Chapter 1

Statistical Mechanics:A brief overview

Lecture-I

1. Introduction:

Statistical mechanics describes the thermodynamic behaviour of macroscopic systems from the laws which govern the behaviour of the constituent elements at the microscopic level. The microscopic elements can be atoms, molecules, dipole moments or magnetic moments, etc. A macroscopic system, generally, is composed of a large number of these elements (of the order of Avogadro number $N_A \approx 6.022 \times 10^{23}$ per mole). Each element may have a large number of internal degrees of freedom associated with different types of motion such as translation, rotation, vibration etc. The constituent elements may interact with the external field applied to the system. There can also be very complex interaction among the constituent elements. The macroscopic properties of a system is thus determined in the thermodynamic limit by the properties of the constituent molecules, their interaction with external field as well as interaction among themselves.

[**Thermodynamic limit:** For a system of N elements of volume V and density ρ, the thermodynamic limit is defined as $\lim N \to \infty$, $\lim V \to \infty$ keeping $\rho = N/V$ finite. In this limit, the extensive properties of the system become directly proportional to the size of the system (N or V), while the intensive properties become independent of the size of the system.]

In the formalism of statistical mechanics, a macroscopic property of a system is obtained by taking a "statistical average" (or "ensemble average") of the property over all possible "microstates" of the system. A microstate of a system is defined by specifying the states of all of its constituent elements.

Thermodynamic equilibrium of a system can be achieved in different ways depending upon the interaction of the system with the rest of the universe (heat bath, pressure bath, etc). Different external conditions leading to thermodynamic equilibrium of a system give rise to different ensembles. Once microstates and ensembles are specified, macroscopic quantities can be obtained by taking appropriate statistical averages corresponding to a given ensemble.

2. Specification of macrostates and microstates:

Macrostate: The macroscopic state of a thermodynamic system at equilibrium is specified by the values of a set of measurable thermodynamic parameters. For example, the macrostate of a fluid system can be specified by pressure, temperature and volume, (P,V,T). For an isolated system for which there is no exchange of energy or mass with the surroundings, the macrostate is specified by the internal energy E, number of particles N and volume V; (E,N,V). In case of a closed system which exchanges only energy with the surroundings (and no particle) and is in thermodynamic equilibrium with a heat bath at temperature T, the macrostate is given by (N,V,T). For an open system, exchange of both energy and particle with the surroundings can take place. For such systems, at equilibrium with a heat bath at temperature T and a pressure bath at pressure P (or a particle bath of chemical potential μ), the macrostate is specified by (N,P,T) (or (μ,V,T)).

The equilibrium of an isolated system corresponds to maximum entropy $S(E,N,V)$, for a closed system it corresponds to minimum Helmholtz free energy $F(N,V,T)$, and for an open system the equilibrium corresponds to minimum of Gibb's free energy $G(N,P,T)$ (or minimum of the grand potential $\Phi(\mu,V.T)$).

Microstate:A microstate of a system is obtained by specifying the states of all of its constituent elements. However, it depends on the nature of the constituent elements (or particles) of the system. Specification of microstates are made differently for classical and quantum particles.

Microstates of classical particles: In order to specify the microstates of a system of classical particles, one needs to specify the position q and the conjugate momentum p ofeach and every constituent particle of the system. In a classical system, the time evolution of q and p is governed by the classical Hamiltonian $\mathsf{H}(p,q)$ and Hamilton's equation of motion

$$\dot{q}_i = \frac{\partial \mathsf{H}(p,q)}{\partial p_i} \quad and \quad \dot{p}_i = -\frac{\partial \mathsf{H}(p,q)}{\partial q_i}; \quad i = 1,2,\cdots,3N$$

For a system of N particles in 3-dimension. The state of a single particle at any time is then given by the pair of conjugate variables (q_i, p_i), a point in the phase space. Each single particle then constitutes a 6-dimensional phase space (3-coordinate and 3-momentum). For N particles, the state of the system is then completely and uniquely defined by $3N$ canonical coordinates $q_1, q_2, \cdots, q_{3N}$ and $3N$ canonical momenta $p_1, p_2, \cdots, p_{3N}$. These $6N$ variables constitute a $6N$-dimensional Γ-space or phase space of the system and each point of the phase space represents a microstate of the system. The locus of all the points in Γ-space satisfying the condition $\mathsf{H}(p,q) = E$, total energy of the system, defines the energy surface.

