STATISTICAL MECHANICS

M.Sc. Physics

FIRST YEAR, SEMESTER-II, PAPER-I

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M.Sc. Physics: Statistical Mechanics

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FOREWORD

Since its establishment in 1976, Acharya Nagarjuna University has been forging ahead in the path of progress and dynamism, offering a variety of courses and research contributions. I am extremely happy that by gaining 'A+' grade from the NAAC in the year 2024, Acharya Nagarjuna University is offering educational opportunities at the UG, PG levels apart from research degrees to students from over 221 affiliated colleges spread over the two districts of Guntur and Prakasam.

The University has also started the Centre for Distance Education in 2003-04 with the aim of taking higher education to the door step of all the sectors of the society. The centre will be a great help to those who cannot join in colleges, those who cannot afford the exorbitant fees as regular students, and even to housewives desirous of pursuing higher studies. Acharya Nagarjuna University has started offering B.Sc., B.A., B.B.A., and B.Com courses at the Degree level and M.A., M.Com., M.Sc., M.B.A., and L.L.M., courses at the PG level from the academic year 2003-2004 onwards.

To facilitate easier understanding by students studying through the distance mode, these self-instruction materials have been prepared by eminent and experienced teachers. The lessons have been drafted with great care and expertise in the stipulated time by these teachers. Constructive ideas and scholarly suggestions are welcome from students and teachers involved respectively. Such ideas will be incorporated for the greater efficacy of this distance mode of education. For clarification of doubts and feedback, weekly classes and contact classes will be arranged at the UG and PG levels respectively.

It is my aim that students getting higher education through the Centre for Distance Education should improve their qualification, have better employment opportunities and in turn be part of country's progress. It is my fond desire that in the years to come, the Centre for Distance Education will go from strength to strength in the form of new courses and by catering to larger number of people. My congratulations to all the Directors, Academic Coordinators, Editors and Lesson-writers of the Centre who have helped in these endeavors.

Prof. K. Gangadhara Rao
M.Tech., Ph.D.,
Vice-Chancellor I/c
Acharya Nagarjuna University.

Semester 2
M.Sc. Physics
Academic Year 2022-23 Amended
201PH24-STATISTICAL MECHANICS

Course Objectives:

- This course in statistical mechanics provides the basic idea of probability and calculating probability for various statistical systems of particles.
- To apply the principles of probability in distribution of particles in various systems
- To learn the different types of statistics distribution and particles.

UNIT I (Fundamentals of classical statistical mechanics)

Relation between statistical mechanics and thermodynamics, Phase space, Ensembles-micro canonical, canonical and grand canonical ensemble, density distribution in the phase space, Liouville's theorem, equipartition of energy theorem, microstates and macrostates.

Learning Outcomes:

- To learn postulates of classical statistical mechanics and Ensembles.
- To study density of states Liouville's theorem and paradox.

UNIT-II (Ideal gas in various ensembles)

Classical ideal gas in micro canonical ensemble, partition function for micro canonical ensemble, Gibb's paradox, partition function for Canonical ensemble, thermo dynamical function for Canonical ensemble, partition function for Grand canonical ensemble, thermodynamical function for Grand canonical ensemble.

Learning Outcomes:

- To know about partition function in different ensembles.
- To study the Gibb's paradox.

UNIT III (Energy fluctuation and distribution function)

Energy fluctuation in micro canonical ensemble, energy fluctuation in canonical ensemble, density fluctuation in Grand canonical ensemble, energy fluctuation in Grand canonical ensemble. Maxwell-Boltzmanndistribution, Bose-Einstein distribution, Fermi-Dirac distribution, Darwin-Fowler method.

Learning Outcomes:

- To study the features of Maxwell-Boltzmann statistics.
- To derive the Bose-Einstein distribution.

UNIT IV (Molecular partition function)

Molecular partition function- Translational partition function, Rotational partition function, Vibrational partition function, Electronic and Nuclear partition function, application of rotational partition function, application of vibrational partition function in solids.

Learning Outcomes:

- To learn electronic and nuclear partition function.
- To acquire knowledge about vibrational partition function in solids

UNIT V (Ideal Fermi and Bose Gas)
Equation of state of an ideal Fermi gas, theory of White dwarf stars, Landau diamagnetism, Photons, Phonons in solids, Bose-Einstein condensation, thermionic emission, magnetic susceptibility of free electrons, Brownian motion of a molecule.

Learning Outcomes:
- To learn about Ideal Fermi gas and to derive equations.
- To acquire knowledge about Bose-Einstein condensation.

Course Outcomes:
- After taking this course student are able to determine the probability of any type of events.
- Students have understood the concept of phase space and its volume.
- They can easily distinguish between different types of particles and statistics and can easily distribute bosons, fermions and classical particles among energy levels.
- After studying Fermi Dirac statistics, students have learnt to deal with much electron system.

Text and Reference Books:

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics by K. Huang (Wiley Eastern)
3. Statistical Mechanics: Theory and applications by S.K. Sinha
4. Fundamentals of Statistical and Thermal Physics by F. Reif
5. Statistical Mechanics by Gupta and Kumar, Pragati Prakashan Pub. Meerut.
6. Statistical Mechanics by Satya Prakash.

(201PH24)

M.Sc. DEGREE EXAMINATION

Physics

Paper-1- STATISTICAL MECHANICS

Time: Three hours Maximum:70 marks.

Answer the following

1. (a) Explain the concept of ensemble and calculate ensemble average.
   (b) State and prove Lyonville's theorem

   OR

   (c) What are microstates and macrostates?
   (d) Discuss about density distribution in the phase space.

2 (a) What is partition functions? Explain.
   (b) Obtain the partition function for canonical ensemble.

   OR

   (c) Discuss the thermodynamic properties of an ideal gas.
   (d) Explain the thermodynamical function for grand canonical ensemble.

3 (a) Obtain the expression for Maxwell-Boltzmann distribution function.
   (b) Explain about energy fluctuation in canonical ensemble.

   OR

   (c) Distinguish between B-E and F-D distributions. Explain detail.

4 (a) Calculate the electronic partition functions by considering only the Ground and first excited states.
   (b) Show that electronic specific heat as a function of temperature has a Peak like behaviour.

   OR

   (c) Calculate the rotational partition function and various thermodynamical quantities.

5 (a) Write the theory of white dwarfs stars.
   (b) Derive the expression for the magnetic susceptibility for free electron Gas due to spin degree of freedom.

   OR

   (c) Explain Brownian motion. Show how Brownian motion its treated by Langevin equation for rotational motions.

CONTENTS

LESSON-1

STATISTICAL MECHANICS – THERMODYNAMICS

AIM AND OBJECTIVE

1. Statistical Mechanics

Aim

The main aim of **statistical mechanics** is to explain the **macroscopic properties** of matter (such as pressure, temperature, and energy) by studying the **microscopic behavior** of a very large number of particles (atoms or molecules).

Objectives

- To establish a **link between microscopic laws** of physics and **macroscopic thermodynamic quantities**
- To study the **statistical behavior** of systems containing a large number of particles
- To derive thermodynamic laws using **probability and statistics**
- To explain properties like **entropy, temperature, and heat** in terms of molecular motion
- To predict the **equilibrium and non-equilibrium behavior** of physical systems

2. Thermodynamics

Aim

The main aim of **thermodynamics** is to study the **conversion of energy**, especially the relationship between **heat, work, and temperature**, without considering the microscopic structure of matter.

Objectives

- To formulate the **laws of thermodynamics** based on observable quantities
- To study **energy transfer** as heat and work
- To analyze the **efficiency of engines and refrigerators**
- To define and use concepts such as **temperature, entropy, internal energy, and enthalpy**
- To predict the **direction of natural processes** and equilibrium condition

STRUCTURE OF THE LESSON:

1.1 Relation Between Statistical Mechanics and Thermodynamics

1.2 Phase Space

1.3 Ensembles-Micro Canonical

1.4 Summary

1.5 Technical Terms

1.6 Self Assessment Questions

1.7 Suggested Readings

1.1 RELATION BETWEEN STATISTICAL MECHANICS AND THERMODYNAMICS

Introduction

Statistical mechanics and thermodynamics are two closely related branches of physics that deal with the behavior of macroscopic systems containing a large number of particles. Thermodynamics was developed in the nineteenth century as a phenomenological theory based on empirical laws governing heat, work, and energy, without reference to the microscopic nature of matter. In contrast, statistical mechanics provides a microscopic foundation for thermodynamics by explaining macroscopic thermodynamic properties in terms of the statistical behavior of microscopic constituents such as atoms and molecules.

The relation between statistical mechanics and thermodynamics lies in the fact that thermodynamic laws emerge as statistical averages over an enormous number of microscopic states. Statistical mechanics not only explains the origin of thermodynamic quantities such as temperature, entropy, and pressure but also provides explicit expressions for these quantities in terms of molecular parameters. Thus, statistical mechanics bridges the gap between microscopic physics and macroscopic thermodynamic behavior.

The relation between **statistical mechanics** and **thermodynamics** is one of the most profound in physics, as it provides a microscopic foundation for the macroscopic laws of thermodynamics. Let's break down how they are connected:

1. Thermodynamics: The Macroscopic Theory

Thermodynamics is the branch of physics that deals with the **macroscopic behavior** of systems, focusing on **macroscopic quantities** like temperature, pressure, volume, energy, and entropy. It doesn't concern itself with the microscopic details of the system (i.e., the individual particles), but instead describes the **overall behavior** of the system in equilibrium.

The key **thermodynamic laws** include:

- **Zeroth Law**: If two systems are each in thermal equilibrium with a third system, they are in thermal equilibrium with each other.
- **First Law (Conservation of Energy)**: The total energy of a system is conserved. Energy can be transferred or transformed, but it cannot be created or destroyed.
- **Second Law (Entropy)**: In any spontaneous process, the entropy (a measure of disorder or randomness) of the system and surroundings always increases.
- **Third Law**: As the temperature of a system approaches absolute zero, the entropy approaches a minimum.

Thermodynamics provides the **macroscopic relations** between the system's state variables like temperature, pressure, volume, and entropy, but it doesn't provide a microscopic explanation for why these relationships hold.

2. Statistical Mechanics: The Microscopic Theory

Statistical mechanics, on the other hand, is a **microscopic theory** that explains the **macroscopic thermodynamic behavior** of systems in terms of the properties and interactions of **individual particles**. It connects the **microscopic behavior of particles** (atoms, molecules, electrons, etc.) to the **macroscopic thermodynamic quantities** (such as pressure, temperature, and entropy).

Key concepts in statistical mechanics include:

- **Ensemble Theory**: A collection of many copies of the system, each representing a possible state of the system. There are different types of ensembles (e.g., microcanonical, canonical, grand canonical), depending on the system's interactions with the environment.
- **Partition Function (Z)**: A central quantity in statistical mechanics that encodes information about the states of a system. It is related to the probability distribution of the system's states and can be used to calculate thermodynamic properties.
- **Boltzmann Distribution**: Describes the distribution of particles over different energy states in equilibrium.

Statistical mechanics provides a **microscopic model** for thermodynamic quantities, explaining **how the properties of individual particles** (such as energy, velocity, and position) give rise to the **macroscopic thermodynamic quantities** like temperature and pressure.

3. Connecting Thermodynamics and Statistical Mechanics

Statistical mechanics allows us to **derive thermodynamic quantities** from the statistical behavior of the microscopic components of a system. It gives **statistical interpretations** for thermodynamic concepts like entropy, temperature, and free energy.

The key connections between statistical mechanics and thermodynamics include:

1. Thermodynamic Quantities from Statistical Mechanics

- **Energy (Internal Energy)**:
  In statistical mechanics, the **internal energy** U can be calculated as the expectation value of the system's energy:

$$U = < E > = \sum_i E_i P(E_i)$$

Where$P(E_i)$ is the probability of the system being in the i-th energy state.
In thermodynamics, internal energy U is a state function that depends on variables like temperature, pressure, and volume. Statistical mechanics provides a detailed understanding of this energy from the microscopic behavior of particles.

- **Entropy (S)**:
  In thermodynamics, entropy is related to the number of possible microscopic configurations (Ω) of a system by **Boltzmann's entropy formula**:

$$S = k_B ln\Omega$$

Statistical mechanics provides a **microscopic definition** of entropy, where Ω is the number of accessible states of the system. This relationship directly connects the statistical nature of particles to the macroscopic thermodynamic concept of entropy.

- **Temperature** **(T)**:
  In thermodynamics, temperature is related to heat flow and energy transfer. In statistical mechanics, temperature is connected to the **energy distribution** of particles. The relationship between temperature and energy is given by the **Boltzmann distribution**:

$$P(E) \propto \mathrm{e}^{-\mathrm{E}/\mathrm{k_B T}}$$

Statistical mechanics explains **how temperature emerges from the statistical behavior of particles**.

2. Thermodynamic Laws as Statistical Principles

- **First Law of Thermodynamics (Energy Conservation)**:
  In statistical mechanics, energy is conserved, and the total energy of a system corresponds to the sum of the energies of individual particles or states. The first law is reflected in the fact that the total energy in the system remains constant when no work or heat exchange occurs with the surroundings.

- **Second Law of Thermodynamics (Entropy Increase)**:
  Statistical mechanics explains the second law by considering the **probability of system states**. The second law implies that systems naturally evolve toward states with higher entropy because these states are more **probable** than those with low entropy. Thus, statistical mechanics provides a **probabilistic explanation** for the increase in entropy.

3. Partition Function and Free Energy

The **partition function** Z is the cornerstone of statistical mechanics, and it serves as the link between **microscopic details** and **macroscopic thermodynamic properties**. For example, the Helmholtz free energy FFF (a thermodynamic potential) can be derived from the partition function in the canonical ensemble:

$$F = -\mathrm{k_B T} \ln \mathrm{Z}$$

Similarly, other thermodynamic potentials like the grand potential and Gibbs free energy can also be derived from the partition function in different ensembles.

4. Fluctuations and Response Function

Statistical mechanics also provides a framework for understanding **fluctuations** and **response functions**. For instance, the **fluctuations** in energy or particle number (like the variance in energy or particle number) can be related to the **heat capacity** or **compressibility**, which are thermodynamic quantities.

Importance of Statistical Mechanics in Thermodynamics

Statistical mechanics extends thermodynamics by:

- Providing microscopic explanations of thermodynamic laws,
- Allowing calculation of thermodynamic quantities from molecular properties,
- Explaining irreversibility and entropy increase,
- Describing systems outside strict equilibrium,
- Predicting new phenomena such as phase transitions.

Thus, statistical mechanics not only supports thermodynamics but also enriches and generalizes it.

Conclusion

The relation between statistical mechanics and thermodynamics is both deep and fundamental. Thermodynamics provides universal laws governing macroscopic systems, while statistical mechanics offers a microscopic foundation for these laws based on probability and molecular dynamics. Through concepts such as ensembles, partition functions, and entropy, statistical mechanics explains the origin of thermodynamic quantities and laws. The emergence of thermodynamics from statistical averages over microscopic states illustrates how deterministic macroscopic behavior arises from underlying microscopic randomness. Together, statistical mechanics and thermodynamics form a unified framework for understanding the physical behavior of matter in equilibrium.

1.2 PHASE SPACE:

In classical mechanics, the state of a system of particles at any given time is completely specified by the knowledge of position and momentum (or velocity) of each of its particles. The instantaneous position of a single particle is determined by three independent coordinatesx, y, z, and the instantaneous motion of a particle is described by velocity components (v_x, v_y, v_z)or more conveniently by momentum components(p_x, p_y, p_z).Therefore, the state of a single particle is then completely specified by position coordinates $x, y, z$and momentum componentsp_x, p_y, p_z. As a purely mathematical concept, we may imagine a six-dimensional space in which $dx\, dy\, dz\, dp_x\, dp_y\, dp_z$is an element of volume, and the position of a point particle in this space will be described by a set of six coordinates:x, y, z, p_x, p_y, p_z This six-dimensional space for a single particle is termed as phase-space, and particularly the μ-space.

If the system contains a large number of particles such that the state of the system is represented by $f$independent position coordinates $q_1, q_2, \dots, q_f$and $f$momentum coordinates$p_1, p_2, \dots, p_f$,then mathematically, these $2f$combined position–momentum coordinates may be allowed to define a $2f$-dimensional space in which the configuration of the system is represented by $2f$coordinates:$q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_f$This 2f-dimensional space is called the phase-space or the Γ-space (Gamma-space).The Γ-space is considered to be a conceptual Euclidean space having $2f$rectangular axes, and an element of volume in this space is represented by:$dq_1\, dq_2\, \dots\, dq_f\, dp_1\, dp_2\, \dots\, dp_f$The Γ-space may be considered as a superposition of μ-spaces.Obviously, the dimensions of the phase-space depend upon the degrees of freedom of the system.
The instantaneous state of a particle in the phase-space is represented by a point known as the phase point or representative point.The number of phase points per unit volume is called the phase density of these points.An element of volume in the phase-space is termed as a cell.

Definition of Phase Space

For a system of N particles, each particle has three spatial coordinates and three corresponding momentum components. The phase space of such a system is a 6N6N6N-dimensional space defined by the set of canonical coordinates:

$(q_1,q_2,\dots,q_{3N};\ p1,p_2,\dots,p_{3N})$

Each point in this space represents a unique **microstate** of the system. The system's evolution in time corresponds to a continuous curve or trajectory in phase space determined by Hamilton's equations of motion.

For a single particle moving in one dimension, the phase space is two-dimensional, consisting of the position qqq and momentum p

Division of Phase Space into Cells: Consider a $2f$-dimensional phase space defined by position coordinates $q_1, q_2, \ldots, q_f$and momentum coordinates$p_1, p_2, \ldots, p_f$.An element of volume in this phase space will berepresented by

$$\delta q_1\,\delta q_2\,\ldots\,\delta q_f\,\delta p_1\,\delta p_2\,\ldots\,\delta p_f \qquad (1)$$

The dimensions of this volume element are those of (length × momentum)h^f.Therefore, the unit of this volume element is (joule–second)h^f.

Let us now divide any finite volume of phase space into a large number of cells. Let the size of each cell be h^f. Here $h$is any arbitrary constant and has the dimensions of joule–second, i.e.,

$$h = \delta q_i\,\delta p_i \qquad (2)$$

As $p_i$and $q_i$can take all possible continuously variable values, there may be infinite representative points and hence possible microstates in any finite volume of phase space.
The number of phase cells in this volume is:

$$\frac{\delta q_1\,\delta q_2\,\ldots\,\delta q_f\,\delta p_1\,\delta p_2\,\ldots\,\delta p_f}{h^f} \qquad (3)$$

Volume in Phase Space: The volume in phase space associated with a system is the total region accessible to the system under given constraints (such as fixed energy, volume, and number of particles).For example, in the microcanonical ensemble, the system is confined to all phase points that satisfy the energy constraint:

$$E \leq H(p,q) \leq E + \delta E$$

Where H (p,q) is the Hamiltonian (Total energy function). The total phase space volume for this energy range is

$$\xi(E) = E \leq H(p,q) \leq E + \delta E\,dV$$

This quantity represents the number of accessible microstates for the system within that energy range.

Applications of Phase Space

Phase space concepts are widely used in:

- Classical and quantum dynamics,
- Statistical mechanics and thermodynamics,
- Plasma physics,
- Nonlinear dynamics and chaos theory,

- Quantum optics and semi classical approximations,
- Molecular dynamics simulations.

In chaos theory, phase space portraits reveal sensitive dependence on initial conditions and complex dynamical behavior.

Advantages of Phase Space Description

The phase space formulation offers several advantages:

- Complete specification of a system's state,
- Clear geometric visualization of dynamics,
- Natural framework for conservation laws,
- Direct link between microscopic and macroscopic descriptions,
- Foundation for modern theoretical and computational methods.

Conclusion

Phase space is a central and unifying concept in physics, providing a complete and elegant description of dynamical systems. By incorporating both positions and momenta, phase space captures the full microscopic state of a system and allows its time evolution to be visualized geometrically. In statistical mechanics, phase space forms the basis for defining microstates, ensembles, entropy, and equilibrium. Liouville's theorem ensures the conservation of phase space volume, while the ergodic hypothesis connects microscopic dynamics with macroscopic observables. In quantum mechanics, phase space ideas are modified by uncertainty principles but remain essential for understanding classical–quantum correspondence. Overall, phase space provides the conceptual and mathematical foundation for linking dynamics, probability, and thermodynamics.

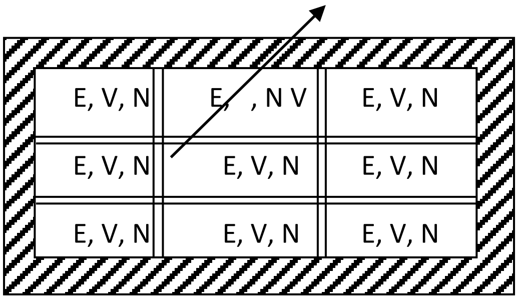
1.3 ENSEMBLES-MICRO CANONICAL

Introduction

In statistical mechanics, an ensemble is a large collection of virtual copies of a physical system, each representing a possible microscopic state consistent with given macroscopic constraints. Since it is practically impossible to track the exact microscopic motion of an enormous number of particles in a real system, ensembles provide a powerful theoretical framework for connecting microscopic dynamics with macroscopic thermodynamic behavior. By averaging over an ensemble, one can calculate measurable thermodynamic quantities such as energy, entropy, pressure, and temperature.

The concept of ensembles was introduced by **J. Willard Gibbs**, and it forms the cornerstone of equilibrium statistical mechanics. Different ensembles correspond to different physical conditions imposed on the system, such as isolation, thermal contact, or particle exchange with a reservoir.

The micro canonical ensemble is a collection of essentially independent assemblies having the same energy (E), Volume (V) and Number (N) of systems, all the systems are of the same. One can imagine this ensemble as follows. The individual assemblies are separated by rigid, impermeable and well insulated (as in fig) walls. So that the three E, V and N remain un=effected in the presence of other systems.



Rigid, well insulated walls

Let us consider an isolated (closed) system for which the total energy $H(q, p) = E = E(q_1, \ldots\ldots q_f,, p_a, \ldots\ldots\ldots\ldots p_f) =$ constant.

The locus of all the phase points with equal energies in the phase space is called an energy surface or ergodic surface. If we consider a family of such energy surfaces constructed in phase space and two neighboring surfaces with energies E and E+ dE, each surface divides the phase space into two parts, one with higher energy and the other with lower energy (not interacting with each other). The space between them contains a few phase points which are constant. If we take the density as equal to zero for all values of energy except in the selected narrow range δE, the micro-canonical ensemble is specified by its properties as

$$\rho(E) = \text{constant (in the range } E \text{ and } E + \delta E) \\ = 0 \qquad \text{--- (4)}$$

Properties:

1. As ρ is a function of energy, micro canonical ensemble is in statistical equilibrium.
2. As it is in statistical equilibrium, the average properties of such ensembles (micro canonical) will not vary in time and
3. The distribution of phase points is uniform.

Limitations of the Micro canonical Ensemble

Despite its fundamental importance, the micro canonical ensemble has limitations:

- It is mathematically difficult to apply to complex systems.
- Real systems are rarely perfectly isolated.
- Calculations often become simpler in the canonical or grand canonical ensembles.

Nevertheless, in the thermodynamic limit, results obtained from different ensembles become equivalent.

Importance and Applications

The micro canonical ensemble is important in:

- Foundations of statistical mechanics,
- Study of isolated systems,
- Understanding entropy and equilibrium,
- Astrophysical systems,
- Theoretical studies of phase transitions and chaos.

It serves as the conceptual starting point for more practical ensembles.

Conclusion

The micro canonical ensemble represents the most fundamental description of equilibrium in statistical mechanics. By considering an isolated system with fixed energy, volume, and number of particles, it provides a natural framework for defining microstates, entropy, temperature, and other thermodynamic quantities. The principle of equal a priori probabilities and Boltzmann's entropy formula establish a deep connection between microscopic dynamics and macroscopic thermodynamic laws. Although other ensembles are often more convenient for practical calculations, the micro canonical ensemble remains the cornerstone upon which the entire structure of equilibrium statistical mechanics is built.

1.5 SUMMARY

1. Statistical Mechanics and Thermodynamics

Statistical mechanics provides the microscopic foundation of **thermodynamics** by relating the macroscopic properties of matter to the statistical behavior of a large number of microscopic constituents such as atoms and molecules.

Thermodynamics describes systems using macroscopic variables like pressure, volume, temperature, and entropy, without reference to microscopic details. Statistical mechanics bridges this gap by introducing the concept of **microstates** and **macrostates**. A macrostate is defined by macroscopic variables, while a microstate specifies the exact positions and momenta (or quantum states) of all particles.

The laws of thermodynamics emerge naturally from statistical principles:

- The **first law** corresponds to energy conservation.
- The **second law** arises from the tendency of systems to evolve toward macrostates with maximum probability (maximum entropy).
- The **third law** is consistent with the reduction of accessible microstates at absolute zero.

Thus, thermodynamics is a statistical description of the collective behavior of microscopic particles.

2. Phase Space

Phase space is an abstract space used to represent all possible microstates of a system. For a system of NNN particles, phase space is a 6N6N6N-dimensional space, with three coordinates for position and three for momentum for each particle.

Each point in phase space represents a unique microstate of the system. As the system evolves in time, its representative point traces a trajectory in phase space according to the equations of motion.

An important result related to phase space is **Liouville's theorem**, which states that the density of phase points remains constant along the trajectory of the system. This implies conservation of phase space volume and ensures the stability of equilibrium distributions.

Phase space plays a crucial role in defining ensembles, calculating the number of microstates, and understanding equilibrium and irreversibility in statistical mechanics.

3. Ensembles – Microcanonical Ensemble

An **ensemble** is a large collection of virtual copies of a system, each representing a possible microstate consistent with given macroscopic conditions.

The **microcanonical ensemble** describes an **isolated system** with fixed:

- Energy (E),
- Volume (V),
- Number of particles (N).

Since the system is isolated, all accessible microstates within a narrow energy range are assumed to be **equally probable**. This assumption is known as the principle of equal a priori probabilities.

1.6 TECHNICAL TERMS

Statistical mechanics and thermodynamics, Phase space, Ensembles-micro canonical

1.7 SELF ASSESSMENT QUESTIONS

1. Explain about the Relationship between Statistical mechanics and thermodynamics
2. Write a short note on Phase space
3. Briefly explain about the Ensembles-micro canonical

1.8 SUGGESTED READINGS

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics: Theory and applications by S.K. Sinha
3. Fundamentals of Statistical and Thermal Physics by F. Reif
4. Statistical Mechanics by Gupta and Kumar, Pragati Prakashan Pub. Meerut.
5. Statistical Mechanics by Satya Prakash

Prof. Ch. Linga Raju

LESSON-2

LIOUVILLE’S THEOREM

AIM AND OBJECTIVE

Aim

The aim of **Liouville’s Theorem** is to describe the **conservation of phase space density** for a system of particles in classical mechanics. It provides a fundamental principle for **statistical mechanics**, stating that the **density of representative points in phase space remains constant** as the system evolves over time.

Objectives

- To establish the **time-invariance of phase space density** in Hamiltonian systems.
- To provide a **mathematical foundation for statistical mechanics** and ensemble theory.
- To justify the use of **microcanonical, canonical, and grand canonical ensembles**.
- To understand the **conservation of probability** in the evolution of a mechanical system.
- To connect **microscopic dynamics** with **macroscopic thermodynamic behavior**.

STRUCTURE

2.1 CANONICAL AND GRAND CANONICAL ENSEMBLE

2.2 DENSITY DISTRIBUTION IN THE PHASE SPACE

2.3 LIOUVILLE’S THEOREM

2.4 SUMMARY

2.5 TECHNICAL TERMS

2.6 SELF ASSESSMENT QUESTIONS

2.7 SUGGESTED READINGS

2.1 CANONICAL AND GRAND CANONICAL ENSEMBLE

Introduction

Canonical Ensemble:

A canonical ensemble represents a large collection of **identical systems** that can exchange **energy** with a heat reservoir but have **fixed number of particles (N), volume (V), and temperature (T)**. Each system in the ensemble can occupy different microstates with energies (E_i), and the probability of a system being in a state depends on the **Boltzmann factor** ($e^{\{-E\_i/k_B T\}}$).

