Unit 3-8: The Quantum Ideal Gas and the Leading Quantum Correction to the Ideal Gas Law

Density of States and Thermodynamic Quantities

The log of the grand partition function for non-interacting, indistinguishable, quantum mechanical particles is,

$$\ln \mathcal{L} = \pm \sum_i \ln\left(1 \pm z\mathrm{e}^{-\beta\epsilon_i}\right) = \pm\sum_i \ln\left(1 \pm \mathrm{e}^{-\beta(\epsilon_i-\mu)}\right) \qquad + \text{ for FD, } - \text{ for BE} \tag{3.8.1}$$

where the sum is over all single particle energy eigenstates i.

For *free particles* (no external potential) and periodic boundary conditions in a cubic box of side length L, single particle states can be labeled by the wavevector $\mathbf{k}$ with $k_\mu = (2\pi/L)n_\mu$, $n_\mu = 0, \pm1, \pm2\ldots$ integer. If the particle has an intrinsic spin s, then there will be $g_s = 2s+1$ spin states for each $\mathbf{k}$.

We will assume that the energy $\epsilon_{\mathbf{k}}$ depends only on the magnitude $|\mathbf{k}|$, and is independent of the spin state (so no applied magnetic field). Then, like we did for phonons and photons, it is useful to define a density of states per unit volume $g(\epsilon)$, where $g(\epsilon)d\epsilon$ is the number of states per unit volume with energy between ϵ and $\epsilon + d\epsilon$.

To find $g(\epsilon)$ we first find $G(\epsilon)$, the number of single-particle states per unit volume with energy $\epsilon_{\mathbf{k}}$ less than or equal to ϵ. Since $\epsilon_{\mathbf{k}}$ depends only on $k = |\mathbf{k}|$, all such states will lie within a sphere in k-space of radius k such that $\epsilon(k) = \epsilon$. The volume of k-space for each allowed wavevector $\mathbf{k}$ is $(\Delta k)^3 = (2\pi/L)^3$, and the number of states at each allowed $\mathbf{k}$ is g_s, the spin degeneracy factor. The number of states per unit volume with $\epsilon_{\mathbf{k}} \le \epsilon$ is then,

$$G(\epsilon) = \frac{g_s}{V}\,\frac{(\text{volume of sphere of radius } k)}{(\text{volume per allowed } \mathbf{k})} = \frac{g_s}{V}\,\frac{\frac{4}{3}\pi k^3}{(\Delta k)^3} = \frac{g_s}{V}\,\frac{\frac{4}{3}\pi k^3}{(2\pi/L)^3} = \frac{g_s k^3}{6\pi^2} \tag{3.8.2}$$

The density of states is then,

$$g(\epsilon) = \frac{dG}{d\epsilon} = \frac{dG}{dk}\,\frac{dk}{d\epsilon} = \frac{g_s k^2}{2\pi^2}\,\frac{dk}{d\epsilon} \tag{3.8.3}$$

For *non-relativistic* particles we have $\quad \epsilon_{\mathbf{k}} = \dfrac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad k = \sqrt{\dfrac{2m\epsilon}{\hbar^2}} \quad \Rightarrow \quad \dfrac{dk}{d\epsilon} = \sqrt{\dfrac{2m\epsilon}{\hbar^2}}\,\dfrac{1}{2\epsilon}$. So we have,

$$g(\epsilon) = \frac{g_s}{2\pi^2}\,\frac{2m\epsilon}{\hbar^2}\sqrt{\frac{2m\epsilon}{\hbar^2}}\,\frac{1}{2\epsilon} \quad \Rightarrow \quad g(\epsilon) = \frac{2g_s}{\sqrt{\pi}}\left(\frac{2\pi m}{h^2}\right)^{3/2}\sqrt{\epsilon} \;\sim\; \sqrt{\epsilon} \qquad \text{with } h = 2\pi\hbar \tag{3.8.4}$$

or using the thermal wavelength $\lambda = \left(\dfrac{h^2}{2\pi m k_B T}\right)^{1/2}$, we can write,

$$\boxed{g(\epsilon) = \frac{2g_s}{\sqrt{\pi}\lambda^3}\,\frac{1}{k_BT}\sqrt{\frac{\epsilon}{k_BT}}} \tag{3.8.5}$$

Note: for phonons and photons we had $g(\omega) \sim \omega^2$, while here for non-relativistic particles we have $g(\epsilon) \sim \sqrt{\epsilon}$. The difference is due to the difference in the dispersion relations. For phonons and photons the dispersion relation is *linear*, $\omega \sim k$, while for non-relativistic particles the dispersion relation is *quadratic*, $\epsilon \sim k^2$.

