Statistical Thermodynamics

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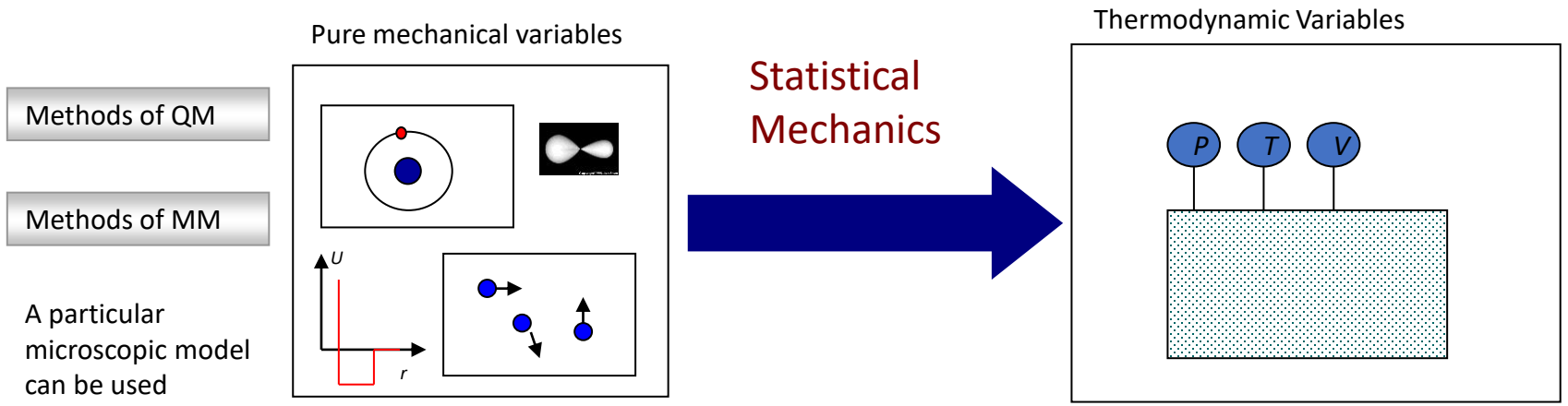
Statistical Thermodynamics

- Thermodynamics
  - Study of the relationships between *macroscopic* properties
    - Volume, pressure, compressibility, …
- Statistical Mechanics (Statistical Thermodynamics)
  - how the various macroscopic properties arise as a consequence of the *microscopic nature* of the system
    - Position and momenta of individual molecules (mechanical variables)

- Statistical Thermodynamics (or Statistical Mechanics) is a link between microscopic properties and bulk (macroscopic) properties



Introduction

- A thermodynamic system is a macrosystem consisting of a large number of molecules.
- It establishing the various thermodynamic function, the structural model of the system is no where required. Without knowing the system is composed of atoms or molecules.
- Statistical thermodynamics develop the thermodynamic properties by expressing the statistical distribution of the molecular properties.
- In statistical mechanics the energy of the system we can express without knowing the motion of individual molecules, only with the number ways the molecules distributed over the available quantum mechanical energy states.
- The various distribution are known as the microstate of the system.
- The object: to interpret the equilibrium thermal properties of macroscopic systems (equal temperature, pressure, and chemical potential)
- **The basic postulate of statistical thermodynamics is that: In a state of thermal equilibrium all the accessible/possible microstates of an isolated assembly are equally probable.**

