

We consider a gas of non-interacting particles, with no internal degree of freedom, confined to a 3D box of volume V . The dispersion relation is

$$\epsilon(\vec{k}) = A|k|$$

We wish to find the equation of state, taking into account quantum statistics.

(a) dispersion relation

Let

$$N(\epsilon) = VH(\epsilon)$$

be the number of single particle states with energy up to ϵ . We define the density of states

$$\frac{dN(\epsilon)}{d\epsilon} = VG(\epsilon)$$

We wish to calculate H, G for the dispersion relation.

First observe

$$VGd\epsilon = dN = V\frac{dH}{d\epsilon}d\epsilon$$

this implies $G = dH/d\epsilon$ or $H = \int_0^\epsilon G(\epsilon)d\epsilon$. We can compute

$$dN = V\frac{d^3k}{(2\pi)^3} = V\frac{k^2dk}{2\pi^2} = \frac{V\epsilon^2}{2\pi^2 A^3}d\epsilon$$

therefore

$$G(\epsilon) = \frac{\epsilon^2}{2\pi^2 A^3}$$

and

$$H(\epsilon) = \frac{\epsilon^3}{6\pi^2 A^3}$$

(b) grand canonical ensemble

We wish to derive expressions for pressure and density. Starting from the ensemble statistics we can write the partition function for a single state $|r\rangle$. Fermions only have two possibilities, occupied or not. But Bosons can have up to $N \rightarrow \infty$ possibilities

$$Z_r^{Fermi} = \sum_{n \in \{0,1\}} e^{-\beta n(\epsilon - \mu)} = 1 + e^{-\beta(\epsilon - \mu)}$$

$$Z_r^{Bose} = \sum_{n=0}^{\infty} e^{-\beta n(\epsilon - \mu)} = \frac{1}{1 - e^{-\beta(\epsilon - \mu)}}$$

Now in either case, the total partition function is the product of all single-state partition functions. If we index the product by energy, then the degeneracy $g(\epsilon) = VG(\epsilon)$ would appear as an exponent. Furthermore let us anticipate dealing with logarithms of the partition function

$$\log Z = \log \left(\prod_{\epsilon} (Z_{\epsilon})^{g(\epsilon)} \right) = \sum_{\epsilon} g(\epsilon) \log Z_{\epsilon} = \int_0^{\infty} g(\epsilon) \log Z_{\epsilon} d\epsilon$$

In the continuum limit the sum over energy levels becomes an integral, and the degeneracy becomes a density of states. Now the total number of particles can be computed from the partition function

$$N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z$$

while the pressure can be written in terms of grand canonical potential ¹

$$pV = -\Phi = \frac{1}{\beta} \log Z$$

Let us now check that taking derivatives of the single state partition function gives us the expected distributions

$$\begin{aligned} \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_r^{Fermi} &= \frac{1}{\beta} \frac{\partial}{\partial \mu} \log(1 + e^{-\beta(\epsilon-\mu)}) = \frac{e^{-\beta(\epsilon-\mu)}}{1 + e^{-\beta(\epsilon-\mu)}} = \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \\ \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_r^{Bose} &= -\frac{1}{\beta} \frac{\partial}{\partial \mu} \log(1 - e^{-\beta(\epsilon-\mu)}) = \frac{e^{-\beta(\epsilon-\mu)}}{1 - e^{-\beta(\epsilon-\mu)}} = \frac{1}{e^{\beta(\epsilon-\mu)} - 1} \end{aligned}$$

Now we just string our results together

$$N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z = \int_0^\infty g(\epsilon) \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_\epsilon d\epsilon = \int_0^\infty \frac{VG(\epsilon)}{e^{\beta(\epsilon-\mu)} \mp 1} d\epsilon$$

For pressure we must use integration by parts

$$pV = \frac{1}{\beta} \log Z = \int_0^\infty g(\epsilon) \frac{1}{\beta} \log Z_\epsilon d\epsilon = - \int_0^\infty VH(\epsilon) \frac{1}{\beta} \frac{\partial}{\partial \epsilon} \log Z_\epsilon d\epsilon = \int_0^\infty \frac{VH(\epsilon)}{e^{\beta(\epsilon-\mu)} \mp 1} d\epsilon$$

therefore we arrive at the result

$$\begin{aligned} n &= \frac{N}{V} = \int_0^\infty \frac{G(\epsilon)d\epsilon}{e^{\beta(\epsilon-\mu)} \mp 1} \\ p &= \int_0^\infty \frac{H(\epsilon)d\epsilon}{e^{\beta(\epsilon-\mu)} \mp 1} \end{aligned}$$

where \mp correspond to boson and fermion statistics respectively.