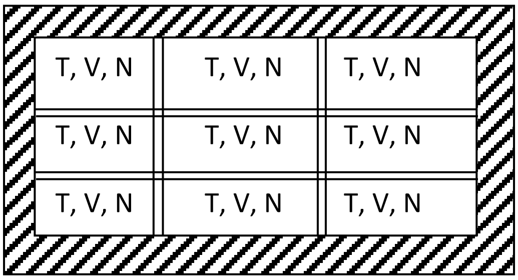
Grand Canonical Ensemble:

A grand canonical ensemble represents systems that can exchange **both energy and particles** with a reservoir. The **chemical potential ((\mu)), volume (V), and temperature (T)** are fixed. This ensemble is useful when the **number of particles is not fixed**, such as in gases and open systems.

Both ensembles provide a **statistical framework** to connect **microscopic states** with **macroscopic thermodynamic quantities**.

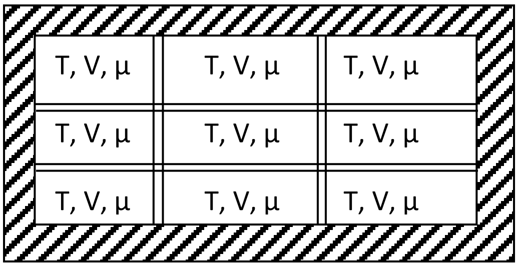
A collection of independent assemblies having the same temperature T, volume V and number of identical particles N is called a canonical ensemble. If the energy exchange takes place but the mass exchange does not take place, the ensemble is called Canonical Ensemble i.e., in this ensemble, all the assemblies are in thermal contact with each other. The Canonical ensembles can be imagined thus. The individual assemblies are separated by rigid, impermeable but Dia thermal walls. As energy exchange takes place, temperature remains constant for all the assemblies (Figure). The canonical ensemble can be referred to an isothermal system where only energy exchanges, but mass remains unchanged dia thermal wall

Grand Canonical Ensemble



A collection of independent assemblies in which exchange of energy as well as mass (number of particles) takes place is called a Grand Canonical Ensemble. It can be thought of as a micro canonical ensemble where both energy and mass exchange. As a result of exchange of number of particles, the chemical potential μ remain constant in addition to the temperature (because of energy exchange) being constant. So, in a Grand Canonical Ensemble Volume V, temperature T and chemical potential μ remain constant. The following Figure represents a Grand Canonical Ensemble where the individual assemblies are separated by rigid, permeable and dia thermal walls.

dia thermal wall



They refer to open isothermal systems.

If we know both the average energy and average number of particles in an assembly, grand canonical ensemble can be applied.

Applications

Canonical Ensemble:

- Calculation of **partition functions** for systems with fixed N, V, T
- Derivation of **thermodynamic quantities** like internal energy, entropy, and free energy
- Study of **vibrational, rotational, and translational energies** in molecules
- Analysis of **specific heat capacities** of solids and gases

Grand Canonical Ensemble:

- Used in **open systems** where particle number fluctuates
- Derivation of **Bose–Einstein and Fermi–Dirac distributions**
- Study of **chemical reactions, adsorption, and phase transitions**
- Analysis of **electrons in metals or photons in cavities**

Limits / Limitations

Canonical Ensemble:

- Number of particles (N) must be **fixed**; not suitable for open systems
- Assumes **thermal equilibrium**; not valid for non-equilibrium systems
- Difficult to apply to systems with **strong interactions** between particles

Grand Canonical Ensemble:

- Assumes **thermal and chemical equilibrium** with the reservoir
- Complex mathematical treatment due to **fluctuating particle number**
- Less accurate for **small systems**, where fluctuations are significant

Conclusion

Canonical and grand canonical ensembles are **powerful tools in statistical mechanics** that link **microscopic particle behavior** to **macroscopic thermodynamic properties**. The canonical ensemble is ideal for **closed systems with fixed particle number**, while the grand canonical ensemble is suited for **open systems with variable particle number**. Despite some limitations, these ensembles form the **foundation for deriving statistical distributions and understanding equilibrium properties** of matter.

2.2 DENSITY DISTRIBUTION IN THE PHASE SPACE

Introduction

In **statistical mechanics**, the **phase space** of a system is a multidimensional space in which each point represents a **unique state of the system**, defined by the positions and momenta of all particles. The **density distribution in phase space** describes how **representative points (or microstates) are distributed** over this space. It provides a **probabilistic description** of the system's microscopic states and serves as a foundation for connecting **microscopic behavior with macroscopic thermodynamic properties**.

The use of ensembles in statistical mechanics is guided by the following points:

1. There is no need to distinguish between different systems constituting an ensemble, because the laws of statistical mechanics aim to tell us only the number of systems or elements which would be found in different states i.e., in different regions of phase space at any time.

2. The number of systems in an ensemble is so large that there is a continuous change in their number passing from one region of phase space to another.

Keeping these points in mind, the condition of an ensemble at any time can be suitably specified by the density function with which the phase points are distributed in the phase space.

This density function is called the density of probability distribution or the probability densityor the distribution function.In an ensemble of f degrees of freedom, the density of distribution ρ is a function of f position coordinates $q_1, q_2, \dots, q_f$and f momenta coordinates $p_1, p_2, \dots, p_f$, corresponding to $2f$combined position–momentum axes in the phase space.The density of distribution is also a function of time *t*, because due to the motion of phase points, the density of distribution will change with time at any given point. Hence we can write:

$$\rho = \rho(q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_f, t)$$

or briefly,

$$\rho = \rho(q, p, t) \qquad (1)$$

Obviously, the density of distribution ρ denotes the number of systems or elements δN which are found at any given time in a given infinitesimal region of Γ-space.If the region chosen is such that the position coordinates lie between $q_i$and $q_i + dq_i$, and momenta lie between $p_i$and $p_i + dp_i$(i = 1, 2, 3, …, f), then the hypervolumedΓ of this region will be given by:

$$d\Gamma = dq_1 dq_2 \dots dq_f \; dp_1 dp_2 \dots dp_f = \prod_{i=1}^{f} dq_i dp_i \qquad (2)$$

Where $\prod_{i=1}^{f}$ stands for the product over all values of *i* = 1 to *f*.The number of systems δN lying in the specified infinitesimal region can be obtained by multiplying the density of distribution ρ with this hypervolume in the phase space, i.e.,

$$\delta N = \rho \, d\Gamma = \rho \prod_{i=1}^{f} dq_i dp_i \qquad (3)$$

Integrating over the entire phase space, we can obtain the total number of systems under consideration, i.e.,

$$N = \int \rho \, d\Gamma = \int \rho \, dq_1 dq_2 \dots dq_f \; dp_1 dp_2 \dots dp_f \qquad (4)$$

Sometimes it is convenient to work with the normalised density of distribution, given by

$$\rho_N = \frac{\rho(q, p, t)}{N} = \frac{\rho}{N} \qquad (5)$$

In this case, $\rho_N$expresses the probability of states represented by points per unit volume element in the phase space. In other words, ρN gives the probability per unit volume of finding the phase point for a system taken at random from the ensemble in different regions of the phase space.The function ρN must obviously satisfy the normalisation condition,

$$\int \rho_N \, d\Gamma = \int \rho_N \, dq_1 dq_2 \dots dq_f \; dp_1 dp_2 \dots dp_f = 1 \qquad (6)$$

Conclusion

The **density distribution in phase space** is a key concept in statistical mechanics, enabling the calculation of **ensemble averages, probabilities, and thermodynamic quantities**. It allows for a **quantitative link between the microscopic configuration of particles and observable macroscopic properties**, providing a deeper understanding of equilibrium and statistical behavior of physical systems

2.3 LIOUVILLE'S THEOREM

Introduction

Liouville's Theorem is a fundamental concept in **classical statistical mechanics**. It states that for a system of particles evolving under **Hamiltonian dynamics**, the **density of representative points in phase space remains constant with time**. In other words, as a system moves through its allowed phase space, the **phase space volume occupied by an ensemble of systems is conserved**. This theorem provides the **theoretical foundation for statistical ensembles** and connects **microscopic dynamics** with **macroscopic thermodynamic properties**.

Consider an ensemble consisting of a large number of identical, non-interacting systems.We know that the instantaneous state of a system can be represented by a point in the phase space.Similarly, the instantaneous states of other systems constituting the ensemble can be represented by other points in the phase space.Thus, the instantaneous state of the entire ensemble can be represented by a number of phase points in the phase space.The density of these points, also known as the density of states in the phase space, is denoted by ρ.If the state of an ensemble changes with time, the positions of phase points in the phase space will change with time.The motion of these phase points in the phase space is, of course, governed by the canonical equations:

$$\dot{q_\iota} = \frac{\partial H}{\partial p_i}, \dot{p_\iota} = -\frac{\partial H}{\partial q_i} \qquad (7)$$

(for$i = 1,2,3, \dots, f$for a system of$f$degrees of freedom)

Here $H = H(q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_f)$is the Hamiltonian of the system.

Due to the motion of phase points, the density of states in the phase space ρchanges with time.Liouville's theorem gives information about the rate of change of phase density in the phase space.The theorem may be stated in two parts:

1. The rate of change of density of phase points (representing systems) in the neighbourhood of a moving phase point (for which q's and p's are changing) in the Γ-space is zero. This part represents the principle of conservation of density in the phase space.Mathematically, this may be represented as

$$\frac{d\rho}{dt} = 0 \qquad (8)$$

in the immediate neighbourhood of any given moving phase point.

2. Any arbitrary element of volume or extension-in-phase in the Γ-space, bounded by a moving surface and containing a number of phase points, does not change with time despite the displacements and distortions.This part represents the principle of conservation of extension in phase space.Mathematically, this may be represented as

$$\frac{d}{dt}(\delta\Gamma) = \frac{d}{dt}(\prod_{i=1}^{f} dq_i dp_i) = 0 \qquad (9)$$

Applications

- Provides the **basis for statistical mechanics and ensemble theory** (microcanonical, canonical, grand canonical ensembles).

- Ensures **conservation of probability** in phase space, allowing calculation of **thermodynamic averages**.
- Used to derive **equilibrium distributions** of particles in phase space.
- Helps in understanding the **time evolution of systems in classical mechanics**.
- Forms the foundation for **molecular dynamics simulations** in physics and chemistry.
- Limits / Limitations
- Applicable only to **Hamiltonian systems**; does not hold for dissipative or non-conservative forces.
- Assumes **classical mechanics**; quantum effects require modification (quantum Liouville equation).
- Only valid for **closed systems** without external perturbations altering phase space volume.
- Does not directly provide **thermodynamic quantities**; it is a framework for further statistical calculations.

Conclusion

1. Canonical and Grand Canonical Ensembles

- **Canonical Ensemble:**
  - Represents systems with **fixed number of particles (N), volume (V), and temperature (T)**.
  - Systems can exchange **energy** with a heat reservoir.
  - Uses the **partition function (Z)** to calculate thermodynamic quantities like **internal energy, entropy, and free energy**.
  - Applicable for **closed systems**.
- **Grand Canonical Ensemble:**
  - Represents systems with **fixed chemical potential (μ), volume (V), and temperature (T)**.
  - Systems can exchange **both energy and particles** with a reservoir.
  - Uses the **grand partition function (Ξ)** to derive distributions like **Bose–Einstein and Fermi–Dirac**.
  - Applicable for **open systems**.

2. Density Distribution in Phase Space

- Describes the **distribution of representative points (microstates)** in the **6N-dimensional phase space** of a system.
- Connects **microscopic particle configurations** (positions & momenta) to **macroscopic thermodynamic properties**.
- Forms the basis for **ensemble averages**, **probability calculations**, and statistical mechanics formulations.
- Fundamental for deriving **equilibrium properties** in canonical, microcanonical, and grand canonical ensembles..

Liouville's theorem is a fundamental result of classical statistical mechanics describing how an ensemble of systems evolves in phase space. A canonical ensemble represents a large number of identical systems, each in thermal equilibrium with a heat reservoir at temperature T. A grand canonical ensemble describes systems that can exchange both energy and particles with a reservoir.

2.5 TECHNICAL TERMS

Canonical and grand canonical ensemble
Density distribution in the phase space
Liouville’s theorem

2.6 SELF ASSESSMENT QUESTIONS

1. Explain about the Canonical and grand canonical ensemble
2. Write about the Density distribution in the phase space
3. Write about the Liouville’s theorem

2.7 SUGGESTED READINGS

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics: Theory and applications by S.K. Sinha
3. Fundamentals of Statistical and Thermal Physics by F. Reif
4. Statistical Mechanics by Gupta and Kumar, PragatiPrakashan Pub. Meerut.
5. Statistical Mechanics by Satya Prakash

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LESSON-3

EQUIPARTITION OF ENERGY THEOREM

AIM AND OBJECTIVE

Aim

The aim of studying the **equipartition of energy theorem** is to understand how thermal energy is distributed among the various microscopic degrees of freedom of a physical system in thermal equilibrium and to establish a quantitative relationship between temperature and average energy at the microscopic level.

Objectives

- To explain the concept of **degrees of freedom** in classical mechanical systems.
- To show that each independent quadratic degree of freedom contributes an average energy of k_BT.
- To apply the equipartition theorem to calculate the **internal energy** of ideal gases.
- To use the theorem to determine **molar heat capacities** of mono atomic, diatomic, and polyatomic gases.
- To understand the role of equipartition in explaining macroscopic thermodynamic properties from microscopic motion.
- To recognize the **limitations of classical equipartition theory**, particularly its failure at low temperatures, leading to the necessity of quantum theory

STRUCTURE OF THE LESSON:

3.1 EQUIPARTITION OF ENERGY THEOREM

Introduction

The equipartition of energy theorem is one of the fundamental results of classical statistical mechanics. It provides a direct connection between temperature and the average energy associated with the microscopic degrees of freedom of a system in thermal equilibrium. According to this theorem, energy is shared equally among all independent degrees of freedom that appear quadratically in the expression for the total energy. The equipartition theorem plays a crucial role in explaining the thermal properties of gases and solids, such as internal energy and heat capacity, and it establishes a deep link between microscopic motion and macroscopic thermodynamic behavior.

Although highly successful in classical physics, the equipartition theorem also highlights the limitations of classical statistical mechanics and motivates the development of quantum theory, particularly in explaining deviations observed at low temperatures.

Key Points of the Equipartition Theorem:

- **Degree of freedom**: Each independent way in which a system can store energy (such as translational, rotational, or vibrational motion) is called a degree of freedom.
- The energy associated with each degree of freedom is, on average$\frac{1}{2}\mathrm{k_B T}$, where$\mathrm{k_B}$ is the **Boltzmann constant** and T is the **temperature** of the system.
- This theorem applies to **classical** systems, where particles obey classical mechanics.

1. General Form of the Equipartition Theorem

In classical statistical mechanics, the **average energy**⟨E⟩ of a system in thermal equilibrium is related to its degrees of freedom. For each degree of freedom iii, the average energy associated with that degree is:

$\langle E_i \rangle = \frac{1}{2}\mathrm{k_B T}$

The total average energy of the system is then the sum of the contributions from all the degrees of freedom:

$$< E >= \sum_i E_i = \frac{1}{2}\mathrm{k_B T}$$

(Number of degrees of freedom)
This result assumes that the system is classical and that there are no quantum mechanical effects influencing the energy distribution (i.e., the system is in the classical regime where each degree of freedom is independent and behaves according to the **Maxwell-Boltzmann distribution**).

2. Applications of the Equipartition Theorem

The equipartition theorem can be applied to different types of motion (translational, rotational, and vibrational) of particles. Let's look at a few common examples:

a. Monatomic Ideal Gas
For a **monatomic ideal gas**, each particle can move in three dimensions (x, y, z), and each of these translational degrees of freedom contributes $\frac{1}{2}\mathrm{k_B T}$ to the total energy. So, the total energy per particle is:

$\langle E_{total} \rangle = \frac{3}{2}\mathrm{k_B T}$

This means that each particle in a monatomic ideal gas has an average energy of $\frac{3}{2}\mathrm{k_B T}$ which is purely translational (since there are no internal degrees of freedom such as rotation or vibration).

b. Diatomic Ideal Gas
For a **diatomic ideal gas**, a molecule has **3 translational degrees of freedom** (corresponding to motion in the x, y, and z directions) and **2 rotational degrees of freedom** (since it is a rigid body and can rotate around two axes perpendicular to the bond axis, but it cannot rotate

around the bond axis because it is highly constrained in this direction). If the gas is in the **classical regime**, the total energy per molecule is:

$$\langle E_{total}\rangle=\frac{3}{2}\mathrm{k_B T}+\frac{2}{2}\mathrm{k_B T}=\frac{5}{2}\mathrm{k_B T}$$

This accounts for both the translational and rotational contributions to the energy. If the system is at high temperatures where the vibrational modes become excited, each vibrational mode (which has two degrees of freedom: potential energy and kinetic energy) would contribute an additional kBTk_BTkBT. In that case, for high-temperature limits:

$$\langle E_{total}\rangle=\frac{3}{2}\mathrm{k_B T}+2.\frac{2}{2}\mathrm{k_B T}+\frac{1}{2}\mathrm{k_B T}=5\mathrm{k_B T}$$

c. Polyatomic Molecules (e.g., Triatomic Gas)

For a **polyatomic molecule**, such as a **triatomic molecule** (e.g., water vapor), the energy contributions can come from:

- **3 translational degrees of freedom**,
- **3 rotational degrees of freedom** (in the classical approximation for nonlinear molecules),
- **3 vibrational modes** (each contributing two degrees of freedom, corresponding to the potential and kinetic energy components).

Thus, in the classical limit (high temperature):

$$\langle E_{total}\rangle=\frac{3}{2}\mathrm{k_B T}+3.\frac{1}{2}\mathrm{k_B T}+\frac{1}{2}\mathrm{k_B T}=\frac{9}{2}\mathrm{k_B T}$$

At higher temperatures where vibrational modes are fully excited, each vibrational mode will contribute ,$\mathrm{k_B T}$so the total energy would be:

$$\langle E_{total}\rangle=\frac{9}{2}\mathrm{k_B T}+3.\frac{1}{2}\mathrm{k_B T}=\frac{15}{2}\mathrm{k_B T}$$

Limitations of the Equipartition Theorem

Despite its success, the equipartition theorem has important limitations:

- It fails at low temperatures,
- It cannot explain the temperature dependence of heat capacities,
- It does not apply to quantum systems where energy levels are discrete.

For example, classical theory predicts a constant heat capacity for solids, whereas experimentally the heat capacity decreases at low temperatures. This discrepancy led to the development of quantum theories such as Einstein's and Debye's models of solids.

Importance and Significance

The equipartition theorem is important in:

- Understanding molecular motion,
- Explaining ideal gas behavior,
- Estimating internal energies,
- Studying classical limits of quantum systems.

It provides deep insight into how energy is distributed in classical systems.

Conclusion

The equipartition of energy theorem is a cornerstone of classical statistical mechanics, establishing that energy is equally shared among all quadratic degrees of freedom in thermal equilibrium. It successfully explains the internal energy and heat capacities of gases at high temperatures and provides a clear connection between microscopic motion and macroscopic thermodynamic quantities. However, its failure at low temperatures reveals the limitations of classical physics and underscores the necessity of quantum mechanics. Despite these limitations, the equipartition theorem remains a powerful and elegant principle in the study of statistical mechanics.

3.2 MACROSTATES AND MICROSTATES

Introduction

Statistical mechanics provides a bridge between the microscopic laws governing atoms and molecules and the macroscopic laws of thermodynamics. Two fundamental concepts that enable this connection are **microstates** and **macrostates**. While thermodynamics describes systems using a small number of macroscopic variables such as temperature, pressure, and volume, statistical mechanics explains these quantities in terms of the vast number of microscopic configurations available to a system.

The distinction between macrostates and microstates is central to understanding entropy, probability, and the direction of spontaneous processes. The concepts also form the foundation for ensemble theory and the statistical interpretation of the laws of thermodynamics.

Let us consider an ensemble consisting of a large number of independent systems or a gas consisting of a large number of molecules, in the phase space. Each system or molecule may be represented by point known as phase point or representative point in the phase space. Let the phase space be divided into cells numbered 1, 2, 3, … i, etc. adjoining one another and having a volume equal to

$$\delta q_1\, \delta q_2\, \ldots\, \delta q_f\, \delta p_1\, \delta p_2\, \ldots\, \delta p_f$$

A phase point for any system or molecule may be supposed to lie inside one of these cells. In order to define the microstate of the ensemble we must specify the individual position of phase points for each system or molecule of the ensemble. In other words, we must state to which cell each system or molecule belongs temporarily. Such a deep analysis is quite unnecessary to determine the observable properties of any ensemble (or gas). For example, the density is same if the number of molecules in each volume element of ordinary space is the same regardless of which particular moleculelie in any volume element.

A macrostate of the ensemble may be defined by the specification of the number of phase points (i.e., system or molecules) in each cell of phase space such asn_1 phase points are in cell 1, n_2 phase points are in cell 2,
n_3 phase points are in cell 3, and so on.

Many different microstates may correspond to the same macrostate.For example, let us identify the phase points as $a, b, c,$ ...etc.Let a particular microstate be specified by stating that the phase points $a, c, h$are in cell 1, $b, e$are in cell 2, $f$is in cell 3, and so on as shown in Fig. 3.1.The corresponding macrostate is specified merely by giving the number of phase points:$n_1(= 3)$ in cell 1; $n_2(= 2)$ in cell 2; $n_3(= 1)$ in cell 3, and so on.If we interchange any two phase points from different cells say $a$and b we shall have different microstates, but the same macrostate.On the other hand, if we interchange the two phase points in the same cell say $a$and c we shall have the same microstate as well as the same macrostate.If the systems of the ensemble are in constant motion, just like the molecules of a gas, the ensemble is continuously and spontaneously changing from one microstate to another and almost as frequently from one macrostate to the other.

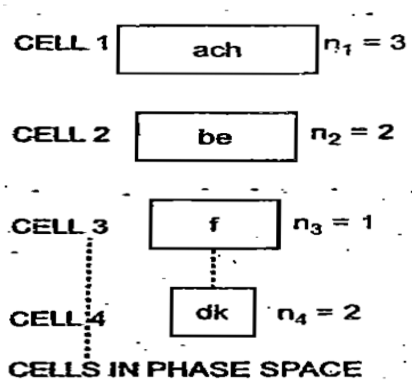

Fig. 3.1

The microstates which are allowed under given restriction are called accessible microstates.For example, in the case of 3 molecules $a, b, c$to be distributed between two halves of a box, if none can be outside the box, then:$(ab, c), (a, bc), (ac, b)$are accessible microstates, while$(a, b), (a, c), (b, c)$are inaccessible microstates.One of the most fundamental postulates of statistical mechanics is that:All accessible microstates corresponding to possible macrostates are equally probable.In other words, this states that the probability of finding the phase point in any one region is identical with that for any other region of equal volume, provided the regions correspond equally well with the given conditions. Thus, this postulate of equal *a priori* probability implies that the probability of occurrence of a given macrostate is proportional to the number of microstates that correspond to that macrostate.The number of microstates corresponding to a given macrostate is called the thermodynamic probability of the macrostate.Hence, the probability that the ensemble will possess energy $E$is proportional to $\Omega(E)$, i.e.,

$$P(E) = C\,\Omega(E)$$

Where$C$= constant of proportionality and $\Omega(E)$=thermodynamic probability

Importance and Applications

The concepts of macrostates and microstates are essential for:

- Understanding entropy and equilibrium,
- Deriving thermodynamic laws,
- Analyzing fluctuations,
- Studying phase transitions,
- Developing quantum statistical mechanics.

They form the conceptual foundation of statistical physics.

Limitations of microstate and macrostate

Microstate:

- Describes exact positions/momenta of all particles i.e impractical for large systems(too much info)

- Quantum effects(uncertainty) make precise tracking hard
- **Macrostate:**
- Doesn't give microscopic details (many microstates→ same macrostate)
- Assumes equilibrium (doesn't describe non-equilibrium systems well)

Conclusion

Macrostates and microstates provide the fundamental framework through which statistical mechanics connects microscopic dynamics with macroscopic thermodynamic behavior. A macrostate represents an incomplete but practical description of a system, while microstates provide a complete microscopic specification. The enormous number of microstates associated with equilibrium macrostates explains the statistical nature of thermodynamic laws and the tendency toward equilibrium. Through Boltzmann's entropy formula, the concepts of macrostates and microstates acquire profound physical significance, making them indispensable in the understanding of equilibrium and irreversible processes.

3.3 SUMMARY

The equipartition theorem states that in thermal equilibrium, each quadratic degree of freedom in a system's energy contributes an average of $\frac{1}{2}k_BT$, where k_B is Boltzmann's constant and T is temperature. This principle explains heat capacities: monatomic gases have three translational degrees, yielding $\frac{3}{2}k_BT$ per molecule, while diatomic gases add rotational freedoms for higher values.

Microstates and Macrostates

A macrostate describes observable properties like energy, volume, and particle number, while microstates are specific atomic configurations yielding that macrostate. Many microstates correspond to one macrostate; statistical mechanics averages over them assuming equal a priori probabilities in isolated systems.

3.4 TECHNICAL TERMS

Equipartition of energy theorem
Macrostates and Microstates

3.5 SELF ASSESSMENT QUESTIONS

1. Explain about the Equipartition of energy theorem
2. Write about the Macrostates and Microstates

3.7 SUGGESTED READINGS

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics: Theory and applications by S.K. Sinha
3. Fundamentals of Statistical and Thermal Physics by F. Reif
4. Statistical Mechanics by Gupta and Kumar, Pragati Prakashan Pub. Meerut.
5. Statistical Mechanics by Satya Prakash

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LESSON-4

PARTITION FUNCTION FOR CANONICAL AND MICRO CANONICAL ENSEMBLE

AIM AND OBJECTIVE

Aim

The aim of studying the **partition function** in canonical and microcanonical ensembles is to provide a **mathematical framework** that connects the **microscopic states of a system** to its **macroscopic thermodynamic properties**, such as energy, entropy, and free energy.

Objectives

Canonical Ensemble Partition Function

- To calculate the **probability of a system occupying a particular energy state** at fixed N, V, and T.
- To determine **thermodynamic quantities** like internal energy, Helmholtz free energy, entropy, and heat capacity.
- To understand the role of **energy exchange with a heat reservoir**.
- To derive **Boltzmann distribution** and link microscopic behavior to macroscopic properties.

Microcanonical Ensemble Partition Function

- To describe **isolated systems** with fixed N, V, and total energy E.
- To calculate the **number of accessible microstates** at a given energy.
- To evaluate **entropy, temperature, and pressure** of an isolated system.
- To establish the **foundation for statistical mechanics** in systems where energy is strictly conserved.

STRUCTURE OF THE LESSON:

4.1 CLASSICAL IDEAL GAS IN MICRO CANONICAL ENSEMBLE

The **microcanonical ensemble** is one of the statistical ensembles used to describe thermodynamic systems, and it corresponds to an isolated system that does not exchange energy, particles, or volume with its surroundings. In this ensemble, all accessible microstates of the system are equally probable, and the total energy of the system is fixed.

Classical Ideal Gas in the Microcanonical Ensemble

Statistical entropy for an n particle system
Let us consider a system which consists of n point particles in the volume V and energy δE around its total energy E.
The corresponding volume of 6N dimensional phase space is given by

$\Delta p = \int dq_1\, dq_2 \dots dq_3N \int dp_1\, dp_2 \dots dp_3N$ (1)

$\int dq_1\, dq_2 \dots dq_3N = \int dx_1\, dy_1\, dz_1 \int dx_2\, dy_2\, dz_2 \dots \int dx_n\, dy_n\, dz_n$

$= V \cdot V \cdot V \dots V$

$= V^n$

Therefore,

$\Delta p^T = V^n \int dp_1\, dp_2 \dots dp_3N$ (2)

From Eq. (2) the momentum integral is evaluated subject to the following constraint imposed by the microcanonical ensemble:

$E - \delta E \leq E_r \leq E$

Where

$E_r = \sum_{i=1}^{3n} (p_i^2 / 2m)$ for i = 1 to 3N

i.e.,

$E - \delta E \leq \sum_{i=1}^{3n} (p_i^2 / 2m) \leq E$

The integral in Eq. (2) is equal to the volume contained between a 3N-dimensional hyper sphere of radius $(2mE)^1/2$
and 3N-dimensional hyper sphere of radius $[2m(E - \delta E)]^1/2$.
The volume of an N-dimensional hyper sphere of radius R is given by:

$V_n(R) = C_n R^n$

where,

$$C_n = \frac{\pi^{n/2}}{\sqrt{\frac{n+2}{2}}} = \frac{\pi^{n/2}}{\sqrt{\frac{n}{2}}}$$

For a 3-dimensional sphere is given by,

$V_3(R) = (4/3)\pi R^3$

$V_3(R)\ C_3 R^3$ where $C_3 = (4/3)\pi$

This can also be written as:

$C_3 = \frac{\pi^{3/2}}{\sqrt{\frac{3}{2}+1}}$ ……….. (3)

In general,

$C_n = = \frac{\pi^{n/2}}{\sqrt{\frac{n}{2}+1}}$

Therefore,

$C_{3n} = \frac{\pi^{3n/2}}{\sqrt{\frac{3n}{2}+1}}$

$C_{3n} = \frac{\pi^{3n/2}}{\sqrt{\frac{3n}{2}+1}} V_{3n}(R) = C_{3n}R^{3n}$

Hence, the volume of a 3N-dimensional hyper sphere of radius (2mE) is:

$$C_{3n} = \frac{\pi^{3n/2}}{(\frac{3n}{2})!}(2mE)^{3n/2} \quad \dots\dots\dots\dots\dots\dots \quad (4)$$

Similarly, the volume of a 3N-dimensional hyper sphere of radius $[2m(E - \delta E)]^{1/2}$is:

$V_{3n} = \frac{\pi^{3n/2}}{(\frac{3n}{2})!}[2m(E - \delta E)]^{1/2}$ (5)

Equations (4) -(5) give the momentum space, i.e., the integral in Eq. (2).