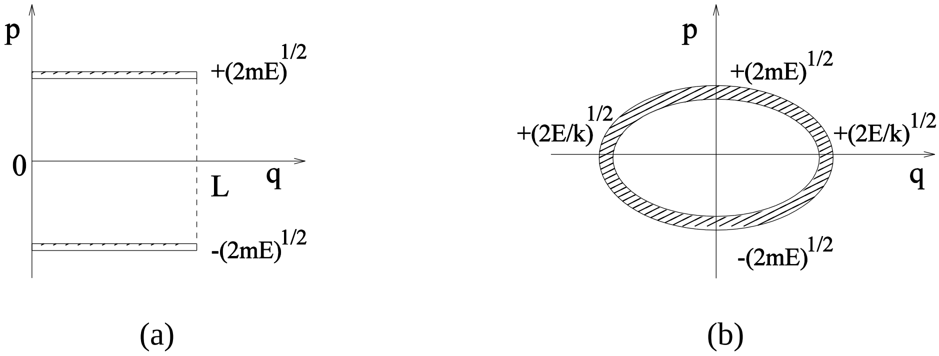


Figure 1.1: (a) Accessible region of phase space for a free particle of mass m and energy E in a one dimensional box of length L. (b) Region of phase space for a one dimensional harmonic oscillator with energy E, mass m and spring constant k.

Example: Consider a free particle of mass m inside a one dimensional box of length L, such that $0 \le q \le L$, with energy between E and $E+\delta E$. The macroscopic state of the system is defined by (E, N, L) with $N=1$. The microstates are specified in certain region of phase space. Since the energy of the particle is $E = p^2/2m$, the momentum will be $p = \pm\sqrt{2mE}$ and the position q is within 0 and L. However, there is a small width in energy δE, so the particles are confined in small strips of width $\delta p = \sqrt{m/2E}\delta E$ as shown in Fig.1.1 (a). Note that if $\delta E = 0$, the accessible region of phase space representing the system would be one dimensional in a two dimensional phase space. In order to avoid this artifact a small width in E is considered which does not affect the final results in the thermodynamic limit. In Fig.1.1 (b), the phase space region of a one dimensional harmonic oscillator with mass m, spring constant k and energy between E and $E+\delta E$ is shown. The Hamiltonian of the particle is: $\mathsf{H} = p^2/2m + kq^2/2$ and for a given energy E, the accessible region is an ellipse: $p^2/(2mE) + q^2/(2E/k) = 1$. With the energy between E and $E+\delta E$, the accessible region is an elliptical shell of area $2\pi\sqrt{m/k}\delta E$.

Microstates of quantum particles: For a quantum particle, the state is characterized by the wave function $\Psi(q_1, q_2, q_3, \cdots)$. Generally, the wave function is written in terms of a complete orthonormal basis of eigenfunctions of the Hamiltonian operator of the system. Thus, the wave function may be written as

$$\Psi = \sum_n c_n \phi_n, \quad \hat{\mathsf{H}}\phi_n = E_n \phi_n$$

where E_n is the eigenvalue corresponding to the state ϕ_n. The eigenstates ϕ_n, characterized by a set of quantum numbers n provides a way to count the microscopic states of the system.

Example: Consider a localized magnetic ion of spin $1/2$ and magnetic moment μ in thermal equilibrium at temperature T. The particle has two eigenstates, $(1,0)$ and $(0,1)$ associated with spin up $(\uparrow)$ and down spin $(\downarrow)$ respectively. In the presence of an external magnetic field $\vec{H}$, the energy is given by

$$E = -\vec{\mu}\cdot\vec{H} = \begin{cases} +\mu H, \textit{for spin}\downarrow \\ -\mu H, \textit{for spin}\uparrow \end{cases}$$

Thus, the system with macrostate (N, H, T) with $N=1$ has two microstates with energy $-\mu H$ and $+\mu H$ corresponding to up spin (parallel to $\vec{H}$) and down spin (antiparallel to $\vec{H}$). If there are two such magnetic ions in the system, it will have four microstates: $\uparrow\uparrow$ with energy $-2\mu H$, $\uparrow\downarrow$ & $\downarrow\uparrow$ with zero energy and $\downarrow\downarrow$ with energy $+2\mu H$. For a system of N spins of spin-$1/2$, there are total 2^N microstates and specification of the spin-states of all the N spins will give one possible microstate of the system.

Lecture-II

3. Statistical ensembles:

An ensemble is a collection of a large number of replicas (or mental copies) of the microstates of the system under the same macroscopic condition or having the same macrostate. However, the microstates of the members of an ensemble can be arbitrarily different. Thus, for a given macroscopic condition, a system of an ensemble is represented by a point in the phase space. The ensemble of a macroscopic system of given macrostate then corresponds to a large number of points in the phase space. During time evolution of a macroscopic system in a fixed macrostate, the microstate is supposed to pass through all these phase points.

