Easy Access to Statistical Physics

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By

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وَإِن تَعُدُّوا نِعْمَةَ اللَّهِ لَا تُحْصُوهَا ۗ إِنَّ اللَّهَ لَغَفُورٌ رَّحِيمٌ

And if they count the grace of God, you do not count them For God is Forgiving, Most Merciful

In memory of my parents, Musa, and Halima.
I dedicate this book to the cherished memory of my late parents, whose unwavering support and encouragement spurred me on to pursue advanced studies.".

CONTENTS

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Writing this book has been a rewarding experience, and I'm very thankful to everyone who played a part in making it possible.

With heartfelt thanks,
Mohammed M. Shabat

PREFACE

Statistical physics delves into the profound study of systems comprised of an extensive array of particles, ranging from minuscule atoms and molecules to the intricate world of spins. The inherent complexity of these systems renders it both impractical and redundant to delve into the microscopic dynamics of each individual constituent

In the captivating realm of statistical physics, the journey to comprehension can prove challenging without a sturdy foundational understanding. While numerous educational resources, including courses and textbooks, have sought to facilitate this voyage, a unique need has arisen for a resource that offers accessibility and simplicity.

This book emerges as a testament to the collective commitment of educators at the Physics Department of IUG, where the aspiration to share the wisdom of statistical physics with undergraduate and postgraduate students has been a driving force. The primary aim here is to endow undergraduate students with the essential framework required for a meaningful exploration of statistical physics.

The book's cover proudly displays an olive branch, symbolizing not only the richness of knowledge within but also the attributes of peace and love. It draws inspiration from the land of olives and the sacred surroundings where its contents were crafted.

In conclusion, I express my deepest appreciation to my beloved wife, Am Obayda, my cherished family, and the entire community of colleagues and students at IUG. Their unwavering support and encouragement have played an irreplaceable role in bringing this book to life, and I am immensely grateful for their contributions to this endeavor.

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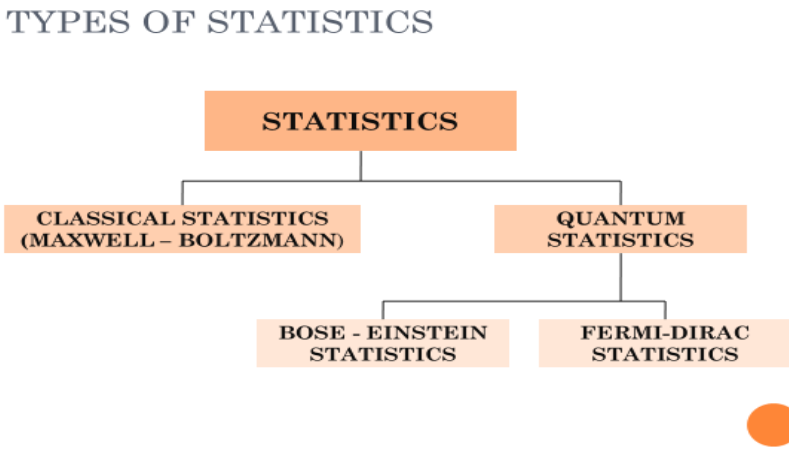
CHAPTER 1

INTRODUCTION

Since I've been unjustly picking on chemists "All science is either physics or stamp collecting."
—Ernest Rutherford,
"The physicist and 1908 Nobel Prize winner in chemistry"



1.1 Introduction

Statistical physics is a field of physics that utilizes statistical methods to study and explain the collective behavior of particles or components within a physical system, enabling insights into thermodynamics, phase transitions, and emergent phenomena in complex systems. It plays a pivotal role in connecting microscopic details to macroscopic observables, offering a comprehensive understanding of the behavior of matter and energy in diverse physical systems.

Statistical physics, also known as statistical mechanics, is a branch of physics that provides a framework for understanding the behavior of systems consisting of a large number of particles, such as atoms or molecules. It emerged in the late 19th century and has played a pivotal role in elucidating the properties of matter and energy. Here is a concise history of statistical physics in five pages:

1. Early Foundations (Late 19th Century)

Ludwig Boltzmann's Kinetic Theory: The roots of statistical physics can be traced back to Ludwig Boltzmann's pioneering work in the late 19th century. Boltzmann formulated the kinetic theory of gases, which described the behavior of gas molecules as tiny particles in constant motion. He introduced the concept of entropy and the Boltzmann equation, which related the macroscopic properties of gases to the statistical behavior of their constituent particles.

2. Maxwell-Boltzmann Distribution and Thermodynamics (Late 19th to Early 20th Century)

Maxwell's Contributions: James Clerk Maxwell made significant contributions to the field by deriving the Maxwell-Boltzmann distribution, which describes the velocity distribution of particles in an ideal gas. This distribution laid the groundwork for understanding the concept of temperature and the equipartition theorem, which relates the energy of particles to temperature.

Statistical Mechanics Formalism: The development of statistical mechanics formalism, incorporating Boltzmann's ideas, provided a unified framework for linking microscopic behavior to macroscopic thermodynamics. This formalism, with equations like the partition function, allowed for the calculation of thermodynamic properties based on the statistical properties of particles.

3. Quantum Mechanics and Statistical Physics (Early to Mid-20th Century)

Quantum Mechanics Revolution: The adv4ent of quantum mechanics in the early 20th century brought about a profound shift in the understanding of particles at the microscopic level. Pioneers like Max Planck, Albert Einstein, and Niels Bohr introduced quantum principles, such as quantization of energy levels and wave-particle duality. These principles were integrated into statistical physics, giving rise to quantum statistical mechanics.

4. Fermi-Dirac and Bose-Einstein Statistics

The development of quantum statistics, including Fermi-Dirac statistics for fermions and Bose-Einstein statistics for bosons, enabled the description of particles obeying quantum principles. These statistics played a crucial role in explaining phenomena like electron behavior in metals (Fermi-Dirac) and the behavior of bosons in low-temperature systems (Bose-Einstein condensation).

5. Modern Advances and Applications (Mid-20th Century to Present)

Statistical Mechanics in Condensed Matter Physics: Statistical mechanics found extensive applications in condensed matter physics, explaining phenomena in materials such as phase transitions, superconductivity, and magnetism. Landau theory, the Ising model, and Monte Carlo simulations are some notable developments in this area.

Statistical Thermodynamics in Biology: Statistical physics also made its way into the biological sciences, explaining phenomena like protein folding and enzyme kinetics. Concepts like the free energy and chemical potential found application in understanding cellular processes.

6. Contemporary Developments and Challenges (21st Century)

Complex Systems and Network Theory: In the 21st century, statistical physics expanded its scope to analyze complex systems, including social networks, traffic patterns, and ecological systems. Tools from statistical physics, such as percolation theory and network analysis, have been instrumental in understanding these complex phenomena.

Nanoscience and Quantum Computing: As technology advanced, statistical physics became essential in nanoscience and quantum computing. Understanding the behavior of nanomaterials and quantum systems relies heavily on statistical mechanics principles.

7. Challenges and Unsolved Problems

Contemporary statistical physics faces challenges such as understanding non-equilibrium dynamics, exploring systems far from equilibrium, and addressing questions related to the arrow of time and the nature of dark matter and dark energy. These challenges continue to drive research in the field.

In summary, the history of statistical physics is a journey from Boltzmann's kinetic theory and the Maxwell-Boltzmann distribution to the integration of quantum mechanics, the development of quantum statistics, and its applications in various scientific disciplines. Today, statistical physics remains a vibrant field at the forefront of understanding complex systems and addressing pressing questions in science and technology.

Thermodynamics explores the relationships among a limited set of observable macroscopic parameters within a system, including variables like pressure, volume, temperature, magnetization, and more. Its fundamental principles are grounded in empirical observations, devoid of microscopic system details. In contrast, Statistical Thermodynamics bridges the gap between the microscopic behaviors of individual atoms and molecules and the observable, bulk properties of materials encountered in our daily experiences. This approach attributes thermodynamic phenomena as natural outcomes of statistical mechanics, encompassing both classical and quantum mechanical principles at the microscopic level. In the realm of physics, there are scenarios where the precise analysis of a system's properties becomes impractical due to the vast number of constituent components. Statistical mechanics, therefore, addresses the behavior of systems comprising numerous particles, employing probability theory and statistics as essential mathematical tools to handle such complexity. Instead of focusing on individual particle dynamics, it centers on determining the most probable system behavior, emphasizing the multitude of ways (represented by "W") in which particles can be arranged to yield a specific energy distribution. Maximizing "W" identifies the most likely state of the system, characterizing its macroscopic properties without delving into the minutiae of individual particle motions. This approach enables the calculation of macroscopic thermodynamic properties, including energy, particle count, volume, pressure, and temperature, based on microscopic considerations, all without the need to specify every dynamic variable governing the system. This state is referred to as a microscopic state. Statistical physics primarily grapples with systems containing a vast number of entities, exceeding Avogadro's number, encompassing atoms, molecules, spins, and more. In such cases, studying the complete microscopic dynamics is not only infeasible but also lacks practical relevance.