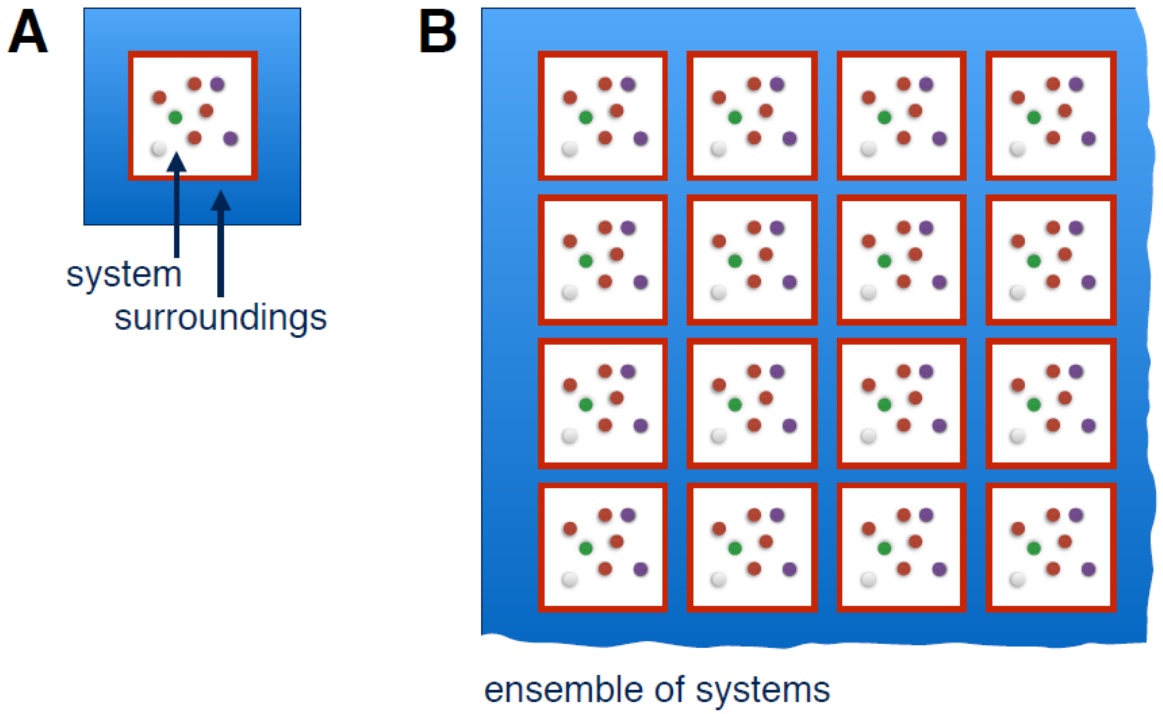
- *Ensemble*: denote a number N of identical entities, such as molecules, atoms, electrons.
- *Macrostate*: is specified by the number of particles in each of the energy levels of the system.
- *Microstate*: is specified by the number of particles in each energy state.
- *Degeneracy*: an energy level contains more than one energy state.
- *Thermodynamic probability*: the number of microstates leading to a given macrostate. It is donated by W_k where k represents the k^{th} macrostate.

Macrostates : T, P, V, … (fewer variables)
Microstates : position, momentum of each particles (~10^{23} variables)

The thermodynamic state also known as the macrostate of a system can be described/fixed by macroscopic parameters like P, T, V & n_i

In contrast, the quantum state of the system (or the microstate) requires a large a large number of variables to describe.

An **ensemble** consists of an infinite (or: very large) number of copies of a particular systems.



- In thermodynamics, the world is always divided into a **system** and its **surroundings**.
- The behavior of the system depends on how the system can interact with its surroundings:
- Statistical thermodynamics introduce the concept of an **ensemble of systems**.

Classification of ensembles

The system in an ensemble are typically not all in the same microstate or macrostate, but all of them interact in the same way with their surroundings. Therefore, ensembles can be classified by the way their systems interacts with their surroundings.

- An isolated system can neither exchange particles nor energy with its surroundings. The energy E, the volume and the number of particles N are constant in these systems $\rightarrow$ **microcanonical ensemble**.
- A closed system cannot exchange particles with its surroundings, but it can exchange energy (in form of heat or work). If the energy exchange occurs via heat but not work, the following parameters are constant: temperature T, volume V and the number of particles N $\rightarrow$ **canonical ensemble**
- In a closed system which exchanges energy with its surrounding via heat and work the following parameters are constant: temperature T, volume p and the number of particles N $\rightarrow$ **isothermal-isobaric ensemble**
- An open system exchanges particles and heat with its surroundings. The following parameters are constant temperature T, volume V and chemical potential μ $\rightarrow$ **grand canonical ensemble**

