Lecture

BOSE GAS

We will study Bose gas first and Fermi gas second.

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

$$(2) \quad \frac{pv}{kT} = -\int_0^\infty d\epsilon\, g(\epsilon) \ln\left(1 - e^{\beta\mu - \beta\epsilon}\right) \quad + \text{ other terms if necessary}$$

First we need to find if other terms are necessary to be added on the right hand side of (1) and (2). To find an answer we go back to the unapproximated formula

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

The minimum value for the energy $\epsilon_{j_1 j_2 j_3}$ is zero, and we can write

$$(3) \quad N = \underbrace{\sum_{\substack{j_1 \neq 0 \\ j_2 \neq 0 \\ j_3 \neq 0}} \frac{1}{e^{-\beta\mu + \beta\epsilon_{j_1 j_2 j_3}} - 1}}_{\text{Excited states}} + \underbrace{\frac{1}{e^{-\beta\mu} - 1}}_{\text{Ground state}}$$

Each term in the sum represents the average number of particles in the state (j_1, j_2, j_3)

$$\langle n_{j_1 j_2 j_3} \rangle = \frac{1}{e^{-\beta\mu + \beta\epsilon_{j_1 j_2 j_3}} - 1}$$

Because bosons can accumulate in many numbers in a state, the value $\langle n_{j_1 j_2 j_3} \rangle$ can be very large.

In view of the fact that for bosons

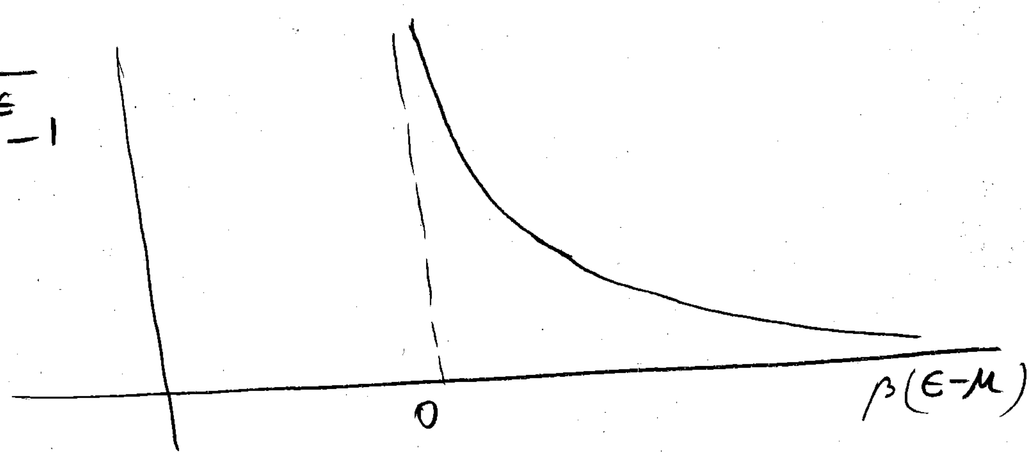
$$\mu \leqslant \epsilon_{j_1 j_2 j_3} \quad \text{for all } (j_1, j_2, j_3)$$

we find that

$$\langle n_{j_1 j_2 j_3} \rangle < \langle n_{i_1 i_2 i_3} \rangle$$

if the energy $E_{j_1 j_2 j_3} > E_{i_1 i_2 i_3}$. The bosons will accumulate on lower energy levels

$$\langle n_\epsilon \rangle = \frac{1}{e^{-\beta\mu + \beta\epsilon} - 1}$$



The ground state ($j_1=0,\ j_2=0,\ j_3=0,\ \epsilon_{j_1 j_2 j_3}=0$) is the moast populated state. The term in (3) $\frac{1}{e^{-\beta\mu}-1}$ which represents the average number of particles in the ground state is higher than any correspondin term $\frac{1}{e^{-\beta\mu+\beta\epsilon_{j_1 j_2 j_3}}-1}$ for the excited states. From Euler- MacLaurin point of view, the ground state is like $f(a)$, and because we noticed that is big, we cannot discard it. Moreover, in the integral (1) the continuous density of states $g(\epsilon)$ is ZERO for $\epsilon=0$; thus $g(\epsilon)$ completely elliminates the ground state. In view of this discussion, we need to start from formula (3) and approximate only the excited states with an integral.

$$(4) \qquad N = \int_0^\infty d\epsilon\, g(\epsilon)\, \frac{1}{e^{-\beta\mu+\beta\epsilon}-1} + \frac{1}{e^{-\beta\mu}-1}$$

