Thermodynamics and Statistical Mechanics

A brief overview

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Contents

1 Thermodynamics **1**

Chapter 1

Thermodynamics

1.1 Introduction

Thermal behaviour of macroscopic matter is of great importance in science and technology. The study of thermal behaviour of matter started a chapter in Physics called *Thermodynamics* during nineteenth century. In the nineteenth century itself, it was first recognized that heat is a form of energy and could be converted into other forms of energy. Thermodynamics is mainly concerned with the conversion of heat into mechanical work and vice versa. The equivalence of heat and mechanical work was then established and the principle of the conservation of energy was proposed. Indeed, that was a great realization. But, it was not clear at that point of time what is the source of this heat energy. If matter is made up of atoms or molecules, then what they do at a given temperature? This particular question receives tremendous attention during the latter part of nineteenth century. The answer to this question leads to another subject in thermal physics called *Statistical Mechanics*. Thermodynamics deals with the basic laws governing heat whereas Statistical Mechanics explains the laws of thermodynamics in terms of kinetics of atoms or molecules in a macroscopic object. Eventually, it was found that all thermal phenomena are linked to disordered motions of atoms and molecules, the constituents of matter. Statistical Mechanics then could be considered as a microscopic theory of the phenomenological subject like Thermodynamics. This article will have two sections, Thermodynamics and Statistical Mechanics. In the first section, the principles or laws of thermodynamics will be discussed. The microscopic theory or the statistical mechanical derivation of these laws will be given in the section of Statistical Mechanics.

Thermodynamics deals with the thermal properties of matter in bulk by determining the relationship between different parameters of the system. In order to determine different relationships between the system parameters, the internal structure of matter is completely ignored in thermodynamics. Atoms in matter and their behaviour with temperature is not considered in this subject. Thermodynamics is purely based on principles formulated by generalizing experimental observations. There are basically four principles in this subject, namely (*i*) the temperature principle, (*ii*) the energy principle, (*iii*) the entropy principle, and (*iv*) the Nernst postulate. These four principles are also known as the zeroth law, first law, second law, and third law of thermodynamics. In the following, these principles will be described and they will be applied to physical problems in order to understand their validity and consequences.

1.2 Basic Concepts of Thermodynamics

Before describing thermodynamic principles and their consequences in different physical situations, few basic concepts necessary for the understanding of these principles are discussed here. These concepts involve the definition of a thermodynamic system and its environment, necessity of using specific thermodynamic parameters in order to describe a thermodynamic system, and most importantly the thermodynamic equilibrium.

1.2.1 Thermodynamic Systems:

Any macroscopic material body could be considered as a thermodynamic system. Macroscopic system means a system composed of atoms or molecules of the order of one Avogadro number ($N_A \approx 6.022 \times 10^{23}$) per mole. The examples of thermodynamic system could be a wire under tension, a liquid film, a gas in a cylinder, radiation, a solid material, magnetic material, dielectrics, and many others. The thermodynamic systems should have a boundary which separates the systems from the surroundings. Consider a drop of liquid as a thermodynamic system. The surface of the liquid is the boundary between the liquid and air. In the language of thermodynamics, the boundary is considered as a wall. This has been demonstrated in Figure 1.1. The nature of the wall classifies the thermodynamic system in different categories. (*i*) If the wall is such that **energy** or **matter** (atoms or molecules) cannot be exchanged between the system and its surroundings, then the system is called **isolated**. Total energy E, and total number of particles N are conserved for this system. (*ii*) The wall is such that only **energy** could be exchanged between the system and the surroundings. If the system is in thermal contact with a heat

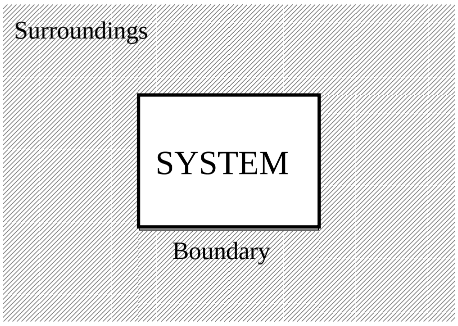


Figure 1.1: Schematic representation of a thermodynamic system. The shaded area is the surroundings or the universe. The thick line represents the boundary. The central white space is the system.

bath in the surroundings, heat energy will be exchanged however total number of particles will remain constant. This system is known as **closed** system. (*iii*) If the wall is porous, then, beside **energy**, **matter** (atoms or molecules) can also be exchanged between the system and the surroundings. If the system is in contact with a heat bath as well as with a particle reservoir, heat energy and number of particles both will be exchanged. Neither energy nor number of particles is conserved in this system. The system is called an **open** system.

1.2.2 Thermodynamic Parameters:

Thermodynamic parameters are measurable macroscopic physical quantities of a system. Consider a gas in a cylinder. Measurable physical quantities are the pressure (P), temperature (T) and the volume (V) of the gas. These physical quantities are called **thermodynamic parameters** or **thermodynamic variables**. The thermodynamic variables are *macroscopic* in nature. They are divided in two categories, *intensive* and *extensive* parameters. In thermodynamic equilibrium, the intensive parameter has the same value everywhere in the system. Pressure is an example of intensive parameter. It is same everywhere in the gas at equilibrium. On the other hand, the value of the extensive variable changes with the size of the system. For example, volume is an extensive parameter. Every intensive parameter has a corresponding independent extensive parameter. They form a conjugate pair of thermodynamic variables. Since they are independent of each other, one could be changed without effecting the other. Keeping the pressure constant the volume of the gas can be changed and vice versa. A partial list of conjugate thermodynamic parameters are given in Table 1.1. For each system, there always exists one more pair of conjugate intensive and extensive parameters. They are temperature (T)

System	Intensive parameter	Extensive parameter
Wire	Tension (τ)	Length (L)
Liquid film	Surface tension (γ)	Surface area (A)
Fluid	Pressure (P)	Volume (V)
Charged particles	Electric potential (ϕ)	Electric charge (q)
Magnetic material	External magnetic field ($\mathbf{B}$)	Total magnetization ($\mathbf{M}$)
Dielectrics	External electric field ($\mathbf{E}$)	Electric polarization ($\mathbf{P}$)

Table 1.1: A partial list of intensive and extensive conjugate variables for different thermodynamic systems.

and entropy (S). Temperature is the other intensive parameter and entropy is the corresponding conjugate extensive parameter.

1.2.3 Thermodynamic State:

Position and momentum coordinates are used to specify the state of a particle in mechanics. Similarly, the state of a thermodynamic system can be specified by the given values of a set of thermodynamic parameters. For example, the state of a fluid system can be specified by the pressure P, volume V, and temperature T and specified as (P, V, T). For an dielectric of polarization $\mathbf{P}$ at temperature T under an external electric field $\mathbf{E}$, the state is defined by $(\mathbf{E}, \mathbf{P}, T)$. For a magnetic system the state can be given by (M, B, T). For every thermodynamic systems there always exists three suitable thermodynamic parameters to specify the state of the system. It is important to notice that thermodynamic parameters are all *macroscopic* measurable quantities. On the other hand, *microscopic* quantities like position or momentum of the constituent particles are not used for specifying the state of a thermodynamic system.

1.2.4 Thermodynamic Equilibrium:

The equilibrium condition in mechanics is defined as: in absence of external forces, if a particle is slightly displaced from its stable equilibrium position it will come back to its original position after some time. Consider a thermodynamic system like gas in a cylinder. Suppose the gas is in a state defined by the given thermodynamic parameter values (P, V, T). The downward force (W) due to the weight of the piston is just balanced by the upward force exerted by the pressure (P) of the gas, and the system is in equilibrium. If the piston is slightly depressed and released, it will oscillate around the equilibrium position for some time and slowly come to rest at the original equilibrium position. It means that if a small external force is applied to the system and released, the system would come back to the thermodynamic state it was in originally, *i.e.*, the values of all the extensive and intensive parameters would recover. This definition is very similar to the definition of equilibrium given in mechanics and known as **mechanical equilibrium** of a thermodynamic system. Apart from mechanical equilibrium, the system should have thermal and chemical equilibrium as well to achieve thermodynamic equilibrium of a system.

Consider an isolated system with two partial systems. Initially each of them are in equilibrium at different temperatures. Temperature at all points of each system are the same. They are now taken into thermal contact, only exchange of heat and no exchange of matter, with each other. Heat would flow from the system of higher temperature to the system of lower temperature until uniform temperature is attained throughout the combined system. The system is then in **thermal equilibrium**. Experience shows, all systems which are in thermal equilibrium with a given system are also in thermal equilibrium with each other. This principle defines the temperature of a thermodynamic system and known as *zeroth law of thermodynamics*. Hence systems which are in thermal equilibrium with each other have a common intensive property, *i.e.*, temperature.

Suppose the system is a mixture of several different chemical components. When the composition of the system remain fixed and definite, the system is said to be in **chemical equilibrium**. Generally, chemical equilibrium takes a long time to achieve. Sometimes the system appears to be in chemical equilibrium, having fixed amount of components but the chemical reaction may continue with an extremely slow reaction rate.

The mechanical equilibrium therefore refers to uniformity of pressure, the thermal equilibrium refers to uniformity of temperature and the chemical equilibrium refers to the constancy of chemical composition. If there exist in the system gradients of macroscopic parameters such as pressure, temperature, density, etc such a state of the system is referred as a non-equilibrium state. A system which satisfies all possible equilibrium conditions is said to be in *thermodynamic equilibrium*. Thermodynamic equilibrium is thus correspond to the situation when the thermodynamic state does not change with time.

1.2.5 The Equation of State:

The equation of state is a functional relationship among the thermodynamic parameters for a given system in equilibrium. If X, Y and Z are the thermodynamic parameters for a system, the equation of state takes the form

$$\mathcal{F}(X, Y, Z) = 0.$$

The equation of state then defines a surface in the three dimensional $X - Y - Z$ space and any point lying on this surface represents an equilibrium state. The parameters (X, Y, Z) correspond to thermodynamic parameters of a given system. Such as, for a fluid system (X, Y, Z) correspond to pressure, volume and temperature (P, V, T), for a surface film (X, Y, Z) correspond to surface tension, surface area, and temperature (γ, A, T), for a magnetic material (X, Y, Z) correspond to magnetic field, magnetization and temperature (H, M, T), and so on. Since the parameters X, Y and Z are related by the equation of state, then all three parameters are not independent, only two of them are independent. If pressure P and volume V of a fluid system are given, the temperature of the fluid is automatically fixed by the equation of state $\mathcal{F}(P, V, T) = 0$ if the fluid is in thermodynamic equilibrium. The equation of state thus reduces the number of independent thermodynamic variables from three to two.

The gaseous system at high temperature and low pressure generally follow the Boyle's law. The equation of state of one mole of a gas is given by

$$PV = RT$$

where $R \approx 8.31$ J/mole.K is a universal constant. This is known as ideal gas equation and the gases which obey this equation are called ideal gas. For ideal paramagnet the equation of state is given by

$$\frac{M}{B} = \frac{C}{T}$$

where C a material dependent constant is known as Curie constant.

However, real gases like O_2, CO_2 etc., generally do not obey Boyle's law at all conditions and a different set of equation of state are proposed for real gases. Such as van der Waals' equation of state

$$(P + \frac{a}{V^2})(V - b) = RT$$

where a and b are specific constants for a particular gas.

1.2.6 Thermodynamic Transformations:

A *thermodynamic transformation* is a change of state. If one or more of the parameters of a system are changed, the state of the system changes. It is said that the system is undergoing a *transformation* or *process*. The transformation is generally from an initial equilibrium state to a final equilibrium state. Thermodynamic processes are classified into two groups (*i*) irreversible and (*ii*) reversible.

1.2.6.1 Irreversible Process:

The water from the slopes of the Himalayas flows down the Ganges into the Indian Ocean. The water in the Indian Ocean will never go back to the hill on itself even if the total energy loss during the down flow producing heat and sound energy is supplied back to the water at the Ocean. This means that the work done in the forward process is not equal to the work done in the backward process. Such natural flow of liquid downward is spontaneous and is irreversible. Almost all natural spontaneous processes are irreversible, just reversing the direction of the process it is not possible to get back the initial state. Consider free expansion of a gas. It does no work during the free expansion however to compress it back to the original volume a large amount of work has to be performed on the gas. A pendulum without a driving force will by itself cease to swing after some time, since its mechanical energy is transformed into heat by friction. The reverse process, that a pendulum starts swing by itself while the surroundings cool, has never been occurred. It is characteristic of irreversible processes that they proceed over non-equilibrium states dissipating energy in various forms during the transformation from one state to the other. Ferromagnets are magnetized by applying external magnetic field. If the external filed is reduced the magnetization curve does not follow the original path and forms a hysteresis loop because during magnetization the system dissipates energy in the form of heat and sound.

1.2.6.2 Reversible Process:

In a reversible process, the change of states occurs only over equilibrium intermediate states. That is to say, all steps between the final and initial states are in equilibrium during a reversible process. A reversible process is then an idealization. Because, if a system is in thermodynamic equilibrium, the parameters should not change with time. On the contrary, in order to change the state one needs to change the parameter values. However, a reversible process could be realized in a quasi static manner. In a quasi static process, infinitesimal change in the parameter values are made sufficiently slowly compared to the relaxation time of the system. Relaxation time is the time required for a system to pass from a non-equilibrium state to an equilibrium state. Thus, if the process rate is considerably less than the rate of relaxation, there will be enough time for the parameters to equalize over the entire system and the system could be considered at equilibrium. The process will represent a continuous succession of equilibrium states infinitely close to each other and could be considered as a reversible process, reversing the direction of the process one could reach to the initial state from the final state following the same path.

The reversible change could be performed under different conditions. Consider a thermally insulated system where no heat exchange is possible, any process under this condition is an *adiabatic process.* Reversible adiabatic process are also known as *iso-entropic* process. If a system undergoes a change keeping temperature constant, it is called an *isothermal process*, it is an *isochoric process* if volume kept constant and it is an *isobaric process* if pressure remains constant.

1.3 Exact and inexact differentials

Thermodynamic parameters are related through the state function or the equation of state

$$\mathcal{F}(X, Y, Z) = 0 \qquad \text{or} \qquad Z = f(X, Y).$$

It is characteristic of the state quantities and the state functions, that they depend only on the values of the state variables, but not on the way, the procedure by which these values are realized. If one changes the state variables (X, Y) by dX and dY amount from their initial values, keeping the other constant, in order to change the parameter Z infinitesimally, the change in Z can be expressed as

$$dZ = \left.\frac{\partial f(X,Y)}{\partial X}\right|_Y dX + \left.\frac{\partial f(X,Y)}{\partial Y}\right|_X dY$$

or more generally

$$dZ = df(\vec{x}) = \nabla f(\vec{x}) \cdot d\vec{x}$$

where $\vec{x} = (X, Y)$. If the state of the system is changed from $\vec{x}_0$ to $\vec{x}$ along a path C then

$$f(\vec{x}) - f(\vec{x}_0) = \int_C \nabla f(\vec{x}) \cdot d\vec{x} = \int_C \vec{F}(\vec{x}) \cdot d\vec{x}$$

where $\vec{F}(\vec{x}) = \nabla f(\vec{x})$ could be considered as a force. Thus a thermodynamic variable to be a state function or its elementary change to be an exact differential if there exists a potential $f(\vec{x})$ whose gradient correspond to a thermodynamic force. Since $\vec{F}(\vec{x}) = \nabla f(\vec{x})$, the necessary and sufficient condition that a given differential to be exact is then given by

$$\nabla \times \vec{F} = 0$$

or

$$\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} = 0, \qquad \frac{\partial F_x}{\partial z} - \frac{\partial F_z}{\partial x} = 0, \qquad \frac{\partial F_z}{\partial y} - \frac{\partial F_y}{\partial z} = 0$$

or

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}, \qquad \frac{\partial^2 f}{\partial z \partial x} = \frac{\partial^2 f}{\partial x \partial z}, \qquad \frac{\partial^2 f}{\partial y \partial z} = \frac{\partial^2 f}{\partial z \partial y}$$

This simply means that the interchange in sequence of differentiation has no effect. This is a property of a *totally differentiable* function.