Ensembles

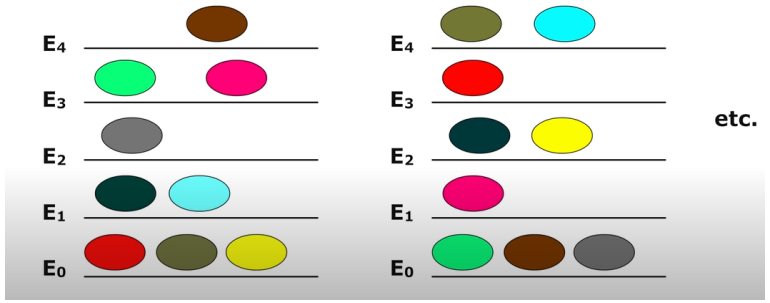
- Micro-canonical ensemble: E,V,N
- Canonical ensemble: T,V,N
- Constant pressure ensemble: T,P,N
- Grand-canonical ensemble: T,V,μ

Assembly of distinguishable particles

- An isolated system consists of N distinguishable particles.
- The macrostate of the system is defined by (N, V, U).
- Particles interact sufficiently, despite very weakly, so that the system is in thermal equilibrium.

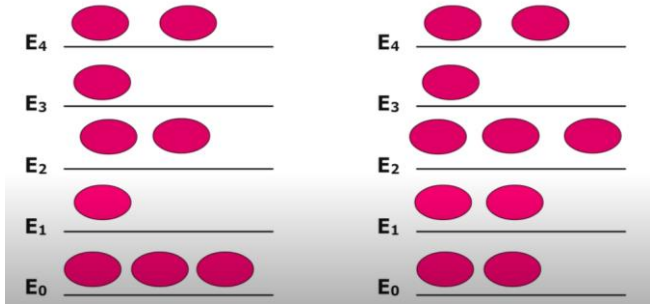
Maxwell-Boltzmann statistics (classical statistic):

- Deal with the distribution of distinguishable particles amongst different energy level (Ex: Ideal gas).
- Do not account about the internal structure are of the molecule.
- No restriction of the concupiscence of the energy level.



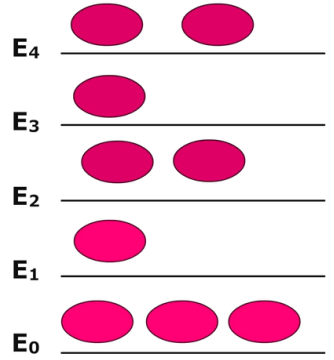
Bose-Einstein Statistic (quantum statistic):

- Indistinguishable particle (Boson: which have integral spin, Ex: Photon, ^4He, deuterium
- Do take into account about the internal structure of the molecules.
- Here also no restriction on the occupancy of the energy level



Fermi-Dirac Statistic:

- Indistinguishable particle (Fermions: which have half integral spin, Ex: electron}
- Do take into account about the internal structure of the molecules.
- Here is a restriction on the occupancy of the energy level



- Two restrictive conditions apply here

$$\sum_{j=1}^{n} N_j = N \quad \text{(conservation of particles)}$$

$$\sum_{j=1}^{n} N_j E_j = U \quad \text{(conservation of energy)}$$

where N_j is the number of particles on the energy level j with the energy E_j.

Concept about “Probability”

In statistics, probabilities are multiplicative.

As an example, consider a true die: The probability of throwing a one is 1/6.
Now if there are two dies, the probability of one coming up on both dies is: $\left(\frac{1}{6}\right)\left(\frac{1}{6}\right)=\left(\frac{1}{36}\right)$

Elementary Statistics

We begin by considering 3 **distinguishable** coins (N D Q)

The possible macrostates are HHH HHT HTT TTT

Let us consider the microstates for the macrostate HHT

H	H	T
N	D	Q
D	N	Q
N	Q	D
Q	N	D
D	Q	N
Q	D	N

The table shows the possible selection of coins.
There are 6 possibilities.
However the pairs shown are not different microstates (the order does not matter).
Hence we have 3 microstates.

