Physics 415 - Lecture 31: Quantum Gases - Classical Limit, Equation of State

April 9, 2025

Summary

- Quantum Ideal Gases (BE or FD): Grand Potential $\Phi = \pm T \sum_r \ln(1 \mp e^{-\beta(\epsilon_r - \mu)})$.
- Mean occupation number: $\overline{n}_r = \frac{1}{e^{\beta(\epsilon_r - \mu)} \mp 1}$.
- Classical Limit (Maxwell-Boltzmann, MB): $\overline{n}_r \approx e^{-\beta(\epsilon_r - \mu)} \ll 1$.
- Relation determining μ: $N = \sum_r \overline{n}_r$.
- Single-particle Density of States (DOS) for free particle (spin J, degeneracy $g = 2J + 1$) in volume V:

$$\sum_r \to gV \int \frac{d^3k}{(2\pi)^3} \quad \text{or} \quad \sum_r \to g \int d\epsilon\, \rho(\epsilon)$$

where $\rho(\epsilon) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\epsilon}$.

Classical Limit Revisited

We previously derived the classical partition function for N identical particles:

$$Z = \frac{1}{N!} \left(\sum_r e^{-\beta\epsilon_r} \right)^N$$

where the factor $1/N!$ was introduced to correct for indistinguishability (resolve Gibbs paradox), and $\sum_r e^{-\beta\epsilon_r}$ is the single-particle partition function Z_1. Let's re-derive this starting from the classical limit of quantum statistics.

Evaluate $Z_1 = \sum_r e^{-\beta\epsilon_r}$ using the DOS integral for a free particle (for simplicity, let spin degeneracy $g = 1$ initially).

$$Z_1 = \sum_r e^{-\beta\epsilon_r} \to V \int \frac{d^3k}{(2\pi)^3} e^{-\beta\hbar^2k^2/(2m)}$$

Change variables from $\vec{k}$ to momentum $\vec{p} = \hbar\vec{k}$, so $d^3k = d^3p/\hbar^3$.

$$Z_1 = V \int \frac{d^3p}{(2\pi\hbar)^3} e^{-\beta p^2/(2m)}$$

The integral is $\int_{-\infty}^{\infty} \frac{dp_x}{h} e^{-\beta p_x^2/(2m)} \times (\dots)_y \times (\dots)_z$. Each 1D integral is $\frac{1}{h}\sqrt{2\pi m/\beta} = \frac{\sqrt{2\pi m T}}{h}$.

$$Z_1 = V \left(\frac{\sqrt{2\pi m T}}{h} \right)^3 = V \left(\frac{2\pi m T}{h^2} \right)^{3/2} = \frac{V}{\lambda_{th}^3} = \xi$$

(If spin degeneracy g is included, $Z_1 = gV/\lambda_{th}^3 = g\xi$).

Now recall the relation derived from the GCE in the classical limit $\Phi \approx -TN$, and $F = \Phi + \mu N$. We found:

$$F = -T \ln \left[\frac{1}{N!} (Z_1)^N \right]$$

Comparing with $F = -T \ln Z$, we identify the classical partition function as

$$Z_{classical} = \frac{(Z_1)^N}{N!}$$

This confirms our previous result, deriving the $1/N!$ factor and the phase space volume h (via λ_{th}) from the quantum statistical starting point.

Equation of State of Quantum Ideal Gas

The pressure p can be obtained from the grand potential Φ:

$$p = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu}$$

Using $\Phi = \pm T \sum_r \ln(1 \mp e^{-\beta(\epsilon_r - \mu)})$ and replacing sum with integral:

$$\Phi = \pm T g \int d\epsilon\, \rho(\epsilon) \ln(1 \mp e^{-\beta(\epsilon - \mu)})$$

Since $\rho(\epsilon) = \frac{V}{4\pi^2}(\frac{2m}{\hbar^2})^{3/2}\sqrt{\epsilon} \propto V$, the grand potential is proportional to V: $\Phi(T, V, \mu) = V \times f(T, \mu)$. Therefore, $p = -(\partial\Phi/\partial V)_{T,\mu} = -\Phi/V$.