1.4 Work, Heat and Internal Energy

1.4.1 Work:

Work appears during a change in state. The definition of work in thermodynamics is borrowed from mechanics and it is given by

$$\delta W = -\vec{F} \cdot \vec{d\ell}$$

where $\vec{F}$ is the force acting on the system during a small displacement $\vec{d\ell}$. The negative sign is a convention in thermodynamics and it is decided by the fact that: work done *by the system* is negative and work done *on the system* is positive. In mechanics, doing work the potential or kinetic energy of the system is changed. Similarly, work is equivalent to energy exchange in thermodynamics. Energy exchange is positive if it is added to a system and it is negative if it is subtracted from a system. Note that, only macroscopic work is considered here, and not on an atomic level.

Consider a gas enclosed in a cylinder at an equilibrium thermodynamic state (P, V, T). Assuming that there is no friction between the piston and the cylinder, the force acting *on the gas*, *i.e.*, the weight on the piston, is $F = PA$ where A is the cross sectional area of the piston. In order to compress the volume by an infinitesimal amount dV, the piston is pushed down by an infinitesimal amount $d\ell$. The corresponding work done is

$$\delta W = -\vec{F} \cdot \vec{d\ell} = PA d\ell = -PdV$$

since pressure is acting in a direction opposite to the displacement and $Ad\ell =$

$-dV$ during compression. The same definition is also valid for expansion. In case of expansion, the pressure will act in the same direction of the displacement and $Ad\ell = dV$.

Thus, work is the product of an intensive state quantity (pressure) and the change of an extensive state quantity (volume). One could easily verify that the same definition can be applied to the other thermodynamic systems. For example, in case of dielectrics and magnetic materials, in order to change the electric polarization $\mathbf{P}$ or magnetization $\mathbf{M}$ by a small amount $d\mathbf{P}$ or $d\mathbf{M}$ in presence of electric field $\mathbf{E}$ or magnetic field $\mathbf{H}$, the amount of work has to be performed on the systems are

$$\delta W = \mathbf{E} \cdot d\mathbf{P} \qquad \text{or} \qquad \delta W = \mathbf{B} \cdot d\mathbf{M}$$

where $\mathbf{E}$ and $\mathbf{B}$ are the intensive parameters and $\mathbf{P}$ and $\mathbf{M}$ are extensive parameters. In order to change the particle number by dN, one should add particles those have energy comparable to the mean energy of other particles otherwise equilibrium will be lost. Let us define

$$\delta W = \mu dN$$

as the work necessary to change the particle number by dN. The intensive field quantity μ is called the chemical potential and represents the resistance of the system against adding particles.

However, this definition is only valid for an infinitesimal displacement because the pressure changes during the change of volume. To calculate the total work done then one needs to know the equation of state $P = f(V, T)$ and the nature of the process. For a reversible process, the total work done can be obtained just by integrating δW from the initial to the final state

$$W = \int_1^2 \delta W = -\int_1^2 P(V,T)dV.$$

In a reversible cyclic path, the work done is then zero. Since the work depends on the process or the path of integration, it is then an inexact differential. Notice that, the above definition is only for reversible process. In an irreversible process (sudden expansion or compression of gas), the work needed to change the state is always larger than the work needed to change the state in a reversible way, $\delta W_{irr} \geq \delta W_{rev}$. In other words, for reversible process one requires the least work or the system produces *the most work*, while for a irreversible process a part of the work is always converted into heat which is radiated out of the system.

1.4.2 Heat:

Heat, another form of energy, is the measure of the temperature of a system. Let us define

$$\delta Q = CdT$$

where δQ is a small amount of heat which causes the increase in the temperature by dT of a system. The proportionality constant C is called the total heat capacity of the system. Though work and heat are just different form of energy transfer, the main difference between work and heat is that work is energy transfer via the *macroscopic* observable degrees of freedom of a system, whereas heat is the direct energy transfer between *microscopic*, *i.e.*, internal degrees of freedom. For example, consider gas in a thermally isolated cylinder with a piston. In order to compress the gas, work has to be performed on the gas by changing the macroscopic coordinate, the position of the piston. On the other hand, the warming up of the gas during the compression is due to the elastic collisions of the gas molecules with the moving piston. The energy gained in elastic collisions with the moving piston is shared between all other molecules by subsequent molecular collisions. Moreover, work can be easily transformed into heat but heat cannot be wholly converted into work. In order to convert heat into work one always needs a thermodynamic engine. Heat always flows from a hotter body to a colder body. Heat is an extensive quantity. Therefore, the total heat capacity C is also an extensive quantity, since temperature is an intensive parameter. However, the specific heat c defined as $c = C/m$ where m is the mass of the substance, is an intensive quantity. It is also possible to define the specific heat on a molar basis, $C = nc_{mol}$, with $n = N/N_A$ where N is the total number of particles and N_A is the Avogadro number. The quantity c_{mol} is the molar specific heat. The heat capacity may depend on the external conditions under which heat is transferred to the system. It matters whether a measurement is performed at constant pressure or at constant volume. The corresponding specific heats are

$$c_P = \frac{1}{m}\left(\frac{\delta Q}{dT}\right)_P, \qquad \text{and} \qquad c_V = \frac{1}{m}\left(\frac{\delta Q}{dT}\right)_V.$$

They are known as specific heat at constant pressure and specific heat at constant volume respectively.

1.4.3 Internal energy:

Let us consider the energy E of a given state of a macroscopic system. According to the laws of mechanics, the energy E is the sum of (i) the energy of the macroscopic mass motion of the system, and (ii) the internal energy of the system.

The energy of the mass motion consists of the kinetic energy of the motion of the center of mass of a system, plus the potential energy due to the presence of an external force field. In thermodynamics, we are interested in the internal properties of the system and not in their macroscopic mass motion. Usually the stationary systems are considered and the potential energy due to any external field becomes unimportant. Thus, energy in thermodynamics means the internal energy.

The internal energy of a system is the energy associated with its internal degrees of freedom. It is the kinetic energy of the molecular motion plus the potential energy of the molecular interaction. In an ideal gas, the internal energy is the sum of the translational kinetic energy of the gas molecules due to their random motion plus the rotational kinetic energy due to their rotations, etc. In a crystal, the internal energy consists of the kinetic and potential energy of the atoms vibrating about their equilibrium positions in the crystal lattice. Thus the internal energy is the energy associated with the random molecular motion of the atoms or molecules or the constituent particles of the system. However, in thermodynamics it is not our interest to calculate internal energy from microscopic interaction. Internal energy will be considered here as a thermodynamic potential.

1.5 The Laws of Thermodynamics

1.5.1 The first law:

The principle of conservation of energy is of fundamental importance in Physics. The first law is a law of conservation of energy in thermodynamics. The principle of conservation of energy is valid in all dimensions, *i.e.*, in macroscopic as well as in microscopic dimensions. Therefore, in thermodynamics one should consider conservation between work done (W) which may be performed by or on a system, heat exchange (Q) with the surroundings and the change in internal energy (E). Suppose there is an isolated system, no heat exchange, and some work ΔW is performed on the system. There is then an increase in the internal energy ΔE of the system. The conservation of energy demands

$$\Delta E = \Delta W.$$

Suppose instead of doing work on a system, an amount of heat ΔQ is exchanged with the surroundings which raises the internal energy by ΔE and one has

$$\Delta E = \Delta Q.$$

The first law says that the change in the internal energy ΔE for an arbitrary (*reversible or irreversible*) change of state is given by the sum of work done ΔW and heat exchange ΔQ with the surroundings. One thus writes

$$\text{First law:} \qquad \Delta E = \Delta W + \Delta Q.$$

The work done and the heat exchange with the surroundings in a small change in state depend on the way in which the procedure takes place. They are then not exact differentials. On the other hand, the change in internal energy is independent of the way the procedure takes place and depends only on the initial and final state of the system. The internal energy is therefore an exact differential. In order to distinguish the exact and inexact differentials in case of infinitesimal change of state, the following notations are used

$$dE = \delta W + \delta Q.$$

Since the internal energy E depends only on the macroscopic state of the system, it is then a state function. For a state function, the infinitesimal change dE is always a total differential. Since dE is a total differential and path independent, for a cyclic process where a system comes back to its initial state after passing through a series of changes of state, the equation

$$\oint dE = 0$$

is always true.

Now, one can write the differential form of the first law in different context:

Fluid system:	$dE = \delta Q - PdV$	**Strained wire:**	$dE = \delta Q + \tau dL$
Surface film:	$dE = \delta Q + \gamma dA$	**Magnetic materials:**	$dE = \delta Q + BdM$

The definitions of heat capacities can be rewritten in terms of energy now. Consider one mole of a fluid and the first law for the fluid can be written as

$$\delta Q = dE + PdV.$$

Since Q is not a state function, the heat capacity depends on the mode of heating the system and one has heat capacities at constant volume and constant pressure. The molar heat capacity at constant volume is then given by

$$C_V = \left(\frac{\delta Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V .$$

The energy is then a function V and T : $\quad E = E(V, T)$. The molar heat capacity at constant pressure then can be written as

$$C_P = \left(\frac{\delta Q}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P .$$

The energy E in this case is a function P and T : $\quad E = E(p, T)$. If the considered fluid is an **ideal gas** for which the specific heat is a constant, the volume occupied by the molecules and their mutual interactions are negligible, the internal energy E is function of temperature T only $E = E(T)$.

1.5.2 Carnot's process and entropy:

Consider one mole of monatomic ideal gas as working substance. In the Carnot process, the working substance is taken back to its original state through four successive reversible steps as illustrated in a $p\,V$ diagram in Figure 1.2.

Step 1. Isothermal expansion from volume V_1 to volume V_2 at constant temperature T_1. For the isotherm, $P_1V_1 = P_2V_2 = RT_1$ where R is the universal gas constant. Since $E = E(T)$ for ideal gas,

$$\Delta E_1 = \Delta W_1 + \Delta Q_1 = 0 \qquad \Longrightarrow \qquad \Delta Q_1 = -\Delta W_1 = RT_1 \ln\left(\frac{V_2}{V_1}\right).$$

Since $V_2 > V_1$, then $\Delta Q_1 > 0$, *i.e.*, the amount of heat ΔQ_1 is absorbed by the gas from the surroundings.

Step 2. Adiabatic expansion of the gas from V_2 to V_3. The temperature decreases from T_1 to T_2 ($T_1 > T_2$). The equation of state is $V_3/V_2 = (T_1/T_2)^{3/2}$. Since $\Delta Q = 0$,

$$\Delta E_2 = \Delta W_2 = C_V(T_2 - T_1).$$

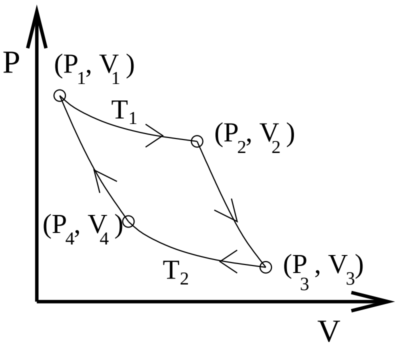


Figure 1.2: Carnot processes of an ideal gas represented on the PV diagram.

Step 3. Isothermal compression from V_3 to V_4 at temperature T_2. The equation of state is: $P_3V_3 = P_4V_4 = RT_2$. Again one has,

$$\Delta E_3 = \Delta W_3 + \Delta Q_2 = 0 \qquad \Longrightarrow \qquad \Delta Q_2 = -\Delta W_3 = -RT_2 \ln\left(\frac{V_3}{V_4}\right).$$

Since $V_3 > V_4$, $\Delta Q_2 < 0$, the amount of heat is released by the gas.

Step 4. Adiabatic compression from V_4 to V_1. Here temperature increases from T_2 to T_1 and the equation of state is $V_1/V_4 = (T_2/T_1)^{3/2}$. Since $\Delta Q = 0$,

$$\Delta E_4 = \Delta W_4 = C_V(T_1 - T_2) = -\Delta W_2.$$

The net change in internal energy $\Delta E = \Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 = 0$ as it is expected. Consider the amount of heat exchanged during the isothermal processes:

$$\Delta Q_1 = RT_1 \ln\left(\frac{V_2}{V_1}\right) \qquad \text{and} \qquad \Delta Q_2 = -RT_2 \ln\left(\frac{V_3}{V_4}\right).$$

During the adiabatic processes, one has combining the equation of states

$$V_3/V_2 = V_4/V_1 \qquad \Longrightarrow \qquad V_2/V_1 = V_3/V_4.$$

This implies that

$$\frac{\Delta Q_1}{T_1} + \frac{\Delta Q_2}{T_2} = 0.$$

If the Carnot's cycle is made of a large number of infinitesimal steps, the above equation modifies to

$$\oint \frac{\delta Q}{T} = 0.$$

This is not only true for Carnot's cycle but also true for any reversible cyclic process.

Suppose that the state of a thermodynamic system is changed from state 1 to state 2 along a path C_1 and the system is taken back to the initial state along another reversible path C_2, as shown in Figure 1.3. Thus, $1C_12C_21$ forms a closed reversible cycle and one has

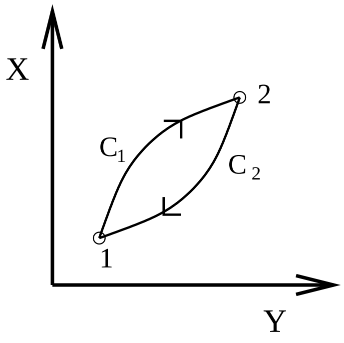


Figure 1.3: A reversible cyclic process on a XY diagram where X and Y form a conjugate pair of thermodynamic variables.

$$\oint_{1C_12C_21} \frac{\delta Q}{T} = 0 \qquad \text{or} \qquad \int_1^2 \left(\frac{\delta Q}{T}\right)_{C_1} + \int_2^1 \left(\frac{\delta Q}{T}\right)_{C_2} = 0$$

Since, the paths are reversible, one also has

$$\int_2^1 \left(\frac{\delta Q}{T}\right)_{C_2} = -\int_1^2 \left(\frac{\delta Q}{T}\right)_{C_2}$$

and therefore

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_{C_1} = \int_1^2 \left(\frac{\delta Q}{T}\right)_{C_2}$$

Thus the integral $\int \delta Q/T$ is path independent, *i.e.*, independent of the process of heating or cooling the system. The integral depends only on the initial and final states of the system and thus represents a state function whose total differential is $\delta Q/T$. Since heat is an extensive quantity, this state function, say S, is also extensive whose conjugate intensive parameter is temperature T. This extensive state function is the entropy S and defined as

$$dS = \frac{\delta Q}{T} \qquad \text{and} \qquad S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}.$$

Note that, only entropy difference could be measure, not the absolute entropy. The statistical mechanical definition of entropy will be given in the section of statistical mechanics.

