Ideal Bose Gas: (See Kardar 7.6). 11/5

- No interactions between the molecules but a virial expansion is going to be needed to obtain the equation of state due to quantum effects.

We found that

$$\ln Z_{BE} = -\sum_r \ln\left(1 - e^{-\alpha - \beta \varepsilon_r}\right) \quad (1) \qquad \alpha = -\beta\mu$$

We also found that

$$\tilde{\Omega} = F - \mu N = -kT \ln \mathcal{Z} \qquad (2)$$

Landau potential

Since $E = TS - PV + \mu N$ then

$$\underbrace{E - TS}_{F} - \mu N = -PV$$

$$F - \mu N = \tilde{\Omega} = -PV \qquad (3)$$

From (3) and (2) we see that knowing $\mathcal{Z}$ we can obtain the equation of state for the gas,

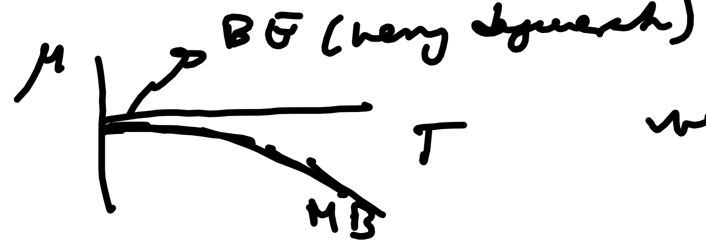
$$\therefore \quad PV = RT \ln \mathcal{Z} \underset{(1)}{=} -kT \sum_r \ln\left(1 - e^{-\beta(\varepsilon_r - \mu)}\right) \qquad (4)$$

also for B-E:

$$N = \sum_r n_r = \sum_r \frac{1}{e^{\beta(\varepsilon_r-\mu)} - 1} > 0 \quad \text{since } N > 0 \qquad (5)$$

$$\therefore \quad \varepsilon_r - \mu > 0 \quad \text{so} \quad e^{\beta(\varepsilon_r-\mu)} > 1$$

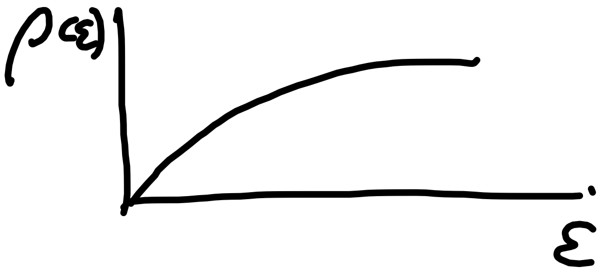
$\mu < \varepsilon_r$(minimum) - If $\varepsilon_r(\text{min}) = 0 \Rightarrow \mu < 0$.



we will see later.

Since the quantum levels are very close to each other we found that we can assume that the discrete levels are continuous and we found for the ideal gas that

$$\rho(\varepsilon)\,d\varepsilon = \frac{2\pi V}{h^3}(2m)^{3/2}\,\varepsilon^{1/2}\,d\varepsilon \qquad (3D)$$



$\rho(\varepsilon=0)=0$ ok for large T

but notice that really

$\rho(\varepsilon=0)=1$ (very small and irrelevant at $T>>0$)

Now let's write the continuous version of (4) and (5):

$$PV = -kT\frac{2\pi V}{h^3}(2m)^{3/2}\int_0^\infty \varepsilon^{1/2}\ln\left(1-e^{-\beta(\varepsilon-\mu)}\right)d\varepsilon \quad (6)$$

$$\cancel{-kT\underbrace{\ln\left(1-e^{\beta\mu}\right)}_{\varepsilon=0}}$$

since it is of the order of N_0 and even if $N_0 \sim N$, the $N \ll$ the other terms.

and

$$N = \underbrace{\frac{2\pi V}{h^3}(2m)^{3/2}\left[\int\frac{\varepsilon^{1/2}d\varepsilon}{e^{\beta(\varepsilon-\mu)}-1}\right.}_{N_e \text{ (\# of molecules in the excited states)}} + \left.\underbrace{\frac{1}{e^{-\beta\mu}-1}}_{N_0}\right] \quad (7)$$

may be important if N_0 gets large.