Instead, statistical physics focuses on assessing macroscopic average values using particle distribution functions, facilitating the calculation of properties such as energy, pressure, heat capacity, entropy, free energies, thermodynamic potentials, and more. This framework provides a means to correlate the microscopic behaviors of individual atoms and molecules with the observable properties of systems. Another perspective on statistical physics is its exploration of the general characteristics of macroscopic systems endowed with numerous degrees of freedom, often involving a colossal number of particles, on the order of 10^{20}, for instance. Despite the mechanical and mathematical complexity of such systems, they are typically characterized by only a handful of physical parameters, such as temperature, pressure, and density, which are sufficient to define the system's "state".

1.2 Specification of macrostates and microstates

In statistical physics, a macrostate refers to a specific macroscopic description or set of macroscopic properties that characterize a physical system, such as temperature, pressure, and volume. A macrostate can encompass a wide range of microscopically distinct configurations or arrangements of individual particles within the system, known as microstates. Microstates represent the fine-grained details of how the particles are distributed in terms of positions and momenta. The relationship between macrostates and microstates is essential in understanding how the statistical behavior of a system arises from the multitude of ways its constituent particles can be arranged while satisfying the macroscopic constraints. Statistical mechanics uses this concept to describe the probabilities of different microstates for a given macrostate, allowing us to make predictions about a system's behavior at the macroscopic level.

The equilibrium state of a thermodynamic system is determined by a specific set of measurable parameters that encapsulate its macroscopic characteristics. To illustrate, consider the example of a fluid system, where equilibrium is defined by the values of pressure (P), volume (V), and temperature (T) – collectively known as the macrostate (P, V, T). In the case of an isolated system, one in which there is no exchange of energy or mass with its surroundings, the macrostate is uniquely specified by the internal energy (E), the number of particles (N), and the volume (V) – represented as (E, N, V) .Now, let's consider a closed system. In this scenario, energy exchange with the surroundings is allowed, but not the transfer of particles. In equilibrium with a heat bath at temperature T, the macrostate can be defined by (N, V, T) . In the realm of open systems, both energy and particle exchange with the surroundings are possible. For such systems, equilibrium with a heat bath at temperature T and a pressure bath at pressure P (or a particle bath with chemical potential μ) is characterized by the macrostate (N, P, T) or (μ, V, T).

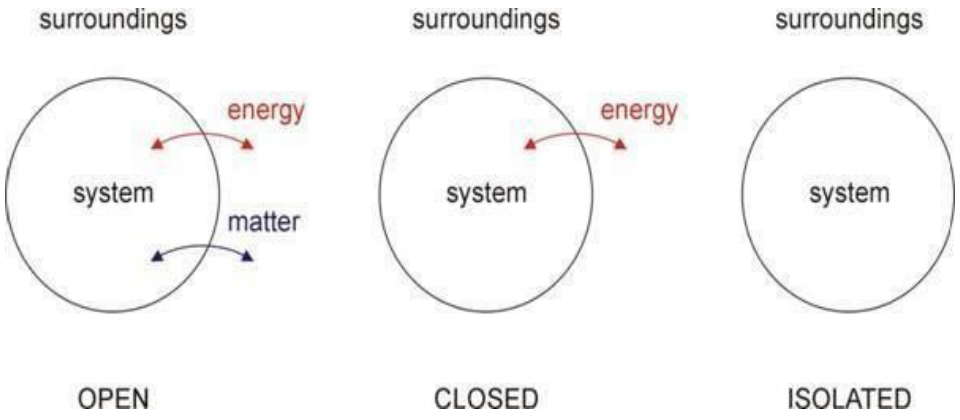


Figure 1.1 Three system, open, closed and isolated.

In the realm of physics, a microstate refers to the specific configuration of every molecule within a system at a particular moment. Conversely, a macrostate is characterized by the system's observable properties, including temperature, pressure, volume, and the like. Within each macrostate, numerous microstates can lead to the same macroscopic outcome. Obtaining a microstate for a system also involves detailing the states of all its constituent elements. However, the approach to specifying microstates varies depending on the nature of these constituent elements or particles within the system. The criteria for describing microstates differ between classical and quantum particles.

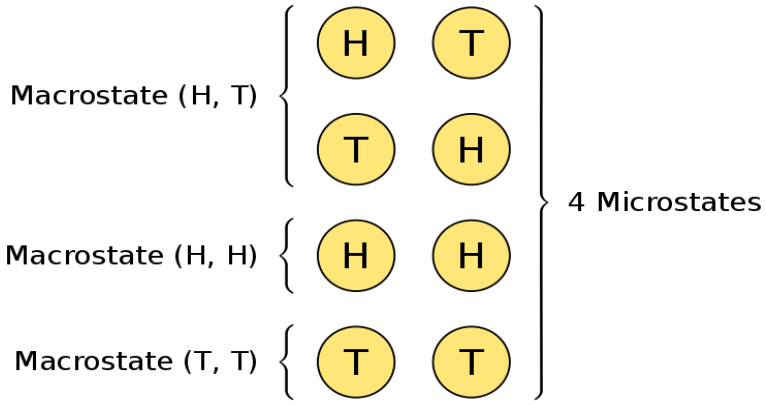


Figure 1.2 Microstates and Macrostates configuration structure

Specific thermodynamic functions characterize equilibrium in different systems. In an isolated system, it corresponds to the maximum entropy (S(E, N, V)), whereas in a closed system, it corresponds to the minimum Helmholtz free energy (F(N, V, T)). In the case of an open system, equilibrium is indicated by the minimum Gibbs free energy (G(N, P, T)) or the minimum grand potential (Φ(μ, V, T)). From a mathematical standpoint, thermodynamics involves mathematical identities derived from well-defined functions. However, in a physical sense, it primarily deals with the equilibrium properties of systems and various transformations like heating, cooling, phase changes, volume compression, magnetization, chemical reactions, and the conversion of work into heat, and vice versa.

Statistical mechanics, on the other hand, seeks to explain how these properties and transformations arise from the microscopic characteristics of a system. At the quantum and small scales, the constant motion and collisions of electrons, atoms, and molecules create a dynamic environment. The challenge lies in reconciling the microscopic and macroscopic perspectives. For instance, why do processes like glass breaking or coffee and milk mixing, which seem reversible at the microscopic level according to Newton's and Schrödinger's equations, often appear irreversible on the macroscopic scale? Why doesn't a broken glass reassemble itself, or why don't coffee and milk spontaneously separate in a cappuccino? Furthermore, how can thermodynamic equilibrium maintain constant temperature, pressure, and other properties in a body, despite the continuous motion of its microscopic constituents?

Statistical mechanics offers insights and solutions to these intriguing and profound questions by bridging the gap between the microscopic realm and macroscopic observations. When dealing with macroscopic bodies, the sheer number of microscopic degrees of freedom is immense, making a deterministic approach for each particle impractical. Instead, a statistical viewpoint is embraced, emphasizing concepts like probability, averages, and fluctuations. Through this perspective, a direct link to the thermodynamic level of description is established, a framework that applies seamlessly at both classical and quantum levels.

1.3 Definitions of micro-state and macro-state

1. Microstate

A ***microstate*** is defined as a state of the system where *all parameters* of constituent particles are specified. Classical thermodynamics describes ***macroscopic systems*** in terms of a few macroscopic variables (T, V, N, …). We can use two approaches to describe such a macroscopic system the classical Mechanics and quantum mechanics.

First: The Classical Mechanics approach

The state of a single particle is specified by its position coordinates (q_1, q_2, q_3) and its momentum coordinates (p_1, p_2, p_3). One needs 6N degrees of freedom for N particles to describe the system in *the phase space representation*. Thus, from the point of view of classical mechanics, the state of a system of N particles is described by 6N variables. This model of matter on a microscopic scale is called *microscopic state or microstate.* In summary, a microstate is defined by the representative point in phase space.

Second: The Quantum Mechanics approach

The energy levels and the state of particles in terms of quantum numbers are used to specify the parameters of a microstate**.**

Example:

a. Micro and macrostates

Consider a system of three coins; this system's macrostate is described by the number of heads facing up. There are four such macrostates, labeled 0, 1, 2, and 3. We might even call these energy levels 0, 1, 2, & 3.