$$pV = -\Phi = \mp g T \int_0^\infty d\epsilon\, \rho(\epsilon) \ln(1 \mp e^{-\beta(\epsilon - \mu)})$$

Substituting $\rho(\epsilon)$:

$$\frac{p}{T} = \mp \frac{g}{V} \int_0^\infty d\epsilon\, \rho(\epsilon) \ln(\dots) = \mp \frac{g}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty d\epsilon\, \sqrt{\epsilon} \ln(1 \mp e^{-\beta(\epsilon - \mu)}) \quad (*)$$

The total number of particles N is given by:

$$N = \sum_r \overline{n}_r = g \int_0^\infty d\epsilon\, \rho(\epsilon) \overline{n}(\epsilon) = g \int_0^\infty d\epsilon\, \rho(\epsilon) \frac{1}{e^{\beta(\epsilon - \mu)} \mp 1}$$

$$\frac{N}{V} = n = \frac{g}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty d\epsilon\, \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon - \mu)} \mp 1} \quad (**)$$

The equations $(*)$ and $(**)$ implicitly define the equation of state $p = p(n, T)$.

Quantum Corrections to Ideal Gas Law

What are the QM corrections to $pV = NT$? First, verify the classical result recovers $pV = NT$. Classical limit: $\overline{n}_r \ll 1 \implies e^{-\beta(\epsilon - \mu)} \ll 1$. Use $\ln(1 \mp x) \approx \mp x$ for small x. From $(*)$: $\frac{p}{T} \approx \mp \frac{g}{V} \int d\epsilon \rho(\epsilon) (\mp e^{-\beta(\epsilon - \mu)}) = \frac{g}{V} \int d\epsilon \rho(\epsilon) e^{-\beta(\epsilon - \mu)}$. From $(**)$: $N \approx g \int d\epsilon \rho(\epsilon) e^{-\beta(\epsilon - \mu)}$. Comparing these gives $p/T \approx N/V$, or $pV \approx NT$. ✓

To compute corrections, simplify integrals using $x = \beta\epsilon = \epsilon/T$, $d\epsilon = T dx$. $\sqrt{\epsilon} = \sqrt{Tx}$. Use $\lambda_{th} = \sqrt{2\pi\hbar^2/(mT)}$. $\rho(\epsilon) = \frac{Vg}{2\pi^2}(\frac{m}{\hbar^2})^{3/2}\sqrt{2\epsilon}d\epsilon$? No. $\rho(\epsilon) = \frac{V}{4\pi^2}(\frac{2m}{\hbar^2})^{3/2}\sqrt{\epsilon}$. $\frac{g}{4\pi^2}(\frac{2m}{\hbar^2})^{3/2} =$

$\frac{g}{4\pi^2}\frac{(2m)^{3/2}}{(2\pi\hbar^2/(mT))^{3/2}}\frac{(2\pi\hbar^2)^{3/2}}{(mT)^{3/2}} = \frac{g}{\lambda_{th}^3}\frac{1}{\sqrt{\pi}T^{3/2}}$. Check this... $g\rho(\epsilon)d\epsilon = \frac{gV}{2\pi^2}(\frac{m}{\hbar^2})^{3/2}\sqrt{2\epsilon}d\epsilon$? Let's use result from notes. $\frac{p}{T} = \mp\frac{2}{\sqrt{\pi}}\frac{g}{\lambda_{th}^3}\int_0^\infty dx\sqrt{x}\ln(1 \mp e^{-(x-\beta\mu)})$. $n = \frac{N}{V} = \frac{2}{\sqrt{\pi}}\frac{g}{\lambda_{th}^3}\int_0^\infty dx\frac{\sqrt{x}}{e^{x-\beta\mu}\mp 1}$.