Depending on the interaction of a system with the surroundings (or universe), a thermodynamic system is classified as isolated, closed or open system. Similarly, statistical ensembles are also classified into three different types. The classification of ensembles again depends on the type of interaction of the system with the surroundings which can either be by exchange of energy only or exchange of both energy and matter (particles or mass). In an isolated system, neither energy nor matter is exchanged and the corresponding ensemble is known as *microcanonical* ensemble. A closed system exchanging only energy (not matter) with its surroundings is described by *canonical* ensemble. Both energy and matter are exchanged between the system and the surroundings in an open system and the corresponding ensemble is called a *grand canonical* ensemble.

4. Statistical equilibrium:

Consider an isolated system with the macrostate (E, N, V). A point in the phase space corresponds to a microstate of such a system and its internal dynamics is described by the corresponding phase trajectory. The density of phase points $\rho(p,q)$ is the number of microstates per unit volume of the phase space and it is the probability to find a state around a phase point (p,q).

By Liouville's theorem, in the absence of any source and sink in the phase space, the total time derivative in the time evolution of the phase point density $\rho(p,q)$ is given by

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{\rho, \mathrm{H}\} = 0$$

where

$$\{\rho, \mathrm{H}\} = \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial \mathrm{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial \mathrm{H}}{\partial q_i} \right)$$

is the Poisson bracket of the density function ρ and the Hamiltonian H of the system.

The ensemble is considered to be in statistical equilibrium if $\rho(p,q)$ has no explicit dependence on time at all points in the phase space, *i.e.*,

$$\frac{\partial\rho}{\partial t} = 0.$$

Under the condition of equilibrium, therefore, $\{\rho, H\} = 0$. It will be satisfied if ρ is an explicit function of the Hamiltonian $\mathsf{H}(q,p)$ or ρ is a constant, independent of p and q. That is

$$\rho(p,q) = constant.$$

The condition of statistical equilibrium then requires no explicit time dependence of the phase point density $\rho(p,q)$ as well as uniform distribution of $\rho(p,q)$ over the relevant region of phase space. The value of $\rho(p,q)$ will, of course, be zero outside the relevant region of phase space. Physically the choice corresponds to an ensemble of systems which at all times are uniformly distributed over all possible microstates and the resulting ensemble is referred to as the microcanonical ensemble. However, in canonical ensemble it can be shown that $\rho(q,p) \propto \exp[-\mathsf{H}(q,p)/k_B T]$.

5. Postulates of statistical mechanics

The principles of statistical mechanics and their applications are based on the following two postulates.

Equal a priori probability: For a given macrostate (E,N,V), specified by the number of particles N in the system of volume V and at energy E, there is usually 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 the fixed energy ensemble, the density $\rho(q,p)$ of the representative points in the phase space corresponding to these microstates is constant or the phase points are uniformly distributed. Thus, any member of the ensemble is equally likely to be in any of the various possible microstates. In case of a quantum system, the various different microstates are identified as the independent solutions $\Psi(r_1, r_2, \cdots, r_N)$ of the Schrödinger equation of the system, corresponding to an eigenvalue E. 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.

Principle of ergodicity: The microstates of a macroscopic system are specified by a set of points in the $6N$-dimensional phase space. 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, say (E,N,V) as for an isolated system. With time, the system passes from one microstate to another. After a sufficiently long time, the system passes through all its possible microstates. In the language of statistical mechanics, the system is considered to be in equilibrium if it samples all the microstates with equal a priori probability. The equilibrium value of the observable X can be obtained by the statistical or ensemble average

$$\langle X \rangle = \frac{\iint X(p,q)\rho(p,q)d^{3N}q d^{3N}p}{\int \rho(p,q)d^{3N}q d^{3N}p}.$$

On the other hand, the mean value of an observable (or a property) is given by its time-averaged value:

$$\overline{X} = \lim_{T\to\infty}\frac{1}{T}\int_0^T X(t)dt.$$

The ergodicity principle suggests that statistical average $\langle X \rangle$ and the mean value $\overline{X}$ are equivalent: $\overline{X} \equiv \langle X \rangle$.

Lecture-III

6. Thermodynamics in different ensembles:

6.1 Microcanonical ensemble (E,N,V): In this ensemble, the macrostate is defined by the total energy E, the number of particles N and the volume V. However, for calculation purpose, a small range of energy E to $E+\delta E$ (with $\delta E \to 0$) is considered instead of a sharply defined energy value E. The systems of the ensemble may be in any one of a large number of microstates between E and $E+\delta E$. In the phase space, the representative points will lie within a hypershell defined by the condition

$$E \le \mathrm{H}(p,q) \le E+\delta E.$$

At statistical equilibrium, all representative points are uniformly distributed and $\rho(q,p) = constant$ between E and $E+\delta E$ otherwise zero. As per equal a priori probability, any accessible state is equally probable and the number of accessible microstates Ω is proportional to the phase space volume enclosed within the hypershell and it is given by