Specifying the orientation of each coin defines a *microstate*. The list the microstates can be displayed, using H for heads and T for tails: TTT, HTT, THT, TTH, HHT, HTH, THH, HHH.

The microstates into the macrostate energy levels are displayed.

Table 1.1 the microstates of the mentioned example.

Energy level	Microstates	multiplicity, Ω
0	TTT	1
1	HTT, THT, TTH	3
2	HHT, HTH, THH	3
3	HHH	1

The *multiplicity* is the number of distinct ways a specified macrostate can be realized. The total multiplicity of the system is the total of all the possible microstates. For these three coins, that means any individual microstate is as likely as any other.

2. Macrostate

A *macrostate* is defined as a state of the system in which the distribution of particles over energy levels is specified. Therefore, the number of particles ($\mathbf{N_i}$) in a particular quantum state (**i**), with a particular energy ($\boldsymbol{\varepsilon_i}$), specify a *macrostate.* If these numbers are known, the mean energy and other average quantities of the system can be calculated. A macrostate contains a huge number of microstates.

The equilibrium thermodynamic macrostate is described by three macroscopic variables (P,V, and T) or (P, V, and N) or (E, V, and N). These macroscopic variables are related by *an equation of state*, which for the case of an ideal gas is given by:

$$PV = NkT \tag{1.1}$$

In statistical mechanics, the equilibrium tends towards a macrostate that is the most stable. The stability of the macrostate depends on the perspective of the microstate.

For many particles, each macrostate k can be realized by a very large number Ω_k of microstates. The main assumption of statistical physics is that all microstates occur with the same probability, which is called *the equal a priori probability concept.*

It may appear easier to use a quantum description that specifies the quantum states of all the atoms the **microstate**. Since the atoms interact, this state changes very rapidly. But the *observed* ***macrostate*** doesn't change. Therefore, a macrostate contains a huge number *of* different microstates (Ω).

Quantum statistics theory offers increased precision when applied to non-interacting particle systems. In the absence of interactions, individual particles possess unique sets of quantum states with discrete energy levels they can occupy. For identical particles, these sets of states are identical. These particles can be distributed across their respective quantum states in numerous distinct arrangements, referred to as realizations. Each such distribution realization represents a microstate of the system.

The true probability of the macrostate **k** is normalized: $\sum_k p_k = 1$. It is important to highlight that both $\boldsymbol{\Omega_k}$ and $\mathbf{p_k}$ depend on the whole set of N_i:

$$p_k = p_k(N_1, N_2, \ldots); \quad \Omega_k = \Omega_k(N_1, N_2, \ldots) \tag{1.2}$$

For an isolated system, the number of particles N and the total energy E are conserved; the following constraints involving N_i are:

$$\sum_i N_i = N \tag{1.3a}$$

$$\sum_i N_i \varepsilon_i = E \tag{1.3b}$$

Where ε_i is the energy of the particle in state i. The number of particles $\overline{\overline{N_i}}$ averaged over all microstates k can be calculated using the true probability p_k and the number of particles in the microstate i corresponding to the macrostate k. In the case of large N, the dominating true probability p_k should be found by maximizing the "ignorance" concerning to all N_i considering the constraints of equation (1.3).

To illustrate the concepts of micro–states and macro–states, we consider the example of a two–state particle, namely the coin tossing, for example:

A tossed coin (a coin thrown in the air) can land on the ground in two positions: **Head up or tail up.** Considering the coin as a particle, one can say that this particle has **two "quantum" states**, one corresponding to the head up and two corresponding to the tail up. If N coins are thrown in the air, this can be considered as a system of N particles **with two quantum states each.** The microstates of the system are specified by the states occupied by each coin. As each coin has 2 states, there are altogether

$$\Omega = 2^N \tag{1.4}$$

microstates. The macrostates of this system are defined by the numbers of particles in each state. Let N_1 be the number of particles in state 1, and N_2 the number of particles in state 2. N_1 and N_2 satisfy the following constraint condition:

$$N_1 + N_2 = N \tag{1.5}$$

Thus, one can take N_1 or N_2 as the number k labeling macrostates. The number of microstates in one macrostate, that is, the number of different ways of picking N_1 particles being in state 1 (all others being in state 2) within N indistinguishable particles, avoiding multiple counting of the same microstates. According to combinatorial analysis Ω_{N_1} is given by:

$$\Omega_{N_1} = \frac{N!}{N_1!(N - N_1)!} \tag{1.6}$$

It can be shown that:

$$\sum_{N1=0}^{N} \Omega_{N1} = \sum_{N1=0}^{N} \frac{N!}{N_1!(N - N_1)!} = 2^N \tag{1.7}$$

The thermodynamic probability Ω_{N_1} has a maximum at $N_1 = N/2$, that is, when half of the coins are in state 1(head up) and half of the coins in state 2(tail up). The corresponding macrostate is the most probable state. Indeed, as for an individual coin, the probability to land head up and tails up is equal to 1/2.

1.4 Basic principles and definitions

1. An isolated system is in equilibrium if all accessible microstates are equally probable, or any individual microstate is as likely as any other individual microstate.

2. Isolated physical systems tend to be in the macrostate that has the greatest number of microstates.

3. In many cases of interest in physics and engineering, the probability of the event x "P(x)" is a continuous function of x. It is important to introduce the probability density or distribution function "f(x)" associated with x and fulfilling the following conditions:

- $f(x) \geq 0$ for all values of x in the range of x "R(x)"

$$\int_{-\infty}^{+\infty} f(\times) d \times = 1$$

- The probability of finding a value x between a and b, is: $P(a \prec\times\prec b) = \int_a^b f(x)dx$
- For discrete case

$$\sum_{n_1=0}^{N} P_N(n_1) = 1$$

- For continues case

$$\int_0^N P_N(n)dn = 1$$

4. Extensive Parameter:

Macroscopic parameters are proportional to the amount of substance in the system, such as volume V, entropy S, and the total energy E and which can be added.

For example: if we mix two systems A_1 with N_1, V_1, S_1, E_1, and system A_2 with N_2, V_2, S_2, E_2 then the total volume $V=V_1+V_2$, the total entropy $S=S_1+S_2$, *the total number of particles* $N=N_1+N_2$, and the total energy $E=E_1+E_2$.

5. Intensive Parameter: Macroscopic parameters that are independent of the amount of substance in the system like (temperature T, pressure P, and density n).

6. If an isolated system at instant time" t=0" is found with equal probability in each accessible microstate, then it is in equilibrium.

In any case, to a given macrostate of a system, there does, in general a large number of microstates (complexion) and it seems natural to assume that at any time (t) the system is equally likely to be in any one of these microstates which it means that all corresponding state of a given energy is equally probable.

7. Phase space

Phase space was introduced by Willard Gibbs in 1901, is a space where all possible states of a system are represented, with each possible state of the system corresponding to one unique point in the phase space. For mechanical systems, the phase space usually consists of all possible values of position and momentum (velocity) variables.

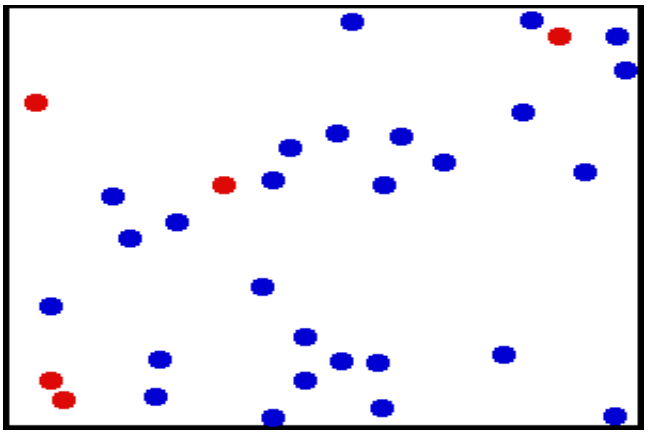


Figure 1.3: The assembly structure of N systems.

A combination of position and momentum space is known as phase space which is a six-dimensional space. So, if a system consists of N particles, then the 6N coordinates are described the behavior of the system in the phase space.

