

Comprehensive Study Notes: Statistical Mechanics

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Contents

1	Phase Space	2
2	Macrostate vs. Microstate	2
3	Density of States	2
4	Statistical Ensembles	3
5	Thermodynamic Probability and Entropy	3
6	Classical vs. Quantum Statistics	3
6.1	Maxwell-Boltzmann (MB) Statistics	3
6.2	Quantum Statistics	4
7	Comparison of Statistics	4

1 Phase Space

To describe the state of a system mechanically, we use the concept of phase space, which combines position and momentum coordinates.

- **μ -space (Molecular Phase Space):** This is the phase space of a *single* particle. It is a 6-dimensional space consisting of:
 - 3 Position coordinates: (x, y, z)
 - 3 Momentum coordinates: (p_x, p_y, p_z)

The smallest volume element (unit cell) in this space is determined by the Uncertainty Principle:

$$(d\tau)_{min} = h^3$$

where h is Planck's constant.

- **Γ -space (Gas Phase Space):** This is the phase space for the *entire* system of N particles. It is a $6N$ -dimensional space. A single point in Γ -space represents the microscopic state of the whole system at a specific instant.

2 Macrostate vs. Microstate

Statistical mechanics relies on distinguishing between the macroscopic observation and the microscopic configuration.

1. **Microstate:** A detailed specification of the system where the state (position and momentum) of *every* constituent particle is specified.
2. **Macrostate:** A specification of the system based on bulk, measurable quantities such as Pressure (P), Volume (V), Temperature (T), and Total Energy (E).

Fundamental Postulate: For an isolated system in equilibrium, all accessible microstates corresponding to the same macrostate are equally probable.

3 Density of States

The density of states, $g(\epsilon)$, is defined as the number of quantum states (or phase space cells) available per unit energy interval.

The number of states in the energy range ϵ to $\epsilon + d\epsilon$ is:

$$g(\epsilon)d\epsilon = \frac{8\sqrt{2}\pi V}{h^3}m^{3/2}\epsilon^{1/2}d\epsilon$$

Significance: This function is crucial for calculating particle distributions, as it weights the probability of finding particles at higher energy levels where more states exist.

4 Statistical Ensembles

An ensemble is a collection of a large number of mental copies of a system, used to average properties.

- **Microcanonical Ensemble:** Represents an isolated system with fixed Energy (E), Volume (V), and Number of particles (N).
- **Canonical Ensemble:** Represents a system in thermal equilibrium with a heat reservoir. Temperature (T), Volume (V), and Number of particles (N) are fixed, but energy can fluctuate.
- **Grand Canonical Ensemble:** Represents an open system that can exchange energy and particles with a reservoir. Temperature (T), Volume (V), and Chemical Potential (μ) are fixed.

5 Thermodynamic Probability and Entropy

- **Thermodynamic Probability (W):** The number of microstates corresponding to a specific macrostate. W is typically a very large number.
- **Boltzmann's Entropy Relation:** Ludwig Boltzmann connected the macroscopic property of entropy (S) to the microscopic probability (W):

$$S = K_B \ln W$$

where K_B is the Boltzmann constant. This equation implies that equilibrium (maximum entropy) corresponds to the macrostate with the maximum number of microstates (W_{max}).

6 Classical vs. Quantum Statistics

6.1 Maxwell-Boltzmann (MB) Statistics

Assumptions:

- Particles are identical but **distinguishable**.
- Any number of particles can occupy a single energy state.
- Valid at high temperatures and low densities (classical limit).

Distribution Function:

$$n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i}}$$

(Where $\beta = 1/K_B T$)

6.2 Quantum Statistics

Applies when particles are indistinguishable and quantum effects are significant (low T , high density).

1. Bose-Einstein (BE) Statistics:

- Applies to **Bosons** (Integral spin: $0, \hbar, \dots$).
- Particles are **indistinguishable**.
- **No** Pauli exclusion principle.
- Example: Photons, Phonons.

$$n_i = \frac{g_i}{e^{(\epsilon_i - \mu)/K_B T} - 1}$$

2. Fermi-Dirac (FD) Statistics:

- Applies to **Fermions** (Half-integral spin: $\frac{1}{2}\hbar, \frac{3}{2}\hbar, \dots$).
- Particles are **indistinguishable**.
- Obey **Pauli Exclusion Principle** (Max 1 particle per state).
- Example: Electrons, Protons.

$$n_i = \frac{g_i}{e^{(\epsilon_i - \epsilon_F)/K_B T} + 1}$$

7 Comparison of Statistics

Table 1: Comparison of MB, BE, and FD Statistics

Property	Maxwell-Boltzmann	Bose-Einstein	Fermi-Dirac
Particle Type	Classical (Boltzons)	Bosons	Fermions
Distinguishability	Distinguishable	Indistinguishable	Indistinguishable
Spin	Any	Integral ($0, 1, 2 \dots$)	Half-Integral ($1/2, \dots$)
Pauli Principle	No	No	Yes
Occupancy Limit	None	None	1 per state
Wave Function	N/A	Symmetric	Antisymmetric
Examples	Ideal Gas	Photons, He-4	Electrons, Metal free e ⁻