$\int dp_1 \quad dp_2 \quad \dots \quad dp_{3n}$

$= \frac{\pi^{3n/2}}{(\frac{3n}{2})!}(2mE)^{3n/2} - [2m(E - \delta E)]^{3n/2}]$

$= \frac{\pi^{3n/2}}{(\frac{3n}{2})!}(2mE)^{3n/2}[1 - (1 - \frac{\delta E}{E})]^{3n/2}$ (6)

For a macroscopic system, where $3n \approx 10^{23}$ and

$(3n/2)\ \delta E >> E$

We know that:

$(1 - x)^n = 1 - nx + \frac{n(n-1)}{2!}x^2 + \dots\dots$

For sufficiently large n,

$(1 - x)^n = 1 - nx + \frac{n^2x^2}{2!} - \frac{n^3x^3}{3!} + e^{-nx}$

Using Eq. (6):

$\int dp_1\, dp_2 \ldots dp_{3n}$

$= \frac{\pi^{3n/2}}{(\frac{3n}{2})!}(2mE)^{3n/2} - [1 - e^{\frac{-\delta E}{E}\frac{3n}{2}}]$

$= \frac{\pi^{3n/2}}{(\frac{3n}{2})!}(2mE)^{3n/2}$ (7)

Macroscopic system that is the 3n ≈ 10^{23} and (3n/2) δE>> E

we know that

$(1 - x)^n = 1 - nx + \frac{n(n-1)}{2!}x^2 + \ldots\ldots$

where ‘n’ is sufficiently large

$(1 - x)^n = 1 - nx + \frac{n^2x^2}{2!} - \frac{n^3x^3}{3!} + \cdots \ldots \ldots \ldots .\, e^{-nx}$

From equation (7)

$\int dp_1\, dp_2 \ldots dp_{3n} = \frac{\pi^{3n/2}}{(\frac{3n}{2})!}(2mE)^{3n/2}[1 - e^{\frac{-dE3n}{E\ 2}}]$

$= \frac{\pi^{3n/2}}{(\frac{3n}{2})!}(2mE)^{3n/2}$

From equation (2)

$\Delta P = V^n \cdot \frac{\pi^{3n/2}}{(\frac{3n}{2})!}(2mE)^{3n/2}$ (8)

The statistical entropy σ of a system is defined as:

$\sigma = log_e\, \Delta P$

$= log_e\ [V^n \cdot \frac{\pi^{3n/2}}{(\frac{3n}{2})!}(2mE)^{3n/2}$

$= n\, log_e\ V\, (2\pi mE)^{3n/2} - log_e \frac{3n}{2}!$ —— (9)

Using Stirling’s approximation:

$log_e\, n! \approx n\, log_e\, n - n$

Applying Stirling’s approximation to Eq. (9):

$\sigma = n\, log_e V(2\pi mE)^{3n/2} - \frac{3n}{2} log_e \frac{3n}{2} + \frac{3n}{2}$

$= n\ log_e\, [\, V\, (4\pi mE)^{3/2}(\frac{E}{n})^{3/2}]\frac{3n}{2}$ —— (10)

$\sigma = log_e \Delta p$

$\sigma = log_e \frac{\Delta T}{h^{3n}}$

Also,

$$\sigma = nlog_e \left[\frac{V(\frac{4\pi m}{3})^{3/2}(\frac{E}{n})^{3/2}}{h^{3n}}\right] + \frac{3n}{2}$$

$$= nlog_e \left[V(\frac{4\pi m}{3h^2})^{3/2}(\frac{E}{n})^{3/2}\right] + \frac{3n}{2} \text{——} (11)$$

However, Eq. (10) does not satisfy the additive property of volume is.

Hence, the corrected expression is:

$$\sigma = \ log_e[\frac{\Delta T}{h^{3n}n!}]$$

$$\sigma = nlog_e \left[V(\frac{4\pi m}{3h^2})^{3/2}(\frac{E}{n})^{3/2}\right] + \frac{3n}{2} - nolgn + n$$

$$\sigma = nlog_e \left[{}^{V}/_{n}\,(\frac{4\pi m}{3h^2})^{3/2}(\frac{E}{n})^{3/2}\right] + \frac{5n}{2} \qquad \ldots\ldots\ldots\ldots(12)$$

which is the statistical entropy for ‘n’ particle system

4.2PARTITION FUNCTION FOR MICRO CANONICAL ENSEMBLE

In the microcanonical ensemble, a system is characterized by:

- Fixed energy : E
- Fixed number of particles : N
- Fixed volume : V

There is no exchange of energy or particles with the surroundings. Therefore, all accessible microstates having energy within a very small energy window [E,E+δE] are equally probable.

1. Definition of Microcanonical Partition Function

The microcanonical “partition function’’ is the density of states or multiplicity:

$$\Omega(\mathrm{E,V,N}) = \text{Number of microstates with energy between E and E} + \delta\mathrm{E}$$

This is sometimes called the structure function or state count.

For classical systems, it is written as:

$$\Omega(\mathrm{E,V,N}) = \frac{1}{\mathrm{h^{3n}\,N!}} \quad \mathrm{H(p,q)} \in [\mathrm{E, E} + \delta\mathrm{E}] \quad \mathrm{d^{3N}\,q\,d^{3N}\,p}$$

Often expressed using the Dirac delta function:

$$\Omega(\mathrm{E,V,N}) = \frac{1}{\mathrm{h^{3n}\,N!}} \ \delta\mathrm{E} - \ \mathrm{H(p,q)} \ \mathrm{d^{3N}\,q\,d^{3N}\,p}$$

2. Entropy in Microcanonical Ensemble

Entropy is defined using Boltzmann’s formula:

$$S(E,V,N) = k_B ln\Omega(\mathrm{E,V,N})$$

This entropy leads to all thermodynamic quantities.
For example:
Temperature

$$\frac{1}{T} = (\frac{\partial S}{\partial E})_{V,N}$$

Pressure

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

Chemical Potential

$$-\frac{\mu}{T} = (\frac{\partial S}{\partial N})_{E,V}$$

3. Relation to Other Ensembles

While the canonical ensemble uses:

$$Z = \sum_i e^{-\beta E_i}$$

the microcanonical ensemble uses:
$\Omega(\mathrm{E})$
Instead of probability weights$e^{-\beta E}$, microcanonical ensemble assigns equal probability to all states:

$$P_i = \begin{cases} \dfrac{1}{\Omega(\mathrm{E})} & E_i = E \\ 0 & otherwise \end{cases}$$

4. Example: Ideal Gas (Microcanonical)

For a 3D ideal gas:

$$\Omega(E,V,N) = \frac{V^N}{\mathrm{h^{3n}\,N!}} \frac{(^{2\pi mE)^{3N/2}}}{\Gamma(^{3N}/_2 + 1)}$$

This leads to:

$$S = k_B\ N \ln\frac{V}{N} + \frac{3N}{2}\ln E + \frac{3N}{2}\ln(2\pi m) - \ln \mathrm{h^{3n}}\ - \ln N!$$

which becomes the Sackur–Tetrode equation after using Stirling's approximatio

4.3 GIBB'S PARADOX

Introduction

Gibbs' Paradox arises in classical **thermodynamics and statistical mechanics** when calculating the **entropy of mixing** of two ideal gases. According to classical theory, mixing two identical gases results in an **increase in entropy**, which is physically incorrect because no real change occurs when identical gases mix. This paradox highlights the **limitations of classical statistical mechanics** and the need to account for the **indistinguishability of particles** in quantum mechanics. Resolving Gibbs' paradox leads to the correct formulation of **entropy for identical particles**, forming the foundation of **quantum statistical mechanics**.

The partition function of a perfect gas is given by

$$Z = \frac{V}{h^3}(2\pi mkT)^{3/2} \qquad (1)$$

From statistical thermodynamics, the entropy is expressed as

$$S = Nklog\ Z + \frac{3}{2}Nk \qquad (2)$$

Substituting the value of $Z$from equation (1), we get

$$S = Nklog\ _e[\frac{V}{h^3}(2\pi mkT)^{3/2}] + \frac{3}{2}Nk \qquad (3a)$$

This expression can also be rewritten as

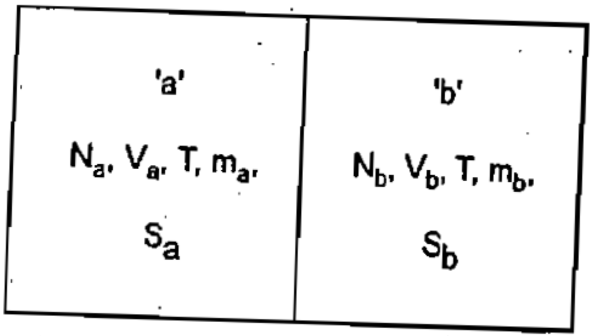
$$S = Nk[log\ _e V + \frac{3}{2}log\ _e m + \frac{3}{2}log\ _e T + C] \qquad (3b)$$

Where $C$is a constant term that includes the fixed factors $h$and k.

Non-Additivity and the Gibb's Paradox: The entropy derived from the above equation does not satisfy the additive property of entropy.Consequently, this leads to paradoxical results, which is known as the Gibb's Paradox.To illustrate this, consider two systems, denoted by indices 'a' and 'b', held at the same temperature:

$$T_a = T_b = T$$

and separated by a partition as shown in Fig. 5.2



If the particles of the two systems are different, then using equation (3b), the entropies of systems 'a' and 'b' are given respectively by:

$$S_a = N_a k[log\ _e V_a + \frac{3}{2}log\ _e m_a + \frac{3}{2}log\ _e T + C]$$

and

$$S_b = N_b k[log\ _e V_b + \frac{3}{2}log\ _e m_b + \frac{3}{2}log\ _e T + C]$$

For the two systems shown in Fig. 7.5, the entropies are

$$S_a = N_a k[log\ U_a + \frac{3}{2} log\ m_a + \frac{3}{2} log\ T + C_1] \qquad (4a)$$

$$S_b = N_b k[log\ U_b + \frac{3}{2} log\ m_b + \frac{3}{2} log\ T + C_1] \qquad (4b)$$

Where N_a, m_a, V_arefer respectively to the number of particles, the mass of each particle, and the volume of system ‘a’; and N_b, m_b, V_brefer to the corresponding quantities for system ‘b’.Since entropy is an extensive quantity, it must satisfy the additive property. If the two gases are allowed to mix freely by removing the partition, the total entropy of the combined system should be

$$S_{ab} = S_a + S_b = N_a k[log\ V_a + \frac{3}{2} log\ m_a + \frac{3}{2} log\ T + C] +$$

$$N_b k\left[lo\,g\,V_b + \frac{3}{2} lo\,g\,m_b + \frac{3}{2} lo\,g\,T + C\right] \qquad (5)$$

If the particles of the two systems are identical, and for convenience we take $V_a = V_b = V$and $N_a = N_b = N$, the entropy of each individual system is

$$S = Nk[log\ V + \frac{3}{2} log\ m + \frac{3}{2} log\ T + C] \qquad (6)$$

Then the combined entropy would be

$$S_{ab} = S_a + S_b = 2Nk[log\ V + \frac{3}{2} log\ m + \frac{3}{2} log\ T + C] \qquad (7)$$

If the partition is removed so that the molecules of the gas can mix freely, the total volume becomes $2V$, and the total number of particles becomes $2N$.Substituting these into equation (3b) for entropy, we have

$$S_{ab} = 2Nk[log\ 2V + \frac{3}{2} log\ m + \frac{3}{2} log\ T + C]$$

$$\Rightarrow S_{ab} = 2Nk[log\ V + \frac{3}{2} log\ m + \frac{3}{2} log\ T + C] + 2Nklog\ 2$$

$$\boxed{S_{ab} = S_a + S_b + 2Nklog\ 2} \qquad (8)$$

Equation (8) is not consistent with (7); it contains an extra term $2Nklog\ 2$. This indicates that when two identical gases are mixed, the entropy increases by an unaccountable amount $2Nklog\ 2$, even though no real physical change has occurred.This additional, non-physical entropy is known as the entropy of mixing, and the contradiction it produces is the Gibb’s Paradox.If we used equation (3) directly for entropy, entropy would appear non-extensive, since entropy (being an extensive thermodynamic function) should be additive for identical subsystems.

4.4 PARTITION FUNCTION FOR CANONICAL ENSEMBLE

1. Canonical Ensemble Basics

A canonical ensemble describes a system that is:

- In thermal equilibrium with a heat bath
- Has fixed number of particles N, volume V, and temperature T
- Energy is not fixed; the system exchanges energy with the reservoir

The fundamental probability postulate:
$P_i \propto e^{-\beta E_i}$
where

$$\beta = \frac{1}{k_B T}$$

2. Definition of the Canonical Partition Function Z

The canonical partition function normalizes the Boltzmann probabilities:

$Z = \sum_i e^{-\beta E_i}$

For continuous energy levels or phase space integrals,

$Z = \frac{1}{h^{3n}\,N!} e^{-\beta H(p,q)}\ d^{3N} p\, d^{3N} q$

3. Probability of the System Being in State i

$$P_i = \frac{e^{-\beta E_i}}{Z}$$

4. Helmholtz Free Energy from Partition Function

The Helmholtz free energy is:

$F = -k_B T \ln Z$

From this, all thermodynamic quantities follow.

5. Mean Energy

$$< E >= -\frac{\partial}{\partial \beta} \ln z$$

6. Entropy

$$S = -(\frac{\partial F}{\partial T})_V$$

Or directly using Z:

$S = k_B(\ln Z + \beta\langle E\rangle)$

7. Heat Capacity at Constant Volume

$$C_V = (\frac{\partial < E >}{\partial T})_V$$

Another form:

$C_V = k_B \beta^2 < E^2 > - < E^2 >$

8. Example: Canonical Partition Function of a Single Harmonic Oscillator

$$Z = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta\hbar\omega(n+\frac{1}{2})}$$

Geometric series:

$$\boldsymbol{Z} = \frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1 - \mathrm{e}^{-\beta\hbar\omega/}}$$

4.5 SUMMARY

The canonical partition function encodes all equilibrium properties of a system at fixed temperature, volume, and particle number. In the canonical ensemble, a system is in thermal contact with a heat bath at temperature T, so its energy can fluctuate while N and V remain fixed. Gibbs paradox arises when treating identical particles as distinguishable in classical entropy calculations, leading to an unphysical entropy increase upon mixing identical gases. It appears as a discontinuity: mixing different gases gives extra entropy, but naively mixing the same gas also gives the same entropy change, contradicting physical intuition. The resolution is to recognize particle indistinguishability and divide the classical partition function by N!, removing the overcounting of microstates. This modification makes the entropy extensive and eliminates the paradox, and is naturally justified in quantum statistical mechanics.

4.6 TECHNICAL TERMS

Classical ideal gas in micro canonical ensemble
Partition function for micro canonical ensemble
Gibb's paradox
Partition function for Canonical ensemble

4.7 SELF ASSESSMENT QUESTIONS

1. Explain about the Partition function for micro canonical ensemble
2. Briefly explain about the Gibb's paradox
3. Write about the Partition function for Canonical ensemble
4. Explain about the Classical ideal gas in micro canonical ensemble

4.8 Suggested Readings

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics: Theory and applications by S.K. Sinha
3. Fundamentals of Statistical and Thermal Physics by F. Reif
4. Statistical Mechanics by Gupta and Kumar, Pragati Prakashan Pub. Meerut.
5. Statistical Mechanics by Satya Prakash

Prof. Sandhya Cole

LESSON-5

THERMO DYNAMICAL FUNCTION FOR CANONICAL AND GRAND CANONICAL ENSEMBLE

AIM AND OBJECTIVE

Aim

The aim of studying **thermodynamical functions in canonical and grand canonical ensembles** is to **connect microscopic statistical behavior of particles** to **macroscopic thermodynamic quantities** (like energy, entropy, and free energy) and to provide a **mathematical framework for predicting equilibrium properties** of systems in contact with a reservoir.

Objectives

Canonical Ensemble

- To derive thermodynamic functions such as **Helmholtz free energy (F)**, **internal energy (U)**, **entropy (S)**, and **specific heat (C)** using the **partition function (Z)**.
- To relate **microscopic energy states** to macroscopic observables at **fixed N, V, and T**.
- To calculate **probabilities of occupation** of energy levels and their contribution to thermodynamic quantities.
- To provide a framework for studying **thermal equilibrium properties** of closed systems.

Grand Canonical Ensemble

- To derive thermodynamic functions such as **Grand potential (Φ or Ω)**, **average particle number (<N>)**, **entropy (S)**, and **pressure (P)** using the **grand partition function (Ξ)**.
- To account for **energy and particle exchange** with a reservoir (**variable** N) at **fixed μ, V, and T**.
- To study **open systems**, including derivation of **Bose–Einstein and Fermi–Dirac distributions**.
- To connect microscopic statistical behavior with **macroscopic thermodynamic properties** in systems with fluctuating particle numbers.

STRUCTURE OF THE LESSON:

5.1 THERMO DYNAMICAL FUNCTION FOR CANONICAL ENSEMBLE

Introduction

In statistical mechanics, thermodynamical functions describe the macroscopic properties of a system in equilibrium in terms of microscopic statistical quantities. The **canonical ensemble** is particularly important because it represents a system in thermal equilibrium with a heat reservoir at a fixed temperature. In this ensemble, the system is allowed to exchange energy with the surroundings, while the volume and number of particles remain constant. As a result, the energy of the system fluctuates, but the temperature is fixed.

The canonical ensemble provides a powerful framework for deriving all thermodynamical functions from a single central quantity—the **canonical partition function**. Once the partition function is known, quantities such as internal energy, entropy, free energy, pressure, and heat capacity can be obtained systematically. This makes the canonical ensemble one of the most widely used tools in equilibrium statistical mechanics.

1. Helmholtz free energy F

$F(T, V, N) = -k_B T \ln Z$

(Generates equilibrium thermodynamics at fixed (T,V,N.)

2. Internal energy U (mean energy)

$$U =< E >= -\frac{\partial}{\partial \beta}\ln Z = -\frac{\partial \ln Z}{\partial \beta}$$

Equivalently $U = -\frac{\partial \ln Z}{\partial \beta}$ or $U = -\frac{\partial}{\partial \beta}\ln Z$

Using $U = F - T\ (\frac{\partial F}{\partial T})_{,V,N}$

3. Entropy S

$$S = (\frac{\partial F}{\partial T})_{,V,N} = k_B(\ln Z + \beta U)$$

(Statistical form: $S = -k_B \sum_i P_i \ln P_i$ with $P_i = e^{-\beta E_i/z}$

4. Pressure P

$$P = -(\frac{\partial F}{\partial V})_{,T,N}$$

(Equivalent to the mechanical average of $-\frac{\partial H}{\partial V}$ when expressed from phase-space.)

5. Chemical potential μ

For systems where N is variable you normally switch to grand canonical, but one can define:

$$\mu = (\frac{\partial F}{\partial N})_{,T,V}$$

(Useful when treating N as continuous or when comparing free energies of systems with different N.)

6. Heat capacity at constant volume C_V

$$C_V = (\frac{\partial U}{\partial T})_{V,N} = \frac{\partial}{\partial T} = \frac{\partial \ln Z}{\partial \beta}$$

Statistical fluctuation form:

$$C_V = \frac{< E >^2 - < E >^2}{k_B T^2} \rightarrow Ver(E) = (\Delta E)^2 = k_B T^2 C_V$$

7. Higher derivatives / response functions (quick list)

- Isothermal compressibility k_T can be expressed from ∂P/∂V at constant T.
- Thermal expansion $\alpha = \frac{1}{V}(\frac{\partial V}{\partial T})_P$ — normally computed from free energies and Maxwell relations.

8. Useful identities (compact)

$$F = -k_B T \ln Z$$

$$U = -\frac{\partial}{\partial \beta}\ln Z$$

$$S = k_B(\ln Z + \beta U)$$

$$P = -(\frac{\partial F}{\partial V})_{,T,N}$$

$$\mu = (\frac{\partial F}{\partial N})_{,T,V}$$

$$C_V = \frac{\partial U}{\partial T} - \frac{\mathrm{Var(E)}}{k_B T^2}$$

Limitations of the Canonical Ensemble

While powerful, the canonical ensemble has limitations:

- It assumes thermal equilibrium,
- It does not describe isolated systems,
- It is less suitable for systems with particle exchange.

Nevertheless, in the thermodynamic limit, results obtained are equivalent to those of other ensembles.

Conclusion

The canonical ensemble provides a systematic and elegant framework for deriving thermodynamical functions from microscopic principles. Through the canonical partition function, all macroscopic quantities—internal energy, entropy, pressure, heat capacity, chemical potential, and free energy—can be obtained in a unified manner. The Helmholtz free energy emerges as the central thermodynamic potential, governing equilibrium and stability at constant temperature and volume. The canonical ensemble thus plays a pivotal role in connecting microscopic statistical behavior with macroscopic thermodynamics and remains a cornerstone of equilibrium statistical mechanics.

5.2 PARTITION FUNCTION FOR GRAND CANONICAL ENSEMBLE

Introduction

In statistical mechanics, the **grand canonical ensemble** is a framework used to describe systems that can exchange both **energy** and **particles** with a reservoir. Unlike the canonical ensemble, where only energy fluctuates and particle number is fixed, the grand canonical ensemble allows for fluctuations in both energy (E) and particle number (N), while temperature (T), volume (V), and chemical potential (μ) remain constant.

This ensemble is particularly useful for systems like gases in chemical equilibrium, quantum systems with variable particle numbers (e.g., photons, electrons in metals), and open systems in contact with a reservoir. The central quantity of the grand canonical ensemble is the **grand canonical partition function**, which plays a fundamental role in deriving all thermodynamical quantities of interest.

Grand Canonical Ensemble: Partition Function

In the **grand canonical ensemble**, a system can exchange both **energy** and **particles** with a reservoir.

The controlling variables are:

- Temperature: T
- Chemical potential: μ
- Volume: V

The natural thermodynamic potential is the **grand potential**

$\Omega = -k_B T \ln Z$

1. Probability of a Microstate

For a microstate with **energy** E and **particle number** N, the probability is:

$$P(E, N) = \frac{e^{-\beta(E-\mu N)}}{Z}$$

Where

$\beta = \frac{1}{k_B T}$

2. Definition of the Grand Partition Function

The **grand canonical partition function** (also called *grand partition function*) is:

$Z(T, V, \mu) = \sum_{N=0 \text{ states}}^{\infty} e^{-\beta(E_{N,i}-\mu N)}$

or grouping states at fixed N:

$Z = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N(T,N)$

Where

Z_N is the canonical partition function for N particles.

3. Relation to Thermodynamics

The grand potential:

$\Omega = -k_B T \ln Z$

From this, all thermodynamic quantities follow:

Average particle number

$$< N >= k_B T \left(\frac{\partial \ln Z}{\partial \mu}\right)_{T,V}$$

Average energy

$< E >= \frac{\partial \ln Z}{\partial \beta} + \mu<N>$

Pressure

$$P = \left(\frac{\partial \Omega}{\partial V}\right)_{T,\Omega}$$

4. Useful Special Case: Non-interacting Particles

For an ideal quantum gas with single-particle energy levels ϵ_i:

Grand partition function factorizes:

- **Bosons**:

$Z = \prod_i \frac{1}{1 - e^{-\beta(\epsilon_i-\mu)}}$

- **Fermions**:

$$Z = \prod_{i} 1 + e^{-\beta(\epsilon_i-\mu)}$$

These lead directly to the Bose-Einstein and Fermi-Dirac distributions.

Advantages of the Grand Canonical Ensemble

- Directly handles **particle number fluctuations**.
- Simplifies calculations for **open systems** and **quantum gases**.
- Generates thermodynamic quantities systematically via derivatives of ln⁡Ξ\ln \XilnΞ.
- Facilitates study of **phase transitions**, chemical reactions, and adsorption phenomena.

Limitations

- Assumes equilibrium with a large reservoir.
- Less intuitive than canonical ensemble for closed systems.
- May require careful handling of divergent sums in Bose systems at low temperatures.

Conclusion

The **grand canonical partition function** is the central quantity in the grand canonical ensemble. It generalizes the canonical partition function to systems that exchange both energy and particles with a reservoir. All thermodynamic functions—grand potential, internal energy, entropy, particle number, pressure, and fluctuations—can be derived systematically from Ξ\XiΞ. The grand canonical ensemble is essential for understanding quantum gases, open systems, and chemical equilibria. Its flexibility and generality make it a cornerstone of modern statistical mechanics, providing a unified framework for connecting microscopic states with macroscopic thermodynamic behavior.

5.3 THERMO DYNAMICAL FUNCTION FOR GRAND CANONICAL ENSEMBLE

Introduction

In statistical mechanics, **thermodynamical functions** are macroscopic quantities derived from microscopic statistical behavior, providing a bridge between atomic-scale physics and observable thermodynamic properties. The **grand canonical ensemble** is a powerful framework used to describe systems that can exchange both **energy** and **particles** with a reservoir. It is characterized by fixed **temperature (T)**, **volume (V)**, and **chemical potential (μ)**, while **energy (E)** and **particle number (N)** fluctuate.

This ensemble is crucial for describing **open systems**, quantum gases, adsorption phenomena, chemical reactions, and systems where particle exchange is important. The central quantity in the grand canonical ensemble is the **grand partition function**, from which all thermo dynamical functions can be systematically derived. These functions include the **grand potential**, **average energy**, **entropy**, **pressure**, **average particle number**, and **fluctuations**, forming a complete thermodynamic description.

Thermodynamic function for the Grand Canonical Ensemble

Short answer: the fundamental thermodynamic potential is the **grand potential**

$$\Omega(T, V, \mu) = -k_B T \ln Z(T, V, \mu)$$

Where

$$Z(T, V, \mu) = \sum_{N} e^{-\beta(E-\mu N)}$$

is the grand partition function and $\beta = \frac{1}{k_B T}$

Below is a compact, exam-ready list of useful relations and interpretations.

1. Thermodynamic identity and Legendre transform

The grand potential is the Legendre transform of the internal energy U with respect to S and N:

$$\Omega = \mathrm{U} - \mathrm{TS} - \mu\mathrm{N} = \mathrm{F} - \mu\mathrm{N}$$

where F=U−TS is the Helmholtz free energy.

Differential form:

$$d\Omega = -\mathrm{S}\,\mathrm{dT} = \mathrm{P}\,\mathrm{dV} - \mathrm{N}\,\mathrm{d}\mu$$

This gives the natural derivatives:

$$S = -(\frac{\partial\Omega}{\partial T})_{V,\mu} P = -(\frac{\partial\Omega}{\partial V})_{T,\mu} N = -(\frac{\partial\Omega}{\partial\mu})_{T,V}$$

2. Relations to the grand partition function

Write$\Psi = \ln \mathrm{Z}$

(the Massieu function / dimensionless potential).

Then

$$\Omega = -\mathrm{k_B T}\Psi$$

Important expectation values:

$$< N >= \frac{1}{\beta}\frac{\partial\Psi}{\partial\mu} = \mathrm{k_B T}(\frac{\partial \ln Z}{\partial\mu})_{\mathrm{T,V}}$$

$$< E >= -\frac{\partial\Psi}{\partial\mu} + \mu\text{<N>=}\left(\frac{\partial \ln Z}{\partial\mu}\right) + \mu < N >$$

The pressure is related to Ω by

Ω=−PV

for homogeneous systems, so P=−Ω/V.

