



**SATHYABAMA**

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

[www.sathyabama.ac.in](http://www.sathyabama.ac.in)

**SCHOOL OF SCIENCE AND HUMANITIES**

**DEPARTMENT OF PHYSICS**

## **UNIT – I - Thermodynamics and Statistical Mechanics – SPHA5202**

# **I. REVIEW OF THE LAWS OF THERMODYNAMICS AND THEIR CONSEQUENCES**

Thermodynamics is essentially the study of the internal motions of many body systems. Virtually all substances which we encounter in everyday life are many body systems of some sort or other (e.g., solids, liquids, gases, and light). Not surprisingly, therefore, thermodynamics is a discipline with an exceptionally wide range of applicability. Thermodynamics is certainly the most ubiquitous sub-field of Physics outside Physics Departments. Engineers, Chemists, and Material Scientists do not study relatively or particle physics, but thermodynamics is an integral, and very important, part of their degree courses. Energy exists in many forms, such as heat, light, chemical energy, and electrical energy. Energy is the ability to bring about change or to do work. Thermodynamics is the study of energy.

**First Law of Thermodynamics:** Energy can be changed from one form to another, but it cannot be created or destroyed. The total amount of energy and matter in the Universe remains constant, merely changing from one form to another. The First Law of Thermodynamics (Conservation) states that energy is always conserved, it cannot be created or destroyed. In essence, energy can be converted from one form into another.

**The Second Law of Thermodynamics** states that "in all energy exchanges, if no energy enters or leaves the system, the potential energy of the state will always be less than that of the initial state." This is also commonly referred to as entropy. A watch spring-driven watch will run until the potential energy in the spring is converted, and not again until energy is reapplied to the spring to rewind it. A car that has run out of gas will not run again until you walk 10 miles to a gas station and refuel the car. Once the potential energy locked in carbohydrates is converted into kinetic energy (energy in use or motion), the organism will get no more until energy is input again. In the process of energy transfer, some energy will dissipate as heat. Entropy is a measure of disorder: cells are NOT disordered and so have low entropy. The flow of energy maintains order and life. Entropy wins when organisms cease to take in energy and die.

Heat capacity or thermal capacity is a measurable physical quantity equal to the ratio of the heat added to (or removed from) an object to the resulting temperature change. The SI

unit of heat capacity is joule per Kelvin (J/K) and the dimensional form is  $L^2MT^{-2}$ . Specific heat is the amount of heat needed to raise the temperature of a certain mass by 1 degree Celsius.

Heat capacity is an extensive property of matter, meaning it is proportional to the size of the system. When expressing the same phenomenon as an intensive property, the heat capacity is divided by the amount of substance, mass, or volume, so that the quantity is independent of the size or extent of the sample. The molar heat capacity is the heat capacity per unit amount (SI unit: mole) of a pure substance and the specific heat capacity, often simply called specific heat, is the heat capacity per unit mass of a material. Occasionally, in engineering contexts, the volumetric heat capacity is used.

## Entropy

Once set up, the checkerboard stays set up until we decide to change it, a situation which we can refer to as static disorder. As we have found, most physical systems change with time, a situation we can refer to as dynamic disorder. Because a system changes with time, the large ratio of the number of disordered situations relative to an ordered situation can be used to predict how the system will change with time. Based on the number of disordered situations compared to the number of ordered situations, it is extremely unlikely that a system will go by itself from a disordered to an ordered condition. If the system is ordered, it is likely to become disordered. It is useful to define a quantity ***S*** called ***entropy***, which is a measure of the degree of disorder in a system. The entropy of a system increases as the disorder of the system increases.

We now focus on the molecular motion of a system, which gives rise to the internal energy of this system. Adding heat to this system increases the disorder because the heat increases the randomness of the molecular motion. So, the entropy of the system increases. The effect of adding heat to a system increases the molecular motion, and this results in more disorder of the system. The effect of adding heat to a

cold system, one that has small molecular motion, produces more disorder than would happen if one added the same amount of heat to the system if it were at a higher temperature. Why? It is because the hot system already has more molecular motion than the cold system, so the percentage change in motion is not as great.

If the change in entropy only comes about because the internal energy of the system changes, the result is called a reversible process. In this case, the change in entropy  $\Delta S$  is given by equation .1.

$$\text{change in entropy} = \frac{\text{change in the heat of the system}}{\text{temperature}}$$

or

$$\Delta S = \frac{\Delta Q}{T} \quad (\text{Equation .1})$$

where

$\Delta S$  = change in entropy of a reversible process (joules/Kelvin or calories/Kelvin)

$\Delta Q$  = change in the heat of the system (joules or calories)

$T$  = temperature (Kelvin)

A good example is found in an ice cube at 0 °C placed in a well-insulated chest at 20 °C. The ice cube is the system and the chest is the environment. Heat flows from the chest to the ice cube because there is a difference in their temperatures. As heat is added to the system (the ice cube), after some time the ice cube becomes a puddle of water at 0 °C. If we wait long enough, the puddle of water and the chest will reach the same temperature, which will be less than 20 °C.

Equation 1 must be applied carefully, because it is valid only if the temperature of the substance remains approximately constant. However, we learned in Chapter 5 the amount of heat needed to change one gram of ice at 0 °C to one gram of water at 0 °C. This is the latent heat, which is 80 calories/gram for ice. If the ice cube has a mass of 100 grams (0.1 kg), we can find the heat added, which equals the increase in thermal energy, using Equation 5.3.

$$Q = L_{\text{heat}} \times M = 80 \text{ cal/g} \times 100 \text{ g} = 8,000 \text{ cal}$$

These 8,000 calories are the difference between the initial and final thermal energy. During this phase change, the temperature remains at 0 °C. This means that we can find the change in entropy by using Equation .1.

## SECOND LAW OF THERMODYNAMICS

Definition by *Clausius*:

” There is no thermodynamic transformation whose *sole* effect is to deliver heat from a reservoir of lower temperature to a reservoir of higher temperature.”

*Summary*: heat does not flow upwards.

Definition by *Kelvin*:

”There is no thermodynamic transformation whose *sole* effect is to extract heat from a reservoir and convert it entirely to work”.

*Summary*: a perpetuum mobile of second type does not exist.

In order to prove that both definition are equivalent, we will show that the falsehood of one implies the falsehood of the other. For that purpose, we consider two heat reservoirs with temperatures  $T_1$  and  $T_2$  with  $T_1 > T_2$ .

- (1) If Kelvin’s statement were false, we could extract heat from  $T_2$  and convert it entirely to work. We could then convert the work back to heat entirely and deliver it to  $T_1$  (there is no law against this) (Fig. 4.5). Thus, Clausius’ statement would be negated.

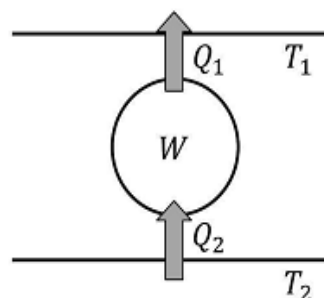
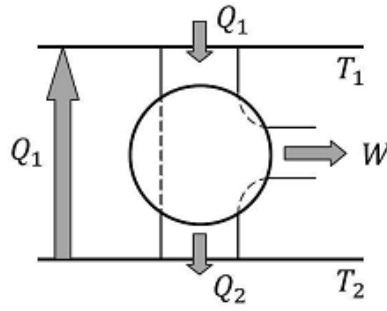


Figure 4.5:  $Q_2 = W = Q_1$  process.

- (2) If Clausius’ statement were false, we could let an amount of heat  $Q_1$  flow from  $T_2$  to  $T_1$  ( $T_2 < T_1$ ). Then, we could connect a Carnot engine between  $T_1$  and  $T_2$  such as to extract  $Q_1$  from  $T_1$  and return an amount  $|Q_2| < Q_1$  back to  $T_2$ . The net work output of such an engine would be  $|Q_1| - |Q_2| > 0$ , which would mean that an amount of heat  $|Q_1| - |Q_2|$  is converted into work, without any other effect. This would contradict Kelvin’s statement.





From the microscopic point of view

- *heat transfer* is an exchange of energy due to the random motion of atoms;
- *work's* performance requires an organized action of atoms.

In these terms, heat being converted entirely into work means chaos changing spontaneously to order, which is a very improbable process.

→ Usually,

- one configuration corresponds to order;
- many configurations correspond to chaos.

# Thermodynamic potentials

Thermodynamic potentials are *state functions* that, together with the corresponding equations of state, describe the equilibrium behavior of a system as a function of so-called "natural variables". The natural variables are a set of appropriate variables that allow to compute other state functions by partial differentiation of the thermodynamic potentials.

## 1 Internal energy $U$

The basic relation of thermodynamics is given by the equation

$$\boxed{dU = TdS + \sum_{i=1}^m F_i dq_i + \sum_{j=1}^{\alpha} \mu_j dN_j}, \quad (1)$$

where  $\{F, q\}$  denote the set of conjugate intensive and extensive variables that characterize a system. For instance, for a gas

$$\{F, q\} \rightarrow \{-P, V\},$$

for a magnetic system

$$\{F, q\} \rightarrow \{\mathcal{B}, \mathcal{M}\}.$$

In (1),  $N$  is the number of particles in the system (an extensive variable); the index  $j$  ( $j = 1, \dots, \alpha$ ) denotes different sets of particles that may constitute the system.

*Chemical potential*  $\mu$  (an intensive variable): is defined as the energy needed to add a particle to a thermally and mechanically isolated system.

The last term in eq. (1),  $\mu dN$ , is needed if the number of particles in the system is not kept constant, i.e. if particles enter or leave the system.

For a gas, eq. (1) is written as

$$dU = TdS - PdV + \sum_{j=1}^{\alpha} \mu_j dN_j,$$

which means that

$$\boxed{U = U(S, V, N)}.$$

Since  $dU$  is a total differential, through differentiation of  $U$  as a function of  $S$ ,  $V$ , and  $N$  one obtains thermal and caloric equations of state:

$$\begin{aligned} T &= \left( \frac{\partial U}{\partial S} \right)_{V,N}, \\ -P &= \left( \frac{\partial U}{\partial V} \right)_{S,N}, \\ \mu_j &= \left( \frac{\partial U}{\partial N_j} \right)_{S,N,N_{i \neq j}}. \end{aligned}$$

The experimentally important *response* functions are obtained by second-order differentiation:

$$\begin{aligned} \left( \frac{\partial^2 U}{\partial S^2} \right)_{V,N} &= \left( \frac{\partial T}{\partial S} \right)_{V,N} = \left[ \left( \frac{\partial S}{\partial T} \right)_{V,N} \right]^{-1} = \frac{T}{C_V} \Rightarrow \\ &\Rightarrow \boxed{C_V = T \left[ \left( \frac{\partial^2 U}{\partial S^2} \right)_{V,N} \right]^{-1}}, \\ \left( \frac{\partial^2 U}{\partial V^2} \right)_{S,N} &= - \left( \frac{\partial P}{\partial V} \right)_{S,N} = \frac{1}{V k_S} \Rightarrow \\ &\Rightarrow \boxed{k_S = \frac{1}{V} \left[ \left( \frac{\partial^2 U}{\partial V^2} \right)_{S,N} \right]^{-1}}. \end{aligned} \tag{2}$$

### Maxwell relations

A *Maxwell relation* follows from the differentiability of  $U$ :

$$\begin{aligned} \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right) &= \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right) \Rightarrow \\ &\Rightarrow \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V \quad (\text{Maxwell relation}). \end{aligned} \tag{3}$$

*Example:* monoatomic ideal gas. The behavior of a monoatomic ideal gas obeys the following relations:

$$PV = nRT,$$



## INTERNAL ENERGY $U$

$$U = \frac{3}{2}nRT,$$

$$C_V = \frac{3}{2}nR.$$

Let us use this information and derive an expression for  $U$  in terms of its natural variables:

$$dS = \frac{dU + PdV}{T} = C_V \frac{dT}{T} + nR \frac{dV}{V},$$

$$\begin{aligned} S(T, V) &= C_V \ln \left( \frac{T}{T_0} \right) + nR \ln \left( \frac{V}{V_0} \right) + S_0 \\ &= C_V \ln \left( \frac{U}{U_0} \right) + nR \ln \left( \frac{V}{V_0} \right) + S_0, \end{aligned}$$

$$\frac{S - S_0}{C_V} = \ln \left( \frac{U}{U_0} \right) + \frac{nR}{C_V} \ln \left( \frac{V}{V_0} \right). \quad (4)$$

Since

$$\begin{aligned} nR &= C_P - C_V \Rightarrow \\ \Rightarrow \frac{nR}{C_V} &= \frac{C_P - C_V}{C_V} = \gamma - 1 = \frac{5}{3} - 1 = \frac{2}{3}, \end{aligned}$$

we can write eq. (4) as

$$e^{\frac{S-S_0}{C_V}} = \left( \frac{U}{U_0} \right) \left( \frac{V}{V_0} \right)^{\frac{nR}{C_V}},$$

from which

$$\boxed{U(S, V) = U_0 \left( \frac{V_0}{V} \right)^{\gamma-1} e^{\frac{S-S_0}{C_V}}} \quad (5)$$

follows. Eq. (5) is the fundamental equation for the ideal gas, with  $U(S, V)$  as the thermodynamic potential and  $S, V$  as independent natural variables.

*Corollary:* the natural variables for  $U$  are  $S$  and  $V$ , which means that if the function  $U(S, V)$  is known for a given system we can obtain all the thermodynamic properties of the system through the differentiation of  $U(S, V)$ .

On the contrary, in the equation of state

$$U = U(T, V, N) \quad (6)$$

$U$  is *not* an appropriate thermodynamic potential any more since from the first derivatives of eq. (6),

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

and

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

we do not obtain the dependent variables  $S$  and  $P$ .

If we rewrite eq. (1) as

$$dS = \frac{1}{T}dU + \frac{1}{T}PdV - \frac{1}{T} \sum_{j=1}^{\alpha} \mu_j dN_j,$$

it becomes clear that

$$S = S(U, V, N)$$

is also a thermodynamic potential.

## HELMHOLTZ FREE ENERGY

By replacing the independent variable  $S$  by  $T$  in  $U(S, V, N)$ , we define the *free energy*  $F$ :

$$F = U - TS = U - T \left(\frac{\partial U}{\partial S}\right)_{V,N} = U - TS,$$

$$F = F(T, V, N) \rightarrow \text{Free energy.}$$

In

$$dF = dU - d(TS) = dU - SdT - TdS$$

we substitute  $dU$  from eq. (5.1) and get

$$dF = -SdT - PdV + \sum_{j=1}^{\alpha} \mu_j dN_j.$$

The natural variables of the free energy are  $\{T, V, N\}$ . The *dependent* variables are obtained out of the first derivatives:

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_T \rightarrow \text{thermal state equations}$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \rightarrow \text{Maxwell relation.}$$

## ENTHALPY

Enthalpy

$$\boxed{H = H(S, P, N)}$$

is obtained when we substitute the variable  $V$  by  $P$  in  $U(S, V, N)$ :

$$\boxed{H = U + PV}.$$

The total differential of  $H$  is derived as follows.

$$\begin{aligned} H &= U - \underbrace{V \left( \frac{\partial U}{\partial V} \right)_{S, N}}_{-P}, \\ dH = dU + d(PV) &= dU + VdP + PdV \\ &= TdS - PdV + \sum_{j=1}^{\alpha} \mu_j dN_j + VdP + PdV \quad \Rightarrow \\ \Rightarrow \quad &\boxed{dH = TdS + VdP + \sum_{j=1}^{\alpha} \mu_j dN_j}. \end{aligned}$$

The natural variables of the enthalpy are  $\{S, P, N\}$ . Out of the first order derivatives we obtain

$$\begin{aligned} T &= \left( \frac{\partial H}{\partial S} \right)_{P, N}, \\ V &= \left( \frac{\partial H}{\partial P} \right)_{S, N}, \end{aligned}$$

and the Maxwell relation

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

## EQUILIBRIUM CONDITIONS

An important property of the thermodynamic potentials is that, by keeping constant certain variables and changing others, one can calculate how the energy exchange with the environment happens.

*Example:* internal energy of a gas.

$$dU = TdS - PdV \quad \Rightarrow \quad \begin{array}{l} \text{a) } S = \text{const} : dU = -PdV \text{ (work)} \\ \text{b) } V = \text{const} : dU = TdS \text{ (heat)} \end{array}$$

The second law of thermodynamics,

$$TdS \geq \delta Q = dU + PdV - \sum_{j=1}^{\alpha} \mu_j dN_j, \quad (7)$$

can be written in very simple forms for the various exchanges between the system and its environment by using various thermodynamic potentials. The thermodynamic potentials allow for the description of the development of a system towards equilibrium state itself. Depending on a specific experimental situation, an adequate potential is to be used.

Both systems will interchange particles and energy until equilibrium is attained. In the equilibrium state

$$\begin{aligned} 0 &= dS = dS_1 + dS_2 \\ &= \left\{ \left( \frac{\partial S_1}{\partial U_1} \right)_{V_1, N_1} - \left( \frac{\partial S_2}{\partial U_2} \right)_{V_2, N_2} \right\} dU_1 \\ &+ \left\{ \left( \frac{\partial S_1}{\partial V_1} \right)_{U_1, N_1} - \left( \frac{\partial S_2}{\partial V_2} \right)_{U_2, N_2} \right\} dV_1 \\ &+ \left\{ \left( \frac{\partial S_1}{\partial N_1} \right)_{U_1, V_1} - \left( \frac{\partial S_2}{\partial N_2} \right)_{U_2, V_2} \right\} dN_1 \\ &= \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left( \frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 \\ &+ \left( -\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2} \right) dN_1. \end{aligned}$$

Since  $U_1$ ,  $V_1$ , and  $N_1$  are independent variables, each curly bracket  $\{\}$  has to be zero. Therefore,

$$T_1 = T_2 = T; \quad P_1 = P_2 = P; \quad \mu_1 = \mu_2 = \mu.$$

## ISOLATED SYSTEMS

In an isolated system

$$dU = 0 \ (\delta Q = 0),$$

$$dV = 0,$$

$$dN = 0.$$

Then, according to eq. ( 7 ),

$$dS \geq 0$$

$$dS = 0 \quad \text{in equilibrium.}$$

★ In all irreversible processes, under the conditions

$$U = \text{const},$$

$$V = \text{const},$$

$$N = \text{const},$$

the entropy increases and is maximum in the stationary equilibrium.  $S$  evolves to a maximum under conditions of fixed  $U, V, N$ . This is an *extremum* principle.



# SUMMARY OF THERMODYNAMIC POTENTIALS

Potential	Natural independent variables	Conjugated dependent variables	Maxwell relations and others
INTERNAL ENERGY $U$	$S, V, N$	$T = \left( \frac{\partial U}{\partial S} \right)_{V,N}$ $P = - \left( \frac{\partial U}{\partial V} \right)_{S,N}$ $\mu = \left( \frac{\partial U}{\partial N} \right)_{S,V}$	$\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V$
ENTROPY $S$	$U, V, N$	$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V,N}$ $\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{U,N}$ $-\frac{\mu}{T} = \left( \frac{\partial S}{\partial N} \right)_{U,N}$	
FREE ENERGY $F = U - TS$	$T, V, N$	$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N}$ $P = - \left( \frac{\partial F}{\partial V} \right)_{T,N}$ $\mu = \left( \frac{\partial F}{\partial N} \right)_{T,V}$	$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V$ $U = -T^2 \frac{\partial}{\partial T} \left( \frac{F}{T} \right)$

ENTHALPY $H = U + PV$	$S, P, N$	$T = \left( \frac{\partial H}{\partial S} \right)_{P,N}$ $V = \left( \frac{\partial H}{\partial P} \right)_{S,N}$ $\mu = \left( \frac{\partial H}{\partial N} \right)_{S,P}$	$\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P$
GIBBS ENTHALPY $G = H - TS = N\mu$	$T, P, N$	$S = - \left( \frac{\partial G}{\partial T} \right)_{P,N}$ $V = \left( \frac{\partial G}{\partial P} \right)_{T,N}$ $\mu = \left( \frac{\partial G}{\partial N} \right)_{T,P}$	$\left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P$ $H = -T^2 \frac{\partial}{\partial T} \left( \frac{G}{T} \right)$

Potential	Natural independent variables	Conjugated dependent variables	Maxwell relations and others
GRAND CANONICAL POTENTIAL $\Omega = F - \mu N = -PV$	$T, V, \mu$	$S = - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu}$ $P = - \left( \frac{\partial \Omega}{\partial V} \right)_{T, \mu}$ $N = - \left( \frac{\partial \Omega}{\partial \mu} \right)_{T, V}$	
CHEMICAL POTENTIAL $\mu = \frac{G}{N}$	$T$ $P$	$s = \frac{S}{N} = - \left( \frac{\partial \mu}{\partial T} \right)_P$ $v = \frac{V}{N} = \left( \frac{\partial \mu}{\partial P} \right)_T$	

## Thermodynamic Potentials and Maxwell's Relations

### The energy and entropy representations

We have noted that both  $S(U, V, N)$  and  $U(S, V, N)$  contain complete thermodynamic information. We will use the fundamental thermodynamic identity

$$dU = TdS - pdV + \mu dN$$

as an aid to memorizing the of temperature, pressure, and chemical potential from the consideration of equilibrium conditions. by calculating the appropriate partial derivatives we have

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

$$\left( \frac{\partial U}{\partial V} \right)_{S, N} = -p,$$

and

$$\left( \frac{\partial U}{\partial N} \right)_{S, V} = \mu.$$

We can also write the fundamental thermodynamic identity in the entropy representation:

$$dS = \frac{dU}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN$$

from which we find

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

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

and

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

By calculating the second partial derivatives of these quantities we find the Maxwell relations. Maxwell relations can be used to relate partial derivatives that are easily measurable to those that are not. Starting from

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T, \text{ and } \left(\frac{\partial U}{\partial V}\right)_{S,N} = -p,$$

we can calculate

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_{S,N}, \text{ and } \frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}.$$

Now since under appropriate conditions

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$$

then

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

This result is called a Maxwell relation. By considering the other second partial derivatives, we find two other Maxwell relations from the energy representation of the fundamental thermodynamic identity. These are:

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

Similarly, in the entropy representation, starting from

$$dS = \frac{dU}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN$$

and the results

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

we find the Maxwell relations:

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

## Enthalpy $H(S,p,N)$

We have already defined enthalpy as  $H = U + pV$ . We can calculate its differential and combine it with the fundamental thermodynamic identity to show that the natural variables of  $H$  are  $S$ ,  $p$ , and  $N$ .

$$H = U + pV$$

we have

$$dH = dU + d(pV) = dU + pdV + Vdp,$$

and so inserting

$$dU = TdS - pdV + \mu dN$$

we have

$$dH = TdS - pdV + \mu dN + pdV + Vdp$$

resulting in

$$dH = TdS + Vdp + \mu dN.$$

Thus, we can see that we can write  $H = H(S, p, N)$ , and as already noted  $S$ ,  $p$ , and  $N$  are the natural variables of  $H$ . We can continue as above to generate the definitions

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

and the Maxwell relations

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

In the above, as we transformed from  $U$  to  $H$ , we changed independent variables, *i.e.*, we replaced the variable  $V$  with its conjugate  $p$ . (Variables  $x$  and  $y$  that are related through the partial derivative of some function  $\xi$  such that  $\frac{\partial \xi}{\partial x} = y$  are called conjugate variables.) This is an example of a *Legendre transform*. In a Legendre transform, to replace one independent variable with its conjugate, a new function  $\zeta$  is defined by the addition or subtraction of the product of the conjugates  $x$  and  $y$ . In other words we define  $\zeta = \xi \pm xy$ . In the case of enthalpy we added  $pV$ , as we shall see, this was due to the presence of the term  $-pdV$  in the fundamental thermodynamic identity. To eliminate the variables  $S$  and  $N$  in terms of their conjugates, it will be necessary to subtract the products of the conjugate variables, as we shall soon see.

## Helmholtz Free Energy $F(T,V,N)$

This time as we transform from  $U$  to  $F$ , we replace the independent variable  $S$  with its conjugate  $T$ . In a Legendre transform, to replace one independent variable with its conjugate, a new function

is defined by the addition or subtraction of the product of the conjugates. Thus in this case we define the new function  $F$  by subtracting  $TS$  from  $U$ .

Starting from

$$F(T, V, N) = U(S, V, N) - TS$$

calculating the differentials

$$dF = dU - d(TS) = dU - TdS - SdT,$$

then inserting

$$dU = TdS - pdV + \mu dN$$

we find

$$dF = TdS - pdV + \mu dN - TdS - SdT$$

resulting in

$$dF = -SdT - pdV + \mu dN.$$

Thus, we have  $F = F(T, V, N)$  as desired. We continue as above to generate the definitions

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

and the Maxwell relations

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

## Gibbs Free Energy $G(T,p,N)$

This time as we transform from  $U$  to  $G$ , we replace the independent variables  $S$  and  $V$  with their conjugates  $T$  and  $p$ . We can think of this as a double Legendre transform of  $U$  or a single Legendre transform of either  $H$  or  $F$ .