At any instant of time, suppose one of the particles has its position coordinates lying between x and x+Δx, y and y+Δy, z and z+Δz and let its momentum coordinates are between p_x and $p_x+\Delta p_x$, p_y and $p_y+\Delta p_y$, p_z and $p_z+\Delta p_z$. Then, the particle is located in a phase space compartment having a volume,

$$d\Gamma = dxdydz.dp_xdp_ydp_z \qquad (1.8)$$

Where, dv =dxdydz

The kinetic energy of a system with coordinates within the small value of dΓ is as

$$\varepsilon = \frac{p_x{}^2 + p_y{}^2 + p_z{}^2}{2m} \tag{1.9}$$

The state of the microstate is defined by specifying the position and the momentum coordinates for each system. For *N*-particles, the coordinates must be *6N*-coordinates, *3N* for the position, and *3N for* the momentum, which is called the phase space (Γ space).

The element of volume in phase space is given by:

$$d\Gamma_{6N} = dx_1 dy_1 dz_1 dp_{x1} dp_{y1} dp_{z1} \rightleftarrows \cdots \rightleftarrows d_{zN}, \tag{1.10}$$

$$d\Gamma_{6N} = \prod_{i=1}^{N} (d\Gamma)_i \tag{1.11}$$

The phase space contains many representation points in the interval region of the phase space.

Consider the compartments in phase space be further divided into a very large number of elementary cells of equal volume dΓ.

Where, h_o has the dimensions of length x momentum.

In Classical Physics, the choice of phase space cell size "h_o" is entirely easy to obtain. But in Quantum Mechanics, we are not free to make h_o as small as we like. The minimum volume of an elementary cell in phase space in the Quantum Mechanical system is h^3, where h is Planck's constant.

Total number of elementary cells in phase space =
Total volume in phase space/ Volume of one elementary cell

$$= (\int dx \int dy \int dz \int dp_x \int dp_y \int dp_z) / \ d\Gamma \tag{1.12}$$

Where, $d\Gamma = h^3{}_o$ which may approach zero in Classical system, and h^3 in the Quantum Mechanical System.

Let's consider now the so-called phase plane for one-dimensional motion. This is the plane constructed by plotting the linear moment of motion versus the position.

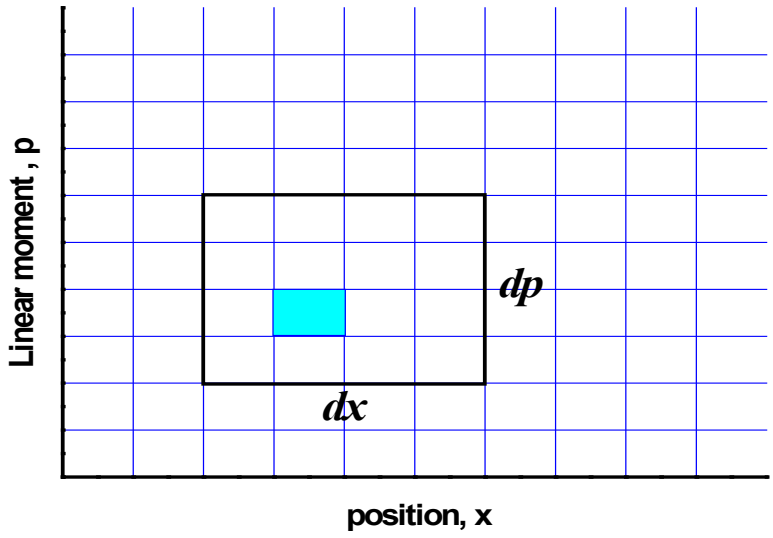


Figure 1.4 The elements of phase space dΓ

The smallest unit in such a plane is *h* (the dashed, cyan rectangle). Each discrete state (defined by the values of *p* and *x*) is represented by such a rectangle in the phase plane, corresponding to an energy $\varepsilon = p_x{}^2/2m$.

8. Group distributions

In a macroscopic volume, there is an enormous number of states for a gas, and the energy levels are closely spaced. This scenario can be described as group distributions.

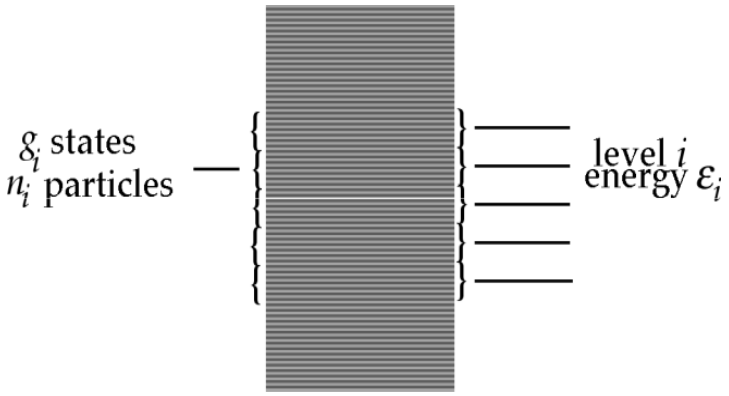


Figure 1.5. Group distribution's structure

So, the number of levels within-group *i*, g_i, is a very large, and such that the number of particles within the group, n_i , also is large, but such that the average distances $\Delta\varepsilon_i$ between the levels in the different groups still is very small. In practice, it turns out that you can g_i of 1010 still have $\Delta\varepsilon_i \propto 10^{-9} \cdot kT$. It also turns out that it is not critical for the final result how we do the grouping.

The next step is to determine the degeneracy g_i of gaseous molecules. These are the energy states that are so close to each other and lie within the energy interval dε. This is the number of states (rectangles) belonging to that bundle represented by the rectangle dp_x. dx. Thus,

$$g_i = \frac{dx \cdot dp_x}{h} \tag{1.13a}$$

For three-dimensional motion:

$$g_i = \frac{dx \cdot dp_x}{h} \cdot \frac{dy \cdot dp_y}{h} \cdot \frac{dz \cdot dp_z}{h} \tag{1.13b}$$

The number of dynamic states available in the phase space μ of a single particle depends on the six – dimensional volume element, $d\Gamma = d^3p_x\, d^3q$ and on the "minimum cell" whose extension is given by $d\Gamma_{min} = h^3$, according to Heisenberg uncertainty principle. Therefore, the maximum number of cells corresponding to dynamic states with energy ranges between ε and ε + dε (see figure 1.4) is given by:

$$g(\varepsilon)d\varepsilon = \frac{d\omega}{h^3} \tag{1.14}$$

g(ε) is the density of states per unit energy, and g(ε)dε is the number of possible dynamic states in the energy range between ε and ε + dε.

9. Assembly

An assembly is defined as a collection of systems, say *N*. The state of an assembly is defined by *6N*.

10. Averaging

The macroscopic properties we observe are the outcome of averaging these variables over the permissible microscopic states. To ensure accurate averaging, we rely on statistical hypotheses regarding the distribution of microscopic states. Averaging serves as the fundamental principle underpinning the statistical method for analyzing macroscopic systems, while the thermodynamic approach hinges on deriving general physical laws from experimental results while disregarding the atomic-molecular structure. Suppose an assembly of N systems with a total energy E is enclosed in a volume V. As the state of the assembly is defined by the value of 6N coordinates, then the state of the assembly is changing with time and described by the motion of the point representing these 6N coordinates in $\Gamma_{6N} - space$. Although the illustration of such a motion can only be given in two dimensions, an attempt is made in fFigure1.6 to indicate the changing state of an assembly. In Figure 1.6 $\vec{p}$(N) represents the momentum coordinates, and $\vec{x}$(N) represents the position coordinate.

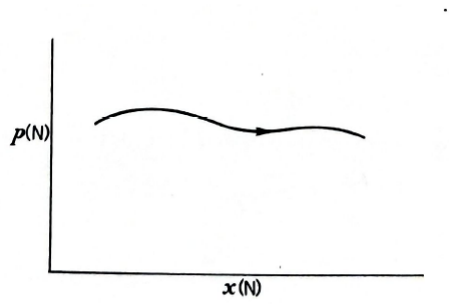


Figure 1. 6 The motion of a point in Γ_6N.

If the properties of an assembly are functions of the position $\vec{x}$(N), $\vec{p}$(N) in $\Gamma_{6N} - space$ (of 6 N coordinates of the system), then the average properties of the assembly are found by averaging the known function overall allowed positions $\vec{x}$(N), $\vec{p}$(N).