The classical limit is when $e^{\beta\mu} \ll 1$. Let $z = e^{\beta\mu}$ be the small parameter ("fugacity"). $e^{-(x-\beta\mu)} = ze^{-x}$. Expand $\ln(1 \mp \zeta) \approx \mp\zeta - \zeta^2/2$ and $(e^{x-\beta\mu} \mp 1)^{-1} \approx e^{-(x-\beta\mu)}(1 \pm e^{-(x-\beta\mu)})$. $\frac{p}{T} \approx \mp\frac{2}{\sqrt{\pi}}\frac{g}{\lambda_{th}^3}\int_0^\infty dx\sqrt{x}(\mp ze^{-x} - \frac{1}{2}z^2e^{-2x})$. $\frac{p}{T} \approx \frac{2}{\sqrt{\pi}}\frac{g}{\lambda_{th}^3}[z\int_0^\infty \sqrt{x}e^{-x}dx \pm \frac{z^2}{2}\int_0^\infty \sqrt{x}e^{-2x}dx]$. Use $\int_0^\infty \sqrt{x}e^{-ax}dx = \frac{\Gamma(3/2)}{a^{3/2}} = \frac{\sqrt{\pi}/2}{a^{3/2}}$. $a = 1 \implies \sqrt{\pi}/2$. $a = 2 \implies (\sqrt{\pi}/2)/2^{3/2}$.

$$\frac{p}{T} \approx \frac{2}{\sqrt{\pi}}\frac{g}{\lambda_{th}^3}[z(\sqrt{\pi}/2) \pm \frac{z^2}{2}(\frac{\sqrt{\pi}/2}{2^{3/2}})] = \frac{g}{\lambda_{th}^3}[z \pm \frac{z^2}{2^{5/2}}]$$

Now expand N/V: $n = \frac{N}{V} \approx \frac{2}{\sqrt{\pi}}\frac{g}{\lambda_{th}^3}\int_0^\infty dx\sqrt{x}[ze^{-x} \pm z^2e^{-2x}]$.

$$n \approx \frac{2}{\sqrt{\pi}}\frac{g}{\lambda_{th}^3}[z(\sqrt{\pi}/2) \pm z^2(\frac{\sqrt{\pi}/2}{2^{3/2}})] = \frac{g}{\lambda_{th}^3}[z \pm \frac{z^2}{2^{3/2}}]$$

We see $p/T \approx n$ to lowest order in z. We need to express p/T in terms of n. From $n \approx (g/\lambda_{th}^3)z$, we get $z \approx n\lambda_{th}^3/g$. Substitute into second term of n: $n \approx \frac{g}{\lambda_{th}^3}[z \pm \frac{1}{2^{3/2}}z(\frac{n\lambda_{th}^3}{g})]$. Solve for z: $z \approx \frac{n\lambda_{th}^3}{g}[1 \mp \frac{1}{2^{3/2}}(\frac{n\lambda_{th}^3}{g})]$. (Approximate inversion). Substitute this z into the expression for p/T:

$$\frac{p}{T} \approx \frac{g}{\lambda_{th}^3}[\frac{n\lambda_{th}^3}{g}(1 \mp \frac{1}{2^{3/2}}\frac{n\lambda_{th}^3}{g}) \pm \frac{1}{2^{5/2}}(\frac{n\lambda_{th}^3}{g})^2]$$

$$\frac{p}{T} \approx n[(1 \mp \frac{1}{2^{3/2}}\frac{n\lambda_{th}^3}{g}) \pm \frac{1}{2^{5/2}}(\frac{n\lambda_{th}^3}{g})]$$

$$\frac{p}{T} \approx n[1 \mp (\frac{1}{2^{3/2}} - \frac{1}{2^{5/2}})(\frac{n\lambda_{th}^3}{g})]$$

Since $1/2^{3/2} - 1/2^{5/2} = 1/(2\sqrt{2}) - 1/(4\sqrt{2}) = 1/(4\sqrt{2}) = 1/2^{5/2}$.

$$\frac{p}{T} = n\left[1 \mp \frac{1}{2^{5/2}}\left(\frac{n\lambda_{th}^3}{g}\right) + \dots\right]$$

Using $n = N/V$ and T in energy units:

$$pV = NT\left[1 \mp \frac{1}{2^{5/2}}\left(\frac{n\lambda_{th}^3}{g}\right) + \dots\right]$$

Quantum corrections modify the ideal gas law.