1.5.3 The second law:

The first law of thermodynamics tells us about the conservation of energy in a thermodynamic process during its change of state. The second law tells us about the direction of a natural process in an isolated system. The entropy $S = \delta Q_{rev}/T$ is the amount of heat reversibly exchanged with the surroundings at temperature T. Since the amount of heat δQ_{irr} exchanged in an irreversible process is always less than that of δQ_{rev} exchanged in a reversible process, it is then always true that

$$\delta Q_{irr} < \delta Q_{rev} = TdS.$$

For an isolated system, $\delta Q_{rev} = 0$. Therefore, in an isolated system the entropy is constant in thermodynamic equilibrium and it has an extremum since $dS = 0$. It is found that in every situation this extremum is a maximum. All irreversible processes in isolated system which lead to equilibrium are then governed by an increase in entropy and the equilibrium will be reestablished only when the entropy will assume its maximum value. This is the second law of thermodynamics. Any change of state from one equilibrium state to another equilibrium state in an isolated system will occur naturally if it corresponds to an increase in entropy.

$$\textbf{Second law:} \qquad dS = 0, \qquad S = S_{max}$$

and for irreversible processes

$$dS > 0.$$

Note that, entropy could be negative if there is heat exchange with the surroundings *i.e.*, the system is not an isolated system. It is positive only for an isolated system.

The first law for reversible changes now can be rewritten in terms of entropy:

Fluid system:	$dE = TdS - PdV$	**Strained wire:**	$dE = TdS + \tau dL$
Surface film:	$dE = TdS + \gamma dA$	**Magnetic materials:**	$dE = TdS + HdM$

If there is exchange of energy of several different forms, the first law should take a form

$$dE = TdS - PdV + HdM + \mu dN + \cdots$$

1.5.4 The third law:

The third law of thermodynamics deals with the entropy of a system as the absolute temperature tends to zero. It is already seen that

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T},$$

and one can only measure the entropy difference between two states. The absolute value of entropy for a given thermodynamic states remains undetermined because of the arbitrary additive constant depending on the choice of the initial state. The third law enables us to determine the additive constant appearing in the definition of entropy. It states that: *the entropy of every system at absolute zero can always be taken equal to zero*,

$$\lim_{T\to 0} S = 0.$$

The zero temperature entropy is then independent of any other properties like volume or pressure of the system. It is generally believed that the ground state at $T = 0$ is a single non-degenerate state. It is therefore convenient to choose this non-degenerate state at $T = 0$ as the standard initial state in the definition of entropy and one could set the entropy of the standard state equal to zero. The entropy of any state A of the system is now defined, including the additive constant, by the integral

$$S(A) = \int_{T=0}^{A} \frac{\delta Q}{T}$$

where the integral is taken along a reversible transformation from $T = 0$ state (lower limit) to the state A. Since $dQ = C(T)dT$, the entropy of a system at temperature

T can also be given as

$$S = \int_0^T \frac{C_V(T)}{T} dT \qquad \text{or} \qquad S = \int_0^T \frac{C_P(T)}{T} dT$$

when the system is heated at constant volume or constant pressure. As a consequence of the third law $S(0) = 0$, the heat capacities C_V or C_P at $T = 0$ must be equal to zero otherwise the above integrals will diverge at the lower limit. Thus, one concludes

$$C_V \quad \text{or} \quad C_P \to 0 \qquad\qquad \text{as} \quad T \to 0.$$

The results are in agreement with the experiments on the specific heats of solid.

1.6 Thermodynamic Potentials and Maxwell relations

By the second law of thermodynamics, an isolated system during a spontaneous change reaches an equilibrium state characterized by maximum entropy:

$$dS = 0, \qquad S = S_{max}.$$

On the other hand, it is known from mechanics, electrodynamics and quantum mechanics that a system which is not isolated minimizes its energy. An interacting thermodynamic system always exchanges heat or perform work on the surroundings during a spontaneous change to minimize its internal energy. However, the entropy of the system plus the surroundings, which could be thought as a whole an isolated system, always increases. Thus, a non-isolated system at constant entropy always leads to a state of minimum energy.

1.6.1 Entropy as a thermodynamic potential:

Both entropy and the internal energy are state functions. If they are known as function of state variables of an isolated system then all other thermodynamic quantities are completely known. Consider the internal energy $E = E(S, V, N)$ then,

$$dE = TdS - PdV + \mu dN$$

and consequently the temperature and pressure are known as functions of other state variables

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

Similarly, consider the entropy $S = S(E, N, V)$, then

$$TdS = dE + PdV - \mu dN$$

and the temperature and pressure can be found as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \quad P = T\left(\frac{\partial S}{\partial V}\right)_{E,N}, \quad \mu = -T\left(\frac{\partial S}{\partial N}\right)_{E,V}.$$

The entropy and the internal energy then can be calculated as functions of the state variables form the equation of state. Since the equilibrium state of the system is given by a maximum of the entropy as a function of (E, V), it gives information about the most stable equilibrium state of the system as potential energy does in mechanics. As the difference in potential energy defines the direction of a natural process in mechanics, the entropy difference determines the direction of a spontaneous change in an isolated system. Thus, the entropy can be called as a thermodynamic potential.

1.6.2 Enthalpy as a thermodynamic potential:

The enthalpy of a system is defined as

$$H = E + PV$$

and in the differential form

$$dH = dE + PdV + VdP \quad \Longrightarrow \quad dH = TdS + VdP + \mu dN.$$

Knowing the enthalpy $H = H(S, P, N)$, the state variables can be calculated as

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N}, \quad V = \left(\frac{\partial H}{\partial P}\right)_{S,N}, \quad \mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}.$$

Consider an isolated system at constant pressure. Process at constant pressure are of special interest in chemistry since most of the chemical reactions occur under constant atmospheric pressure. In an isolated-isobaric system, $\delta Q = 0$ and P is constant, thus

$$dE + PdV = 0 \quad \Longrightarrow \quad d(E + PV) = 0 \quad \Longrightarrow \quad dH = 0.$$

In a spontaneous process of an adiabatic-isobaric system, the equilibrium corresponds to the minimum of the enthalpy

$$dH = 0, \qquad H(S, P) = H_{min}.$$

1.6.3 Helmholtz free energy as a thermodynamic potential:

The Helmholtz potential (free energy) is defined as

$$F = E - TS$$

and differentially,

$$dF = dE - SdT - TdS \quad \Longrightarrow \quad dF = -SdT - PdV + \mu dN$$

since $dE = TdS - PdV + \mu dN$. Thus, knowing $F = F(T, V, N)$, S, P and μ could be determined as

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad -P = \left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}.$$

The Helmholtz potential is useful in defining the equilibrium of a non-isolated system in contact with heat bath at constant temperature T. The system is interacting with the heat bath through heat exchange only. Consider an arbitrary isothermal transformation of this system from a state A to state B. By the second law , one have

$$\int_A^B \frac{dQ}{T} \leq S(B) - S(A).$$

Since T is constant,

$$\frac{\Delta Q}{T} \leq \Delta S$$

where ΔQ is the amount of heat absorbed during the transformation and $\Delta S = S(B) - S(A)$. Using the first law, the inequality could be written as

$$\Delta W \leq -\Delta E + T\Delta S \quad \Longrightarrow \quad \Delta W \leq -\Delta F$$

where ΔW is the work done by the system. Thus, the equilibrium of an isothermal system which does not perform work (mechanically isolated) always looks for a minimum of Helmholtz potential. Irreversible process happen spontaneously, until the minimum

$$dF = 0, \qquad F = F_{min}$$

is reached.

1.6.4 Gibbs free energy as a thermodynamic potential:

The Gibb's potential (free energy) is defined as

$$G = E - TS + PV = F + PV$$

or differentially

$$dG = -SdT + VdP + \mu dN$$

since $E = TS - PV + \mu N$ for a system attached with heat bath as well as with a bariostat. System exchanges heat and does some work due to volume expansion at constant pressure. The thermodynamic variables can be obtained in terms of $G(P, T, N)$ as

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,N}, \qquad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}, \qquad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}.$$

Notice that the chemical potential μ can be defined as Gibb's free energy per particle. Consider a system at constant pressure and temperature. For isothermal process,

$$\Delta W \leq -\Delta F$$

as it is already seen. If the pressure remain constant $\Delta W = P\Delta V$, then

$$P\Delta V + \Delta F \leq 0 \quad \Longrightarrow \quad \Delta G \leq 0.$$

Thus, a system kept at constant temperature and pressure, the Gibb's free energy never increases and the equilibrium state corresponds to minimum Gibb's potential. Irreversible spontaneous process in an isothermal isobaric system

$$dG = 0 \qquad G = G_{min}$$

are always achieved.

1.6.5 Grand potential as a thermodynamic potential:

The grand potential is defined as

$$\Phi = E - TS - \mu N = F - \mu N = -PV$$

since $E = TS - PV + \mu N$. The system attached with heat bath as well as with a particle reservoir. System exchanges heat with heat bath and exchanges particle with the particle reservoir. Differentially the grand potential can be expressed as

$$d\Phi = dE - TdS - SdT - \mu dN - Nd\mu = -SdT - PdV - Nd\mu$$

since $dE = TdS - PdV + \mu dN$. The thermodynamic variables are then obtained in terms of $\Phi(V, T, \mu)$ as

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

Consider an isothermal system at constant chemical potential. For an isothermal system

$$\Delta W \leq -\Delta F$$

and $\Delta W = -\mu \Delta N$ since μ is constant and the inequality leads to

$$\Delta F - \mu \Delta N \leq 0 \qquad \Longrightarrow \qquad \Delta \Phi \leq 0.$$

Thus, a system kept at constant temperature and chemical potential, the grand potential never increase and the equilibrium state corresponds to minimum grand potential. Irreversible spontaneous process in an isothermal system with constant chemical potential correspond to

$$d\Phi = 0 \qquad \Phi = \Phi_{min}.$$

1.6.6 Maxwell relations for a fluid system:

A number of relations between the thermodynamic state variables can be obtained since the thermodynamic potentials E, H, F and G (also Φ) are state functions and have exact differentials.

1. Form Internal Energy E:

$$dE = TdS - PdV = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV.$$

   Since

$$\frac{\partial}{\partial V}\left(\frac{\partial E}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial E}{\partial V}\right) \qquad \Longrightarrow \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

2. From enthalpy H:

$$dH = TdS + VdP \qquad \Longrightarrow \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

3. From Helmholtz potential F:

$$dF = -SdT - PdV \qquad \Longrightarrow \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

4. From Gibbs potential G:

$$dG = -SdT + VdP \qquad \Longrightarrow \qquad -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

1.7 Response functions for fluid systems

Definitions of the thermodynamic response functions will be given here.

1.7.1 Specific heats:

The specific heats C_V and C_P are measures of the heat absorption from a temperature stimulus. The definition of heat capacities are already given as follows:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

and

$$C_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P.$$

1.7.2 Compressibilities:

Compressibility κ is defined as

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right).$$

Isothermal and adiabatic compressibilities are then defined accordingly

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T,$$

and

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = -\frac{1}{V}\left(\frac{\partial^2 H}{\partial P^2}\right)_S.$$

1.7.3 Coefficient of volume expansion:

The change of volume generally is made under constant pressure for the solid system. The coefficient of volume expansion α_P is defined as the change in volume of a system for unit change in temperature at constant pressure per unit volume

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial^2 G}{\partial T \partial P}\right).$$

1.7.4 Relations among response functions:

The response functions are not all independent of one another. It can be shown that

$$C_P/C_V = \kappa_T/\kappa_S.$$

Two more useful relations among them are

$$\kappa_T(C_P - C_V) = TV\alpha^2 \quad \text{and} \quad C_P(\kappa_T - \kappa_S) = TV\alpha^2.$$

1.8 Thermodynamics of a magnetic system

In order to study magnetic properties of matter one requires the expression for the work of magnetizing a material. One needs to be careful in defining precisely the system and the processes in order to calculate magnetic work done. Let us assume that the effects of pressure and volume on a magnetic system is negligible. The thermodynamic parameters of a magnetic system are going to be the external magnetic induction B, total magnetization M and temperature T instead of P, V and T of a fluid system. The first law of thermodynamics: the differential change in internal energy E for a reversible change of state can be written in two different but equivalent forms as

$$dE = TdS - MdB \tag{1.1}$$

or

$$dE = TdS + BdM. \tag{1.2}$$

The difference between between Eq.1.1 and Eq.1.2 is that the later one includes the mutual filed energy but the first one does not. This particular issue is discussed in many texts such as Statistical Physics by F. Mandl, Elementary Statistical Physics by C. Kittle, and Introduction to Thermodynamics and thermostatics by H. B. Callen. The internal energy in Eq.1.1 includes the potential energy of the magnetic moments (spins) in the field and the lattice energy whereas in Eq.1.2 it includes mutual field energy along with the spin and lattice energies. It is worth looking at M. Barrett and A. Macdonald, Am. J. Phys. **67**, 613 (1999) and G. Castellano, J. Mag. Mag. Mat. **206**, 146 (2003).

We will be using the second form of the first law $dE = TdS + BdM$ and define other state functions and thermodynamic potentials such as enthalpy $H(N, S, B)$, the Helmholtz free energy $F(N, M, T)$ and the Gibbs free energy $G(N, B, T)$. The definitions of these thermodynamics state functions and differential change in a reversible change of state are given by

$$\begin{array}{lcl} H(N,S,B) = E - MB & \text{and} & dH = TdS - MdB \\ F(N,M,T) = E - TS & \text{and} & dF = -SdT + BdM \\ G(N,B,T) = E - TS - MB & \text{and} & dG = -SdT - MdB \end{array} \tag{1.3}$$

where explicit N dependence is also avoided. If one wants to take into account of number of particles there must be another term μdN in all differential forms of the state functions. It can be noticed that the thermodynamic relations of a magnetic system can be obtained from those in fluid system if V is replaced by $-M$ and P is replaced by B.

Note that if the other form of the first law $dE = TdS - MdB$ in Eq.1.1 is used it can be checked that the differential change in Helmholtz free energy would be given by $dF = -SdT - MdB$ same as Gibbs free energy given in Eq.1.3. The Helmholtz free energy becomes $F(B,T)$ function of B and T instead of $F(M,T)$ function of M and T. In many text books, $F(B,T)$ is used as free energy and the reader must take a note that in this situation a different definition of magnetic work and energy is used.

Now one can obtain all the thermodynamic parameters from the state functions defined in Eqs.1.2 and 1.3 by taking appropriate derivatives as given below

$$\begin{aligned}
T &= \left(\frac{\partial E}{\partial S}\right)_M \quad \text{or} \quad T = \left(\frac{\partial H}{\partial S}\right)_B, \\
S &= -\left(\frac{\partial F}{\partial T}\right)_M \quad \text{or} \quad S = -\left(\frac{\partial G}{\partial T}\right)_B, \\
B &= \left(\frac{\partial E}{\partial M}\right)_S \quad \text{or} \quad B = \left(\frac{\partial F}{\partial M}\right)_T, \\
M &= -\left(\frac{\partial H}{\partial B}\right)_S \quad \text{or} \quad M = -\left(\frac{\partial G}{\partial B}\right)_T.
\end{aligned} \tag{1.4}$$

1.8.1 Maxwell relations for a magnetic system:

A number of relations between the thermodynamic state variables can be obtained since the thermodynamic potentials E, H, F and G (also Φ) are state functions and have exact differentials.