Likewise, formula (2) becomes

$$(5) \qquad \frac{pV}{KT} = \underbrace{-\int_0^\infty d\epsilon\, g(\epsilon)\, \ln\left(1-e^{\beta\mu-\beta\epsilon}\right)}_{\text{excited states}} \underbrace{+\ln\left(1-e^{\beta\mu}\right)}_{\text{ground state}}$$

We will introduce a common notation for $e^{\beta\mu}$

$$z = e^{\beta\mu} \quad , \quad 0 < z \leq 1$$

because $\mu \leq 0$

jargon name : FUGACITY

Also, in view of the thermodynamic limit which asks for $N \to \infty$, $V \to \infty$ with $\frac{N}{V} \to$ <u>constant density</u>, we will write (4) and (5) as

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

$$(6) \quad \frac{N}{V} = \frac{2\pi}{h^3} (2m)^{\frac{3}{2}} \int_0^\infty d\epsilon \frac{\epsilon^{\frac{1}{2}}}{z^{-1} e^{\beta\epsilon} - 1} + \frac{1}{V} \frac{z}{1-z}$$

$$(7) \quad \frac{p}{kT} = -\frac{2\pi}{h^3} (2m)^{\frac{3}{2}} \int_0^\infty d\epsilon \, \epsilon^{\frac{1}{2}} \ln(1 - z e^{-\beta\epsilon}) - \frac{1}{V} \ln(1-z)$$

Denote with N_0 the number of particles in the ground state, then

$$N = N_e + N_0$$

\# of particles in the excited states

From (6) N_e is the integral, and

$$N_0 = \frac{z}{1-z}$$

So

$$z = \frac{N_0}{N_0+1}$$

As N_0 increases, z gets close to 1.

Now the term $\frac{1}{V}\ln(1-z)$ which corrects the ratio $\frac{P}{kT}$ in (7) is

$$-\frac{1}{V}\ln(1-z) = -\frac{1}{V}\ln\left(1-\frac{N_0}{N_0+1}\right) = \frac{\ln(N_0+1)}{V} =$$

$$= \frac{\ln(N_0+1)}{N\cdot\left(\frac{V}{N}\right)}$$

In the thermodynamic limit $\left(N\to\infty, V\to\infty, \frac{V}{N}\to\text{CONST}\right)$ this term goes to ZERO

$$\frac{\ln(N_0+1)}{N\cdot\text{CONST}} < \frac{\ln(N+1)}{N\cdot\text{CONST}} \xrightarrow[\text{when } N\to\infty]{} 0$$

thus the term $-\frac{1}{V}\ln(1-z)$ is negligible, unlike the term

$$\frac{1}{V}\,\frac{z}{1-z} = \frac{N_0}{N\,\frac{V}{N}} \to \frac{N}{N\cdot\text{CONST}} \to \frac{1}{\text{CONST}}$$

here N_0 can go to N when all bosons are accumulated in the ground state.

This possibility, that all bosons can accumulate in the ground state is called

BOSE-EINSTEIN CONDENSATION

At this point we succeeded to master the influence of the ground state on our formulas. We will neglect the term $-\frac{1}{V}\ln(1-z)$ in (7) but we cannot neglect the term $\frac{1}{V}\frac{z}{1-z}$ in (6). Thus.

$$(8) \quad \frac{N}{V} = \frac{2\pi}{h^3}(2m)^{\frac{3}{2}}\int_0^\infty d\epsilon\, \frac{\epsilon^{\frac{1}{2}}}{z^{-1}e^{\beta\epsilon}-1} + \frac{1}{V}\underbrace{\frac{z}{1-z}}_{N_0}$$

$$(9) \quad \frac{P}{kT} = -\frac{2\pi}{h^3}(2m)^{\frac{3}{2}}\int_0^\infty d\epsilon\, \epsilon^{\frac{1}{2}}\ln\left(1 - z e^{-\beta\epsilon}\right)$$

The next steps require to find z from (8) and then substitute it in (9). To achieve this, we will change the energy variable ϵ so that β will not be part of the integral. In this way the integral will become some standard functions

$$\beta\epsilon = x$$

We also move the term $\frac{N_0}{V}$ in (8) on the left side

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

Notations

$$\frac{P}{kT} = -\underbrace{\frac{2\pi}{h^3}(2mkT)^{\frac{3}{2}}}_{\frac{1}{\lambda^3}} \underbrace{\int_0^\infty x^{\frac{1}{2}} \ln(1 - z e^{-x})\,dx}_{g_{\frac{5}{2}}(z)}$$

with

$$\boxed{\lambda = \frac{h}{\sqrt{2\pi m k T}}}$$

Thermal wavelength

and

$$g_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{x^{\nu-1}}{z^{-1}e^x - 1}\,dx$$

are BOSE – EINSTEIN functions

$$g_\nu(z) = z + \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} + \cdots$$

