Derivation of Equation of State for Ideal Quantum Gases in the Microcanonical Ensemble

Section 6.1 Overview: Quantum Microcanonical Formulation (Based on Pathria 3rd Edition)

We begin by considering an ideal quantum gas in the microcanonical ensemble, as outlined in Section 6.1 of Pathria. The total energy E, particle number N, and volume V are fixed.

Microstates and Constraints

Each microstate is described by occupation numbers $\{n_i\}$ satisfying:

$$\sum_i n_i = N$$

$$\sum_i n_i \varepsilon_i = E$$

where ε_i are the one-particle energy levels (with degeneracy g_i).

Counting Microstates

The number of microstates $\Omega(E, N)$ is the number of distributions $\{n_i\}$ satisfying the constraints above. For different statistics:

- Bose-Einstein: $n_i = 0, 1, 2, \ldots$
- Fermi-Dirac: $n_i = 0, 1$

We approximate the entropy as:

$$S = k_B \ln \Omega$$

Approximate Maximization

Since direct computation of $\Omega(E, N)$ is difficult, we maximize $\ln \Omega(\{n_i\})$ subject to the constraints:

$$\sum_i n_i = N$$

$$\sum_i n_i \varepsilon_i = E$$

using Lagrange multipliers α, β:

$$\delta \left[\ln \Omega - \alpha \sum_i n_i - \beta \sum_i n_i \varepsilon_i \right] = 0$$

This yields:

$$n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} \pm 1}$$

("+" for fermions, "−" for bosons)

With $\beta = 1/(k_B T)$ and $\alpha = -\mu/(k_B T)$.

Entropy Expressions

Using the equilibrium distribution, entropy becomes:

- Bose:

$$S = k_B \sum_i g_i \left[(1 + f_i) \ln(1 + f_i) - f_i \ln f_i \right]$$

- Fermi:

$$S = -k_B \sum_i g_i \left[f_i \ln f_i + (1 - f_i) \ln(1 - f_i) \right]$$

where $f_i = n_i / g_i$

Pressure via Entropy

We use:

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N} \Rightarrow P = T \left(\frac{\partial S}{\partial V} \right)$$

In 3D, the density of states $g(\varepsilon) \propto V \varepsilon^{1/2}$, so $S \propto V$, and:

$$P \propto \frac{S}{V} \Rightarrow \text{Obtain Equation of State}$$

Final Results

- **Classical (MB)**:

$$PV = N k_B T$$

- **Bose–Einstein**:

$$PV = N k_B T \cdot \frac{g_{5/2}(z)}{g_{3/2}(z)}$$

- **Fermi–Dirac**:

$$PV = N k_B T \cdot \frac{f_{5/2}(z)}{f_{3/2}(z)}$$

where:

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

Overview

This note elaborates Section 6.1 from Pathria (3rd Edition), which discusses the formulation of quantum ideal gases in the **microcanonical ensemble**. The goal is to compute thermodynamic quantities for ideal Bose and Fermi gases by considering the number of accessible microstates consistent with fixed energy E, particle number N, and volume V.

Definition of the Ensemble

We consider a system of N indistinguishable, non-interacting quantum particles confined in a box of volume V with total energy E.

In quantum mechanics, the microstates are specified by the set of occupation numbers $\{n_i\}$ corresponding to single-particle energy levels ε_i (with degeneracy g_i), subject to:

$$\sum_i n_i = N,$$
$$\sum_i n_i \varepsilon_i = E.$$

The total number of accessible microstates $\Omega(E, N, V)$ is the number of distinct configurations $\{n_i\}$ satisfying the above constraints.

Nature of the Counting Problem

- For **bosons**, $n_i = 0, 1, 2, \ldots$ - For **fermions**, $n_i = 0$ or 1

Thus:

- *A microstate is defined by the set of occupation numbers.*
- *There is no overcounting, since particles are indistinguishable.*

However, computing $\Omega(E, N)$ exactly is extremely hard due to discrete energy levels and the two constraints. So Pathria proceeds by seeking the *most probable distribution.*

Approximate Evaluation via Entropy Maximization

Define the entropy:

$$S = k_B \ln \Omega(E, N)$$

We assume that the system is large enough that the most probable distribution dominates. Therefore, we consider maximizing $\ln \Omega(\{n_i\})$ with constraints:

$$\sum_i n_i = N,$$
$$\sum_i n_i \varepsilon_i = E.$$

Form of $\Omega(\{n_i\})$

- **Bose-Einstein statistics**:

$$\Omega = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

- **Fermi-Dirac statistics**:

$$\Omega = \prod_i \binom{g_i}{n_i}$$

Apply Stirling's approximation: $\ln n! \approx n \ln n - n$ for large n.

Use of Lagrange Multipliers

Define:

$$\mathcal{F} = \ln \Omega - \alpha \sum_i n_i - \beta \sum_i n_i \varepsilon_i$$

The equilibrium configuration satisfies:

$$\delta \mathcal{F} = 0$$

This yields, for each i:

$$\frac{\partial \ln \Omega}{\partial n_i} = \alpha + \beta \varepsilon_i$$

Solving this gives the familiar distributions:
- **Bosons**:

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

- **Fermions**:

$$\bar{n}_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} + 1}$$

Interpretation

Let $\beta = 1/(k_B T)$ and $\alpha = -\mu/(k_B T)$, where T and μ are introduced as parameters arising from maximization.

Conversion to Integrals and Appearance of $g_n(z)$ and $f_n(z)$

To compute N and P, convert sums over i to integrals over energy using the density of states:

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

Let $z = e^{\beta \mu}$ (fugacity), and change variables: $x = \beta \varepsilon$.

Then:

$$N = \int_0^\infty \frac{g(\varepsilon)}{z^{-1}e^{\beta\varepsilon} \pm 1} d\varepsilon$$
$$= \frac{V}{\lambda^3} \times \begin{cases} g_{3/2}(z) & \text{(bosons)} \\ f_{3/2}(z) & \text{(fermions)} \end{cases}$$

where:

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

Equation of State

Similarly, one derives:

$$P = \frac{k_B T}{\lambda^3} \times \begin{cases} g_{5/2}(z) & \text{(bosons)} \\ f_{5/2}(z) & \text{(fermions)} \end{cases}$$

Thus the equation of state becomes:

$$PV = N k_B T \cdot \begin{cases} \frac{g_{5/2}(z)}{g_{3/2}(z)} & \text{(bosons)} \\ \frac{f_{5/2}(z)}{f_{3/2}(z)} & \text{(fermions)} \end{cases}$$

Remarks

Although the starting point is the microcanonical ensemble, Pathria uses entropy maximization via Lagrange multipliers, which leads to expressions formally identical to those obtained from the grand canonical ensemble.