The number of particles and their total energy must satisfy

$$\sum_{j=0}^{3} N_j = 3$$

(here the index j starts from 0)

$$\sum_{j=0}^{3} N_j E_j = 3E$$

	# particles on Level 0	# Particles on Level 1 E	# particles on Level 2E	# particles on Level 3E
Case 1	2	0	0	1
Case 2	1	1	1	0
Case 3	0	3	0	0

So far, there are only THREE macrostates satisfying the conditions provided.

Configurations for case 1

Level 0	Level 1E	Level 2E	Level 3E
A, B			C
A, C			B
B, C			A

Thermodynamic probability for case 1 is 3

Configurations for case 2

Level 0	Level 1E	Level 2E	Level 3E
A	B	C	
A	C	B	
B	A	C	
B	C	A	
C	A	B	
C	B	A	

Configuration for case 3

Level 0	Level 1E	Level 2E	Level 3E
	A, B and C		

Therefore, $W_1 = 3$, $W_2 = 6$, and $W_3 = 1$

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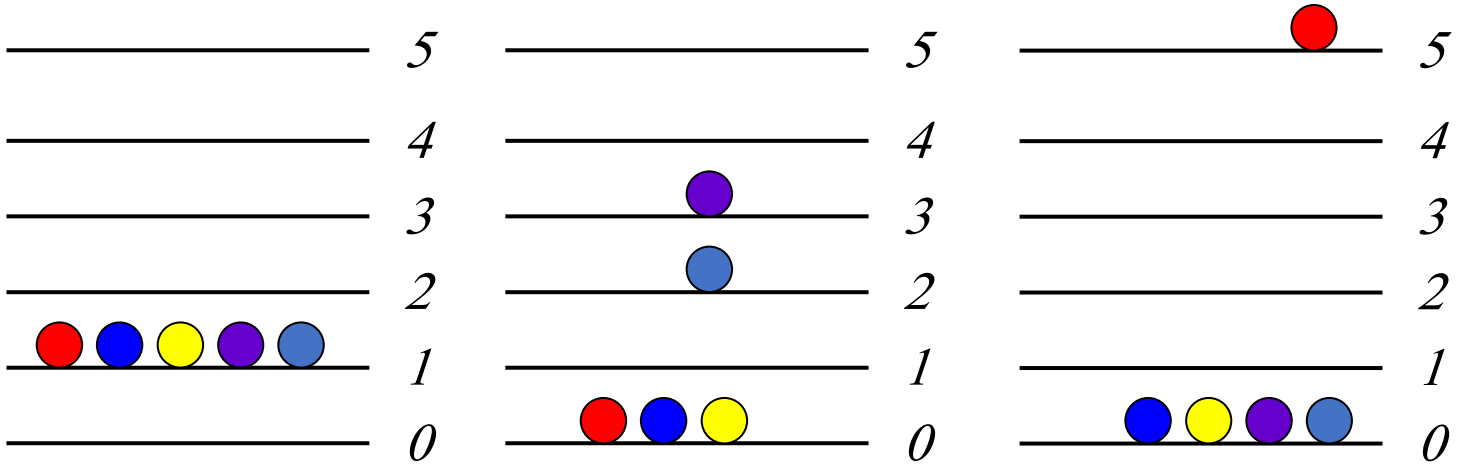
Principles of Equal a Priori Probability

