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**B.Sc. (Prog), Thermal Physics
Chapter - 5
Statistical Mechanics**

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Chapter- 5

Statistical Mechanics: Phase space, Macrostate and Microstate, Entropy and Thermodynamic probability, Maxwell-Boltzmann law, distribution of velocity, Quantum statistics, Fermi-Dirac distribution law, Bose-Einstein distribution law, comparison of three statistics.

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Que1: Explain concept of phase space in detail.

Ans: Phase Space: A Framework for Statistics involves the counting of states, and the state of a classical particle is completely specified by the measurement of its position and momentum. If we know the six quantities

$$x, y, z, p_x, p_y, p_z$$

then we know its state. It is often convenient in statistics to imagine a six-dimensional space composed of the six position and momentum coordinates. It is conventionally called "phase space". The counting tasks can then be visualized in a geometrical framework where each point in phase space corresponds to a particular position and momentum. That is, each point in phase space represents a unique state of the particle. The state of a system of particles corresponds to a certain distribution of points in phase space.

The counting of the number of states available to a particle amounts to determining the available volume in phase space. One might preclude that for a continuous phase space, any finite volume would contain an infinite number of states. But the uncertainty principle tells us that we cannot simultaneously know both the position and momentum, so we cannot really say that a particle is at a mathematical point in phase space. So when we contemplate an element of "volume" in phase space

$$du = dx.dy.dz.dp_x.dp_y.dp_z$$

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then the smallest "cell" in phase space which we can consider is constrained by the uncertainty principle to be

$$dU_{\min} = h^3$$

Que 2: What is a microstate and microstate.

Ans: A 'microstate' refers to a description of the system which relies on the states of each element of the system. Applied to a thermodynamic system, each microstate M_i of the system is a set of positions $\{q_i\}$ and velocities $\{q_i\}$ for $i=1, \dots, 3N$ (in three dimensions, add another set of coordinates for internal degrees of freedom, such as rotation) which describe the position and velocity of each particle. As you can imagine, for large N^N (say, $N=10^{23}$), this gets out of hand. Furthermore, the probability that the system is in microstate M_i is quite low as there are many, many different microstates the system could occupy.

A 'macrostate' on the other hand is a state description relying on the macroscopic properties of the system: its temperature, pressure, volume, internal energy and such. For each macrostate, there are many, many microstates which result in the same macrostate: for example, if you interchange velocity (but not position) of two gas particles, the macrostate does not change, but you have a different microstate.

Que 3: Enumerate the number of microstates for a given microstate (N, V, E) of a system.

Ans: Enumeration of microstates:

It is important to enumerate the number of microstates for a given microstate (N, V, E) of a system. For a classical particle, the microstate is specified by a phase point. Consider an infinitesimal change in the position and momentum coordinates in the phase space. The phase point of this particle then under go a small displacement in the phase space and the microscopic state of the system will be modified. However, if the change in the microstate is so small that it is not measurable by the most accurate experiment, then it can be assumed that there is no change in the macroscopic state of the system. Thus, the state of a system is given by a small

volume element $\delta\Omega$ of the Γ -phase space. If $\delta q\delta p = h$, then

$$\delta\Omega = \delta q_1\delta q_2\cdots\delta q_{3N}\delta p_1\delta p_2\cdots\delta p_{3N} = h^{3N}.$$

By Heisenberg's uncertainty principle in quantum mechanics it can be shown that h is the Planck's constant. Thus, the number of states of a system of N particles of energy $\leq E$ is given by

$$\Gamma = \frac{1}{h^{3N}} \int d\Omega = \frac{1}{h^{3N}} \int \int d^{3N}q d^{3N}p.$$

The number of microstates is then proportional to the volume of the phase space.

The enumeration of number of microstates however depends on the *distinguishable* and *indistinguishable* nature of the particles. If the constituent particles are distinguishable, the two microstates corresponding to the interchange of two particles of different energy are distinct microstates. On the other hand, if the constituent particles are indistinguishable, these two microstates are not distinct microstates. Thus, for a system of N indistinguishable, identical classical particles having different energy states, the number of microstates is then given by

$$\Gamma = \frac{1}{h^{3N}N!} \int \int d^{3N}q d^{3N}p$$

as suggested by Gibbs.