Starting from

$$G(T, p, N) = U(S, V, N) - TS + pV$$

calculating the differentials

$$dG = dU - d(TS) + d(pV) = dU - TdS - SdT + pdV + Vdp,$$

then inserting

$$dU = TdS - pdV + \mu dN$$

we find

$$dG = TdS - pdV + \mu dN - TdS - SdT + pdV + Vdp$$



resulting in

$$dG = -SdT + Vdp + \mu dN.$$

Thus, we have  $G = G(T, p, N)$  as desired. We continue as above to generate the definitions

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

and the Maxwell relations

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

## The Grand Potential $\Omega(T, V, \mu)$

This time as we transform from  $U$  to  $\Omega$ , we replace the independent variables  $V$  and  $N$  with their conjugates,  $p$  and  $\mu$ . We can think of this as a double Legendre transform of  $U$  or a single transform of  $F$ . The grand potential is far less common in elementary work than the other potentials. It is used in open systems, that is systems that can exchange particles with the environment. We will, however, make some use of it.

Starting from

$$\Omega(T, V, \mu) = U(S, V, N) - TS - \mu N$$

calculating the differentials

$$d\Omega = dU - d(TS) - d(\mu N) = dU - SdT - TVdS - \mu dN - Nd\mu,$$

then inserting

$$dU = TdS - pdV + \mu dN$$

we find

$$d\Omega = TdS - pdV + \mu dN - TdS - SdT - \mu dN - Nd\mu$$

resulting in

$$d\Omega = -pdV - SdT - Nd\mu.$$

Thus, we have  $\Omega = \Omega(T, V, \mu)$  as desired. We continue as above to generate the definitions

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

and the Maxwell relations

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

## The Gibbs-Helmholtz Equation

### Derivation of the Gibbs-Helmholtz Equation

The Gibbs-Helmholtz equation provides information about the temperature dependence of the Gibbs free energy. The derivation of the Gibbs-Helmholtz equation begins with the fundamental equation for the Gibbs free energy  $G$ ,

$$dG = -SdT + VdP. \quad (1)$$

Using the relationships for an exact differential, we have that

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

Substituting this result for  $-S$  into the equation defining the Gibbs free energy,  $G = H - TS$ , yields

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P. \quad (3)$$

Dividing both sides of Eq. (3) by  $T$  leads to the result

$$\frac{G}{T} = \frac{H}{T} + \left(\frac{\partial G}{\partial T}\right)_P. \quad (4)$$

The Gibbs-Helmholtz equation involves the partial derivative with respect to temperature (at constant pressure) of the quantity on the left side of Eq. (4),  $G/T$ . Taking the partial derivative gives

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P. \quad (5)$$

Note that in Eq. (5), since  $G$  is a function of temperature,  $G = G(T)$ , the product rule was employed in order to evaluate the derivative of  $G/T$ . Factoring  $1/T$  out from the right side of Eq. (5) yields

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{1}{T}\left[-\frac{G}{T} + \left(\frac{\partial G}{\partial T}\right)_P\right]. \quad (6)$$

Substituting the relation for  $G/T$  from Eq. (4) gives the result

$$\begin{aligned} \left(\frac{\partial(G/T)}{\partial T}\right)_P &= \frac{1}{T}\left[-\frac{G}{T} + \left(\frac{\partial G}{\partial T}\right)_P\right] \\ &= \frac{1}{T}\left\{-\left[\frac{H}{T} + \left(\frac{\partial G}{\partial T}\right)_P\right] + \left(\frac{\partial G}{\partial T}\right)_P\right\} \\ \left(\frac{\partial(G/T)}{\partial T}\right)_P &= -\frac{H}{T^2}. \end{aligned} \quad (7)$$

Equation (7) provides one form of the Gibbs-Helmholtz equation.

Another useful form of the Gibbs-Helmholtz equation may be obtained by considering the derivative

$$\left( \frac{\partial(G/T)}{\partial(1/T)} \right)_P = -T^2 \left( \frac{\partial(G/T)}{\partial T} \right)_P. \quad (8)$$

The result in Eq. (8) may be derived by making the substitution  $u = 1/T$  such that  $du = -dT/T^2$ . Substituting the result for the partial derivative on the right from Eq. (7) leads to the primary form for the Gibbs-Helmholtz equation,

$$\left( \frac{\partial(G/T)}{\partial(1/T)} \right)_P = H. \quad (9)$$

Written in terms of the change in free energy, the Gibbs-Helmholtz equation is

$$\boxed{\left( \frac{\partial(\Delta G/T)}{\partial(1/T)} \right)_P = \Delta H.} \quad (10)$$

### Nernst's Heat Theorem of third law

The third law of thermodynamics is concerned with the limiting behavior of systems as the temperature approaches zero. The bulk of the thermodynamics does not require this postulate because in thermodynamics calculations usually only entropy differences are used. Consequently, the zero point of the entropy scale is often not important. However, we discuss the third law at this point because it closes the postulatory basis of thermodynamics.

The temperature is defined as

$$T \equiv \left( \frac{\partial U}{\partial S} \right)_{V, N_i} \quad (1)$$

Therefore, the third law states that

$$\lim_{T \rightarrow 0} S = 0 \quad (2)$$

Historically, Walter Nernst's formulation of the third law, called *Nernst's Heat Theorem*, in 1907 was somewhat weaker. He stated:

**"Any entropy changes in an isothermal reversible process approach zero as the temperature approaches zero, or**

$$\lim_{T \rightarrow 0} \Delta S_{T,rev} = 0 \quad (3)$$

We shall see in the following that Nernst's Heat Theorem is enclosed in the definition of the third law. The formulation of the third law that we are using (equation (2)) emerged several decades later through the work of *Francis Simons* and the formulation of *Max Planck*.

There are several ways to state the third law of thermodynamics. It turns out that all of them are equivalent, and that one can derive one from the other. Let us start with the following form, a statement that summarizes a lot of experimental observations:

**"It is impossible reduce the temperature of any systems to absolute zero in a finite number of steps."**

Let's discuss this in more detail.

Assume a system to be cooled by varying a parameter  $X$  from the initial state  $i$  to the finale state  $f$   $X_i$  to  $X_f$ . This cools the system from the temperature  $T_i$  to  $T_f$ . Using only the second law we can write for the entropy of the initial state

$$S(T_i, X_i) = S(0, X_i) + \int_0^{T_i} \left( \frac{\partial S}{\partial T} \right)_{X=X_i} dT \quad (4)$$

and for the final state

$$S(T_f, X_f) = S(0, X_f) + \int_0^{T_f} \left( \frac{\partial S}{\partial T} \right)_{X=X_f} dT \quad (5)$$

We can write  $dS$  as

$$dS = \frac{C_X}{T} dT \quad (6)$$

Equations (6) can be rewritten as:

$$\left( \frac{\partial S}{\partial T} \right)_X = \frac{C_X}{T} \quad (7)$$

Heat capacities are positive. Thus, maximum cooling can be obtained only if the process is reversible and only without thermal contact to the environment, i.e. adiabatically.

Reversibility implies:

$$S(0, X_i) + \int_0^{T_i} \left( \frac{\partial S}{\partial T} \right)_{X=X_i} dT = S(0, X_f) + \int_0^{T_f} \left( \frac{\partial S}{\partial T} \right)_{X=X_f} dT \quad (8)$$

According to the third law (2)

$$S(0, X_i) = S(0, X_f) \quad (9)$$

The temperature of the final state is zero, i.e.,  $T_f = 0$ . This implies:

$$\int_0^{T_i} \left( \frac{\partial S}{\partial T} \right)_{X=X_i} dT = 0 \quad (10)$$

This is impossible. We showed that absolute zero temperature cannot be achieved in a finite step and, consequently, on a finite number of steps. The fact that the entropies of all systems must be equal (zero) at  $T=0$ .

## Chemical Potential

The chemical potential of a substance  $i$  is the partial molar derivative of the free energy  $G$ , the enthalpy  $H$ , the Helmholtz energy  $A$ , or the internal energy  $U$  of substance  $i$ :

$$\mu_i = \left[ \frac{\partial G}{\partial n_i} \right]_{T,P,n_j} = \left[ \frac{\partial H}{\partial n_i} \right]_{S,P,n_j} = \left[ \frac{\partial A}{\partial n_i} \right]_{T,V,n_j} = \left[ \frac{\partial U}{\partial n_i} \right]_{S,V,n_j}$$

Matter flows spontaneously from a region of high chemical potential to a region of low chemical potential just like electric current flows from a region of high electric potential to a region of low electric potential and mass flows from a position of high gravitational potential to a position of low gravitational potential. The chemical potential can therefore be used to determine whether or not a system is in equilibrium. When the system is in equilibrium, the chemical potential of each substance will be the same in all the phases appearing in the system.



The ideal solution can be defined as a solution in which the chemical potential of each species is given by the expression:

$$\mu_i = \mu_i^0(T, P) + RT \ln x_i$$

In this expression,  $\mu_i^0(T, P)$  is the chemical potential of pure species i in the same state of aggregation as the solution; i.e. in a liquid mixture  $\mu_i^0(T, P)$  is the chemical potential of pure liquid i at temperature T and pressure P.  $\mu_i^0(T, P)$  is referred to as the standard state chemical potential. From the expression above, it is seen that the chemical potential of a species in an ideal solution is lower than the chemical potential of the pure component: the mole fraction is less than one and the second term is therefore negative.

### **TEXT / REFERENCE BOOKS**

1. F. Reif, Statistical and Thermal physics, McGraw Hill, International Edition, Singapore, 1979.
2. B.R. Agarwal and N. Eisnor, Statistiactal Mechanics, 2nd ed, Wiley Eastern Limited, New Delhi.
3. R. Huang, Statistical Mechanics, Wiley Eastern Ltd., New Delhi, 1983.
4. F. Mandl, Statistical physics, John Wiley, London, 1971.
5. C. Kittel, W. H. Freeman, Thermal Physics, 2nd ed. 1980.
6. F.W.Sears and G.L.Salinger, Thermodynamics, kinetic theory and statistical thermodynamics, 3rd edition, Narosa publishing house, 1998.

## QUESTION BANK

### PART-A

1. State and explain first law of thermodynamics.
2. Explain Heat capacity of gas molecules.
3. What is specific heat capacity?
4. Explain entropy and enthalpy in kinetics?
5. State and explain the second law of thermodynamics.
6. What is thermodynamic potential of a gas?
7. What is thermal equilibrium?
8. State and explain the third law of thermodynamics?
9. Explain about chemical potential of gas.
10. Explain the energy of particles in kinetics?
11. Write a note on Gibb's phase rule.

### PART-B

1. Explain entropy of a gas? Obtain an expression of entropy with its energy? Show that the entropy is constant in all reversible process of thermodynamic system.
2. Derive Maxwell's thermodynamic expression and deduce the other relations.
3. Derive Gibb's Helmholtz equations and obtain an expression for H.
4. Derive the first and second TdS equation.
5. a. Explain Nernst theorem of kinetics.  
b. Derive the expressions for thermodynamic potential.



**SATHYABAMA**

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

[www.sathyabama.ac.in](http://www.sathyabama.ac.in)

**SCHOOL OF SCIENCE AND HUMANITIES**

**DEPARTMENT OF PHYSICS**

## **UNIT – II - Thermodynamics and Statistical Mechanics – SPHA5202**

## II. KINETIC THEORY

### Equilibrium states dilute gas

A gas consists of a very large number of particles (typically  $10^{24}$  or many orders of magnitude more) occupying a volume of space that is very large compared to the size ( $10^{-10}$  m) of any typical atom or molecule. A system may be characterized as dilute based on the “average” spacing between its molecules

$$\delta \approx \sqrt[3]{\frac{1}{n}} \quad \text{or} \quad \frac{\delta}{\sigma} \approx \sqrt[3]{\frac{1}{n\sigma^3}}$$

where  $n$  is the number density (number of atoms per unit volume) and  $\sigma$  is the effective “diameter” of the molecule. We see that the relevant quantity here is the non-dimensional number density  $n^* = n\sigma^3$ . If  $n^* \ll 1$ , then the system can be described as dilute, in other words, the volume per particle ( $\sim n^{-1}$ ) is much larger than the volume of the particle ( $\sim \sigma^3$ ), or alternatively, the relative spacing  $\delta/\sigma$  is large.

In a dilute system one expects collisions between particles to be infrequent and, because of the absence of other interactions, particles to travel most of the time in straight lines.

### Binary collisions

The molecular collisions are responsible for establishing the equilibrium condition. In the absence of equilibrium, intermolecular interactions result in transport of macroscopic gas quantities, such as mass, momentum and energy. Under equilibrium conditions the distribution of molecular velocities is the same Maxwell-Boltzmann distribution at every configuration space location. In other words the effects of molecular collisions cancel each other (the distribution function is constant in time and configuration space) and therefore the details of individual collisions do not play a role in determining the distribution of molecular velocities. The situation is entirely different if we allow even the slightest deviation from equilibrium. In this case molecular collisions result in the transport of macroscopic quantities (such as mass, momentum and energy) accompanied by a gradual approach to the equilibrium velocity distribution. The details of the macroscopic transport and change of the distribution function are controlled by the specific nature of the molecular collision process. Molecular collisions represent the microscopic process governing all macroscopic transport phenomena.

We consider the process of two particle (or binary) collisions. For the sake of simplicity it will be assumed that the gas is composed of monatomic molecules which do not possess any internal degrees of freedom (or if the molecules are not monatomic their states of internal motion are assumed to be unaffected by the collisions).

### ***Center of mass and relative position coordinates***

It will be assumed that the molecules can be represented as point centers of force and they interact via conservative forces directed along the line connecting the two molecules.

Let us consider two molecules with masses  $m_1$  and  $m_2$ , position vectors  $r_1$  and  $r_2$ , and velocities  $v_1$  and  $v_2$ . It can be shown that the interaction between these two molecules depends only on their relative position and velocity. We introduce the radius vector of center of mass,  $r_c$ :

$$r_c = \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2} \quad \text{----- (1)}$$

The other quantity of physical interest is the relative position vector of the two particles,  $r$ :

$$r = r_1 - r_2 \quad \text{----- (2)}$$

The two molecules move under each other's influence and the two equations of motion can be written in the following form:

$$m_1 \frac{d^2 r_1}{dt^2} = F_{12} \quad m_2 \frac{d^2 r_2}{dt^2} = F_{21} \quad \text{----- (3)}$$

Here  $F_{12}$  and  $F_{21}$  are forces acting on molecules 1 and 2 due to the presence of the other molecule, respectively. These forces depend only on the relative position of the molecules,  $r$ , and the fact that the forces acting on the two particles are of equal magnitude and point in opposite directions,  $\mathbf{F}_{12}(\mathbf{r}) = -\mathbf{F}_{21}(\mathbf{r})$ . It can be easily seen that there is no force acting on the center of mass and consequently it does not accelerate (moves with constant velocity):

$$\frac{d^2 r_c}{dt^2} = \frac{1}{m_1 + m_2} \left[ m_1 \frac{d^2 r_1}{dt^2} + m_2 \frac{d^2 r_2}{dt^2} \right] = \frac{F_{12} + F_{21}}{m_1 + m_2} = 0 \quad \text{----- (4)}$$

One can also readily calculate the relative acceleration of the two molecules with respect to each other:

$$\frac{d^2 r}{dt^2} = \frac{d^2 r_1}{dt^2} - \frac{d^2 r_2}{dt^2} = \frac{F_{12}}{m_1} - \frac{F_{21}}{m_2} = \left( \frac{1}{m_1} + \frac{1}{m_2} \right) F_{12} \quad \text{----- (5)}$$



Equation (5) can be written as an equation of motion for a single particle with mass  $m^*$  (where  $m^*$  is the reduced mass of the two molecules) in a central field of force:

$$m^* \frac{d^2 r}{dt^2} = - \frac{dU(r)}{dr} e_r \quad \text{-----} \quad (6)$$

where  $e_r$  represents the unit vector along the relative position vector of the two molecules and  $U(r)$  is the potential of the conservative intermolecular force,  $F_{12}$ :

$$F_{12} = - \frac{dU(r)}{dr} e_r \quad \text{-----} \quad (7)$$

These results show that one may introduce a new set of independent variables which simplify the description of the collision. These new variables refer to the center of mass of the two molecules and to their relative position, velocity and acceleration. It was shown that the center of mass velocity remains constant during the interaction of the two molecules, while the relative motion of the molecules can be described as the motion of a single particle with mass  $m^*$  under the influence of a conservative central field of force characterized by potential  $U(r)$ .

### **Boltzmann Transport Equation**

In physics, specifically non-equilibrium statistical mechanics, the Boltzmann equation or Boltzmann transport equation (BTE) describes the statistical behaviour of a thermodynamic system not in thermodynamic equilibrium. It was devised by Ludwig Boltzmann in 1872. The classic example is a fluid with temperature gradients in space causing heat to flow from hotter regions to colder ones, by the random transport of particles. In the modern literature the term Boltzmann equation is often used in a more general sense and refers to any kinetic equation that describes the change of a macroscopic quantity in a thermodynamic system, such as energy, charge or particle number.

The equation arises not by statistical analysis of all the individual positions and momenta of each particle in the fluid; rather by considering the probability that a number of particles all occupy a very small region of space (mathematically written  $d^3r$ , where  $d$  means "differential", a very small change) centered at the tip of the position vector  $r$ , and have very nearly equal small changes in momenta from a momentum vector  $p$ , at an instant of time.

The Boltzmann equation can be used to determine how physical quantities change, such as heat energy and momentum, when a fluid is in transport, and other properties characteristic to fluids such as viscosity, thermal conductivity also electrical conductivity (by

treating the charge carriers in a material as a gas) can be derived. The equation is a linear stochastic partial differential equation, since the unknown function in the equation is a continuous random variable.

### The phase space and density function

The set of all possible positions  $\mathbf{r}$  and momenta  $\mathbf{p}$  is called the phase space of the system; in other words a set of three coordinates for each position coordinate  $x, y, z$ , and three more for each momentum component  $p_x, p_y, p_z$ . The entire space is 6-dimensional: a point in this space is  $(\mathbf{r}, \mathbf{p}) = (x, y, z, p_x, p_y, p_z)$ , and each coordinate is parameterized by time  $t$ .

The small volume ("differential volume element") is written

$$d^3r d^3p = dx dy dz dp_x dp_y dp_z$$

Since the probability of  $N$  molecules which *all* have  $\mathbf{r}$  and  $\mathbf{p}$  within  $d^3r d^3p$  is in question, at the heart of the equation is a quantity  $f$  which gives this probability per unit phase-space volume at an instant of time  $t$ . This is a probability density function:  $f(\mathbf{r}, \mathbf{p}, t)$ , defined so that,

$$dN = F(r, p, t) d^3r d^3p$$

is the number of molecules which *all* have positions lying within a volume element  $d^3r$  about  $\mathbf{r}$  and momenta lying within a momentum space element  $d^3p$  about  $\mathbf{p}$ , at time  $t$ . Integrating over a region of position space and momentum space gives the total number of particles which have positions and momenta in that region:

$$N = \int_{\text{positions}} d^3r \int_{\text{momenta}} d^3p f(r, p, t)$$

which is a 6-fold integral. While  $f$  is associated with a number of particles, the phase space is for one-particle (not all of them, which is usually the case with deterministic many-body systems), since only one  $\mathbf{r}$  and  $\mathbf{p}$  is in question. It is not part of the analysis to use  $\mathbf{r}_1, \mathbf{p}_1$  for particle 1,  $\mathbf{r}_2, \mathbf{p}_2$  for particle 2, etc. up to  $\mathbf{r}_N, \mathbf{p}_N$  for particle  $N$ .

It is assumed the particles in the system are identical (so each has an identical mass  $m$ ). For a mixture of more than one chemical species, one distribution is needed for each, see below.

## Principal statement

The general equation can then be written:

$$\frac{\partial f}{\partial t} = \left( \frac{\partial f}{\partial t} \right)_{force} + \left( \frac{\partial f}{\partial t} \right)_{diff} + \left( \frac{\partial f}{\partial t} \right)_{coll}$$

Where the "force" term corresponds to the forces exerted on the particles by an external influence (not by the particles themselves), the "diff" term represents the diffusion of particles, and "coll" is the collision term - accounting for the forces acting between particles in collisions. Expressions for each term on the right side are provided below.

## The force and diffusion terms

Consider particles described by  $f$ , each experiencing an *external* force  $\mathbf{F}$  not due to other particles. Suppose at time  $t$  some number of particles all have position  $\mathbf{r}$  within element  $d^3\mathbf{r}$  and momentum  $\mathbf{p}$  within  $d^3\mathbf{p}$ . If a force  $\mathbf{F}$  instantly acts on each particle, then at time  $t + \Delta t$  their position will be  $\mathbf{r} + \Delta\mathbf{r} = \mathbf{r} + \mathbf{p}\Delta t/m$  and momentum  $\mathbf{p} + \Delta\mathbf{p} = \mathbf{p} + \mathbf{F}\Delta t$ .

Then, in the absence of collisions,  $f$  must satisfy

$$f\left(r + \frac{p}{m}\Delta t, p + F\Delta t, t + \Delta t\right) d^3r d^3p = f(r, p, t) d^3r d^3p$$

Note that we have used the fact that the phase space volume element  $d^3\mathbf{r}d^3\mathbf{p}$  is constant, which can be shown using Hamilton's equations. However, since collisions do occur, the particle density in the phase-space volume  $d^3\mathbf{r}d^3\mathbf{p}$  changes, so

$$\begin{aligned} dN_{coll} &= \left( \frac{\partial f}{\partial t} \right)_{coll} \Delta t^3 d^3r d^3p & \text{----- (1)} \\ &= f\left(r + \frac{p}{m}\Delta t, p + F\Delta t, t + \Delta t\right) d^3r d^3p - f(r, p, t) d^3r d^3p \\ &= \Delta f \cdot d^3r d^3p \end{aligned}$$

Where  $\Delta f$  is the *total* change in  $f$ .

Dividing (1) by  $d^3\mathbf{r}d^3\mathbf{p}\Delta t$  and taking the limits  $\Delta t \rightarrow 0$  and  $\Delta f \rightarrow 0$ , we have

$$\left( \frac{df}{dt} \right) = \left( \frac{\partial f}{\partial t} \right)_{coll} \text{----- (2)}$$

The total differential of  $f$  is:

$$\begin{aligned}
df &= \frac{\partial f}{\partial t} dt + \left( \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy + \frac{\partial f}{\partial z} dz \right) + \left( \frac{\partial f}{\partial p_x} dp_x + \frac{\partial f}{\partial p_y} dp_y + \frac{\partial f}{\partial p_z} dp_z \right) \\
&= \left( \frac{\partial f}{\partial t} dt + \nabla f \cdot dr + \frac{\partial f}{\partial p} \cdot dp \right) \text{-----} (3) \\
&= \left( \frac{\partial f}{\partial t} dt + \nabla f \cdot \frac{p dt}{m} + \frac{\partial f}{\partial p} \cdot F dt \right)
\end{aligned}$$

Where  $\nabla$  is the gradient operator,  $\cdot$  is the dot product,

Dividing (3) by  $dt$  and substituting into (2), we get;

$$\frac{\partial f}{\partial t} + \frac{p}{m} \cdot \nabla f + F \cdot \frac{\partial f}{\partial p} = \left( \frac{\partial f}{\partial t} \right)_{coll} \text{-----} (4)$$

In this context,  $\mathbf{F}(\mathbf{r}, t)$  is the force field acting on the particles in the fluid, and  $m$  is the mass of the particles. The term on the right hand side is added to describe the effect of collisions between particles; if it is zero then the particles do not collide. The collisionless Boltzmann equation is often called the Vlasov equation.

### Validity of Boltzmann Transport Equation

This equation was originally derived for dilute gases. In the following some of the approximations of the Boltzmann transport equation and their implications are addressed. The solution of the Boltzmann transport equation with an external force  $F(\mathbf{r})$  provides the distribution function  $f_n(\mathbf{r}, P, t)$  from which macroscopic quantities can be derived. The right-hand side of (4) describes the changes to the distribution function induced by scattering. The particle's Group velocity is determined from the semiconductor band structure  $E_n(P)$  as  $v_n(P) = \hbar^{-1} \nabla_P E_n(P)$ .

In the parabolic band approximation,  $\hbar^{-1} \nabla_K E_n(P) = \hbar P / m^*$  and the particle's group velocity can be calculated from the effective mass tensor  $\hat{m}^*$ . The distribution function  $f_n(\mathbf{r}, P, t) d^3 P d^3 r$  defines the probability density to find a particle in  $d^3 P d^3 r$  at a given time  $t$ . Obviously, such a statistical description can only be appropriate when the number of carriers is large. Extremely down-scaled devices may contain too few carriers to justify this kind of statistical treatment.