So, from now on, whenever we have a quantity X that is independent of the spin s and depends on $\mathbf{k}$ only via $\epsilon_{\mathbf{k}}$, we can write

$$\frac{1}{V}\sum_i X_i \;=\; \frac{1}{V}\sum_s\sum_{\mathbf{k}} X_{\mathbf{k}} \;=\; \frac{g_s}{V}\sum_{\mathbf{k}} X_{\mathbf{k}} \;=\; \int d\epsilon\, g(\epsilon) X(\epsilon) \tag{3.8.6}$$

Pressure:

Recall, the grand potential is given by $-pV = \Phi = -k_B T \ln \mathcal{L}$. So we can write for the pressure of the gas,

$$\frac{p}{k_B T} = \frac{1}{V} \ln \mathcal{L} = \pm \frac{1}{V} \sum_i \ln\left(1 \pm z\mathrm{e}^{-\beta\epsilon_i}\right) = \pm \int_0^\infty d\epsilon\, g(\epsilon)\, \ln\left(1 \pm z\mathrm{e}^{-\beta\epsilon}\right) \tag{3.8.7}$$

$$= \pm \frac{2g_s}{\sqrt{\pi}\lambda^3} \frac{1}{k_B T} \int_0^\infty d\epsilon \sqrt{\frac{\epsilon}{k_B T}} \ln\left(1 \pm z\mathrm{e}^{-\beta\epsilon}\right) \tag{3.8.8}$$

Let $y \equiv \beta\epsilon = \epsilon/k_B T$. We then have,

$$\frac{p}{k_B T} = \pm \frac{2g_s}{\sqrt{\pi}\lambda^3} \int_0^\infty dy\, \sqrt{y}\, \ln\left(1 \pm z\mathrm{e}^{-y}\right) \tag{3.8.9}$$

Now integrate by parts to get,

$$\frac{p}{k_B T} = \pm \frac{2g_s}{\sqrt{\pi}\lambda^3} \left[\frac{2}{3} y^{3/2} \ln\left(1 \pm z\mathrm{e}^{-y}\right)\Big|_0^\infty - \int_0^\infty dy\, \frac{2}{3}\, y^{3/2}\, \frac{\mp z\mathrm{e}^{-y}}{1 \pm z\mathrm{e}^{-y}} \right] \tag{3.8.10}$$

The boundary term vanishes since at the upper limit $y \to \infty$, $y^{3/2} \ln\left(1 \pm z\mathrm{e}^{-y}\right) \to y^{3/2}\left(\pm z\mathrm{e}^{-y}\right) \to 0$, while at the lower limit $y \to 0$, $y^{3/2} \ln\left(1 \pm z\mathrm{e}^{-y}\right) \to y^{3/2} \ln\left(1 \pm z\right) \to 0$.

We thus have,

$$\boxed{\frac{p}{k_B T} = \frac{4g_s}{3\sqrt{\pi}\lambda^3} \int_0^\infty dy\, \frac{y^{3/2}}{z^{-1}\mathrm{e}^{y} \pm 1}} \qquad \text{with + for FD, − for BE} \tag{3.8.11}$$

Density of particles:

The density of particles is given by,

$$n = \frac{N}{V} = \frac{1}{V} \sum_i \langle n_i \rangle = \frac{1}{V} \sum_i \frac{1}{z^{-1}\mathrm{e}^{\beta\epsilon_i} \pm 1} = \int_0^\infty d\epsilon\, g(\epsilon)\, \frac{1}{z^{-1}\mathrm{e}^{\beta\epsilon} \pm 1} \tag{3.8.12}$$

$$= \frac{2g_s}{\sqrt{\pi}\lambda^3} \frac{1}{k_B T} \int_0^\infty d\epsilon \sqrt{\frac{\epsilon}{k_B T}}\, \frac{1}{z^{-1}\mathrm{e}^{\beta\epsilon} \pm 1} = \frac{2g_s}{\sqrt{\pi}\lambda^3} \int_0^\infty dy\, \frac{y^{1/2}}{z^{-1}\mathrm{e}^{y} \pm 1} \qquad \text{with } y = \beta\epsilon \tag{3.8.13}$$

$$\boxed{n = \frac{N}{V} = \frac{2g_s}{\sqrt{\pi}\lambda^3} \int_0^\infty dy\, \frac{y^{1/2}}{z^{-1}\mathrm{e}^{y} \pm 1}} \qquad \text{with + for FD, − for BE} \tag{3.8.14}$$