Consider a system of N particles of total energy E and corresponds to a macrostate (N, V, E) . If the particles are distributed among the different energy levels as, n_i particles in the energy level ϵ_i , the following conditions has to be satisfied

$$N = \sum_i n_i \quad \text{and} \quad E = \sum_i n_i \epsilon_i.$$

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The total number of possible distributions of N such particles is then given by

$$\frac{N!}{\prod n_i!}$$

If the particles are distinguishable, then all these permutations would lead to distinct microstate whereas if the particles are indistinguishable, these permutations must be regarded as one and the same microstate.

Que 4: Explain “Equal a priori probability”.

Ans:

As it is already seen that for a given macrostate (N, V, E) , there is a large number of possible microstates of the system. In case of classical non-interacting system, the total energy E can be distributed among the N particles in a large number of different ways and each of these different ways corresponds to a microstate. In case of a quantum system, the various different microstates are identified as the independent solutions $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ of the Schrödinger equation of the system, corresponding to an eigenvalue E . In any case, to a given macrostate of the system there exists a large number of microstates and it is assumed in statistical mechanics that at any time t the system is **equally likely** to be in any one of these microstates. This is generally referred as the postulate of *equal a priori probability* for all microstates of a given macrostate of the system.

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Que 5: What is an ensemble and classify different statistical ensembles.

Ans: Statistical ensembles: The microstate of a macroscopic system is specified by a point in $6N$ -dimensional phase space where N is of the order of Avogadro number (10^{23}). At any time t , the system is equally likely to be in any one of the large number of microstates corresponding to a given macrostate (N, V, E) . As the dynamical system evolves with time, the system moves from one microstate to another. After a sufficiently long time, the system passes through a large number of microstates. The behaviour of

the system then can be obtained as averaged over those microstates through which the system passes. Thus, in a single instant of time, one could consider a collection of large number of replicas (mental copies) of the original system characterized by the same macrostate but could be in any of the possible microstates to obtain the average behaviour of the system. This collection of large number of copies of the same system is called an ensemble. It is expected that the ensemble averaged behaviour of a system would be identical with the time averaged behaviour of the given system. Since the values of (q, p) at any instant are different for a system of an ensemble, they are represented by different points in the phase space. Thus, the ensemble will be represented by a cloud of phase points in the phase space.

Ensembles and Thermodynamic quantities

Like thermodynamic systems, statistical ensembles are also classified in three different types. The classification of ensembles depends on the type of interaction of the system with the surroundings. The interactions of the systems with the surroundings are either through energy exchange or through energy and matter (number particles) exchange. In an isolated system, neither energy nor matter is exchanged and the corresponding ensemble is known as microcanonical ensemble. A system exchanging only energy (not matter) with its surroundings is described by canonical ensemble. If both energy and matter are exchanged between the system and the surroundings the corresponding ensemble is called a grand canonical ensemble. The equilibrium thermodynamic properties of a system can be calculated using any ensemble formalism in statistical mechanics. However, choice of a specific ensemble to calculate physical properties of a specific system always reduces the mathematical task enormously.

Que 6: Explain Boltzmann formula of entropy using Microcanonical ensemble.

Ans:

Consider two physical systems, A and B as shown in Fig.2.1. The systems are independently in thermodynamic equilibrium at the macrostates (N_1, V_1, E_1) and (N_2, V_2, E_2) respectively. The number of microscopic states of the corresponding systems are $\Omega_A(N_1, V_1, E_1)$ and $\Omega_B(N_2, V_2, E_2)$. Now the two systems are kept in thermal contact and the combined system $AB \equiv A+B$ remain an isolated system. In thermal contact, only energy exchange between the two systems is possible keeping the other thermodynamic parameters (N or V) fixed. Thus, the energy of the

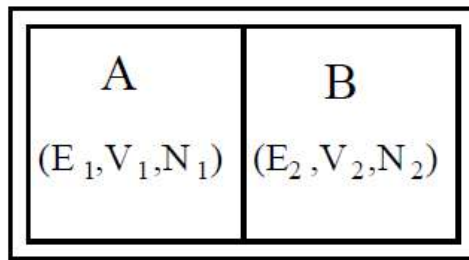


Figure 2.1: Two physical systems A and B are in thermal contact.