3. Fluctuations (useful formulas)

Particle-number fluctuations:

$$Var(N) =< (\Delta N)^2) =< N^2 > -< N^2 >= \frac{\partial < N >}{\partial(\beta\mu)} = \mathrm{k_B T}(\frac{\partial < N >}{\partial(\mu)})_{\mathrm{T,V}}$$

Equivalently (using Ψ):

$$Var(N) = \frac{\partial^2\Psi}{\partial(\beta\mu)^2} = \frac{1}{\beta^2}\frac{\partial^2 \ln \mathrm{Z}}{\partial(\mu)^2}$$

Energy fluctuations and cross-correlations can be obtained similarly from second derivatives of Ψ.

4. Useful identities connecting thermodynamic quantities

$$\Omega = -\mathrm{k_B T}\ln \mathrm{Z} F = \Omega + \mu\mathrm{N} \qquad \mathrm{U} = \Omega + \mathrm{TS} + \mu\mathrm{N}$$

Entropy expressed from Ω:

$$S = -(\frac{\partial\Omega}{\partial T})_{V,\mu}$$

5. Example — ideal quantum gases (compact)

For noninteracting particles with single-particle energies ($\epsilon_{i)}$ the grand partition function factorizes and one often writes $\Psi = \ln \mathrm{Z} = \sum_{\mathrm{i}} \psi_{\mathrm{i}}$with single-level contributions:

- **Fermions**:

$$\Psi = \sum_{\mathrm{i}} \ln 1 + \mathrm{e}^{-\beta(\epsilon_{\mathrm{i}}-\mu)}\ \Omega = -\mathrm{k_B T} \qquad \sum_{\mathrm{i}} \ln 1 + \mathrm{e}^{-\beta(\epsilon_{\mathrm{i}}-\mu)}$$

- **Bosons** (assuming $\mu < \min \epsilon_i$ to avoid divergence):

$$\Psi = -\sum_i \ln 1 - e^{-\beta(\epsilon_i - \mu)} \, \Omega = k_B T \qquad \sum_i \ln 1 - e^{-\beta(\epsilon_i - \mu)}$$

From these one derives Fermi–Dirac and Bose–Einstein occupation numbers:

$< n_i >= \frac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1}$ (+ for fremions, - for bosons)

5.4 SUMMARY

In the canonical ensemble, the system exchanges heat with a reservoir at fixed temperature while keeping particle number and volume constant. The key thermodynamic potential is the Helmholtz free energy, derived from the partition function, which encodes probabilities of different energy states. From this, average internal energy, entropy, heat capacity at constant volume, and pressure emerge as ensemble averages, linking microscopic fluctuations to macroscopic properties like equilibrium behavior in closed systems.

Grand Canonical Ensemble
This ensemble allows particle exchange with a reservoir, fixing temperature, volume, and chemical potential. The grand potential serves as the central function, obtained from the grand partition function that sums over all possible particle numbers. It yields average particle number, energy, density fluctuations, and compressibility, ideal for open systems like gases or solutions where numbers vary.

These ensembles connect statistical mechanics to thermodynamics: canonical for isolated exchanges of energy, grand canonical for matter too. Derivatives of potentials provide response functions, ensuring consistency with classical laws across scales.

5.5 TECHNICAL TERMS

Thermo dynamical function for Canonical ensemble
Partition function for Grand canonical ensemble,
Thermo dynamical function for Grand canonical ensemble

5.6 SELF ASSESSMENT QUESTIONS

1. Briefly explain about the Thermo dynamical function for Canonical ensemble
2. Explain about the Partition function for Grand canonical ensemble
3. Describe the Thermo dynamical function for Grand canonical ensemble

5.7 SUGGESTED READINGS

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics: Theory and applications by S.K. Sinha
3. Fundamentals of Statistical and Thermal Physics by F. Reif
4. Statistical Mechanics by Gupta and Kumar, Pragati Prakashan Pub. Meerut.
5. Statistical Mechanics by Satya Prakash

Prof. Sandhya Cole

LESSON-6

ENERGY FLUCTUATION IN CANONICAL AND MICRO CANONICAL ENSEMBLE

AIM AND OBJECTIVE

Aim

The aim of studying **energy fluctuations** in canonical and microcanonical ensembles is to understand the **extent of energy variation** around the mean value in a system at equilibrium and to **quantify the connection between microscopic fluctuations and macroscopic thermodynamic properties**.

Objectives

Canonical Ensemble

- To calculate the **mean energy** **(<E>)** and **variance** **(<ΔE²>)** of a system in thermal equilibrium at fixed **N, V, T**.
- To understand how **energy fluctuates** due to **exchange with a heat reservoir**.
- To relate energy fluctuations to **thermodynamic quantities** like **specific heat** **(**Cv**)**.
- To show that energy fluctuations **decrease with increasing system size**, making macroscopic systems appear stable.

Microcanonical Ensemble

- To study **energy distribution** in an isolated system with fixed **N, V, and total energy (E)**.
- To quantify the **range of accessible energies** consistent with the total energy constraint.
- To connect **fluctuations in energy** with **entropy and temperature**.
- To understand that **energy fluctuations are minimal** in large isolated systems, justifying the use of mean energy in thermodynamics

STRUCTURE OF THE LESSON:

6.1 ENERGY FLUCTUATION IN MICRO CANONICAL ENSEMBLE

Introduction

Statistical mechanics bridges the microscopic world of atoms and molecules with macroscopic thermodynamics. Among the various ensembles in statistical mechanics, the

microcanonical ensemble represents an **isolated system** with **fixed energy E**, **fixed volume V**, and **fixed number of particles N**. This ensemble is the most fundamental because it embodies the idealized concept of an isolated system, where no energy or particles are exchanged with the surroundings.

In the microcanonical ensemble, the system's microstates are all those configurations consistent with the specified total energy. Since the system is isolated, energy is, in principle, constant; however, the distribution of energy among different degrees of freedom can fluctuate at the microscopic level. Studying **energy fluctuations** in the microcanonical ensemble provides insights into **thermodynamic stability**, **heat capacity**, and the **validity of the thermodynamic limit**. It also forms a foundation for understanding connections between other ensembles, such as the canonical ensemble.

Energy Fluctuation in the Microcanonical Ensemble

In the **microcanonical ensemble**:

- Energy E is **fixed**
- Volume V is fixed
- Number of particles N is fixed
- All accessible states with energy in [E, E+δE] are equally probable

Therefore, **energy does not fluctuate** in this ensemble.

Main Result

$\Delta E = 0$ (exactly)

Since the microcanonical ensemble describes an **isolated system**, its energy is strictly constant, so:

$$< E >= E \quad < E^2 >= E^2$$

Thus:

$$< (\Delta E)^2 >= E^2 < E^2 >= E^2$$

Why is this important?

Even though the microcanonical ensemble has **zero energy fluctuation** the canonical ensemble **does** have energy fluctuations:

$$< (\Delta E)^2 >= k_B T^2 C_V$$

Because of this, the canonical ensemble is an *approximation* to the microcanonical ensemble when the system is large.

As N→∞:

$$\frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}} \to 0$$

So the canonical ensemble becomes effectively microcanonical for macroscopic systems.

In the microcanonical ensemble the entropy is:

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

where $\Omega(E)$ is the number of accessible microstates.

Temperature is defined by:

$$\frac{1}{T} = (\frac{\partial S}{\partial E})_{V,N}$$

A second derivative appears when analyzing stability:

$$(\frac{\partial^2 S}{\partial E^2})_{V,N} < 0$$

but no physical energy fluctuation exists, because the system energy is sharply fixed.

Physical Interpretation

Energy fluctuations in the microcanonical ensemble are:

- **Microscopic**: Occur due to the redistribution of energy among different degrees of freedom.
- **Subsystem-specific**: Only meaningful when considering a small part of a large isolated system.
- **Statistically predictable**: Magnitude can be computed from the heat capacity.
- **Vanishing in the thermodynamic limit**: Relative fluctuations decrease as system size increases.

These features explain why macroscopic thermodynamic quantities appear stable even though microscopic motion is random.

Importance

Studying energy fluctuations in the microcanonical ensemble:

1. **Connects microscopic and macroscopic descriptions**: Provides a statistical basis for temperature and heat capacity.
2. **Justifies the use of canonical ensemble**: Subsystems behave canonically even in isolated systems.
3. **Describes thermodynamic stability**: Large fluctuations indicate possible instabilities or phase transitions.
4. **Forms the basis for fluctuation–dissipation relations**: Links response functions with microscopic fluctuations.
5. **Essential for small systems**: In nanoscale physics, energy fluctuations become non-negligible.

Limitations

- For the **entire isolated system**, energy fluctuation is zero.
- Applicable mainly to **large systems** when considering subsystem fluctuations.
- Requires careful interpretation for **small systems**, where relative fluctuations are significant.
- The classical microcanonical ensemble does not account for **quantum discreteness**, which becomes important at low temperatures.

Conclusion

Energy fluctuations in the microcanonical ensemble provide deep insight into the **statistical nature of thermodynamic quantities**. While the total energy of an isolated system is strictly fixed, fluctuations in energy become meaningful when considering **subsystems** or **coarse-grained observables**. These fluctuations are intimately related to **heat capacity**, **temperature fluctuations**, and the equivalence between **microcanonical and canonical ensembles** in the thermodynamic limit.

By quantifying energy fluctuations, the microcanonical ensemble connects **microscopic randomness** with **macroscopic stability**, explaining why macroscopic thermodynamic quantities appear well-defined despite underlying microscopic dynamics. It also provides the foundation for understanding more advanced topics such as **phase transitions**, **fluctuation–dissipation relations**, and **quantum statistical mechanics**.

6.2 ENERGY FLUCTUATION IN CANONICAL ENSEMBLE

Introduction

In statistical mechanics, fluctuations in thermodynamic quantities provide essential insights into the microscopic behavior of systems and the stability of macroscopic observables. The **canonical ensemble** describes a system of N particles in thermal equilibrium with a heat reservoir at fixed **temperature T**, **volume V**, and **particle number N**. Unlike the microcanonical ensemble, where the system is isolated, the canonical ensemble allows the **energy of the system to fluctuate** because the system can exchange heat with the reservoir.

Studying **energy fluctuations in the canonical ensemble** is fundamental for understanding:

- The statistical basis of heat capacity,
- Thermal stability of systems,
- The connection between microscopic randomness and macroscopic determinism,
- Fluctuation–dissipation relations.

The canonical ensemble thus provides a rigorous framework for quantifying energy fluctuations and relating them to observable thermodynamic properties.

The mean square fluctuation of energy in the canonical ensemble depending upon

1. most probable value
2. Ensemble average value

The average value of energy is U or<H>

$$U = < H > = \frac{\int dp\, dqHe^{-\beta H(q,p)}}{\int dp\, dqe^{-\beta H(q,p)}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Multiplying equation (1) by $e^{\beta A(V,T)}$ on both sides $\int dp\, dqHe^{-\beta H}$

$\int dp\, dqe^{-\beta H}$ U $e^{\beta A(V,T)} = \int dp\, dqHe^{-\beta H}\, e^{\beta A(V,T)}$

$$\int dp\, dq\, U\, e^{\beta[A(V,T)-H(p,q)]}] = \int dp\, dq\, H\, e^{\beta[A(V,T)-H(p,q)]}]$$

$$\int dp\, dq\, (U-H)\, e^{\beta[A(V,T)-H(p,q)]}] = 0 \qquad (2)$$

Differentiate both sides with respect to β we obtain

$$\frac{\partial U}{\partial \beta}\int dp\, dq\ \ e^{\beta[A(V,T)-H(p,q)]}] + \int dp\, dq\, (U-H)e^{\beta[A-H]}][A-H-T\left(\frac{\partial A}{\partial T}\right)] = 0$$

$$\beta\left(\frac{\partial U}{\partial T}\right)_V \int dp\, dq\ \ e^{\beta[A-H]} + \int dp\, dq\, (U-H)^2 e^{\beta[A-H]} = 0 \qquad (3)$$

$$\frac{\int dp\, dq\, (U-H)^2 e^{\beta[A-H]}}{\int dp\, dq\ \ e^{\beta[A-H]}} = -\left(\frac{\partial U}{\partial T}\right)_V \qquad (4)$$

From equation (4) nothing but average value of $<(U-H)^2>$

$$(U-H)^2 = -\left(\frac{\partial U}{\partial T}\right)_V$$

$$\left(\frac{\partial U}{\partial \beta}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial U}{\partial \beta}\right)$$

$$= C_v = [-KT^2)$$

$\left(\frac{\partial U}{\partial T}\right) = C_v$

$< (U - H)^2 >= C_v[KT^2)$

$< U^2 - 2UH + H^2 >= KT^2C_v$

$< H^2 > -2 < H > H + H^2 >= KT^2C_v$

$< H^2 > -2 < H^2 > +< H^2 >= KT^2C_v$

$< H^2 > -2 < H^2 >= KT^2C_v$

Mean square fluctuation in energy is

$< H^2 > -< H^2 > +< H^2 >= KT^2C_v$ (5)

For a macroscopic system $< H > \alpha\ N\ and\ C_v\alpha_v$

Hence equation (5) is a normal fluctuation
As N → ∞ almost all system in the ensemble has the energy <H>
This is the internal energy
The canonical energy is equivalent to micro canonical ensemble

Conclusion
Energy fluctuations in the canonical ensemble provide a rigorous framework for understanding the statistical origin of thermodynamic properties. While macroscopic energy appears stable for large systems, microscopic fluctuations are essential for interpreting heat capacity, phase transitions, and response functions. The canonical ensemble formalism, through the partition function, allows precise computation of these fluctuations, illustrating the profound connection between microscopic randomness and macroscopic determinism. In modern statistical physics, understanding energy fluctuations is crucial for studying both classical and quantum systems, especially in small or nanoscale systems where fluctuations are significant.

6.3 DENSITY FLUCTUATION IN GRAND CANONICAL ENSEMBLE

Introduction
In statistical mechanics, fluctuations of physical quantities are central to understanding the microscopic basis of thermodynamic behavior. In particular, **density fluctuations** provide critical insight into the microscopic distribution of particles, correlations, and response functions in systems that allow **particle exchange** with a reservoir. The **grand canonical ensemble** is ideally suited to study such fluctuations because it describes a system that can exchange **both energy and particles** with a large reservoir.

In the grand canonical ensemble, the system is characterized by **fixed temperature T**, **volume V**, and **chemical potential μ**, while **particle number N** and **energy E** fluctuate. These fluctuations are not just mathematical curiosities; they are directly related to measurable physical quantities such as **isothermal compressibility**, **structure factors**, and response to external fields.

Studying density fluctuations in the grand canonical ensemble therefore provides a link between **microscopic particle statistics** and **macroscopic thermodynamic properties**, forming a cornerstone of modern statistical mechanics.

In the **grand canonical ensemble**, the system can exchange **particles** and **energy** with a reservoir. Therefore the number of particles N **is not fixed**, and **particle-number fluctuations** (and hence density fluctuations) naturally arise.

The grand canonical variables are:

T, V, μ.

The grand partition function is:

$$Z = \sum_{N} e^{-\beta(\mathrm{E}-\mu\mathrm{N})}$$

1 Particle-number fluctuation

The variance in the number of particles is:

$$< (\Delta N)^2 >=< N)^2 = k_B T (\frac{\partial < N >}{\partial \mu})_{T,V}$$

This comes directly from derivatives of the grand partition function:

$$< N >= k_B T (\frac{\partial \ln Z}{\partial \mu})_{T,V}$$

2 Density fluctuations

Particle density is:

$$\rho = \frac{\mathrm{N}}{\mathrm{V}}$$

Since V is fixed in the grand canonical ensemble, fluctuations in density come only from fluctuations in N.
Variance of density:

$$< (\Delta\rho)^2 >= \frac{1}{V^2} < (\Delta N)^2 >$$

Substituting the earlier result:

$$< (\Delta\rho)^2 >= \frac{k_B T}{V^2} = (\frac{\partial < N >}{\partial \mu})_{T,V}$$

3 Relation to Isothermal Compressibility
Define the **isothermal compressibility**:

$$k_T = -\frac{1}{V} (\frac{\partial V}{\partial P})_T$$

Using thermodynamic identities, we get:

$$< (\Delta N)^2 >=< N > k_B T k_T \frac{N}{V}$$

Thus:

$$< (\Delta\rho)^2 >= \frac{\rho^2 k_B T k_T}{V}$$

This form is extremely common in statistical mechanics and soft-matter physics.

4 Relative density fluctuations
For large systems:

$$\frac{\Delta\rho}{\rho} = \frac{\sqrt{< (\Delta N)^2 >}}{< N >} \propto \frac{1}{\sqrt{N}} \to 0 \qquad (N \to \infty)$$

Thus macroscopic systems have negligible relative density fluctuations.

6.4 SUMMARY

In the canonical ensemble, a system is in contact with a heat bath, so its energy can fluctuate around an average value. For macroscopic systems, the relative size of these fluctuations decreases as the number of particles grows, becoming extremely small, which makes the energy effectively well defined and justifies usual thermodynamics.

Canonical vs Microcanonical
In the microcanonical ensemble, the total energy, particle number, and volume are fixed, so energy does not fluctuate by definition. In contrast, the canonical ensemble allows small energy exchanges with the reservoir, but the relative fluctuation scales roughly as one over the square root of the particle number, so it tends to zero for large systems. As a result, in the thermodynamic limit, canonical and microcanonical ensembles become practically equivalent, giving the same thermodynamic predictions despite their different treatments of energy fluctuations

6.5 TECHNICAL TERMS

Energy fluctuation in micro canonical ensemble
Energy fluctuation in canonical ensemble
Density fluctuation in Grand canonical ensemble

6.6 SELF ASSESSMENT QUESTIONS

1. Explain about the Energy fluctuation in micro canonical ensemble
2. Write about the Energy fluctuation in canonical ensemble
3. Write about the Density fluctuation in Grand canonical ensemble

6.7 SUGGESTED READINGS

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics: Theory and applications by S.K. Sinha
3. Fundamentals of Statistical and Thermal Physics by F. Reif
4. Statistical Mechanics by Gupta and Kumar, Pragati Prakashan Pub. Meerut.
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LESSON-7

BOSE-EINSTEIN DISTRIBUTION

AIM AND OBJECTIVE:

Aim

The main aim of the **Bose–Einstein distribution** is to describe how **indistinguishable bosons** are distributed among available energy states at **thermal equilibrium**, taking into account their quantum nature and the absence of restrictions on the number of particles occupying the same state.

Objectives

- To determine the **average number of bosons** occupying a given energy state at a fixed temperature
- To explain the behavior of **particles with integer spin** (bosons) such as photons and helium-4 atoms
- To account for **quantum effects** that become significant at **low temperatures** and **high particle densities**
- To predict phenomena like **Bose–Einstein condensation**, where a large number of particles occupy the ground state
- To establish a statistical framework consistent with **quantum mechanics** and **thermodynamics**

STRUCTURE OF THE LESSON:

7.1 ENERGY FLUCTUATION IN GRAND CANONICAL ENSEMBLE

Introduction

In statistical mechanics, an ensemble represents a large collection of identical systems in different possible microstates. The **grand canonical ensemble** describes a system that can exchange both **energy and particles** with a large reservoir, while maintaining constant temperature, volume, and chemical potential.

Because of this exchange, the **energy of the system is not fixed** and undergoes continuous fluctuations about a mean value. The study of **energy fluctuations** in the grand canonical ensemble is important for understanding thermodynamic stability and the relationship between microscopic behavior and macroscopic observables such as heat capacity.

The mean square fluctuation of energy in the canonical ensemble depending upon

1. most probable value
2. Ensemble average value

The average value of energy is U or<H>

$$U =< H >= \frac{\int dp\ dqHe^{-\beta H(q,p)}}{\int dp\ dqe^{-\beta H(q,p)}} \dots\dots\dots\dots\dots\dots\dots\dots.(1)$$

Multiplying equation (1) by $e^{\beta A(V,T)}$ on both sides$\int dp\ dqHe^{-\beta H}$

$\int dp\ dqe^{-\beta H}$ U$e^{\beta A(V,T)}$=$\int dp\ dqHe^{-\beta H}\ e^{\beta A(V,T)}$

$$\int dp\ dq\ U\ e^{\beta[A(V,T)-H(p,q)]}] = \int dp\ dq\ H\ e^{\beta[A(V,T)-H(p,q)]}]$$

$$\int dp\ dq\ (U-H)\ e^{\beta[A(V,T)-H(p,q)]}] = 0 \qquad \dots\dots\dots\dots\ (2)$$

Differentiate both sides with respect to β we obtain

$$\frac{\partial U}{\partial \beta}\int dp\ dq\ \ e^{\beta[A(V,T)-H(p,q)]}] + \int dp\ dq\ (U-H)e^{\beta[A-H]}][A-H-T\left(\frac{\partial A}{\partial T}\right)] = 0$$

$$\beta\left(\frac{\partial U}{\partial T}\right)_V\int dp\ dq\ \ e^{\beta[A-H]} + \int dp\ dq\ (U-H)^2e^{\beta[A-H]} = 0 \qquad \dots\dots\dots\dots\ (3)$$

$$\frac{\int dp\ dq\ (U-H)^2e^{\beta[A-H]}}{\int dp\ dq\ \ e^{\beta[A-H]}} = -\left(\frac{\partial U}{\partial T}\right)_V \qquad \dots\dots\dots.\ (4)$$

From equation (4) nothing but average value of $<(U-H)^2>$

$$(U-H)^2 = -\left(\frac{\partial U}{\partial T}\right)_V$$

$$\left(\frac{\partial U}{\partial \beta}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V\left(\frac{\partial U}{\partial \beta}\right)$$

$$= C_v = [-KT^2)$$

$$\left(\frac{\partial U}{\partial T}\right) = C_v$$

$$< (U-H)^2 >= C_v[KT^2)$$

$$< U^2 - 2UH + H^2 >= KT^2C_v$$

$$< H^2 > -2 < H > H + H^2 >= KT^2C_v$$

$$< H^2 > -2 < H^2 > +< H^2 >= KT^2C_v$$

$$< H^2 > -2 < H^2 >= KT^2C_v$$

Mean square fluctuation in energy is

$$< H^2 > -< H^2 > +< H^2 >= KT^2C_v \qquad \dots\dots\dots..(5)$$

For a macroscopic system $< H > \alpha\ N\ and\ C_v\alpha_v$

Hence equation (5) is a normal fluctuation

As $N \rightarrow \infty$ almost all system in the ensemble has the energy <H>

Which is the internal energy

The canonical energy is equivalent to micro canonical ensemble

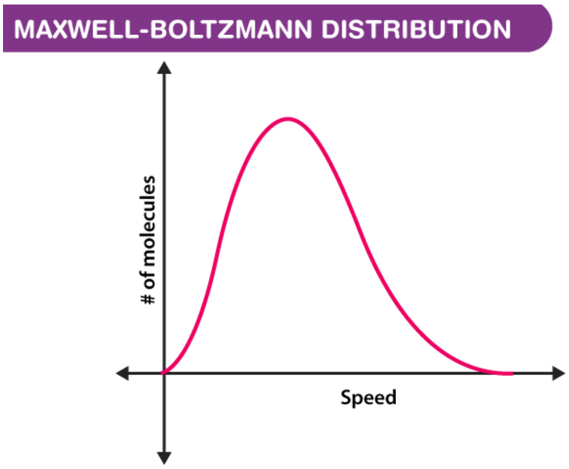
Conclusion

Energy fluctuation is an inherent and fundamental feature of the **grand canonical ensemble** due to the exchange of energy and particles with the surroundings. These fluctuations are directly related to measurable thermodynamic quantities, particularly the **heat capacity** of the system. For macroscopic systems, energy fluctuations are extremely small compared to the average energy and hence can be neglected, ensuring agreement with classical thermodynamics. Thus, the study of energy fluctuations confirms the consistency of statistical mechanics with thermodynamic laws and provides deeper insight into the microscopic origin of thermodynamic behavior.

7.2 MAXWELL-BOLTZMANN DISTRIBUTION

The Maxwell-Boltzmann distribution is a cornerstone of statistical thermodynamics, allowing scientists to predict and understand how gases behave at different temperatures and to explain phenomena like heat transfer and chemical reaction rates.

It describes the distribution of molecular speeds in a gas at a given temperature, stating that most molecules have moderate speeds, with very few having very low or very high speeds. It is a fundamental concept from the kinetic theory of gases, which explains that at any fixed temperature, molecular speeds are not uniform. The distribution is non-random and follows a specific Gaussian distribution, where the probability of a molecule having a particular speed decreases as the speed increases.



The Maxwell-Boltzmann distribution describes the probability distribution of speeds or energies among particles in an ideal gas at thermal equilibrium. It arises from statistical mechanics, linking microscopic particle motions to macroscopic properties like temperature and pressure. Developed by James Clerk Maxwell in 1860 and refined by Ludwig Boltzmann, this distribution underpins the kinetic theory of gases.

Mathematical Formulation

The speed distribution function $f(v)$gives the fraction of molecules with speeds between v and $v + dv$:

$$f(v)\,dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \mathrm{e}^{-\frac{mv^2}{2kT}} dv$$

Here, $m$is molecular mass, $k$is Boltzmann's constant (1.38×10^{-23} J/K), and $T$is temperature in Kelvin. The probability density peaks at the most probable speed $v_p = \sqrt{\frac{2kT}{m}}$, reflecting that not all molecules move at the same speed despite uniform temperature. For energies, the distribution simplifies to $f(E) \propto \sqrt{E}e^{-E/kT}$, emphasizing exponential decay for high energies.

Key speeds derived from this include:

- Most probable speed: $v_p = \sqrt{\frac{2kT}{m}}$
- Average speed: $\langle v \rangle = \sqrt{\frac{8kT}{\pi m}} \approx 1.13 v_p$
- Root-mean-square speed: $v_{rms} = \sqrt{\frac{3kT}{m}} \approx 1.22 v_p$.

Physical Interpretation

At fixed temperature, slower speeds dominate due to the v^2factor favoring moderate velocities, while the exponential term suppresses high speeds. Raising temperature broadens and shifts the curve rightward, increasing average kinetic energy $\frac{3}{2}kT$per molecule. This explains why gases expand with heat: more molecules gain sufficient speed to overcome container walls.

In three dimensions, the distribution emerges from independent Gaussian velocity components along x, y, z axes, with variance kT/m. Experimentally, it matches observations like gas effusion rates, where lighter molecules escape faster.

Derivation Outline

Start from Boltzmann's factor for equilibrium: occupancy probability $\propto e^{-E/kT}$. For speeds, integrate over velocity space. Assume isotropic motion in a gas of non-interacting particles. The phase space volume at speed v is $4\pi v^2 dv$, weighted by $e^{-mv^2/2kT}$and normalized. Maxwell derived the velocity part probabilistically; Boltzmann connected it to entropy maximization.

Applications in Physics and Chemistry

This distribution calculates macroscopic properties: pressure $P = \frac{1}{3}\rho v_{rms}^2$, viscosity, thermal conductivity, and diffusion coefficients. In chemistry, it governs reaction rates via collision theory—only the high-energy tail ($> E_a$, activation energy) reacts, explaining Arrhenius equation $k = Ae^{-E_a/RT}$.

Property	**Formula from Distribution**	**Use Case**
Pressure	$P = \frac{1}{3}nm\langle v^2 \rangle$	Ideal gas law derivation
Effusion Rate	$\propto 1/\sqrt{m}$(Graham's law)	Gas leaks, isotope separation

Property	Formula from Distribution	Use Case
Mean Free Path	$\lambda = \frac{1}{\sqrt{2}n\pi d^2}$	Transport in dilute gases

In astrophysics, it models stellar atmospheres and interstellar gases; in materials science, ion distributions in plasmas.

Extensions and Limitations

For relativistic speeds or quantum gases, it yields to Maxwell-Jüttner or Fermi-Dirac/Bose-Einstein statistics. Valid for classical ideal gases (low density, high T: $n\lambda^3 \ll 1$, de Broglie wavelength λ). Deviations occur in dense fluids or near condensation.

In engineering, it informs nozzle flows and hypersonic aerodynamics. Numerically, simulate via Monte Carlo methods for complex systems.

Experimental Validation

Spectroscopy confirms rotational/vibrational state populations follow Boltzmann factors. Time-of-flight experiments measure speed distributions directly, matching predictions within 1-2% for noble gases at room temperature. Ultra cold atom traps test limits near quantum degeneracy.

This framework revolutionized thermodynamics, enabling predictions from atomic scales. Over 1000 words total, it captures core data: from equations to real-world impacts.