Since carriers interact through their electric fields, the distribution function  $f_n(r, P, t)$  at a particular point in the six dimensional position-momentum (phase) space at a given time can only be determined from the knowledge of  $f_n$  in all other points. This would involve a treatment using an N-particle system and an N-particle distribution function. However, if the carrier-carrier correlations are weak, the N-particle distribution function can be contracted to a one-particle distribution function. Alternatively, the influence of other carriers can be treated through the self-consistent electric field and schemes where the Pauli exclusion principle is included.

A main assumption of the Boltzmann transport equation is that particles can be treated semi-classically, obeying Newton's law. Quantum mechanics enters the equation only through the band structure and the description of the collision term. Since both the position and the momentum of a particle are arguments of the distribution function, apparently the quantum mechanical uncertainty principle is  $\Delta p \Delta r \geq \hbar/2$  violated. Assuming a spread in particle energy of  $k_B T$ , one finds that the spread in position is

$$\Delta r \geq \hbar / (2 \sqrt{2 m^* k_B T}) = \lambda_B / 2 . \quad (5)$$

Here,  $\lambda_B$  denotes the particle's thermal average wavelength. Thus, one should not attempt to localize the particle's position exactly with respect to its thermal average wavelength. If the potential varies sharply on the scale of  $\lambda_B$ , which is typically in the order of 10 nm to 20 nm at room temperature, condition (5) is not satisfied, and instead of the Boltzmann equation a wave equation must be solved to study the propagation of a carrier wave through the device.

## THE H-THEOREM

$$H = \sum f_i \ln f_i dx dy dz dp_x dp_y dp_z \quad \text{-----} (1)$$

Boltzmann began by defining the function H for a dilute gas comprised of spherical particles where f is a distribution function which determines the number of particles  $n_i$  located in the spatial region (dx, dy, dz) and having momentum in the range (dp<sub>x</sub>, dp<sub>y</sub>, dp<sub>z</sub>) through the relation

$$n_i = f(x, y, z, p_x, p_y, p_z, t) dx dy dz dp_x dp_y dp_z \quad \text{-----} (2)$$

The term  $dx dy dz dp_x dp_y dp_z$ , is denoted  $\pi dV_\mu$  and is referred to as the "volume" of a cell in 6-dimensional  $\mu$ -space. The cells occupy equal "volumes" of  $\mu$ -space. Each particle has six degrees of freedom and could be completely specified by a point in  $\mu$ -space. Thus, a quantity of gas containing  $N$  particles can be represented by a swarm of  $N$  points in  $\mu$ -space and the distribution function  $f$  tells us how these  $N$  points are partitioned among the cells of  $\mu$ -space. The summation in Eq. (1) is taken over all of the cells in  $\mu$ -space. As indicated in Eq. (2), the distribution function could depend upon position, momentum, and time.

The function  $H$  can be restated as

$$H = N \sum_i \frac{n_i}{N} \ln \frac{n_i}{N} + \text{cons tan } t \quad \text{----- (3)}$$

If  $n_i/N$  could be taken as the probability of a particle being found in the  $i^{\text{th}}$  cell of  $\mu$ -space, we could write Eq. (3) as

$$H = N \sum_i P_i \ln P_i + \text{cons tan } t \quad \text{----- (4)}$$

The first right-hand term of Eq. (4) would appear to be related to the statistical mechanical entropy, but it must be remembered that the latter quantity refers to an equilibrium state and therefore the  $P_i$ 's should be the cell occupation probabilities when the equilibrium distribution prevails. Our substitution of  $n_i/N$  for  $P_i$  implies that the following relationship between  $H$  and  $S$  is valid only as equilibrium is approached

$$H = -\frac{S}{k} + \text{cons tan } t \quad \text{----- (5)}$$

(or)

$$-k \frac{dH}{dt} = \frac{dS}{dt} \quad \text{----- (6)}$$

The time derivative of  $S$  can therefore be obtained from the time derivative of  $H$  which in turn depends on the change in  $f$  with time. Particle collisions provide the mechanism for changes in  $f$  and when molecular chaos is assumed, it can be shown that

$$\frac{dH}{dt} \leq 0 \quad \text{----- (7)}$$

As per Eq. (6) this results in

$$\frac{dS}{dt} \geq 0 \quad \text{-----} \quad (8)$$

Thus, H can never increase and if Eq. (5) is valid, S can never decrease. These derivatives become zero at equilibrium where together forward and reverse collisions zero out and the Maxwell-Boltzmann distribution prevails

## Maxwell-Boltzmann Distributions

The Maxwell-Boltzmann equation, which forms the basis of the kinetic theory of gases, defines the distribution of speeds for a gas at a certain temperature. From this distribution function, the most probable speed, the average speed, and the root-mean-square speed can be derived.

## Introduction

The kinetic molecular theory is used to determine the motion of a molecule of an ideal gas under a certain set of conditions. However, when looking at a mole of ideal gas, it is impossible to measure the velocity of each molecule at every instant of time. Therefore, the Maxwell-Boltzmann distribution is used to determine how many molecules are moving between velocities  $v$  and  $v + dv$ . Assuming that the one-dimensional distributions are independent of one another, that the velocity in the  $y$  and  $z$  directions does not affect the  $x$  velocity, for example, the Maxwell-Boltzmann distribution is given by

$$\frac{dN}{N} = \left( \frac{m}{2\pi k_B T} \right)^{1/2} e^{\frac{-mc^2}{2k_B T}} dv \quad \text{-----} \quad (1)$$

Where

$dN/N$  is the fraction of molecules moving at velocity  $v$  to  $v + dv$ ,

$m$  is the mass of the molecule,

$k_b$  is the Boltzmann constant, and

$T$  is the absolute temperature.

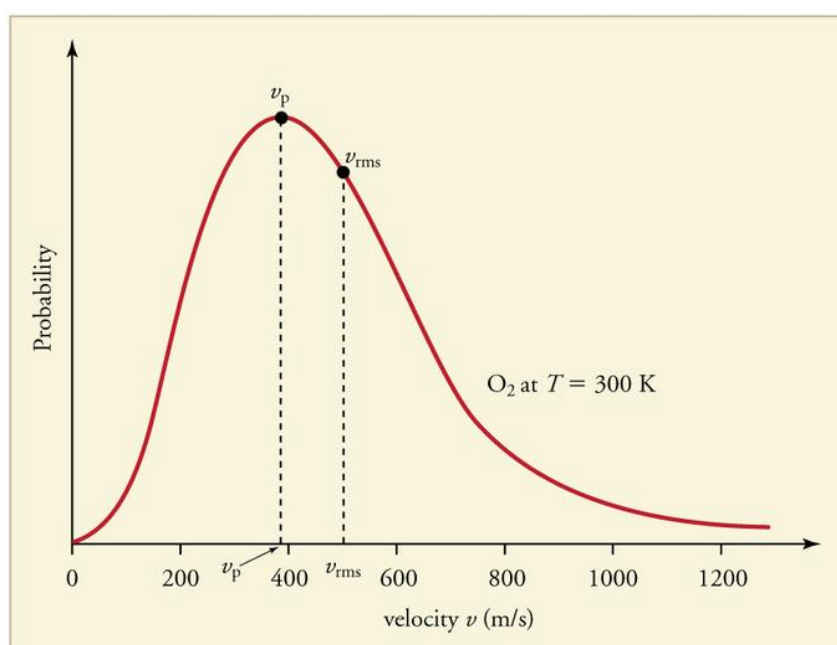
Additionally, the function can be written in terms of the scalar quantity speed  $c$  instead of the vector quantity velocity. This form of the function defines the distribution of the gas molecules moving at different speeds, between  $c_1$  and  $c_2$ , thus

$$f(c) = 4\pi c^2 \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mc^2}{2k_B T}} \quad \text{----- (2)}$$

Finally, the Maxwell-Boltzmann distribution can be used to determine the distribution of the kinetic energy of for a set of molecules. The distribution of the kinetic energy is identical to the distribution of the speeds for a certain gas at any temperature.

### Plotting the Maxwell-Boltzmann Distribution Function

Figure 1 shows the Maxwell-Boltzmann distribution of speeds for a certain gas at a certain temperature, such as nitrogen at 298 K. The speed at the top of the curve is called the most probable speed because the largest number of molecules has that speed.



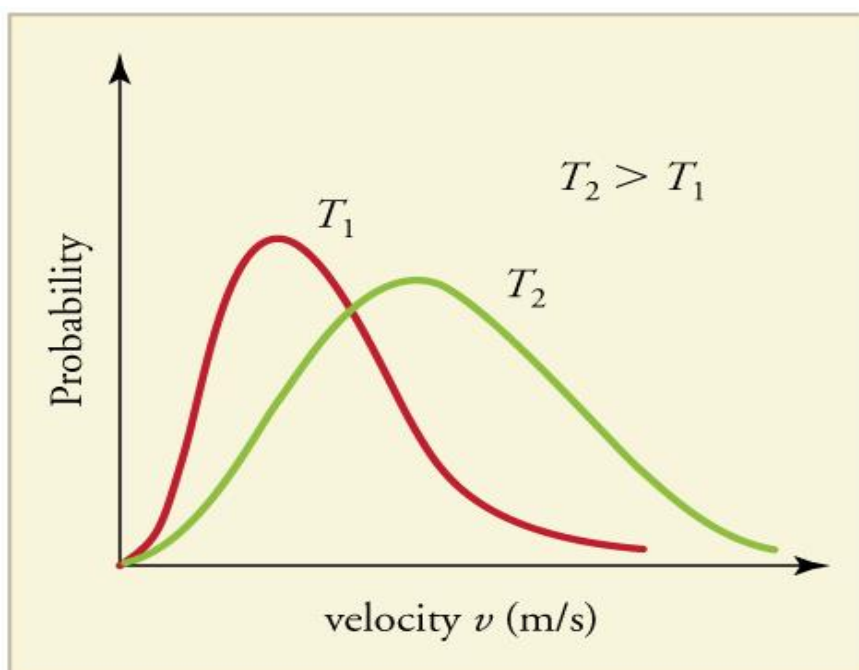
**Figure 1** The Maxwell-Boltzmann distribution is shifted to higher speeds and is broadened at higher temperatures.

Figure 2 shows how the Maxwell-Boltzmann distribution is affected by temperature. At lower temperatures, the molecules have less energy. Therefore, the speeds of the molecules are lower and the distribution has a smaller range. As the temperature of the molecules increases, the distribution flattens out. Because the molecules have greater energy at higher temperature, the molecules are moving faster.

Figure 3 shows the dependence of the Maxwell-Boltzmann distribution on molecule mass. On average, heavier molecules move more slowly than lighter molecules. Therefore,

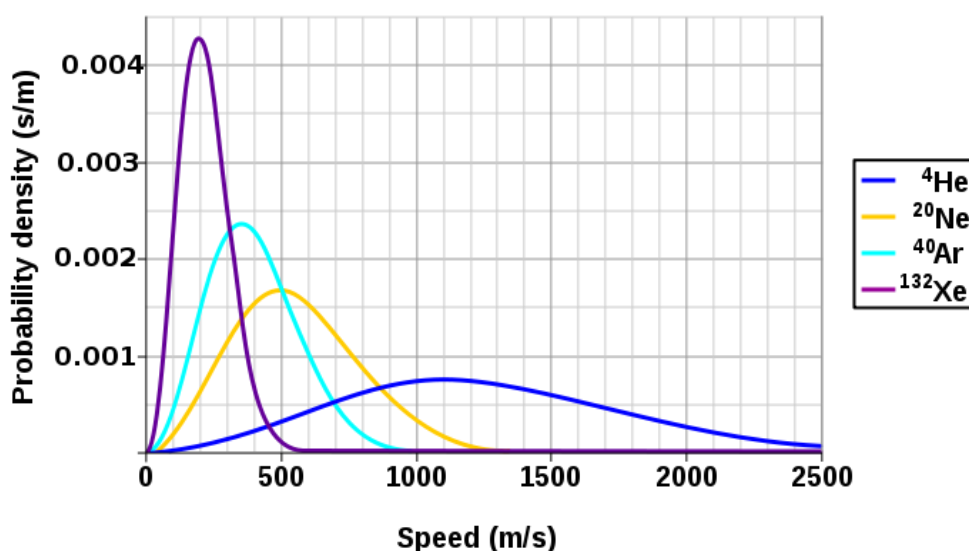


heavier molecules will have a smaller speed distribution, while lighter molecules will have a speed distribution that is more spread out.



**Figure 2:** The Maxwell-Boltzmann distribution is shifted to higher speeds and is broadened at higher temperatures.

#### Maxwell-Boltzmann Molecular Speed Distribution for Noble Gases



**Figure 3:** The speed probability density functions of the speeds of a few noble gases at a temperature of 298.15 K (25 °C). The y-axis is in s/m so that the area under any section of the curve (which represents the probability of the speed being in that range) is dimensionless.

## Related Speed Expressions

Three speed expressions can be derived from the Maxwell-Boltzmann distribution: the most probable speed, the average speed, and the root-mean-square speed. The most probable speed is the maximum value on the distribution plot. This is established by finding the velocity when the following derivative is zero.

$$\left. \frac{df(c)}{dc} \right|_{c_{mp}} = 0$$

which is  $C_{mp} = \sqrt{\frac{2RT}{M}}$  ----- (3)

The average speed is the sum of the speeds of all the molecules divided by the number of molecules.

$$C_{avg} = \int_0^{\infty} cf(c)dc = \sqrt{\frac{8RT}{\pi M}}$$
 ----- (4)

The root-mean-square speed is square root of the average speed-squared.

$$C_{rms} = \sqrt{\frac{3RT}{M}}$$
 ----- (5)

Where

$R$  is the gas constant,

$T$  is the absolute temperature and

$M$  is the molar mass of the gas.

It *always* follows that for gases that follow the Maxwell-Boltzmann distribution (if thermallized)

$$C_{mp} < C_{avg} < C_{rms}$$

## The Most probable Distribution

We are ultimately interested in the probability that a given distribution will occur. The reason for this is that we must have this information in order to obtain useful thermodynamic averages. The method used to obtain the distribution function of the ensemble of systems is known as the *method of the most probable distribution*. We begin with the statistical entropy,

$$S = k \ln W.$$

The weight,  $W$  (or thermodynamic probability) is the number of ways that distinguishable particles can be arranged into groups such  $a_0$  is the number in the zeroth group,  $a_1$  is the number in the first group etc. where  $A$  is the total number of systems in the ensemble.

$A$  = total number of systems.

$a_0, a_1, a_2 \dots$  = occupation numbers for system in each quantum state.

The overall probability that  $P_j$  that a system is in the  $j$ th quantum state is obtained by averaging  $a_j/A$  over all the allowed distributions.

Thus,  $P_j$  is given by

$$P_j = \frac{\langle a_j \rangle}{A} = \frac{1}{A} \frac{\sum_a W(a) a_j(a)}{\sum_a W(a)}$$

where the angle brackets indicate an ensemble average. Using this definition we can calculate any average property (i.e. any thermodynamic property) using the Gibbs postulate.

$$\langle M \rangle = \sum_j M_j P_j$$

The method of the most probable distribution is based on the idea that the average over  $a_j/A$  is identical to the most probable distribution (i.e. that the distribution is arbitrarily narrow in width). Physically, this results from the fact that we have so many particles in a typical system that the fluctuations from the mean are extremely (immeasurably) small.

If we think only of translation motion, McQuarrie shows that the number of states increases dramatically as the energy (and quantum number increase). Although the number of states is an increasing function the kinetic energy is fixed and must be distributed in some statistical manner among all of the available molecules.

The equivalence of the average probability of an occupation number and the most probable distribution is expressed as follows:

$$P_j = \frac{\langle a_j \rangle}{A} = \frac{a_j^*}{A}$$

To find the most probable distribution we maximize the probability function subject to two constraints.

Conservation of energy requires:

$$\sum_j a_j \epsilon_j = E$$

where  $\epsilon_j$  is the energy of the  $j$ th system in its quantum state.

Conservation of mass requires:

$$\sum_j a_j = A$$

which says only that the total number of the all of the systems in the ensemble must be A.

Using  $S = k \ln W$  we can reason that the system will tend towards the distribution among the  $a_j$  that maximizes S. This can be expressed as  $S_j(\nabla S / \nabla a_j) = 0$ .

This condition is satisfied by

$$S_j(\nabla \ln W / \nabla a_j) = 0$$

Subject to constraints

$$\sum_j \varepsilon_j da_j = 0$$

The most probable distribution is  $a_j/A = e^{a-be_j}$

$$\sum_j \frac{a_j}{A} = e^a \sum_j e^{-\beta \varepsilon_j}$$

Now we need to find the undetermined multipliers a and b.

The left hand side is 1. Thus, we have

$$\frac{a_j}{A} = \frac{e^{-\beta \varepsilon_j}}{\sum_i e^{-\beta \varepsilon_i}}$$

This determines a and defines the Boltzmann distribution.

We will show that  $b=1/kT$ . This identification will show the importance of temperature in the Boltzmann distribution. The distribution represents a thermally equilibrated most probable distribution over all energy levels.

The sum over all factors  $e^{-\beta \varepsilon_j}$  is given a name. It is called the molecular partition function, q.

$$q = \sum_j e^{-\beta \varepsilon_j}$$

The molecular partition function q gives an indication of the average number of states that are thermally accessible to a molecule at the temperature of the system.

## Transport Phenomena

In engineering, physics and chemistry, the study of **transport phenomena** concerns the exchange of mass, energy, and momentum between observed and studied systems. Mass, momentum, and heat transport all share a very similar mathematical framework, and the parallels between them are exploited in the study of transport phenomena. The fundamental analyses in all three subfields of mass, heat, and momentum transfer are often grounded in

the simple principle that the sum total of the quantities being studied must be conserved by the system and its environment. Thus, the different phenomena that lead to transport are each considered individually with the knowledge that the sum of their contributions must equal zero.

In physics, **transport phenomena** are all irreversible processes of statistical nature stemming from the random continuous motion of molecules, mostly observed in fluids. Every aspect of transport phenomena is grounded in two primary concepts: the conservation laws, and the constitutive equations. The conservation laws, which in the context of transport phenomena are formulated as continuity equations, describe how the quantity being studied must be conserved. The constitutive equations describe how the quantity in question responds to various stimuli via transport. Prominent examples include Fourier's Law of Heat Conduction and the Navier-Stokes equations, which describe, respectively, the response of heat flux to temperature gradients and the relationship between fluid flux and the forces applied to the fluid. These equations also demonstrate the deep connection between transport phenomena and thermodynamics, a connection that explains why transport phenomena are irreversible. Almost all of these physical phenomena ultimately involve systems seeking their lowest energy state in keeping with the principle of minimum energy. As they approach this state, they tend to achieve true thermodynamic equilibrium, at which point there are no longer any driving forces in the system and transport ceases. The various aspects of such equilibrium are directly connected to a specific transport: heat transfer is the system's attempt to achieve thermal equilibrium with its environment, just as mass and momentum transport move the system towards chemical and mechanical equilibrium.

Examples of transport processes include heat conduction (energy transfer), fluid flow (momentum transfer), molecular diffusion (mass transfer), radiation and electric charge transfer in semiconductors.

Transport phenomena have wide application. For example, in solid state physics, the motion and interaction of electrons, holes and phonons are studied under "transport phenomena". Another example is in biomedical engineering, where some transport phenomena of interest are thermoregulation, perfusion, and microfluidics. In chemical engineering, transport phenomena are studied in reactor design, analysis of molecular or diffusive transport mechanisms, and metallurgy.

The transport of mass, energy, and momentum can be affected by the presence of external sources:

- An odor dissipates more slowly (and may intensify) when the source of the odor remains present.
- The rate of cooling of a solid that is conducting heat depends on whether a heat source is applied.
- The gravitational force acting on a rain drop counteracts the resistance or drag imparted by the surrounding air.

### Mean Free Path

**Mean Free Path** ( $l$ ), the mean length of the path traversed by a particle between two successive collisions with other particles. The concept of mean free path is used extensively in calculations of various transfer processes, such as viscosity, heat conduction, diffusion, and electrical conduction.

According to the kinetic theory of gases, molecules move uniformly and rectilinearly from collision to collision. If a molecule traverses an average path  $v$  in 1 sec, undergoing in the process  $\nu$  elastic collisions with similar molecules, then

$$\bar{l} = v/\nu = 1/n\sigma\sqrt{2}$$

where  $n$  is the number of molecules per unit volume (the density of the gas) and  $\sigma$  is the effective cross section of the molecule. As the density of the gas (its pressure) increases, the mean free path decreases, since the number of collisions  $\nu$  per sec increases. A rise in temperature or in the intensity of motion of the molecules leads to a certain decline in  $\nu$  and consequently to an increase in  $\sigma$ . For ordinary molecular gases under normal conditions (at atmospheric pressure and 20°C),  $l \sim 10^{-5}$  cm, which is approximately 100 times greater than the average distance between molecules.

In many cases the concept of mean free path is also applicable to particles whose motion and interaction conform to the laws of quantum mechanics (such as conduction electrons in a solid, neutrons in weakly absorbing mediums, and photons in stars), but the calculation of the mean free path for such particles is more difficult.

## Commonalities among phenomena

An important principle in the study of transport phenomena is analogy between phenomena.

### Diffusion

There are some notable similarities in equations for momentum, energy, and mass transfer which can all be transported by diffusion, as illustrated by the following examples:

- Mass: the spreading and dissipation of odors in air is an example of mass diffusion.
- Energy: the conduction of heat in a solid material is an example of heat diffusion.
- Momentum: the drag experienced by a rain drop as it falls in the atmosphere is an example of momentum diffusion (the rain drop loses momentum to the surrounding air through viscous stresses and decelerates).

The molecular transfer equations of Newton's law for fluid momentum, Fourier's law for heat, and Fick's law for mass are very similar. One can convert from one transfer coefficient to another in order to compare all three different transport phenomena.

### Momentum transfer

In momentum transfer, the fluid is treated as a continuous distribution of matter. The study of momentum transfer or fluid mechanics can be divided into two branches: fluid statics (fluids at rest), and fluid dynamics (fluids in motion). When a fluid is flowing in the  $x$  direction parallel to a solid surface, the fluid has  $x$ -directed momentum, and its concentration is  $\rho v_x$ . By random diffusion of molecules there is an exchange of molecules in the  $z$  direction. Hence the  $x$ -directed momentum has been transferred in the  $z$ -direction from the faster- to the slower-moving layer. The equation for momentum transport is Newton's Law of Viscosity written as follows:

$$T_{zx} = -\frac{\partial \rho v_x}{\partial z}$$

where  $\tau_{zx}$  is the flux of  $x$ -directed momentum in the  $z$  direction,  $\nu$  is  $\mu/\rho$ , the momentum diffusivity  $z$  is the distance of transport or diffusion,  $\rho$  is the density, and  $\mu$  is the viscosity. Newton's Law is the simplest relationship between the flux of momentum and the velocity gradient.

## Mass transfer

When a system contains two or more components whose concentration vary from point to point, there is a natural tendency for mass to be transferred, minimizing any concentration difference within the system. Mass Transfer in a system is governed by Fick's First Law: Diffusion flux from higher concentration to lower concentration is proportional to the gradient of the concentration of the substance and the diffusivity of the substance in the medium. Mass transfer can take place due to different driving forces. Some of them are:

- Mass can be transferred by the action of a pressure gradient (pressure diffusion)
- Forced diffusion occurs because of the action of some external force
- Diffusion can be caused by temperature gradients (thermal diffusion)
- Diffusion can be caused by differences in chemical potential

This can be compared to Fourier's Law for conduction of heat:

$$J_{AY} = -D_{AB} \frac{\partial C_A}{\partial y}$$

where D is the diffusivity constant.

## Energy transfer

All process in engineering involves the transfer of energy. Some examples are the heating and cooling of process streams, phase changes, distillations, etc. The basic principle is the first law of thermodynamics which is expressed as follows for a static system:

$$q = -K \frac{dT}{dx}$$

The net flux of energy through a system equals the conductivity times the rate of change of temperature with respect to position.

For other systems that involve turbulent flow, complex geometries or difficult boundary conditions another equation would be easier to use:

$$Q = h.A.\Delta T$$



where  $A$  is the surface area,  $\Delta T$  is the temperature driving force,  $Q$  is the heat flow per unit time, and  $h$  is the heat transfer coefficient.

Within heat transfer, two types of convection can occur:

Forced convection can occur in both laminar and turbulent flow. In the situation of laminar flow in circular tubes, several dimensionless numbers are used such as Nusselt number, Reynolds number, and Prandtl. The commonly used equation is:

$$Nu_a = \frac{h_a D}{K}$$

Natural or free convection is a function of Grashof and Prandtl numbers. The complexities of free convection heat transfer make it necessary to mainly use empirical relations from experimental data.