$$\Omega(E,N,V) = \frac{1}{h^{3N}} \int_E^{E+\delta E} d^{3N}q\, d^{3N}p$$

for a system of N particles and of total energy E. If the particles are indistinguishable, the number of microstates Ω should be divided by $N!$ as the Gibb's correction. However, if the energy states are discrete, the particles are distributed among the different energy levels as, n_i particles in the energy level ε_i and satisfies the following conditions

$$N = \sum_i n_i \quad and \quad E = \sum_i n_i \varepsilon_i,$$

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

$$\Omega = \frac{N!}{n_1! n_2! \cdots}.$$

The thermodynamic properties can be obtained by associating entropy S of the system to the number of accessible microstates Ω. The statistical definition of entropy by Boltzmann is given by

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

where k_B is the Boltzmann constant, 1.38×10^{-23} JK^{-1}. In a natural process the equilibrium corresponds to maximum Ω or equivalently maximum entropy S as is stated in the second law of thermodynamics. It is to be noted that, as $T \to 0$, the system is going to be in its ground state and the value of Ω is going to be 1. Consequently, the entropy $S \to 0$ which is the third law of thermodynamics. If a thermodynamic potential like entropy S is known in terms of the number of microstates, the thermodynamic properties of the system can be obtained by taking suitable derivative of S with respect to the relevant parametersas given below.

Fluid System:

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

Temperature

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

Pressure

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

Chemical potential

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

6.2 Canonical ensemble (N,V,T):

In the micro-canonical ensemble, a macrostate was defined by a fixed number of particles N, a fixed volume V and a fixed energy E. However, the total energy E of a system is generally not measured. Furthermore, it is difficult to keep the total energy fixed. Instead of energy E, temperature T is a better alternate parameter of the system which is directly measurable and controllable. Let us consider an ensemble whose macrostate is defined by N, V and T. Such an ensemble is known as *canonical* ensemble. In the canonical ensemble, the energy E can vary from zero to infinity. The set of microstates can be continuous as in most classical systems or it can be discrete like the eigenstates of a quantum mechanical Hamiltonian. Each microstate s is characterized by the energy E_s of that state. If the system is in thermal equilibrium with a heat-bath at temperature T, then the probability p_s that the system to be in the microstate s is $\propto e^{-E_s/k_BT}$, the Boltzmann factor. The **canonical partition function** Z is the sum of the Boltzmann factor over all possible microstates

$$Z(N,V,T) = \sum_s e^{-E_s/k_BT} = \sum_s e^{-\beta E_s}$$

where $\beta = 1/k_BT$ .The expectation (or average) value of a macroscopic quantity X is given by

$$\langle X \rangle = \frac{\sum_s X_s \exp(-\beta E_s)}{\sum_s \exp(-E_s/k_BT)} = \frac{1}{Z}\sum_s X_s e^{-E_s/k_BT}$$

where X_s is the property X measured in the microstate s.

In the classical limit, the consecutive energy levels are very close and can be considered as continuous. In this limit, the canonical partition function can be written as

$$Z(N,V,T) = \frac{1}{h^{3N} N!} \iint \exp\{-\beta \mathcal{H}(p,q)\} d^{3N} q\, d^{3N} p$$

($N!$ is for indistinguishable particles only) and the expectation value of X is given by

$$\langle X \rangle = \frac{1}{Z} \iint X(q,p) \exp\{-\beta \mathcal{H}(p,q)\} d^{3N} q\, d^{3N} p$$

Helmholtz free energy $F(N,V,T) = E - TS$ is the appropriate potential or free energy to describe the thermodynamic system when the system is in thermal equilibrium with a heat-bath at temperature T. It can be shown that the Helmholtz free energy $F(N,V,T)$ of the system is related to the logarithm of the partition function $Z(N,V,T)$ and it is given by