1. Form Internal Energy E:

$$dE = TdS + BdM \qquad \Longrightarrow \qquad \left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial B}{\partial S}\right)_M$$

2. From enthalpy H:

$$dH = TdS - MdB \qquad \Longrightarrow \qquad \left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_B$$

3. From Helmholtz potential F:

$$dF = -SdT + BdM \qquad \Longrightarrow \qquad \left(\frac{\partial S}{\partial M}\right)_T = -\left(\frac{\partial B}{\partial T}\right)_M$$

4. From Gibbs potential G:

$$dG = -SdT - MdB \qquad \Longrightarrow \qquad \left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$$

1.9 Response functions for a magnetic system

Definitions of the thermodynamic response functions will be given here.

1.9.1 Specific heats:

The specific heats C_M and C_B are the measures of the heat absorption from a temperature stimulus at constant magnetization and constant external magnetic field respectively. The definition of heat capacities are :

$$C_M = T\left(\frac{\partial S}{\partial T}\right)_M = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_M$$

and

$$C_B = T\left(\frac{\partial S}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_B .$$

1.9.2 Susceptibilities:

In case of magnetic systems, instead of isothermal and adiabatic compressibilities one have the isothermal and the adiabatic magnetic susceptibilities

$$\chi_T = \left(\frac{\partial M}{\partial B}\right)_T = -\left(\frac{\partial^2 G}{\partial B^2}\right)_T ,$$

and

$$\chi_S = \left(\frac{\partial M}{\partial B}\right)_S = -\left(\frac{\partial^2 H}{\partial B^2}\right)_S$$

where M is the total magnetization and B is the external magnetic field. Note that the normalizing factor of $1/V$ is absent here.

1.9.3 Coefficient α_B:

The change of magnetization M with respect to temperature T under constant external magnetic field α_B, is defined as

$$\alpha_B = \left(\frac{\partial M}{\partial T}\right)_B = \left(\frac{\partial^2 G}{\partial T \partial B}\right) .$$

1.9.4 Relations among response functions:

The response functions are not all independent of one another. It can be shown that

$$C_B/C_M = \chi_T/\chi_S.$$

Two more useful relations among them are

$$\chi_T(C_B - C_M) = T\alpha_B^2 \quad \text{and} \quad C_B(\chi_T - \chi_S) = T\alpha_B^2.$$

1.10 Some applications

Let us apply the principles of thermodynamics developed from phenomenology only to few simple physical situations.

1.10.1 Heat capacities of materials:

The difference between heat capacities is given by

$$C_P - C_V = TV\alpha^2/\kappa_T$$

where $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ is the volume expansion coefficient and $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ is the isothermal compressibility. Using this relation, the difference between heat capacities of an ideal gas could be easily obtained. For one mole of an ideal gas, the equation of state is $PV = RT$ where R is the universal gas constant. Thus,

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\frac{R}{P} = \frac{1}{T}$$

and

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(-\frac{V}{P}\right) = \frac{1}{P}.$$

Therefore the difference in heat capacities is given by

$$C_P - C_V = TV\left(\frac{1}{T}\right)^2\frac{1}{1/P} = \frac{PV}{T} = R$$

is a well known equation.

As $T \to 0$, by third law of thermodynamics, the entropy $S \to S_0 = 0$ becomes independent of all parameters like pressure, volume and temperature. Therefore, in the limit $T \to 0$ the heat capacities also tend to zero,

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \to 0 \qquad \text{and} \qquad C_P = T\left(\frac{\partial S}{\partial T}\right)_P \to 0$$

This is because of the fact that as $T \to 0$, the system tends to settle down in its non-degenerate ground state. The mean energy of the system then become essentially equal to its ground state energy, and no further reduction of temperature can result in a further reduction of mean energy.

Not only the individual heat capacity goes to zero but also their difference goes to zero as $T \to 0$. Because, the volume expansion coefficient α also goes to zero

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \to 0.$$

However, the compressibility κ_T, a purely mechanical property, remains well-defined and finite as $T \to 0$. Thus,

$$\text{as} \quad T \to 0 \qquad\qquad C_P - C_V \to 0.$$

This is not in contradiction to the ideal gas result $C_P - C_V = R$ because as $T \to 0$, the system approaches its ground state and quantum mechanical effects become very important. Hence the classical ideal gas equation $PV = RT$ is no longer valid as $T \to 0$.

1.10.2 Gibbs paradox:

An isolated system with two parts of equal volume V each contains N number of molecules of the same monatomic perfect gas at the same temperature T, pressure P. Initially, the two parts were separated by a membrane and then the membrane was removed. The system is allowed to equilibrate. The change in entropy is given by

$$\Delta S = \int \frac{\delta Q}{T} = \frac{1}{T}\int \delta Q.$$

From first law, for a perfect gas $dE(T) = \delta Q + \delta W = 0$ and thus $\delta Q = -\delta W = PdV$. The volume changes from V to $2V$ for the each part. Therefore,

$$\Delta S = \frac{1}{T}\int PdV = Nk_B \int_V^{2V} \frac{dV}{V} + Nk_B \int_V^{2V} \frac{dV}{V} = 2Nk_B \ln 2 > 0.$$

The entropy of the system then may increase indefinitely by putting more and more membranes and removing them. However, the process is reversible. By putting back the membranes one would recover the initial state. According to Clausius theorem, the change in entropy must be $\Delta S = 0$ in a reversible process. This discrepancy is known as Gibb's paradox. The paradox would be resolved only by applying quantum statistical mechanics. The same problem will be discussed again in the next section again.

1.10.3 Radiation:

According to electromagnetic theory, the pressure P of an isotropic radiation field is equal to 1/3 of the energy density:

$$P = u(T)/3 = U(T)/3V$$

where V is the volume of the cavity, U is the total energy. Using the thermodynamic principles, one could obtain Stefan's law: $u = aT^4$, where a is a constant. By the second law $dU = TdS - PdV$, thus

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \qquad \Longrightarrow \qquad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

since $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ by Maxwell equation. Since $U = u(T)V$,

$$\left(\frac{\partial U}{\partial V}\right)_T = u(T) \qquad \text{and} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{3}\frac{du}{dT}.$$

Thus,

$$u(T) = \frac{T}{3}\frac{du}{dT} - \frac{1}{3}u \qquad \Longrightarrow \qquad T\frac{du}{dT} = 4u \qquad \Longrightarrow \qquad u = aT^4$$

where a is constant of integration.

1.10.4 Paramagnet:

For a paramagnetic system, if the temperature T is held constant and the magnetic field B is changed to $B + \Delta B$, the change in entropy is found as

$$\Delta S = -CB\Delta B/T^2$$

where C is a material dependent constant. The rate of change of S with the external field B at a fixed temperature is then given by

$$\left(\frac{\partial S}{\partial B}\right)_T = -\frac{CB}{T^2}.$$

Since the elementary Gibb's potential for a magnetic system is given by

$$dG = -SdT - MdB \qquad \Longrightarrow \qquad \left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$$

and one has

$$\left(\frac{\partial M}{\partial T}\right)_B = -\frac{CB}{T^2} \qquad \Longrightarrow \qquad M = \frac{CB}{T}.$$

This is the Cure law.

Thermodynamic principles are applied to different physical situations and useful relations among the thermodynamic parameters are obtained. However, no microscopic understanding has been achieved. Although motion of atom or molecules are completely ignored in these calculations, a rich mathematical structure has come out from the phenomenology. The microscopic theory will be developed in the next section, Statistical Mechanics, and will be applied to the similar problems in order to understand the same problems from the atomic or molecular point of view.

Problems:

1.1 Experimentally one finds that for a rubber band

$$\left(\frac{\partial \tau}{\partial L}\right)_T = \frac{aT}{L_0}\left[1 + 2\left(\frac{L_0}{L}\right)^3\right]$$

$$\left(\frac{\partial \tau}{\partial T}\right)_L = \frac{aL}{L_0}\left[1 - \left(\frac{L_0}{L}\right)^3\right]$$

where τ is the tension, $a = 1.0 \times 10^3$ dyne/K, and $L_0 = 0.5$m is the length of the band when no tension is applied. The mass of the rubber band is held fixed.

(a) Compute $(\partial L/\partial T)_\tau$ and discuss its physical meaning.

(b) Find the equation of state and show that $d\tau$ is an exact differential.

(c) Assume that heat capacity at constant length is $C_L = 1.0$ J/K. Find the work necessary to stretch the band reversibly and adiabatically to a length 1 m. Assume that when no tension is applied, the temperature of the band is $T = 290$ K. What is the change in temperature?

1.2 For pure water in contact with air at normal pressure, the surface tension has a constant value γ_0 at all temperatures for which the water is a liquid. If certain surfactant molecules, such as pentadecylic acid, are added to the water, they remain on the free surface and alter the surface tension. For water of area A containing N surfactant molecules, it was found experimentally

$$\left(\frac{\partial \gamma}{\partial A}\right)_T = \frac{Nk_BT}{(A-b)^2} - \frac{2a}{A}\left(\frac{N}{A}\right)^2$$

$$\left(\frac{\partial T}{\partial \gamma}\right)_A = -\frac{A-b}{Nk_B}$$

where k_B is Boltzmann constant and a and b are constants. Find an expression for $\gamma(A,T)$ that reduces to the result for pure water when $N = 0$.

1.3 Blackbody radiation in a box of volume V and at temperature T has internal energy $U = aVT^4$ and pressure $P = (1/3)aT^4$, where a is the Stefan-Boltzmann constant.

(a) What is the fundamental equation for the blackbody radiation (the entropy)?

(b) Compute the chemical potential.

1.4 Two vessels, insulated from the outside world, one of volume V_1 and the other of volume V_2 , contain equal numbers N of the same ideal gas. The gas in each vessel is originally at temperature T_i. The vessels are then connected and allowed to reach equilibrium in such a way that the combined vessel is also insulated from the outside world. The final volume is $V = V_1+V_2$. What is the maximum work, δW_{free}, that can be obtained by connecting these insulated vessels? Express your answer in terms of T_i, V_1, V_2, and N.

1.5 Compute the Helmholtz free energy F for a van der Waals gas. The equation of state is

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

where a and b are constants which depend on the type of gas and n is the number of moles. Assume that heat capacity is $C_{V,n} = (3/2)nR$.

1.6 Compute the entropy S, enthalpy H, Helmholtz free energy F, and Gibbs free energy G for a paramagnetic substance and write them explicitly in terms of their natural variables if possible. Assume that mechanical equation of state is $m = (C/T)B$ and the molar heat capacity at constant magnetization c_m is a constant, where m is the molar magnetization, B is the magnetic field, C is a constant, and T is the temperature.

1.7 Compute the molar heat capacity c_P , the compressibilities, κ_T and κ_S , and the thermal expansivity α_P of a monoatomic van der Waals gas. Start from the fact that the mechanical equation of state is

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

and the molar heat capacity is $c_v = 3R/2$, where $v = V/n$ is the molar volume.

1.8 Compute the heat capacity at constant magnetic field $C_{B,n}$, the susceptibilities $\chi_{T,n}$ and $\chi_{S,n}$, and the thermal expansivity $\alpha_{B,n}$ for a magnetic system, given that the mechanical equation of state is

$$M = \frac{nCB}{T}$$

and the heat capacity $C_{M,n} = nc$, where M is the magnetization, B is the magnetic field, n is the number of moles, c is the molar heat capacity, and T is the temperature.

1.9 Show that for a fluid system,

$$C_P - C_V = T\alpha_P^2/\kappa_T \quad \text{and} \quad C_P/C_V = \kappa_T/\kappa_S$$

where $\alpha_P = (1/V)(\partial V/\partial T)_P$.

1.10 Show that for a magnetic system,

$$C_B - C_M = T\alpha_B^2/\chi_T \quad \text{and} \quad \chi_T - \chi_S = T\alpha_B^2/C_B$$

where $\alpha_B = (\partial M/\partial T)_B$.

Chapter 2

Statistical Mechanics

2.1 Introduction

The properties of thermodynamic, *i.e.*, macroscopic systems are needed to be understood form microscopic point of view. Statistical mechanics will be used as a tool for this purpose. The basis of the subject is laid on the dynamical behaviour of the *microscopic* constituents, *i.e.*, atoms or molecules of the system. Theory of statistical mechanics is thus made up of mathematical statistics and classical Hamiltonian dynamics or quantum mechanics. The dynamics of a physical system can be represented by a set of quantum states and the thermodynamics of the system can be determined by the multiplicity of these states. On can write the equation of motion of any particle of these large systems quantum mechanically accurately but the complexity of the system containing many particles is enormous and it leads to the impossibility of having a solution. The difficulties involved is just not quantitative. The complexity of the interaction may give rise to unexpected qualitative features in the behaviour of a macroscopic system. The fundamental connection between the microscopic and the macroscopic description of a system is established by investigating the conditions of equilibrium between two physical systems in thermodynamic contact. One, in principle, could work in the frame work of quantum mechanics and develop a quantum statistical mechanical theory of the macroscopic properties. The classical results can then be obtained as a limiting situation. However, the subject of classical statistical mechanics and quantum statistical mechanics will be developed independently here and finally the connection will be made by taking the classical limit of the quantum results.

2.2 Basic Concepts of Statistical Mechanics

Consider a physical system composed of N identical particles confined in a volume V. For a macroscopic system, N is of the order of Avogadro number $N_A \approx 6.022 \times 10^{23}$ per mole. In this view, all the analysis in statistical mechanics are carried out in the so-called *thermodynamic limit.* It is defined as: both number of particles N and volume V of the system tends to infinity whereas the density of particles $\rho = N/V$ remains finite.

$$N \to \infty, \quad V \to \infty, \quad \rho = N/V = \mathsf{finite}.$$

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. The particle density becomes an important parameter for all physical properties of the system.

In order to develop a microscopic theory of a macroscopic system, it is necessary to specify the state of micro-particles, atoms or molecules as a first step. Next is to construct the macro-state from the micro-states of N number of particles when N is very large. Finally, one needs to extract the macroscopic properties in terms of the micro-states of a macroscopic system. In this section, all these essential definitions will be given.

2.2.1 Specification of states:

The specification of the state of a particle depends on the nature of the particle, *i.e.*, whether the particle's dynamics is described by classical mechanics or by quantum mechanics. The dynamics of a classical system is determined by its Hamiltonian $\mathcal{H}(p,q)$ where q and P are the generalized position and momentum conjugate variables. The motion of a particle is described by the canonical Hamilton's equation of motion

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

The state of a single particle at any time is then given by the pair of conjugate variables (q_i, p_i). The state of a system composed of N particles is then completely and uniquely defined by $3N$ canonical coordinates $q_1, q_2, \cdots, q_{3N}$ and $3N$ canonical momentum $p_1, p_2, \cdots, p_{3N}$. These $6N$ variables constitute a $6N$-dimensional Γ-space or phase space of the system and each point of the phase space represents a state of the system. Each single particle constitutes a 6-dimensional μ-space. Γ-space is evidently built up of N such 6-dimensional μ-space of each particle. The locus of all the points in Γ-space satisfying the condition $\mathcal{H}(p,q) = E$, total energy of the system, defines a surface called energy surface. Specification of states of quantum particles will be discussed later.

2.2.2 Enumeration of microstates:

It is important to enumerate the number of microstates for a given macrostate (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

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

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.

2.2.3 Equal a priori probability:

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 $\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$ 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.

2.2.4 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. As time passes, every member of the ensemble undergoes a continuous change in microstates and accordingly the system moves from one place to another on the phase space describing a phase trajectory. The density of the cloud of phase points at a particular place then may vary with time or at a given time the density may vary place to place. It must be emphasized here that the systems of an ensemble are independent systems, that is, there is no interaction between them and hence the trajectories do not intersect.