combined system E_0 is given by alllabexperiments.com

$$E_0 = E_1 + E_2 = \text{constant.}$$

At any time t , the subsystem A is equally likely in any of the microstates $\Omega_A(E_1)$ and the subsystem B is equally likely if any of the microstate $\Omega_B(E_2)$. The combined system AB is then in any of the microstate $\Omega_{AB}(E_1, E_2)$ given by

$$\Omega_{AB}(E_1, E_2) = \Omega_A(E_1)\Omega_B(E_2) = \Omega_A(E_1)\Omega_B(E_0 - E_1) = \Omega_{AB}(E_0, E_1)$$

At equilibrium, the value of $\Omega_{AB}(E_0, E_1)$ will be maximum. A system evolves naturally in a direction that enables it to assume an ever increasing number of macrostates. If \bar{E}_1 is the equilibrium value of E_1 and \bar{E}_2 is that of E_2 ,

$$\Omega_B(E_2) \left(\frac{\partial \Omega_A}{\partial E_1} \right)_{\bar{E}_1} + \Omega_A(E_1) \left(\frac{\partial \Omega_B}{\partial E_2} \right)_{\bar{E}_2} \left(\frac{\partial E_2}{\partial E_1} \right) = 0.$$

Since $\partial E_2 / \partial E_1 = -1$, the above equation reduces to

$$\frac{1}{\Omega_A} \left(\frac{\partial \Omega_A}{\partial E_1} \right)_{\bar{E}_1} = \frac{1}{\Omega_B} \left(\frac{\partial \Omega_B}{\partial E_2} \right)_{\bar{E}_2} \quad \Rightarrow \quad \left(\frac{\partial \ln \Omega_A}{\partial E_1} \right)_{\bar{E}_1} = \left(\frac{\partial \ln \Omega_B}{\partial E_2} \right)_{\bar{E}_2}.$$

The condition of equilibrium is then equality of two parameters β_1 and β_2 where

$$\beta = \frac{\partial \ln \Omega(N, V, E)}{\partial E}.$$

From thermodynamics, it is already known that

$$k_B T = \frac{1}{\beta} \quad \text{and} \quad \frac{1}{T} = \frac{\partial S}{\partial E}$$

where T is the temperature, k_B is the Boltzmann constant and S is the entropy. It suggests that the entropy of the system is given by

$$S = k_B \ln \Omega.$$

This is the Boltzmann definition of entropy. Since, in a natural process the equilibrium corresponds to maximum Ω then the equilibrium corresponds to maximum entropy S and one gets the second law of thermodynamics. The condition of equilibrium $\beta_1 = \beta_2$ also reduces to $T_1 = T_2$ as in thermodynamics. In case of movable wall or penetrable wall the equilibrium conditions could be obtained as $P_1 = P_2$ and $\mu_1 = \mu_2$ respectively by taking derivative of $\Omega(E, N, V)$ with respect to volume V and number of particles N . Notice that as $T \rightarrow 0$, the system is going to be in its ground state and the value of Ω is going to be 1. Consequently, the entropy $S \rightarrow 0$, the third law of thermodynamics.

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Que 7: Explain Maxwell-Boltzmann Distribution.**Ans: Maxwell-Boltzmann Distribution**

The Maxwell-Boltzmann distribution is the classical distribution function for distribution of an amount of energy between identical but distinguishable particles.

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Besides the presumption of distinguishability, classical statistical physics postulates further that:

- There is no restriction on the number of particles which can occupy a given state.
- At thermal equilibrium, the distribution of particles among the available energy states will take the most probable distribution consistent with the total available energy and total number of particles.
- Every specific state of the system has equal probability.

One of the general ideas contained in these postulates is that it is unlikely that any one particle will get an energy far above the average (i.e., far more than its share). Energies lower than the average are favored because there are more ways to get them. If one particle gets an energy of 10 times the average, for example, then it reduces the number of possibilities for the distribution of the remainder of the energy. Therefore it is unlikely because the probability of occupying a given state is proportional to the number of ways it can be obtained.

