \infty$

Volume $V \to \infty$

such that $\frac{N}{V} \to$ constant density

the thermodynamic results should be independant on the boundary conditions we imposed. For this reason, for the gas we will use periodic boundary conditions because this boundary condition will set the ground state to zero, and thus will be easy to manipulate the 1- particle energy spectrum.

Periodic boundary conditions:

$$\phi(0,y,z) = \phi(L,y,z)$$
$$\phi(x,0,z) = \phi(x,L,z)$$
$$\phi(x,y,0) = \phi(x,y,L)$$

In this case the 1-particle energy and states are
$$\epsilon_{\text{1-particle states}} = \frac{\hbar^2}{2mL^2}(j_1^2 + j_2^2 + j_3^2)$$

$$j_1 = 0, \pm 1, \pm 2, \ldots$$
$$j_2 = 0, \pm 1, \pm 2, \ldots$$
$$j_3 = 0, \pm 1, \pm 2, \ldots$$

Notice that the j_1, j_2, j_3 can be now positive or <u>negative</u>, and that the energy formula changed (from $\frac{1}{8}\ldots$ to $\frac{1}{2}\ldots$)

The minimum energy is now

$$\boxed{\epsilon_{\text{1-particle state, minimum}} = 0}$$

ground state for periodic boundary conditions

as opposed to

$$\epsilon_{\text{1-particle state, minimum}} = \frac{h^2}{8mL^2}\cdot 3$$

ground state for "zero on the walls" boundary conditions.

At this point the problem of a perfect gas is encapsulated in the following formulas

(I) The 1-particle states and energy

$$\epsilon_{j_1 j_2 j_3} = \frac{\hbar^2}{2mL^2}\left(j_1^2 + j_2^2 + j_3^2\right)$$

$$j_1 = 0, \pm 1, \pm 2, \ldots$$
$$j_2 = 0, \pm 1, \pm 2, \ldots$$
$$j_3 = 0, \pm 1, \pm 2, \ldots$$

(II) The average number of particles

$$\langle N \rangle = \sum_{j_1, j_2, j_3} \frac{1}{e^{-\beta\mu + \beta \epsilon_{j_1 j_2 j_3}} \mp 1}$$

(III) The thermodynamic equation of state

$$\frac{pV}{kT} = \mp \sum_{j_1, j_2, j_3} \ln\left(1 \mp e^{\beta\mu - \beta \epsilon_{j_1 j_2 j_3}}\right)$$

with (−) for BOSONS and (+) for FERMIONS

(IV) Here we have to add the following logic. Because we are using a grand canonical approximation for a canonical distribution, we need to interpret (II) as an equation for the chemical potential μ, given $\langle N \rangle$ and the temperature T $\left(\beta = \frac{1}{kT}\right)$. We have to write then

$$N = \sum_{j_1 j_2 j_3}' \frac{1}{e^{-\beta\mu + \beta \epsilon_{j_1 j_2 j_3}} \mp 1}$$

the number of particles in volume V.

The logical scheme is thus:

Find $\displaystyle \sum_{j_1 j_2 j_3}' \frac{1}{e^{-\beta\mu + \beta \epsilon_{j_1 j_2 j_3}} \mp 1}$

Solve for $\mu(T, V, N)$ from

$$N = \sum_{j_1 j_2 j_3}' \frac{1}{e^{-\beta\mu + \beta \epsilon_{j_1 j_2 j_3}} \mp 1}$$

Substitute $\mu(T, V, N)$ into the following sum and compute it

$$\frac{pV}{kT} = \mp \sum_{j_1 j_2 j_3}' \ln\left(1 \mp e^{\beta\mu - \beta \epsilon_{j_1 j_2 j_3}}\right)$$

the above scheme cannot be completed without approximations. The approximation we will use is to go from the sum $\sum$ to an integral $\int$

Continous approximation

Let $f(n)$ be a function defined on the integers between $n=a$ and $n=b$, admitting a continuous extension on the real numbers. Then

$$\sum_{n=a}^{n=b}{}' f(n) = \int_a^b f(n)\,dn + \frac{1}{2}\left(f(a)+f(b)\right) +$$

$$+ \sum_{j=1}^{\infty}{}' (-1)^j \frac{B_{2j}}{(2j)!}\left(f^{(2j-1)}(a) - f^{(2j-1)}(b)\right)$$

Where B_j are the Bernoulli numbers, $B_2 = \frac{1}{6}$, $B_4 = -\frac{1}{30}$, ...
This is known as the Euler-MacLaurin sum formula.
the Bernoulli polinomials $B_n(x)$, $n=0,1,2,\ldots$ may be defined recursively as follows:

$$B_0(x) = 1,$$

$$B_n'(x) = n\,B_{n-1}(x) \quad \text{and} \quad \int_0^1 B_n(x)\,dx = 0 \quad \text{for } n \geq 1.$$

the Bernoulli numbers are $B_n = B_n(1)$

the Bernoulli polinomials value for $x=1$

When we can neglect the contributions from the boundaries a and b of the interval, we have

$$\sum_{n=a}^{b} f(n) \cong \int_a^b f(n)\,dn .$$

Neglecting or not the boundary influence, we need to compute $\int_a^b f(n)\,dn$.

Our sum is over three integer variables

$$\sum_{j_1, j_2, j_3}{}'$$

and for each variable $a = -\infty$ and $b = +\infty$.