2.2.5 Phase point density:

Since a phase point corresponds to a microstate of a system and its dynamics is described by the phase trajectory, the density of phase points $\rho(p, q)$ is then determining the number of microstates per unit volume, that is, the probability to find a state around a phase point (p, q). The phase point density $\rho(p, q)$ is given by

$$\rho(p, q) = \frac{\textsf{Number of states}}{\textsf{Volume element}}.$$

At any time t, the number of representative points in the volume element $d^{3N}qd^{3N}p$ around the point (p, q) of the phase space is then given by

$$\rho(p, q)d^{3N}qd^{3N}p.$$

The density function $\rho(p, q)$ then represents the manner in which the members of the ensemble are distributed over all possible microstate at different instant of time.

2.2.6 Statistical average and mean values:

Consider any physical property of the system $X(p, q)$, which may be different in different microstates for a system. The macroscopic value of X must be the average of it over all possible microstates corresponding to a given macrostate. The ensemble average or the statistical average $\langle X \rangle$ of the physical quantity X at a given instant of time, is defined as

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

where $\rho(p,q)$ is the density of phase points. Note that the integration is over the whole phase space. However, it is only the populated region of phase space that really contribute.

The mean value $\bar{X}$ of the physical quantity X depends how it evolves with time t. In a sufficiently long time, the phase trajectory passes through all possible phase points. If the duration of time is T, the mean value is defined as

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

The statistical average $\langle X \rangle$ and the mean value $\bar{X}$ are equivalent. This is known as *ergodic hypothesis.*

2.2.7 Condition of Equilibrium:

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

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

where

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

is known as Poisson bracket of the density function ρ and the Hamiltonian $\mathcal{H}$ of the system. Thus, the cloud of phase points moves in the phase space like an incompressible fluid.

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,

$$\{\rho, \mathcal{H}\} = \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right) = 0$$

and it will be satisfied only if ρ is independent of P and q. That is

$$\rho(p,q) = \text{constant}$$

which means that the representative points are distributed uniformly over the phase space. The condition of statistical equilibrium then requires no explicit time dependence of the phase point density $\rho(p,q)$ as well as independent of the coordinates (p,q).

2.3 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.

The ensemble theory will be developed for each ensemble to calculate thermodynamic properties of a given system.

2.3.1 The microcanonical ensemble:

In this ensemble, the macrostate is defined by the number molecules N, the volume V and the energy E. However, for calculation purpose, a small range of energy E to $E+\delta E$ (with $\delta E \to 0$) variation 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 with in a hypershell defined by the condition

$$E \leq \mathcal{H}(p,q) \leq E + \delta E.$$

The phase space volume $\Omega(E,N,V)$ of the enclosed shell is given by

$$\Omega(E,N,V) = \int_{E}^{E+\delta E} d^{3N}q d^{3N}p.$$

In the microcanonical ensemble, the density function $\rho(q,p)$ is given by

$$\rho(q,p) = \begin{cases} \mathsf{C} \ \ \textsf{if} & E \leq E_x \leq E + \delta E \\ 0 & \textsf{otherwise} \end{cases}$$

where C is a constant and can be determined from the normalization condition $\int \rho(q,p) d^{3N}q d^{3N}p = 1$ between E and $E+\delta E$. The number of accessible microstates is then proportional to the phase space volume Ω enclosed within the shell.

2.3.1.1 Thermodynamics in Microcanonical Ensemble:

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 combined system E_0 is given by

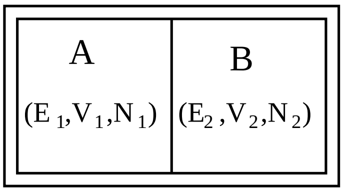


Figure 2.1: Two physical systems A and B are in thermal contact.

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

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

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

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

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

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 $T \to 0$, the system is going to be in its ground state and the value of Ω is going to be 1. Consequently, the entropy $S \to 0$, the third law of thermodynamics.

Example: The ideal gas

Consider an ideal gas of N molecules enclosed in a volume V at temperature T. The ideal gas law, $PV = Nk_BT$, now should be derivable from statistical mechanics. The Hamiltonian of the system is given by

$$\mathcal{H} = \frac{1}{2m}\sum_i^N p_i^2.$$

The number of accessible states Ω is given by the phase volume as

$$\Omega = \frac{1}{h^{3N}}\int d^3q_1\cdots d^3q_N d^3p_1\cdots d^3p_N.$$

The integration over q will give V^N. If $R = \sqrt{2mE}$, then

$$\Omega = \left(\frac{V}{h^3}\right)^N \Sigma_{3N}(R)$$

where $\Sigma_{3N}(R)$ is the volume of a sphere of radius R in $3N$ dimensional momentum space. It can be shown that

$$\Omega = \frac{\pi^{3N/2}}{((N/2)!)^3}\left(\frac{V}{h^3}\right)^N (2mE)^{3N/2}.$$

Using Stirling's formula, $\ln n! = n\ln n - n$, one could obtain the entropy as

$$S = k_B\ln\Omega = Nk_B\ln\left[V\left(\frac{4\pi mE}{3h^2N}\right)^{3/2}\right] + \frac{3}{2}Nk_B$$

or

$$E = \left(\frac{3h^2}{4\pi m}\right)\frac{N}{V^{2/3}}\exp\left(\frac{2}{3}\frac{S}{Nk_B} - 1\right).$$

The temperature and pressure of the system are obtained as

$$T = \left(\frac{\partial E}{\partial S}\right)_V = \frac{2}{3}\frac{E}{Nk_B}, \qquad P = -\left(\frac{\partial E}{\partial V}\right)_S = \frac{2}{3}\frac{E}{V}$$

Combining these two, one could easily verify that

$$PV = Nk_BT \quad \text{or} \quad PV = \frac{2}{3}E.$$

Gibbs paradox:

The entropy for ideal gas is given by

$$\begin{aligned} S &= Nk_B \ln\left[V\left(\frac{4\pi m E}{3h^2N}\right)^{3/2}\right] + \frac{3}{2}Nk_B \\ &= Nk_B \ln\left(VE^{3/2}\right) + NS_0, \qquad S_0 = \frac{3k_B}{2}\left(1 + \ln\frac{4\pi m}{3h^2}\right). \end{aligned}$$

Consider an ideal gas of same density ($\rho_1 = \rho_2$) in two chambers at a common temperature T. If the separation between the two chambers is now removed, the change in entropy ΔS will be

$$\Delta S = k_B\left(N_1 \ln\frac{V}{V_1} + N_2 \ln\frac{V}{V_2}\right) > 0$$

where $V = V_1 + V_2$ is the total volume of the system. For $N_1 = N_2$ and $V_1 = V_2$, the change in entropy is $\Delta S = 2Nk_B \ln 2$. However, the change in entropy ΔS should be zero in this situation because the process is reversible. Thus, the Gibb's paradox is not yet resolved even after calculating the entropy from statistical mechanics.

Let us calculate the number of accessible states by

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

where $N!$ in the denominator takes care of the indistinguishability of the gas molecules. Correspondingly, the value of entropy will be now

$$\begin{aligned} S &= Nk_B \ln\left(VE^{3/2}\right) + NS_0 - Nk_B \ln N + Nk_B \\ &= Nk_B \ln\left(\frac{V}{N}E^{3/2}\right) + \text{Constant}. \end{aligned}$$

Since, V/N and E both remains unchanged in this process, the change in entropy will be

$$\Delta S = 0.$$

Gibb's paradox is then resolved. The origin of Gibb's paradox is associated with the indistinguishable property of the particles which is a property of quantum particles.

2.3.2 The canonical ensemble:

In a micro-canonical ensemble, a microstate 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 observable and controllable. Let us consider an ensemble whose microstate 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. One then needs to find out the probability P_r that a system in the ensemble is in one of the states characterized by E_r.

Consider a system A in contact with a large heat reservoir B at temperature T as shown in Fig.2.2. At equilibrium, the system will have the same temperature T of the reservoir. However, the energy could lie between 0 and E_0, the total energy of the system and the reservoir. The total energy E_0 is then given by

$$E_r + E_r' = E_0 = \text{constant}, \qquad \text{and} \qquad \frac{E_r}{E_0} \ll 1.$$

For a given state r of the system A, the reservoir B can still be in any one of the large number of states $\Omega'(E_r')$ compatible with the energy value E_r'. If the number of states available to the reservoir is large, the probability of the reservoir in the state E_r' is also going to be large and correspondingly the probability to find the system in E_r. Since all the states are equally likely to occur, the probability P_r that a system in a state r is directly proportional to $\Omega'(E_r')$

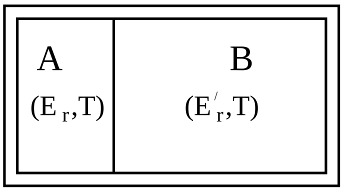


Figure 2.2: A given system A immersed in a heat reservoir B in equilibrium.

$$P_r \propto \Omega'(E_r') = \Omega'(E_0 - E_r)$$

or

$$P_r = C\Omega'(E_0 - E_r) \qquad \Longrightarrow \qquad \ln P_r = \ln C + \ln \Omega'(E_0 - E_r).$$

Since $E_r/E_0 \ll 1$, $\ln\Omega'(E_0-E_r)$ can be expanded in a Taylor series around $E_r = E_0$. Thus,

$$\begin{aligned}\ln\Omega'(E_0-E_r) &= \ln\Omega'(E_0) + \left(\frac{\partial \ln\Omega'}{\partial E'}\right)_{E'=E_0}(E'_r - E_0) + \cdots \\ &\approx \text{constant} - \beta' E_r.\end{aligned}$$

where $\beta = \partial\ln\Omega/\partial E$, and in equilibrium $\beta' = \beta$. The probability P_r is then given by

$$P_r \propto \exp(-\beta E_r)$$

by normalizing

$$P_r = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}, \quad \text{since} \quad \sum_r P_r = 1$$

where the sum is over all possible states of the system A. The numerator $\exp(-\beta E_r)$ is called the Boltzmann factor and the denominator $Z = \sum_r \exp(-\beta E_r)$ is called the canonical partition function.

The partition function or sum over states Z is a function of temperature T naturally. It also depends on the number of particle N and volume V through the energy E. In most physical systems, the energy levels are degenerate, *i.e.*, a group of states g_r in number have the same energy E_r. In these situations, the canonical probability distribution and the partition function are given by

$$P_r = \frac{g_r \exp(-\beta E_r)}{\sum_r g_r \exp(-\beta E_r)}, \quad \text{and} \quad Z(N,V,T) = \sum_r g_r \exp(-\beta E_r).$$

In the thermodynamic limit $N \to \infty$ and $V \to \infty$, the consecutive energy levels are very close. In a small width of energy E to $E + dE$, there lies a large number of states and the energy E can be considered as continuous. In these cases, the probability to find a state between E and $E + dE$ is then given by

$$P(E)dE = \frac{\exp(-\beta E) g(E) dE}{\int_0^\infty \exp(-\beta E) g(E) dE}$$

and the corresponding partition function is given by

$$Z = \int_0^\infty \exp(-\beta E) g(E) dE.$$

2.3.2.1 Thermodynamics in Canonical Ensemble:

Consider the canonical distribution function P_r for a system of non-degenerate discrete energy levels

$$P_r = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}.$$

The average of a physical quantity X is then

$$\langle X \rangle = \sum_r X_r P_r = \frac{\sum_r X_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}.$$

According to the above definition, the mean energy of the system $\langle E \rangle$ is given by

$$\langle E \rangle = E = \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} = -\frac{\partial}{\partial \beta} \ln\{\sum_r e^{-\beta E_r}\} = -\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}.$$

From thermodynamics one knows that

$$E = F + TS \qquad \text{and} \qquad S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}.$$

Rewriting E in terms of F one has

$$E = F - T\left(\frac{\partial F}{\partial T}\right)_{N,V} = -T^2\left[\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right]_{N,V} = \frac{\partial(F/T)}{\partial(1/T)} = \frac{\partial(F/k_BT)}{\partial(1/k_BT)}.$$

Comparing the thermodynamic and statistical definitions of the mean energy one finds

$$F = -k_BT \ln Z \qquad \text{and} \qquad \beta = \frac{1}{k_BT}.$$

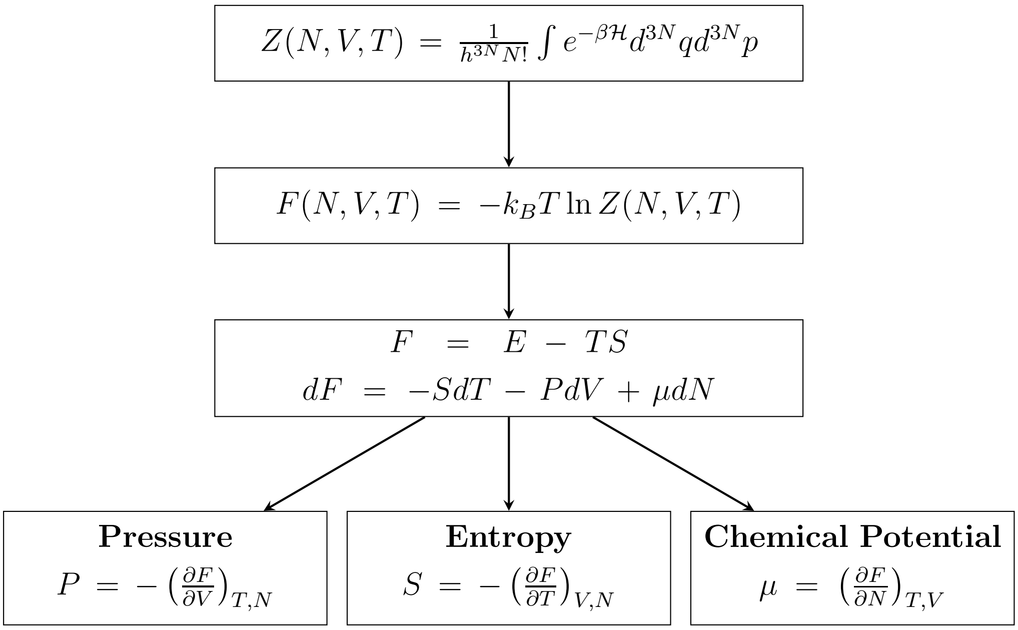
In the case of a thermodynamic system in equilibrium with a heat reservoir, all thermodynamic quantities are different derivatives of the Helmholtz free energy F. Thus, knowing partition function as well as F from statistical mechanics, one could in principle calculate all thermodynamic quantities statistical mechanically. For example: entropy S is given by

$$\begin{aligned} S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} &= \frac{\partial}{\partial T}(k_BT \ln Z) = k_B \ln Z + k_BT\frac{\partial \ln Z}{\partial T} \\ &= k_B \ln Z + \frac{1}{T}\left(-\frac{\partial \ln Z}{\partial \beta}\right) = k_B(\ln Z + \beta E). \end{aligned}$$

The pressure and chemical potential are given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = k_B T \frac{\partial \ln Z}{\partial V} \quad \text{and} \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -k_B T \frac{\partial \ln Z}{\partial N}.$$

Since we will be using these relations frequently, we present here different derivatives of the Helmholtz free energy $F(N, V, T)$ with respect to its parameters for a fluid system at constant volume in the following flowchart.