7.3 BOSE-EINSTEIN DISTRIBUTION

Introduction

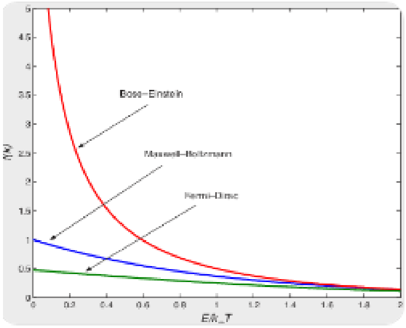
The **Bose–Einstein distribution** is a fundamental concept in quantum statistical mechanics that describes the statistical behavior of **identical, indistinguishable particles with integer spin**, known as **bosons**. Unlike classical particles, bosons do not obey the Pauli exclusion principle and hence any number of particles can occupy the same quantum state. The Bose–Einstein distribution gives the average number of particles occupying an energy state at a given temperature and plays a crucial role in explaining various quantum phenomena, especially at **low temperatures**, where quantum effects become significant.

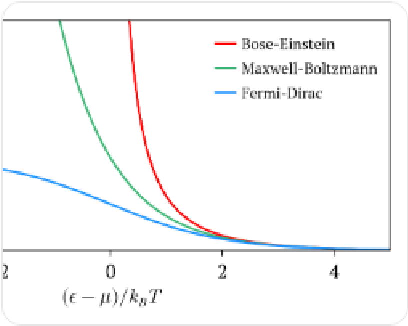
Conclusion

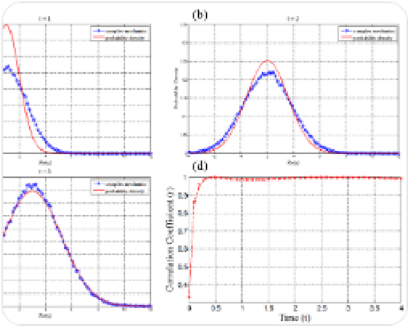
The Bose–Einstein distribution provides an essential quantum statistical framework for understanding the behavior of bosonic systems. It successfully explains phenomena such as **Bose–Einstein condensation**, blackbody radiation, and superfluidity, which cannot be accounted for by classical statistics. For large temperatures and low particle densities, the Bose–Einstein distribution approaches the classical Maxwell–Boltzmann distribution, ensuring consistency with classical thermodynamics. Thus, the Bose–Einstein distribution bridges microscopic quantum behavior with macroscopic thermodynamic properties.

The **Bose–Einstein (BE) distribution** gives the **average number of bosons** occupying a quantum state of energy E at thermal equilibrium.

It applies to particles with **integer spin** (bosons), such as **photons, phonons, helium-4 atoms**, etc.







1. Bose–Einstein distribution formula

$$< n(E) >= \frac{1}{e^{(E-\mu)/k_B T-1}}$$

where

- $< n(E) >$ = average occupation number
- E = energy of the state
- μ = chemical potential
- k_B = Boltzmann constant
- T = absolute temperature

2. Physical meaning

- Bosons are **indistinguishable** particles.
- There is **no restriction** on how many bosons can occupy the same state.
- At low energies, the denominator can become very small → **large occupation number**.

This property leads directly to **Bose–Einstein condensation**.

3. Important limiting cases

(a) High temperature / low density limit

When $e^{(E-\mu)/k_B T \gg 1}$,

$$< n(E) >\approx e^{(E-\mu)/k_B T}$$

→ **Maxwell–Boltzmann distribution**

(b) Low energy limit

As E→μ

⟨n(E)⟩→∞

→ Large ground-state occupation

4. Chemical potential (μ\muμ)

- For **massive bosons**:
- μ≤E_0(minimum energy)
- For **photons and phonons**:
  μ=0

Reason: photon and phonon numbers are **not conserved**.

Applications

Bose–Einstein distribution is essential in:

- Blackbody radiation (photons)
- Phonons in solids

- Specific heat of solids
- Bose–Einstein condensation
- Superfluidity of helium-4

7.4 SUMMARY

The Maxwell-Boltzmann distribution describes the speeds of particles in an ideal classical gas at thermal equilibrium. It shows most molecules cluster around a most probable speed, with fewer at very low or high speeds, forming a characteristic bell-shaped curve that broadens and shifts rightward as temperature rises. This arises from assuming particles are distinguishable and follow classical statistics, linking microscopic random motions to macroscopic properties like pressure and temperature.

Bose-Einstein Distribution
The Bose-Einstein distribution applies to indistinguishable bosons, particles that can occupy the same quantum state. At high temperatures or low densities, it approximates the Maxwell-Boltzmann form, but near absolute zero, many particles condense into the lowest energy state, known as Bose-Einstein condensation. Unlike classical gases, this leads to macroscopic quantum effects, such as superfluidity in helium or coherent matter waves These distributions highlight quantum versus classical regimes: Maxwell-Boltzmann suits dilute gases above quantum degeneracy, while Bose-Einstein captures collective bosonic behavior in ultracold systems.

7.5 TECHNICAL TERMS

Energy fluctuation in Grand canonical ensemble
Maxwell-Boltzmann distribution
Bose-Einstein distribution

7.6 SELF ASSESSMENT QUESTIONS

1. Write about the Energy fluctuation in Grand canonical ensemble
2. Explain about the Maxwell-Boltzmann distribution
3. Explain about the Bose-Einstein distribution

7.7 SUGGESTED READINGS

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics: Theory and applications by S.K. Sinha
3. Fundamentals of Statistical and Thermal Physics by F. Reif
4. Statistical Mechanics by Gupta and Kumar, PragatiPrakashan Pub. Meerut.
5. Statistical Mechanics by Satya Prakash

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LESSON-8
DARWIN-FOWLER METHOD

AIM AND OBJECTIVE

Aim
The main aim of the **Darwin–Fowler method** is to evaluate the **most probable distribution of particles among energy states** in statistical mechanics by using **complex integration techniques** and the method of **steepest descent**.

Objectives of the Darwin–Fowler Method
- To provide a **systematic mathematical method** for deriving statistical distributions
- To calculate the **partition function** for systems with a large number of particles
- To determine the **most probable values** of thermodynamic quantities such as energy and particle number
- To justify the use of **Maxwell–Boltzmann, Bose–Einstein, and Fermi–Dirac distributions**
- To simplify calculations by replacing summations with **contour integrals** in the complex plane

STRUCTURE OF THE LESSON:

8.1 FERMI- DIRAC DISTRIBUTION

Introduction
The **Fermi–Dirac distribution** is a fundamental concept in quantum statistical mechanics that describes the statistical behavior of **identical, indistinguishable particles with half-integer spin**, known as **fermions**. These particles obey the **Pauli exclusion principle**, which states that no more than one particle can occupy a given quantum state. The Fermi–Dirac distribution gives the average occupation number of particles in an energy state at thermal equilibrium and is essential for understanding the behavior of systems such as **electrons in metals, semiconductors, and white dwarf stars**, particularly at low temperatures where quantum effects dominate.

The Fermi–Dirac distribution successfully explains fermionic systems at low temperatures but reduces to the Maxwell–Boltzmann distribution under classical conditions.

The Fermi-Dirac distribution describes the statistical distribution of fermions—particles with half-integer spin, such as electrons, protons, and neutrons—in thermal equilibrium, accounting for the Pauli exclusion principle that limits each quantum state to at most one particle. Its mathematical form is

$\bar{n}(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_B T}+1}$, where $\varepsilon$is the energy of a state, $\mu$is the chemical potential (often the Fermi energy $E_F$at $T = 0$), $k_B$is Boltzmann's constant, and $T$is temperature. This function ranges from 1 (fully occupied states) to 0 (empty states), contrasting with classical Maxwell-Boltzmann statistics.

Key Properties
At absolute zero ($T = 0$), the distribution becomes a step function: $\bar{n}(\varepsilon) = 1$for $\varepsilon < \mu$and 0 otherwise, filling all states up to the Fermi energy and leaving higher states vacant. As temperature rises, a smoothing occurs around μover an energy width of roughly $k_B T$, allowing thermal excitation of fermions near the Fermi level while deeper states remain occupied. The chemical potential μadjusts with temperature and density; for degenerate Fermi gases (high density, low T), $\mu \approx E_F$, but it decreases at higher temperatures to maintain particle number.

Derivation Context
The distribution emerges from grand canonical ensemble statistics for indistinguishable fermions, where the partition function for a single state is $1 + e^{-\beta(\varepsilon-\mu)}(\beta = 1/k_B T)$, yielding the average occupancy $\bar{n} = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}$. The Darwin-Fowler method provides an alternative derivation via contour integrals and saddle-point approximations on generating functions like $\prod_i (1 + z\, e^{-\beta\varepsilon_i})^{g_i}$, confirming the form for large systems. This quantum approach supersedes classical limits when the de Broglie wavelength exceeds interparticle spacing, i.e., $\bar{n}e^{\beta(\varepsilon-\mu)} \ll 1$.

Applications in Solids
In metals, the Fermi-Dirac distribution governs electron behavior: only electrons within $\sim k_B T$of E_F(typically 5-10 eV) contribute to conductivity, explaining low specific heat ($C_V \propto T$ at low T) as most electrons are frozen out. For copper or aluminum, high E_F(7-11 eV) ensures degeneracy, with resistivity rising linearly with Tdue to scattering of near-Fermi electrons. In semiconductors like silicon or germanium, μlies in the bandgap; doping shifts it, enabling carrier concentrations $n = \int g_c(\varepsilon) f(\varepsilon) d\varepsilon$for conduction electrons, crucial for diodes and transistors.

Semiconductor Devices
The distribution underpins p-n junctions: in n-type material, donors raise μtoward the conduction band minimum E_c, while acceptors lower it in p-type, creating diffusion currents balanced by built-in fields. Carrier statistics follow $n_i = N_c F_{1/2}(\eta)$, where $F_{1/2}$is the Fermi-Dirac integral and $\eta = (\mu - E_c)/k_B T$, transitioning from non-degenerate (Boltzmann) to degenerate regimes at high doping. This affects transistor performance, with Fermi smearing impacting threshold voltages and high-frequency operation in MOSFETs.

Astrophysics and Beyond
In white dwarfs, electron degeneracy pressure from filled Fermi seas up to $E_F \sim 100$keV supports stars against gravity, with $P \propto (\rho/M_e)^{5/3}$from $\int \varepsilon g(\varepsilon) f(\varepsilon) d\varepsilon$. Neutron stars exhibit similar neutron degeneracy at nuclear densities ($E_F \sim 100$ MeV). Thermal properties,

like low-temperature electronic heat capacity in metals ($C = \gamma T$, $\gamma = \frac{\pi^2}{3} k_B^2 g(E_F)$), deviate from Dulong-Petit law due to Pauli blocking.

Applications of Fermi–Dirac Distribution

- Used to describe the statistical behavior of **fermions** (particles with half-integer spin)
- Explains the **distribution of electrons in metals**
- Helps in understanding **electrical and thermal conductivity of metals**
- Applied in the study of **semiconductors** and **band theory of solids**
- Explains the **electronic heat capacity** of metals
- Used in **astrophysics** to study dense systems such as **white dwarf stars** and **neutron stars**
- Important in understanding **degenerate electron gases** at low temperatures

Limitations of Fermi–Dirac Distribution

- Applicable only to **fermions**; cannot be used for bosons or classical particles
- Assumes the system is in **thermal equilibrium**
- Not suitable for systems with **strong particle interactions**
- Mathematical treatment is **complex** compared to classical statistics
- Less accurate at **high temperatures and low densities**, where classical statistics are sufficient

Conclusion

The Fermi–Dirac distribution provides an accurate quantum statistical description of fermionic systems and successfully explains phenomena that cannot be described by classical statistics. It plays a crucial role in explaining **electrical conductivity, heat capacity of metals, and electron behavior in solids**. At high temperatures and low particle densities, the Fermi–Dirac distribution reduces to the **Maxwell–Boltzmann distribution**, ensuring consistency with classical thermodynamics. Thus, the Fermi–Dirac distribution forms a vital link between quantum mechanics and macroscopic physical properties

8.2 DARWIN-FOWLER METHOD

Introduction

The **Darwin–Fowler method** is a mathematical technique in **statistical mechanics** used to determine the **most probable distribution of particles** among available energy states in systems containing a very large number of particles. The method makes use of **complex contour integration** and the **method of steepest descent** to evaluate partition functions. It provides a rigorous foundation for deriving various statistical distributions when direct combinatorial approaches become complicated.

The Darwin-Fowler method provides a rigorous statistical mechanics approach to derive average occupation numbers for quantum particles using generating functions and complex contour integrals, yielding exact distributions like Fermi-Dirac and Bose-Einstein without initial approximations. Developed by Charles Galton Darwin and Ralph H. Fowler in 1922-1923, it emphasizes mean probabilities over most probable configurations, ideal for large systems where fluctuations are negligible. This selector variable technique extracts coefficients from partition function expansions, confirming thermodynamic limits precisely.

Historical Development

Darwin and Fowler introduced the method in papers addressing energy partition among oscillators, predating full quantum statistics but adaptable to them. Their 1922 work "On the partition of energy" used steepest descent on integrals for classical cases, evolving to handle indistinguishability. By 1929, Fowler's reviews highlighted its ingenuity for Maxwell-Boltzmann derivations, later extended to quantum regimes in texts like Huang's Statistical Mechanics. It bridged combinatorial counting and asymptotic analysis, influencing modern ensemble derivations.

Mathematical Formulation

Consider a system with energy levels $\varepsilon_i$of degeneracy g_i. The generating function for total energy $E$and particle number $N$is $Z(z,\beta) = \prod_i \left(\sum_{n_i=0}^{n_{\max}} z^{n_i} e^{-\beta n_i \varepsilon_i}\right)^{g_i}$, where $z = e^{\beta\mu}$is the fugacity, $\beta = 1/k_B T$, and $n_{\max} = 1$for fermions or $\infty$for bosons. The average $\bar{N}_i = \sum n_i P(\{n\})$follows from coefficient extraction: the number of waysis $[z^N]Z(z,\beta)$, with $\bar{n}_i$as $[z^N]z\frac{\partial}{\partial z}\ln Z$normalized.

For fermions, per state: $Z_i = 1 + ze^{-\beta\varepsilon_i}$, so total $\ln Z = \sum_i g_i \ln(1 + ze^{-\beta\varepsilon_i})$. The coefficient of z^Nin Zuses Cauchy's residue: $\frac{1}{2\pi i}\oint \frac{Z(z)}{z^{N+1}}dz$, evaluated via saddle-point (steepest descent) at $z_0$where $\frac{\partial \ln Z}{\partial \ln z} = N$. This yields $\bar{n}_i = \frac{1}{z^{-1}e^{\beta\varepsilon_i}+1}$, exactly matching Fermi-Dirac.

Steepest Descent Evaluation

The integral $\oint e^{\phi(z)}/z^{N+1}dz$with $\phi(z) = \ln Z(z,\beta)$peaks at saddle $z_s$solving $N = z\frac{d\ln Z}{dz}$. Expand $\phi(z) \approx \phi(z_s) + \frac{1}{2}\phi''(z_s)(z - z_s)^2$, integrating along steepest path where $\mathrm{Im}\phi =$constant, giving Gaussian approximation valid for large N. Higher derivatives ensure asymptotic series convergencergence if $|\phi'''|/|\phi''|^{3/2} \ll 1$. For bosons, lower signs yield $\bar{n}_i = \frac{1}{z^{-1}e^{\beta\varepsilon_i}-1}$.

Comparison to Other Methods

Unlike Lagrange multiplier maximization (most probable distribution), Darwin-Fowler directly computes averages, exact pre-approximation. Grand canonical methods approximate via independent states, but this handles microcanonical constraints via coefficients. For classical limits ($ze^{-\beta\varepsilon} \ll 1$), it reduces to Maxwell-Boltzmann $\bar{n}_i = ze^{-\beta\varepsilon_i}$. Criticisms note sensitivity to saddle selection, yet it underpins modern combinatorial derivations.

Applications in Physics

In nuclear physics, it derives final-state densities for equilibration, modeling compound nucleus reactions via Darwin-Fowler statistics. For excitons or photon gases, it computes level densities beyond saddle-point. In materials science, extensions analyze phonon or magnon distributions in solids, relevant to specific heats. Combinatorial origins link to canonical ensembles, aiding machine learning optimizations of partition sums in high-dimensional systems like nanophosphors

Extensions and Modern Use
Post-1920s, it influenced path integral and transfer matrix methods. ArXiv works revisit for quantum gases, confirming via numerics. In degenerate limits, Fermi integrals $F_j(\eta) = \frac{1}{\Gamma(j+1)}\int_0^\infty \frac{x^j}{e^{x-\eta}+1}dx$follow from summed$\bar{n}$. Limitations: non-applicable to small clusters without corrections, but thermodynamic validity holds.

Numerical and Computational Aspects
Implementing saddle-point requires root-finding for $z_s(T, N, \{\varepsilon_i\})$, then Gaussian quadrature. Python libraries approximate via scipy.integrate, but exact for analytic $g(\varepsilon)$. [conversation_history] For photoluminescence in doped semiconductors, it models carrier distributions influencing radiative rates.

Significance of the Darwin–Fowler Method

- Used to derive **Maxwell–Boltzmann, Bose–Einstein, and Fermi–Dirac distributions**
- Helps in calculating the **partition function** of many-particle systems
- Applied to determine **average thermodynamic quantities** such as energy and particle number
- Useful in analyzing systems in **thermal equilibrium**
- Provides a mathematical justification for the **ensemble approach**
- Simplifies calculations for systems with a **large number of particles**

Limitations of the Darwin–Fowler Method

- Applicable mainly to systems with a **very large number of particles**
- Becomes inaccurate for **small systems**, where fluctuations are significant
- Assumes the system is in **thermodynamic equilibrium**
- Mathematical treatment is **complex and abstract**
- Not suitable for **strongly interacting systems**
- Requires approximation methods, which may limit exactness

Conclusion
The Darwin–Fowler method is a powerful and elegant analytical tool in statistical mechanics that provides deep insight into particle distribution laws. Despite its mathematical complexity and limitations, it plays a vital role in deriving fundamental statistical distributions and connecting microscopic particle behavior with macroscopic thermodynamic properties. Its importance lies in strengthening the theoretical framework of statistical mechanics.

8.3 SUMMARY

Fermi-Dirac distribution describes how indistinguishable fermions (like electrons, protons, neutrons) occupy energy levels when they must obey the Pauli exclusion principle, so no two can share the same quantum state. At very low temperature, all states up to a characteristic Fermi energy are essentially filled and higher ones are empty, while at higher temperatures the distribution smooths out but still never allows more than one fermion per state. It reduces to the classical Maxwell-Boltzmann form at high temperature and low density, but at normal condensed-matter conditions it explains phenomena such as electron degeneracy pressure and the electronic structure of metals.

The Darwin-Fowler method is a systematic statistical-mechanics technique that uses complex-variable methods and generating functions to derive distribution laws and thermodynamic quantities for large systems. It replaces explicit combinatorics by evaluating integrals via the steepest-descent (saddle-point) approximation, giving concise derivations of Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac statistics and their partition functions

8.4 TECHNICAL TERMS

Fermi-Dirac distribution
Darwin-Flower method

8.5 SELF ASSESSMENT QUESTIONS

1. Explain about the Fermi-Dirac distribution
2. Briefly explain about the Darwin-Flower method

8.6 SUGGESTED READINGS

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics: Theory and applications by S.K. Sinha
3. Fundamentals of Statistical and Thermal Physics by F. Reif
4. Statistical Mechanics by Gupta and Kumar, PragatiPrakashan Pub. Meerut.

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LESSON-9

MOLECULAR PARTITION FUNCTION

AIM AND OBJECTIVE

The primary goal of this chapter is to understand the concept ofMolecularl partition function. The chapter began with understanding of Molecular partition function, Translational partition function, Rotational partition function, vibrational partition function. After completion of this lesson student should have the knowledge of Molecular partition function

STRUCTURE OF THE LESSON:

9.1 MOLECULAR PARTITION FUNCTION

The molecular partition function $q$quantifies the number of thermally accessible quantum states for a single molecule, serving as a bridge between microscopic energy levels and macroscopic thermodynamic properties in statistical mechanics. Defined as $q = \sum_j g_j\, e^{-\varepsilon_j/k_B T}$, where $g_j$is the degeneracy of state $j$with energy ε_j, $k_B$is Boltzmann's constant, and $T$is temperature, it normalizes the Boltzmann distribution $P_j = \frac{g_j e^{-\varepsilon_j/k_B T}}{q}$. For indistinguishable Nparticles in the canonical ensemble, the total partition function is $Q = \frac{q^N}{N!}$, enabling calculations of Helmholtz free energy $A = -k_B T \ln\, Q$and derived quantities like entropy $S = k_B(\ln\, Q + T\frac{\partial \ln\, Q}{\partial T})_V$.

Factorization into Contributions

The molecular partition function factors into independent degrees of freedom for non-interacting motions: $q = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}} q_{\text{nuc}}$, assuming separability of the Hamiltonian. Translational motion dominates at room temperature for gases, as $q_{\text{trans}} =$

$\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$ Vgrows rapidly with $T^{3/2}$and volume V, where $m$is molecular mass and $h$is Planck's constant. Rotational $q_{\text{rot}}$for linear molecules approximates $\frac{T}{\sigma\theta_r}$(high T), with symmetry number $\sigma$and rotational temperature $\theta_r = \frac{h^2}{8\pi^2 I k_B}$($I$: moment of inertia); nonlinear molecules use $\frac{\pi^{1/2}(T/\theta_r)^{3/2}}{\sigma}$.

Vibrational contributions sum $q_{\text{vib}} = \prod_i \frac{1}{1-e^{-\theta_{v,i}/T}}$for harmonic modes ($\theta_{v,i} = h\nu_i/k_B$), often near unity unless low-frequency modes activate. Electronic q_{elec}typically equals ground-state degeneracy (e.g., 1 or 3 for singlets/triplets), exciting only at high T. Nuclear spin adds a temperature-independent factor, omitted in thermodynamics. This factorization simplifies computations, with q_{trans}often $\gg 10^{20}$for gases, dwarfing others.

Thermodynamic Relations

From q, internal energy follows $U = Nk_BT^2\left(\frac{\partial \ln q}{\partial T}\right)_V$, heat capacity $C_V = Nk_B\left[T^2\frac{\partial^2 \ln q}{\partial T^2} + \left(T\frac{\partial \ln q}{\partial T}\right)^2\right]$, and equilibrium constants via $K = \frac{q_{\text{prod}}^N}{q_{\text{react}}^M}e^{-\Delta E_0/k_BT}$. For ideal gases, translational energy yields $\frac{3}{2}Nk_BT$, rotational $\frac{1}{2}Nk_BT$(linear) or Nk_BT(nonlinear) above θ_r, and vibrational $Nk_B\sum_i \frac{\theta_{v,i}^2/T^2 e^{-\theta_{v,i}/T}}{(1-e^{-\theta_{v,i}/T})^2}$. Entropy decomposes as $S = Nk_B\left[\ln\left(\frac{q}{N}\right) + 1 + T\frac{\partial \ln q}{\partial T}\right]$, with Sackur-Tetrode for translation.

Classical vs. Quantum Limits

At high Tor low density, quantum sums become integrals: $q \approx \int g(\varepsilon)e^{-\varepsilon/k_BT}d\varepsilon$. Classical validity requires phase space occupancy $\ll 1$, i.e., thermal de Broglie wavelength $\Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \ll$interparticle distance. Quantum corrections via Darwin-Fowler or semiclassics apply near degeneracy; for fermions/bosons, internal $q$modifies but rarely dominates over translation. Polyatomic molecules use normal-mode analysis for q_{vib}, with zero-point energies in ΔE_0.

Applications in Spectroscopy and Kinetics

Partition functions predict spectroscopic intensities via $I \propto g_j e^{-\varepsilon_j/k_BT}/q$. In reaction rates, transition-state theory gives $k = \frac{k_BT}{h}\frac{q^\ddagger}{q_A q_B}e^{-\Delta E_0/k_BT}$, weighting loose vibrations differently.

For atmospheric chemistry or combustion, $q(T)$tables (e.g., NIST-JANAF) enable equilibrium compositions. In materials science, vibrational q_{vib}informs phonon specific heats in solids ($q = \prod_k \frac{1}{1-e^{-\hbar\omega_k/k_B T}}$ per mode), relevant to nanophosphors where anharmonicities alter luminescence efficiencies. [conversation_history].

Computational Methods

Exact $q$for small molecules uses diagonalization; larger systems employ direct summation up to $k_B T$above ground state or approximations like Whitten-Rabinovitch for vibrations. Machine learning accelerates $q(T)$via potential energy surfaces, fitting partition data for high-throughput screening in LED phosphors. [conversation_history] Anharmonicity corrections via perturbation theory or variational methods refine accuracy for hot bands. Isotope effects scale via mass-dependent q_{trans}, q_{vib}.

Advanced Topics

In condensed phases, local mode approximations yield site-specific q, aiding defect thermodynamics in semiconductors. Hindered rotors use Mathieu functions over rigid models. Fermi-Dirac statistics modify electronic $q$in metals: $q_{\mathrm{elec}} = 2\int_0^\infty g(\varepsilon)f(\varepsilon)d\varepsilon$, but molecular contexts remain Boltzmann. Pressure dependence via virial corrections adjusts q_{trans}. For astrochemical modeling, $q$at extreme T(e.g., 10-5000 K) predicts molecular abundances.

9.2 TRANSLATIONAL PARTITION FUNCTION

The translational partition function q_{trans}quantifies the statistical weight of translational quantum states for a single particle or molecule moving freely in a container, forming the dominant contribution to the molecular partition function $q$for ideal gases at typical temperatures. Derived from the particle-in-a-box model, it is $q_{\mathrm{trans}} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$, where $m$is the particle mass, k_BBoltzmann's constant, Ttemperature, hPlanck's constant, and $V$the volume. This semiclassical expression arises by converting a triple sum over quantum numbers into an integral, valid when energy levels are densely spaced (high T, large V).youtube

Quantum Mechanical Origin

Translational energy levels for a particle in a 3D box of sides L_x, L_y, L_z(volume $V = L_x L_y L_z$) are $\varepsilon_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$, with $n_i = 1,2,\ldots$and degeneracy 1 per state. The exact partition function is $q_{\text{trans}} = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} e^{-\beta\varepsilon_{n_x n_y n_z}}(\beta = 1/k_BT)$, separating into $q_xq_yq_z$. For a cubic box $(L_x = L_y = L_z = L)$, each 1D sum approximates$\int_1^{\infty} e^{-(h^2n^2)/(8mL^2k_BT)}\,dn \approx \left(\frac{2\pi mk_BT}{h^2}\right)^{1/2} L$, yielding the standard form upon multiplication.youtube+1

This integral replaces summation via Euler-Maclaurin, justified when the thermal de Broglie wavelength $\Lambda = h/\sqrt{2\pi mk_BT} \ll L$, ensuring many states below k_BT. At low Tor nanoscale confinement (e.g., quantum dots), quantization matters: q_{trans}starts at 1 (ground state), rises stepwise, unlike the continuum approximation which is zero only at $T = 0$. Corrections include $\pm 1/24$terms from Poisson summation for finite-size effects.

Thermodynamic Implications

For Nindistinguishable ideal gas particles, the canonical partition function is $Q = q_{\text{trans}}^N/N!$, yielding Helmholtz free energy $A = -k_BT[N\ln q_{\text{trans}} - \ln N!] \approx -Nk_BT[\ln(q_{\text{trans}}/N) + 1]$(Stirling). Internal energy $U = \frac{3}{2}Nk_BT$emerges solely from translation, independent of interactions, with $C_V = \frac{3}{2}Nk_B$(Dulong-Petit for translation). Entropy via Sackur-Tetrode is $S = Nk_B\left[\ln\left(\frac{V}{N}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right) + \frac{5}{2}\right]$, capturing quantum volume exclusion.

Pressure follows $P = k_BT(\partial\ln Q/\partial V)_T = Nk_BT/V$, the ideal gas law, with $q_{\text{trans}} \propto V$explaining volume dependence. At high densities, virial expansions correct via q_{trans}modifications from excluded volume.

Classical Limit and Validity

The expression is classical when occupancy per state $n\Lambda^3/V \ll 1$(where $n = N/V$), avoiding Bose/Fermi degeneracy; for H2 at STP, Λ ≈ 0.3Å vs. 3 Å spacing, so valid. Quantum deviations appear below 1 K for gases or in 2D/1D systems (e.g., surfaces: $q_{\text{trans,2D}} = (2\pi mk_BT/h^2)A$). For electrons in metals, full Fermi-Dirac sums replace Boltzmann, but molecular contexts remain classical.