Let's work with ⑥ a bit:

$$PV = -kT\frac{2\pi V}{h^3}(2m)^{3/2}\int_0^\infty \underbrace{\varepsilon^{1/2}}_{u'} \underbrace{\ln\left(1-e^{-\beta(\varepsilon-\mu)}\right)}_{v} d\varepsilon =$$

$$u = \frac{2}{3}\varepsilon^{3/2} \qquad v' = \frac{\beta e^{-\beta(\varepsilon-\mu)}}{1-e^{-\beta(\varepsilon-\mu)}}$$

$$\int_a^b u'v\,dx = uv\Big|_a^b - \int_a^b uv'\,dx$$

$$= -kT\frac{2\pi V}{h^3}(2m)^{3/2}\Bigg\{\underbrace{\Big[\frac{2}{3}\varepsilon^{3/2}\ln\big(1-e^{-\beta(\varepsilon-\mu)}\big)\Big]\Big|_0^\infty}_{0 \text{ in } \varepsilon=0 \quad \text{in } \varepsilon\to\infty \quad 0} -$$

$$-\frac{2}{3}\int_0^\infty \varepsilon^{3/2}\frac{\beta e^{-\beta(\varepsilon-\mu)}}{1-e^{-\beta(\varepsilon-\mu)}}d\varepsilon$$

Then

$$PV = \cancel{k}T \frac{2\pi V}{h^3} (2m)^{3/2} \frac{2}{3} \frac{1}{\cancel{k}T} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)}-1} d\varepsilon$$

Define $x = \beta\varepsilon \Rightarrow dx = \beta d\varepsilon$ (*)

$$PV = \frac{2\pi V}{h^3} (2m)^{3/2} \frac{2}{3} \frac{1}{\beta^{5/2}} \int_0^\infty \frac{x^{3/2}\, dx}{e^{-\beta\mu} e^x - 1}$$

$$PV = \frac{2\pi V}{h^3} (2m)^{3/2} \frac{2}{3} (kT)^{5/2} \underbrace{\int_0^\infty \frac{x^{3/2}\, dx}{z^{-1} e^x - 1}}_{I(z)} \qquad (8)$$

Def.

$$\boxed{z = e^{\beta\mu}}$$

Also from (7) we obtain (applying (*)):

$$N - N_0 = \frac{2\pi V}{h^3} (2m)^{3/2} (kT)^{3/2} \int_0^\infty \frac{x^{1/2}}{z^{-1} e^x - 1} dx$$

(7')

In addition:

$$\langle E \rangle = \sum_r n_r \varepsilon_r = \sum_r \frac{\varepsilon_r}{e^{\beta(\varepsilon_r - \mu)} - 1}$$

in the continuum it becomes

$$\langle E \rangle = \int_0^\infty \frac{2\pi V}{h^3} \frac{(2m)^{3/2} \varepsilon^{1/2} \varepsilon \, d\varepsilon}{e^{\beta(\varepsilon - \mu)} - 1}$$

(*)

$$= \frac{2\pi V (2m)^{3/2}}{h^3} (kT)^{5/2} \int_0^\infty \frac{x^{3/2}\, dx}{z^{-1} e^{x} - 1} \quad (9)$$

Comparing (9) with (8) we find that

$$PV = \frac{2}{3} \langle E \rangle$$

or $$P = \frac{2}{3} \frac{\langle E \rangle}{V} \quad (10)$$

To obtain the equation of state consider the case in which $e^{\mu\beta} = z \ll 1$ (this is for $\mu \ll 0$ ~ ideal gas limit)

This will lead to a Virial expansion.

Consider the integrand in our integrals:

$$\frac{1}{z^{-1}e^{x}-1} = \frac{z e^{-x}}{1 - z e^{-x}} \simeq z e^{-x}\left(1 + z e^{-x} + z^2 e^{-2x} + \cdots\right)$$

expansion in powers of z.