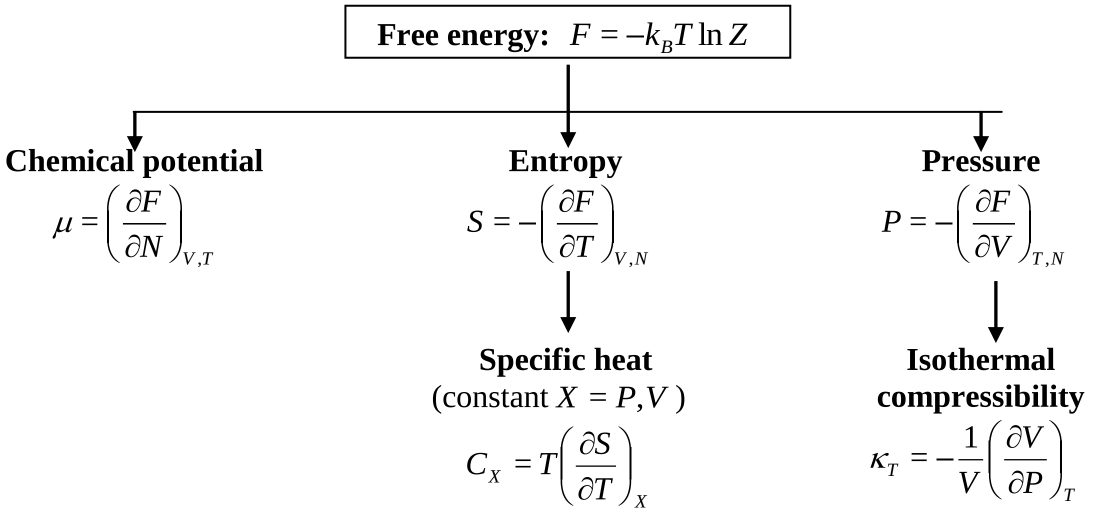
$$F(N,V,T) = -k_B T \ln Z(N,V,T).$$

Thermal equilibrium corresponds to the minimum free energy or maximum entropy at finite temperature. All equilibrium thermodynamic properties can be calculated by taking appropriate derivatives of the free energy $F(N,V,T)$ with respect to its parameters.

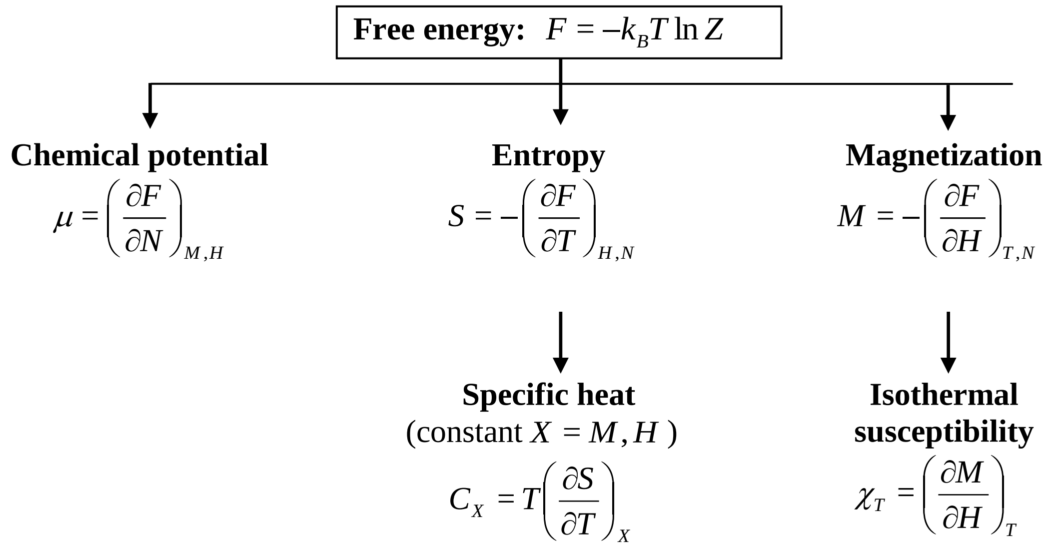
Note: For non-interacting system of N particles, the partition function Z can be written as $Z = Z_1^N$ where Z_1 is the partition function for a single particle. Consequently one obtains ideal gas behaviour for $N \to \infty$.

Thermodynamic quantities can be calculated by taking different derivatives of the free energy F as given below:

Fluid System:



Magnetic System:



5.3 Grand canonical ensemble (μ,V,T): Consider a system in contact with an energy reservoir as well as a particle reservoir and the system could exchange energy as well as particles (mass) with the reservoirs. Canonical ensemble theory has limitations in dealing these systems and needs generalization. It comes from the realization that not only the energy E but also the number of particles N of a physical system is difficult to measure directly. However, their average values, $\langle E \rangle$ and $\langle N \rangle$, are measurable quantities. The system interacting with both energy and particle reservoirs comes to equilibrium when a common temperature T and a common chemical potential μ with the reservoir is established. In this ensemble, each microstate (r, s) corresponds to energy E_s and number of particles N_r in that state. If the system is in thermodynamic equilibrium at temperature T and chemical potential μ, the**grand canonical partition function**is given by

$$Q = \sum_{r,s} \exp\left(\frac{\mu N_r}{k_B T} - \frac{E_s}{k_B T}\right) = \sum_{r,s} z^{N_r} e^{-E_s/k_B T}$$

where $z = e^{\mu/k_B T}$ is the fugacity of the system. In case of a system of continuous energy levels, the grand partition function can be written as

$$Q = \sum_{N=1}^{\infty} \frac{1}{h^{3N} N!} \iint \exp\left\{-\beta H(p,q) + \frac{\mu N}{k_B T}\right\} d^{3N}q d^{3N}p.$$

Note that division by $N!$ is only for indistinguishable particles.