### Special Cases of Navier-Stoke equation:

- **Incompressible fluid** - In fluid dynamics, an incompressible fluid is a fluid whose density is constant. It is the same throughout space and it does not change through time. According to the continuity equation, it also implies  $\nabla \cdot \mathbf{u} = 0$ . It is an idealization used to simplify analysis. In reality, all fluids are compressible to some extent.
- **Inviscid or Stokes flow** - Viscous problems are those in which fluid friction have significant effects on the solution. Problems for which friction can safely be neglected are called inviscid. The Reynolds number ( $Re = (\rho u_s L) / \mu$ , where  $u_s$  is the mean fluid velocity, and  $L$  is the characteristic length, e.g., the cross-section of the pipe) can be used to evaluate whether viscous or inviscid equations are appropriate to the problem. High Reynolds numbers indicate that the inertial forces are more significant than the viscous forces. However, even in high Reynolds number regimes certain problems require that viscosity be included. In particular, problems calculating net forces on bodies (such as the wings on aircraft) should use viscous equations. Stokes flow occurs at very low Reynold's numbers, such that inertial forces can be neglected compared to viscous forces.

- **Steady flow** - Another simplification of the equations is to set all changes of fluid properties with time to zero. These are called steady flow, and are applicable to a large class of problems, such as lift and drag on a wing or flow through a pipe.
- **Boussinesq approximation** - In fluid dynamics, the Boussinesq approximation is used in the field of buoyancy-driven flow. It states that density differences are sufficiently small to be neglected, except where they appear in terms multiplied by  $g$ , the acceleration due to gravity. The essence of the Boussinesq approximation is that the difference in inertia is negligible but gravity is sufficiently strong to make the specific weight appreciably different between the two fluids. Boussinesq flows are common in nature (such as atmospheric fronts, oceanic circulation, downhill winds), industry (dense gas dispersion, fume cupboard ventilation), and the built environment (natural ventilation, central heating). The approximation is extremely accurate for many such flows, and makes the mathematics and physics simpler.

**Laminar vs turbulent flow** - Turbulence is flow dominated by recirculation, eddies, and apparent randomness (see Figure 01). Flow in which turbulence is not exhibited is called laminar (see Figure 02). It is believed that turbulent flows obey the Navier-Stokes equations. However, the flow is so complex that it is not possible to solve turbulent problems from first principles with the computational tools available today or likely to be available in the near future. Turbulence is instead modeled using one of a number of turbulence models and coupled with a flow solver that assumes laminar flow outside a turbulent region. Turbulence usually occurs below a Reynold's numbers of 3000. It causes increased energy loss (as heat), more drag (on the moving body), and generates sound wave (noise). Modern vehicle and aircraft designs always try to minimize the turbulence by adopting a smooth surface and streamlined contour.

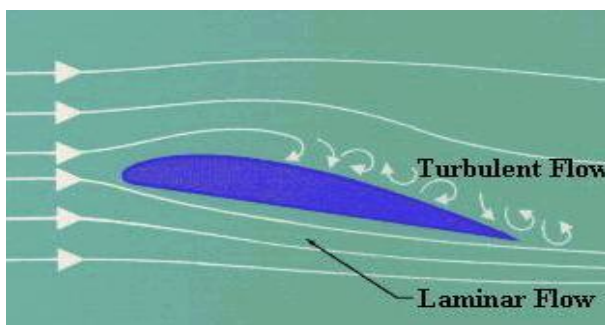


Figure 1 Turbulent Flow

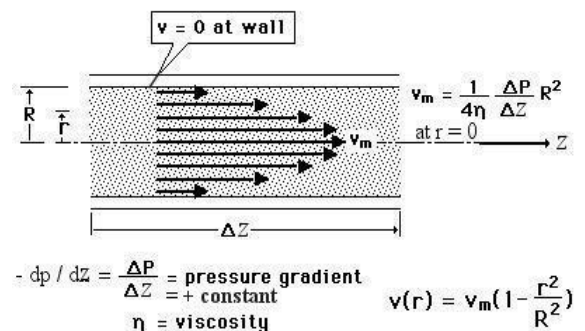


Figure 02 Laminar Flow

## **TEXT / REFERENCE BOOKS**

1. F. Reif, Statistical and Thermal physics, McGraw Hill, International Edition, Singapore, 1979.
2. B.R. Agarwal and N. Eisnor, Statistiactal Mechanics, 2nd ed, Wiley Eastern Limited, New Delhi.
3. R. Huang, Statistical Mechanics, Wiley Eastern Ltd., New Delhi, 1983.
4. F. Mandl, Statistical physics, John Wiley, London, 1971.
5. C. Kittel, W. H. Freeman, Thermal Physics, 2nd ed. 1980.
6. F.W.Sears and G.L.Salinger, Thermodynamics, kinetic theory and statistical thermodynamics, 3rd edition, Narosa publishing house, 1998.

## QUESTION BANK

### Part-A

1. Explain mean free path of a gas molecules and describe " $\lambda$ " of a gas molecules.
2. Explain transport phenomena of a gas.
3. Explain different conservation laws in kinetics.
4. What is hydrodynamics-Explain viscous hydrodynamics?
5. Describe TdS equation in Thermodynamics.
6. Explain binary collisions in gas molecules.
7. What are the limitations of Boltz-Man distribution law?
8. What is zero order approximation?
9. What is first order approximation?
10. What are the postulates of kinetic theories of gases?

### PART-B

1. Derive Boltzmann-H theorem of gas molecules.
2. Derive Maxwell's Boltzmann distribution law and obtain most probable distribution equation of velocity.
3. Explain about the transport phenomena of gas molecules and obtain the expression for  $\lambda$  using viscous hydrostatics.
4. Explain different types of conservation laws of mass, energy and momentum.
5. Obtain the expression for Navier-Stokes equation. What is the importance of this equation in Thermodynamics
6. Describe Zero and first order approximation of a gas and deduce the expression.
7. Describe the theory of viscous hydrodynamics and give one example in viscous hydrodynamics.



**SATHYABAMA**

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

[www.sathyabama.ac.in](http://www.sathyabama.ac.in)

**SCHOOL OF SCIENCE AND HUMANITIES**

**DEPARTMENT OF PHYSICS**

## **UNIT – III - Thermodynamics and Statistical Mechanics – SPHA5202**

### III. CLASSICAL STATISTICAL MECHANICS

#### Microstate and Macrostate

In statistical mechanics, a **microstate** is a specific microscopic configuration of a thermodynamic system that the system may occupy with a certain probability in the course of its thermal fluctuations. In contrast, the **macrostate** of a system refers to its macroscopic properties, such as its temperature, pressure, volume and density. Treatments on statistical mechanics, define a macrostate as follows. A particular set of values of energy, number of particles and volume of an isolated thermodynamic system is said to specify a particular macrostate of it. In this description, microstates appear as different possible ways the system can achieve a particular macrostate.

A macrostate is characterized by a probability distribution of possible states across a certain statistical ensemble of all microstates. This distribution describes the probability of finding the system in a certain microstate. In the thermodynamic limit, the microstates visited by a macroscopic system during its fluctuations all have the same macroscopic properties.

Kinetic theory studies the macroscopic properties of large numbers of particles, starting from their (classical) equations of motion. Thermodynamics describes the equilibrium behavior of macroscopic objects in terms of concepts such as work, heat, and entropy. The phenomenological laws of thermodynamics tell us how these quantities are constrained as a system approaches its equilibrium. At the microscopic level, we know that these systems are composed of particles (atoms, molecules), whose interactions and dynamics are reasonably well understood in terms of more fundamental theories. If these microscopic descriptions are complete, we should be able to account for the macroscopic behavior, i.e. derive the laws governing the macroscopic state functions in equilibrium. Kinetic theory attempts to achieve this objective.

## Statistical equilibrium

Statistical equilibrium is that state of closed statistical system in which the average values of all the physical quantities characterizing the state are independent of time.

Statistical equilibrium is one of the basic concepts of statistical mechanics, where it plays the same role as the thermodynamics

equilibrium in thermodynamics. Statistical equilibrium is not balanced in the mechanical sense, since small fluctuations

do not cease in the system when this state obtains. The theory of statistical equilibrium is given in statistical mechanics, which describes statistical equilibrium in terms of Gibbs's microcanonical, canonical or grand canonical ensembles depending on the type of contact between the system and its surroundings.

## Phase Space

- Phase Space: a concept of classical Statistical Mechanics
- Each Phase Space dimension corresponds to a particle degree of freedom
- 3 dimensions correspond to Position in (real) space:  $x, y, z$
- • 3 dimensions correspond to Momentum:  $p_x, p_y, p_z$  (or Energy and direction:  $E, \theta, \phi$ )
- More dimensions may be envisaged, corresponding to other possible degrees of freedom, such as quantum numbers: spin, etc.
- Each particle is represented by a point in phase space
- Time can also be considered as a coordinate, or it can be considered as an independent variable: the variation of the other phase space coordinates as a function of time (the trajectory of a phase space point) constitutes a particle "history".

Consider an isolated system with  $N$  particles (components). The complete description of this system is given by the generalized coordinates:

$$q = (q_1, \dots, q_{3N}),$$

$$p = (p_1, \dots, p_{3N}).$$

We define the phase space as follows.

Phase space:  $6N$ -dimensional space whose points are given by the  $6N$  values of

$$(q_1, \dots, q_{3N}, p_1, \dots, p_{3N}).$$

**Properties of phase space:**

- Phase space is a cartesian space;
- It is non-metric, i.e., one cannot define invariant distances in the phase space. This is also the case for the PV -state space.

For N particles, the total numbers of degrees of freedom is 6N, and therefore the total phase space is 6N-dimensional. The motion of the particles is governed deterministically by the Hamiltonian

$$H(p, q) = \sum_{i=1}^N \frac{\vec{P}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} V(\vec{q}_i - \vec{q}_j)$$

Where  $V(\vec{q}_i - \vec{q}_j)$  is the inter-particle potential. The equations of motion of the particles are

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

$i = 1, \dots, 6N$ , with certain initial conditions.

The phase space is also called  $\Gamma$ -space. A point (representative point) in this space corresponds to a state of the N-body system at a given time, i.e, to the microstate of the system.

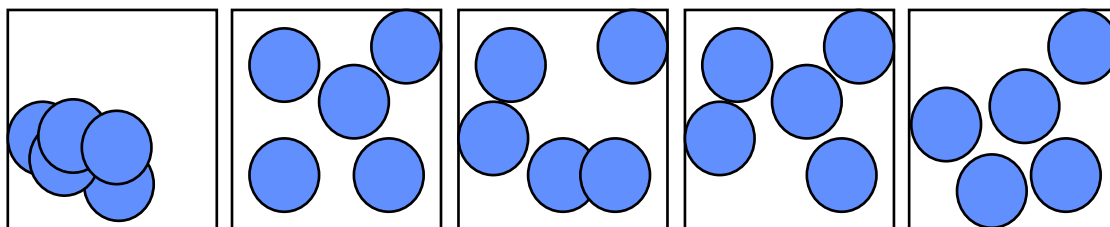
A trajectory in the phase space corresponds to the time evolution of the microstate. This trajectory never intersects with itself since the solution of the system of equations of motion is unique given certain initial conditions (self-avoiding random walk).

If H does not depend explicitly on time, in which case energy is a conserved quantity, all trajectories in phase space lie on an energy surface which is a hypersurface in  $\Gamma$ -space.

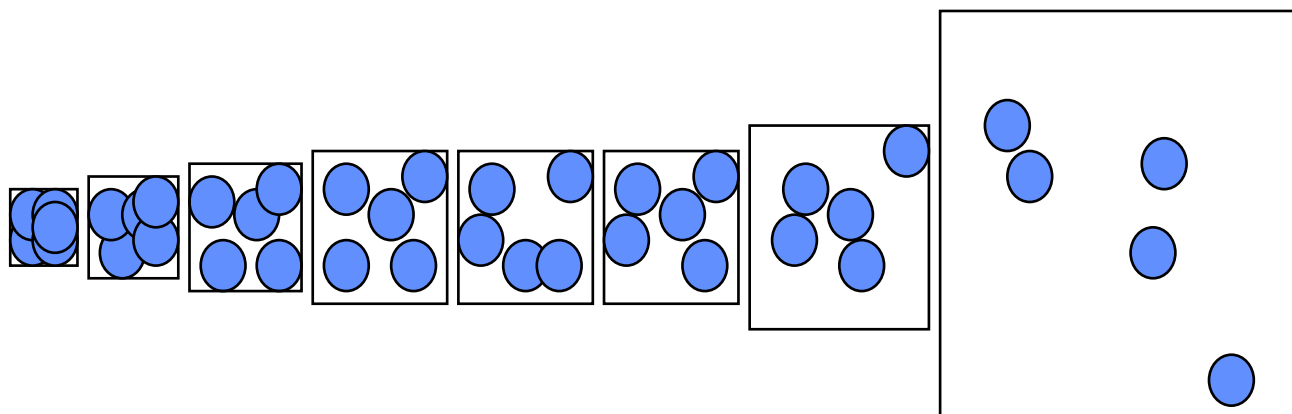


## Ensembles

A key concept in statistical mechanics is the *ensemble*. An ensemble is a collection of microstates of system of molecules, all having in common one or more extensive properties. An ensemble is also defined as a large number of points in the phase space that can be described by a density function  $\rho(q_i, p_i)$ . Additionally, an ensemble defines a probability distribution  $\pi$  accords a weight to each element (microstate) of the ensemble. These statements require some elaboration. A *microstate* of a system of molecules is a complete specification of all positions and momenta of all molecules (*i.e.*, all atoms in all molecules, but for brevity we will leave this implied). This is to be distinguished from a thermodynamic state, which entails specification of very few features, *e.g.* just the temperature, density and total mass. An extensive quantity is used here in the same sense it is known in thermodynamics—it is a property that relates to the total amount of material in the system. Most frequently we encounter the total energy, the total volume, and/or the total number of molecules (of one or more species, if a mixture) as extensive properties. Thus an ensemble could be a collection of all the ways that a set of  $N$  molecules could be arranged (specifying the location and momentum of each) in a system of fixed volume. As an example, in Illustration 1 we show a few elements of an ensemble of five molecules.



If a particular extensive variable is not selected as one that all elements of the ensemble have in common, then all physically possible values of that variable are represented in the collection. For example, Illustration 2 presents some of the elements of an ensemble in which only the total number of molecules is fixed.



The elements are not constrained to have the same volume, so all possible volumes from zero to infinity are represented. Likewise in both Illustrations 1 and 2 the energy is not selected as one of the common extensive variables. So we see among the displayed elements configurations in which molecules overlap. These high-energy states are included in the ensemble, even though we do not expect them to arise in the real system. The likelihood of observing a given element of an ensemble—its physical relevance—comes into play with the probability distribution  $\pi$  that forms part of the definition of the ensemble.

Any extensive property omitted from the specification of the ensemble is replaced by its conjugate intensive property. So, for example, if the energy is not specified to be common to all ensemble elements, then there is a temperature variable associated with the ensemble. These intensive properties enter into the weighting distribution  $\pi$  in a way that will be discussed shortly. It is common to refer to an ensemble by the set of independent variables that make up its definition. Thus the TVN ensemble collects all microstates of the same volume and molecular number, and has temperature as the third independent variable. The more important ensembles have specific names given to them. These are

- Microcanonical ensemble (EVN)
- Canonical ensemble (TVN)
- Isothermal-isobaric ensemble (TPN)
- Grand-canonical ensemble ( $TV\mu$ )

## Microcanonical ensemble (EVN)

In statistical mechanics, a **microcanonical ensemble** is the statistical ensemble that is used to represent the possible states of a mechanical system which has an exactly specified total energy. The system is assumed to be isolated in the sense that the system cannot exchange energy or particles with its environment, so that (by conservation of energy) the energy of the system remains exactly known as time goes on. The system's energy, composition, volume, and shape are kept the same in all possible states of the system.

The macroscopic variables of the microcanonical ensemble are quantities such as the total number of particles in the system (symbol:  $N$ ), the system's volume (symbol:  $V$ ) each which influence the nature of the system's internal states, as well as the total energy in the system (symbol:  $E$ ). This ensemble is therefore sometimes called the  **$NVE$  ensemble**, as each of these three quantities is a constant of the ensemble.

In simple terms, the microcanonical ensemble is defined by assigning an equal probability to every microstate whose energy falls within a range centered at  $E$ . All other microstates are given a probability of zero. Since the probabilities must add up to 1, the probability  $P$  is the inverse of the number of microstates  $W$  within the range of energy,

$$P = \frac{1}{W}$$

The range of energy is then reduced in width until it is infinitesimally narrow, still centered at  $E$ . In the limit of this process, the microcanonical ensemble is obtained.

The microcanonical ensemble is sometimes considered to be the fundamental distribution of statistical thermodynamics, as its form can be justified on elementary grounds such as the principle of indifference: the microcanonical ensemble describes the possible states of an isolated mechanical system when the energy is known exactly, but without any more information about the internal state. Also, in some special systems the evolution is ergodic in which case the microcanonical ensemble is equal to the time-ensemble when starting out with a single state of energy  $E$  (a time-ensemble is the ensemble formed of all future states evolved from a single initial state).

In practice, the microcanonical ensemble does not correspond to an experimentally realistic situation. With a real physical system there is at least some uncertainty in energy, due to uncontrolled factors in the preparation of the system. Besides the difficulty of finding an experimental analogue, it is difficult to carry out calculations that satisfy exactly the

requirement of fixed energy since it prevents logically independent parts of the system from being analyzed separately. Moreover there are ambiguities regarding the appropriate definitions of quantities such as entropy and temperature in the microcanonical ensemble.

Systems in thermal equilibrium with their environment have uncertainty in energy, and are instead described by the canonical ensemble or the grand canonical ensemble, the latter if the system is also in equilibrium with its environment in respect to particle exchange.

## Properties

- *Statistical equilibrium* (steady state): A microcanonical ensemble does not evolve over time, despite the fact that every constituent of the ensemble is in motion. This is because the ensemble is defined strictly as a function of a conserved quantity of the system (energy).
- *Maximum information entropy*: For a given mechanical system (fixed  $N$ ,  $V$ ) and a given range of energy, the uniform distribution of probability over microstates (as in the microcanonical ensemble) maximizes the ensemble average  $-\langle \log P \rangle$ .
- Three different quantities called "entropy" can be defined for the microcanonical ensemble. Each can be defined in terms of the phase volume function  $\nu(E)$  which counts the total number of states with energy less than  $E$ .

## Grand canonical ensemble

In statistical mechanics, a **grand canonical ensemble** is the statistical ensemble that is used to represent the possible states of a mechanical system of particles that is being maintained in thermodynamic equilibrium (thermal and chemical) with a reservoir. The system is said to be open in the sense that the system can exchange energy and particles with a reservoir, so that various possible states of the system can differ in both their total energy and total number of particles. The system's volume, shape, and other external coordinates are kept the same in all possible states of the system.

The thermodynamic variables of the grand canonical ensemble are chemical potential (symbol:  $\mu$ ) and absolute temperature (symbol:  $T$ ). The ensemble is also dependent on mechanical variables such as volume (symbol:  $V$ ) which influence the nature of the system's

internal states. This ensemble is therefore sometimes called the  **$\mu VT$  ensemble**, as each of these three quantities are constants of the ensemble.

## Properties

- *Uniqueness*: The grand canonical ensemble is uniquely determined for a given system at given temperature and given chemical potentials, and does not depend on arbitrary choices such as choice of coordinate system (classical mechanics) or basis (quantum mechanics).
- *Statistical equilibrium (steady state)*: A grand canonical ensemble does not evolve over time, despite the fact that the underlying system is in constant motion. Indeed, the ensemble is only a function of the conserved quantities of the system (energy and particle numbers).
- *Thermal and chemical equilibrium with other systems*: Two systems, each described by a grand canonical ensemble of equal temperature and chemical potentials, brought into thermal and chemical contact<sup>[note 2]</sup> will remain unchanged, and the resulting combined system will be described by a combined grand canonical ensemble of the same temperature and chemical potentials.
- *Maximum entropy*: For given mechanical parameters (fixed  $V$ ), the grand canonical ensemble average of the log-probability  $-\langle \log P \rangle$  (also called the "entropy") is the maximum possible for any ensemble (i.e. probability distribution  $P$ ) with the same  $\langle E \rangle$ ,  $\langle N_1 \rangle$ , etc.
- *Minimum grand potential*: For given mechanical parameters (fixed  $V$ ) and given values of  $T$ ,  $\mu_1$ , ...,  $\mu_s$ , the ensemble average  $\langle E + kT \log P - \mu_1 N_1 - \dots - \mu_s N_s \rangle$  is the lowest possible of any ensemble.

## Liouville's Theorem

Consider a large number of particles, perhaps in a beam. These particles can be described by one point in phase space per particle. For really large numbers of particles in a system, or if we consider a theoretical ensemble of particles, the system can be described as a density  $\rho(q_i, p_i)$  which is a function of the position in phase space.

Liouville's Theorem states that the density of particles in phase space is a constant

$\frac{d\rho}{dt} = 0$ , so we wish to calculate the rate of change of the density of particles. Imagine we shoot a burst of particles at the moon. The burst is localized in space and in momentum. The burst moves toward the moon and so clearly the density near the earth is decreased, however, the density we are interested in is essentially, the density around one of the particles, not the density at some fixed point. That is, the point in phase space at which we wish to measure the density, moves with the particles. The bunch of particles spreads out in coordinates space but the coordinate is highly correlated with the momentum so the density in phase space can remain constant.

To prove Liouville's theorem, we will calculate the rate of change of the number of particles in an infinitesimal hypercube in phase space. Consider the cube face perpendicular to  $q_k$  for example. The flow of particles through the face is  $\rho \dot{q}_k dp_k$  times all the other dimensions of the face  $dq_j dp_j$  for  $j \neq k$ . Then the rate of change of the number of particles in the hypercube, due to flow through this face and the one opposite it is,

$$\frac{\partial N}{\partial t} = - \frac{\partial(\rho \dot{q}_k)}{\partial q_K} \prod_j dq_j dp_j$$

and the net flow into the hypercube due to all of the faces is

$$\frac{\partial N}{\partial t} = - \sum_k \left[ \frac{\partial(\rho \dot{q}_k)}{\partial q_K} + \frac{\partial(\rho \dot{p}_k)}{\partial p_K} \right] \prod_j dq_j dp_j.$$

Calculate the rate of change of the density by dividing by the volume of the hypercube.

$$\frac{\partial \rho}{\partial t} = - \sum_k \left[ \frac{\partial(\rho \dot{q}_k)}{\partial q_K} + \frac{\partial(\rho \dot{p}_k)}{\partial p_K} \right]$$

So that is the rate of change due to the other particles flowing, the partial derivative. To this we should add the rate of change due to the particle we are following moving.

$$\begin{aligned}
\frac{d\rho}{dt} &= \frac{\partial \rho}{\partial t} + \sum_k \left[ \frac{\partial \rho}{\partial q_K} \dot{q}_k + \frac{\partial \rho}{\partial p_K} \dot{p}_k \right] \\
\frac{d\rho}{dt} &= - \sum_k \left[ \frac{\partial(\rho \dot{q}_k)}{\partial q_K} + \frac{\partial(\rho \dot{p}_k)}{\partial p_K} \right] + \sum_k \left[ \frac{\partial \rho}{\partial q_K} \dot{q}_k + \frac{\partial \rho}{\partial p_K} \dot{p}_k \right] \\
\frac{d\rho}{dt} &= \sum_k \left[ -\frac{\partial \rho}{\partial q_K} \dot{q}_k - \frac{\partial \dot{q}_k}{\partial q_K} \rho - \frac{\partial \rho}{\partial p_K} \dot{p}_k - \frac{\partial \dot{p}_k}{\partial p_K} \rho + \frac{\partial \rho}{\partial q_K} \dot{q}_k + \frac{\partial \rho}{\partial p_K} \dot{p}_k \right] \\
\frac{d\rho}{dt} &= \sum_k \left[ -\frac{\partial \dot{q}_k}{\partial q_K} - \frac{\partial \dot{p}_k}{\partial p_K} \right] \rho
\end{aligned}$$

Now, we apply Hamilton's equations.

$$\begin{aligned}
\dot{q}_i &= \frac{\partial H}{\partial p_i} \\
\dot{p}_i &= -\frac{\partial H}{\partial q_i}
\end{aligned}$$

$$\frac{d\rho}{dt} = \sum_k \left[ -\frac{\partial^2 H}{\partial q_K \partial p_K} + \frac{\partial^2 H}{\partial p_K \partial q_K} \right] \rho = 0$$

This is true in the presence of any external forces or focusing elements. One cannot change the density in phase space of a bunch of particles, a beam of light, or any other collection of particles.

### Maxwell-Boltzmann distribution law

In statistics, the **Maxwell-Boltzmann distribution** is a particular probability distribution named after James Clerk Maxwell and Ludwig Boltzmann. It was first defined and used in physics (in particular in statistical mechanics) for describing particle speeds in idealized gases where the particles move freely inside a stationary container without interacting with one

another, except for very brief collisions in which they exchange energy and momentum with each other or with their thermal environment. Particle in this context refers to gaseous particles (atoms or molecules), and the system of particles is assumed to have reached thermodynamic equilibrium. While the distribution was first derived by Maxwell in 1860 on heuristic grounds, Boltzmann later carried out significant investigations into the physical origins of this distribution.