2.3.2.2 Specific Heat as Energy Fluctuation:

In statistical mechanics, specific heat is nothing but fluctuation in energy. The fluctuation in energy is defined as

$$\langle(\Delta E)^2\rangle = \langle(E - \langle E\rangle)^2\rangle = \langle E^2\rangle - \langle E\rangle^2.$$

Let us calculate the average of squared energy:

$$\begin{aligned}
\langle E^2\rangle &= \frac{\sum\limits_s E_s^2 \exp(-\beta E_s)}{\sum\limits_s \exp(-\beta E_s)} = \frac{1}{Z}\sum_s E_s^2 \exp(-\beta E_s) = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} \\
&= \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) + \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 = -\frac{\partial \langle E\rangle}{\partial \beta} + \langle E\rangle^2
\end{aligned}$$

since $\langle E\rangle = -(1/Z)(\partial Z/\partial\beta)$. Thus the fluctuation in energy is given by

$$\langle(\Delta E)^2\rangle = \langle E^2\rangle - \langle E\rangle^2 = -\frac{\partial\langle E\rangle}{\partial\beta} = -\left(\frac{\partial E}{\partial T}\right)\left(\frac{\partial T}{\partial\beta}\right) = k_B T^2 C_V$$

where $\beta = 1/k_B T$.

2.3.2.3 The equipartition theorem:

The equipartition theorem states that each square term in the Hamiltonian contributes $k_B T/2$ amount of energy to the free energy of a system. In statistical mechanics, one then needs to calculate the mean energy per degrees of freedom. Consider a system with a Hamiltonian

$$\mathcal{H}(p,q) = H_0 + \sum_{i=1}^{f} ap^2$$

where $a = 1/2m$ and f is the number of degrees of freedom and equal to the number of square terms in the Hamiltonian here. The mean energy in one degree of freedom is given by

$$\begin{aligned}
\langle\epsilon_i\rangle = \langle ap_i^2\rangle &= \frac{\displaystyle\int_{-\infty}^{+\infty} ap_i^2 \exp(-\beta H_0 - \beta ap_i^2) dq_1\cdots dq_f dp_1\cdots dp_f}{\displaystyle\int_{-\infty}^{+\infty} \exp(-\beta H_0 - \beta ap_i^2) dq_1\cdots dq_f dp_1\cdots dp_f} \\
&= \frac{\displaystyle\int_{-\infty}^{+\infty} ap_i^2 \exp(-\beta ap_i^2) dp_i}{\displaystyle\int_{-\infty}^{+\infty} \exp(-\beta ap_i^2) dp_i} = -\frac{\partial}{\partial\beta}\ln\left(\int_{-\infty}^{+\infty} e^{-\beta ap_i^2} dp_i\right) \\
&= -\frac{\partial}{\partial\beta}\ln\left(\beta^{-1/2}\int_{-\infty}^{+\infty} e^{-ay^2} dy\right), \quad y = \sqrt{\beta}p_i \\
&= \frac{1}{2\beta} = \frac{1}{2}k_B T.
\end{aligned}$$

Thus, the total energy of the system is

$$E = \frac{f}{2}k_B T.$$

The theorem is then proved by statistical mechanics.

Let us consider an example of 3-dimensional solid whose atoms could be considered as independent localized harmonic oscillators, oscillating about their mean positions.

The Hamiltonian of the solid can be written as

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \frac{1}{2}kq_i^2$$

where k is the strength of the harmonic potential. The system has $3N$ degrees of freedom, however, there are $6N$ square terms in this Hamiltonian. Thus, the mean energy of the solid is given by

$$E = 6N \times \frac{1}{2}k_BT = 3Nk_BT = 3RT.$$

the specific heat of the solid C_V is then given by

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3R.$$

This is known as Dulong-Petit's law. The same result can be obtained calculating canonical partition function from this classical Hamiltonian. However, instead of classical oscillators if quantum harmonic oscillators are considered which constitutes Einstein solid, an exponential decay of specific heat at low temperature is observed.

2.3.2.4 Constant pressure Canonical ensemble

The NPT ensemble is also called the isothermal-isobaric ensemble. It describes systems in contact with a thermostat at temperature T and a bariostat at pressure P. The system not only exchanges heat with the thermostat, it also exchanges volume (and work) with the bariostat. The total number of particles N remains fixed. But the total energy E and volume V fluctuate at thermal equilibrium.

In the NPT canonical ensemble, the energy E as well as the volume V can vary from zero to infinity. Each microstate s is now characterised by the energy E_s of that state and the volume of the system V. The probability p_s that the system to be in the microstate s is proportional to $e^{-(E_s+PV)/k_BT}$. Since the system has to be in a certain state, the sum of all p_s has to be unity, *i.e.*; $\sum_s p_s = 1$. The normalized probability

$$\begin{aligned} p_s &= \frac{\exp\{-(E_s+PV)/k_BT\}}{\int_0^\infty dV \sum_s \exp\{-(E_s+PV)/k_BT\}} \\ &= \frac{1}{Z(N,P,T)} e^{-(E_s+PV)/k_BT} \end{aligned} \tag{2.1}$$

is the Gibbs probability and the normalization factor

$$\begin{aligned} Z\left(N,P,T\right) &= \int_0^\infty dV \sum_s e^{-\frac{(E_s+PV)}{k_BT}} \\ &= \int_0^\infty dV \sum_s e^{-\beta(E_s+PV)} \end{aligned} \tag{2.2}$$

where $\beta = 1/(k_BT)$ and $Z\left(N,P,T\right)$ is the **constant pressure canonical partition function**.

It can be noted here that the canonical partition function $Z(N,V,T)$ under constant volume is related to the canonical partition function $Z(N,P,T)$ under constant pressure by the following *Laplace transform.*

$$\begin{aligned} Z\left(N,P,T\right) &= \int_0^\infty dV \sum_s e^{-\beta(E_s+PV)} = \int_0^\infty e^{-\beta PV} dV \sum_s e^{-\beta E_s} \\ &= \int_0^\infty Z\left(N,V,T\right) e^{-\beta PV} dV \end{aligned} \tag{2.3}$$

The expectation (or average) value of a macroscopic quantity X is given by

$$\begin{aligned} \langle X \rangle &= \frac{\int_0^\infty dV \sum_s X_s \exp\{-\beta(E_s+PV)\}}{\int_0^\infty dV \sum_s \exp\{-(E_s+PV)/k_BT\}} \\ &= \frac{1}{Z(N,P,T)} \int_0^\infty dV \sum_s X_s e^{-(E_s+PV)/k_BT} \end{aligned} \tag{2.4}$$

where X_s is the property X measured in the microstate s when system volume is V. Under this macroscopic condition, both the enthalpy $H = E + PV$ and the volume V of the system fluctuate. The average enthalpy $\langle H \rangle$ of the system is given by

$$\begin{aligned} \langle H \rangle &= \langle E \rangle + P\langle V \rangle \\ &= \frac{1}{Z(N,P,T)} \int_0^\infty dV \sum_s \left(E_s + PV\right) e^{-(E_s+PV)/k_BT} \\ &= -\frac{\partial}{\partial\beta} \left\{ \ln \left(\int_0^\infty dV \sum_s e^{-\beta(E_s+PV)} \right) \right\} \\ &= -\frac{\partial}{\partial\beta} \ln Z(N,P,T) \end{aligned} \tag{2.5}$$

Immediately, one could calculate a thermal response function, the specific heat at constant pressure C_P as

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{2.6}$$

where $H \equiv \langle H \rangle$.

In the continuum limit of the energy levels, the summations in the above expressions should be replaced by integrals. In this limit, the constant pressure canonical partition function can be written as

$$Z(N,P,T) = \frac{1}{h^{3N}N!}\int_0^\infty dV \int\int \exp\left\{-\beta\left[\mathcal{H}(p,q) + PV\right]\right\} d^{3N}q d^{3N}p \tag{2.7}$$

where $\mathcal{H} = \sum_i^N \mathcal{H}_i(q_i,p_i)$ and the volume element $d^{3N}qd^{3N}p = \prod_i^N d^3q_i d^3p_i$. $N!$ is for indistinguishable particles only.

The expectation value of X is given by

$$\langle X \rangle = \frac{1}{Z(N,P,T)}\int_0^\infty dV \int\int X(q,p) \exp\left\{-\beta\left[\mathcal{H}(p,q) + PV\right]\right\} d^{3N}q d^{3N}p \tag{2.8}$$

The Gibbs free energy $G(N,P,T) = E - TS + PV$ is the appropriate potential or free energy to describe a thermodynamic system of fixed number of particles in thermal equilibrium with a heat-bath at temperature T as well as in mechanical equilibrium at a constant pressure P. The statistical definition of entropy S under this macroscopic condition The statistical definition of entropy under this conditions can be obtained from the ensemble average of $-k_B \ln p_s$, p_s is the probability to find the system in the state s. The entropy S in terms of p_s then can be obtained as

$$\begin{aligned} S &= \langle -k_B \ln p_s \rangle \\ &= -k_B\,\frac{1}{Z}\int dV \sum_s e^{-\beta(E_s+PV)}\ \ln p_s \\ &= -k_B \int dV \sum_s\ \left\{\frac{1}{Z}e^{-\beta(E_s+PV)}\right\}\ \ln p_s \\ &= -k_B \int dV \sum_s p_s \ln p_s \end{aligned} \tag{2.9}$$

Following the definition of p_s given in Eq. 2.1, one has

$$\begin{aligned} S &= -k_B \int dV \sum_s \frac{e^{-\beta(E_s+PV)}}{Z} \{-\beta(E_s+PV) - \ln Z\} \\ &= \frac{1}{T}\left\{\frac{1}{Z}\int dV \sum_s (E_s+PV)e^{-\beta(E_s+PV)}\right\} + k_B \ln Z \\ &= \frac{1}{T}(E+PV) + k_B \ln Z \end{aligned} \tag{2.10}$$

where $E \equiv \langle E \rangle$ and $V \equiv \langle V \rangle$. Therefore, the Gibbs free energy $G(N,P,T)$ of the system is given by

$$G(N,P,T) = E - TS + PV = -k_B T \ln Z(N,P,T). \tag{2.11}$$

The thermodynamic equilibrium here corresponds to the minimum of Gibbs free energy. All equilibrium, thermodynamic properties can be calculated by taking appropriate derivatives of the Gibbs free energy $G(N,P,T)$ with respect to an appropriate parameter of it. Since the differential form of the first law of thermodynamics given by

$$dE = TdS - PdV + \mu dN \tag{2.12}$$

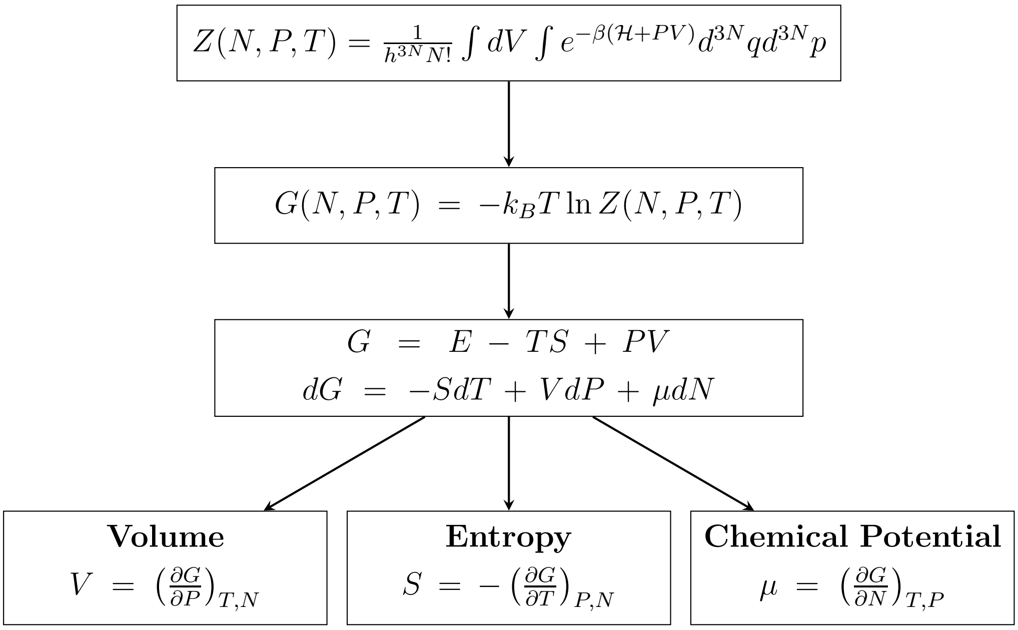
where μ is the chemical potential, the differential form of the Gibbs free energy $G(N,P,T) = E - TS + PV$ is given by

$$\begin{aligned} dG &= dE - SdT - TdS + PdV + VdP \\ &= -SdT + VdP + \mu dN \end{aligned} \tag{2.13}$$

Then, the thermodynamic parameters of the system can be obtained as

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}, \quad V = -\left(\frac{\partial G}{\partial P}\right)_{T,N}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} \tag{2.14}$$

Since we will be using these relations frequently, we present here different derivatives of the Gibbs free energy $G(N,P,T)$ with respect to its parameters for a fluid system at constant pressure in the following flowchart.



The thermodynamic response functions now can be calculated by taking second derivatives of the Gibbs free energy $G(N,P,T)$. The specific heat at constant pressure can be obtained as

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N}, \tag{2.15}$$

the isothermal compressibility κ_T can be obtained as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N}, \tag{2.16}$$

and the volume expansion coefficient α_P is given by

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} = \frac{1}{V}\left(\frac{\partial^2 G}{\partial T \partial P}\right)_{N}. \tag{2.17}$$

Another response function, iso-entropic compressibility κ_S can be calculated from the enthalpy $H = E + PV$. Since $dH = TdS + VdP + \mu dN$, volume V and the iso-entropic compressibility κ_S are given by

$$V = \left(\frac{\partial H}{\partial P}\right)_{S,N} \quad \text{and} \quad \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,N} = -\frac{1}{V}\left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N}. \tag{2.18}$$

2.3.3 Canonical ensemble for magnetic system

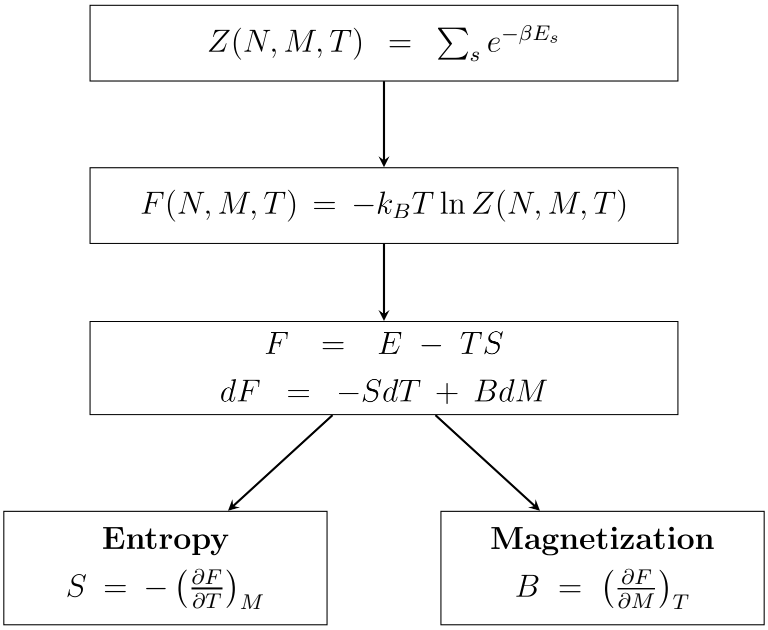
Canonical ensemble for a magnetic system can be fixed in two different st of parameters as in fluid. Let us first take (N, M, T), the number of magnetic moments N, the total magnetization M and the temperature T as our system parameters. Under such macroscopic condition, Helmholtz free energy $F(N, M, T)$ describes the equilibrium condition of the system. It is similar to the constant volume canonical ensemble for a fluid system. If a microstate s of the (N, M, T) canonical ensemble is characterised by an energy E_s and 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 must be $\propto e^{-E_s/k_BT}$, the Boltzmann factor. The constant field canonical partition function $Z(N, M, T)$ would be given by

$$Z\left(N, M, T\right) = \sum_s e^{-\frac{E_s}{k_BT}} = \sum_s e^{-\beta E_s} \tag{2.19}$$

where $\beta = 1/(k_BT)$ and the Gibbs free energy is then given by

$$F(N, B, T) = -k_BT \ln Z\left(N, M, T\right). \tag{2.20}$$

Different derivatives of the Helmholtz free energy $F(N, M, T)$ with respect to its parameters for a magnetic system at constant external field are given in the following flowchart.



