Ideal Quantum Gases in the Grand Canonical Ensemble (Pathria Section 6.3)

Objective

To derive expressions for macroscopic quantities of quantum ideal gases using the grand canonical ensemble, which is particularly suited for systems with variable particle number (Bose and Fermi gases).

Grand Canonical Formalism

- Non-interacting, indistinguishable particles (bosons or fermions)
- Fixed: Temperature T, Volume V, Chemical potential μ
- Number of particles N can fluctuate

Grand Partition Function

The grand partition function factorizes:

$$\mathcal{Z} = \prod_i \mathcal{Z}_i$$

- For **bosons**:

$$\mathcal{Z}_i = \sum_{n_i=0}^{\infty} e^{-\beta n_i(\varepsilon_i - \mu)} = \frac{1}{1 - z e^{-\beta \varepsilon_i}}$$

- For **fermions**:

$$\mathcal{Z}_i = \sum_{n_i=0}^{1} e^{-\beta n_i(\varepsilon_i - \mu)} = 1 + z e^{-\beta \varepsilon_i}$$

Therefore:

$$\ln \mathcal{Z}_{\text{Bose}} = -\sum_i \ln\left(1 - z e^{-\beta \varepsilon_i}\right)$$

$$\ln \mathcal{Z}_{\text{Fermi}} = \sum_i \ln\left(1 + z e^{-\beta \varepsilon_i}\right)$$

Mean Occupation Number

$$\bar{n}_i = -\frac{1}{\beta}\frac{\partial \ln \mathcal{Z}_i}{\partial \varepsilon_i}$$

Yields:

- **Bosons**:

$$\bar{n}_i = \frac{1}{z^{-1}e^{\beta\varepsilon_i} - 1}$$

- **Fermions**:

$$\bar{n}_i = \frac{1}{z^{-1}e^{\beta\varepsilon_i} + 1}$$

Density of States and Thermal Wavelength

Define:

$$g(\varepsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}, \quad \lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}$$

Mean Total Particle Number

$$N = \int_0^\infty \bar{n}(\varepsilon)g(\varepsilon)d\varepsilon = \frac{V}{\lambda^3}\begin{cases} g_{3/2}(z) & \text{(bosons)} \\ f_{3/2}(z) & \text{(fermions)} \end{cases}$$

Pressure

$$P = \frac{1}{\beta V}\ln \mathcal{Z} = \frac{k_BT}{\lambda^3}\begin{cases} g_{5/2}(z) & \text{(bosons)} \\ f_{5/2}(z) & \text{(fermions)} \end{cases}$$

Polylogarithmic Functions

$$g_n(z) = \frac{1}{\Gamma(n)}\int_0^\infty \frac{x^{n-1}}{z^{-1}e^x - 1}dx$$
$$f_n(z) = \frac{1}{\Gamma(n)}\int_0^\infty \frac{x^{n-1}}{z^{-1}e^x + 1}dx$$

Fluctuations in Occupation Numbers

In the grand canonical ensemble, the variance in the occupation number of a single-particle state is:

$$\sigma_i^2 = \langle n_i^2 \rangle - \bar{n}_i^2 = \bar{n}_i(1 \pm \bar{n}_i)$$

Where:

- The plus sign is for bosons.

- The minus sign is for fermions.

Interpretation:

- Bosons tend to bunch together ⇒ large fluctuations.
- Fermions are restricted by Pauli exclusion ⇒ smaller fluctuations.
- In the classical limit $\bar{n}_i \ll 1$: $\sigma_i^2 \approx \bar{n}_i$ (Poisson statistics).

Limiting Cases

- **Classical limit**: $z \ll 1 \Rightarrow$ Maxwell-Boltzmann statistics.
- **Fermions at** $T \to 0$: $f_n(z) \to$ step function at Fermi energy.
- **Bosons at** $z \to 1$: $g_n(z) \to \infty \Rightarrow$ Bose-Einstein condensation.

Summary Table

Quantity	Bosons	Fermions
$\bar{n}_i$	$\dfrac{1}{z^{-1}e^{\beta\varepsilon_i} - 1}$	$\dfrac{1}{z^{-1}e^{\beta\varepsilon_i} + 1}$
σ_i^2	$\bar{n}_i(1 + \bar{n}_i)$	$\bar{n}_i(1 - \bar{n}_i)$
$\ln \mathcal{Z}$	$-\sum \ln\left(1 - ze^{-\beta\varepsilon_i}\right)$	$\sum \ln\left(1 + ze^{-\beta\varepsilon_i}\right)$
N	$\dfrac{V}{\lambda^3} g_{3/2}(z)$	$\dfrac{V}{\lambda^3} f_{3/2}(z)$
P	$\dfrac{k_B T}{\lambda^3} g_{5/2}(z)$	$\dfrac{k_B T}{\lambda^3} f_{5/2}(z)$