Energy density:

The energy density is given by,

$$\frac{E}{V} = \frac{1}{V} \sum_i \epsilon_i \langle n_i \rangle = \frac{1}{V} \sum_i \frac{\epsilon_i}{z^{-1}\mathrm{e}^{\beta\epsilon_i} \pm 1} = \int_0^\infty d\epsilon\, g(\epsilon)\, \frac{\epsilon}{z^{-1}\mathrm{e}^{\beta\epsilon} \pm 1} \tag{3.8.15}$$

$$= \frac{2g_s}{\sqrt{\pi}\lambda^3} \frac{1}{k_B T} \int_0^\infty d\epsilon \sqrt{\frac{\epsilon}{k_B T}}\, \frac{\epsilon}{z^{-1}\mathrm{e}^{\beta\epsilon} \pm 1} = \frac{2g_s}{\sqrt{\pi}\lambda^3}\, k_B T \int_0^\infty dy\, \frac{y^{3/2}}{z^{-1}\mathrm{e}^{y} \pm 1} \qquad \text{with } y = \beta\epsilon \tag{3.8.16}$$

$$\boxed{\frac{E}{V} = \frac{2g_s}{\sqrt{\pi}\lambda^3}\, k_BT \int_0^\infty dy\, \frac{y^{3/2}}{z^{-1}\mathrm{e}^y \pm 1}} \qquad \text{with + for FD, } - \text{ for BE} \tag{3.8.17}$$

Comparing to Eq. (3.8.11) for the pressure, we then have,

$$\frac{E}{V} = \left(\frac{3}{2}k_BT\right)\left(\frac{p}{k_BT}\right) = \frac{3}{2}p \qquad \Rightarrow \qquad \boxed{p = \frac{2}{3}\frac{E}{V}} \qquad \text{holds for } \textit{both} \text{ fermions and bosons} \tag{3.8.18}$$

Recall, we earlier found the same result to hold for the *classical* ideal gas of *non-relativistic* particles; for classical particles, $pV = Nk_BT$ and $E = \frac{3}{2}Nk_BT$, which gives $p = \frac{2}{3}\frac{E}{V}$.

<u>The standard functions</u>:

Because of their appearance in the above expressions for p/k_BT, N/V, and E/V, it is customary to define the integrals that appear in terms of the following "standard functions" (see Pathria and Beale Appendices D and E),

$$f_n(z) \equiv \frac{1}{\Gamma(n)}\int_0^\infty dy\, \frac{y^{n-1}}{z^{-1}\mathrm{e}^y + 1} = \sum_{\ell=1}^\infty (-1)^{\ell+1}\frac{z^\ell}{\ell^n} \tag{3.8.19}$$

$$g_n(z) \equiv \frac{1}{\Gamma(n)}\int_0^\infty dy\, \frac{y^{n-1}}{z^{-1}\mathrm{e}^y - 1} = \sum_{\ell=1}^\infty \frac{z^\ell}{\ell^n} \tag{3.8.20}$$

where $\Gamma(n)$ is the gamma function that has the following properties,

$$\Gamma(n+1) = n\Gamma(n), \quad \Gamma(1/2) = \sqrt{\pi} \quad \Rightarrow \quad \Gamma(3/2) = \frac{1}{2}\sqrt{\pi} \quad \Rightarrow \quad \Gamma(5/2) = \frac{3}{4}\sqrt{\pi} \tag{3.8.21}$$

In terms of these we have:

<u>fermions</u> | <u>bosons</u>

$$\frac{p}{k_BT} = \frac{g_s}{\lambda^3}\, f_{5/2}(z) \qquad\qquad \frac{p}{k_BT} = \frac{g_s}{\lambda^3}\, g_{5/2}(z) \tag{3.8.22}$$

$$\frac{N}{V} = \frac{g_s}{\lambda^3}\, f_{3/2}(z) \qquad\qquad \frac{N}{V} = \frac{g_s}{\lambda^3}\, g_{3/2}(z) \tag{3.8.23}$$

$$\frac{E}{V} = \frac{3}{2}k_BT\frac{g_s}{\lambda^3}\, f_{5/2}(z) \qquad\qquad \frac{E}{V} = \frac{3}{2}k_BT\frac{g_s}{\lambda^3}\, g_{5/2}(z) \tag{3.8.24}$$

$$\frac{E}{N} = \frac{3}{2}k_BT\frac{f_{5/2}(z)}{f_{3/2}(z)} \qquad\qquad \frac{E}{N} = \frac{3}{2}k_BT\frac{g_{5/2}(z)}{g_{3/2}(z)} \tag{3.8.25}$$

Leading Quantum Correction to the Ideal Gas Law

We now apply the above results to compute the leading quantum correction to the classical equation of state!