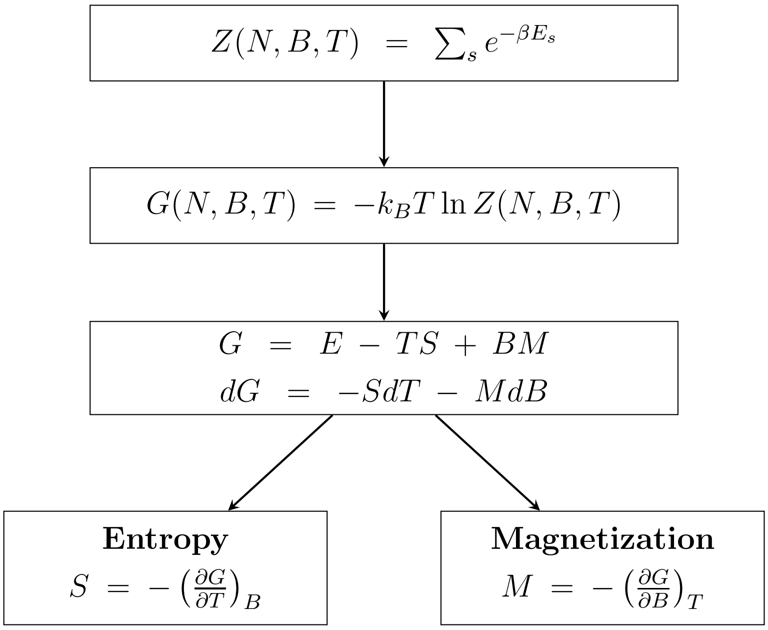
However, the natural parameters for a magnetic system are the number of magnetic moments N, the external magnetic induction B and the temperature T. Under this macroscopic condition, the Gibbs free energy $G(N, B, T)$ of the system defines the thermodynamics equilibrium. It is similar to the constant pressure canonical ensemble for a fluid system. One needs to calculate the constant field canonical partition function $Z(N, B, T)$ and which would be given by

$$Z\left(N, B, T\right) = \sum_{s} e^{-\frac{E_s}{k_B T}} = \sum_{s} e^{-\beta E_s} \tag{2.21}$$

where $\beta = 1/(k_B T)$ and the Gibbs free energy is then given by

$$G(N, B, T) = -k_B T \ln Z\left(N, B, T\right). \tag{2.22}$$

Different derivatives of the Gibbs free energy $G(N, B, T)$ with respect to its parameters for a magnetic system at constant external field are given in the following flowchart.



The magnetic response functions now can be calculated by taking second derivatives of the Gibbs free energy $G(N, B, T)$. The specific heat at constant magnetization and constant external field B can be obtained as

$$C_M = T\left(\frac{\partial S}{\partial T}\right)_{M,N} = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{M,N}, \tag{2.23}$$

and

$$C_B = T\left(\frac{\partial S}{\partial T}\right)_{B,N} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{B,N} \tag{2.24}$$

respectively. The isothermal susceptibility χ_T can be obtained as

$$\chi_T = \left(\frac{\partial M}{\partial B}\right)_{T,N} = -\left(\frac{\partial^2 G}{\partial B^2}\right)_{T,N}, \tag{2.25}$$

and the coefficient α_B is given by

$$\alpha_B = \left(\frac{\partial M}{\partial T}\right)_{B,N} = \left(\frac{\partial^2 G}{\partial T \partial B}\right)_{N}. \tag{2.26}$$

Another response function, iso-entropic susceptibility χ_S can be calculated from the enthalpy $H = E + BM$. Since $dH = TdS + MdB$, magnetization M and the iso-entropic susceptibility χ_S are given by

$$M = -\left(\frac{\partial H}{\partial B}\right)_S \quad \text{and} \quad \chi_S = \left(\frac{\partial M}{\partial B}\right)_S = -\left(\frac{\partial^2 H}{\partial B^2}\right)_S. \tag{2.27}$$

Example: Paramagnet

Consider a system of N localized magnetic ions, of spin-1/2 and magnetic moment μ. An external magnetic field B is applied to the system. The system is in contact with a heat bath at temperature T. The Hamiltonian of the system is given by

$$\mathcal{H} = -\mu B \sum_{j=1}^{N} \sigma_j$$

where $\sigma_j = \pm 1$, for $j = 1, 2 \cdots, N$. A microscopic state of this system is characterized by the values of set of spin variables $\{\sigma_j\}$. The canonical partition function then can be written as

$$Z(N,B,T) = \sum_{\{\sigma_j\}} \exp(-\beta\mathcal{H}) = \sum_{\sigma_1,\sigma_2,\cdots,\sigma_N} \exp\left(\beta\mu B \sum_{j=1}^{N} \sigma_j\right).$$

The sum can be factorized into multiples of partition function of individual particles and may be written as

$$Z = \left[\sum_{\sigma_1} \exp\left(\beta\mu B\sigma_1\right)\right] \cdots \left[\sum_{\sigma_N} \exp\left(\beta\mu B\sigma_N\right)\right] = Z_1^N$$

where Z_1 is the single particle partition function and is given by

$$Z_1 = \sum_{\sigma=\pm 1} \exp\left(\beta\mu B\sigma\right) = 2\cosh(\beta\mu B).$$

The Gibbs free energy is then readily obtained as

$$G(N,B,T) = -k_BT\ln Z(N,B,T) = -Nk_BT\ln\left\{2\cosh\left(\frac{\mu B}{k_BT}\right)\right\}.$$

As soon as the free energy is known other thermodynamic quantities can also be obtained. In the following, the expressions for entropy S, internal energy E, specific heat C_B, magnetization M and susceptibility χ are derived.

$$S = -\left(\frac{\partial G}{\partial T}\right)_B = Nk_B\left[\ln\left\{2\cosh\left(\frac{\mu B}{k_BT}\right)\right\} - \frac{\mu B}{k_BT}\tanh\left(\frac{\mu B}{k_BT}\right)\right],$$

$$C_B = T\left(\frac{\partial S}{\partial T}\right)_B = Nk_B\left(\frac{\mu B}{k_BT}\right)^2\cosh^{-2}\left(\frac{\mu B}{k_BT}\right),$$

$$M = -\left(\frac{\partial G}{\partial B}\right)_T = N\mu\tanh\left(\frac{\mu B}{k_BT}\right),$$

$$\chi_T = \left(\frac{\partial M}{\partial B}\right)_T = \frac{N\mu^2}{k_BT}\cosh^{-2}\left(\frac{\mu B}{k_BT}\right).$$

At high temperature $k_BT \gg \mu H$, and $\tanh x \approx x$ then

$$M \approx \frac{N\mu^2B}{k_BT} \qquad \chi \approx \frac{N\mu^2}{k_BT} = \frac{C}{T}$$

where $C = N\mu^2/k_B$ is a constant. This is the Curie's law of paramagnetism.

2.3.3.1 Susceptibility as fluctuation in magnetization:

Consider a system on N localized non-interacting paramagnetic ions of spin-$\frac{1}{2}$ and magnetic moment μ in an external magnetic field B, is in thermal equilibrium with a heat bath at temperature T. The square deviation in magnetization M is defined as

$$\left\langle \Delta M^2 \right\rangle = \left\langle M^2 \right\rangle - \langle M \rangle^2.$$

The average and square magnetic moments are given by

$$\langle \mu \rangle = \frac{1}{Z_1}\left(\sum_{s=\pm 1} \mu_s e^{-\beta E_s}\right) = \mu \tanh \frac{\mu B}{k_B T} \quad \text{and} \quad \left\langle \mu^2 \right\rangle = \frac{1}{Z_1}\left(\sum_{s=\pm 1} \mu_s^2 e^{-\beta E_s}\right) = \mu^2$$

Therefore,

$$\left\langle \Delta M^2 \right\rangle = \left\langle M^2 \right\rangle - \langle M \rangle^2 = N\left(\left\langle \mu^2 \right\rangle - \langle \mu \rangle^2\right)$$

Plugging the values of $\langle \mu \rangle$ and $\langle \mu^2 \rangle$ one has

$$\left\langle \Delta M^2 \right\rangle = N\mu^2 \left[1 - \left(\tanh \frac{\mu B}{k_B T}\right)^2\right] = N\mu^2 \left(\cosh \frac{\mu B}{k_B T}\right)^{-2} = k_B T \chi_T$$

2.3.4 The grand canonical ensemble:

Consider a system which could exchange energy as well as particles (mass) with the surroundings. 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 is difficult to measure directly of a physical system. However, their average values $\langle E \rangle$ and $\langle N \rangle$ are measurable quantities. Consider a given system A which is exchanging energy as well as matter, *i.e.*, number of particles with a large particle-energy reservoir B as shown in Fig. 2.3. The system A is regarded as a member of a grand canonical ensemble. Say, the system A is any one of its states characterized by N_r particles and E_s energy. In the reservoir, the number of particles and the energy would be N'_r and E'_s such that

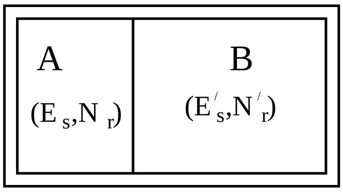


Figure 2.3: A system A is in equilibrium with a particle-energy reservoir B .

$$N_r + N'_r = N_0 = \text{constant}, \qquad \text{where} \qquad \frac{N_r}{N_0} \ll 1.$$

and

$$E_r + E_r' = E_0 = \textsf{constant}, \qquad \textsf{where} \qquad \frac{E_r}{E_0} \ll 1.$$

The probability P_{rs} to find the system in a state (N_r, E_s) would be directly proportional to the number of microstates $\Omega'(N_r', E_s')$. Thus,

$$P_{rs} \propto \Omega'(N_r', E_s') = \Omega'(N_0 - N_r, E_0 - E_s).$$

Since N_r and E_s are small quantities with respect to N_0 and E_0, a Taylor series expansion of Ω' is possible around (N_0, E_0) and can be written as

$$\begin{aligned} \ln \Omega'(N_0 - N_r, E_0 - E_s) &= \ln \Omega'(N_0, E_0) + \left(\frac{\partial \ln \Omega'}{\partial N'}\right)_{N'=N_0} (-N_r) \\ &\quad + \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{E'=E_0} (-E_s) + \cdots \\ &\approx \textsf{constant} - \alpha' N_r - \beta' E_s. \end{aligned}$$

where $\alpha = \partial \ln \Omega / \partial N$ and $\beta = \partial \ln \Omega / \partial E$. In equilibrium $\alpha' = \alpha$ and $\beta' = \beta$. Thus the probability P_{rs} is given by

$$P_{rs} = C \exp(-\alpha N_r - \beta E_s).$$

After normalizing,

$$P_{rs} = \frac{\exp(-\alpha N_r - \beta E_s)}{\sum\limits_{rs} \exp(-\alpha N_r - \beta E_s)}, \qquad \textsf{since} \qquad \sum_{rs} P_{rs} = 1$$

where the sum is over all possible states of the system A. The numerator $\exp(-\alpha N_r - \beta E_s)$ is the Boltzmann factor here and the denominator $\mathcal{Z} = \sum_{rs} \exp(-\alpha N_r - \beta E_r)$ is called the grand canonical partition function.

The mean energy $\langle E \rangle$ and the mean number of particle $\langle N \rangle$ of the system are then given by

$$\langle E \rangle = E = \frac{\sum_{rs} E_s \exp(-\alpha N_r - \beta E_s)}{\sum_{rs} \exp(-\alpha N_r - \beta E_s)} = -\frac{\partial}{\partial \beta} \ln\{\sum_{rs} e^{-\alpha N_r - \beta E_s}\} = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \beta}$$

and

$$\langle N \rangle = N = \frac{\sum_{rs} N_r \exp(-\alpha N_r - \beta E_s)}{\sum_{rs} \exp(-\alpha N_r - \beta E_s)} = -\frac{\partial}{\partial \alpha} \ln\{\sum_{rs} e^{-\alpha N_r - \beta E_s}\} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \alpha}.$$

2.3.4.1 Thermodynamics in Grand Canonical Ensemble:

From second law of thermodynamics one has

$$TdS = dE + PdV - \mu dN$$

where μ is the chemical potential. Consequently the thermodynamic parameters are defined as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}, \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,E} \quad \text{and} \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}.$$

On the other hand, the entropy here is given by

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

Thus,

$$dS = k_B \left(\frac{\partial \ln \Omega}{\partial E}\right) dE + k_B \left(\frac{\partial \ln \Omega}{\partial N}\right) dN$$

It is then straight forward to obtain α and β as given below

$$\left(\frac{\partial S}{\partial E}\right)_N = k_B \left(\frac{\partial \ln \Omega}{\partial E}\right) = k_B \beta = \frac{1}{T} \quad \Longrightarrow \quad \beta = \frac{1}{k_B T}$$

and

$$\left(\frac{\partial S}{\partial N}\right)_E = k_B \left(\frac{\partial \ln \Omega}{\partial N}\right) = k_B \alpha = -\frac{\mu}{T} \quad \Longrightarrow \quad \alpha = -\frac{\mu}{k_B T}.$$

The grand canonical partition function then can be written as

$$\mathcal{Z} = \sum_{rs} \exp\left(\frac{\mu N_r}{k_B T} - \frac{E_s}{k_B T}\right) = \sum_{rs} \mathfrak{z}^{N_r} e^{-E_s/k_B T}$$

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

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

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

As soon as the partition function is known, one could calculate the thermodynamic quantities in terms of the partition function. The grand partition function $\mathcal{Z}$ is a function of β, α and the volume V, and can be written as

$$\mathcal{Z} = \mathcal{Z}(\beta, \alpha, V).$$

Therefore,

$$\begin{aligned} d\ln\mathcal{Z} &= \frac{\partial \ln\mathcal{Z}}{\partial\beta}d\beta + \frac{\partial \ln\mathcal{Z}}{\partial\alpha}d\alpha + \frac{\partial \ln\mathcal{Z}}{\partial V}dV \\ &= -Ed\beta - Nd\alpha + \beta PdV. \end{aligned}$$

or

$$d\left(\ln\mathcal{Z} + \beta E + \alpha N\right) = \beta dE + \alpha dN + \beta PdV = \beta(dE - \mu N + PdV) = \frac{1}{k_B}dS.$$

or

$$S = k_B(\ln\mathcal{Z} + \beta E - \mu\beta N) \quad \Longrightarrow \quad TS = k_BT\ln\mathcal{Z} + E - \mu N.$$

The grand potential $\Phi(T, V, \mu)$ then can be obtained as

$$\Phi(T, V, \mu) = E - TS - \mu N = -k_BT\ln\mathcal{Z}.$$

Since grand potential characterizes a thermodynamic system exchanging particle and energy with surroundings, the thermodynamic quantities of such a system then can be obtained by statistical mechanics by calculating grand canonical partition function.