Then

$$I_{1/2} = \int_0^\infty \frac{x^{1/2}\,dx}{z^{-1}e^{x}-1} \simeq \frac{\sqrt{\pi}}{2}\left[z + \frac{z^2}{2^{3/2}} + \cdots\right] \quad (11)$$

$$I_{3/2} = \int_0^\infty \frac{x^{3/2}\,dx}{z^{-1}e^{x}-1} \simeq \frac{3\sqrt{\pi}}{4}\left[z + \frac{z^2}{2^{5/2}} + \cdots\right] \quad (12)$$

Divide 8 by 7':

$$\frac{PV}{N-N_0} = \frac{2}{3} kT \frac{I_{3/2}}{I_{1/2}} = kT \frac{\cancel{3}}{\cancel{2}} \frac{\cancel{2}}{\cancel{3}} \frac{\left[z + \frac{z^2}{2^{3/2}} + \cdots\right]}{\left[z + \frac{z^2}{2^{5/2}} + \cdots\right]}$$

For T high enough so that $N \gg N_0$

$$\frac{PV}{NkT} = \frac{I_{3/2}}{I_{1/2}}$$

also at high T

$$N = \sum_r n_r = \sum_r \frac{1}{z^{-1} e^{\beta \varepsilon_r} - 1} \xrightarrow{\text{high } T} \sum_r z\, e^{-\beta \varepsilon_r} =$$

$$= z \sum_r e^{-\beta \varepsilon_r} = z Z$$

Then $N = z Z$ or $z = \frac{N}{Z}$

but $Z = \frac{V(2\pi m kT)^{3/2}}{h^3}$ partition function for ~~the~~ ideal gas.

$$z = e^{\beta\mu} = \frac{N}{Z} = \frac{h^3 N}{(2\pi m kT)^{3/2} V} = \frac{h^3}{(2\pi m kT)^{3/2}} \underbrace{\frac{N}{V}}_{n}$$

An expansion in powers of z is equivalent to an expansion in powers of n like a Virial expansion.

Then

$$\frac{PV}{NkT} = \frac{\left(1 + \frac{h^3}{2^{5/2}(2\pi mkT)^{3/2}}\frac{N}{V} + \cdots\right)}{\left(1 + \frac{h^3}{2^{3/2}(2\pi mkT)^{3/2}}\frac{N}{V} + \cdots\right)} \simeq$$

$$\simeq 1 - \frac{h^3}{2^{3/2}(2\pi mkT)^{3/2}}\frac{N}{V} + \cdots$$

then

$$PV = NkT\left[1 - \frac{h^3}{2^{3/2}(2\pi mkT)^{3/2}}\frac{N}{V} + \cdots\right]$$

We see that if $\frac{N}{V}$ is negligible then the BE gas has the eq. of state of the ideal gas but as $\frac{N}{V}$ increases we start finding corrections. This is valid at high temperatures.

Notice that we can write:

$$PV = NkT \sum_{l=1}^{\infty} a_l \left(\frac{\lambda^3}{v}\right)^{l-1} \qquad v = \frac{V}{N} = \frac{1}{n}$$

$$= NkT \sum_{l=1}^{\infty} a_l \left(\lambda^3 n\right)^{l-1}$$

a_l → Virial coefficients.

$$\lambda = \frac{h}{(2\pi mkT)^{1/2}}$$

$a_1 = 1 \qquad a_2 = -\frac{1}{4\sqrt{2}} < 0$

Since $E = \frac{3}{2} PV$

we see that E is smaller than for the ideal gas and the quantum statistics is equivalent to the effect of an attractive interaction (although the particles are non interacting).

Note: If you do the same for F-D statistics you will find out that the energy is larger than for the ideal case. Pauli exclusion principle is equivalent to a repulsive interaction.

Let's see what happens with C_V (at high T);

