Lecture Notes: Maximization Principles and Entropy of Classical, Bose, and Fermi Gases

1 Introduction

1. Expressions for $W\{n_i\}$

Given a distribution $\{n_i\}$ of particles among energy levels $\{\varepsilon_i\}$, the number of microstates $W\{n_i\}$ for each statistical ensemble is:

- **Classical (MB):**

$$W\{n_i\}_{MB} = \frac{N!}{\prod_i n_i!} \prod_i g_i^{n_i}$$

- **Bose-Einstein (BE):**

$$W\{n_i\}_{BE} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

- **Fermi-Dirac (FD):**

$$W\{n_i\}_{FD} = \prod_i \binom{g_i}{n_i}$$

g_i is the degeneracy of level ε_i.

2. Maximization in Multiple Variables

Let $f(x_1, x_2, ..., x_n)$ be a function of n variables. The function attains an extremum when:

$$\frac{\partial f}{\partial x_i} = 0 \quad \text{for all } i$$

One then examines the second derivatives to classify the critical point (maximum, minimum, saddle).

3. Maximization with Constraints (Lagrange Multipliers)

Often, we want to maximize a function $f(x_1, ..., x_n)$ subject to constraints:

$$\phi_k(x_1, ..., x_n) = 0, \quad \text{for } k = 1, ..., m$$

We define the function:

$$\mathcal{L} = f + \sum_{k=1}^{m} \lambda_k \phi_k$$

and solve:

$$\frac{\partial \mathcal{L}}{\partial x_i} = 0, \quad \frac{\partial \mathcal{L}}{\partial \lambda_k} = 0$$

This ensures the extremum of f under the given constraints. Lagrange multipliers λ_k have physical significance (e.g., temperature, chemical potential).

2 Obtaining n_i^*

1. Microstate Expressions $W\{n_i\}$

Let:

- n_i: number of particles in energy level ε_i
- g_i: degeneracy of level ε_i
- $N = \sum_i n_i$, $E = \sum_i n_i \varepsilon_i$

Classical (MB)

$$W_{MB} = \frac{N!}{\prod_i n_i!} \prod_i g_i^{n_i}$$

Bose-Einstein (BE)

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

Fermi-Dirac (FD)

$$W_{FD} = \prod_i \binom{g_i}{n_i}$$

2. Goal: Maximize Entropy $S = k_B \ln W$

Subject to constraints:

$$\sum_i n_i = N$$

$$\sum_i n_i \varepsilon_i = E$$

This is a constrained optimization problem.

3. Lagrange Multipliers: Why and How

We can't vary n_i freely. Instead, define:

$$\mathcal{L} = \ln W - \alpha \left(\sum_i n_i - N \right) - \beta \left(\sum_i n_i \varepsilon_i - E \right)$$

Where:

- α: enforces particle number conservation
- β: enforces energy conservation (turns out $\beta = 1/k_B T$)

We then extremize $\mathcal{L}$ without constraints.

4. Using Stirling and Logarithms

- Take $\ln W$ to convert products into sums.
- Use Stirling's formula: $\ln n! \approx n \ln n - n$.

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(a) Classical (MB)

$$\ln W_{MB} \approx N \ln N - N - \sum_i (n_i \ln n_i - n_i) + \sum_i n_i \ln g_i$$
$$= - \sum_i n_i \ln \left(\frac{n_i}{g_i} \right) + \text{const}$$

Maximize:

$$\mathcal{L} = - \sum_i n_i \ln \left(\frac{n_i}{g_i} \right) - \alpha \left(\sum_i n_i - N \right) - \beta \left(\sum_i n_i \varepsilon_i - E \right)$$

Derivative:

$$\frac{d\mathcal{L}}{dn_i} = - \ln \left(\frac{n_i}{g_i} \right) - 1 - \alpha - \beta \varepsilon_i = 0 \Rightarrow n_i = g_i e^{-\alpha - \beta \varepsilon_i}$$

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(b) Bose-Einstein (BE)

Using Stirling:

$$\ln W_{BE} \approx \sum_i \left[(n_i + g_i)\ln(n_i + g_i) - n_i \ln n_i - g_i \ln g_i\right]$$

Then:

$$\mathcal{L} = \ln W_{BE} - \alpha \left(\sum_i n_i - N\right) - \beta \left(\sum_i n_i \varepsilon_i - E\right)$$

Derivative:

$$\frac{d\mathcal{L}}{dn_i} = \ln\left(1 + \frac{g_i}{n_i}\right) - \alpha - \beta\varepsilon_i = 0 \Rightarrow n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i} - 1}$$

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(c) Fermi-Dirac (FD)

$$\ln W_{FD} \approx \sum_i \left[g_i \ln g_i - n_i \ln n_i - (g_i - n_i)\ln(g_i - n_i)\right]$$

Maximize:

$$\mathcal{L} = \ln W_{FD} - \alpha \left(\sum_i n_i - N\right) - \beta \left(\sum_i n_i \varepsilon_i - E\right)$$

Derivative:

$$\ln\left(\frac{g_i - n_i}{n_i}\right) - \alpha - \beta\varepsilon_i = 0 \Rightarrow n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i} + 1}$$

5. Final Entropy Expressions

Classical (MB)

$$S = -k_B \sum_i n_i \left[\ln\left(\frac{n_i}{g_i}\right) - 1\right]$$

Bose-Einstein

$$S = -k_B \sum_i g_i \left[\frac{n_i}{g_i}\ln\left(\frac{n_i}{g_i}\right) - \left(1 + \frac{n_i}{g_i}\right)\ln\left(1 + \frac{n_i}{g_i}\right)\right]$$

Fermi-Dirac

$$S = -k_B \sum_i g_i \left[\frac{n_i}{g_i}\ln\left(\frac{n_i}{g_i}\right) + \left(1 - \frac{n_i}{g_i}\right)\ln\left(1 - \frac{n_i}{g_i}\right)\right]$$

6. Summary of Steps

1. Write expression for $W\{n_i\}$
2. Take $\ln W$ to simplify the product into a sum
3. Use Stirling's approximation
4. Add constraints using Lagrange multipliers
5. Take derivatives w.r.t. n_i and set to zero
6. Solve for n_i
7. Plug back into $\ln W$ to get entropy