Consider some physical property X of an assembly is written as a function of the 6N coordinates (momentum and position) as $X(\vec{x}(N), \vec{p}(N))$, and if the probability that the point representing the assembly lies in the element of volume $d\Gamma_{6N}$ at $(\vec{x}(N), \vec{p}(N))$ is $\mathrm{P}(\vec{x}(N), \vec{p}(N))d\Gamma_{6N}$ then the average property $\bar{X}$ will be given by the normal statistical value

$$\bar{X} = \frac{\int_{\Gamma_{6N}} property * . probability}{\int_{\Gamma_{6N}} probability} \tag{1.15a}$$

$$\bar{X} = \frac{\int_{\Gamma_{6N}} X(\vec{x}(N),\vec{p}(N))\mathrm{P}(\vec{x}(N),\vec{p}(N))d\Gamma_{6N}}{\int_{\Gamma_{6N}} \mathrm{P}(\vec{x}(N),\vec{p}(N))d\Gamma_{6N}} \tag{1.15b}$$

If the total probability has normalized to unity over the whole space Γ_{6N} then

$$\int_{\Gamma_{6N}} \mathrm{P}(\vec{x}(N), \vec{p}(N))d\Gamma_{6N} = 1 \tag{1.16}$$

So,

$$\bar{X} = \int_{\Gamma_{6N}} X(\vec{x}(N), \vec{p}(N))\mathrm{P}(\vec{x}(N), \vec{p}(N))d\Gamma_{6N} \tag{1.17}$$

If the property has a value of X_i where the assembly in the state i and the probability of that assembly in the state i is p_i , then the average is taken as a summation of overall states of the assembly as:

$$\bar{X} = \frac{\sum_i p_i X_i}{\sum_i p_i} \tag{1.18a}$$

If the probabilities are normalized→ $\sum_i p_i = 1$ then,

$$\bar{X} = \sum_i p_i X_i \tag{1.18b}$$

where the summation is over all possible states.

11. Mathematics

Challenges often arise within the realm of statistical physics when considering the myriad arrangements of particles in terms of order, placement within states, or allocation within boxes or containers. Several fundamental principles and laws in statistical mechanics can address these issues, as outlined below:

- **Theorem (1)**

The number of ways of distributing N Distinguishable objects equals:

W (N) = N.(N-1). (N-2).(N-3)!……3.2.1 = N! (1.10.1)

- **Theorem (2)**

The number of ways of arranging N Distinguishable objects into groups equals:

$$W(N) = \frac{N!}{n_0!n_1!n_2!\ldots} = \frac{N!}{\prod_i n_i!} \quad (1.10.2)$$

- **Theorem (3)**

The number of ways of selecting N Distinguishable objects from a set of M distinguishable objects irrespective of the order of choice.

$$W(N) = \frac{N!}{N!(M-N)!} \quad (1.10.3)$$

- **Theorem (4)**

The number of ways of arranging N Indistinguishable objects into M distinguishable containers such that there is not more than one object per container, provided that M$\gg N$.

$$W(N) = \frac{M!}{N!(M-N)!} \quad (1.10.4)$$

- **Theorem (5)**

The number of ways of arranging N Indistinguishable objects into M distinguishable containers with no restriction on the number of objects per container provided that M$\gg N$.

$$W(N) = \frac{(M+N-1)!}{N!(M-1)!} \quad (10.1.5)$$

- **Theorem (6)**

The number of ways of arranging N Distinguishable objects into M distinguishable containers with no restriction on the number of objects per container.

$$\mathbf{W\ (N) = M^N} \quad (10.1.6)$$

Example:

I. Calculate the Number of ways of putting 4 Distinguishable objects into 5 distinguishable boxes.

II. How many ways (2) indistinguishable balls may be placed in three boxes?

a- Without any restriction.
b- One ball can be in one box.
c- The balls are distinguishable.

Solution

I. $\mathbf{W\ (N) = M^N = 4^5}$

II. From equation (10.1. 5), M= 3, N=2.

$$W(2) = \frac{(3+2-1)!}{2!(3-1)!} = \frac{4!}{2!2!} = 6$$

a. From equation (10.1 .4), M=3, N= 2.

$$W(2) = \frac{M!}{N!(M-N)!} = \frac{3!}{2!(3-2)!} = 3$$

b. From equation (10.1.6), M= 3, N= 2.

$$\mathbf{W\ (2) = } M^N = 3^2 = 9$$

12. Types of systems:

In assemblies, three categories of systems exist: particles, atoms, ions, and the like. Within these assemblies, two categories pertain to indistinguishable systems, while one category falls under classical distinguishable systems. Notably, classical statistics and quantum statistics diverge in two significant aspects: in quantum theory, micro-particles of the same species are indistinguishable, and energy levels are discrete. Conversely, classical systems within the assembly are localized, allowing them to be individually traced and distinguished from one another.

I. Classical distinguishable systems:

In the context of systems, they are classified as classical distinguishable systems when they share identical physical properties but remain distinguishable based on their positions, paths, or trajectories. This classification pertains to classical physics particles, such as those found in an ideal gas, where each particle is localized and can be uniquely identified. Notably, in these systems, the system size is relatively small compared to the average distance separating the individual components.

II. Quantum indistinguishable systems:

Identical or indistinguishable systems refer to particles that, in principle, cannot be differentiated from one another. These systems primarily fall into two main categories:

Bosons:

Bosons are a class of subatomic particles characterized by integer values of spin, such as 0, 1, or 2, according to the principles of quantum mechanics. Unlike fermions, another class of particles with half-integer spin, bosons do not obey the Pauli exclusion principle and can occupy the same quantum state simultaneously, making them essential in forming states of matter like Bose-Einstein condensates. The Bose-Einstein distribution applies to *bosons.* Examples of bosons are photons, phonons, Helium-4atoms, etc., whose total spin angular momentum has integral values ($|\vec{S}| = 0, \hbar, 2\hbar, 3\hbar, \ldots$). The wave function describing bosons is completely symmetric, that is, if we interchange two particles with one another, the wave functions remain unchanged. Thus, the occupation numbers will be (n_k =0, 1, 2, 3, 4…).

- **Fermions:**

Fermions are a class of subatomic particles, such as electrons and quarks, that obey the Pauli Exclusion Principle, meaning no two fermions can occupy the same quantum state simultaneously. This principle underlies the stability of matter and is responsible for the behavior of electrons in atoms and the structure of the periodic table.

Examples of fermions are electrons, neutrinos, quarks, protons and neutrons, and helium-3 atoms whose total spin angular momentum in $\hbar$ units w the following values ($|\vec{S}| = \frac{1}{2}\hbar, \frac{3}{2}\hbar, \frac{5}{2}\hbar, \ldots$). The wave function describing fermions is completely antisymmetric, that is, if we exchange two particles with one another, the wave function changes. In a multi-electron atom, the Pauli Exclusion Principle states that no two electrons can have the same set of the four quantum numbers *(n, l, n_l, n_S)*. Therefore, the occupation numbers are n_k =0 or 1.

Table 1.1 Differences between Boson and Fermions

Description	Fermions	Bosons
Wave function	Antisymmetric (−)	Symmetric (+)
Statistics	Fermi–Dirac	Bose–Einstein
Examples	Electrons, protons, neutrons	Photons (α particle), phonons
Pauli exclusion principle	Yes	No
Spin quantum number	Half-integral	Integral
Applies to the systems	Identical, indistinguishable systems, that obey exclusion principle	Identical, indistinguishable systems, that do not obey exclusion principle
Properties 0f distribution	Never more than 1	No limits of systems per state

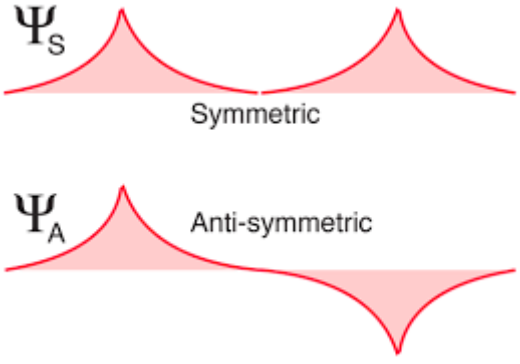


Figure 1.7: Symmetric vs. Antisymmetric Quantum Functions

Table 1.2 : Three statistical distribution functions

	Maxwell-Boltzmann	Bose-Einstein	Fermi-Dirac
Applies to systems of	Identical, distinguishable particles	Identical, indistinguishable particles that do not obey exclusion principle	Identical, indistinguishable particles that obey exclusion principle
Category of particles	Classical	Bosons	Fermions
Properties of particles	Any spin, particles far enough apart so wave functions do not overlap	Spin 0, 1, 2, . . . ; wave functions are symmetric to interchange of particle labels	Spin $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$; wave functions are antisymmetric to interchange of particle labels
Examples	Molecules of a gas	Photons in a cavity; phonons in a solid; liquid helium at low temperatures	Free electrons in a metal; electrons in a star whose atoms have collapsed (white dwarf stars)
Distribution function (number of particles in each state of energy ϵ at the temperature T)	$f_{MB}(\epsilon) = Ae^{-\epsilon/kT}$	$f_{BE}(\epsilon) = \frac{1}{e^{\alpha}e^{\epsilon/kT} - 1}$	$f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1}$
Properties of distribution	No limit to number of particles per state	No limit to number of particles per state; more particles per state than f_{MB} at low energies; approaches f_{MB} at high energies	Never more than 1 particle per state; fewer particles per state than f_{MB} at low energies; approaches f_{MB} at high energies

Chapter summary

- **Statistical Physics:**

A branch of physics is studying the physical properties of the macroscopic system from the microscopic system.