The expectation value of a thermodynamic quantity $\langle X \rangle$ is given by

$$\langle X \rangle = \frac{\sum_{r,s} X_s \exp(-\alpha N_r - \beta E_s)}{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)}$$

The grand potential $\Phi(T,V,\mu) = E - TS - \mu N$ is the appropriate potential or free energy to describe the thermodynamic system in equilibrium with temperature T and chemical potential μ. It can be shown that

$$\Phi(\mu,V,T) = -k_B T \ln Q.$$

All equilibrium thermodynamic properties can now be calculated by taking appropriate derivatives of the grand potential $\Phi(T,V,\mu)$ with respect to its parameters as given below.

Fluid System:

Grand potential: $\Phi(\mu,V,T) = -k_B T \ln Q$

Entropy

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

Pressure

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

Number of Particles

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$$

In the table below, statistical quantities and the corresponding thermodynamic functions in cases of different ensembles are given. Thermodynamic quantities and response functions are different derivatives of these potential functions.

Ensemble	**Statistical quantity**	**Thermodynamic functions**
Microcanonical	Number of microstates: $\Omega(E,N,V)$	Entropy: $S = k_B \ln \Omega$
Canonical	Canonical partition function: $Z(N,V,T)$	Helmholtz free energy: $F = -k_B T \ln Z$
Grand Canonical	Grand partition function: $Q(\mu,V,T)$	Grand potential: $\Phi = -k_B T \ln Q$

Lecture-IV

11 Nature of Particles and Statistics:

Consider a gas of N non-interacting particles described by the Hamiltonian

$$\hat{\mathrm{H}}(q,p)=\sum_{i=1}^{N}\hat{\mathrm{H}}_i(q_i,p_i)$$

where (q_i,p_i) are the coordinate and momentum of the i th particle, $\hat{\mathrm{H}}_i$ is the Hamiltonian operator.A stationary system of N particles in a volume V then can be in any one of the quantum states determined by the solutions of the time independent Schödinger equation

$$\hat{\mathrm{H}}\psi_E(q)=E\psi_E(q)$$

where E is the eigenvalue of the Hamiltonian and ψ_E is the corresponding eigenfunction.

If there are n_i particles in an eigenstate ε_i, then the distribution should satisfy

$$\sum_i n_i=N \quad and \quad \sum_i n_i\varepsilon_i=E.$$

and the wave functions for N particles $\{a_1,a_2,\cdots,a_N\}$ with a_i particle in the n_i th state can be written as

(i) $$\psi(a_1,a_2,\cdots,a_N)=\prod_{i=1}^{N}\phi_{n_i}^{a_i} \qquad Product$$

(ii) $$\psi(a_1,a_2,\cdots,a_N)=\frac{1}{\sqrt{N!}}\sum\prod_{i=1}^{N}\phi_{n_i}^{a_i} \qquad Symmetric$$

(iii) $$\psi(a_1,a_2,\cdots,a_N)=\frac{1}{\sqrt{N!}}\begin{bmatrix}\phi_{n_1}^{a_1} & \phi_{n_1}^{a_2} & \cdots & \phi_{n_1}^{a_N}\\ \phi_{n_2}^{a_1} & \phi_{n_2}^{a_2} & \cdots & \phi_{n_2}^{a_N}\\ \vdots & \vdots & \ddots & \vdots\\ \phi_{n_N}^{a_1} & \phi_{n_N}^{a_2} & \cdots & \phi_{n_N}^{a_N}\end{bmatrix} \qquad Anti-symmetric$$

where ϕ_i is the eigenfunction of the single particle Hamiltonian $\hat{\mathrm{H}}_i$ with eigenvalue ε_i. Each single particle wave function ϕ_i is always a linear combination of a set of orthonormal basis functions $\{\varphi_j\}$, $\phi_i=\sum_j c_{ij}\varphi_j$. The particles described by these three wave functions obey different statistics. (i) The particles described by the product function correspond to different microstate by interchanging particles between states. These are then distinguishable particles and obey Maxwell-Boltzmann statistics. (ii) In the case of symmetric wave functions, interchanging of particles does not generate a new microstate. Thus, the particles are indistinguishable. Also, all the particles in a single state correspond to a non-vanishing wave function. That means accumulation of all the particles in a single state is possible. These particles obey Bose-Einstein statistics and are called **bosons**. (iii) For the anti-symmetric wave function, if the two particles are exchanged, the two columns of the determinant are exchanged and leads to the same wave function with a different sign. Thus, the particles are again indistinguishable. However, if any two particles are in one state then the corresponding rows of the determinant are the same and the wave function vanishes. This means that a state cannot be occupied by more than one particle. This is known as Pauli principle. These particles obey Fermi-Dirac statistics and they are called **fermions**.