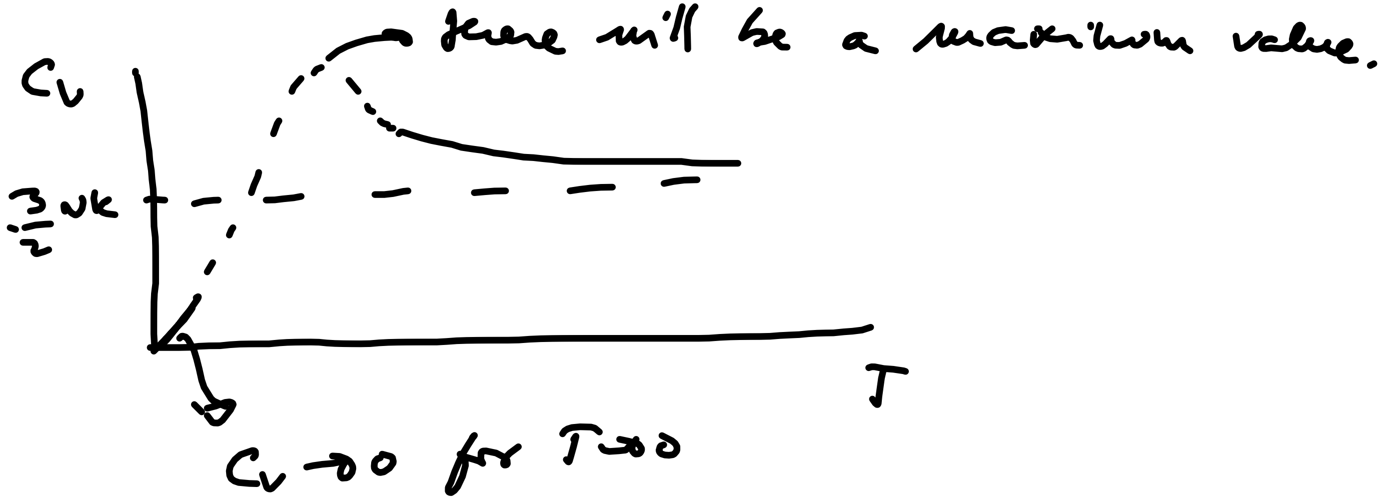
$$C_V = \frac{\partial \bar{E}}{\partial T}\Big|_{N,V} = \frac{3}{2}\left(\frac{\partial}{\partial T} PV\right)\Big|_{N,V} =$$

$$= \frac{3}{2} N k \sum_{\ell=1}^{\infty} \frac{5-3\ell}{2} a_\ell \, (n\lambda^3)^{\ell-1}$$

$$\therefore \; C_V = \frac{3}{2} N k \left(1 + \frac{(-1)}{2} a_2 (n\lambda^3) + \dots \right) =$$

$$= \frac{3}{2} N k \left(1 - \frac{1}{2^{5/2}} (n\lambda^3) + \dots \right) > C_V \text{ for ideal gas}$$

$$= \frac{3}{2} N k$$



Low T limit: Bose-Einstein condensation.

If T is low then $e^{-\beta\mu} \longrightarrow 1$ $(z^{-1} \longrightarrow 1)$

$z = e^{\beta\mu}$ and $0 \leq z \leq 1$

$\mu = \mu(T)$ and when $T \to 0$ then $\mu \to 0$ as well.

If $z \to 1$ then

$$N_e = (N - N_0) = \frac{2\pi V}{h^3}(2mkT)^{3/2} \underbrace{\int_0^\infty \frac{x^{1/2}}{z^{-1}e^x - 1}\,dx}_{I_{1/2}}$$

From this equation you can obtain $z = e^{\mu\beta}$ which allows you to obtain $\mu = \mu(T)$.

But when $z \to 1$ $I_{1/2} \to I_{1/2\,max}$ independent of T. and $\mu = 0$.

$$\int_0^\infty \frac{x^{1/2}}{e^x - 1}\,dx \simeq 2.3 = I_{1/2\,max}.$$

$N_e \sim N$ except when $e^{\beta\mu} \approx 1$ - then

$$N_e \leq \frac{V(2\pi m k T)^{3/2}}{h^3} I_{1/2\,max}$$

But when $z = e^{-\beta\mu} \to 1$ (for $\mu \to 0$ and $T \to 0$)

then

$$N_e = \frac{V(2\pi m k T)^{3/2}}{h^3} I_{1/2\,max}$$

and

$$N_0 = N - N_e = N - V\frac{(2\pi m k T)^{3/2}}{h^3} I_{1/2\,max}.$$

But $N_0 = \dfrac{e^{-\mu\beta}}{1-e^{-\mu\beta}} = \dfrac{z}{1-z}$

B-E dist.

$z = \dfrac{N_0}{1+N_0} \simeq 1 - \dfrac{1}{N_0} \simeq 1$

In this situation ($z \to 1$) N_0 is rather large.