- **System:**

The individual components of any physical body these components which may be electrons, photons, atoms, or molecules. In some cases, the components may be quite complex.

- **Assembly:**

An assembly is defined as a collection of systems say *N*. The state of an assembly is defined by *6N*.

- **Macrostate:**

The state of a system is described, without attention to microscopic details, by specifying quantities that can be determined by macroscopic measurements. (*P*, *V*, *T*, and *N*)

- **Microstate:**

The state of a system is described in microscopic detail by the most complete specification, according to the laws of mechanics, of all the atoms in the system.

- **Macroscopic Systems:**

Systems consist of a very large number of atoms and molecules. e.g. one liter of gas or an apiece of copper of few grams.

Problems

I. Define a symmetric function, antisymmetric function, and draw the functions?

II. Define and give examples of micro and macro states of systems?

CHAPTER 2

MAXWELL-BOLTZMANN STATISTICS

2.1 Introduction

Maxwell-Boltzmann statistics, a fundamental concept in statistical mechanics, provides insight into the distribution of velocities among particles within an ideal gas. This statistical model elucidates that gas particles exhibit a wide spectrum of velocities, forming a characteristic bell-shaped curve known as the Maxwellian distribution. Its practical applications span various domains of physics and chemistry, encompassing phenomena like pressure, diffusion, electron transport, and laser theory. The Maxwell-Boltzmann distribution, coined after James Clerk Maxwell and Ludwig Boltzmann, originates from Statistical Mechanics, and is rooted in the concept of the most probable energy distribution within a system comprising numerous classical, non-interacting particles. This statistical approach is particularly suitable for analyzing the behavior of ideal gases, where molecular interactions are minimal, and quantum effects are negligible, typically at high temperatures or low particle densities. The conditions of Maxwell-Boltzmann distribution are summarized below in the Figure 2.1.

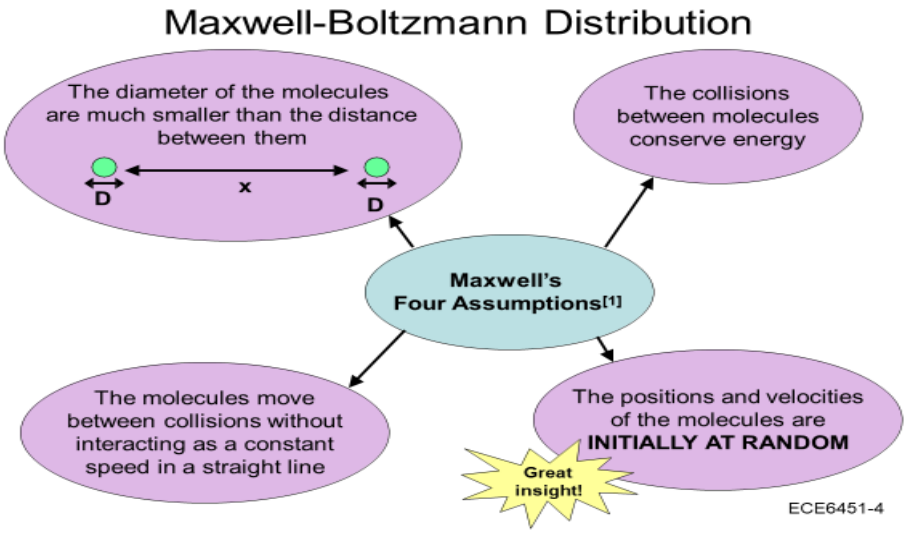


Figure 2-1 The condition of Maxwell-Boltzmann statistics.

The Maxwell-Boltzmann distribution applies to assemblies comprising classical distinguishable systems (particles) where the average distance between particles, denoted as 'd,' significantly exceeds the quantum uncertainty in particle position**.**

$$\frac{\hbar}{2\sqrt{mkT}} \leq \Delta x \ll d \qquad (2.1)$$

Where,$\hbar = \frac{h}{2\pi}$ h is the Planck constant and m is the particle mass.

In such cases, where the particles are distinguishable and the wave properties of particles can be neglected, some algebraic calculations reveal that

$$\left(\frac{N}{V}\right)\frac{\hbar^3}{8\sqrt{(mkT)^3}} \ll 1 \qquad (2.2)$$

Hence, when the particle concentration (density, N/V) is low, the particle mass (m) is high (indicating classical distinguishable particles), and the temperature is elevated.

Example 1:

Prove that the Maxwell-Boltzmann statistics valid for hydrogen gas at standard temperature and pressure (abbreviated typically STP, 273 K, 1 atmosphere)?

Under STP 1 mol H_2 gas = 6.02* 10^{23} molecules occupies 22.4 liter $dm^{3,}$ Mass of H_2 molecule 3.34 10^{-27} kg, h = 6.626 10^{-34} $W.s^2$, k = 1.381 10^{-23} J/K = 8.617 10^{-5} eV/K.

Solution:

$$\left(\frac{N}{V}\right)\frac{\hbar^3}{8\sqrt{(mkT)^3}} = 8.83.10^{-8} \ll 1$$

Example 2:

Show that if the Maxwell-Boltzmann statistics are valid for electrons in Silver?

Silver has a density of 10.5 g/cm^{-3} and a molar weight of 197.9 g. assuming one free electron per silver atom, the density of free electrons is $\frac{10.5}{197.9} * 6.02 \cdot 10^{23}\text{electrons/m}^3 = 5.86 \cdot 10^{28}\text{electrons/m}^3$, mass of electron 9.109 10^{-31} kg assuming the room temperature, T = 300 K, then, k*T = 4.14 10^{-21} J $\approx$ 25meV.

Solution:

$$\left(\frac{N}{V}\right)\frac{\hbar^3}{8\sqrt{(mkT)^3}} = 4.64$$

In this example, the Maxwell-Boltzmann statistic is not valid, because of the small mass of the electron, and the density of electrons in silver about 2000 times higher than the density of H_2 at STP, electrons are fermions, and so Fermi-Dirac statistics is valid.

2.2 Distribution over energies

To find the distribution of the systems over their possible energy states, we consider an assembly having total energy (E) and number of systems (N). The energies of the systems are then related to the total energy by the condition $\sum_i \varepsilon_i = E$ (2.3)

Consider that the energies of the systems can be divided into levels or states (s), so that level (s) will include all the energy states in the range ε_s to $\varepsilon_s + d\varepsilon_s$ of and the energy of a system is ε_s.

Each energy level or state is divided into sublevels, called the state's weight. The distribution of the systems over the various energies is then given by specifying the occupation numbers n_s. There are several ways of distributing energy among systems. Consider that the energy of systems is arranged over total energy levels, then the distribution may be written in terms of the occupation numbers as follows:

Level or state number	1	2	3	4	$\dots\dots\dots s$	$\dots\dots r$
Level energy	ε_1	ε_2	ε_3	ε_4	$\dots\dots\dots \varepsilon_s$	$\dots\dots \varepsilon_r$
Weight of levels	g_1	g_2	g_3	g_4	$\dots\dots\dots g_s$	$\dots\dots g_r$
Occupation numbers	n_1	n_2	n_3	n_4	$\dots\dots\dots n_s$	$\dots\dots n_r$

The number of systems is written as:

$$\sum_{s=1}^{r} n_s = N = \text{constant} \qquad (2.3.\text{ a})$$

The total energy (E) is written as:

$$\sum_{s=1}^{r} n_s \varepsilon_s = E = constant \qquad (2.3.\text{ b})$$

If we combine theorem 2 in chapter 1, where a number of ways of arranging N distinguishable objects into groups (n_s) , $W(N) = \frac{N!}{n_0!n_1!n_2!\ldots} = \frac{N!}{\prod_s n_s!}$ with theorem 6, number of ways of arranging N distinguishable objects into M distinguishable containers with no restriction on the number of objects per container, W(N) = M^N . Here M represents g_s and N represents n_s . Then, we have: ${g_s}^{n_s}$.