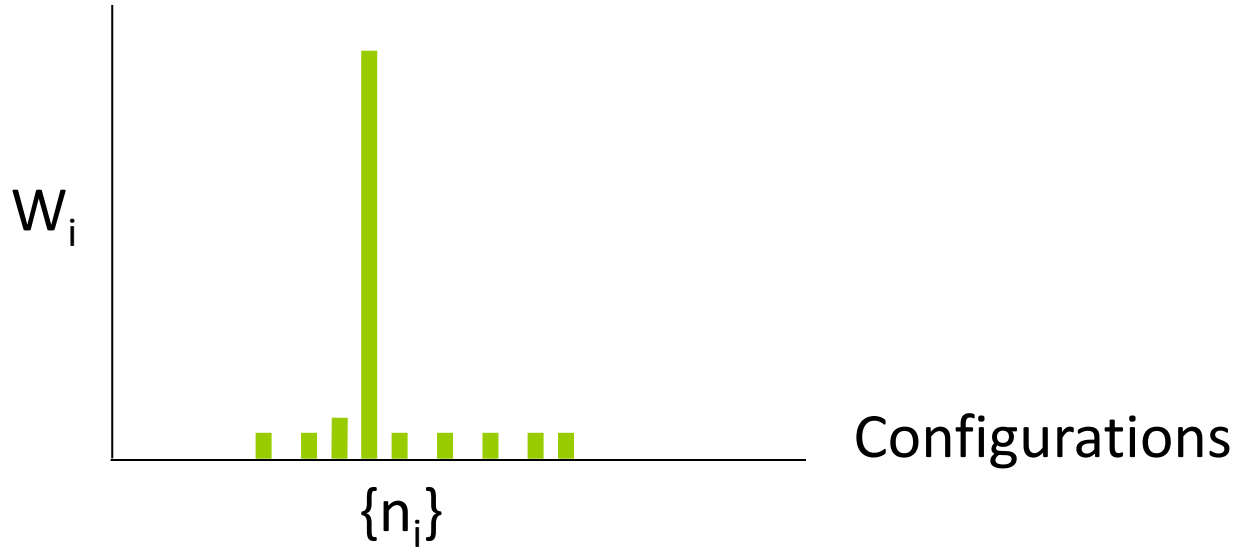
- All distributions of energy are equally probable
- If E = 5 and N = 5 then



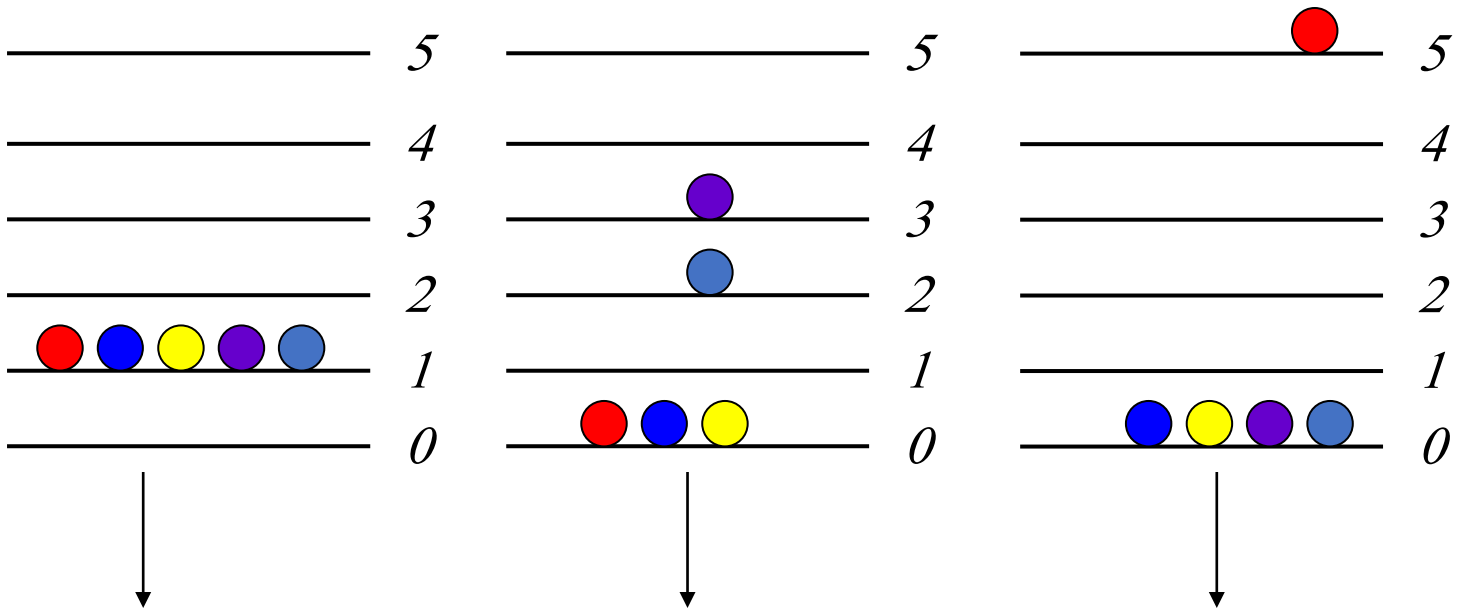
All configurations have equal probability, but possible number of way (weight) is different.