A particle speed probability distribution indicates which speeds are more likely: a particle will have a speed selected randomly from the distribution, and is more likely to be within one range of speeds than another. The distribution depends on the temperature of the system and the mass of the particle. The Maxwell–Boltzmann distribution applies to the classical ideal gas, which is an idealization of real gases. In real gases, there are various effects (e.g., van der Waals interactions, vertical flow, relativistic speed limits, and quantum exchange interactions) that can make their speed distribution different from the Maxwell–Boltzmann form. However, rarefied gases at ordinary temperatures behave very nearly like an ideal gas and the Maxwell speed distribution is an excellent approximation for such gases. Thus, it forms the basis of the Kinetic theory of gases, which provides a simplified explanation of many fundamental gaseous properties, including pressure and diffusion. The Maxwell–Boltzmann distribution is the function

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

Where  $m$  is the particle mass and  $KT$  is the product of Boltzmann's constant and thermodynamic temperature.

This probability density function gives the probability, per unit speed, of finding the particle with a speed near  $v$ . This equation is simply the Maxwell distribution with distribution parameter  $a = \sqrt{kT/m}$ . In probability theory the Maxwell–Boltzmann distribution is a chi distribution with three degrees of freedom and scale parameter  $a = \sqrt{kT/m}$ .

The simplest ordinary differential equation satisfied by the distribution is:

$$kTv f'(v) + f(v)(mv^2 - 2kT) = 0,$$

$$f(1) = \sqrt{\frac{2}{\pi}} e^{-\frac{m}{2kT}} \left(\frac{m}{kT}\right)^{3/2}$$

or in unit less presentation:



$$a^2 x f'(x) + (x^2 - 2a^2) f(x) = 0,$$

$$f(1) = \frac{\sqrt{\frac{2}{\pi}} e^{-\frac{1}{2a^2}}}{a^3}$$

### Distribution of energy

The energy distribution is found imposing

$$f_E(E)dE = f_p(P)d^3P \quad \text{-----} \quad (1)$$

Where  $d^3P$  is the infinitesimal phase-space volume of momenta corresponding to the energy interval  $dE$ . Making use of the spherical symmetry of the energy-momentum dispersion relation  $E = |P|^2/2m$ , this can be expressed in terms of as

$$d^3P = 4\pi|P|^2 d|P| = 4\pi m \sqrt{2mE} dE \quad \text{-----} \quad (2)$$

Using then **(2)** in **(1)**, and expressing everything in terms of the energy  $E$ , we get

$$f_E(E) = \frac{1}{(2\pi m kT)^{3/2}} e^{-\frac{E}{kT}} 4\pi m \sqrt{2mE} dE$$

$$f_E(E)dE = 2\sqrt{\frac{E}{\pi}} \left(\frac{1}{kT}\right)^{3/2} \exp\left(\frac{-E}{kT}\right) dE$$

And finally,

$$f_E(E) = 2\sqrt{\frac{E}{\pi}} \left(\frac{1}{kT}\right)^{3/2} \exp\left(\frac{-E}{kT}\right) \quad \text{-----} \quad (3)$$

Since the energy is proportional to the sum of the squares of the three normally distributed momentum components, this distribution is a gamma distribution; in particular, it is a chi-squared distribution with three degrees of freedom.

By the equipartition theorem, this energy is evenly distributed among all three degrees of freedom, so that the energy per degree of freedom is distributed as a chi-squared distribution with one degree of freedom:

$$f_{\epsilon}(\epsilon)d\epsilon = \sqrt{\frac{\epsilon}{\pi kT}} \exp\left(\frac{-\epsilon}{kT}\right) \text{-----} (4)$$

Where,  $\epsilon$  is the energy per degree of freedom. At equilibrium, this distribution will hold true for any number of degrees of freedom. For example, if the particles are rigid mass dipoles of fixed dipole moment, they will have three translational degrees of freedom and two additional rotational degrees of freedom. The energy in each degree of freedom will be described according to the above chi-squared distribution with one degree of freedom, and the total energy will be distributed according to a chi-squared distribution with five degrees of freedom. This has implications in the theory of the specific heat of a gas.

### Distribution for the velocity vector

Recognizing that the velocity probability density  $f_v$  is proportional to the momentum probability density function by

$$f_v d^3v = f_p \left( \frac{dP}{dv} \right)^3 d^3v$$

And using  $p=mv$ , we get

$$f_v(v_x, v_y, v_z) = \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left[ -\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT} \right]$$

which is the Maxwell–Boltzmann velocity distribution. The probability of finding a particle with velocity in the infinitesimal element  $[dv_x, dv_y, dv_z]$  about velocity  $\mathbf{v} = [v_x, v_y, v_z]$  is

$$f_v(v_x, v_y, v_z) dv_x dv_y dv_z$$

Like the momentum, this distribution is seen to be the product of three independent normally distributed variables  $v_x, v_y$  and  $v_z$  but with variance  $kT/m$ . It can also be seen that the Maxwell–Boltzmann velocity distribution for the vector velocity  $[v_x, v_y, v_z]$  is the product of the distributions for each of the three directions:

$$f_v(v_x, v_y, v_z) = f_v(v_x) f_v(v_y) f_v(v_z)$$

Where the distribution for a single direction is

$$f_v(v_x) = \left( \frac{m}{2\pi kT} \right)^{1/2} \exp \left[ -\frac{mv_x^2}{2kT} \right]$$

Each component of the velocity vector has a normal distribution with mean

$\mu_{vx} = \mu_{vy} = \mu_{vz} = 0$  and standard deviation  $\sigma_{vx} = \sigma_{vy} = \sigma_{vz} = \sqrt{\frac{kT}{m}}$ , so the vector has a 3-

dimensional normal distribution, a particular kind of multivariate normal distribution, with

mean  $\mu_v = 0$  and standard deviation  $\sigma_v = \sqrt{\frac{kT}{m}}$

The Maxwell–Boltzmann distribution for the speed follows immediately from the distribution of the velocity vector, above.

Note that the speed is

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

And the volume element in spherical coordinates

$$dv_x dv_y dv_z = v^2 \sin \theta dv d\theta d\phi$$

Where  $\phi$  and  $\theta$  are the "course" (azimuth of the velocity vector) and "path angle" (elevation angle of the velocity vector).

Integration of the normal probability density function of the velocity, above, over the course (from 0 to  $2\pi$ ) and path angle (from 0 to  $\pi$ ), with substitution of the speed for the sum of the squares of the vector components, yields the speed distribution.

## Equipartition of energy

**Equipartition of energy**, law of statistical mechanics stating that, in a system in thermal equilibrium, on the average, an equal amount of energy will be associated with each independent energy state. Based on the work of physicists James Clerk Maxwell of Scotland and Ludwig Boltzmann of Germany, this law states specifically that a system of particles in equilibrium at absolute temperature  $T$  will have an average energy of  $\frac{1}{2}kT$  associated with each degree of freedom, in which  $k$  is the Boltzmann constant. In addition, any degree of freedom contributing potential energy will have another  $\frac{1}{2}kT$  associated with it. For a system of  $s$  degrees of freedom, of which  $t$  have associated potential energies, the total average energy of the system is  $\frac{1}{2}(s + t)kT$ .

For example, an atom of a gas has three degrees of freedom (the three spatial, or position, coordinates of the atom) and will, therefore, have an average total energy of  $\frac{3}{2}kT$ .

For an atom in a solid, vibratory motion involves potential energy as well as kinetic energy, and both modes will contribute a term  $\frac{1}{2}kT$ , resulting in an average total energy of  $3kT$ .

## Energy Fluctuation

In the canonical ensemble, the system acquire a temperature by having a thermal contact with a thermostat (heat bath) with temperature  $T$ . Thus the system is no longer isolated any more. Its total energy, i.e., Hamiltonian  $H(q_i, p_i)$  is no longer conserved. In other words, we should expect some fluctuation of total energy in the canonical ensemble. On the other hand, fluctuations are not considered in thermodynamics. At constant  $N, V, T$  the appropriate thermodynamics potential is  $A(N, V, T)$ , from which we can compute a definite value for energy  $E = A + TS$ , with  $S \equiv -\left(\frac{\partial A}{\partial T}\right)_{N,V}$ .

Hence, in thermodynamics, we expect the system to simultaneously have a definite temperature  $T$  and total energy  $E$ . In statistical mechanics, if the system has a well defined temperature, its total energy  $E$  must fluctuate.

## Partition functions

Partition functions describe the statistical properties of a system in thermodynamic equilibrium. It is a function of temperature and other parameters, such as the volume enclosing a gas. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives. There are actually several different types of partition functions, each corresponding to different types of statistical ensemble (or, equivalently, different types of free energy). The canonical partition function applies to a canonical ensemble, in which the system is allowed to exchange heat with the environment at fixed temperature, volume, and number of particles. The grand canonical partition function applies to a grand canonical ensemble, in which the system can exchange both heat and particles with the environment, at fixed temperature, volume, and chemical potential. Other types of partition functions can be defined for different circumstances.

### *Meaning and significance*

It may not be obvious why the partition function, as we have defined it above, is an important quantity. First, let us consider what goes into it. The partition function is a function of the temperature  $T$  and the microstate energies  $E_1, E_2, E_3$ , etc. The microstate energies are determined by other thermodynamic variables, such as the number of particles and the volume, as well as microscopic quantities like the mass of the constituent particles. This dependence on microscopic variables is the central point of statistical mechanics. With a model of the microscopic constituents of a system, one can calculate the microstate energies, and thus the partition function, which will then allow us to calculate all the other thermodynamic properties of the system.

The partition function can be related to thermodynamic properties because it has a very important statistical meaning. The probability  $P_s$  that the system occupies microstate  $s$  is

$$P_s = \frac{1}{Z} e^{-\beta E_s}$$

$e^{-\beta E_s}$  is the well-known Boltzmann factor. The partition function thus plays the role of a normalizing constant (note that it does not depend on  $s$ ), ensuring that the probabilities sum up to one:

$$\sum_s P_s = \frac{1}{Z} \sum_s e^{-\beta E_s} = \frac{1}{Z} Z = 1$$

This is the reason for calling  $Z$  the "partition function": it encodes how the probabilities are partitioned among the different microstates, based on their individual energies. The letter  $Z$  stands for the German word Zustandssumme, "sum over states". This notation also implies another important meaning of the partition function of a system: it counts the (weighted) number of states a system can occupy. Hence if all states are equally probable (equal energies) the partition function is the total number of possible states. Often this is the practical importance of  $Z$ .

### *Relation to thermodynamic variables*

In this section, we will state the relationships between the partition function and the various thermodynamic parameters of the system. These results can be derived using the method of the previous section and the various thermodynamic relations.

As we have already seen, the thermodynamic energy is

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

The variance in the energy (or "energy fluctuation") is

$$\langle (\Delta E)^2 \rangle \equiv \langle (E - \langle E \rangle)^2 \rangle = \frac{\partial^2 \ln Z}{\partial^2 \beta}$$

The heat capacity is

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{k_B T^2} \langle (\Delta E)^2 \rangle$$

The entropy is

$$S \equiv -k_B \sum_s P_s \ln P_s = k_B (\ln Z + \beta \langle E \rangle) = \frac{\partial}{\partial T} (k_B \ln Z) = -\frac{\partial A}{\partial T}$$

where A is the Helmholtz free energy defined as  $A = U - TS$ , where  $U = \langle E \rangle$  is the total energy and S is the entropy, so that

$$A = \langle E \rangle - TS = -k_B T \ln Z.$$

### Boltzmann's Entropy equation

**Boltzmann's equation** is a probability equation relating the entropy  $S$  of an ideal gas to the quantity  $W$ , which is the number of microstates corresponding to a given macrostate:

$$S = k_B \ln W$$

where  $k_B$  is the Boltzmann constant, which is equal to  $1.38065 \times 10^{-23}$  J/K.

In short, the Boltzmann formula shows the relationship between entropy and the number of ways the atoms or molecules of a thermodynamic system can be arranged. In 1934, Swiss physical chemist Werner Kuhn successfully derived a thermal equation of state for rubber molecules using Boltzmann's formula, which has since come to be known as the entropy model of rubber.

The term **Boltzmann entropy** is also sometimes used to indicate entropies calculated based on the approximation that the overall probability can be factored into an identical separate term for each particle i.e., assuming each particle has an identical independent probability distribution, and ignoring interactions and correlations between the particles. This is exact for an ideal gas of identical particles, and may or may not be a good approximation for other systems.

The Boltzmann entropy is obtained if one assumes one can treat all the component particles of a thermodynamic system as statistically independent. The probability distribution of the system as a whole then factorises into the product of  $N$  separate identical terms, one term for each particle; and the Gibbs entropy simplifies to the Boltzmann entropy

$$S_B = -N k_B \sum_i p_i \ln p_i$$

Where the summation is taken over each possible state in the 6-dimensional phase space of a *single* particle (rather than the  $6N$ -dimensional phase space of the system as a whole).

This reflects the original statistical entropy function introduced by Ludwig Boltzmann in 1872. For the special case of an ideal gas it exactly corresponds to the proper thermodynamic entropy.

However, for anything but the most dilute of real gases, it leads to increasingly wrong predictions of entropies and physical behaviours, by ignoring the interactions and correlations between different molecules. Instead one must follow Gibbs, and consider the ensemble of states of the system as a whole, rather than single particle states.

## **TEXT / REFERENCE BOOKS**

1. F. Reif, Statistical and Thermal physics, McGraw Hill, International Edition, Singapore, 1979.
2. B.R. Agarwal and N. Eisnor, Statistiocal Mechanics, 2nd ed, Wiley Eastern Limited, New Delhi.
3. R. Huang, Statistical Mechanics, Wiley Eastern Ltd., New Delhi, 1983.
4. F. Mandl, Statistical physics, John Wiley, London, 1971.
5. C. Kittel, W. H. Freeman, Thermal Physics, 2nd ed. 1980.
6. F.W.Sears and G.L.Salinger, Thermodynamics, kinetic theory and statistical thermodynamics, 3rd edition, Narosa publishing house, 1998.



## **QUESTION BANK**

### **PART-A**

1. What are macroscopic and microscopic states?
2. Explain statistical equilibrium in Thermodynamics?
3. Explain the phase space
4. What is an ensemble of thermodynamic system? Give an example?
5. Explain the principles of equi-partition of energy.
6. What do you mean by energy fluctuations?
7. What is grand canonical ensemble of statistical mechanics?
8. Compare the basic concepts of Bose-Einstein's statistics and Fermi-Dirac statistics
9. Compare the basic concepts of Fermi-Dirac statistics and Maxwell-Boltzmann statistics.
10. What are the different kinds of ensemble?

### **PART-B**

1. Show that the density of phase points is an integral of motion by Liouville's Theorem.
2. Explain the basic concepts of Bose-Einstein's and Fermi Dirac statistics?
3. Derive the relation between the partition function and thermodynamic quantities.
4. Explain distribution of energy and velocity of particles by Maxwell-Boltzmann distribution law.



**SATHYABAMA**

INSTITUTE OF SCIENCE AND TECHNOLOGY  
(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

[www.sathyabama.ac.in](http://www.sathyabama.ac.in)

**SCHOOL OF SCIENCE AND HUMANITIES**

**DEPARTMENT OF PHYSICS**

## **UNIT – IV - Thermodynamics and Statistical Mechanics – SPHA5202**

## IV. QUANTUM STATISTICAL MECHANICS

Quantum statistical mechanics is based on the quantum-mechanical description of many-particle systems. Therefore, even before introducing statistical distributions (for microscopic states), we have to face the intrinsic probabilistic nature of quantum mechanical predictions. It is very important to distinguish carefully between the intrinsic statistical nature of quantum mechanics and the statistical aspects introduced by the probability distribution of quantum-mechanical states.

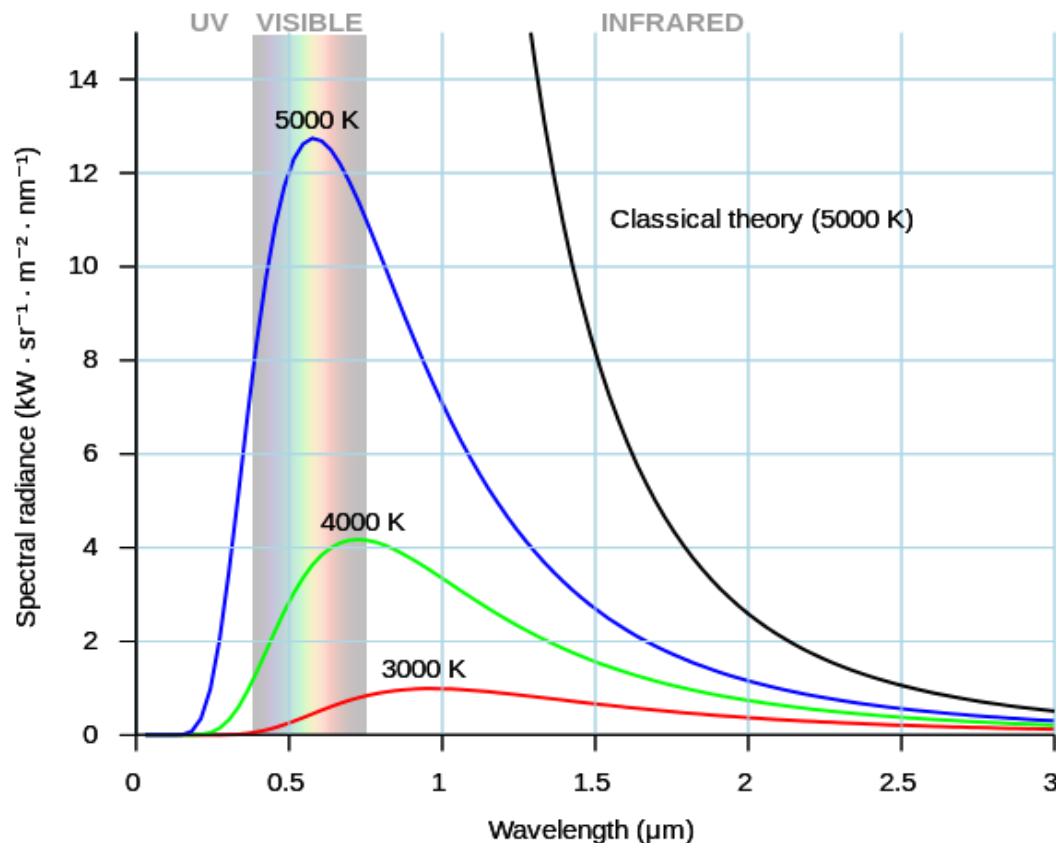
### **Black body**

An idealized physical body that absorbs all incident electromagnetic radiation, regardless of frequency or angle of incidence, is called Black body. Although black body is a theoretical concept, you can find approximate realizations of black body in nature.

A black body in thermal equilibrium (i.e. at a constant temperature) emits electromagnetic radiation called black body radiation. Black body radiation has a characteristic, continuous frequency spectrum that depends only on the body's temperature. Max Planck, in 1901, accurately described the radiation by assuming that electromagnetic radiation was emitted in discrete packets (or quanta). Planck's quantum hypothesis is a pioneering work, heralding advent of a new era of modern physics and quantum theory.

Explaining the properties of black-body radiation was a major challenge in theoretical physics during the late nineteenth century. Predictions based on classical theories failed to explain black body spectra observed experimentally, especially at shorter wavelength . The puzzle was solved in 1901 by Max Planck in the formalism now known as Planck's law of black-body radiation. Contrary to the common belief that electromagnetic radiation can take continuous values of energy, Planck introduced a radical concept that electromagnetic radiation was emitted in discrete packets (or quanta) of energy.

## Black body radiation spectrum



Typical spectrum from a black body at different temperatures is shown in blue, green and red curves. As the temperature decreases, the peak of the black-body radiation curve moves to lower intensities and longer wavelengths. Black line is a prediction of a classical theory for an object at 5,000K, showing catastrophic discrepancy at shorter wavelength.

**Planck's radiation law**, a mathematical relationship formulated in 1900 by German physicist Max Planck to explain the spectral-energy distribution of radiation emitted by a blackbody (a hypothetical body that completely absorbs all radiant energy falling upon it, reaches some equilibrium temperature, and then reemits that energy as quickly as it absorbs it). Planck assumed that the sources of radiation are atoms in a state of oscillation and that the vibrational energy of each oscillator may have any of a series of discrete values but never any value between. Planck further assumed that when an oscillator changes from a state of energy  $E_1$  to a state of lower energy  $E_2$ , the discrete amount of energy  $E_1 - E_2$ , or quantum of radiation, is equal to the product of the frequency of the radiation, symbolized by the Greek

letter  $\nu$  and a constant  $h$ , now called Planck's constant, that he determined from blackbody radiation data; i.e.,  $E_1 - E_2 = h\nu$ .

Planck's law for the energy  $E_\lambda$  radiated per unit volume by a cavity of a blackbody in the wavelength interval  $\lambda$  to  $\lambda + \Delta\lambda$  ( $\Delta\lambda$  denotes an increment of wavelength) can be written in terms of Planck's constant ( $h$ ), the speed of light ( $c$ ), the Boltzmann constant ( $k$ ), and the absolute temperature ( $T$ ):

$$E_\lambda = \frac{8\pi hc}{\lambda^5} \times \frac{1}{\exp(hc/kT\lambda) - 1}.$$

The wavelength of the emitted radiation is inversely proportional to its frequency, or  $\lambda = c/\nu$ . The value of Planck's constant is found to be  $6.62606957 \times 10^{-34}$  Js.

For a blackbody at temperatures up to several hundred degrees, the majority of the radiation is in the infrared radiation region of the electromagnetic spectrum. At higher temperatures, the total radiated energy increases, and the intensity peak of the emitted spectrum shifts to shorter wavelengths so that a significant portion is radiated as visible light.

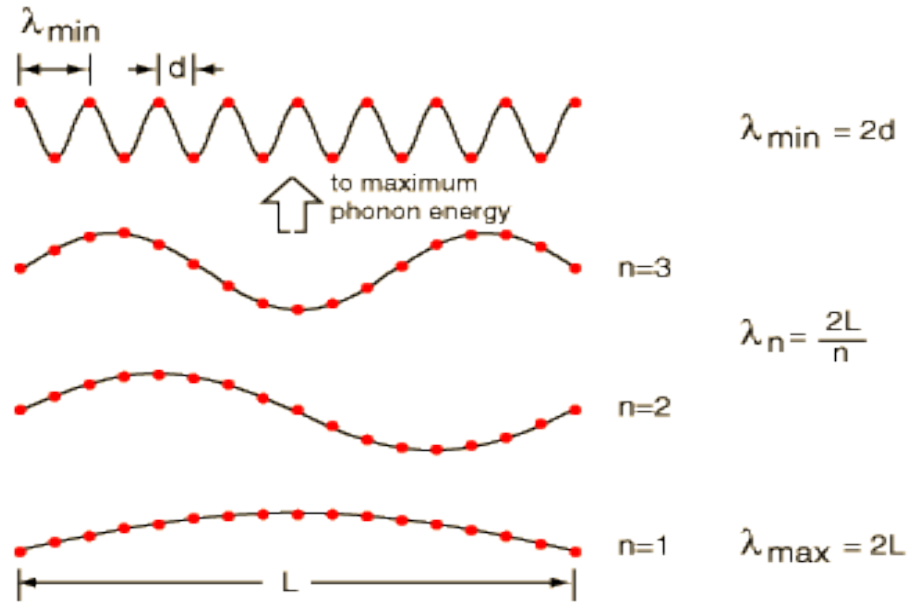
### Phonons

Considering the regular lattice of atoms in a uniform solid material, you would expect there to be energy associated with the vibrations of these atoms. But they are tied together with bonds, so they can't vibrate independently. The vibrations take the form of collective modes which propagate through the material. Such propagating lattice vibrations can be considered to be sound waves, and their propagation speed is the speed of sound in the material.

The vibrational energies of molecules, e.g., a diatomic molecule, are quantized and treated as quantum harmonic oscillators. Quantum harmonic oscillators have equally spaced energy levels with separation  $\Delta E = h\nu$ . So the oscillators can accept or lose energy only in discrete units of energy  $h\nu$ .

The evidence on the behavior of vibrational energy in periodic solids is that the collective vibrational modes can accept energy only in discrete amounts, and these quanta of energy have been labeled "phonons". Like the photons of electromagnetic energy, they obey Bose-Einstein statistics. Phonons are bosons possessing zero spin.

Considering a solid to be a periodic array of mass points, there are constraints on both the minimum and maximum wavelength associated with a vibrational mode.



By associating a phonon energy

$$h\nu = \frac{h\nu_s}{\lambda} = \frac{h\nu_s n}{2L}$$

with the modes and summing over the modes, Debye was able to find an expression for the energy as a function of temperature and derive an expression for the specific heat of the solid. In this expression,  $v_s$  is the speed of sound in the solid.