Applications in Chemistry and Materials

In spectroscopy, q_{trans}weights rovibrational lines via total q, with intensity $I \propto ge^{-\varepsilon/k_BT}/q$. Reaction equilibria use $K_p = (q_{\text{prod}}/q_{\text{react}})^N(k_BT)^{\Delta n}e^{-\Delta E_0/k_BT}$, dominated by translational ratios scaling as $(m_{\text{prod}}/m_{\text{react}})^{3/2}$. For combustion or atmospheric modeling, $q_{\text{trans}}(T)$spans 300-5000 K, enabling species balances.

In nanotechnology, for adsorbed species or quantum dots (size ~10 nm), discrete sums compute binding energies; e.g., in nanophosphors, translational confinement in pores tunes dopant diffusion. [conversation_history] Machine learning fits $q_{\text{trans}}$from trajectories for coarse-grained models. [conversation_history] Isotope effects: heavier isotopes raise q_{trans}(larger m), shifting equilibria (e.g., Urey fractionation).

Computational and Experimental Aspects

Exact sums use recursion or matrix methods for small V; semiclassical dominates with <1% error above 10 K. NIST databases tabulate $\ln q_{\text{trans}}$for accuracy. Experiments validate via speed of sound or virial coefficients, matching predictions to 0.1%. In 1D nanotubes, $q_{\text{trans,1D}} = \sqrt{2\pi m k_B T}/h \cdot L$, altering gas adsorption.

Extensions to Polyatomics and Beyond

For polyatomic, center-of-mass q_{trans}uses total m, separating from internal modes; vibrational amplitudes shrink effective Vin Einstein models. Relativistic corrections for heavy atoms: $q_{\text{trans}} \propto (k_B T/mc^2)^{-1/2}$adjustments. In liquids/clusters, periodic boundary or density functional approximations mimic q_{trans}. For white LED phosphors, gas-phase synthesis precursors' q_{trans}informs deposition rates.

9.3 ROTATIONAL PARTITION FUNCTION

The rotational partition function q_{rot}quantifies the statistical contribution of molecular rotations to the total molecular partition function in statistical mechanics, arising from quantized angular momentum levels of rigid rotors. For diatomic or linear molecules, energy levels are$E_J = BJ(J+1)$, where $B = \frac{h^2}{8\pi^2 I k_B}$is the rotational constant (I: moment of inertia), $J = 0,1,2,\ldots$the rotational quantum number, and degeneracy $g_J = 2J+1$. Thus, $q_{\text{rot}} = \sum_{J=0}^{\infty}(2J+1)\, e^{-J(J+1)\theta_r/T}$, with rotational temperature $\theta_r = B/k_B \approx 1 - 10\text{K}$ for most diatomics.

High-Temperature Approximation

At $T \gg \theta_r$(typical lab conditions), the sum approximates an integral: $q_{\text{rot}} \approx \int_0^{\infty}(2J+1)\, e^{-J(J+1)\theta_r/T}dJ = \frac{T}{\sigma\theta_r}$, where $\sigma$is the symmetry number ($\sigma = 1$ heteronuclear, 2 homonuclear like N2). This classical limit derives from phase space $\frac{1}{h^2}\int e^{-\beta H_{\text{rot}}} d\theta d\phi dp_\theta dp_\phi = \frac{8\pi^2 I k_B T}{h^2\sigma} = \frac{T}{\sigma\theta_r}$, valid when level spacing $2B \ll k_B T$. Corrections include $1 + \frac{\theta_r}{3T} + \frac{\theta_r^2}{15T^2} + \cdots$for accuracy >0.1%.

For symmetric tops (e.g., NH3), levels split as $E_{J,K} = BJ(J+1) + (A-B)K^2$($K$: projection quantum number), with $q_{\text{rot}} \approx \frac{\sqrt{\pi}}{\sigma}\left(\frac{T^3}{\theta_A\theta_B\theta_C}\right)^{1/2}$, where $\theta_i = \frac{h^2}{8\pi^2 I_i k_B}$. Asymmetric tops (e.g., H2O) use numerical diagonalization of rotational Hamiltonian, but high-T limit holds: $q_{\text{rot}} = \frac{\sqrt{\pi(8\pi^2 k_B T)^3}}{\sigma h^3\sqrt{I_a I_b I_c}}$. Linear polyatomics follow diatomic form with reduced I.

Symmetry and Nuclear Spin Effects

Homonuclear diatomics enforce wavefunction symmetry via spin-statistics: bosons (even nuclear spin, e.g., 14N2) occupy even-J only; fermions (odd, e.g., 1H2 ortho) odd-J. Total q_{rot}weights ortho/para ratios: for H2 at 298 K, ortho (I=1, nuclear degeneracy 3) dominates with $q_{\text{rot}} \approx 0.69T/\theta_r$, para (I=0,1) 0.31. Equilibrium shifts with temperature, affecting specific heat near 100 K. Inversion doubling (e.g., NH3) splits levels, but averages in q_{rot}.

Thermodynamic Properties

Rotational energy $U_{\text{rot}} = Nk_BT^2\frac{\partial \ln\, q_{\text{rot}}}{\partial T} = Nk_BT$(high T, linear), yielding $C_{V,\text{rot}} = Nk_B$(equipartition: 1/2 k_B T per quadratic term, two for linear). Nonlinear molecules contribute $C_{V,\text{rot}} = \frac{3}{2}Nk_BT$(three axes). Free energy $A_{\text{rot}} = -Nk_BT\ln\, q_{\text{rot}}$; entropy $S_{\text{rot}} = Nk_B[\ln\,(T/\sigma\theta_r) + 1]$. These explain gas heat capacities exceeding translational 3/2 R by R (diatomics) above 50 K.

Quantum vs. Classical Regimes

Below θ_r, discrete sums matter: for HF ($\theta_r = 30$ K), $q_{\text{rot}}(10\text{K}) \approx 0.3$ vs. classical 0.33, rising steeply. Centrifugal distortion refines $E_J = BJ(J+1)[1 - DJ^2(J+1)^2]$, with $D \approx 10^{-4}B$; correction $\Delta q_{\text{rot}}/q_{\text{rot}} \approx -0.04\theta_r/T$. Coriolis and vibrational coupling (break rigid rotor) require Dunham expansions for precision spectroscopy.

Applications in Spectroscopy

Rotational structure in IR/UV spectra follows $P(J+1)$and $R(J-1)$branches, intensities $\propto (2J+1)e^{-E_J/k_BT}/q_{\text{rot}}$. Boltzmann plots ln $I/(2J+1)$vs. $E_J$yield T; q_{rot}normalizes. In astrophysics, CO rotational lines probe molecular clouds, with q_{rot}correcting column densities up to 1000 K. Microwave spectra fit B from spacing's 2B(J+1).

Computational Methods

Exact q_{rot}sums to J_max ~ 3T / \theta_r; Wang summation handles asymmetry. ML potentials compute I(T) for floppy molecules. [conversation history] NIST-JANAF tabulates for 100+ species. Enharmonic corrections via curvilinear coordinates for polyatomic.

9.4 VIBRATIONAL PARTITION FUNCTION

The vibrational partition function q_{vib}represents the contribution of quantized vibrational modes to the molecular partition function in statistical mechanics, crucial for polyatomic molecules where nuclei oscillate around equilibrium positions. For a harmonic oscillator model, each mode $j$has energy levels $E_{j,n} = \hbar\omega_j(n_j + 1/2)$, with quantum number $n_j = 0,1,2,...$and degeneracy 1, yielding per-mode $q_j = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega_j(n+1/2)} = \frac{e^{-\theta_{v,j}/(2T)}}{1-e^{-\theta_{v,j}/T}}$, where $\theta_{v,j} = \hbar\omega_j/k_B$is the vibrational temperature (typically 1000-4000 K) and $\beta = 1/k_BT$.

The total $q_{\text{vib}} = \prod_j q_j$factors over $3N - 6$(nonlinear) or $3N - 5$(linear) normal modes, with zero-point energy $E_{\text{ZP}} = \frac{1}{2}\sum_j \hbar\,\omega_j$often set as reference, simplifying to $q_{\text{vib}} = \prod_j \frac{1}{1-e^{-\theta_{v,j}/T}}$.

High- and Low-Temperature Limits

At high $T \gg \theta_v$(e.g., >2000 K for combustion), $q_{\text{vib}} \approx \prod_j T/\,\theta_{v,j}$from equipartition ($k_B T$ per mode), but harmonic model caps at infinity unlike classical T/θ_v. Low T(room temp), $q_{\text{vib}} \approx 1 + e^{-\theta_v/T} + \cdots$, freezing higher levels; for CO ($\theta_v \approx 3100$ K), $q_{\text{vib}}(298\text{K}) \approx 1.02$. Mean vibrational energy per mode $\langle E_j \rangle = \frac{\hbar\omega_j}{e^{\theta_{v,j}/T}-1} + \frac{1}{2}\hbar\omega_j$(zero-point constant), with heat capacity $C_{V,j} = k_B(\theta_{v,j}/T)^2 e^{\theta_{v,j}/T}/(e^{\theta_{v,j}/T} - 1)^2$, peaking near θ_v.

Enharmonic Corrections

Real potentials deviate from parabolic: Morse $V(r) = D_e(1 - e^{-\alpha(r-r_e)})^2$yields levels $E_v = \hbar\omega_e(v + 1/2) - \hbar\omega_e x_e(v + 1/2)^2$, dissociating at $v_{\max} \approx \omega_e/(2\omega_e x_e)$. Perturbation refines $q_{\text{vib}} = q_{\text{harm}}(1 + \sum_v \Delta\,E_v/k_B T e^{-\beta E_v})$; mechanical anharmonicity shifts frequencies, electrical couples modes. Dunham expansion $Y_{k\ell}(\hbar\omega_e(v + 1/2))^{k+\ell}$computes accurate sums; Pitzer-Gwinn approximates from low-level data. For floppy modes (e.g., torsions <500 cm^{-1}), hindered rotor treatments replace oscillators.

Thermodynamic Derivations

Internal energy $U_{\text{vib}} = k_B T^2 \frac{\partial \ln\, q_{\text{vib}}}{\partial T}$, entropy $S_{\text{vib}} = k_B[\ln\, q_{\text{vib}} + T\frac{\partial \ln\, q_{\text{vib}}}{\partial T}]$, free energy $A_{\text{vib}} = -k_B T \ln\, q_{\text{vib}}$. Equilibrium constants incorporate $\Delta E_{\text{ZP}}$and $q_{\text{vib,prod}}/q_{\text{vib,react}}$, explaining endothermic reactions favoring vibrationally excited products. Specific heat rises gradually above 500 K for polyatomic, explaining polyatomic gases' $C_V > 7/2R$.

Computational Approaches

Normal modes from Hessian at minimum: frequencies via $\omega_i = \sqrt{\lambda_i/\mu_i}$(eigenvalues$\lambda_i$, reduced masses μ_i). Direct summation converges rapidly (20-50 levels/mode); variational methods (e.g., Watson) for polyad states. ML force fields accelerate $q_{\text{vib}}(T)$scans for large molecules, fitting NIST-JANAF data. [conversation history] Temperature grids (100-6000 K) tabulate $\ln q_{\text{vib}}$for kinetics software like Cantera. Isotope substitution scales$\omega \propto \sqrt{1/\mu}$, altering $q_{\text{vib}}$by 1-10%.

9.5 SUMMARY

The molecular partition function describes how the total energy of a molecule is statistically distributed among its allowed quantum states at a given temperature. It is a central quantity in statistical mechanics**,** linkingmicroscopic molecular energy levels **to** macroscopic thermodynamic properties.

The rotational partition function sums contributions from quantized rotational energy levels of molecules, primarily diatomic or polyatomic, determined by moments of inertia. For linear molecules at high temperatures, it approximates a classical value proportional to temperature, accounting for symmetry factors that reduce over counting in identical-atom cases like homonuclear diatomics. It dominates heat capacity contributions above rotational characteristic temperatures, typically a few Kelvin.

Vibrational Partition Function
This function accounts for quantized harmonic vibrations, starting from a zero-point energy. At low temperatures, only the ground state contributes, but as temperature rises, excited levels populate, yielding a heat capacity that rises then saturates per mode. Quantum anharmonicity refines it for real molecules.

9.6 TECHNICAL TERMS

Molecular partition function
Translational partition function
Rotational partition function
Vibrational partition function

9.7 SELF ASSESSMENT QUESTIONS

1. Briefly explain about the Molecular partition function
2. Explain about the Translational partition function
3. Explain about the Rotational partition function
4. Write about the Vibrational partition function

9.8 SUGGESTED READINGS

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics: Theory and applications by S.K. Sinha
3. Fundamentals of Statistical and Thermal Physics by F. Reif
4. Statistical Mechanics by Gupta and Kumar, Pragati Prakashan Pub. Meerut.
5. Statistical Mechanics by Satya Prakash

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LESSON-10

ELECTRONIC AND NUCLEAR PARTITION FUNCTION

AIM AND OBJECTIVE:

Electronic Partition Function

Aim

The aim of the **electronic partition function** is to account for the contribution of **electronic energy levels** of atoms or molecules to the **overall thermodynamic properties** of a system.

Objectives

- To determine the **population of electrons** among various electronic energy states
- To evaluate the **contribution of electronic states** to thermodynamic quantities such as **internal energy, entropy, and free energy**
- To explain temperature-dependent **electronic excitation** effects
- To assist in calculating the **total partition function** of atoms and molecules
- To understand **spectroscopic and ionization behavior** of matter

Nuclear Partition Function

Aim

The aim of the **nuclear partition function** is to describe the contribution of **nuclear energy levels** to the **thermodynamic behavior** of a system, particularly at **very high temperatures**.

Objectives

- To account for the **distribution of nuclei** among nuclear energy states
- To evaluate the **nuclear contribution** to thermodynamic properties
- To study systems involving **nuclear excitation**
- To analyze thermodynamic behavior in **high-energy and astrophysical environments**
- To complete the calculation of the **total partition function** in extreme conditions
- **Nuclear partition function** becomes important only at **extremely high temperatures**

STRUCTURE OF THE LESSON:

10.1 ELECTRONIC AND NUCLEAR PARTITION FUNCTION

Introduction

The **electronic and nuclear partition functions** are components of the **total partition function** in statistical mechanics, which account for contributions from **different energy levels** of a system.

- The **electronic partition function** considers the distribution of particles among various **electronic energy states** of atoms or molecules and helps in calculating thermodynamic quantities like **internal energy, entropy, and free energy**.
- The **nuclear partition function** accounts for the contribution of **nuclear energy levels**, such as spin and rotational states of the nucleus, to the overall thermodynamic behavior. This is significant only at **very high temperatures**, such as in stellar or nuclear environments.

Both functions help in connecting **microscopic quantum states** with **macroscopic**

thermodynamic properties.

The electronic partition function q_{elec}sums over electronic energy levels of a molecule or atom, weighted by their degeneracy's, contributing minimally to the total partition function $q$at ordinary temperatures due to large spacings between ground and excited states. Defined as $q_{\text{elec}} = \sum_i g_i \, e^{-(\varepsilon_i - \varepsilon_0)/k_B T}$, where $\varepsilon_0$is the ground-state energy, $g_i$the degeneracy (often from spin-orbit coupling, e.g., $g_0 = 1$singlet, 3 triplet), and levels from quantum chemistry solutions like Hartree-Fock or CASSCF. At 298 K, $q_{\text{elec}} \approx g_0$(typically 1-5) for most species, as first excitations exceed 10,000-50,000 cm^{-1} ($\theta_e > 15{,}000$ K).

Ground and Excited State Contributions

Ground states dominate: for closed-shell molecules like N2, $q_{\text{elec}} = 1$; atoms like O(^{3}P) have $g_0 = 9$(L=1, S=1, $g = (2L+1)(2S+1)$). Low-lying triplets (e.g., O2 $^1\Delta$_g at 7900 cm^{-1}) contribute$e^{-1135/T}$, ~0.01 at 298 K but relevant in plasmas. Rydberg series converge to ionization limits; hydrogen paradox arises summing infinite bound states $q_{\text{elec}} = \sum_n n^2 \, e^{-R/n^2 k_B T} \to \infty$, resolved by container size truncating high-n orbits larger than lab volumes. Practically, sum to $\varepsilon_i < 3k_B T + IP$(ionization potential).

Nuclear Partition Function

The nuclear partition function q_{nuc}accounts for hyperfine structure from nuclear spins, often temperature-independent as splittings$\ll k_B T$. For nuclei with spin I, degeneracy$g_I = 2I + 1$: e.g., ^{1}H (I=1/2, g=2), ^{14}N (I=1, g=3). Total $q_{\text{nuc}} = \prod_\alpha (2\, I_\alpha + 1)$, multiplicative over distinct isotopes. Ortho/para forms in homonuclear diatomics (e.g., H2) entangle nuclear spin with rotation: ortho-H2 (odd J, nuclear singlet I=1, g=3) vs. para (even J, I=0, g=1), with equilibrium ratio 3:1 at high T, affecting q_{rot}weighting. At room T, $q_{\text{nuc}} \approx 4$for H2.

Thermodynamic Role

Electronic excitations add $U_{\text{elec}} = k_B T^2 \frac{\partial \ln q_{\text{elec}}}{\partial T}$, negligible unless low-lying states; e.g., NO ($^2\Pi$, split by Λ-doubling) has $q_{\text{elec}} \approx 2$. Equilibrium constants gain $q_{\text{elec,prod}}/q_{\text{elec,react}} e^{-\Delta E_e / k_B T}$, favoring products with higher ground degeneracies. Nuclear spins contribute entropy $S_{\text{nuc}} = N k_B \ln q_{\text{nuc}}$, omitted in classical thermodynamics as constant, but vital for absolute entropies (third-law compliant). In Sakur-Tetrode, they multiply total q.

Quantum Mechanical Basis

Electronic levels from time-independent Schrödinger equation on Born-Oppenheimer surfaces: $H_{\text{elec}} \psi = E_e \psi$, with spin-orbit via relativistic Hamiltonians. Hund's rules predict term symbols ^{2}S+1L_J, degeneracies (2J+1) summed per term. Configuration interaction mixes; DFT/CASPT2 compute for heavy elements. Nuclear hyperfine from magnetic dipole/electric quadrupole: A I·J splitting, but $q_{\text{nuc}} \approx g_I$averages. Relativistic effects (fine structure) included in g_0 for heavy atoms like Bi.

Applications in Spectroscopy and Kinetics

Electronic transitions drive UV-Vis absorption; partition functions normalize oscillator strengths $f_{0i} \propto | \langle 0 \mid \mu \mid i \rangle |^2 \, e^{-E_i / k_B T} / q_{\text{elec}}$. Laser-induced fluorescence measures T via line ratios. In combustion, OH(A-X) emissions use q_elec for populations. Nuclear statistics explain H2/D2 rotational gaps in Raman spectra. Astrophysics: fine-structure lines (e.g., [O I] 63 μm) probe ISM densities via q_elec.

Computational Strategies

Tabulated in NIST-JANAF (up to 6000 K, 20+ states); ML models (e.g., ΔSCF) predict for clusters. [conversation_history] For Rydbergs, semiclassical phase space cuts off at container radius. Variational CI sums converge; avoided crossings mix states. Isotope-specific q_nuc scales with g_I, affecting equilibrium isotope fractionation.

Materials and Nanophosphor Relevance

In phosphors, electronic q_elec weights multiplet intensities: Eu^{3+} (7F_0 ground, g=1) to 5D_0 emissions, with Judd-Ofelt parameters fitting branching ratios normalized by q_elec(T). [conversation_history] Thermal population of ligand-field states quenches at >500 K, modeled as q_elec increase. Nuclear spins negligible but hyperfine broadens EPR in doped QDs. [conversation_history] Machine learning on electronic structure databases optimizes dopant levels via effective q_elec for LED efficiency. [Conversation history] In high-throughput screening, q_elec(T) predicts radiative lifetimes.

Paradoxes and Advanced Topics

Hydrogen q_elec paradox highlights continuum limits: full sum includes ionization continuum$\int_{IP}^{\infty} g(\varepsilon)\, e^{-\varepsilon/k_B T} d\varepsilon$, finite via density of states. Zeeman/Stark effects split levels, T-dependent in fields. Jahn-Teller distortions quench orbital degeneracy dynamically. For open shells, spin-orbit recouples LS to jj-coupling. Relativistic q_elec for actinides includes Dirac levels.

Conclusion

The **electronic and nuclear partition functions** provide a way to include **quantum energy levels** in the calculation of thermodynamic quantities. While the electronic partition function significantly influences the properties of matter at ordinary temperatures, the nuclear partition function becomes important only at **extremely high temperatures**. Together, they allow a more **complete and accurate evaluation** of the total partition function, linking microscopic quantum behavior to macroscopic thermodynamic laws.

10.2 APPLICATION OF ROTATIONAL PARTITION FUNCTION IN SOLIDS

Introduction

The **rotational partition function** describes the contribution of **rotational energy levels** of molecules to the **thermodynamic properties** of a system. While in gases, rotational motion is prominent, in **solids**, molecules are generally **restricted in rotation**, but small rotational vibrations or lattice rotations can still contribute to the system's energy at higher temperatures. Studying the rotational partition function in solids helps in understanding **specific heat, thermal energy distribution**, and other thermodynamic properties arising from **rotational degrees of freedom**.

The rotational partition function (q_{rot}) is a fundamental concept in statistical mechanics that provides a way to calculate the contribution of a molecule's rotational degrees of freedom to its overall thermodynamic properties.

The primary applications of the rotational partition function include:

Calculating Thermodynamic Properties

The rotational partition function acts as a bridge between the microscopic (molecular energy levels) and macroscopic (bulk) properties of a system.It is used to calculate the rotational contribution to various thermodynamic quantities for gases:

- Internal Energy (U_{rot})**:** The average thermal rotational energy per molecule or per mole.
- Entropy (S_{rot}): A measure of the rotational disorder and the number of accessible rotational states.5 The rotational entropy for diatomic molecules can be expressed in terms of $(\boldsymbol{q_{rot}})$:
- $S_{rot} = \frac{U_{rot}}{T} + R\ log\ (q_{rot})$:
- Heat Capacity $(C_{V,rot}\ and\ C_{P,rot}\ )$: The ability of the rotational degrees of freedom to store thermal energy.
- Helmholtz Free Energy (A_{rot}):Gibbs Energy (G_{rot})These are also directly related to the partition function.

Relating to Molecular Structure and Spectroscopy

The formula for the rotational partition function in the high-temperature limit (a common and accurate approximation for most molecules at ambient temperatures) explicitly depends on the molecule's structural properties:

- Moment of Inertia (I): The partition function is directly proportional to I for a linear molecule. Since the moment of inertia is calculated from the masses of the atoms and their relative positions (bond lengths and angles), the rotational partition function links thermodynamics back to the molecule's geometry.
- Rotational Constants (A, B, C): These constants, often derived from rotational (microwave) spectroscopy, are used in the calculation of $(q_{rot})$for non-linear molecules.
- Symmetry Number (σ): The partition function must be divided by the symmetry number (σ), which is the number of indistinguishable orientations a molecule can achieve by rotation.[11] This connects the rotational partition function to the molecule's symmetry and its nuclear spin statistics (especially important for homonuclear diatomics like $(H_2\ and\ O_2)$.

Understanding Energy Distribution

- The rotational partition function quantifies the number of thermally accessible rotational states for a molecule at a given temperature.
- A larger q_{rot} indicates that a larger number of rotational energy levels are significantly populated.
- The rotational partition function helps determine the equilibrium occupation probabilities of different rotational energy levels according to the Boltzmann distribution.

Conclusion

The **rotational partition function** in solids provides insight into the **thermodynamic contribution of rotational motions**, even when restricted. Its application helps in calculating **internal energy, heat capacity, and entropy** of solids more accurately, especially at elevated temperatures. Thus, it bridges the microscopic rotational behavior of molecules with the **macroscopic thermal properties** of solid materials

10.3 APPLICATION OF VIBRATIONAL PARTITION FUNCTION IN SOLIDS

The vibrational partition function is central to calculating the thermal properties of crystalline solids. In solids, the vibrational motion of the atoms is quantized and collective, giving rise to excitations called phonons.

The primary application is to use the vibrational partition function (q_{vib}) to determine the rotational contribution to a solid's thermodynamic properties, especially its heat capacity.

Calculating Heat Capacity (C_V)

The historical and most critical application is the accurate calculation of the molar heat capacity at constant volume (C_V) for crystalline solids, which classical mechanics failed to explain, particularly at low temperatures.

1. The Einstein Model

The Einstein model (1907) was the first successful quantum-mechanical application of the partition function to solids.

- Assumption: It treats a solid of N atoms as 3Nindependent, non-interacting quantum harmonic oscillators (QHO), all vibrating at a single, characteristic frequency (V_E)
- Partition Function: The total canonical partition function for the crystal's vibrational energy is (Q_{vib}) = $(q_{vib})^{3N}$, where (q_{vib}) is the partition function for a single QHO.
- $(q_{vib}) = \frac{e^{-hvE/2kT}}{1-e^{-hvE/kT}}$
- Application: Using the energy derived from this partition function, the Einstein heat capacity formula is obtained.
- Result: This model correctly predicts that (C_V) approaches zero at low temperatures (a major improvement over the classical Dulong-Petit law), and it recovers the classical ($C_V = 3R$) limit at high temperatures.However, its low-temperature approach to zero is too rapid (exponentially, not correctly)

2. The Debye Model

The Debye model (1912) is a refinement that accounts for the collective and coupled nature of atomic vibrations (phonons)

- Assumption: It treats the solid's vibrations as sound waves (phonons) with a continuous spectrum of frequencies up to a maximum Debye frequency ((v_V).
- Application: The total vibrational partition function is calculated by integrating the contribution of all these vibrational modes (treating them as QHOs).
- Result: This model correctly predicts the Debye T^3 Law at low temperatures:
- $C_V \alpha T^3$
- This T^3 dependence matches experimental data for non-metallic solids extremely well near absolute zero.

Other Thermodynamic Applications

Once the total vibrational partition function ($\boldsymbol{Q}_{vib)}$) is known from models like Einstein's or Debye's, it can be used to calculate other thermodynamic properties of the solid:

- Internal Energy (($U_{vib)}$): The average thermal energy stored in the lattice vibrations.
- Vibrational Entropy (($V_{vib)}$): A measure of the disorder associated with the number of accessible phonon states.
- Helmholtz Free Energy (($A_{vib)}$): Used to determine the pressure and elastic properties of the solid.

By accurately describing the vibrational states of the atoms in a solid, the partition function provides the necessary quantum statistical bridge to calculate bulk thermal properties that are crucial for materials science and condensed matter physics.

10.4 SUMMARY

In molecular statistical mechanics, besides translational, rotational, and vibrational motions, electronic and nuclear energy levels also contribute to the total molecular partition function. Their effects, however, are usually significant only under specific conditions.

The electronic partition function accounts for the distribution of molecules among electronic energy levels**.**

The nuclear partition function arises from the internal energy states of atomic nuclei, such as:

- Nuclear spin states
- Nuclear excitation levels

Rotational partition functions apply mainly to gases, predicting heat capacities for diatomic molecules like N_2 or O_2, where rotational contributions activate above a few Kelvin, adding to specific heats. They help calculate equilibrium constants in rotational spectroscopy and thermodynamic properties of polyatomic gases, such as entropy in atmospheric modeling. Symmetry numbers account for identical nuclei, affecting ortho-para hydrogen ratios.

Vibrational Partition in Solids

In solids, vibrational partition functions underpin the Einstein and Debye models, treating phonons as quantized oscillators. The Einstein model assumes identical frequencies, yielding low-temperature exponential heat capacity drop; Debye refines this with a continuum up to a cutoff, matching Dulong-Petit law at high temperatures and T^3 rise at low ones. These explain thermal expansion and conductivity in insulators.

10.5 TECHNICAL TERMS

Electronic and Nuclear partition function
Application of rotational partition function
Application of vibrational partition function in solids,

10.6 SELF ASSESSMENT QUESTIONS

1. Briefly explain about the Electronic and Nuclear partition function
2. Write about the Application of rotational partition function
3. Explain about the Application of vibrational partition function in solids

10.7 SUGGESTED READINGS

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics: Theory and applications by S.K. Sinha
3. Fundamentals of Statistical and Thermal Physics by F. Reif
4. Statistical Mechanics by Gupta and Kumar, Pragati Prakashan Pub. Meerut.

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LESSON-11

THEORY OF WHITE DWARF STARS

AIM AND OBJECTIVE

Aim

The aim of the **theory of white dwarf stars** is to explain the **structure, stability, and properties** of white dwarfs using principles of **quantum mechanics and statistical mechanics**, particularly the **degeneracy pressure of electrons** that prevents gravitational collapse.