- BE (upper sign): $pV \approx NT[1 - \frac{1}{2^{5/2}}(\frac{n\lambda_{th}^3}{g})]$. Pressure is reduced. Quantum statistics lead to an effective "attraction".
- FD (lower sign): $pV \approx NT[1 + \frac{1}{2^{5/2}}(\frac{n\lambda_{th}^3}{g})]$. Pressure is increased. Quantum statistics (Pauli exclusion) lead to an effective "repulsion".

The correction term involves $(n\lambda_{th}^3)$, consistent with the condition for classicality.

Relation between E and p ($pV = \frac{2}{3}E$)

We can obtain an exact result relating average energy E and pressure p for non-relativistic particles ($\epsilon \propto k^2 \propto p^2$) in 3D, regardless of statistics. $E = \overline{E} = \sum_r \overline{n}_r \epsilon_r = g \int d\epsilon \rho(\epsilon) \overline{n}(\epsilon)\epsilon$. $pV = -\Phi = \mp Tg \int d\epsilon \rho(\epsilon) \ln(1 \mp e^{-\beta(\epsilon-\mu)})$. Use $\rho(\epsilon) = AV\sqrt{\epsilon}$ where $A = \frac{1}{4\pi^2}(\frac{2m}{\hbar^2})^{3/2}$. Integrate pV expression by parts: Let $u = \ln(1 \mp \dots)$ and $dv = \rho(\epsilon)d\epsilon = AV\epsilon^{1/2}d\epsilon \implies v = \frac{2}{3}AV\epsilon^{3/2}$.

$$pV = \mp Tg \left\{ [\frac{2}{3}AV\epsilon^{3/2} \ln(1 \mp e^{-\beta(\epsilon-\mu)})]_0^\infty - \int_0^\infty (\frac{2}{3}AV\epsilon^{3/2}) \frac{\mp(-\beta)e^{-\beta(\epsilon-\mu)}}{1 \mp e^{-\beta(\epsilon-\mu)}} d\epsilon \right\}$$

Boundary terms vanish (at $\epsilon = 0$ because of $\epsilon^{3/2}$, at $\epsilon = \infty$ because $\ln(1) = 0$).

$$pV = \mp Tg \left\{ -\int_0^\infty \frac{2}{3}AV\epsilon^{3/2} \frac{\pm\beta e^{-\beta(\epsilon-\mu)}}{1 \mp e^{-\beta(\epsilon-\mu)}} d\epsilon \right\}$$

$$pV = Tg\beta \int_0^\infty \frac{2}{3}AV\epsilon^{3/2} \frac{e^{-\beta(\epsilon-\mu)}}{1 \mp e^{-\beta(\epsilon-\mu)}} d\epsilon$$

Since $T\beta = 1$:

$$pV = \frac{2}{3}g \int_0^\infty (AV\epsilon^{1/2})\epsilon \frac{1}{e^{\beta(\epsilon-\mu)} \mp 1} d\epsilon$$

Recognize $AV\epsilon^{1/2} = \rho(\epsilon)$ and $1/(e^{\cdots} \mp 1) = \overline{n}(\epsilon)$.

$$pV = \frac{2}{3}g \int_0^\infty d\epsilon \rho(\epsilon) \overline{n}(\epsilon)\epsilon$$

The integral is just the average energy E.

$$pV = \frac{2}{3}E$$

This exact relation holds for non-relativistic ideal gases in 3D under BE, FD, or MB statistics. Check classical limit: $E = \frac{3}{2}NT \implies pV = \frac{2}{3}(\frac{3}{2}NT) = NT$. ✓