### Partition function for a Harmonic oscillator

Consider a one-dimensional harmonic oscillator in equilibrium with a heat reservoir at temperature  $T$ . The energy of the oscillator is given by

$$E = \frac{p^2}{2m} + \frac{1}{2}\kappa x^2, \quad (1)$$

where the first term on the right-hand side is the kinetic energy, involving the momentum  $P$  and mass  $m$ , and the second term is the potential energy, involving the displacement  $x$  and the force constant  $\kappa$ . Each of these terms is quadratic in the respective variable. So, in the classical approximation the equipartition theorem yields:

$$\frac{\overline{P^2}}{2m} = \frac{1}{2}kT \quad (2)$$

$$\frac{1}{2}\kappa \overline{x^2} = \frac{1}{2}kT \quad (3)$$

That is, the mean kinetic energy of the oscillator is equal to the mean potential energy which equals  $(1/2)kT$ . It follows that the mean total energy is

$$\overline{E} = \frac{1}{2} k T + \frac{1}{2} k T = k T. \quad (4)$$

According to quantum mechanics, the energy levels of a harmonic oscillator are equally spaced and satisfy

$$E_n = (n + 1/2) \hbar \omega, \quad (5)$$

where  $n$  is a non-negative integer, and

$$\omega = \sqrt{\frac{\kappa}{m}}. \quad (6)$$

The partition function for such an oscillator is given by

$$Z = \sum_{n=0}^{\infty} \exp(-\beta E_n) = \exp[-(1/2) \beta \hbar \omega] \sum_{n=0}^{\infty} \exp(-n \beta \hbar \omega). \quad (7)$$

Now,

$$\sum_{n=0}^{\infty} \exp(-n \beta \hbar \omega) = 1 + \exp(-\beta \hbar \omega) + \exp(-2 \beta \hbar \omega) + \cdots \quad (8)$$

is simply the sum of an infinite geometric series, and can be evaluated immediately,

$$\sum_{n=0}^{\infty} \exp(-n \beta \hbar \omega) = \frac{1}{1 - \exp(-\beta \hbar \omega)}. \quad (9)$$

Thus, the partition function takes the form

$$Z = \frac{\exp[-(1/2) \beta \hbar \omega]}{1 - \exp(-\beta \hbar \omega)}, \quad (10)$$

and

$$\ln Z = -\frac{1}{2} \beta \hbar \omega - \ln[1 - \exp(-\beta \hbar \omega)] \quad (11)$$

The mean energy of the oscillator is given by

$$\overline{E} = -\frac{\partial}{\partial \beta} \ln Z = -\left[ -\frac{1}{2} \hbar \omega - \frac{\exp(-\beta \hbar \omega) \hbar \omega}{1 - \exp(-\beta \hbar \omega)} \right], \quad (12)$$

or

$$\overline{E} = \hbar \omega \left[ \frac{1}{2} + \frac{1}{\exp(\beta \hbar \omega) - 1} \right]. \quad (13)$$

Consider the limit

$$\beta \hbar \omega = \frac{\hbar \omega}{k T} \ll 1, \quad (14)$$

in which the thermal energy  $k T$  is large compared to the separation  $\hbar \omega$  between the energy levels. In this limit,

$$\exp(\beta \hbar \omega) \simeq 1 + \beta \hbar \omega, \quad (15)$$

so

$$\overline{E} \simeq \hbar \omega \left[ \frac{1}{2} + \frac{1}{\beta \hbar \omega} \right] \simeq \hbar \omega \left[ \frac{1}{\beta \hbar \omega} \right], \quad (16)$$

giving

$$\overline{E} \simeq \frac{1}{\beta} = k T. \quad (17)$$

Thus, the classical result (4) holds whenever the thermal energy greatly exceeds the typical spacing between quantum energy levels.

Consider the limit

$$\beta \hbar \omega = \frac{\hbar \omega}{k T} \gg 1, \quad (18)$$

in which the thermal energy is small compared to the separation between the energy levels. In this limit,

$$\exp(\beta \hbar \omega) \gg 1, \quad (19)$$



and so

$$\overline{E} \simeq \hbar \omega \left[ 1/2 + \exp(-\beta \hbar \omega) \right] \simeq \frac{1}{2} \hbar \omega. \quad (20)$$

Thus, if the thermal energy is much less than the spacing between quantum states then the mean energy approaches that of the ground-state (the so-called *zero point energy*). Clearly, the equipartition theorem is only valid in the former limit, where  $kT \gg \hbar \omega$ , and the oscillator possess sufficient thermal energy to explore many of its possible quantum states.

### Specific heats of solids

The amount of energy required to raise the temperature of one kilogram of the substance by one kelvin is called specific heat. The SI unit for specific heat capacity is the joule per kilogram kelvin,  $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ . By heat capacity, it is often referred that heat capacity at constant volume, which is more fundamental than the heat capacity at constant pressure. The heat capacity at constant volume is defined as

$$C_v = T \sum \left( \frac{\partial S}{\partial T} \right)_v = \left( \frac{\partial U}{\partial T} \right)_v \quad \text{-----} (1)$$

Where S is the entropy, U is the energy, and T is temperature.

The experimental facts about the heat capacity of solids are these:

1. In room temperature range the value of the heat capacity of nearly all monoatomic solids is close to  $3Nk$ , or  $25 \text{ J mol}^{-1} \text{ deg}^{-1}$ .
2. At lower temperatures the heat capacity drops rapidly and approaches zero as  $T^3$  in insulators and as  $T$  in metals. If metal becomes semiconductor, the drop is faster than  $T$ .

The Debye model is developed by Peter Debye in 1912. He estimated the phonon contribution to the heat capacity in solids. The Debye model treats the vibration of the lattice as phonons in a box, in contrast to Einstein model, which treats the solid as non-interacting harmonic oscillators. The Debye model predicts the low temperature dependence of heat capacity  $T^3$  that confirms the experimental results. Moreover, it covers the high temperature limits like the Einstein model.

## EINSTEIN MODEL

The average energy of an oscillator of frequency  $\omega$ , is  $\langle n \rangle \hbar \omega$ . For N oscillators in one dimension, all having same frequency, the thermal energy is

$$U = N \langle n \rangle \hbar \omega = \frac{N \hbar \omega}{e^{\hbar \omega / \tau} - 1} \quad \text{----- (2)}$$

Where  $\tau = kT$ , k Boltzmann constant and  $\langle n \rangle$  is the thermal average of the number of phonons in an elastic wave of given frequency.

Then the heat capacity of oscillator is

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = Nk \left( \frac{\hbar \omega^2}{\tau} \right) \frac{e^{\hbar \omega / \tau}}{(e^{\hbar \omega / \tau} - 1)^2} \quad \text{----- (3)}$$

(a) At high temperatures  $\hbar \omega \ll kT$  and  $e^{\frac{\hbar \omega}{kT}} \approx 1 + \hbar \omega / kT$

$$U = \frac{3N\hbar}{\hbar \omega / kT} = 3NkT = 3RT \quad \text{----- (4)}$$

Also  $C = dU/dT = 3R$ , in agreement with experiment.

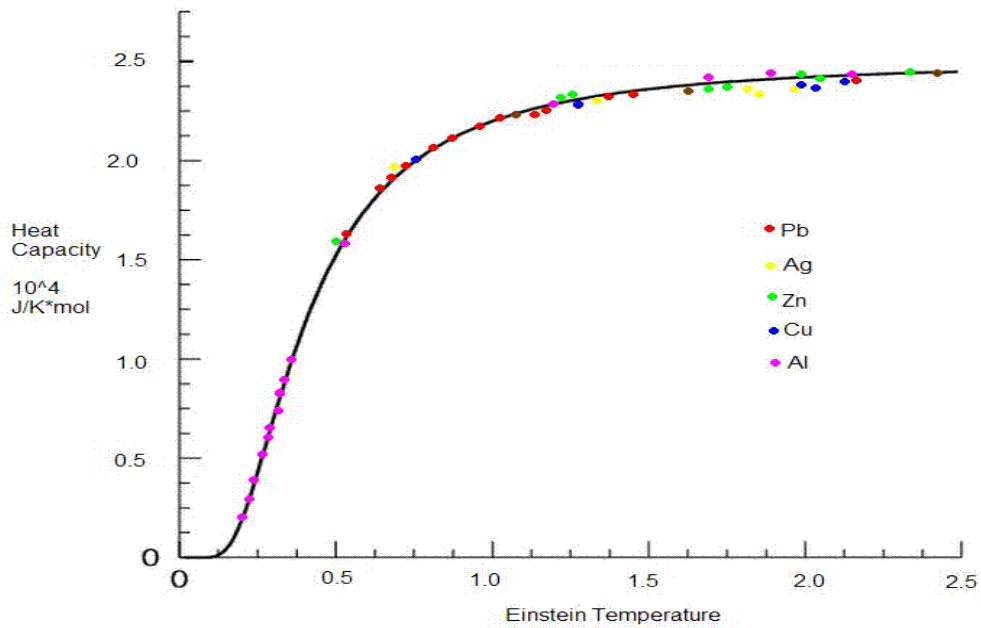
(b) At low temperatures  $\hbar \omega \gg kT$  and  $e^{\frac{\hbar \omega}{kT}} \gg 1$

$$U = 3N\hbar \omega e^{-\frac{\hbar \omega}{kT}} \quad \text{----- (5)}$$

And C can be found as follows,

$$\begin{aligned} C &= 3Nk \left( \frac{\hbar \omega}{kT} \right)^2 e^{-\frac{\hbar \omega}{kT}} \\ &= 3R \left( \frac{\theta_E}{T} \right)^2 e^{-\frac{\theta_E}{T}} \end{aligned} \quad \text{----- (6)}$$

Therefore, it can be seen that Einstein model successfully predicts that C decreases with decreasing T. However, exponential decrease is not observed; if low frequencies are present, then  $\hbar \omega$  will be small, much smaller than kT even at low temperatures; C will remain at 3kT to much lower frequencies and the fall off is not as dramatic as predicted by the Einstein model.



This graph indicates the heat capacity of several solid metals as a function of the Einstein temperature:  $\theta_E = h\nu/kB$ .

## DEBYE MODEL

Debye improved on Einstein's theory by treating the coupled vibrations of the solid in terms of  $3N$  normal modes of vibration of the whole system, each with its own frequency. The lattice vibrations are therefore equivalent to  $3N$  independent harmonic oscillators with these normal mode frequencies. For low frequency vibrations, defined as those for which the wavelength is much greater than the atomic spacing,  $\lambda \gg a$ , the crystal may be treated as a homogeneous elastic medium. The normal modes are the frequencies of the standing waves that are possible in the medium.

Debye derived an expression for the number of modes with frequency between  $\nu$  and  $\nu + d\nu$  in such a medium.

$$g(\nu)d\nu = \frac{4\pi V \nu^2}{\nu^3} d\nu = \alpha \nu^2 d\nu$$

where  $V$  is the crystal volume and  $\nu$  is the propagation velocity of the wave. This expression applies only to low frequency vibrations in a crystal. Debye used the approximation that it applied to all frequencies, and introduced a maximum frequency  $\nu_D$

(the Debye frequency) such that there were  $3N$  modes in total. i.e.  $\int_0^D g(\nu)d\nu = 3N$

The Debye frequency corresponds to  $\lambda = 2a$ , when neighbouring atoms vibrate in antiphase with each other. With this approximation in place, Debye integrated over all of the frequencies to find the internal energy of the crystal, and then calculated the heat capacity

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

The resulting expression is given below.

$$C_V = 3NK \left( \frac{3}{x_D^3} \int_0^{x_D} \frac{x^4 e^x dx}{(e^e - 1)^2} \right)$$

where  $x = \hbar\nu/kT$ , and  $x_D = \hbar\nu_D/kT = \theta_D/T$ . The Debye heat capacity depends only on the Debye temperature  $\theta_D$ . The integral cannot be evaluated analytically, but the bracketed function is tabulated.

At high temperatures ( $T \gg \theta_D$ ,  $x_D \ll 1$ ), we may rewrite the integrand as follows:

$$\begin{aligned} \frac{x^4 e^x}{(e^e - 1)^2} &= \frac{x^4}{(e^e - 1)(1 - e^x)} \\ &= \frac{x^4}{2(2 \cosh(x) - 1)} = \frac{x^4}{(x^2/2 + x^4/4 + \dots)} \end{aligned}$$

Retaining only the  $x^2$  term in the denominator gives

$$C_V = 3Nk \left( \frac{3}{x_D^3} \int_0^{x_D} x^2 dx \right) = 3Nk$$

To determine the low temperature limit ( $T \ll \theta_D$ ,  $x_D \gg 1$ ), we note that the integrand tends towards zero rapidly for large  $x$ . This allows us to replace the upper limit by  $\infty$  and turn the integral into a standard integral, to give

$$C_V = 3Nk \left( \frac{T}{\theta_D} \right)^3 \left( 3 \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} \right) = \frac{12}{5} \pi^4 Nk \left( \frac{T}{\theta_D} \right)^3$$

We see that the Debye heat capacity decreases as  $T^3$  at low temperatures, in agreement with experimental observation. This is a marked improvement on Einstein's theory.

### Extension: Einstein-Debye Specific Heat

This  $T^3$  dependence of the specific heat at very low temperatures agrees with experiment for nonmetals. For metals the specific heat of highly mobile conduction electrons is approximated by Einstein Model, which is composed of single-frequency quantum harmonic oscillators. The temperature dependence of Einstein model is just  $T$ . It becomes significant at low temperatures and is combined with the above lattice specific heat in the Einstein-Debye specific heat.

$$C_{metal} = C_{electron} + C_{phonon} = \frac{\pi^2 N k^2}{2 E_f} T + \frac{12 \pi^4 N k_B}{5 T_D^3} T^3$$

Finally, experiments suggest that amorphous materials do not follow the Debye  $T^3$  law even at temperatures below  $0.01 T_D$ .

### Diatomic molecule

In case of an ideal gas of diatomic molecules, the presence of internal degrees of freedom are apparent. In addition to the three translational degrees of freedom, there are rotational and vibrational degrees of freedom. In general, the number of degrees of freedom,  $f$ , in a molecule with  $n_a$  atoms is  $3n_a$ :

$$f = 3n_a$$

Mathematically, there are a total of three rotational degrees of freedom, one corresponding to rotation about each of the axes of three-dimensional space. However, in practice only the existence of two degrees of rotational freedom for linear molecules will be considered. This approximation is valid because the moment of inertia about the internuclear axis is vanishingly small with respect to other moments of inertia in the molecule (this is due to the very small rotational moments of single atoms, due to the concentration of almost all their mass at their centers; compare also the extremely small radii of the atomic nuclei compared to the distance between them in a diatomic molecule). Quantum mechanically, it can be shown that the interval between successive rotational energy Eigen states is inversely proportional to the moment of inertia about that axis. Because the moment of inertia about the internuclear axis is vanishingly small relative to the other two rotational axes, the energy

spacing can be considered so high that no excitations of the rotational state can occur unless the temperature is extremely high. It is easy to calculate the expected number of vibrational degrees of freedom (or vibrational modes). There are three degrees of translational freedom, and two degrees of rotational freedom, therefore

$$f_{vib} = f - f_{trans} - f_{rot} = 6 - 3 - 2 = 1$$

Each rotational and translational degree of freedom will contribute  $R/2$  in the total molar heat capacity of the gas. Each vibrational mode will contribute  $R$  to the total molar heat capacity, however. This is because for each vibrational mode, there is a potential and kinetic energy component. Both the potential and kinetic components will contribute  $R/2$  to the total molar heat capacity of the gas. Therefore, a diatomic molecule would be expected to have a molar constant-volume heat capacity of

$$C_{v,m} = \frac{3R}{2} + R + R = \frac{7R}{2} = 3.5R$$

Where the terms originate from the translational, rotational, and vibrational degrees of freedom, respectively.

The following is a table of some molar constant-volume heat capacities of various diatomic gases at standard temperature ( $25\text{ }^{\circ}\text{C} = 298\text{ K}$ )

<b>Diatomic gas</b>	<b><math>C_{V,m}</math> (J/(mol·K))</b>	<b><math>C_{V,m} / R</math></b>
H <sub>2</sub>	20.18	2.427
CO	20.2	2.43
N <sub>2</sub>	19.9	2.39
Cl <sub>2</sub>	24.1	3.06
Br <sub>2</sub> (vapour)	28.2	3.39

From the above table, clearly there is a problem with the above theory. All of the diatomics examined have heat capacities that are lower than those predicted by the equipartition

theorem, except Br<sub>2</sub>. However, as the atoms composing the molecules become heavier, the heat capacities move closer to their expected values. One of the reasons for this phenomenon is the quantization of vibrational, and to a lesser extent, rotational states. In fact, if it is assumed that the molecules remain in their lowest energy vibrational state because the inter-level energy spacings for vibration-energies are large, the predicted molar constant volume heat capacity for a diatomic molecule becomes just that from the contributions of translation and rotation:

$$C_{v,m} = \frac{3R}{2} + R = \frac{5R}{2} = 2.5R$$

which is a fairly close approximation of the heat capacities of the lighter molecules in the above table. If the quantum harmonic oscillator approximation is made, it turns out that the quantum vibrational energy level spacings are actually inversely proportional to the square root of the reduced mass of the atoms composing the diatomic molecule. Therefore, in the case of the heavier diatomic molecules such as chlorine or bromine, the quantum vibrational energy level spacings become finer, which allows more excitations into higher vibrational levels at lower temperatures. This limit for storing heat capacity in vibrational modes, as discussed above, becomes  $7R/2 = 3.5 R$  per mole of gas molecules, which is fairly consistent with the measured value for Br<sub>2</sub> at room temperature. As temperatures rise, all diatomic gases approach this value.

### **Ideal Bose gas**

We consider an ideal gas of Bose particles. This is a gas of any integral spin (e.g. zero spin) particles at a temperature low enough that quantum effects are important. Quantum effects become important when the thermal wavelength  $\lambda_T = (h^2 / 2\pi m k T)^{1/2}$  of the particles is comparable or greater than the interparticle spacing, i.e.  $n\lambda_T^3 \geq 1$ .

The prime physical example is a gas of <sup>4</sup>He atoms. In fact the <sup>4</sup>He-<sup>4</sup>He interatomic interaction is strong enough that the gas condenses into a liquid at low temperature, below 4.2 K. In spite of this, liquid <sup>4</sup>He properties are often compared with similar properties in the perfect Bose gas. In 1924 Einstein proposed that a Bose gas at low temperature would undergo a "condensation" in which a macroscopic or large fraction of the particles condense into the lowest energy single particle state (the zero momentum state). This Bose-Einstein condensation was a logical consequence of the new statistics introduced by Bose. Although

there is not yet a fully satisfactory theory of Liquid  $^4\text{He}$  this condensation is observed in liquid  $^4\text{He}$  at  $T - T_\lambda = 2.17 \text{ K}$ . At  $T_\lambda$  a fraction of atoms begin to condensate into the condensate state. At  $T = 0 \text{ K}$  7.25: 75 % of the fluid is in the condensate state.

### **Bose-Einstein condensation**

A Bose-Einstein condensate (BEC) is a state of matter of a dilute gas of bosons cooled to temperatures very close to absolute zero (that is, very near  $0 \text{ K}$  or  $-273.15 \text{ }^\circ\text{C}$ ). Under such conditions, a large fraction of bosons occupy the lowest quantum state, at which point macroscopic quantum phenomena become apparent.

The statistical description of a collection of non-interacting bosons was first considered by Bose in 1924 in the context of photons and the Planck's distribution. In 1925, Einstein realized that for material particles whose number must be conserved, these statistics (now known as Bose-Einstein statistics) could force the particles to undergo a phase transition in which they form a macroscopic occupation of the lowest energy level of the container. This phase transition is known as Bose-Einstein condensation, and it occurs when the temperature and density are such that the deBroglie waves of the atoms begin to overlap.

Ideal-gas atoms are considered as non-interacting quantum mechanical version of a classical ideal gas. It is composed of bosons, which have an integer value of spin, and obey Bose-Einstein statistics. Considering, properties of a system of  $N$  noninteracting particles (say bosonic atoms) of mass  $m$ , in thermodynamic equilibrium at temperature  $T$ , the mean number of particles occupying a single quantum state of energy  $\epsilon_v$  is given by the Bose-Einstein distribution.

$$f(\epsilon_v) = \frac{1}{e^{(\epsilon_v - \mu_c)/k_B T} - 1} \quad \text{----- (1)}$$

Where  $\mu_c$  and  $k_B$  corresponds to chemical potential and Boltzmann constant, respectively. Note that the exponential part of this distribution function is bounded below by 1, this function allows arbitrarily high occupancy of any state. This surprising result allows for the possibility that certain number of massive particles may exist simultaneously in a single quantum state. That is, more than one particle may be described by exactly the same single-particle Schrodinger wave function. The physical implications of this statement indicate that two or more bosons are observed at the same position. The chemical potential  $\mu_c$  as a function



of temperature and the total number of particles gives the dependence of Bose-Einstein distribution on  $N$ .

The chemical potential is the energy required to add a particle to the system while keeping the entropy and volume are fixed. It is determined from the constraint that the total number of particles in the system is fixed, so we have

$$N = \sum_{\varepsilon_v} \frac{1}{e^{(\varepsilon_v - \mu_c)/k_B T} - 1} \quad \text{----- (2)}$$

If the Bose-Einstein distribution varies slowly on the scale of the energy level spacing, then the summation in Eq. (2) can be replaced by an integral over a density of states. If  $\mu_c \rightarrow 0$ , however, the distribution has a singularity at  $\varepsilon_v = 0$ , which signifies the possibility of the ground state to accommodate very large number of particles. In addition, this state is actually neglected by the density of states, which does not provide a good description of the lowest energy levels. The simplest way to deal with these problems is it correct usage ground state contribution for special treatment, and use a density of states for the remaining levels. Eq. (2) can therefore be written as

$$N = N_0 + \int f(\varepsilon)g(\varepsilon)d\varepsilon \quad \text{----- (3)}$$

where  $N_0$  is the number of particles in the ground state and  $G(\varepsilon)$  is the density of states for the homogeneous gas in three-dimensional (3D) box and is given by

$$G(\varepsilon) = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} \quad \text{----- (4)}$$

where  $V$  is the volume of the system. The integral over the density of states in Eq. (3) gives the number of excited particles  $N_{ex}$ , i.e. those which are not in the ground state. Eq. (1) shows that the Bose-Einstein distribution is a monotonically increasing function of both  $\mu$  and  $T$ . If the system is cooled,  $\mu_c$  must therefore increase so that the total number of particles is constant. Since we must also have  $\mu_c < 0$ , we can find maximum number of particles in the excited states by setting  $\mu_c = 0$  in the integral of Eq. (3), we have

$$N_{ex} = V\zeta(3/2) \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \quad \text{----- (5)}$$

where  $\zeta(\alpha)$  is the Riemann zeta function. For uniform ideal Bose gas in a 3D box, the value of  $\zeta(3/2) = 2.612$ . At high temperature  $\mu_c \ll 0$ ,  $N_{ex} > N$  and essentially all the particles are in the excited states. As the system is cooled, however,  $\mu_c$  increases towards zero and we eventually reach a critical temperature  $T_c$  at which  $N_{ex} = N$ .

From Eq. (5) the transition temperature  $T_c$  is given by

$$T_c \approx 3031 \left( \frac{\hbar^2}{mk_B} \right) n^{2/3} \quad \text{----- (6)}$$

Where  $n = N/V$  is the particle number density. At the transition temperature, the number of particles in the excited state is given by

$$N_{ex} = N \left( \frac{T}{T_c} \right)^{3/2} \quad \text{----- (7)}$$

Below the critical temperature, the particles can no longer be accommodated in the excited states, so further cooling results in the formation of a macroscopic population of the lowest energy level. In this regime, the chemical potential is essentially fixed at zero. Upon substitution Eq. (7) into Eq. (3), the condensate population varies with temperature as

$$N_0 = N - N_{ex} = \left[ 1 - \left( \frac{T}{T_c} \right)^{3/2} \right] \quad \text{----- (8)}$$

Thus, below the critical temperature a finite fraction of all the particles occupy a single state. This is one of the defining features of Bose-Einstein condensation. The particle in a box model is simple to deal with, there are practical difficulties in implementing exactly cubic traps experimentally. As such, its primary purpose lies in providing the most basic theoretical illustration of BEC. An alternative model which is no more complicated to deal with but far more practicable is obtained by replacing the box containment with a radially symmetric harmonic potential,

$$V(r) = \frac{1}{2} m (\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2)$$

Rigorously speaking, for an ideal Bose gas of  $N$  bosonic atoms in a harmonic potential, the condition of phase-space density  $n(2\pi\hbar^2/mk_B)^{3/2} > 2.612$  is replaced by  $N(\hbar\omega_{ho}/k_B T)^{3/2} > 1.202$  where  $\omega_{ho} \equiv (\omega_x\omega_y\omega_z)^{1/3}$  is the geometric means of the harmonic trapping frequencies. Using exactly the same arguments that are usually employed to solve the box model, the density of states is

$$G(\varepsilon) = \frac{1}{2\hbar\omega_{ho}} \left( \frac{\varepsilon}{\hbar\omega_{ho}} \right)^2 \quad \text{----- (9)}$$

and the critical temperature  $T_c \approx 0.94 \left( \frac{\hbar\omega}{k_B} \right) N^{1/3}$

Below  $T_c$ , the condensate population varies with temperature as

$$N_0 = N \left[ 1 - \left( \frac{T}{T_c} \right)^3 \right] \quad \text{----- (10)}$$

The above relation indicates that the number of particles condensed into the single quantum state in harmonic potential varies with temperature.