Thus

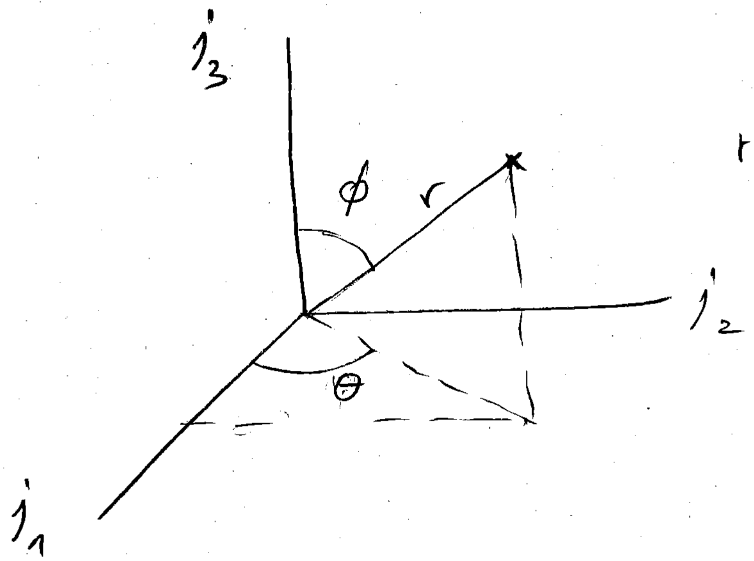
$$\sum_{j_1 j_2 j_3}{}' f(j_1, j_2, j_3) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(j_1, j_2, j_3)\, dj_1\, dj_2\, dj_3$$

In our case:

$$\sum_{j_1 j_2 j_3}{}' \frac{1}{e^{-\beta\mu + \beta \epsilon_{j_1 j_2 j_3}} \mp 1} = \int_{-\infty}^{\infty} dj_1\, dj_2\, dj_3 \frac{1}{e^{-\beta\mu + \beta \epsilon_{j_1 j_2 j_3}} \mp 1}$$

Because $\epsilon_{j_1 j_2 j_3} = \frac{\hbar^2}{2mL^2}(j_1^2 + j_2^2 + j_3^2)$

we will change the variables from (j_1, j_2, j_3) to spherical coordinates (r, θ, ϕ) $\begin{cases} r \text{ in } [0, \infty) \\ \theta \text{ in } [0, 2\pi) \\ \phi \text{ in } [0, \pi] \end{cases}$



$$r^2 = j_1'^2 + j_2'^2 + j_3'^2$$

$$j_1' = r \sin\phi \cos\theta$$

$$j_2' = r \sin\phi \sin\theta$$

$$j_3' = r \cos\phi$$

The volume element

$$dj_1' \, dj_2' \, dj_3' = r^2 \sin\phi \, d\phi \, d\theta \, dr$$

$$\int_{-\infty}^{\infty} dj_1 \, dj_2 \, dj_3 \, \frac{1}{e^{-\beta\mu + \beta\epsilon_{j_1 j_2 j_3}} \mp 1} =$$

$$= \int_0^{2\pi} d\theta \int_0^{\pi} \sin\phi \, d\phi \int_0^{\infty} r^2 dr \, \frac{1}{e^{-\beta\mu + \beta\epsilon_{r\theta\phi}} \mp 1} =$$

$$= 2\pi\left(-\cos\phi\right)\Big|_0^{\pi} \int_0^{\infty} \Bigg(\underbrace{\left[\frac{\epsilon}{\frac{\hbar^2}{2mL^2}}\right]^{\frac{1}{2}}}_{r}\Bigg)^2 d\Bigg(\underbrace{\left[\frac{\epsilon}{\frac{\hbar^2}{2mL^2}}\right]^{\frac{1}{2}}}_{r}\Bigg)$$

from $\epsilon_{j_1 j_2 j_3} = \frac{\hbar^2}{2mL^2}\left(j_1'^2 + j_2'^2 + j_3'^2\right)$

and $r^2 = j_1'^2 + j_2'^2 + j_3'^2$

$$\frac{1}{e^{-\beta\mu + \beta\epsilon} \mp 1}$$

we do not need any index on ϵ because now ϵ is the variable over which we integrate

$$\int_0^{\infty} d\epsilon \; 2\pi \cdot 2 \cdot \frac{2mL^2}{\hbar^2} \cdot \left(\frac{2mL^2}{\hbar^2}\right)^{\frac{1}{2}} \cdot \epsilon \cdot \frac{1}{2}\, \epsilon^{-\frac{1}{2}} \cdot \frac{1}{e^{-\beta\mu+\beta\epsilon} \mp 1} =$$

$$= \int_0^{\infty} d\epsilon \; \frac{2\pi V}{\hbar^3} (2m)^{\frac{3}{2}} \epsilon^{\frac{1}{2}} \frac{1}{e^{-\beta\mu+\beta\epsilon} \mp 1}$$

thus

$$\boxed{N = \int_0^\infty d\epsilon\, g(\epsilon)\, \frac{1}{e^{-\beta\mu+\beta\epsilon} \mp 1} \quad + \text{ other terms if necessary}}$$

with

$$g(\epsilon) = \frac{2\pi V}{h^3} (2m)^{\frac{3}{2}}\, \epsilon^{\frac{1}{2}}$$

The meaning of $g(\epsilon)d\epsilon$ is simple. It represents the <u>number</u> of 1-particle states in the energy interval $[\epsilon, \epsilon+d\epsilon]$.

The scheme for the continuous approximation is thus

Find $\mu(T,V,N)$ from

$$N = \int_0^\infty d\epsilon\, g(\epsilon)\, \frac{1}{e^{-\beta\mu+\beta\epsilon} \mp 1} \quad + \text{ other terms if necessary}$$

$\downarrow$

Substitute $\mu(T,V,N)$ in

$$\frac{pV}{kT} = \mp \int_0^\infty d\epsilon\, g(\epsilon) \ln\left(1 \mp e^{\beta\mu-\beta\epsilon}\right) \quad + \text{ other terms if necessary}$$