A Dominating Configuration

- For large number of molecules and large number of energy levels, there is a dominating configuration.
- The weight of the dominating configuration is much more larger than the other configurations.



Dominating Configuration



W = 1 (5!/5!)

W = 20 (5!/3!)

W = 5 (5!/4!)

→ Difference in W becomes larger when N is increased !

→ In molecular systems ($N \sim 10^{23}$) considering the most dominant configuration is enough for average

How to find most dominant configuration ?

- The Boltzmann Distribution
  - Task : Find the dominant configuration for given *N* and total energy *E*
  - Method : Find maximum value of *W* which satisfies,

$$N = \sum_i n_i \qquad E = \sum_i \varepsilon_i n_i$$

$$\Rightarrow \quad \sum_i dn_i = 0 \qquad \sum_i \varepsilon_i dn_i = 0$$

Method of Undetermined Multipliers

- Maximum weight , W

  →Recall the method to find min, max of a function…

$$d \ln W = 0$$

$$\left(\frac{\partial \ln W}{dn_i} \right) = 0$$

- Method of undetermined multiplier :
  - Constraints should be multiplied by a constant and added to the main variation equation.

Stirling's approximation

- A useful formula when dealing with factorials of large numbers.

$$\ln N! = N \ln N - N$$

$$\ln W = \ln \frac{N!}{n_1! n_2! n_3! \ldots} = \ln N! - \sum_i \ln n_i!$$

$$= N \ln N - N - \sum_i n_i \ln n_i + \sum_i n_i$$

$$= N \ln N - \sum_i n_i \ln n_i$$

A Typical Example of Distribution

Let five distinguishable particles be distributed over the five energy levels with energies 0, ε, 2ε, 3ε and 4ε, respectively. Let the total energy of the system in any one distribution be 4ε. Assuming equal accessibility of all energy levels to all particles, the possible microstates are shown in Table which also includes the number of ways of achieving the microstates and the corresponding mathematical probabilities of their occurrence in the system.

Analysis of Distribution

The following comments regarding the microstates of a system may be made.

- The number of microstates in a distribution is given by

$$W = \frac{N!}{\Pi_i N_i}$$

where N is the total number of particles and N_is are the number of particles in various energy levels.

Reference: K.L Kapoor

Number of Ways of Distributing Five Distinguishable Particles

Distribution	*Number of Particles in the Energy Levels* 0	ε	2ε	3ε	4ε	*Procedure of Distribution*	*Number of Microstates*	*Mathematical Probability of Occurrence*
I	4	0	0	0	1	Any one of the 5 molecules can be placed in the 4ε level	5	$\frac{5}{70} = 0.071$
II	3	1	0	1	0	5 ways of placing 1st molecule 4 ways of placing 2nd molecule	$5 \times 4 = 20$	$\frac{20}{70} = 0.286$
III	3	0	2	0	0	5 ways of placing 1st molecule 4 ways of placing 2nd molecule Since the molecules are placed in the same energy level, the distribution containing the same molecules is counted twice, hence division by two.	$\frac{5 \times 4}{2} = 10$	$\frac{10}{70} = 0.143$
IV	2	2	1	0	0	5 ways of placing 1st molecule 4 ways of placing 2nd molecule 3 ways of placing 3rd molecule In the energy level ε, each distribution is counted twice, hence divison by two.	$\frac{5 \times 4 \times 3}{2} = 30$	$\frac{30}{70} = 0.429$
V	1	4	0	0	0	5 ways of placing 1st molecule 4 ways of placing 2nd molecule 3 ways of placing 3rd molecule 2 ways of placing 4th molecule In the energy level ε, each distribution is counted $4 \times 3 \times 2$ ways, hence division by 4!	$\frac{5 \times 4 \times 3 \times 2}{4 \times 3 \times 2} = 5$	$\frac{5}{70} = 0.071$
						Total Number of Distributions	70	