Or, if the (N) particles are first placed into groups, cells, the (s^{th}) cells or groups having (n_s) as in theorem (2) in chapter (1). This can be done in $N!\frac{N!}{\prod_s ns!}$ ways. The second and all subsequent ones can also occupy the levels or states in g_s ways.

Therefore, there are ${g_s}^{n_s}$ ways, where $n_s!$ particles can occupy $g_s!$ levels or states as discussed in theorem 6 in chapter 1. Hence, we may get the following by this combination

$$W = N! \prod_s \left\{ \frac{{g_s}^{n_s}}{n_s!} \right\} \tag{2.4}$$

2.3 The most probable configuration

Certain values of the occupation numbers lead to the highest possible weight for configurations. Consequently, as the probability of the assembly assuming a specific configuration is directly proportional to its weight, the configuration with the maximum weight becomes the most likely configuration for the assembly. Therefore, in order to determine the occupation numbers under these conditions, it is essential to maximize the weight (representing the most probable configuration).

$$d \ln W = \sum_s \frac{\partial \ln w}{\partial n_s} dn_s = 0 \tag{2.5}$$

$$\sum_s n_s = N = constant \tag{2.6a}$$

Then,

$$dN = \sum_s dn_s = 0 \tag{2.6b}$$

$$\sum_s n_s \varepsilon_s = E = constant \tag{2.6c}$$

Then,

$$dE = \sum_s d\epsilon_s \; dn_s = 0 \tag{2.6d}$$

To maximize W, the most probable configuration as if w is a function of N, E, with two conditions, N = constant, E = constant, then, d W = 0, as a maximum, or minimum. Recalling the Lagrange undetermined multipliers in the Appendix 1, We introduce the Lagrange undetermined multipliers, a, b leading to

$$dW + a\, dN + b\, dE = 0 \tag{2.7}$$

Where a, b are undetermined lagrange multiplier, so equation 2.7 becomes

$$\sum_s \frac{\partial W}{\partial n_s} dn_s + a \sum_s dn_s + b \sum_s d\epsilon_s \; dn_s = 0 \tag{2.8}$$

It is convenient for large values of W to work with ln W rather than W, then,

$$d\ln W + \alpha dN + \beta dE = 0 \tag{2.9}$$

Combining equation 2.8 and 2.9, we get:

$$\sum_s \frac{\partial \ln W}{\partial n_s} dn_s + \alpha \sum_s dn_s + \beta \sum_s d\epsilon_s \; dn_s = 0 \tag{2.10}$$

This equation 2.10 can be rewritten as:

$$\sum_s \left\{ \frac{\partial \ln W}{\partial n_s} + \alpha + \beta \varepsilon_s \right\} dn_s = 0 \tag{2.11}$$

The variations are arbitrary, $dn_s \neq 0$ and therefore, then, we get

$$\frac{\partial lnW}{\partial n_s} + \alpha + \beta\varepsilon_s = 0 \tag{2.12}$$

We know from equation (2.4) that:

$$W = N! \prod_s \left\{ \frac{{g_s}^{n_s}}{n_s!} \right\} \tag{2.4}$$

Then,

$$\ln W = \ln N! + \ln \prod_s \left\{ \frac{{g_s}^{n_s}}{n_s!} \right\} \tag{2.13}$$

Using the usual notation

$$\prod_s XY = \sum_s (X + Y) \tag{2. 14}$$

Equation 2. 13 will be rewritten

$$\ln W = \ln N! + \sum_s \ln \left\{ \frac{{g_s}^{n_s}}{n_s!} \right\} \quad \text{or} \tag{2. 15a}$$

$$\ln W = \ln N! + \sum_s (\ln {g_s}^{n_s} - \ln n_s!) \tag{2. 15b}$$

Since N is a large arbitrary number, as in Appendix 2, Stirling's approximation, $\ln N! = Nln\,N - N$ is applied to equation 2. 15b giving

$$\ln W = NlnN - N + \sum_s (n_s \ln g_s - n_s \ln n_s + n_s) \quad or \tag{2.15c}$$

$$\ln W = N \ln \mathrm{N} - N + \sum_s n_s + \sum_s (n_s \ln g_s - n_s \ln n_s) \tag{2.15d}$$

Using the notation, $\sum_s \mathrm{n_s} = \mathrm{N}$, we get

$$\ln W = NlnN + \sum_s (n_s\, ln\, g_s - n_s \ln n_s) \tag{2.16}$$

By partial differentiation of equation (2. 16), then

$$\frac{\partial \ln W}{\partial n_s} = \frac{\partial}{\partial n_s} (NlnN + \sum_s (n_s \ln g_s - n_s \ln n_s)) \tag{2.17a}$$

$$\frac{\partial \ln W}{\partial n_s} = \frac{\partial NlnN}{\partial n_s} + \frac{\partial}{\partial n_s} (\sum_s (n_s \ln g_s - n_s \ln n_s) \tag{2. 17b}$$

Since N is a constant, then, $\frac{\partial \mathrm{N} \ln N}{\partial n_s} = 0$, therefore, we get

$$\frac{\partial \ln W}{\partial n_s} = \frac{\partial}{\partial n_s} (n_s \ln g_s - n_s \ln n_s) \tag{2. 18a}$$

$$\frac{\partial \ln W}{\partial n_s} = n_s \frac{\partial \ln g_s}{\partial n_s} + \ln g_s * \frac{\partial n_s}{\partial n_s} - n_s \frac{\partial \ln n_s}{\partial n_s} - \ln n_s * \frac{\partial n_s}{\partial n_s} \tag{2. 18b}$$

Since, $\frac{\partial\, ln\, g_s}{\partial n_s} = 0$, $\frac{\partial n_s}{\partial n_s} = 1, n_s \frac{\partial \ln n_s}{\partial n_s} = 1$

Then,

$$\frac{\partial \ln W}{\partial n_s} = \ln g_s - \ln n_s - n_s \frac{\partial \ln n_s}{\partial n_s} \quad or \tag{2. 19a}$$

$$\frac{\partial \ln W}{\partial n_s} = \ln g_s - \ln n_s - 1 \tag{2. 19b}$$

Since ($\mathrm{n_s}$) is very large $\mathrm{n_s} \gg 10^{23}$, then, equation (2. 19b) becomes

$$\frac{\partial \ln W}{\partial n_s} = \ln g_s - \ln n_s \quad \text{or} \tag{2. 20a}$$

$$\frac{\partial \ln W}{\partial n_s} = \ln\left(\frac{g_s}{n_s}\right) \qquad (2.20b)$$

Substituting equation (2. 20b) into equation (2. 19b), we get:

$$\mathbf{ln}\left(\frac{g_s}{n_s}\right) + \alpha + \beta\,\epsilon_s = 0 \qquad \text{Or} \qquad (2.\ 21a)$$

$$-\ln\left(\frac{g_s}{n_s}\right) = \alpha + \beta\,\epsilon_s \qquad (2.\ 21b)$$

Take exponential of equation (2. 21b) leading to

$$\ln\left(\frac{n_s}{g_s}\right) = \alpha + \beta\,\epsilon_s \qquad (2.\ 21c)$$

$$\frac{n_s}{g_s} = e^{\alpha+\beta\,\epsilon_s} \qquad (2.\ 21d)$$

Then, we have

$$n_s = g_s e^{\alpha+\beta\,\epsilon_s} \qquad (2.22)$$

The result obtained in equation (2. 22) gives the distribution of the systems over the various energy states for the most probable configuration and is known as the "Maxwell-Boltzmann distribution or statistics".

If the assembly is non-degenerate, where $g_s = 1$,, then equation (2. 22) becomes

$$n_s = e^{\alpha+\beta\,\epsilon_s} \qquad (2.23)$$

This equation represents the distribution of the most probable state at the equilibrium. Fluctuations from this state are limitingly small.

Equation 2.22 remains applicable even when energy states are not perfectly degenerate but closely spaced within the energy range of dε. In such instances, we consider energy bundles of width dε, and g_{ss} represents the number of energy states.

It's worth noting that no system possesses infinite energy, so β must be negative (as $e^{-\infty} = 0$). Since α remains constant, we treat exp(α) as a constant, denoted as A.