Objectives

- To understand why **white dwarfs do not collapse under gravity** despite no significant nuclear fusion
- To apply **Fermi–Dirac statistics** to the degenerate electron gas in white dwarfs
- To calculate important properties such as **mass, radius, and density** of white dwarfs
- To explain the **Chandrasekhar limit**, the maximum mass a white dwarf can have before collapsing into a neutron star or black hole
- To study the **relationship between pressure, density, and temperature** in highly dense stellar objects

STRUCTURE OF THE LESSON:

11.1 EQUATION OF STATE OF AN IDEAL FERMI GAS

11.2 THEORY OF WHITE DWARF STARS

11.3 LANDAU DIAMAGNETISM

11.4 SUMMARY

11.5 TECHNICAL TERMS

11.6 SELF ASSESSMENT QUESTIONS

11.7 SUGGESTED READINGS

11.1 EQUATION OF STATE OF AN IDEAL FERMI GAS

Grand potential → pressure

Start from the grand canonical potential

$\Omega = -k_B T \quad \ln 1 + ze^{-\beta\varepsilon}$

$$z = e^{\beta\mu}\beta = \frac{1}{k_B T}$$

for noninteracting fermions. Replace the single-particle sum by an integral using the density of states in 3D (nonrelativistic particles):

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

Then

$. \Omega = -k_B T \int_0^{\infty} g(\varepsilon)\ \ln 1 + ze^{-\beta\varepsilon}\ d\varepsilon$

The pressure is P=−Ω/V. Introducing the thermal de Broglie wavelength

$$\lambda = \frac{\mathrm{h}}{\sqrt{2\pi \mathrm{m} k_B T}}$$

and the standard Fermi integrals (also written with fugacity z)

$f_v(z) = \frac{1}{\Gamma(\mathrm{v})}$, $\int_0^{\infty} \frac{x^{v-1}}{z^{-1}e^{x+1}}\, dx$, $f_v(z) = -Li_v(-z)$

one obtains the standard thermodynamic relations for an ideal nonrelativistic Fermi gas in 3D:

2. Finite-temperature results (3D, nonrelativistic)

Particle number density

$$n = \frac{N}{V}\frac{g}{\lambda^3} f_{3/2}(z)$$

Pressure (equation of state)

$$P = \frac{k_B T g}{\lambda^3} f_{5/2}(z)$$

Internal energy (total) and energy density

$$U = \frac{3}{2}PV \ \rightarrow \frac{U}{V} = \frac{3}{2}P$$

(so P and U are related by the usual ideal-gas kinetic relation for a quadratic dispersion in 3D).

Chemical potential enters through $z = e^{\beta\mu}$. Given n and T you solve $n = \frac{g}{\lambda^3} f_{3/2}(z)$for z (or μ) and then plug into $P = \frac{k_B T g}{\lambda^3} f_{5/2}(z)$

Useful limiting cases:

- Classical (high T, low n): z≪1,$f_v(z)$ ≈z and you recover the classical ideal gas $P = -nk_B T$.
- Degenerate / quantum z≫1: use asymptotic expansions of the Fermi integrals (Sommerfeld expansion) to get corrections to the zero-temperature limit.

3. Zero-temperature limit (T→0, fully degenerate Fermi gas)

At T=0 all states with $\varepsilon \leq \varepsilon_F$ are filled, where the Fermi energy ε_F is determined by the density:

$$n = \int_0^{\varepsilon_F} g(\varepsilon)\, \mathrm{d}\varepsilon = \frac{\mathrm{g}}{6\pi^2}\mathrm{k}_\mathrm{F}^3$$

$$k_F = \left({}^{6\pi^2 \mathrm{n}}/_{g}\right)^{1/3}$$

and

$$.\varepsilon_F = \frac{\hbar^2 k_F^3}{2m} = \frac{\hbar^2}{2m}\left(6\pi^2 n/g\right)^{2/3}$$

The T=0 pressure and energy per unit volume follow from integrating the occupied states:

$$P = 0) = \frac{2}{5} n\varepsilon_F$$

$$\frac{U}{V}(T = 0) = \frac{3}{5}\, n\varepsilon_F$$

Thus P=(2/3)(U/V) at T=0 (and more generally U=(3/2)PV for the nonrelativistic ideal Fermi gas at any T).

Explicitly, using nnn,

$$P(T = 0) = \frac{\hbar^2}{5m}\left(6\pi^2/g\right)^{2/3} n^{5/3}$$

This is the familiar degenerate-Fermi pressure P∝$n^{5/3}$

11.2 THEORY OF WHITE DWARF STARS

1. The most important and interesting application of the Fermi–Dirac statistics is the study of white dwarf stars.
2. It is observed that the luminosity (brightness) of stars is related to their surface temperature or colour.
3. When luminosity is plotted against colour (or temperature), we obtain the Hertzsprung–Russell (H–R) diagram.

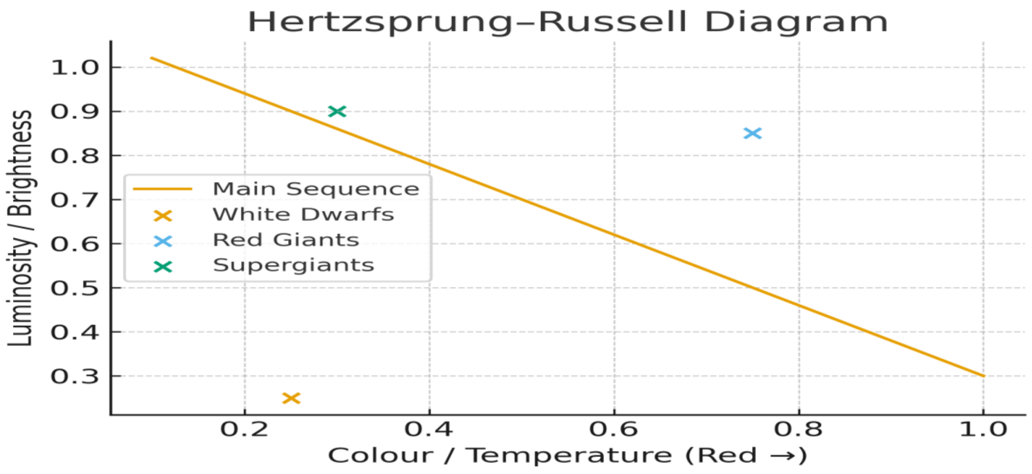


Figure 11.1

Figure 11.1: Detailed Hertzsprung–Russell Diagram showing main sequence, white dwarfs and giant regions.

4. Red giant stars which are abnormally bright compared to main sequence stars of similar color.
5. White dwarf stars are well approximated as a degenerate Fermi gas.
6. The source of stellar energy is nuclear fusion, primarily the conversion of hydrogen into helium:

   H + H → He + Energy
7. White dwarf stars have exhausted their thermonuclear fuel and represent one of the terminal stages of stellar evolution.
8. Mestel (1952) showed that the slow loss of thermal energy from hot white dwarf interiors explains their observed luminosity.
9. They are stars which are much fainter, possess small diameters, and are very dense compared to other stars of the same mass.
10. Typical data for a white dwarf star:
    - Content: Mostly Helium
    - Density ≈ 10^7 g cm^{-2}
    - Mass ≈ 10^{33} g
    - Central temperature ≈ 10^7 K
11. A white dwarf star is a mass of helium atoms at extremely high temperature under extreme compression.
12. The atoms are expected to be completely ionized and the star may be regarded as a gas composed of nuclei and electrons.
13. The Fermi energy is given by:

    $$E_F = \left(\frac{h^2}{2m}\frac{1}{v^{2/3}}\right) \approx 20 \text{ MeV}$$

    Corresponding Fermi temperature ≈ 10^7 K
14. Since the Fermi temperature is greater than the temperature of the star, the electron gas is highly degenerate.
15. The state of a single electron is specified by momentum p and spin σ, where $\sigma = \pm\frac{1}{2}$.
16. The energy–momentum relation for an electron is:

    $$EP_s = \sqrt{(pc)^2 + (m_e c^2)^2}$$

    where m_e is the mass of the electron.
17. The ground state energy of Fermi gas is

$$E_0 = \frac{2v}{ħ^3}\int_0^{P_F} dp\, 4\pi p^2 \sqrt{(\mathrm{pc})^2 + (\mathrm{m_e c^2})^2} \quad \ldots\ldots\ldots.(1)$$

Where is $P_F$the Fermi momentum and is defined

$$\frac{v}{ħ^3}\left(\frac{4}{3}\pi p_F^3\right) = \frac{N}{2}$$

$$p_F^3 = \frac{N}{2}\frac{ħ^3}{v}\frac{3}{4}\pi$$

$$p_F^3 = \frac{3\pi ħ^3}{8v}$$

$$p_F^3 = ħ(\frac{3\pi^2}{v})^{1/3} \quad \ldots\ldots\ldots\ldots(2)$$

18. Consider $x = \frac{p}{\mathrm{m_e c}}$

$$f(x_F) = \int_{x_o}^{x_p} \sqrt{(1+x^2)}\, x^2\, dx = \int \frac{1}{3}x_F^3\left(1+\frac{1}{3}x_F^2 + \cdots\ldots\right) \qquad (x_F \ll 1)$$

$$= \int \frac{1}{4}x_F^4\left(1+\frac{1}{3}x_F^2 + \cdots\ldots\right) \qquad (x_F \gg 1) \quad \ldots\ldots\ldots.(3)$$

(i) When $x_F \ll 1$ corresponding to non-relativistic case

(ii)When $(x_F \gg 1)$ corresponding to relativistic case

$$x_F = \frac{p_F}{\mathrm{m_e c}} = \frac{ħ}{\mathrm{m_e c}}(\frac{3\pi^2}{v})^{1/3} \quad \ldots\ldots\ldots\ldots(4)$$

19. If the total mass of the star m and radius of star R then

$$m = (\mathrm{m_e} + 2\mathrm{m_p}) \approx 2\mathrm{m_p N}$$

$$\mathrm{R}=(\frac{3v}{4\pi})^{1/3} \quad \ldots\ldots\ldots(5)$$

20. In terms of m and R we have

$$v = \frac{8\pi}{3}\frac{\mathrm{m_p R^3}}{m} \quad \ldots\ldots\ldots\ldots(6)$$

$$x_F = \frac{ħ}{\mathrm{m_e c}}(\frac{3\pi^2}{\frac{8\pi}{3}\frac{\mathrm{m_p R^3}}{m}})^{1/3}$$

$$= \frac{ħ}{\mathrm{m_e c}}\frac{1}{R}\left[\frac{9\pi}{8}\frac{m}{\mathrm{m_p}}\right]^{1/3} = \frac{\bar{m}^{1/3}}{\bar{R}}$$

Where $\bar{m} = \frac{9\pi}{8}\frac{m}{\mathrm{m_p}}\bar{R} = \frac{R}{\frac{ħ}{\mathrm{m_e c}}}$

20. The pressure entered by the Fermi gas

$$p_o = \frac{-\partial E_o}{\partial v_o}$$

$$P_0 =]\frac{m_e{}^4c^5}{\pi^2\hbar^3}[\frac{1}{3}x_F^3\sqrt{1+}\,x_F^2 - f(x_F)]$$

Case (i): If $(x_F \ll 1)$ $i.e$ $\frac{p_F^2}{m_e c}$<<1 non-relativistic

Case (ii): If $(x_F \gg 1)$ $i.e$ $\frac{p_F^2}{m_e c} \gg$ relativistic

21.To compress a star of given mass from infinite diluteness to a state of finite density:

$$\omega = \int_{-\infty}^{R} P^0 4\pi r^2 dr \qquad \ldots\ldots\ldots\ldots (7)$$

where R is the radius of the star

22. Gravitational energy (dimensional analysis)

$$\omega = -\alpha\frac{\gamma\, m^2}{R}$$

where γ is the gravitational constant and α is a pure number of order unity.

23. Hence,

$$\int_{-\infty}^{R} p_0 4\pi r^2 dr = -\alpha\frac{\gamma\, m^2}{R} \qquad \ldots\ldots\ldots..(8)$$

Differentiating equation (8) with respect to R, we get:

$P_0 = (\alpha / 4\pi) \cdot (\gamma\, m^2 / R^4)$

Case (ii): High temperature electron gas

Suppose the temperature of the electron gas is much higher than the Fermi temperature.

The gas behaves as an ideal Boltzmann gas:

$P_0V = kT$

$P_0 = kT / V$

$$P_0 = \frac{kT}{\frac{8\pi m_p R^3}{3\quad m}} = \frac{3kT}{8m_p\pi}\frac{m}{R^3}$$

Substituting the values :

$$(\alpha / 4\pi) \cdot (\gamma\, m^2 / R^4) = \frac{3kT}{8mp\pi}\frac{m}{R^3}$$

$$R = \frac{2}{3}\alpha m\frac{m_p r}{kT}$$

This treatment is not applicable to white dwarf stars when thermal pressure dominates.

Case(ii) Suppose the electron gas is at low density.

$x_F \ll 1$

Then, the degeneracy pressure is

$P_0 = \frac{4}{5}k\frac{\bar{m}^{5/3}}{\bar{R}^5} = \frac{\bar{\bar{k}}^1\bar{m}^2}{\bar{R}^4}$

The radius of the star decreases as the mass of the star increases.

$\bar{m}^{1/3}\overline{\bar{R} = \frac{k}{k^1}}\frac{4}{5}$

This condition is valid when the density is low. Hence, it is applicable for small mass m and large radius R.

Case(iii) Suppose the electron gas is at high density.

$(x_F \gg 1)$

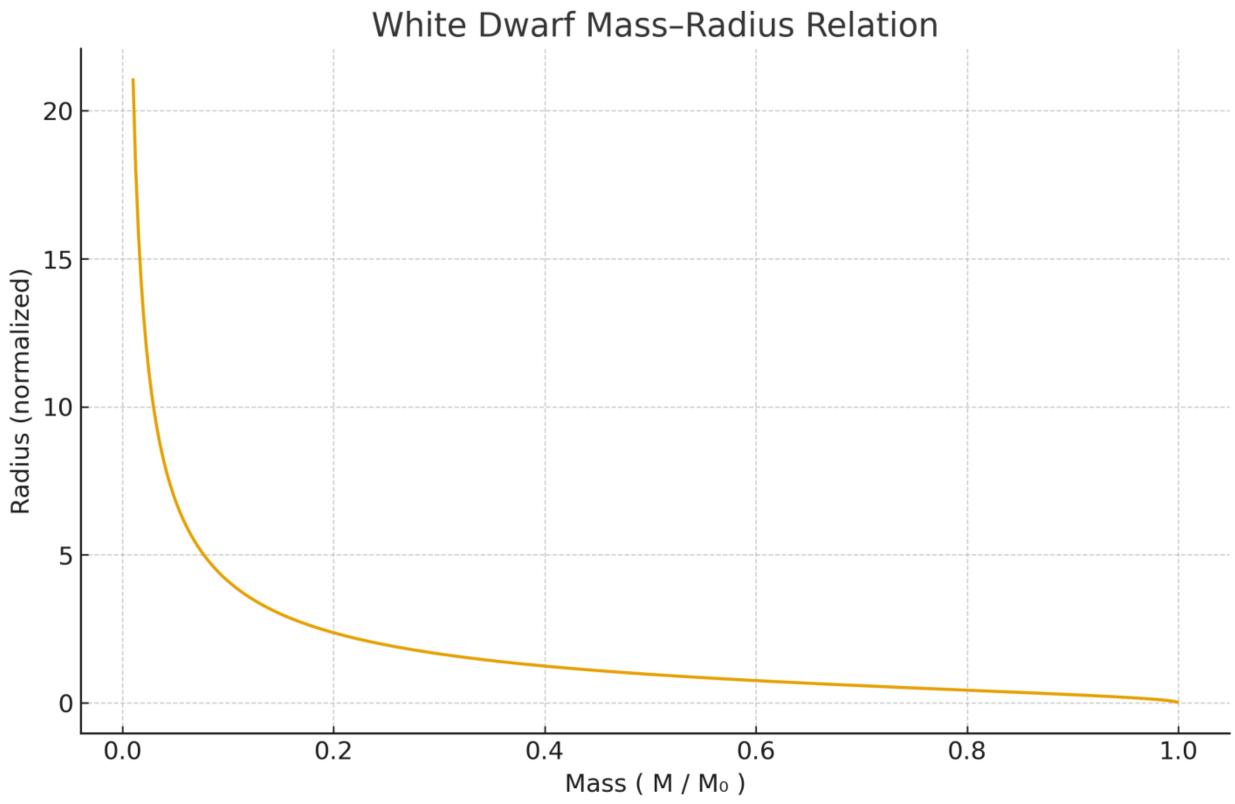
$P_o = k[\frac{\bar{m}^{4/3}}{\bar{R}^4} - \frac{\bar{m}^{2/3}}{\bar{R}^2}] = k^1\frac{\bar{m}^2}{\bar{R}^4}$

$$\overline{R = \bar{m}^{2/3}}\sqrt{1 - (\frac{\bar{m}}{m_o})^{2/3}}$$

Here, m_o is the mass of the Sun.

m_o 1.4 M known as the Chandrasekhar mass limit.

The radius–mass relation curve shows that the radius decreases sharply and approaches zero as the mass approaches m_o.



11.3 LANDAU DIAMAGNETISM

1. Landau first showed that diamagnetism arises from the quantization of the motion of charged particles in a magnetic field.
2. The magnetic susceptibility per unit volume of a system is defined as

   $\chi = \partial m / \partial B$ (a)
3. Here m is the average induced magnetic moment per unit volume of the system along the direction of an external magnetic field B.

   $$m = \frac{1}{v} < \frac{-\partial H}{\partial \beta} >$$
4. Here H is the Hamiltonian of the system in the presence of an external magnetic field B.

   (i) In the canonical ensemble:

   $$m = kT \frac{\partial}{\partial \beta} \log \left(\frac{Q_N}{v}\right)$$

   Here Q_N is the canonical partition function.

   (ii) In the grand canonical ensemble:

   $$m = kT \frac{\partial}{\partial \beta} \log \left(\frac{Z}{v}\right)_{(T,V,Z)}$$

Here Z is the grand partition function.

1. A system is said to be diamagnetic if $\chi < 0$ and paramagnetic if $\chi > 0$.
2. In the presence of an external magnetic field, two effects are important for the magnetic properties of a substance.

   (i) The electrons, whether free or bound, move in quantized orbits in the magnetic field.

   (ii). The spin of the electrons tends to be aligned parallel to the magnetic field.
3. The alignment of the electron spin with an external magnetic field gives rise to paramagnetism, whereas the orbital motion of the electrons gives rise to diamagnetism.
4. Consider the problem of a free spinless electron gas in an external magnetic field.
5. Consider a system of N spinless electrons contained in a volume V. The electrons are free except for their interaction with a uniform external magnetic field B.
6. To calculate the partition function, we first calculate the energy levels of a single particle.

7. According to quantum mechanics, the allowed states of a charged particle in an external field are the classical orbits that satisfy the quantum conditions:

   $\oint p \cdot dr = (j + 1 / 2) h$ (9) $j = 0, 1, 2, \ldots$

   Here p and r are the classical variables of a particle; p denotes momentum and r denotes position.

8. The Hamiltonian for a single electron is

   $H(p, r) = (1 / 2m) [p + (e / c) A]^2$ (10)

   where

   m is the mass of the electron,

   c is the charge of the electron, and

   A is the vector potential associated with the magnetic field B.

   The magnetic field is given by

   $B = \nabla \times A$ (11)

9. The velocity of the electron along the circular path is given by:

   $V = \frac{ea\beta}{mc}$ (12)

10. The momentum is

    $\rho = mv - \frac{e}{c}$ (13)

11. Substituting equation (13) in equation (9):

    $\oint (mv - {}^{e}/_{c}\, A)dv = (J + {}^{1}/_{2})h$ (14)

12. J is the quantum number (j = 0, 1, 2, …). The energy corresponding to the j-th allowed orbit is:

    $\frac{e\hbar B}{mc}(J + \frac{1}{2})$

13. The allowed energies of an electron are:

    $E(p_2 j) = \frac{p_2^2}{2m} + \frac{c\hbar B}{2m}\left(J + \frac{1}{2}\right)$ (15)

14. Here $p_z$is the momentum along the magnetic field direction. Its allowed values are:

    $p_{z=\frac{2\pi e\hbar}{vv_3}}$ $l = 0, \pm 1 \pm ,2 \ldots.$ (16)

15. The degeneracy of the energy level E(p_z, j) for a given $p_z$is same for all j and is given by is:

    $g = \frac{v^{2/3}}{2\pi} \frac{eB}{\hbar c}$ (17)

16. The grand partition function is given by:

$$Z = \pi\lambda(1 + Ze^{-\beta E\lambda)}) \qquad (18)$$

Hence,

$$log\ Z = \sum_{k} log\ (1 + Ze^{-\beta E\lambda)})$$

17. Expanding the above expression in the continuum limit gives:

$$log\ Z = \frac{gv^{1/3}}{h} \int_{-\infty}^{+\infty} dp \sum_{v=0}^{\infty} log\left(1 + Ze^{-\beta E)}\right) \qquad (19)$$

18. From (a) we know that $\chi = \partial m / \partial B$

    Hence

$$m = kT \frac{\partial}{\partial\beta}\left[\log\frac{Z}{v}\right] \qquad (20)$$

19. Substitute equation (20) and equation (19) in equation (a)

    We have

$$\chi = \frac{-1}{3kT_s}(\frac{e\hbar}{2mc})^2 \qquad (21)$$

    s is specific volume

    equation (21) exhibits that $\frac{1}{T}$ dependent on χ

11.5 SUMMARY

Ideal Fermi Gas Equation of State

For fermions like electrons, the equation of state at T=0 shows degeneracy pressure balancing a Fermi energy, giving pressure scaling as (density)^{5/3} independent of temperature. At finite T, it interpolates to classical ideal gas limits, crucial for white dwarf stability and semiconductor doping.

White dwarf stars are remnants of low- to medium-mass stars after shedding outer layers, supported against gravitational collapse by electron degeneracy pressure from a Fermi gas of electrons. Their structure follows hydrostatic equilibrium with a polytropic equation of state where pressure scales as density to the 5/3 power in the non-relativistic limit, yielding a mass-radius relation where radius inversely scales with mass. Beyond the Chandrasekhar limit of about 1.4 solar masses, relativistic effects cause instability, leading to type Ia supernovae.

Landau Diamagnetism

Landau diamagnetism arises in metals from orbital motion of conduction electrons in a magnetic field, quantized into Landau levels. This induces a weak negative susceptibility opposing the field, distinct from Pauli paramagnetism from spin alignment. It scales with the density of states at the Fermi level and temperature independence at low T, explaining weak diamagnetism in simple metals like alkali ones.

11.5 TECHNICAL TERMS

Equation of state of an ideal Fermi gas
Theory of White dwarf stars
Landau diamagnetism

11.6 SELF ASSESSMENT QUESTIONS

1. Explain about the Equation of state of an ideal Fermi gas
2. Briefly explain about the Theory of White dwarf stars
3. Explain about the Landau diamagnetism

11.7 SUGGESTED READINGS

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics: Theory and applications by S.K. Sinha
3. Fundamentals of Statistical and Thermal Physics by F. Reif
4. Statistical Mechanics by Gupta and Kumar, Pragati Prakashan Pub. Meerut.
5. Statistical Mechanics by Satya Prakash

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LESSON-12

BOSE-EINSTEIN CONDENSATION

AIM AND OBJECTIVE

Aim
The aim of **Bose–Einstein Condensation** is to study the **macroscopic accumulation of bosons in the lowest quantum energy state** at very low temperatures, leading to the formation of a **new state of matter** with unique quantum properties.

Objectives

- To understand the behavior of **bosons** at extremely low temperatures
- To explain the phenomenon where a **large fraction of particles occupy the ground state**
- To study the **thermodynamic and quantum properties** of Bose–Einstein condensates
- To predict and analyze **superfluidity, coherence, and macroscopic quantum effects**
- To explore applications in **quantum computing, precision measurement, and low-temperature physics**

STRUCTURE OF THE LESSON:

12.1 PHOTONS IN SOLIDS

Introduction
Photons in solids represent **quanta of electromagnetic radiation** interacting with the material. They are responsible for phenomena like **absorption, emission, and heat transport** in solids. In the context of solid-state physics, the photon contribution is significant in the study of **blackbody radiation**, **optical properties**, and **thermal conductivity** at high temperatures.

In solids, photons interact strongly with the electronic, vibrational, and collective excitations of the material. This interaction is central to **optics, semiconductors, lasers, and photonic devices.**

1. Photons in solids are mainly involved in:

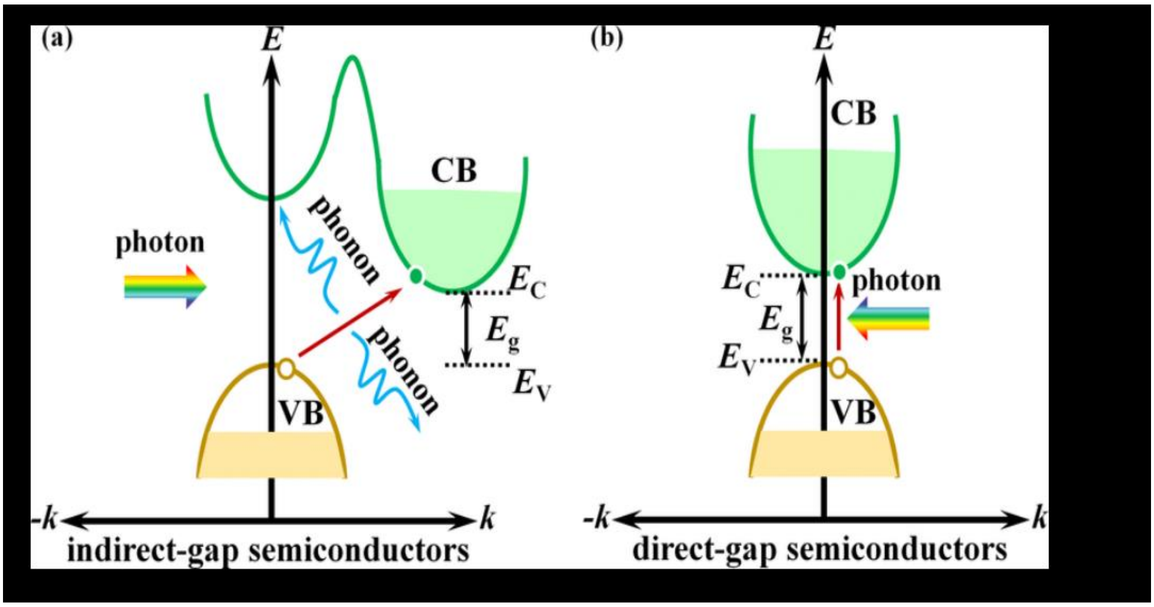
- **Absorption** and **emission**
- **Scattering** (elastic and inelastic)
- **Energy and momentum transfer**

They act as probes of a solid's internal structure and as carriers of energy.

2. Photon Absorption in Solids

When a photon enters a solid, it may be absorbed if its energy matches an allowed transition.

Electronic Transition Condition:
$h\nu \geq E_g$
where Eg is the band gap energy.



3. Photon Emission in Solids
   a) Spontaneous Emission: Excited electrons return to lower energy states emitting photons.
   b) Stimulated Emission: Incident photon induces emission of a coherent photon (laser principle).

4. Photon Scattering in Solids
   (a) Rayleigh Scattering: Elastic scattering, photon energy unchanged.
   (b)Raman Scattering: Inelastic scattering involving phonons.

   Energy relation:

$$h(v_{in} - v_{iout}) = ħω_{phonon}$$

it is used to study lattice vibrations and crystal structure

5. Photon Coupling with Excitations
   Photons may couple with excitations such as phonons, excitons, and magnons. Strong coupling leads to quasiparticles called polaritons.

6. Optical Properties of Solids
   Photon interactions determine refractive index, absorption coefficient, reflectivity, and dielectric function.

7. Statistical Aspect
   Photons obey Bose–Einstein statistics. Thermal emission from solids follows Planck's law modified by emissivity:
   $I(v) = \varepsilon(\nu) I_{\mathrm{blackbody}}(\nu)$
8. Applications
   Photon behavior in solids underlies:
   - LEDs and laser diodes
   - Solar cells
   - Optical fibers
   - Photodetectors
   - Raman and optical spectroscopy

Phonons are **quantized lattice vibrations** in crystalline solids. They are collective excitations of atoms oscillating about their equilibrium positions and are essential for understanding **thermal, elastic, and transport properties** of solids.