Distribution functions: Consider an ideal gas of N identical particles. Let s represents the single particle state and S denotes the state of the whole system. Total energy E and the number of particles N are given by

$$E = \sum_s n_s \varepsilon_s \quad \text{and} \quad N = \sum_s n_s .$$

The distribution functions can be calculated by obtaining the appropriate partition function.

MB Statistics: In this case the particles are distinguishable. The canonical partition function is given by

$$\ln Z = N \ln\left(\sum_{s_i} e^{-\beta\varepsilon_{s_i}}\right).$$

The mean number of particles in state s is then given by

$$\langle n_s \rangle_{MB} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_s} = \frac{Ne^{-\beta\varepsilon_s}}{\sum_s e^{-\beta\varepsilon_s}}.$$

This is the Maxwell-Boltzmann (MB) distribution as already obtained classical statistical mechanics.

BE Statistics: The grand canonical partition function Z of N indistinguishable bosons is given by

$$\ln \mathrm{Z} = -\sum_s \ln\left(1 - e^{-\beta(\varepsilon_s - \mu)}\right).$$

The number of particles in a grand canonical ensemble is given by

$$N = \frac{1}{\beta}\frac{\partial \ln \mathrm{Z}}{\partial \mu} = -\frac{1}{\beta}\frac{\partial}{\partial \mu}\left\{\sum_s \ln\left(1 - e^{-\beta(\varepsilon_s - \mu)}\right)\right\} = \sum_s \langle n_s \rangle$$

Thus the average number of molecules in the s level is

$$\langle n_s \rangle_{BE} = -\frac{1}{\beta}\frac{\partial}{\partial \mu}\left\{\ln\left(1 - e^{-\beta(\varepsilon_s - \mu)}\right)\right\} = \frac{e^{-\beta(\varepsilon_s - \mu)}}{1 - e^{-\beta(\varepsilon_s - \mu)}} = \frac{1}{e^{\beta(\varepsilon_s - \mu)} - 1}.$$

This is Bose-Einstein (BE) distribution where always $\mu < \varepsilon_s$, otherwise $\langle n_s \rangle$ couldbe negative.

FD Statistics: The fermions have only two states, $n_s = 0$ or 1. Thus, the grand canonical partition function for N indistinguishable fermions is given by

$$\ln Z = \sum_s \ln\left(1 + e^{\beta(\mu - \varepsilon_s)}\right)$$

The number of particles is given by

$$N = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \mu} = \sum_s \frac{e^{-\beta(\varepsilon_s - \mu)}}{1 + e^{-\beta(\varepsilon_s - \mu)}} = \sum_s \langle n_s \rangle$$

Thus the average number of molecules in the s level is

$$\langle n_s \rangle_{FD} = \frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1}.$$

This is the Fermi-Dirac (FD) distribution.

However, in the classical limit $T \to \infty$ and $\rho \to 0,$ BE and FD statistics lead to the classical MB statistics.

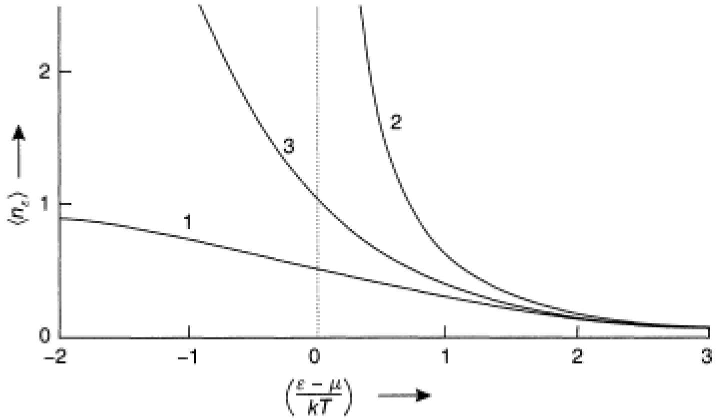


Fig. 1.2. plot of mean occupation number $\langle n_s \rangle$ of a single-particle energy state ϵ in a systemof non-interacting particles: curve 1 is for fermions, curve 2 for bosons and curve 3 forthe particles obeying Maxwell-Boltzmann statistics.

In the discussion of critical phenomena in the coming chapters we will mostly consider either fluid system or localized spins. Both of them are well described by classical distinguishable particles and thus will follow MB statistics.