Conclusion

$$\boxed{\begin{aligned} &(10) \quad \frac{N-N_0}{V} = \frac{1}{\lambda^3}\, g_{\frac{3}{2}}(z) \\ &(11) \quad \frac{P}{kT} = \frac{1}{\lambda^3}\, g_{\frac{5}{2}}(z) \end{aligned}}$$

With $0 < z \leq 1$

Because $N_0 = \dfrac{z}{1-z}$, we see that for small z (that is for z close to zero) the number of particles in the ground state N_0 is small

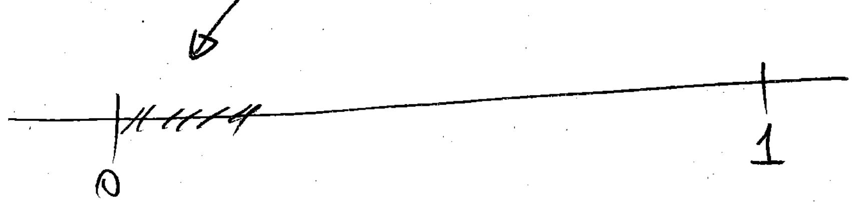
$$N_0 \ll N$$

In this case

$$\frac{N-N_0}{V} \simeq \frac{N}{V} = \rho$$

Notation for the number of particles per unit volume (= particle density)

For z small



the range for z

For small z

$$\frac{N-N_0}{V} = \frac{1}{\lambda^3}\, g_{\frac{3}{2}}(z)$$

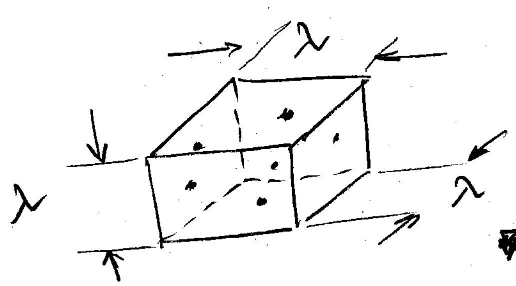
becomes

$$\rho\lambda^3 = g_{3/2}(z) \qquad (12)$$

If the gas is at not very low temperatures, the number of particles in a thermal wavelength cube is small

$\rho\lambda^3$ is small if T is high

$$\lambda \sim \frac{1}{\sqrt{T}}$$



$\rho\lambda^3$ = # of particles

For a dilute gas, $\rho\lambda^3 < 1$ and the relation (12) can be inverted with the help of a series expansion.

Mathematical technique for finding z given $\rho\lambda^3$ from

$$\rho\lambda^3 = g_{\frac{3}{2}}(z)$$

We are lucky here, because for $0 \approx z << 1$, $0 \approx \rho\lambda^3 << 1$. In mathematical jargon we say that we have two <u>small</u> <u>parameters</u>, z and $\rho\lambda^3$. When we have small parameters we can expand the functions in series and use only few terms.

From the definition of $g_{\frac{3}{2}}(z)$ we have the following expantion

$$g_{\frac{3}{2}}(z) = z + \frac{z^2}{2^{\frac{3}{2}}} + \frac{z^3}{3^{\frac{3}{2}}} + \cdots$$

Expressing z in terms of $\rho\lambda^3$ means that z is some function (unknown to us now) of $\rho\lambda^3$

$$z = f(\rho\lambda^3)$$

Because $\rho\lambda^3$ <u>is small</u> we can expand the function $f(\rho\lambda^3)$ in a Taylor series about $\rho\lambda^3 = 0$

So

$$z = b_0 + b_1(\rho\lambda^3) + b_2(\rho\lambda^3)^2 + \cdots \tag{13}$$

If we can find the coefficients $b_0, b_1, b_2, \ldots$ we are done, because these coefficients determines the function $f(\rho\lambda^3)$.