In summary, the classical statistical mechanical problems then can be studied using three ensembles: microcanonical, canonical and grand canonical depending on the basis of interaction of the system with its surroundings. Microcanonical ensemble corresponds to an isolated system, canonical ensemble corresponds a system in equilibrium with a heat bath and grand canonical ensemble corresponds to a system in equilibrium with a particle-energy bath. The corresponding statistical quantities and thermodynamic functions of different ensembles are listed in the table below. Using thermodynamic potentials, obtained from statistical mechanics, thermodynamic quantities can be calculated in statistical mechanical way. Thus, it is possible to derive microscopically all observational quantities of thermodynamics by the application of statistical mechanics.

Ensemble	Statistical quantity		Thermodynamic functions
Microcanonical	Number of microstates:	Ω	Entropy: $S = k_B \ln \Omega$
Canonical	Canonical partition function:	Z	Helmholtz free energy: $F = -k_B T \ln Z$
Grand Canonical	Grand partition function:	$\mathcal{Z}$	Grand potential: $\Phi = -k_B T \ln \mathcal{Z}$

Table 2.1: The statistical quantities and their corresponding thermodynamic functions of different ensembles.

2.4 Quantum Statistical Mechanics

In this section, statistical mechanics of N identical quantum particles will be formulated. For simplicity, a gas of non-interacting N particles is considered. Since the particles are non-interacting, the Hamiltonian of the system is just the sum of N individual Hamiltonian and it is given by

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

where (q_i, p_i) are the coordinate and momentum of the ith particle, $\hat{\mathcal{H}}_i$ 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 Schrödinger equation

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

where E is the eigenvalue of the Hamiltonian and ψ_E is the corresponding eigenfunction. The solution of the above Schrödinger equation of N non-interacting particles can be written as

$$\psi_E(\mathbf{q}) = \prod_{i=1}^{N} \phi_{\epsilon_i}(q_i), \quad \text{with} \quad E = \sum_{i=1}^{N} \epsilon_i$$

and

$$\hat{\mathcal{H}}_i \phi_{\epsilon_i}(q_i) = \epsilon_i \phi_{\epsilon_i}(q_i)$$

where ϕ_i is the eigenfunction of the single particle Hamiltonian $\hat{\mathcal{H}}_i$ with eigenvalue

ϵ_i. Each single particle wave function ϕ_i is always a linear combination of a set of orthonormal basis functions $\{\varphi_j\}$, $\phi_i = \sum_j c_{ij}\varphi_j$. If there are n_i particles in an eigenstate ϵ_i, then the distribution should satisfy

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

2.4.1 Symmetry of wave functions and particle statistics:

For simplicity, first consider a two-particle system described by $\psi(a,b)$. If the particle a described by ϕ_n^a when it is in the nth state of energy E_n and the particle b described by ϕ_k^b when it is in the kth state of energy E_k, then the wave function for the combined two particle system is given by

$$\psi(a,b) = \phi_n^a\phi_k^b \quad \text{with} \quad E = E_n + E_k$$

where E is the energy of the system. If the two particles are exchanged so that a in the kth state and b in the nth state, the corresponding wave function is

$$\psi(a,b) = \phi_n^b\phi_k^a \quad \text{with} \quad E = E_n + E_k.$$

Since both the states corresponds to the same energy value, the states are then degenerate. The most general wave function is the linear combinations of these two wave functions. There are two possible combinations and they are given by

$$(i)\;\; \psi(a,b) = \frac{1}{\sqrt{2!}}\left[\phi_n^a\phi_k^b + \phi_n^b\phi_k^a\right] \qquad \text{Symmetric}$$

and

$$(ii)\;\; \psi(a,b) = \frac{1}{\sqrt{2!}}\left[\phi_n^a\phi_k^b - \phi_n^b\phi_k^a\right] = \frac{1}{\sqrt{2!}}\begin{vmatrix} \phi_n^a & \phi_n^b \\ \phi_k^a & \phi_k^b \end{vmatrix} \qquad \text{Anti-symmetric}$$

If a and b are interchanged, (i) remains unchanged and it is called symmetric wave function, (ii) the absolute vale remains unchanged but reverses the sign and it is called anti-symmetric wave function. However, the wave functions $\phi_n^a\phi_k^b$ and $\phi_n^b\phi_k^a$ individually are neither symmetric nor anti-symmetric. The interchange of the particles leads to different microstates which means the particles are distinguishable as classical particles.

Now, one could write the wave functions for N particles $\{a_1, a_2, \cdots, a_N\}$ with a_i particle in the n_ith state. The corresponding wave functions are

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

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

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

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 corresponds 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**.

2.4.2 The quantum 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. At the state S, the total energy E_S and the number of particles N are given by

$$E_S = \sum_s n_s \epsilon_s \quad \text{and} \quad N = \sum_s n_s.$$

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

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

$$Z = \sum_S e^{-\beta E_S} = \sum_S e^{-\beta \sum_s n_s \epsilon_s}$$

where the sum is all states S. All states is the collection of states with all possible values of n_s. This, the partition function can be written as

$$Z = \sum_{\{s_i\}} e^{-\beta(\epsilon_{s_1} + \epsilon_{s_2} + \cdots + \epsilon_{s_N})}$$

where the sum is now over the all possible states of individual particles. The summation in the partition function can be carried out in the following manner.

$$\begin{aligned} Z &= \sum_{s_1, s_2 \cdots, s_N} e^{-\beta\epsilon_{s_1}} e^{-\beta\epsilon_{s_2}} \dots e^{-\beta\epsilon_{s_N}} \\ &= \left[\sum_{s_1} e^{-\beta\epsilon_{s_1}}\right] \left[\sum_{s_2} e^{-\beta\epsilon_{s_2}}\right] \cdots \left[\sum_{s_N} e^{-\beta\epsilon_{s_N}}\right] \\ &= \left[\sum_{s_i} e^{-\beta\epsilon_{s_i}}\right]^N \end{aligned}$$

and

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

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

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

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

(ii) BE Statistics: The grand canonical partition function $\mathcal{Z}$ of N indistinguishable bosons is given by

$$\mathcal{Z} = \sum_s e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots) + \mu\beta(n_1 + n_2 + \cdots)}$$

where the sum is over all possible single particle states s. The number of particles n_i in each state i could be $0, 1, 2, \cdots$ subject to the condition $\sum n_i = N$. Therefore,

$$\mathcal{Z} = \left(\sum_{n_1} e^{-\beta(\epsilon_1 - \mu)n_1} \right) \left(\sum_{n_2} e^{-\beta(\epsilon_2 - \mu)n_2} \right) \cdots$$

Since,

$$\sum_{n=0}^{\infty} e^{-\beta(\epsilon_1 - \mu)n} = \frac{1}{1 - e^{-\beta(\epsilon - \mu)}},$$

the partition function then can be written as

$$\mathcal{Z} = \left(\frac{1}{1 - e^{-\beta(\epsilon_1 - \mu)}} \right) \left(\frac{1}{1 - e^{-\beta(\epsilon_2 - \mu)}} \right) \cdots$$

and

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

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

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

Thus the average number of molecules in the s level is

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

This is Bose-Einstein distribution where always $\mu < \epsilon_s$, otherwise $\langle n_s \rangle$ could be negative.

(iii) 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

$$\mathcal{Z} = \left(1 + e^{\beta(\mu - \epsilon_1)} \right) \left(1 + e^{\beta(\mu - \epsilon_2)} \right) \cdots$$

and

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

The number of particles is given by

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

Thus the average number of molecules in the s level is

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

This is the Fermi-Dirac Distribution.

2.4.3 Boltzmann limit of Boson and Fermion gasses:

The Bose-Einstein (BE) and Fermi-Dirac (FD) distributions are given by

$$\langle n_s \rangle = \frac{1}{e^{\beta(\epsilon_s - \mu)} \pm 1}$$

where + corresponds to FD and − corresponds to BE distribution. Suppose that,

$$e^{-\beta\mu} \gg 1 \quad \text{that is} \quad e^{\beta(\epsilon_s - \mu)} \gg 1$$

In this case,

$$\langle n_s \rangle \approx \frac{1}{e^{\beta(\epsilon_s - \mu)}} = e^{\beta\mu} e^{-\beta\epsilon_s}$$

and

$$\sum \langle n_s \rangle = N = e^{\beta\mu} \sum_s e^{-\beta\epsilon_s} \quad \text{or} \quad e^{\beta\mu} = \frac{N}{\sum\limits_s e^{-\beta\epsilon_s}}$$

Thus the distribution becomes

$$\langle n_s \rangle = \frac{N e^{-\beta\epsilon_s}}{\sum\limits_s e^{-\beta\epsilon_s}}$$

as that of classical Maxwell-Boltzmann distribution. Thus the quantum statistics will behave like a classical statistics in the limit of

$$e^{-\beta\mu} \gg 1.$$

where μ is chemical potential of an ideal gas of N molecules in a volume V at temperature T. Since the partition function of an ideal gas of N molecules in a volume V at temperature T is given by

$$Z(N, V, T) = \frac{1}{N!}\left[\frac{V}{h^3}(2m\pi k_B T)^{3/2}\right]^N$$

and correspondingly the free energy will be

$$F = -k_B T \ln Z = -Nk_B T \ln \frac{V}{N}\left(\frac{2m\pi k_B T}{h^2}\right)^{3/2} - Nk_B T.$$

The chemical potential of the ideal gas is then given by

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -k_B T \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\frac{V}{N}\right]$$

Thus one has,

$$\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\frac{V}{N} \gg 1 \quad \Longrightarrow \quad \frac{1}{\lambda^3}\frac{V}{N} \gg 1$$

where $\lambda = h/\sqrt{2\pi m k_B T}$ is the thermal wavelength. The above condition will be then satisfied only for the values of the physical parameters $T \to \infty$ and $\rho \to 0$. This is known as the classical limit of the quantum gas.

2.5 Equation of state of a quantum Ideal Gas

Consider a gas of N non-interacting identical quantum particles enclosed in a volume V. The distribution function for the particles of the gas is given by

$$\langle n \rangle = \frac{1}{e^{\beta(\epsilon - \mu)} \pm 1}$$

where $+$ sign corresponds to FD and $-$ sign corresponds to BE distribution. In order to obtain the equation of state, one needs to establish a relationship between the pressure P, volume V and energy E. The mean energy E of the system is given by

$$E = \int_0^\infty \epsilon g(\epsilon)\langle n \rangle d\epsilon$$

where $g(\epsilon)$ is the density of states between energy ϵ and $\epsilon + d\epsilon$. The number of states $g(p)$ between momentum p and $p + dp$ is

$$g(p)dp = \frac{1}{h^3} d^3q d^3p = \frac{V}{h^3} d^3p = \frac{V}{h^3} 4\pi p^2 dp.$$

Since $p^2 = 2m\epsilon$, the number of states $g(\epsilon)$ between energy ϵ and $\epsilon + d\epsilon$ is then

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

The energy E of the system is then given by

$$E = \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}}{e^{\beta(\epsilon - \mu)} \pm 1} d\epsilon.$$

In order to calculate the pressure P of the gas as

$$P = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial V},$$

one needs to know the grand canonical partition function of the gas. The grand canonical partition function of the gas is given by

$$\ln \mathcal{Z} = \int_0^\infty \ln \left(1 \pm e^{-\beta(\epsilon - \mu)}\right)^{\pm 1} g(\epsilon) d\epsilon$$

where $+$ sign corresponds to FD and $-$ sign corresponds to BE distribution as before. The pressure P of the gas is then

$$\begin{aligned} P &= \frac{1}{\beta} \frac{\partial}{\partial V} \int_0^\infty \ln \left(1 \pm e^{-\beta(\epsilon - \mu)}\right)^{\pm 1} \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon \\ &= \frac{1}{\beta} \frac{2\pi}{h^3} (2m)^{3/2} \int_0^\infty \ln \left(1 \pm e^{-\beta(\epsilon - \mu)}\right)^{\pm 1} \epsilon^{1/2} d\epsilon. \end{aligned}$$

Integrating by parts, one could get the pressure as

$$P = \frac{2}{3V} \left(\frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}}{e^{\beta(\epsilon - \mu)} \pm 1} d\epsilon \right) = \frac{2}{3} \frac{E}{V}.$$

Thus, the equation of state is given by

$$PV = \frac{2}{3} E$$

as that of classical monatomic ideal gas. The equation of state is then independent of the statistics the particles obey.

Application of quantum statistical mechanics is enormous in physics and beyond the scope of this article. A major application can be found in solid state physics books. Phonons and electrons are two common example of boson and fermion. It is then left to reader's interest.

Problems:

2.1 A system consists of N noninteracting, distinguishable two-level atoms. Each atom can exist in one of two states, $E_0 = 0$, and $E_1 = \varepsilon$. The number of atoms in energy level E_1 is n_1 . The internal energy of the system is $E = n_0 E_0 + n_1 E_1$. (a) Compute the entropy S of the system as a function of internal energy. (b) Compute the heat capacity C of a fixed number of atoms, N.

2.2 A lattice contains N normal lattice sites and N interstitial lattice sites. N identical atoms sit on the lattice, M on the interstitial sites and $N-M$ on the normal sites ($N \gg M \gg 1$). If an atom occupies a normal sites, its energy $E = 0$. If an atom occupies an interstitial site, its energy is $E = \varepsilon$. Compute the internal energy E and heat capacity C as a function of temperature T for this lattice.

2.3 Consider N localized one dimensional classical Harmonic oscillators of frequency ω in an isolated system with fixed energy E. Show that the number of microstates of the system is given by

$$\Omega = \frac{1}{N!}\left(\frac{E}{\hbar\omega}\right)^N$$

Calculate the the temperature T of the system and check that $E = Nk_BT$.

2.4 Consider N localized one dimensional quantum Harmonic oscillators of frequency ω in an isolated system with fixed energy E. Show that the entropy S of the system is given by

$$\frac{S}{Nk_B} = \left(\frac{E}{N\hbar\omega} + \frac{1}{2}\right)\ln\left(\frac{E}{\hbar\omega} + \frac{N}{2}\right) - \left(\frac{E}{N\hbar\omega} - \frac{1}{2}\right)\ln\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)$$

Calculate the the temperature T of the system and check that

$$E = \frac{N\hbar\omega}{2} + \frac{N\hbar\omega}{e^{\frac{\hbar\omega}{k_BT}} - 1}.$$

2.5 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 the entropy of the system is given by

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

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?

2.6 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 $PV = Nk_BT$.

2.7 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.

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

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

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

2.9 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 $PV = Nk_BT$.

2.10 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

$$Q = \left[1 - \frac{e^{\mu/k_BT}}{2\sinh\left(\hbar\omega/2k_BT\right)}\right]^{-1} .$$

2.11 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,

$$f\left(T\right) = \left[2\pi m k_B T/h^2\right]^{3/2} \quad \text{and} \quad \phi(T) = \left[2\sinh\left(\hbar\omega/2k_BT\right)\ \right]^{-1}.$$

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