## Liquid Helium

The chemical element helium exists in a liquid form only at the extremely low temperature of  $-269^\circ\text{C}$  (about 4 K or  $-452.2^\circ\text{F}$ ). Its boiling point and critical point depend on which isotope of helium is present: the common isotope helium-4 or the rare isotope helium-3. These are the only two stable isotopes of helium. See the table below for the values of these physical quantities. The density of liquid helium-4 at its boiling point and a pressure of one atmosphere (101.3 kilopascals) is about 0.125 grams per  $\text{cm}^3$ , or about 1/8th the density of liquid water.

## Characteristics

The temperature required to produce liquid helium is low because of the weakness of the attractions between the helium atoms. These interatomic forces in helium are weak to begin with because helium is a noble gas, but the interatomic attractions are reduced even more by the effects of quantum mechanics. These are significant in helium because of its low atomic mass of about four atomic mass units. The zero point energy of liquid helium is less if its atoms are less confined by their neighbors. Hence in liquid helium, its ground state energy can decrease by a naturally-occurring increase in its average interatomic distance. However at greater distances, the effects of the interatomic forces in helium are even weaker.

Because of the very weak interatomic forces in helium, this element would remain a liquid at atmospheric pressure all the way from its liquefaction point down to absolute zero. Liquid

helium solidifies only under very low temperatures and great pressures. At temperatures below their liquefaction points, both helium-4 and helium-3 undergo transitions to superfluids. (See the table below).

Liquid helium-4 and the rare helium-3 are not completely miscible. Below 0.9 kelvin at their saturated vapor pressure, a mixture of the two isotopes undergoes a phase separation into a normal fluid (mostly helium-3) that floats on a denser superfluid consisting mostly of helium-4. This phase separation happens because the overall mass of liquid helium can reduce its thermodynamic enthalpy by separating.

At extremely low temperatures, the superfluid phase, rich in helium-4, can contain up to 6% of helium-3 in solution. This makes possible the small-scale use of the dilution refrigerator, which is capable of reaching temperatures of a few milli-kelvins. Superfluid helium-4 has substantially different properties than ordinary liquid helium.

### **Fermi-Dirac statistics**

The counting is the same as in the boson case, except that the 3 states of the system where the particles are in the same single particle state are excluded. Thus there are 3 states in total. The relative probability for finding two particles in the same state is zero, of course.

We can see how the statistics controls the number of states. More interestingly, we can see that the relative probability for finding particles in the same state is greatest for identical bosons and least for identical fermions, with distinguishable particles somewhere in between. Thus one can say that by their very nature, identical bosons “like” to be in the same state compared to identical fermions and other particles.

### **Degenerate Fermi Gas**

It is easy to check that for an electron at room temperature the quantum length is about 4 nm so the quantum volume is about  $64 \text{ nm}^3$ . Consider a metal where, with about one conduction electron per atom, the volume per conduction electron is approximately  $10^{-2} \text{ nm}^3$ . Thanks to the relatively low mass of the electron and the relatively low (room) temperature, the conduction electrons in a metal must be treated quantum mechanically-the fermionic nature of the particle can be expected to be important. We will now explore the simplest possible model of a quantum electrons { the degenerate Fermi gas. This provides an elementary model of conduction electrons in a metal as well as an explanation for phenomena like white dwarf stars.

The degenerate Fermi gas is obtained by treating a collection of electrons as non-interacting fermions at zero temperature. As  $T \rightarrow 0$  you expect the system to settle into its

unique lowest energy state. If it weren't for the fact that the electrons were fermions, this lowest energy state would arise by putting all the particles in the lowest single-particle state. But we can only put 1 electron per single particle state, so we have to fill more and more states. Eventually we have placed all the particles, say  $N$  of them, in the lowest available energy states. The particles will have occupied all (1-particle) energies up to some value, call it  $\epsilon_F$  – the Fermi energy. This leads to behavior with thermodynamic features – even at zero temperature!

As a simple illustration of the Fermi energy, let us return to our identical particles A and B. Let us suppose that states 1, 2, 3, have energies 1eV, 2eV, 3eV, respectively. The Fermi energy is 2eV. What we'd like to do now with the degenerate Fermi gas is to compute the Fermi energy as well as a few other observables like the internal energy and pressure of the gas, all as functions of the volume and number of particles. To do this we need to get a handle on the 1-particle states. We will model the electrons as a “particle in a box”. This means the following.

For a free particle in a cubic box with sides of length  $L$ , the states of a particle with a given energy  $\epsilon$  have wave functions of the form

$$\Psi(x, y, z) = (const.) \sin\left(\frac{n_x x \pi}{L}\right) \sin\left(\frac{n_y y \pi}{L}\right) \sin\left(\frac{n_z z \pi}{L}\right)$$

Where the  $n$ 's can be any integer greater than equal to 1. Note that the wave function vanishes on the edges of the box which are taken to be at  $x; y; z = 0; L$ . The state is determined by the choice of the  $n$ 's and the spin state of the electron, the latter can be up or down along some (arbitrarily chosen) axis. The ground state is when  $n_x = n_y = n_z = 1$ , irrespective of the spin state (so the ground state is doubly degenerate). The first excited states are obtained by setting 2 of the 3  $n$ 's to unity and the third  $n$  is set equal to 2, e.g.,  $n_x = n_y = 1, n_z = 2$ . Thus the ground state is doubly degenerate and the first excited state is 6-fold degenerate. The energy  $\epsilon$  of a single particle state determined by a given choice of the  $n$ 's is

$$\epsilon = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

Where  $m$  is the electron mass.

So much for the energy states of a single particle. The idea is now that, for the  $T \approx 0$  ground state of the gas, each electron occupies one of the energy states such that the gas has the lowest possible energy. Actually, one can put two electrons in each energy state because there

are two spin states the electron can be in for any given energy. The maximum 1-particle energy which occurs is the Fermi energy, which we write as

$$\varepsilon_F = \frac{h^2}{8mL^2} n_{\max}^2$$

Where  $n_{\max}^2$  is the largest value for  $n_x^2 + n_y^2 + n_z^2$  which occurs. To get a handle on  $\varepsilon_F$  we use a geometric interpretation of this formula which arises for a macroscopic gas. The filled 1-particle states determine a sphere of radius  $n_{\max}$ . Actually, only 1/8 of a sphere is used since the vectors  $\vec{n}$  have all components being non-negative. For a large enough number of particles, it is not too hard to see that the volume of this 1/8 of a sphere is approximately 1/2 the number of states which are filled, which is 1/2 the number of particles  $N$ . (The 1/2 comes because there are two particles per energy state due to the two spin states of an electron). Thus, for  $N \gg 1$ , we have

$$N = 2 \times \frac{1}{8} \times \frac{4\pi}{3} n_{\max}^3$$

Use this formula to eliminate  $n_{\max}$  in  $\varepsilon_F$  and set  $V = L^3$ .

We then get a nice formula for the Fermi energy:

$$\varepsilon_F = \frac{h^2}{8m} \left( \frac{3N}{\pi V} \right)^{2/3}$$

For a typical metal the Fermi energy is on the order of an electron volt or so. At room temperature, the average thermal energy per electron is about  $kT = 1/40$  eV. We see that the internal energy per electron is at least an order of magnitude bigger than the average thermal energy of an electron. What this means is that at room temperature the fermionic effects are dominating the thermal effects, although the latter effects aren't completely negligible. This justifies setting  $T = 0$  as a first approximation.

More generally, we can define a Fermi temperature:

$$T_F = \frac{\varepsilon_F}{k} = \frac{h^2}{8mk} \left( \frac{3N}{\pi V} \right)^{2/3}$$

## Pauli paramagnetism

The ground state of a noninteracting Fermi gas is nonmagnetic, with spin up and down states equally populated. On general grounds we therefore expect that in the presence of an external magnetic field these spin states will be split by the eigen values of the Zeeman

$$H_Z = -\boldsymbol{\mu} \cdot \mathbf{B} = \frac{g\mu_B}{\hbar} \mathbf{S} \cdot \mathbf{B} = \mu_B B \sigma_z,$$

$$\epsilon_{\uparrow, \downarrow} = \pm \mu_B B.$$

Ignoring orbital effects of the magnetic field (that we will consider in the next subsection), together with the kinetic energy the single-electron spectrum is then given by

$$\epsilon_{k\sigma} = \frac{\hbar^2 k^2}{2m} + \sigma \mu_B B, \quad \sigma = \pm 1$$

Pauli linear susceptibility is

$$\chi_{\text{Pauli}} = \mu_B^2 g(\epsilon_F)$$

to be compared to the Curie susceptibility  $\chi_{\text{Curie}} = \mu_B^2 / k_B T$ , with the role of  $k_B T$  replaced by  $\epsilon_F$ . As with the qualitative discussion of the low-temperature excitation energy and the heat capacity, above, here too we can understand the result of the temperature-independent Pauli susceptibility in terms of Curie susceptibility of the reduced, temperature dependent number of excitations confined by the Pauli principle to the  $k_B T / \epsilon_F$  shell around the Fermi surface. This reproduces the detailed result via

$$\chi_{\text{Pauli}} \approx \frac{k_B T}{\epsilon_F} \chi_{\text{Curie}} = \frac{k_B T}{\epsilon_F} \frac{\mu_B^2}{k_B T} = \frac{\mu_B^2}{\epsilon_F}$$

Above we have focused on magnetic response to an external field due to spins, ignoring orbital effects of charged electrons.

## The density matrix and partition function

The density matrix or density operator is an alternate representation of the state of a quantum system for which we have previously used the wave function. Although describing a quantum system with the density matrix is equivalent to using the wave function, one gains significant practical advantages using the density matrix for certain time-dependent problems – particularly relaxation and nonlinear spectroscopy in the condensed phase.

The density matrix is formally defined as the outer product of the wave function and its conjugate.

$$\rho(t) \equiv |\psi(t)\rangle\langle\psi(t)| \quad \text{-----} \quad (1)$$

This implies that if you specify a state  $|\chi\rangle$ ,  $\langle\chi|\rho|\chi\rangle$  the integral gives the probability of finding a particle in the state  $|\chi\rangle$ . Its name derives from the observation that it plays the

quantum role of a probability density. If you think of the statistical description of a classical observable obtained from moments of a probability distribution  $P$ , then  $\rho$  plays the role of  $P$  in the quantum case:

$$\langle A \rangle = \int A P(A) dA \quad \text{----- (2)}$$

$$\langle A \rangle = \langle \psi | A | \psi \rangle = \text{Tr}[A\rho] \quad \text{----- (3)}$$

Where  $\text{Tr}[\dots]$  refers to tracing over the diagonal elements of the matrix.

The last expression is obtained as follows. For a system described by a wave function.

$$|\psi(t)\rangle = \sum_n C_n(t) |n\rangle \quad \text{----- (4)}$$

The expectation value of an operator is

$$\langle \hat{A}(t) \rangle = \sum_{n,m} C_n(t) C_m^*(t) \langle m | \hat{A} | n \rangle \quad \text{----- (5)}$$

Also, from eq. (1) we obtain the elements of the density matrix as

$$\begin{aligned} \rho(t) &= \sum_{n,m} C_n(t) C_m^*(t) |n\rangle \langle m| \\ &\equiv \sum_{n,m} \rho_{nm}(t) |n\rangle \langle m| \end{aligned} \quad \text{----- (6)}$$

We see that  $\rho_{nm}$ , the density matrix elements, are made up of the time-evolving expansion Coefficients.

Substituting into eq. (5) we see that

$$\langle \hat{A}(t) \rangle = \sum_{n,m} A_{nm} \rho_{nm}(t) = \text{Tr}[\hat{A}\rho(t)] \quad \text{----- (7)}$$

In practice this makes evaluating expectation values as simple as tracing over a product of matrices.

It is a practical tool when dealing with mixed states. Pure states are those that are characterized by a single wave function. Mixed states refer to statistical mixtures in which we have imperfect information about the system, for which we must perform statistical averages in order to describe quantum observables. A mixed state refers to any case in which we subdivide a microscopic or macroscopic system into an ensemble, for which there is initially



no phase relationship between the elements of the mixture. Examples include an ensemble at thermal equilibrium, and independently prepared states.

### **TEXT / REFERENCE BOOKS**

1. F. Reif, Statistical and Thermal physics, McGraw Hill, International Edition, Singapore, 1979.
2. B.R. Agarwal and N. Eisnor, Statistiocal Mechanics, 2nd ed, Wiley Eastern Limited, New Delhi.
3. R. Huang, Statistical Mechanics, Wiley Eastern Ltd., New Delhi, 1983.
4. F. Mandl, Statistical physics, John Wiley, London, 1971.
5. C. Kittel, W. H. Freeman, Thermal Physics, 2nd ed. 1980.
6. F.W.Sears and G.L.Salinger, Thermodynamics, kinetic theory and statistical thermodynamics, 3rd edition, Narosa publishing house, 1998.

## **QUESTION BANK**

### **PART-A**

1. Explain the black body radiation (or) Photon Gas?
2. State and explain the Bose-Einstein Statistics.
3. How to find the degeneracy of gas molecules.
4. Discuss the electron gas by quantum mechanics.
5. What is called Fermi Energy level?
6. How do electrons contribute to specific heat of solids?
7. Distinguish between Einstein and Debye models of solids.

### **PART-B**

1. Discuss the specific heat capacity of solids by Debye's Theory.
2. Discuss how the properties of Liquid Helium vary using its Phase diagram.
3. Explain Pauli paramagnetism by quantum mechanics.
4. Explain the density matrix of a thermodynamic system by quantum statistical mechanics.



**SATHYABAMA**

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

[www.sathyabama.ac.in](http://www.sathyabama.ac.in)

**SCHOOL OF SCIENCE AND HUMANITIES**

**DEPARTMENT OF PHYSICS**

**UNIT – V - Thermodynamics and Statistical Mechanics – SPHA5202**

## V. ADVANCED TOPICS IN STATISTICAL MECHANICS

### Phase transitions and critical Phenomena

As an introduction to the physics of phase transitions and critical phenomena, we explain in this chapter a number of basic ideas such as phases, phase transitions and critical phenomena. Intuitive accounts are given to the concepts of scaling and renormalization, which are powerful, systematic tools to analyze critical behavior of macroscopic systems. Also explained are several model systems, on the basis of which phase transitions and critical phenomena have been studied.

#### Phase and phase diagram

We are surrounded by a number of substances in different states. A *phase* is a state of matter in which the macroscopic physical properties of the substance are uniform on a macroscopic length scale, e.g. 1 mm. Familiar examples are ice, liquid water, and water vapor, each of which is a phase of water as a collection of macroscopic numbers of H<sub>2</sub>O molecules. Roughly speaking, we call the length scale that we encounter in our daily life the *macroscopic* scale, which is to be contrasted with the *microscopic* scale as the standard of length in the atomic world. The goal of statistical mechanics is to elucidate physical phenomena occurring on the macroscopic scale as a result of the interactions among microscopic constituents. A phase is characterized by a thermodynamic function, typically the free energy. A thermodynamic function is a function of a few macroscopic parameters such as the temperature and the pressure. Thus, the phase of a macroscopic substance is determined by the values of these parameters. A *phase diagram* is a graph with those parameters as the axes, on which the phase is specified for each point. An example of a phase diagram is given in Fig. 1.1. A typical phase diagram has several specific features including *phase boundaries*, a *critical point* (point C in Fig. 1.1), and a *triple point* (point TP). A phase boundary separates different phases. A change in parameters such as the temperature across a phase boundary causes a sudden change in the phase of a substance. For example, a solid phase changes into a liquid phase at the melting temperature. This is a *phase transition*. A phase boundary sometimes disappears at a critical point, where the two phases become indistinguishable and the substance shows anomalous behavior. The

theory of *critical phenomena* explains this anomalous behaviour.

## Phase transitions

A phase transition is a phenomenon in which a drastic change between thermodynamic phases occurs as the system parameters such as the temperature and pressure are varied. A familiar example is the melting of ice at 0 °C near 1 atm. The characterization of a phase transition as a drastic change of macroscopic properties is described theoretically as the emergence of singularities (non-analyticities) in functions representing physical quantities. As shown in Fig. 1.2, quantities such as the entropy  $S$ , the volume  $V$  and the specific heat  $C$  show such singularities as a discontinuity (jump), a *cusp* or a divergence. An example is the melting of ice, in which latent heat must be supplied to the system and consequently the entropy jumps as illustrated in Fig. 1.2(a). When water boils and changes to vapor, the volume changes discontinuously. From a physics standpoint the reason behind the occurrence of a phase transition is the competition between the (internal) energy  $E$  and the entropy  $S$  of the system, which together determine its free energy  $F = E - TS$ . While the first term ( $E$ ) favors order, the second ( $S$ ) privileges disorder, and depending on the value of the external parameters (such as  $T$ ), one of the two terms dominates. According to the conventional classification, phase transitions are roughly divided into two types by the degree of singularity in physical quantities. When the first-order derivative of the free energy  $F$  shows a discontinuity, the transition is of *first order*. The transition is called *continuous* if the second- or higher-order derivatives of the free energy show a discontinuity or a divergence. It is also common to name phase transitions by the order of the derivative that first shows a discontinuity or divergence, e.g. it is called *second order* if it is the second-order derivative of the free energy that first displays the discontinuity or divergence.

## Mean field theories

Very few models of statistical mechanics have been solved exactly; in most of the cases one has to rely on approximative methods. Among them, the mean-field approximation (MFA) is one of the most widely used. The advantage of the mean-field theory is its simplicity and that it correctly predicts the qualitative features of a system in most cases.

The essence of the mean-field theory is the assumption of statistical independence of the local ordering (spins in the case of magnetic systems). The interaction terms in the Hamiltonian are replaced by an effective, "mean field" term. In this way, all the information on correlations in the fluctuations is lost. Therefore, the mean-field theory is usually inadequate in the critical regime. It usually gives wrong critical exponents, in particular at low spatial dimensions when the number of NN is small.

The MFA becomes exact in the limit as the number of interacting neighbours  $z \rightarrow \infty$ . This is the case when the range of interaction  $z \rightarrow \infty$  or if the spatial dimension is high. In both cases, a site "feels" contributions from many neighbours and therefore the fluctuations average out or become even irrelevant (for Ising systems, they become irrelevant in  $d \geq 4$ ). At low  $d$ , the MFA must be used with caution. Not only that it predicts wrong critical exponents, its predictions are even qualitatively wrong sometimes. For example, it predicts long-range order and finite critical temperature for the  $d = 1$  Ising model. In the following, we shall introduce and formulate the MFA for magnetic systems. In the Appendix A we summarize basic thermodynamic relations for magnetic systems. The results,

## Weiss-Molecular Field of an Ising System

**Two formulations of the mean-field approximation.** We will now formulate the mean-field approximation in two different ways.

- A: The "Weiss molecular field theory" according to its "inventor" Pierre Weiss. This method is straightforward and easy to understand. It gives us an expression for the order parameter but does not tell us anything about the free energy or partition function.
- B: The second method will be the Bragg-Williams approximation which is more sophisticated and is based on the free energy minimization.

We will develop the mean-field approximation on the Ising model in an external magnetic field.

Weiss formulated a theory of ferromagnetism in which he assumed that the effect of the neighbouring spins on a given spin can be described by a fictitious “molecular field” which is proportional to the average magnetization of the system.

We start with the Ising Hamiltonian in an external magnetic field:

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i. \quad (1)$$

The local field acting on the spin at the site  $i$  is:

$$H_i = J \sum_j S_j + H. \quad (2)$$

It depends on the configuration of all the neighbouring spins around the site  $i$ . If the lattice is such that each spin has many neighbours, then it is not a bad approximation to replace the actual value of the neighbouring spins by the *mean value* of all spins,

$$\sum_j S_j \rightarrow zm, \quad (3)$$

where  $z$  is the number of nearest neighbours and  $m$  is the mean (average) magnetization per site,  $m = \frac{1}{N} \sum_j S_j$ . With (3), the local field becomes

$$H_i = zJm + H, \quad (4)$$

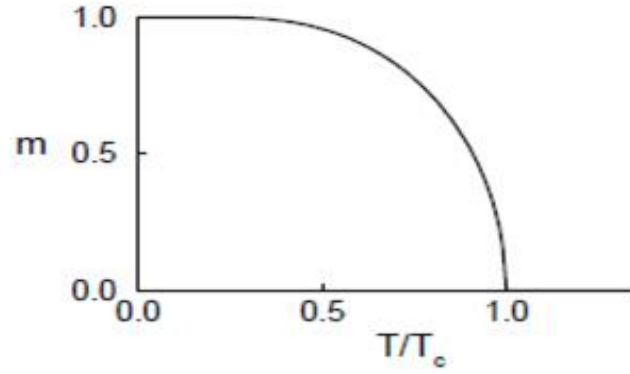


Figure 1: Temperature dependence of the order parameter in the mean-field approximation.

The actual local field acting on the site  $i$  was replaced by its mean value and is independent of the site,  $H_i \rightarrow H_{MF}$ . In the *mean-field* approximation the original Hamiltonian is replaced by a mean-field Hamiltonian

$$\mathcal{H}_{MF} = -H_{MF} \sum_i S_i, \quad (5)$$

which is equivalent to the Hamiltonian of a non-interacting spin system in an external magnetic field and can be solved exactly:

$$m = \tanh(\beta H_{MF}) = \tanh[\beta(zJm + H)]. \quad (6)$$

This is a self-consistent, transcendental equation for  $m$ . It has a non-trivial solution ( $m \neq 0$ ) for  $\beta zJ > 1$ , i.e., at low temperatures. The temperature dependence of the order parameter  $m$  for  $H = 0$  is shown in Fig. 1. It vanishes at the *critical temperature*  $T_C = zJ$ .

### Phase transition

A **phase transition** is the transformation of a thermodynamic system from one phase or state of matter to another one by heat transfer. The term is most commonly used to describe transitions between solid, liquid and gaseous states of matter, and, in rare cases, plasma. A phase of a thermodynamic system and the states of matter have uniform physical properties. During a phase transition of a given medium certain properties of the medium change, often discontinuously, as a result of the change of some external condition, such as temperature, pressure, or others. For example, a liquid may become gas upon heating to the boiling point, resulting in an abrupt change in volume. The measurement of the external conditions at which the transformation occurs is termed the phase transition. Phase transitions are common in nature and used today in many technologies.



Phase transitions occur when the thermodynamic free energy of a system is non-analytic for some choice of thermodynamic variables (cf. phases). This condition generally stems from the interactions of a large number of particles in a system, and does not appear in systems that are too small. It is important to note that phase transitions can occur and are defined for non-thermodynamic systems, where temperature is not a parameter. Examples include: quantum phase transitions, dynamic phase transitions, and topological (structural)

phase transitions. In these types of systems other parameters take the place of temperature. For instance, connection probability replaces temperature for percolating networks.

At the phase transition point (for instance, boiling point) the two phases of a substance, liquid and vapor, have identical free energies and therefore are equally likely to exist. Below the boiling point, the liquid is the more stable state of the two, whereas above the gaseous form is preferred.

## **Critical Indices**

**Critical indices** describe the behaviour of physical quantities near continuous phase transitions. It is believed, though not proven, that they are universal, i.e. they do not depend on the details of the physical system, but only on, the dimension of the system, the range of the interaction, the spin dimension.

These properties of critical exponents are supported by experimental data. The experimental results can be theoretically achieved in mean field theory for higher-dimensional systems (4 or more dimensions). The theoretical treatment of lower-dimensional systems (1 or 2 dimensions) is more difficult and requires the renormalization group. Phase transitions and critical exponents appear also in percolation systems. However, here the critical dimension above which mean field exponents are valid is 6 and higher dimensions.<sup>[1]</sup> Mean field critical exponents are also valid for random graphs, such as Erdős–Rényi graphs, which can be regarded as infinite dimensional systems.

## Ising Model

The Ising model is one of the simplest and most fundamental models of statistical mechanics. It can be used to describe such diverse phenomena as *magnets*; *liquid/gas coexistence*; *alloys of two metals*; and many others, even outside of physics.

Each such system can be described by elementary variables  $s_i$ , usually called “*spins*” with 2 possible values  $s_i = \pm 1$ . The 2 values stand for, e.g., an elementary magnet pointing *up* or *down*; a piece of *liquid* or *gas*; an atom of metal *A* or *B*; etc.). These variables usually live on the sites  $i$  of some lattice. One associates an energy

$$E = -J \sum_{\text{neighbors } i,j} s_i s_j \quad (1)$$

with each configuration of spins, where  $J$  is some constant. Each state of the system occurs with probability given by the *Boltzmann factor*

$$p = \frac{1}{Z} \exp\left(-\frac{E}{k_B T}\right), \quad (2)$$

where  $T$  is temperature,  $k_B$  the Boltzmann constant, and  $Z$  a normalization factor.