Problems

Problem 1: Consider a monatomic ideal gas of N molecules confined in a volume V having total energy E in thermodynamic equilibrium. Calculate the number of microstates of the system considering

$$\Omega(E,N,V)=\frac{1}{h^{3N}}\int_E^{E+\delta E} d^{3N}q\,d^{3N}p \quad \text{and} \quad \Omega(E,N,V)=\frac{1}{h^{3N}N!}\int_E^{E+\delta E} d^{3N}q\,d^{3N}p.$$

Calculate the entropy S of the system as a function of (E,N,V) considering both the formulae and calculate the temperature of the system..

Problem 2: Consider a system with two compartments with an impenetrable partition. Both the compartments of equal volume V are filled with the same monatomic ideal gas of N molecules and total energy E each. The whole system is in thermodynamic equilibrium. Calculate the change in entropy ΔS after removing the partition once without dividing Ω by $N!$ and then dividing Ω by $N!$. Check that $\Delta S = 2Nk_B \ln 2$ in the first case and $\Delta S = 0$ in the second case. (Gibb's paradox is resolved only if the gas molecules are assumed to be indistinguishable).

Problem 3: Consider a system of N localized spin-1/2 magnetic ions of magnetic moment μ in an external magnetic field H having total energy E. Calculate the entropy of the system $S(E,N,H)=k_B \ln\Omega$ where $\Omega = N!/(N_1!N_2!)$ is total number of accessible states with N_1 up spins and N_2 down spins configurations. Check that

$$\frac{S}{Nk_B}=-\frac{N\mu H-E}{2N\mu H}\ln\left(\frac{N\mu H-E}{2N\mu H}\right)-\frac{N\mu H+E}{2N\mu H}\ln\left(\frac{N\mu H+E}{2N\mu H}\right).$$

Treating E to be continuous, plot S/Nk_B versus $E/N\mu H$. Show that this system can have negative absolute temperature for the positive energy region. Why negative absolute temperature is possible here but not for a gas in a box?

Problem 4: Consider a monatomic ideal gas of N particles enclosed in a volume V. The system is in thermodynamic equilibrium with a heat bath at temperature T. Calculate the canonical partition function Z, obtain internal energy E, Helmholtz free energy F and entropy S. Verify the equation of state $PV=Nk_BT$.

Problem 5: Consider N localized one dimensional classical Harmonic oscillators of frequency ω in thermal equilibrium at temperature T. Obtain the canonical partition function $Z=(\hbar\omega/k_BT)^{-N}$. Calculate the internal energy E of the system. Check that the energy obtained is satisfying the equipartition theorem, $k_BT/2$ thermal energy per square term in the Hamiltonian.

Problem 6: Consider N localized one dimensional quantum Harmonic oscillators of frequency ω in thermal equilibrium at temperature T. Obtain the canonical partition function $Z = [2\sinh(\hbar\omega/2k_B T)]^{-N}$. Show that the internal energy E of the system is given by

$$E = N\left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}\right].$$

(Note that E is not satisfying equipartition theorem.) Check that $E \approx Nk_B T$ as $T \to \infty$ and $E \approx N\hbar\omega/2$ as $T \to 0$ as expected.

Problem 7: Consider a system on N localized noninteracting paramagnetic ions of spin- ½ and magnetic moment μ in an external magnetic field H is in thermal equilibrium at temperature T. Obtain the canonical partition function Z. Calculate magnetization M and susceptibility χ. Check that at high temperature, χ is inversely proportional to T.

Problem 8: Consider a monatomic ideal gas of N particles enclosed in a volume V. The system is in thermodynamic equilibrium with a heat bath at temperature T and at constant chemical potential μ. Calculate the grand canonical partition function Q, obtain the grand potential $\Phi = -k_B T ln Q$. Verify the equation of state $PV=Nk_BT$.

Problem 9: Consider N localized one dimensional quantum Harmonic oscillators of frequency ω in thermodynamic equilibrium at temperature T and chemical potential μ. Obtain the grand canonical partition function $Q = [1 - e^{\mu/k_B T} / 2\sinh(\hbar\omega/2k_B T)]^{-1}$.

Problem 10: Consider a single component system of volume V, having two phases - solid and vapour, in equilibrium at temperature T. Treating the vapour as a monatomic ideal gas and the solid as quantum harmonic oscillator, show that a solid phase exists below a characteristic temperature T_c given by $f(T_c)/\phi(T_c) = N/V$ where N is the total number of particles in the system, $f(T) = [2\pi m k_B T/h^2]^{3/2}$ and $\phi(T) = [2\sinh(\hbar\omega/k_B T)]^{-1}$.

[These problems are usual text book problems and can be found as examples in the text books given in the references.]

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