To find $b_0, b_1, b_2, \ldots$ we insert (13) into (12) and obtain a sequence of equations:

$$\rho\lambda^3 = \underbrace{b_0 + b_1(\rho\lambda^3) + b_2(\rho\lambda^3)^2 + \cdots}_{z}$$

$$+ \frac{1}{2^{\frac{3}{2}}}\left(b_0 + b_1(\rho\lambda^3) + b_2(\rho\lambda^3)^2 + \cdots\right)^2$$

$$+ \frac{1}{3^{\frac{3}{2}}}\left(b_0 + b_1(\rho\lambda^3) + b_2(\rho\lambda^3)^2 + \cdots\right)^3 + \cdots$$

On the left hand side we have only one term, namely $\rho\lambda^3$. On the right hand side $b_0, b_1, b_2, \ldots$, should have such values that again only the term $\rho\lambda^3$ is present.

So

(A) $\quad 0 = b_0 + 2^{-\frac{3}{2}} b_0^2 + 3^{-\frac{3}{2}} b_0^3 + \cdots$

(B) $\quad 1 = b_1 + 2^{-\frac{3}{2}}\, 2 b_0 b_1 + 3^{-\frac{3}{2}} \cdot 3 b_0^2 b_1 + \cdots$

(C) $\quad 0 = b_2 + 2^{-\frac{3}{2}}\left(b_1^2 + 2 b_0 b_2\right) + 3^{-\frac{3}{2}}\left(3 b_0 b_1^2 + 3 b_0 b_2\right) + \cdots$

From (A) we get

$$b_0 = 0$$

From (B) $\quad b_1 = 1$

From (C) $\quad b_2 = -2^{-\frac{3}{2}}$

thus

$$\boxed{z = \rho\lambda^3 - 2^{-\frac{3}{2}}(\rho\lambda^3)^2 + \cdots} \qquad (14)$$

Now introduce (14) into (1)

$$\frac{p}{KT} = \frac{1}{\lambda^3}\, g_{\frac{5}{2}}(z)$$

with

$$g_{\frac{5}{2}}(z) = z + \frac{z^2}{2^{\frac{5}{2}}} + \frac{z^3}{3^{\frac{5}{2}}} + \cdots$$

and get

$$\frac{p}{KT} = \frac{1}{\lambda^3}\Big[\Big(\underbrace{\rho\lambda^3 - 2^{-\frac{3}{2}}(\rho\lambda^3)^2 + \cdots}_{z}\Big) +$$

$$+\, 2^{-\frac{5}{2}}\Big(\underbrace{\rho\lambda^3 - 2^{-\frac{3}{2}}(\rho\lambda^3)^2 + \cdots}_{z^2}\Big)^2 +$$

$$+\, 3^{-\frac{5}{2}}\Big(\underbrace{\rho\lambda^3 - 2^{-\frac{3}{2}}(\rho\lambda^3)^2 + \cdots}_{z^3}\Big)^3 + \cdots\Big]$$

Simplifying the right side, we get

$$\frac{p}{kT} = \frac{1}{\lambda^3}\left[\rho\lambda^3 + \underbrace{\left(2^{-\frac{5}{2}} - 2^{-\frac{3}{2}}\right)}_{-\frac{1}{4\sqrt{2}} = -0.17678}(\rho\lambda^3)^2 + \cdots\right]$$

If you collect all the terms you obtain

$$\frac{p}{kT} = \frac{1}{\lambda^3}\left[\rho\lambda^3 - 0.17678\,(\rho\lambda^3)^2 - 0.00011\,(\rho\lambda^3)^3 + \cdots\right]$$

and then Dividing by λ^3 on the right side, and the dividing by ρ both the left side and the right side, we get (remember that $\rho = \frac{N}{V}$)

$$\boxed{\frac{pV}{NkT} = 1 - 0.17678\,\underbrace{\rho\lambda^3}_{\text{equals } \frac{N}{V}\left(\frac{h}{\sqrt{2\pi m kT}}\right)^3} - 0.00011\,(\rho\lambda^3)^2 + \cdots}$$

classical case : $\frac{pV}{NkT} = 1$. The other terms on the right side are quantum corrections to the classical case

BOSE GAS Appendix

A piece of mathematics for the Bose gas.

$$\begin{cases} \dfrac{N-N_0}{V} = \dfrac{2\pi}{h^3}(2mkT)^{\frac{3}{2}} \displaystyle\int_0^\infty \frac{x^{\frac{1}{2}}}{z^{-1}e^{x}-1}\,dx \\[2ex] \dfrac{p}{kT} = -\dfrac{2\pi}{h^3}(2mkT)^{\frac{3}{2}} \displaystyle\int_0^\infty x^{\frac{1}{2}} \ln(1-ze^{-x})\,dx \end{cases}$$

with $0 < z \leq 1$

We want to express the formulas in terms of Bose-Einstein functions

$$g_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{x^{\nu-1}}{z^{-1}e^{x}-1}\,dx$$

defined for ν a real number.