We saw how the classical limit results from the quantum case when $z \ll 1$. This is called the "non-degenerate" limit. Using the standard functions, and their series expansions at small z to lowest order, we have,

$$\frac{p}{k_BT} = \frac{g_s}{\lambda^3}\left\{\begin{array}{c} f_{5/2}(z) \\ g_{5/2}(z) \end{array}\right\} = \frac{g_s}{\lambda^3}\left(z \mp \frac{z^2}{2^{5/2}} + \cdots\right) \qquad \text{+ for FD, } - \text{ for BE} \tag{3.8.26}$$

$$\frac{N}{V} = \frac{g_s}{\lambda^3}\left\{\begin{array}{c} f_{3/2}(z) \\ \\ g_{3/2}(z) \end{array}\right\} = \frac{g_s}{\lambda^3}\left(z \mp \frac{z^2}{2^{3/2}} + \cdots\right) \qquad + \text{ for FD, } - \text{ for BE} \tag{3.8.27}$$

Using the above two results to eliminate g_s/λ^3, we can then write,

$$\frac{p}{k_BT} = \frac{N}{V}\frac{\left(z \mp \frac{z^2}{2^{5/2}} + \cdots\right)}{\left(z \mp \frac{z^2}{2^{3/2}} + \cdots\right)} \approx \frac{N}{V}\left(1 \mp \frac{z}{2^{5/2}} + \cdots\right)\left(1 \pm \frac{z}{2^{3/2}} + \cdots\right) \tag{3.8.28}$$

$$= \frac{N}{V}\left(1 \pm \frac{z}{2^{3/2}} \mp \frac{z}{2^{5/2}} + \cdots\right) \qquad \text{to } O(z) \tag{3.8.29}$$

Now use $\dfrac{1}{2^{3/2}} - \dfrac{1}{2^{5/2}} = \dfrac{2}{2^{5/2}} - \dfrac{1}{2^{5/2}} = \dfrac{1}{2^{5/2}}$ to write,

$$pV = Nk_BT\left(1 \pm \frac{z}{2^{5/2}} + \cdots\right) \qquad \text{with } + \text{ for FD, } - \text{ for BE} \tag{3.8.30}$$

The term $\dfrac{\pm z}{2^{5/2}}$ thus gives the leading quantum correction to the classical ideal gas law!

To finish the calculation, we need to express z in terms of the density of particles $n = N/V$.

For small z, the leading term in Eq. (3.8.27) gives, $\dfrac{N}{V} = \dfrac{g_s}{\lambda^3} z \;\Rightarrow\; z = \left(\dfrac{N}{V}\dfrac{\lambda^3}{g_s}\right) = \dfrac{N}{Q_1}$. This is the same result we had classically, $N = zQ_1$, except now we include the spin degeneracy factor g_s in Q_1.

From the above (and as we also saw before at the end of Notes 3-5) the small $z \ll 1$ limit corresponds to $n\lambda^3 \ll 1$ ($n = N/V$ is the particle density). Since $\lambda(T)$ decreases as T increases, this is the low density, high temperature, limit. In this limit we therefore have,

$$\boxed{pV = Nk_BT\left(1 \pm \frac{1}{2^{5/2}g_s}\frac{N}{V}\lambda^3 + \cdots\right)} \qquad \text{with } + \text{ for FD, } - \text{ for BE} \tag{3.8.31}$$

or

$$p = nk_BT\left(1 \pm \frac{n\lambda^3}{2^{5/2}g_s} + \cdots\right) \qquad \text{with } + \text{ for FD, } - \text{ for BE} \tag{3.8.32}$$

The leading quantum correction to the ideal gas law thus goes as $\propto (N/V)\lambda^3 = n\lambda^3$.

This result is in accord with what we would expect from our discussion in Notes 3-3 of the non-interacting two particle density matrix. We saw that BE statistics led to an effective attraction between bosons, hence we would expect the pressure to decrease compared to a classical ideal gas. However, FD statistics led to an effective repulsion between fermions, hence we would expect the pressure to increase compared to a classical ideal gas. This is exactly what we find in Eq. (3.8.31) above.

Note, the above calculation is for the case of *non-relativistic* particles only.