¹Grand Canonical Potential

$$\Phi = F - \mu N$$

Since the first law of thermodynamics states $dU = TdS - pdV + \mu dN$ we have

$$d\Phi = -SdT - pdV - Nd\mu$$

While $\Phi(T, V, \mu)$ is extensive, all but one of its variables are intensive. Therefore $\lambda\Phi(T, V, \mu) = \Phi(T, \lambda V, \mu)$. This implies

$$\Phi = -p(T, \mu)V$$

One can derive the relation $\Phi = -kT \log Z$ in the grand canonical partition by leveraging the result from free energy $F = -kT \log Z_*$ in the canonical partition. Note $Z \neq Z_*$.

(c) equation of state (low density limit)

In the low density limit $\mu \rightarrow -\infty$. This means the fugacity

$$z = e^{\beta\mu} \rightarrow 0$$

so $z^{-1} \rightarrow \infty$ and we can approximate the distributions in the thermodynamic limit

$$\frac{1}{z^{-1}e^{\beta\epsilon} \mp 1} \approx ze^{-\beta\epsilon}$$

But this means ²

$$p = \int_0^\infty H(\epsilon)ze^{-\beta\epsilon}d\epsilon = \frac{z}{6\pi^2A^3} \int_0^\infty \epsilon^3e^{-\beta\epsilon}d\epsilon = \frac{z}{\pi^2A^3\beta^4}$$

while

$$n = \int_0^\infty G(\epsilon)ze^{-\beta\epsilon}d\epsilon = \frac{z}{2\pi^2A^3} \int_0^\infty \epsilon^2e^{-\beta\epsilon}d\epsilon = \frac{z}{\pi^2A^3\beta^3}$$

Therefore

$$p = \frac{n}{\beta} = nkT$$

which recovers the ideal gas law.

(d) equation of state (higher order correction)

Now we can calculate the next order correction by expanding

$$\frac{1}{z^{-1}e^{\beta\epsilon} \mp 1} = ze^{-\beta\epsilon}[1 \mp ze^{-\beta\epsilon}]^{-1} = ze^{-\beta\epsilon}(1 \pm ze^{-\beta\epsilon} + \dots)$$

so the first correction is

$$p^1 = \pm \int_0^\infty H(\epsilon)(ze^{-\beta\epsilon})^2d\epsilon = \pm \frac{z^2}{\pi^2A^3(2\beta)^4}$$

$$n^1 = \pm \int_0^\infty G(\epsilon)(ze^{-\beta\epsilon})^2d\epsilon = \pm \frac{z^2}{\pi^2A^3(2\beta)^3}$$

Thus

$$\tilde{p} = p^0 + p^1 = p^0 \left(1 \pm \frac{z}{16}\right)$$

$$\tilde{n} = n^0 + n^1 = n^0 \left(1 \pm \frac{z}{8}\right)$$

and we conclude

$$\tilde{p} = \frac{n_0}{\beta} \left(1 \pm \frac{z}{16}\right) = \frac{\tilde{n}}{\beta} \left(\frac{1 \pm \frac{z}{16}}{1 \pm \frac{z}{8}}\right) = \tilde{n}kT \left(1 \pm \frac{z}{16}\right) \left(1 \mp \frac{z}{8}\right) = \tilde{n}kT \left(1 \mp \frac{z}{8}\right)$$

We find that bosons have a slightly lower pressure while fermions have a slightly higher than ideal gas. This agrees with intuition that fermions have 'degeneracy pressure' while bosons can form 'condensates.'

²

$$\int_0^\infty x^m e^{-ax} dx = \frac{m!}{a^{m+1}}$$