For $\dfrac{N-N_0}{V}$ it is easy to see that

$$\frac{N-N_0}{V} = \frac{2\pi}{h^3}(2mkT)^{\frac{3}{2}} \cdot \Gamma\left(\frac{3}{2}\right) \underbrace{\boxed{\frac{1}{\Gamma(\frac{3}{2})} \int_0^\infty \frac{x^{\frac{1}{2}}}{z^{-1}e^{x}-1}\,dx}}_{g_{\frac{3}{2}}(z)}$$

The Gamma function value at $\frac{3}{2}$ is $\frac{1}{2}\sqrt{\pi}$

$$\Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\sqrt{\pi}$$

So

$$\frac{N-N_0}{V} = \frac{2\pi}{h^3}(2mkT)^{\frac{3}{2}}\sqrt{\pi}\; g_{\frac{3}{2}}(z)$$

In terms of the thermal wavelength

$$\lambda = \frac{h}{\sqrt{2\pi m k T}}$$

we can write

$$\boxed{\frac{N-N_0}{V} = \frac{1}{\lambda^3} g_{\frac{3}{2}}(z)}$$

Now we need to write $\frac{p}{kT}$ in terms of the thermal wavelength λ and a Bose-Einstein function. The goal is achieved with the help of an integration by parts

$$\int_0^\infty x^{\frac{1}{2}} \ln(1-ze^{-x})\,dx = \int_0^\infty \ln(1-ze^{-x})\,\frac{2}{3}\,d(x^{\frac{3}{2}}) =$$

$$= \frac{2}{3}\Bigg(\underbrace{x^{\frac{3}{2}}\ln(1-ze^{-x})\Big|_0^\infty}_{\text{we will show that this term is zero}} - \int_0^\infty x^{\frac{3}{2}}\, d[\ln(1-ze^{-x})]\Bigg) =$$

$$= -\frac{2}{3}\int_0^\infty x^{\frac{3}{2}} \frac{ze^{-x}}{1-ze^{-x}}\,dx \underset{\substack{\uparrow \\ \text{divide by} \\ ze^{-x}}}{=} -\frac{2}{3}\int_0^\infty \frac{x^{\frac{3}{2}}}{z^{-1}e^{-x}-1}\,dx =$$

$$= -\frac{2}{3}\,\Gamma\left(\frac{5}{2}\right) \boxed{\frac{1}{\Gamma\left(\frac{5}{2}\right)} \int_0^\infty \frac{x^{\frac{3}{2}}}{z^{-1} e^{x} - 1}\, dx}$$

$$\uparrow$$

$$g_{\frac{5}{2}}(x)$$

Now $\quad \Gamma\left(\frac{5}{2}\right) = \frac{3}{2} \cdot \Gamma\left(\frac{3}{2}\right) = \frac{3}{2} \cdot \frac{1}{2} \sqrt{\pi}$

So $\quad \int_0^\infty x^{\frac{1}{2}} \ln\left(1 - z e^{-x}\right) dx = -\frac{1}{2}\sqrt{\pi}\; g_{\frac{5}{2}}(x)$

Inserting this form of the integral into $\frac{P}{kT}$ we obtain

$$\boxed{\frac{P}{kT} = \frac{1}{\lambda^3}\, g_{\frac{5}{2}}(z)}$$

Annex $\quad$ there is one more thing to show

$$x^{\frac{3}{2}} \ln\left(1 - z\, e^{-x}\right)\Big|_0^\infty = 0$$

At $x=0$ the expression is zero. So we need to show that

$$\lim_{x \to \infty} x^{\frac{3}{2}} \ln\left(1 - z e^{-x}\right) = 0$$

$$\lim_{x\to\infty} x^{\frac{3}{2}} \ln(1-2e^{-x}) = \ln\left[\lim_{x\to\infty} (1-2e^{-x})^{x^{\frac{3}{2}}}\right] =$$

$$= \ln\left(\lim_{x\to\infty} \underbrace{\left[\left(1-\frac{2}{e^x}\right)^{e^x}\right]}_{\text{this goes to } e;\ \text{compare with } \left(1+\frac{1}{n}\right)^n}^{\frac{x^{\frac{3}{2}}}{e^x}}\right) =$$

$$= \ln e^{\lim_{x\to\infty} \frac{x^{\frac{3}{2}}}{e^x}} \xrightarrow{\text{goes to zero}} = \ln e^{0} = \ln 1 = 0$$