Que 8: Explain Fermi-Dirac and Bose-Einstein Distribution in detail.**Ans: Fermi-Dirac Distribution**

The Fermi-Dirac distribution applies to fermions, particles with half-integer spin which must obey the Pauli exclusion principle. Each type of distribution function has a

normalization term multiplying the exponential in the denominator which may be temperature dependent. For the Fermi-Dirac case, that term is usually written:

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The significance of the Fermi energy is most clearly seen by setting $T=0$. At absolute zero, the probability is =1 for energies less than the Fermi energy and zero for energies greater than the Fermi energy. We picture all the levels up to the Fermi energy as filled, but no particle has a greater energy. This is entirely consistent with the Pauli exclusion principle where each quantum state can have one but only one particle.

The probability that a particle will have energy E

At absolute zero, fermions will fill up all available energy states below a level E_F called the Fermi energy with one (and only one) particle. They are constrained by the Pauli exclusion principle. At higher temperatures, some are elevated to levels above the Fermi level.

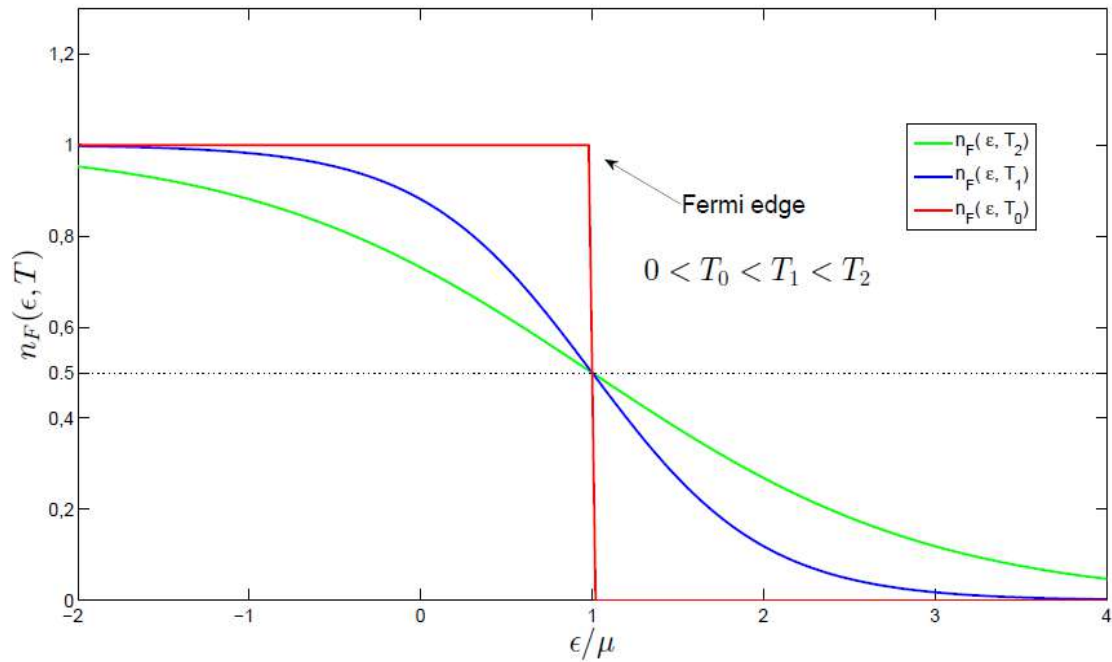
$$f(E) = \frac{1}{e^{(E - E_F)/kT} + 1}$$

Fermi-Dirac

See the Maxwell-Boltzmann distribution for a general discussion of the exponential term.

For low temperatures, those energy states below the Fermi energy E_F have a probability of essentially 1, and those above the Fermi energy essentially zero.

The quantum difference which arises from the fact that the particles are indistinguishable.



Bose-Einstein Distribution

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The Bose-Einstein distribution describes the statistical behavior of integer spin particles (bosons). At low temperatures, bosons can behave very differently than fermions because an unlimited number of them can collect into the same energy state, a phenomenon called "condensation".