Even though the Ising model is drastically simplified from realistic situations, it is able to describe, often quantitatively, the occurrence of *order* at low temperatures and *disorder* at high temperatures, and especially the *phase transition* between those situation, in which spin correlations over very large length scales become essential.

The Ising model can be solved exactly only in the simplest cases (in one spatial dimension, and on a two-dimensional square lattice). In most cases of practical interest, one has to resort to either *analytical approximations* like series expansions for high or for low temperature, or to *numerical techniques* like *Markov Chain Monte Carlo simulations*.

## Interactive simulation

The simulation shows the two-dimensional Ising model. Every little box of the spin field represents one of the two possible states  $s_i = \pm 1$ . The constants  $J$  and  $k_B$  are omitted.

You can control the temperature either by typing a positive real number into the temperature field or by adjusting the slide rule with the mouse. The critical temperature of the model is  $T_{crit} = \frac{2}{\ln(1+\sqrt{2})} = 2.269\dots$  The magnetization is simply the mean of all spins.

You can also adjust the lattice size.

The graphs show magnetization and energy of the current configuration.

**Observe the following:**

1. Set the temperature to be well above the critical temperature (2.26...). You will see that the spin arrangement converges to a nearly random arrangement, independent of the starting state: "Cold", or "Hot", and fluctuates quickly. Hence, above the critical temperature, there is a single thermodynamic state, with zero magnetization. At infinite temperature the spin arrangement is truly random.
2. Start well below the critical temperature with initial state "Cold". All the spins will start with equal value. You will see that just a few small clusters of opposite spins appear, and there is a non-zero magnetization. The analogous situation would occur if initially all spins were reversed. Hence, below the critical temperature, there are two thermodynamic states (the "up spin" state with positive magnetization and the "down spin" state negative magnetization). With the Metropolis method the system stays in one or the other depending on how the spins are initialized.
3. Start well below the critical temperature with initial state "Hot". You see that the system initially cannot make up its mind whether to go into the "up spin" or "down spin" state. Large clusters of each spin form. Eventually, if you let the simulation run for a long time, one of the states will win. Which one wins depends on the random thermal fluctuations. There is equal probability for it to be in the "up spin" or "down spin" state.
4. Start at or close to the critical temperature. You will see large clusters of spins with the same orientation, which fluctuate only very slowly. The typical size of these clusters is the so called *correlation length*  $\xi$  which is maximal at the critical temperature, where it would diverge on an infinitely large system.

The slow fluctuation of spins with the Metropolis method is called *critical slowing down*. Fluctuations of spins travel through the lattice locally in this method, like in a random walk. Therefore they are associated with a time scale of  $\tau \simeq \xi^2$  iterations. The system thus keeps a long memory of its initial state, and many iterations must be discarded before useful averages can be taken. These then need many iterations to converge, especially on large systems.

## Heisenberg model

The Heisenberg model is a statistical mechanical model used in the study of critical points and phase transitions of magnetic systems, in which the spins of the magnetic systems are treated quantum mechanically. In the prototypical Ising model, defined on a  $d$ -dimensional lattice, at each lattice site, a spin  $\sigma_i \in \{\pm 1\}$  represents a microscopic magnetic dipole to which the magnetic moment is either up or down. Except the coupling between magnetic dipole moments, there is also a multi-polar version of Heisenberg model called the multipolar exchange interaction.

For quantum mechanical reasons (see exchange interaction or the subchapter "quantum-mechanical origin of magnetism" in the article on magnetism), the dominant coupling between two dipoles may cause nearest-neighbors to have lowest energy when they are *aligned*. Under this assumption (so that magnetic interactions only occur between adjacent dipoles) the Hamiltonian can be written in the form

$$\hat{H} = -J \sum_{j=1}^N \sigma_j \sigma_{j+1} - h \sum_{j=1}^N \sigma_j$$

Where,  $J$  is the coupling constant for a 1-dimensional model consisting of  $N$  dipoles, represented by classical vectors (or "spins")  $\sigma_j$ , subject to the periodic boundary condition  $\sigma_{N+1} = \sigma_1$ . The Heisenberg model is a more realistic model in that it treats the spins quantum-mechanically, by replacing the spin by a quantum operator (Pauli spin-1/2 matrices at spin 1/2), and the coupling constants  $J_x, J_y$  and  $J_z$ . As such in 3-dimensions, the Hamiltonian is given by

$$\hat{H} = -\frac{1}{2} \sum_{j=1}^N (J_x \sigma_j^x \sigma_{j+1}^x + J_y \sigma_j^y \sigma_{j+1}^y + J_z \sigma_j^z \sigma_{j+1}^z + h \sigma_j^z)$$

Where the  $h$  on the right-hand side indicates the external magnetic field, with periodic boundary conditions, and at spin  $s = 1/2$ ,

The spin matrices are given by

$$\sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\sigma^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The Hamiltonian then acts upon the tensor product , of dimension  $2^N$  . The objective is to determine the spectrum of the Hamiltonian, from which the partition function can be calculated, from which the thermodynamics of the system can be studied.

A simplified version of Heisenberg model is the one-dimensional Ising model, where the transverse magnetic field is in the x-direction, and the interaction is only in the z-direction:

$$\hat{H} = -J_z \sum_{j=1}^N \sigma_j^z \sigma_{j+1}^z - gJ_z \sum_{j=1}^N \sigma_j^x$$

At small g and large g, the ground state degeneracy is different, which implies that there must be a quantum phase transition in between. It can be solved exactly for the critical point using

the duality analysis. The duality transition of the Pauli matrices is  $\sigma_i^z = \prod_{j \leq i} S_j^x$  and  $\sigma_i^x = S_i^z S_{i+1}^z$ , where  $S_i^z$  and  $S_i^x$  are also Pauli matrices which obey the Pauli matrix algebra. Under periodic boundary conditions, the transformed Hamiltonian can be shown is of a very similar form:

$$\hat{H} = -gJ_z \sum_{j=1}^N S_j^z S_{j+1}^z - J_z \sum_{j=1}^N S_j^x$$

but for the  $g$  attached to the spin interaction term. Assuming that there's only one critical point, we can conclude that the phase transition happens at  $g = 1$  .

The most widely known type of Heisenberg model is the Heisenberg XXZ model, which occurs in the case  $J = J_x = J_y \neq J_z = \Delta$ . The spin 1/2 Heisenberg model in one



dimension may be solved exactly using the Bethe ansatz, while other approaches do so without Bethe ansatz.

The physics of the Heisenberg model strongly depends on the sign of the coupling constant  $J$  and the dimension of the space. For positive  $J$  the ground state is always ferromagnetic. At negative  $J$  the ground state is antiferromagnetic in two and three dimensions; it is from this ground state that the Hubbard model is given. In one dimension the nature of correlations in the antiferromagnetic Heisenberg model depends on the spin of the magnetic dipoles. If the spin is integer then only short-range order is present.

### Energy fluctuations in the canonical ensemble

In the canonical ensemble, the total energy is not conserved. (  $H(\mathbf{x}) \neq \text{const}$  ).

What are the fluctuations in the energy? The energy fluctuations are given by the root mean square deviation of the Hamiltonian from its average  $\langle H \rangle$

$$\Delta E = \sqrt{\langle (H - \langle H \rangle)^2 \rangle} = \sqrt{\langle H^2 \rangle - \langle H \rangle^2}$$

$$\langle H \rangle = -\frac{\partial}{\partial \beta} \ln Q(N, V, T)$$

$$\langle H^2 \rangle = \frac{1}{Q} C_N \int d\mathbf{x} H^2(\mathbf{x}) e^{-\beta H(\mathbf{x})}$$

$$= \frac{1}{Q} C_N \int d\mathbf{x} \frac{\partial^2}{\partial \beta^2} e^{-\beta H(\mathbf{x})}$$

$$= \frac{1}{Q} \frac{\partial^2}{\partial \beta^2} Q$$

$$= \frac{\partial^2}{\partial \beta^2} \ln Q + \frac{1}{Q^2} \left( \frac{\partial Q}{\partial \beta} \right)^2$$

$$= \frac{\partial^2}{\partial \beta^2} \ln Q + \left[ \frac{1}{Q} \frac{\partial Q}{\partial \beta} \right]^2$$

$$= \frac{\partial^2}{\partial \beta^2} \ln Q + \left[ \frac{\partial}{\partial \beta} \ln Q \right]^2$$

Therefore

$$\langle H^2 \rangle - \langle H \rangle^2 = \frac{\partial^2}{\partial \beta^2} \ln Q$$

But

$$\frac{\partial^2}{\partial \beta^2} \ln Q = kT^2 C_V$$

Thus,

$$\Delta E = \sqrt{kT^2 C_V}$$

Therefore, the relative energy fluctuation  $\Delta E/E$  is given by

$$\frac{\Delta E}{E} = \frac{\sqrt{kT^2 C_V}}{E}$$

Now consider what happens when the system is taken to be very large. In fact, we will define a formal limit called the *thermodynamic limit*, in which  $N \rightarrow \infty$

and  $V \rightarrow \infty$  such that  $N/V$  remains constant.

Since  $C_V$  and  $E$  are both extensive variables,  $C_V \sim N$  and  $E \sim N$ ,

$$\frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}} \rightarrow 0 \text{ as } N \rightarrow \infty$$

But  $\Delta E/E$  would be exactly 0 in the micro canonical ensemble. Thus, in the thermodynamic limit, the canonical and micro canonical ensembles are equivalent, since the energy fluctuations become vanishingly small.

## Wiener-Khinchin Theorem

The Wiener–Khinchin theorem (also known as the Wiener–Khintchine theorem and sometimes as the Wiener–Khinchin–Einstein theorem or the Khinchin–Kolmogorov theorem) states that the power spectral density of a wide-sense-stationary random process is the Fourier transform of the corresponding autocorrelation function.

---

Recall the definition of the autocorrelation function  $C(t)$  of a function  $E(t)$ ,

$$C(t) \equiv \int_{-\infty}^{\infty} \overline{E}(\tau) E(t + \tau) d\tau. \quad (1)$$

Also recall that the Fourier transforms of  $E(t)$  is defined by

$$E(\tau) = \int_{-\infty}^{\infty} E_{\nu} e^{-2\pi i \nu \tau} d\nu, \quad (2)$$

Giving a complex conjugate of

$$\overline{E}(\tau) = \int_{-\infty}^{\infty} \overline{E}_{\nu} e^{2\pi i \nu \tau} d\nu. \quad (3)$$

Plugging  $\overline{E}(\tau)$  and  $E(t + \tau)$  into the autocorrelation function therefore gives

$$C(t) = \int_{-\infty}^{\infty} \left[ \int_{-\infty}^{\infty} \overline{E}_{\nu} e^{2\pi i \nu \tau} d\nu \right] \left[ \int_{-\infty}^{\infty} E_{\nu'} e^{-2\pi i \nu' (t + \tau)} d\nu' \right] d\tau \quad (4)$$

$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \overline{E}_{\nu} E_{\nu'} e^{-2\pi i \tau (\nu' - \nu)} e^{-2\pi i \nu' t} d\tau d\nu d\nu' \quad (5)$$



$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \bar{E}_\nu E_{\nu'} \delta(\nu' - \nu) e^{-2\pi i \nu' t} d\nu d\nu' \quad (6)$$

$$(7)$$

$$= \int_{-\infty}^{\infty} \bar{E}_\nu E_\nu e^{-2\pi i \nu t} d\nu \quad (8)$$

$$= \int_{-\infty}^{\infty} |E_\nu|^2 e^{-2\pi i \nu t} d\nu \quad (9)$$

$$= \mathcal{F}_\nu [|E_\nu|^2] (t),$$

so, amazingly, the autocorrelation is simply given by the Fourier transform of the absolute square of  $E_\nu$ . The Wiener-Khinchin theorem is a special case of the cross-correlation theorem with  $f = g$ .

### Reversible and Irreversible Thermodynamic process

In science, a process that is not reversible is called irreversible. This concept arises most frequently in thermodynamics. In thermodynamics, a change in the thermodynamic state of a system and all of its surroundings cannot be precisely restored to its initial state by infinitesimal changes in some property of the system without expenditure of energy. A system that undergoes an irreversible process may still be capable of returning to its initial state; however, the impossibility occurs in restoring the environment to its own initial conditions. An irreversible process increases the entropy of the universe. However, because entropy is a state function, the change in entropy of the system is the same whether the process is reversible or irreversible. The second law of thermodynamics can be used to determine whether a process is reversible or not.

All complex natural processes are irreversible. The phenomenon of irreversibility results from the fact that if a thermodynamic system, which is any system of sufficient complexity, of interacting molecules is brought from one thermodynamic state to another, the configuration or arrangement of the atoms and molecules in the system will change in a way that is not easily predictable. A certain amount of "transformation energy" will be used as the molecules of the "working body" do work on each other when they change from one state to another. During this transformation, there will be a certain amount of heat energy loss or dissipation due to intermolecular friction and collisions; energy that will not be recoverable if the process is reversed.

## Onsager reciprocal relations

In thermodynamics, the **Onsager reciprocal relations** express the equality of certain ratios between flows and forces in thermodynamic systems out of equilibrium, but where a notion of local equilibrium exists. "Reciprocal relations" occur between different pairs of forces and flows in a variety of physical systems. For example, consider fluid systems described in terms of temperature, matter density, and pressure. In this class of systems, it is known that temperature differences lead to heat flows from the warmer to the colder parts of the system; similarly, pressure differences will lead to matter flow from high-pressure to low- pressure regions. What is remarkable is the observation that, when both pressure and temperature vary, temperature differences at constant pressure can cause matter flow (as in convection) and pressure differences at constant temperature can cause heat flow. Perhaps surprisingly, the heat flow per unit of pressure difference and the density (matter) flow per unit of temperature difference are equal. This equality was shown to be necessary by Lars Onsager using statistical mechanics as a consequence of the time reversibility of microscopic dynamics (microscopic reversibility). The theory developed by Onsager is much more general than this example and capable of treating more than two thermodynamic forces at once, with the limitation that "the principle of dynamical reversibility does not apply when (external) magnetic fields or Coriolis forces are present", in which case "the reciprocal relations break down"

## ONSAGER's Theorem

A rigorous description of thermal influences on the electrical current and vice versa has been presented by ONSAGER in 1931. His theory discusses the relations of reciprocity of reversible and irreversible processes, where the coupling of the electrical and the thermal subsystems are investigated. For instance, if the electrical driving force is denoted as  $X_1 = E$  and the thermodynamic driving force is expressed as,

$$X_2 = -\frac{1}{T} \nabla T, \quad (1)$$

Where  $T$  has been identified as the absolute temperature by CARNOT, the corresponding equation system can be formulated with independent equations as

$$\mathbf{X}_1 = R_1 \mathbf{J}_1 \quad (2)$$

$$\mathbf{X}_2 = R_2 \mathbf{J}_2, \quad (3)$$

Where  $R_1$  and  $R_2$  are the electrical resistivity and the thermal "heat resistance", respectively. The heat resistance is also called thermal resistance  $\mathbf{R}_{th}$  in this thesis.

The quantities  $\mathbf{J}_1$  and  $\mathbf{J}_2$  are the electrical and the thermal current, respectively.

The thermal current density  $\mathbf{J}_2$  is also called heat flow density  $\mathbf{q}_{th}$ . Equations  $\mathbf{R}_{12}$  and  $\mathbf{R}_{21}$  are coupled. Introducing the standard notation, these equations can be adapted by cross coefficients and represent the ONSAGER relations

$$\mathbf{X}_1 = R_{11} \mathbf{J}_1 + R_{12} \mathbf{J}_2, \quad (4)$$

$$\mathbf{X}_2 = R_{21} \mathbf{J}_1 + R_{22} \mathbf{J}_2. \quad (5)$$

For this equation system, THOMSON proposed the relation

$$R_{12} = R_{21}, \quad (6)$$

Which is also called "reciprocity theorem" of the ONSAGER relations. However, implies that this relation follows from symmetric principles of thermodynamic theory. Hence, the reciprocity theorem neglects the loss during heat conduction and energy conversion and relation assumes a balanced energy flow between the two subsystems. Thus, a steady stage is assumed with the request of, where equilibrium conditions are applicable only within short range.

The principle of microscopic reversibility in  $\mathbf{R}_{ij}$  is less general than the second fundamental law of thermodynamics. For further investigated coupled systems, the currents may have different signs due to the different directions of the energy flows.

Therefore,  $\partial_t S \geq 0$  is not sufficient enough to fulfill the second law of thermodynamics. Hence, the necessary condition for the equation system consisting of and to guarantee the second law with yields

$$R_{12} + R_{21} \leq 2\sqrt{R_{11}R_{22}}. \quad (7)$$

This necessary condition has been originally proposed by BOLTZMANN in 1887.

Writing the ONSAGER relations and as functions of driving forces  $\mathbf{X}_i$

$$\mathbf{J}_1 = L_{11}\mathbf{X}_1 + L_{12}\mathbf{X}_2 \quad (8)$$

$$\mathbf{J}_2 = L_{21}\mathbf{X}_1 + L_{22}\mathbf{X}_2, \quad (9)$$

where the necessary condition of type remains valid accordingly for  $L_{ij}$  as

$$L_{12} + L_{21} \leq 2\sqrt{L_{11}L_{22}}. \quad (10)$$

To consider the ONSAGER relations in terms of energy, and can be multiplied by  $\mathbf{X}_1$  and  $\mathbf{X}_2$ , respectively, leading to

$$\mathbf{J}_1 \cdot \mathbf{X}_1 = L_{11}\mathbf{X}_1 \cdot \mathbf{X}_1 + L_{12}\mathbf{X}_2 \cdot \mathbf{X}_1, \quad (11)$$

$$\mathbf{J}_2 \cdot \mathbf{X}_2 = L_{21}\mathbf{X}_1 \cdot \mathbf{X}_2 + L_{22}\mathbf{X}_2 \cdot \mathbf{X}_2. \quad (12)$$

These equations represent the products of the driving forces  $\mathbf{X}_i$  and displacements of types of flow  $\mathbf{J}_i$ .

The result of and can be described as the dissipated energy per volume and per time and reads

$$T\theta = \sum_i \mathbf{J}_i \cdot \mathbf{X}_i, \quad (13)$$

where  $\theta$  is the entropy generation rate per unit volume and follows from the second law of thermodynamics

$$\partial_t S \geq 0 \implies T\partial_t S \geq 0, \quad (14)$$

$$T\theta = \frac{\partial(T\partial_t S)}{\partial V} = \sum_i \mathbf{J}_i \cdot \mathbf{X}_i \geq 0, \quad (15)$$

$$\implies \theta = \frac{\partial(\partial_t S)}{\partial V} = \frac{1}{T} \sum_i \mathbf{J}_i \cdot \mathbf{X}_i \geq 0, \quad (16)$$

where the entropy generation rate  $\partial_t S$  can be determined by the sum of the power densities of all contributing subsystems. Hereby, the parts of the sums can be identified as the power densities of the participating systems which are determined by chemical reactions, the power loss due to heat transfer and JOULE's self-heating, and the power loss due to diffusion processes. The power density of chemical reactions can be expressed by scalar-valued quantities as

$$T\theta^{\text{chem}} = \sum_i J_i^{\text{chem}} X_i^{\text{chem}} = \left( \frac{1}{V} \partial_t \xi_j \right) \left( - \sum_j \nu_j \mu_j \right),$$

$\partial_t \xi_j$

(17)

Where,  $J_i^{\text{chem}}$  is determined by the chemical reaction rate  $\partial_t \xi_j$  per unit volume  $V$ .

The chemical driving force is represented by,  $X_i^{\text{chem}} = - \sum_j \nu_j \mu_j$

Where,  $\nu_j$  denotes the chemical potential and the  $\mu_j$  stoichiometric coefficient of the participating atom. The electrical power density can be identified by

$$T\theta^{\text{el}} = \sum_i \mathbf{J}_i^{\text{el}} \cdot \mathbf{X}_i^{\text{el}} = \sum_i \mathbf{J}_i \cdot \mathbf{E}_i = - \sum_i \mathbf{J}_i \cdot \nabla \varphi_i,$$

(18)

Where  $\mathbf{J}$  and  $\mathbf{E}$  are the electrical current density and the electrical field, respectively. The electric field can be expressed by the spatial gradient of an electrical potential. For electro- magnetical subsystems, the power density has to be appropriately adapted as discussed in Section . Another important contribution to the global entropy increase is the power loss due to thermal heat flow, which can be expressed in terms of by

$$\begin{aligned} T\theta^{\text{heat}} &= \sum_i \mathbf{J}_i^{\text{heat}} \cdot \mathbf{X}_i^{\text{heat}} = \sum_i \mathbf{q}_{\text{th},i} \cdot \left( T_i \nabla \left( \frac{1}{T_i} \right) \right) = \\ &= \sum_i \mathbf{q}_{\text{th},i} \cdot \left( -\frac{1}{T_i} \nabla T_i \right), \end{aligned} \quad (19)$$

Where,  $q_{th}$  represents the local heat flux density. The second term in depicts the thermal driving force according to FOURIER's empirical law. For diffusion processes, the power density can be identified as

$$\begin{aligned} T\theta^{\text{diff}} &= \sum_i \mathbf{J}_i^{\text{diff}} \cdot \mathbf{X}_i^{\text{diff}} = \sum_i \mathbf{J}_i^{\text{mol}} \cdot \left( -T_i \nabla \left( \frac{\mu_i}{T_i} \right) \right) = \\ &= \sum_i \mathbf{J}_i^{\text{mol}} \cdot \left( -\nabla \mu_i + \frac{\mu_i}{T_i} \nabla T_i \right), \end{aligned} \quad (20)$$

Where  $J_i^{\text{mol}}$  is the mole number per unit area and time of the contributing species  $i$ .

The driving force of diffusion processes is determined by the gradient of the chemical potential and by the gradient of the temperature.

Since the power density of diffusion processes has been determined for no external forces, an extension for the applied electrical field has to be made by introducing an additional term that depicts the force acting on charged particles inside the simulation domain. Hence, equation has to be modified as

$$T\theta = \sum_i \mathbf{J}_i^{\text{mol}} \cdot \left( -\nabla \mu_i + \frac{\mu_i}{T_i} \nabla T_i - Z_i^* n_i \nabla \varphi_i \right), \quad (21)$$

Where  $Z_i^*$  is the effective valence charge of the species  $i$ ,  $n_i$  is the species concentration per mole, and  $\varphi_i$  is the corresponding electrical potential.

To conclude ONSAGER's thermodynamical treatment, the overall power density is thus given by the sum of the power densities of all contributing subsystems as

$$T\theta = T \sum_i \theta_i = T \left( \theta^{\text{chem}} + \theta^{\text{el}} + \theta^{\text{heat}} + \theta^{\text{diff}} \right) \quad (22)$$

$$\begin{aligned} T\theta = & -\frac{1}{V} \partial_t \xi_j \sum_j \nu_j \mu_j \\ & - \sum_i \mathbf{J}_i \cdot \nabla \varphi_i \\ & + \sum_i \mathbf{q}_i \cdot \left( -\frac{1}{T_i} \nabla T_i \right) \\ & + \sum_i \mathbf{J}_i^{\text{mol}} \cdot \left( -\nabla \mu_i + \frac{\mu_i}{T_i} \nabla T_i - Z_i^* n_i \nabla \varphi_i \right), \end{aligned} \quad (23)$$

where, the thermodynamic power density  $T\theta$  is determined by the contributing chemical reactions, the electrical burden, heat flows, and molar diffusion processes.

### TEXT / REFERENCE BOOKS

1. F. Reif, Statistical and Thermal physics, McGraw Hill, International Edition, Singapore, 1979.
2. B.R. Agarwal and N. Eisnor, Statistiactal Mechanics, 2nd ed, Wiley Eastern Limited, New Delhi.
3. R. Huang, Statistical Mechanics, Wiley Eastern Ltd., New Delhi, 1983.
4. F. Mandl, Statistical physics, John Wiley, Londn, 1971.
5. C. Kittel, W. H. Freeman, Thermal Physics, 2nd ed. 1980.
6. F.W.Sears and G.L.Salinger, Thermodynamics, kinetic theory and statistical thermodynamics, 3rd edition, Narosa publishing house, 1998.

## **QUESTION BANK**

### **PART-A**

1. What is called Critical Phenomena?
2. Describe the Phase Transitions in Thermodynamics.
3. Explain the process of Ferromagnetic Transition by statistical mechanics.
4. How to get the Critical indices in Thermodynamics
5. Explain the irreversible process in Thermodynamics.
6. What do you mean by Fluctuations?
7. Explain the elements of non-equilibrium phenomena in Thermodynamics?

### **PART-B**

1. Discuss in detail the Mean Field Theory of Ferromagnetism (or) Weiss theory of Ferromagnetism.
2. Explain the Phase Transition phenomena in Ferromagnetic materials.
3. Discuss and derive Weiner-Khinchine Theorem
4. Derive Onsagar's reciprocity relations in statistical mechanics.