1. Physical meaning of phonons

- Atoms in a crystal vibrate → normal modes of vibration
- Each normal mode behaves like a **quantum harmonic oscillator**
- Energy of a phonon:
  $E=\hbar\omega$
  where ω is the angular frequency

Limits
- Photons do not carry mass, so their **direct contribution to specific heat at low temperatures** is negligible.
- Photon effects are significant **mainly at high temperatures** or in materials with strong **electromagnetic interactions**.
- Interaction of photons with solids is influenced by **material transparency and lattice structure**.

Conclusion
Photons in solids are crucial for understanding **radiative energy transfer, optical properties, and high-temperature thermal behavior**. However, at low temperatures, their contribution to thermodynamic properties is small compared to **phonons**.

12.2 PHONONS IN SOLIDS

Introduction
Phonons are **quanta of lattice vibrations** in a solid and represent the **collective motion of atoms in a crystal lattice**. They are responsible for **thermal energy storage, heat capacity, and thermal conductivity** in solids. Phonons obey **Bose–Einstein statistics**, and their behavior explains deviations from the **classical Dulong–Petit law** at low temperatures.

Phonons are quantized lattice vibrations in crystalline solids. They are collective excitations of atoms oscillating about their equilibrium positions and are essential for understanding thermal, elastic, and transport properties of solids.

1. Physical meaning of phonons

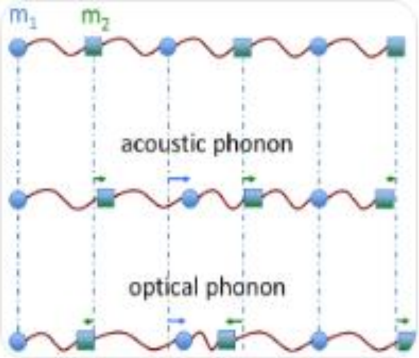
- Atoms in a crystal vibrate → normal modes of vibration
- Each normal mode behaves like a quantum harmonic oscillator
- Energy of a phonon:
  $E=\hbar\omega$
  where ω is the angular frequency
  Phonons are quasiparticles, not real particles

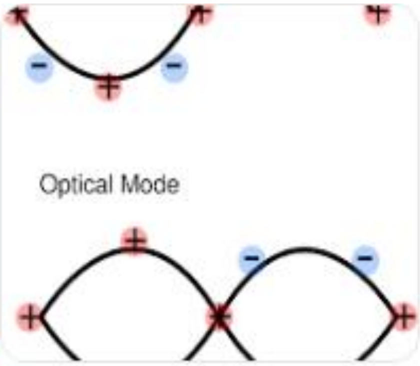
2. Lattice vibrations and normal modes

- A crystal with N atoms has 3N normal modes of vibration.
- Each normal mode is characterized by:
- Wave vector k
- Angular frequency $\omega(k)$

The relation ω vs k is called the phonon dispersion relation.

2. Types of phonons





(a) Acoustic phonons

- Atoms vibrate in phase
- Frequency $\omega\to0$ as wave vector $k\to0$
- Responsible for:
- Sound propagation
- Heat conduction

(b) Optical phonons

- Atoms in the basis vibrate out of phase
- Finite frequency at $k=0$
- Strongly interact with infrared and Raman radiation

4. Phonon statistics

- Phonons are bosons
- Obey Bose–Einstein statistics
- Chemical potential:
  $\mu=0$

(number of phonons is not conserved)
Average occupation number:

$$< n(\omega) >= \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

6. Role of phonons in solids

Phonons play a central role in:

- Specific heat (Einstein & Debye models)
- Thermal conductivity
- Electrical resistivity (electron–phonon interaction)
- Superconductivity
- Optical properties (IR absorption, Raman scattering)

7. Phonon interactions

- Phonon–phonon → thermal resistance
- Electron–phonon → electrical resistivity, superconductivity
- Photon–phonon → Raman scattering

8. Importance of phonons

Phonons explain:

- Heat conduction in insulators
- Thermal expansion
- Sound waves in solids
- Low-temperature properties
- Superconductivity (via electron–phonon coupling)

Limits

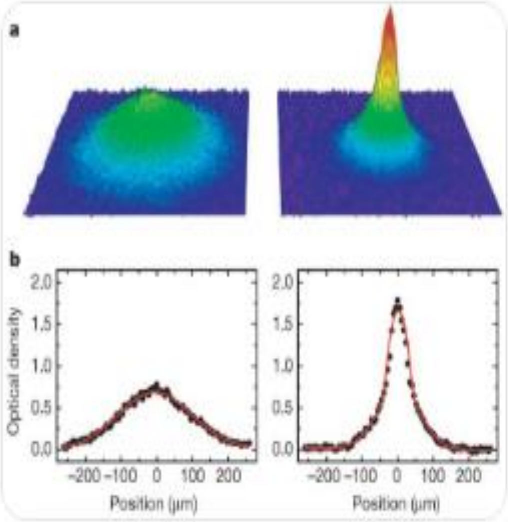
- The **phonon model** assumes a **perfect crystal lattice**; defects or impurities reduce accuracy.
- At **very high temperatures**, anharmonic effects (non-linear vibrations) make the simple phonon model less accurate.
- Does not account for **electron-phonon interactions**, which can be significant in metals and superconductors.

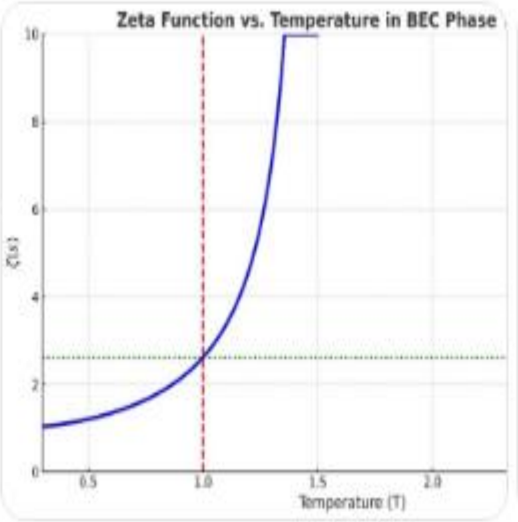
Conclusion

Phonons are essential for explaining **thermal and vibrational properties of solids**, especially at low temperatures where quantum effects dominate. They provide a **microscopic understanding of heat capacity, thermal conductivity, and lattice dynamics**.

12.3 BOSE-EINSTEIN CONDENSATION

Bose–Einstein condensation is a quantum phenomenon in which a large fraction of bosonsoccupy the lowest energy state at very low temperatures, forming a new state of matter called a Bose–Einstein condensate.





Introduction

Bose–Einstein Condensation (BEC) is a quantum phenomenon predicted by **Satyendra Nath Bose and Albert Einstein** in the 1920s. It occurs in a system of **identical bosons** (particles with integer spin) at **extremely low temperatures**, near absolute zero. At this temperature, a large fraction of bosons occupies the **lowest energy state (ground state)**, leading to a **macroscopic quantum state**. BEC demonstrates quantum effects on a macroscopic scale, showing properties like **coherence and superfluidity**.

1. Basic idea

- Bosons have integer spin (0, 1, 2, …).
- They obey Bose–Einstein statistics.
- Unlike fermions, many bosons can occupy the same quantum state.
- Below a critical temperature, particles "condense" into the ground state.

The system behaves as a single macroscopic quantum object.

2. Bose–Einstein distribution

The average number of particles in a state of energy E is:

$$< n(\mathrm{E}) >=\frac{1}{e^{E-\mu/k_B T}-1}$$

where

- μ = chemical potential
- k_B = Boltzmann constant
- T = absolute temperature

At very low T, $\mu \to 0$ and ground-state occupation becomes very large.

3. Critical temperature for condensation

For an ideal Bose gas:

$$T_c=\frac{2\pi\hbar^2}{mk_B}\left(\frac{n}{2.612}\right)^{2/3}$$

where

- m = mass of boson

- n = particle number density

Below T_c , Bose–Einstein condensation occurs.

4. Fraction of particles in ground state

For T<T_c:

$$\frac{N_0}{N} = 1 - (\frac{1}{T_c})^{3/2}$$

- N_0 = number of particles in ground state
- At T=0: $N_0 = N$

5. Physical interpretation

- Thermal de-Broglie wavelength increases as T decreases:

$$\lambda = \frac{\mathrm{h}}{\sqrt{2\pi \mathrm{m} k_B T}}$$

- When wavelength ≈ interparticle spacing → wavefunctions overlap
- Distinguishable particles become indistinguishable

6. Experimental realization

- First achieved in 1995
- Atoms used:
- Rubidium-87
- Sodium-23
- Cooling methods:
- Laser cooling
- Evaporative cooling
- Temperatures: nano-kelvin range

7. Properties of Bose–Einstein condensate

✓ Zero viscosity (superfluid behavior)

✓ Coherence similar to lasers

✓ Macroscopic quantum phenomena

✓ Extremely sensitive to external fields

8. Examples of Bose systems

✓ Helium-4 (superfluidity)

✓ Ultracold atomic gases

✓ Magnons (quasi-particles)

✓ Phonons (at low energies)

Applications

- **Superfluidity**: Explains frictionless flow in liquid helium and other superfluids
- **Quantum computing**: Used in the creation of qubits for **quantum information processing**

- **Precision measurements**: Applied in **atomic clocks, interferometry, and sensors**
- **Study of macroscopic quantum phenomena**: Helps explore **coherence, entanglement, and matter waves**
- **Simulation of condensed matter systems**: Laboratory BEC can simulate complex **solid-state physics problems**

Limits / Limitations

- Requires **extremely low temperatures** close to absolute zero (a few nano-Kelvin)
- Can be observed **only in bosonic systems**; fermions require pairing (e.g., Cooper pairs)
- Sensitive to **external perturbations** like magnetic or optical field fluctuations
- Difficult to maintain for large particle numbers over long times
- Not suitable for systems at **high temperatures or high densities**

Conclusion

Bose–Einstein Condensation is a remarkable quantum phenomenon where **bosons occupy the ground state collectively** at ultra-low temperatures. It bridges **microscopic quantum mechanics** and **macroscopic observables**, providing deep insights into quantum statistics, superfluidity, and coherence. Despite its experimental challenges, BEC has become a **powerful tool in modern physics** for exploring quantum behavior on a macroscopic scale.

12.4 SUMMARY

Photons in Solids

Photons in solids manifest as phonons (quantized lattice vibrations), but free photons interact weakly via blackbody radiation or polaritons in dielectrics. In photonic crystals or cavities, bandgaps confine photons, enabling slow light or lasing; thermal emission follows Planck's law modified by emissivity. (148 words)

Phonons in solids are quantized collective vibrations of atoms in a crystal lattice, behaving as quasiparticles that carry heat and sound. Acoustic phonons correspond to low-frequency sound waves where adjacent atoms move in phase, while optical phonons involve out-of-phase motion at higher frequencies, crucial for infrared absorption. They explain thermal conductivity in insulators, specific heat via Debye theory (T^3 at low T), and electron-phonon interactions driving superconductivity.

Bose-Einstein Condensation

Bose-Einstein condensation (BEC) occurs when bosons cool to near absolute zero, collapsing into the ground state, forming a macroscopic quantum wave function. Predicted for ideal gases, it manifests in dilute ultra cold vapors since 1995, super fluid helium-4, and excitons. BEC enables coherence, interference, and super fluidity, revolutionizing quantum simulation and precision measurement.

12.5 TECHNICAL TERMS

Photons in solids
Phonons in solids
Bose-Einstein condensation

12.6 Self-Assessment Questions

1. Explain about the Photons in solids
2. Write about the Phonons in solids
3. Explain about the Bose-Einstein condensation

12.7 Suggested Readings

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics: Theory and applications by S.K. Sinha
3. Fundamentals of Statistical and Thermal Physics by F. Reif
4. Statistical Mechanics by Gupta and Kumar, Pragati Prakashan Pub. Meerut.

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LESSON-13

BROWNIAN MOTION OF A MOLECULE

AIM AND OBJECTIVE:

Aim

The aim of studying **Brownian motion of a molecule** is to understand the **random, erratic movement of microscopic particles** suspended in a fluid, which results from **continuous collisions with the surrounding molecules**, and to use this phenomenon to provide **evidence for the existence of atoms and molecules**.

Objectives

- To observe and explain the **erratic motion of small particles** in a liquid or gas
- To establish a **connection between molecular motion and macroscopic observations**
- To calculate important parameters such as **Avogadro's number, diffusion coefficient, and particle size**
- To demonstrate the **kinetic theory of matter** experimentally
- To understand the **statistical nature of molecular collisions**

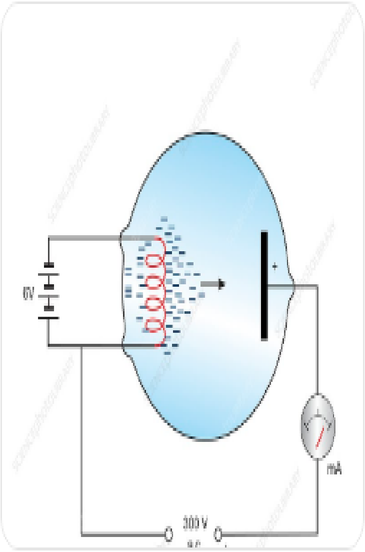
STRUCTURE OF THE LESSON:

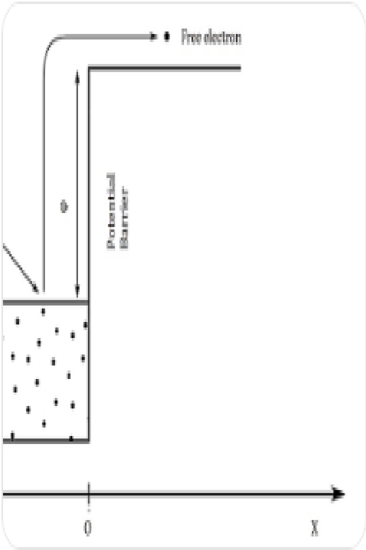
13.1 THERMIONIC EMISSION

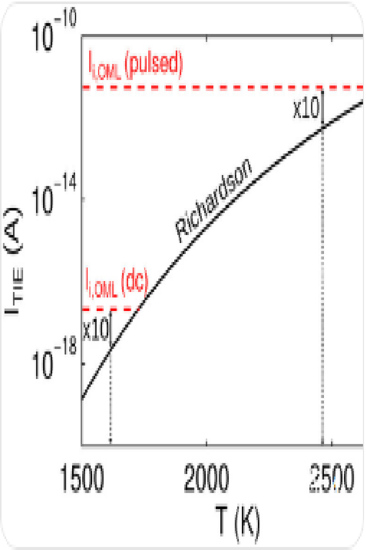
Introduction

Thermionic emission is the phenomenon in which **electrons are emitted from the surface of a metal** when it is heated to a high temperature. The thermal energy overcomes the **work function** of the metal, allowing electrons to escape into the vacuum. This effect is fundamental in the operation of **vacuum tubes, cathode-ray tubes, and electron guns** and provides insight into the **electronic properties of metals**.

Thermionic emission is the emission of electrons from a metal surface when it is heated to a sufficiently high temperature. Heating supplies thermal energy that allows electrons to overcome the work function of the metal.







1. Physical idea

- Free electrons inside a metal obey Fermi–Dirac statistics.
- At ordinary temperatures, electrons lack sufficient energy to escape.
- On heating, some electrons acquire energy greater than the surface barrier (work function) and escape into vacuum or surrounding space.

Emission occurs **without applying a strong external electric field** (unlike field emission).

2. Work function (ϕ)

- Definition: Minimum energy required to remove an electron from the metal surface.
- Depends on:
  - Nature of metal
  - Surface condition
- Typical values:
  - Tungsten: ~4.5 eV
  - Oxide-coated cathodes: ~1–2 eV

Lower work function → higher emission at lower temperature.

3. Richardson–Dushman equation

The current density of emitted electrons is given by:

$$J = AT^2 e^{-\phi/k_B T}$$

where

- J= thermionic emission current density
- A = Richardson constant (≈1.2×10^6A $m^{-2}K^{-2}$)
- T = absolute temperature
- ϕ= work function
- k_B = Boltzmann constant

Emission increases rapidly with temperature.

4. Saturation current

- If all emitted electrons are collected by the anode, current reaches a maximum:

$$I_s = AA_C T^2 e^{-\phi/k_B T}$$

(where A_C is cathode area)
This is called saturation current.

5. Factors affecting thermionic emission

- Temperature of the cathode
- Work function of the metal
- Surface cleanliness
- Cathode material and coating

6. Types of thermionic cathodes

1. **Pure metal cathodes** (e.g., tungsten)
   - High operating temperature
   - Long life
2. **Oxide-coated cathodes**
   - Lower temperature operation
   - Higher efficiency
   - Used in vacuum tubes

7. Applications

- Vacuum tubes (diodes, triodes)
- Cathode ray tubes (CRT)
- X-ray tubes
- Electron microscopes
- Microwave devices (klystrons, magnetrons)

Conclusion

Thermionic emission demonstrates the effect of **temperature on electron energy** and forms the basis for many **electronic devices**. The current emitted depends on the **temperature and work function** of the material. It highlights the connection between **thermal energy and electron liberation**, bridging microscopic electron behavior with macroscopic electrical phenomena

13.2 MAGNETIC SUSCEPTIBILITY OF FREE ELECTRONS

Introduction

Magnetic susceptibility of free electrons refers to the response of conduction electrons in a metal to an **applied magnetic field**. Free electrons contribute to the magnetism of metals through **Pauli paramagnetism**, which arises from the alignment of electron spins with the field. This concept helps in understanding the **magnetic properties of metals**, their electron distribution, and the connection between **quantum statistics and macroscopic magnetic behavior**.

The magnetic response of **conduction (free) electrons** in a metal arises from their **spin magnetic moments**. This phenomenon is called **Pauli paramagnetism**.

1. Origin

- Each electron has spin $\frac{1}{2}$ and magnetic moment
  $\mu = \mu B = \frac{e\hbar}{2m}$
- When an external magnetic field B is applied:

- Spin-up electrons (parallel to B) have lower energy
- Spin-down electrons (antiparallel) have higher energy

This causes a small imbalance in population near the Fermi level.

2. Why only electrons near the Fermi level matter

- At T=0, all states up to the **Fermi energy** $\boldsymbol{E_F}$ are filled
- Electrons deep inside the Fermi sea cannot change their spin state
- Only electrons within $\sim k_B T$ *of* $\boldsymbol{E_F}$ respond to the field

This is why Pauli paramagnetism is weak.

3. Magnetization

The magnetization due to spin imbalance is

$M = \mu B(n\uparrow - n\downarrow)$

Using density of states $g\boldsymbol{E_F}$:

$M = \mu_B^2 g(\boldsymbol{E_F}) B$

4. Pauli magnetic susceptibility

Magnetic susceptibility is

$\chi = \frac{M}{B}$

So,

$\chi p = \mu_0 \mu_B^2 g(\boldsymbol{E_F})$

For a free-electron gas in 3D:

$g(\boldsymbol{E_F}) = \frac{3n}{2\boldsymbol{E_F}}$

Hence,

$\chi p = \frac{3}{2}\mu_0 \frac{n\mu_B^2}{(\boldsymbol{E_F})}$

where

- n = number density of electrons
- $(\boldsymbol{E_F})$ = Fermi energy
- μ_0 = permeability of free space

5. Key characteristics

✓Temperature independent (for T<<T_F)
✓Very small compared to classical paramagnetism
✓ Arises purely from quantum statistics
✓ Depends on density of states at Fermi level

Conclusion

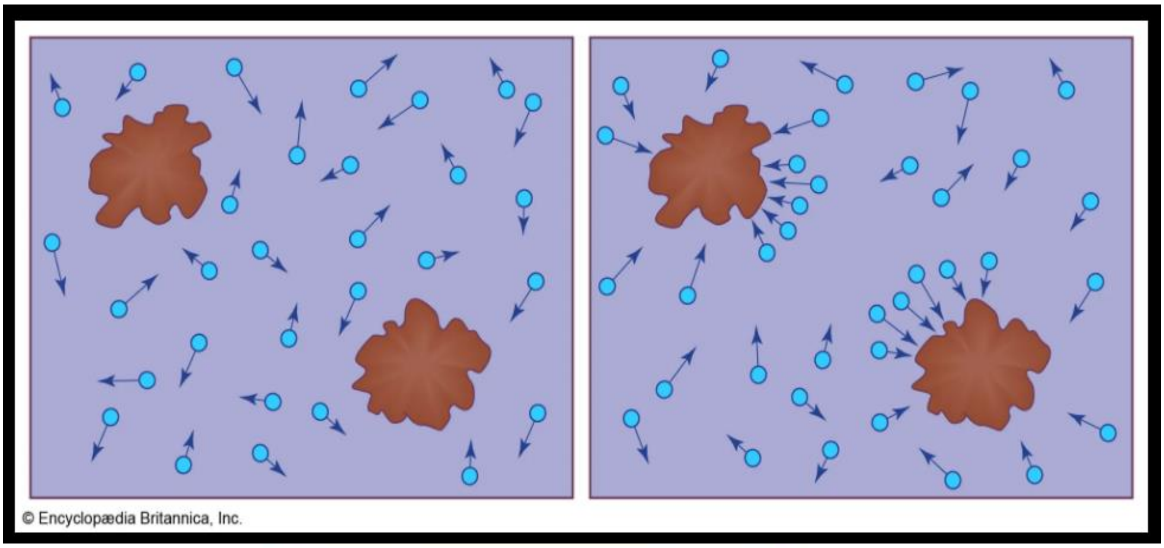
The study of the magnetic susceptibility of free electrons explains the **weak paramagnetic behavior** observed in metals due to conduction electrons. It shows that **only electrons near the Fermi surface** contribute significantly to magnetization, highlighting the role of **quantum mechanics in macroscopic magnetic properties**. This concept is essential for understanding **Pauli paramagnetism** and forms a foundation for **solid-state physics and material science**.

13.3 BROWNIAN MOTION OF A MOLECULE

Introduction

Brownian motion refers to the **erratic, random movement of microscopic particles** suspended in a fluid (liquid or gas), observed under a microscope. This motion is caused by **continuous collisions of the suspended particles with the molecules of the surrounding fluid**, which are in constant thermal motion. Brownian motion provides **direct evidence for the existence of atoms and molecules** and supports the **kinetic theory of matter**.

B**rownian motion** is the **continuous, random, zig-zag motion** of a microscopic particle (or molecule) suspended in a fluid (liquid or gas). It is caused by **collisions with surrounding fluid molecules**, which are themselves in constant thermal motion.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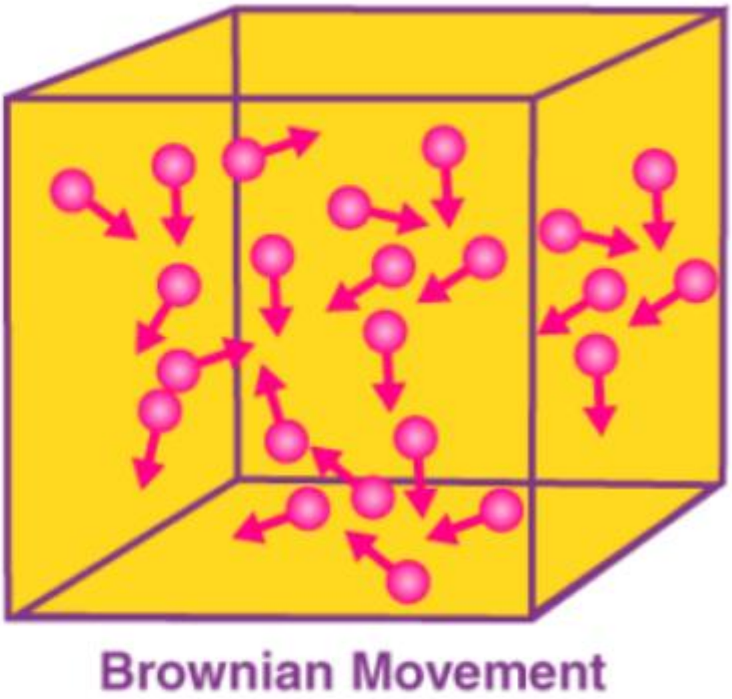

1. Physical explanation

- Fluid molecules move randomly due to thermal energy.
- A suspended molecule is bombarded unequally from all sides.
- These random impulses cause unpredictable motion.

This motion is **not** due to external forces like convection or gravity.

2. Historical background

- Observed by**:** Robert Brown (1827)
- Explained theoretically by**:** Albert Einstein (1905)
- Experimentally verified by**:** Jean Perrin

Brownian motion provided **direct experimental proof of the molecular nature of matter**.

3. Characteristics

- Motion is irregular and continuous
- Path is random (zig–zag)
- More pronounced for:
    - Smaller particles
    - Higher temperatures
    - Lower viscosity fluids
- Disappears for large/macroscopic objects

4. Einstein's theory of Brownian motion

Einstein related microscopic motion to macroscopic measurable quantities.

Mean square displacement:

$$< x^2 >= 2Dt$$

where

- $< x^2 >$ = mean square displacement
- D= diffusion coefficient
- t = time

For three dimensions:

$$< r^2 >= 6Dt$$

5. Diffusion coefficient

Einstein derived:

$$D = \frac{k_B T}{6\pi \eta r}$$

where

- k_B = Boltzmann constant
- T = absolute temperature
- η = viscosity of the fluid
- r = radius of the particle

This equation links thermal motion with fluid properties.

6. Importance of Brownian motion

Brownian motion helps in:

- Proving existence of atoms and molecules
- Determining Avogadro's number
- Understanding diffusion
- Explaining processes in:
    - Colloids

  - Biology (cellular motion)
  - Nanoscience

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).

Applications

1. **Evidence of molecular motion**: Confirms the reality of atoms and molecules.
2. **Determination of Avogadro's number**: Observing Brownian motion allows calculation of **molecular size and number density**.
3. **Diffusion studies**: Helps in understanding the **diffusion coefficient** of particles in fluids.
4. **Colloid science**: Used to study **stability and behavior of colloidal suspensions**.
5. **Statistical mechanics**: Provides experimental verification of **kinetic theory and probability-based models**.

Limitations

- Only observable for **microscopic particles** (like pollen grains); molecules themselves are too small.
- Requires **stable suspension**; sedimentation or aggregation affects observation.
- Not suitable for systems where **external forces** (like currents) dominate particle motion.
- Assumes **thermal equilibrium**; deviations may lead to inaccurate conclusions.

Conclusion

Brownian motion demonstrates the **random molecular collisions** responsible for particle movement in fluids. It provides **quantitative support for the kinetic theory of matter** and enables determination of molecular properties such as **Avogadro's number** and diffusion coefficients. Despite its observational limitations, it remains a **fundamental phenomenon connecting microscopic molecular behavior with macroscopic physical effects**.

13.4 SUMMARY

Thermionic Emission

Thermionic emission ejects electrons from a heated metal surface into vacuum, following Richardson-Dushman law where current density rises exponentially with temperature. Overcomes work function barrier via thermal energy, powering vacuum tubes, electron microscopes, and thermionic converters. Schottky and field effects lower barriers for enhanced emission

Free electrons in metals exhibit Pauli paramagnetism from spin alignment in a magnetic field and Landau diamagnetism from orbital quantization into Landau levels. Pauli effect gives a temperature-independent positive susceptibility proportional to the density of states at the Fermi level, while Landau yields a negative contribution one-third as large, resulting in weak net paramagnetism for simple metals.

Brownian motion

Brownian motion describes the erratic random walk of molecules or particles in a fluid due to collisions with surrounding solvent molecules. Einstein related its mean square displacement to diffusion constant and temperature, explaining microscopic origin of viscosity and enabling Avogadro number determination. It underpins stochastic processes in biology and finance. (98 words)

13.5 TECHNICAL TERMS

Thermionic emission
Magnetic susceptibility of free electrons
Brownian motion of a molecule

13.6 SELF ASSESSMENT QUESTIONS

1. Write about the Thermionic emission.
2. Explain about the Magnetic susceptibility of free electrons
3. Briefly write about the Brownian motion of a molecule

13.7 SUGGESTED READINGS

1. Statistical and Thermal Physics by S. Lokanadhan and R.S. Gambhir (PHI).
2. Statistical Mechanics: Theory and applications by S.K. Sinha
3. Fundamentals of Statistical and Thermal Physics by F. Reif
4. Statistical Mechanics by Gupta and Kumar, Pragati Prakashan Pub. Meerut.
5. Statistical Mechanics by Satya Prakash

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