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The probability that a particle will have energy E

Describing integer spin bosons, this distribution allows an unlimited number of particles to condense into a single level.

$$f(E) = \frac{1}{Ae^{E/kT} - 1}$$

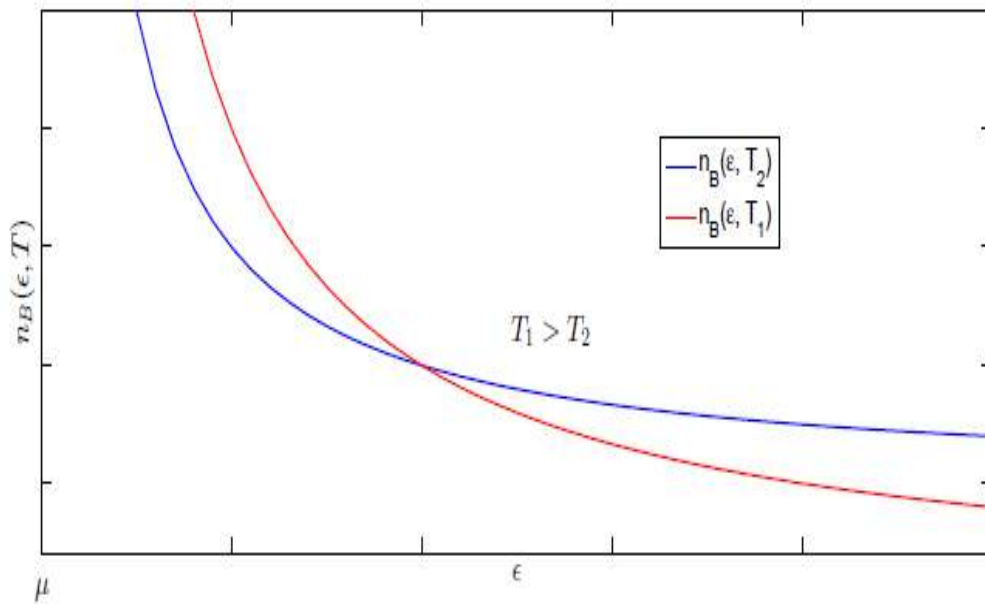
Bose-Einstein

For photons, A=1, so the occupation of very low energy states can increase without limit.

The quantum difference which arises from the fact that the particles are indistinguishable.

The exponential dependence upon energy and temperature. See the classical Boltzmann distribution for more description.

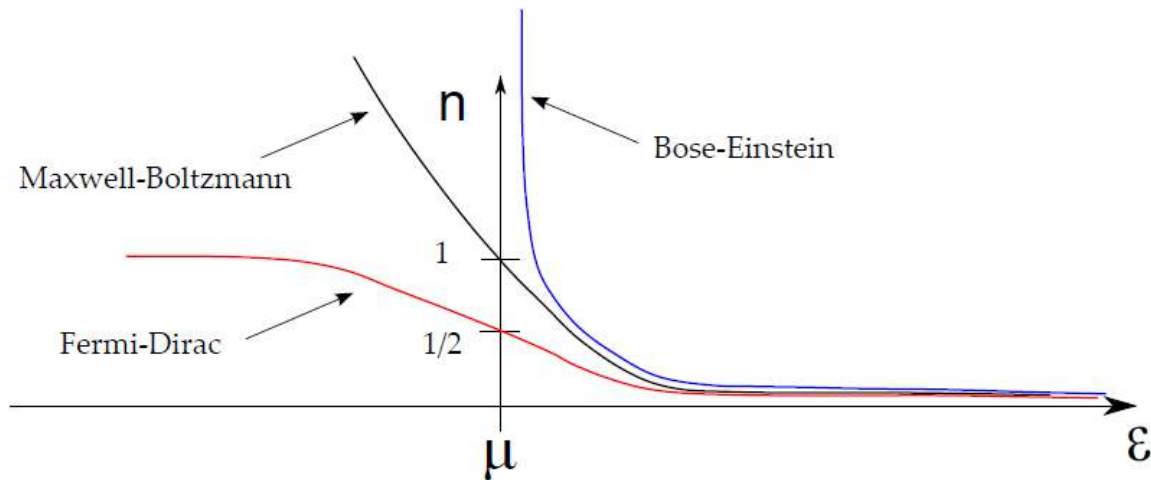
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Que9: Give a short comparison on three statistics.

Ans:

Identical but distinguishable particles.	Identical indistinguishable particles with integer spin (bosons).	Identical indistinguishable particles with half-integer spin (fermions).
Examples: Molecular Speed Distribution	Examples: Thermal Radiation, Specific Heat	Examples: Electrons in a metal, Conduction in Semiconductors



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