The proportion of particles with energy ε_s can be determined using equation 2.22, which yields the probability of locating the particle in the "th" energy level:

$$\frac{n_i}{N} = \frac{n_i}{\sum n_i} = \frac{Ae^{\beta\varepsilon_i}}{\sum Ae^{\beta\varepsilon_i}} = \frac{Ae^{\beta\varepsilon_i}}{A\sum e^{\beta\varepsilon_i}} = \frac{e^{\beta\varepsilon_i}}{\sum_i e^{\beta\varepsilon_i}} \qquad \text{Or,} \qquad (2.24)$$

$$\frac{n_i}{N} = \frac{g_i e^{\beta\varepsilon_i}}{\sum_i g_i e^{\beta\varepsilon_i}} \qquad (2.24b)$$

The ratio of particles in the i^{th} energy level to those in the j^{th} energy level is given by

$$\frac{n_i}{n_j} = \frac{e^{\beta\varepsilon_i}}{e^{\beta\varepsilon_j}} = e^{\beta(\varepsilon_i-\varepsilon_j)} \qquad (2.25a)$$

$$\frac{n_i}{n_j} = \frac{g_i e^{\beta\varepsilon_i}}{g_j e^{\beta\varepsilon_j}} = \frac{g_i}{g_j} e^{\beta(\varepsilon_i-\varepsilon_j)} \qquad (2.25b)$$

This equation holds significant importance within the realm of laser theory. It plays a pivotal role in understanding and describing laser operation, particularly in elucidating the conditions for laser amplification and emission of coherent light. Researchers and engineers heavily rely on this equation as a fundamental building block for laser design, optimization, and practical applications, making it a cornerstone in the field of laser science and technology.

2.4. The sharpness of the configuration maxim

The occupation numbers provided in equation 2.22 correspond to a stationary point for the weight W. To examine the characteristics of W in the vicinity of this stationary point, it is most effectively approached by expanding the natural logarithm of W, (ln W) as a Taylor series centered at this point. The resulting expansion takes the following form:

$$ln\, W = ln\, W_{max} + \sum_s \left\{\frac{\partial\, ln\, w}{\partial n_s}\right\}_{max} \Delta n_s + \sum_s \left\{\frac{\partial^2\, ln\, w}{\partial {n_s}^2}\right\}_{max} \frac{\Delta {n_s}^2}{2} + \cdots \quad (2.26)$$

There would be additional terms in equation 2.26 of the form $\sum_s \sum_t \left\{\frac{\partial^2 ln}{\partial n_s n_t}\right\} \Delta n_s \Delta n_t$, *but* $\frac{\partial\, ln\, w}{\partial n_s}$ is function of n_s only, so these terms will be zero.

We know by the definition at a stationary point

$$\sum \left\{\frac{\partial\, ln\, w}{\partial n_s}\right\}_{max} \Delta n_s = 0 \quad (2.27)$$

From equation 2.20b, we have

$$\frac{\partial \ln W}{\partial n_s} = \ln\left(\frac{g_s}{n_s}\right) \quad (2.20b)$$

The second term in equation 2.26 is obtained from 2.20b

$$\frac{\partial^2\, ln\, w}{\partial {n_s}^2} = \frac{-1}{n_s} \quad (2.28)$$

Suppose that n_{sm} is equal to n_s at the stationary point, and substitution equation 2.28 into equation 2.26 leads to

$$ln\, W = ln\, W_{max} - \frac{1}{2}\sum_s \frac{\Delta {n_s}^2}{n_{sm}} \quad (2.29)$$

Take exponential of equation 2.29, we get

$$W = W_{max}\, exp\left(-\frac{1}{2}\sum_s \frac{\Delta {n_s}^2}{n_{sm}}\right) \quad (2.30)$$

The quantity W_{max} represents the maximum value of W. Equation (2.30) showing that any deviation Δn_s, positive or negative of n_s from the value n_{sm} will produce a weight W less than W_{max}.

To achieve the sharpness of configuration maximum, let

$$\frac{\Delta n_s}{n_{sm}} = \delta_s \quad (2.31)$$

So, the equation 2.30 becomes

$$W = W_{max}\, exp\left(-\frac{1}{2}\sum_s n_{sm} {\delta_s}^2\right) \quad (2.32)$$

Then, if that case is considered where all the fractional derivations have the same magnitude $|\delta_s| = \delta$ but with the sign chosen to give $\sum_s n_s\, \delta_s = 0$, equation 2.32

$$W = W_{max}\, exp\left(-\frac{1}{2}{\delta_s}^2 \sum_s n_{sm}\right) \quad \text{or} \quad (2.32)$$

$$W = W_{max}\, exp\left(-\frac{1}{2}\delta^2 N\right) \quad (2.33)$$

The average assembly under consideration consists of an exceedingly large number of systems, N >> 10^{20}. Consequently, even a slight deviation, δ, from the most probable configuration, as small as one part in 10^8 (i.e., $\delta = 10^{-8}$), results in a significant reduction in the configuration's weight.

$$W = W_{max}\, exp\left(-\frac{1}{2}(10^{-8})^2 * 10^{20}\right) \quad (2.34)$$
$$W = 10^{-2150}\, .\, W_{max}$$

Figure 2.2 illustrates the swift decline in W when fractional deviations reach the scale of approximately one part in 10^{-10} for $N = 10^{20}$.

These calculations demonstrate that the peak of W is exceptionally narrow, closely resembling the most probable configuration. This sensitivity implies a noticeable margin of error when the most probable configuration aligns precisely with the equilibrium configuration and the calculated properties reflect the assembly's average properties. Reducing the number of systems within the assembly mitigates the sharpness of the configuration peak, causing fluctuations away from the most probable configuration to become significant, as exemplified in the following.

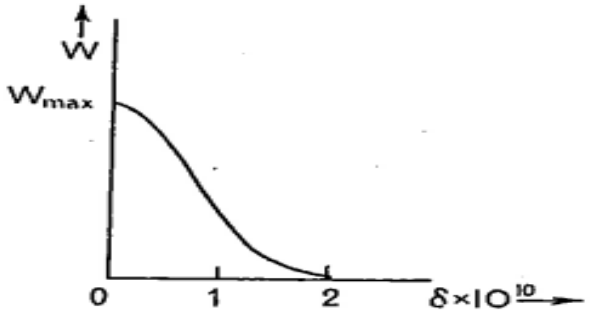


Figure 2-2 Rapid decrease of W with very small deviations from the most probable point.

2.5 The multiplier

We can anticipate that the value of β is negative based on the premise that there are no systems with infinite energy in the Maxwell-Boltzmann equation. Since it appears that no system possesses infinite energy (as expressed by $(e^{-\infty} = 0)$, β is expected to be negative.

$$n_s = g_s\, e^{\alpha + \beta \epsilon_s} \tag{2.5.1}$$

It is an easy approach to prove that the undetermined β Lagrange's Multiplier is a function of temperature only.

Consider two assemblies $\grave{A}$ $(\grave{N}, \grave{E}\ and\ \grave{W})$ and $\grave{\grave{A}}$ $(\grave{\grave{N}}, \grave{\grave{E}}\ and\ \grave{\grave{W}})$ in thermal contact $\grave{T} = \grave{\grave{T}}$ (zeroth law).

$$d\grave{N} = 0,\ d\grave{\grave{N}} = 0\ ,\ \mathrm{dE} = 0\ , \tag{2.5.2a}$$

The total energy of two assemblies is

$$E = \grave{E} + \grave{\grave{E}}\ \ = \sum_S \grave{n}_s \grave{\epsilon}_S + \sum_S \grave{\grave{n}}_s \grave{\grave{\epsilon}}_S \tag{2.5.2b}$$

Since the assemblies divided into states and the state, s having energy $\grave{\epsilon}_S$ and $\grave{\grave{\epsilon}}_S$ and the occupation number $\grave{n}_s$ and $\grave{\grave{n}}_s$.

$$dE = \sum_S \grave{\epsilon}_S\ d\grave{n}_s + \sum_S \grave{\grave{\epsilon}}_S\, d\grave{\grave{n}}_s = 0 \tag{2.5.2c}$$

The total configuration number of two assemblies is

$$W_T = \grave{W}\grave{\grave{W}} \tag{2.5.3a}$$

Then,

$$\ln W_T = \ln \grave{W} + \ln \grave{\grave{W}} \tag{2.5.3b}$$

Differentiating equation 2.5.3b, we get:

$$\mathrm{d} \ln W_T = \mathrm{d} \ln \grave{W} + \mathrm{d} \ln \grave{\grave{W}} \tag{2.5.3c}$$

Since $\grave{W}$ and $\grave{\grave{W}}$ depend only on the occupation number, we can write:

$$\mathrm{dln}\, \grave{W} = \sum_s \frac{\partial \ln \grave{W}}{\partial \grave{n}_s} dn_s \tag{2.5.4a}$$

and