Reference: K.L Kapoor

- The total number of microstates in all distributions may be computed by using the expression

$$W_{\text{total}} = \frac{(N + E - 1)!}{(N - 1)!\,E!}$$

where E is the number of quanta of energy in the maximum energy level.

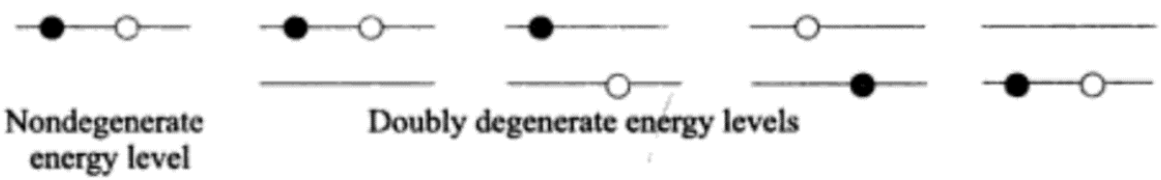
- The mathematical probability of occurrence of a distribution is given by

$$p = \frac{W}{W_{\text{total}}} = \frac{W}{\sum_i W_i}$$

- The most probable distribution corresponds to the maximum probability of occurrence.

Reference: K.L Kapoor

- With the increase in the number of particles, the probability of the most probable distribution increases towards the maximum value of unity (e.g. for $N = 10$, $P = 0.503$; $N = 20$, $P = 0.547$; $N = 50$, $P = 0.786$ and $N = 100$, $P = 0.887$). In a real system where very large number of particles (e.g. 10^{23}) is involved, the probability of the most probable distribution will be almost equal to one.
- The macroscopic properties of a system depend upon the various microscopic states of the system. The fact that the probability of the most probable distribution is nearly unity, the macroscopic properties of a system at equilibrium is largely governed by the most probable distribution.
- In a real system, energy levels may involve degeneracy (i.e. more than one energy state is involved in an energy level). In such a case, the number of ways of distributing the particles is enhanced. For example, the number of ways of distributing two distinguishable particles is increased from **one** in a nondegenerate energy level to **four** in a doubly degenerate energy levels, as shown in the following.



Reference: K.L Kapoor

The general expression for computing the number of microstates for distinguishable particles occupying degenerate energy levels with no restriction on the number of particles in any energy level is given by

$$W = (N!)\left(\Pi_i \frac{g_i^{N_i}}{N_i!}\right)$$

where g_i is the degeneracy of ith energy level.

- The quantity W is frequently called the thermodynamic probability,

For indistinguishable particles, $W = \Pi_i (g_i^{N_i}/N_i!)$

Reference: K.L Kapoor

1. The total number of particles in a system has a constant value, i.e.

$$N = \sum_i N_i = \text{constant} \tag{4.2.5}$$

or equivalently,

$$dN = \sum_i dN_i = 0 \tag{4.2.6}$$

2. The total energy of the system has a constant value, i.e.

$$U = \sum_i N_i \varepsilon_i = \text{constant} \tag{4.2.7}$$

Comment All energies ε_i are measured with respect to the lowest available energy at $T = 0$ K. For translational and rotational motions, $\varepsilon_0 = 0$, but for vibrational motion, $\varepsilon_0 = (1/2)h\nu_0$. Correctly speaking, the internal energy of a system is given by

$$U' = U_0 + \sum_i N_i \varepsilon_i$$

Throughout this chapter, we represent $U' - U_0$ as U.

The condition of constant U implies that

$$dU = \sum_i \varepsilon_i \, dN_i = 0 \tag{4.2.8}$$

The expression of $\ln W$ is

$$\ln W = \ln \left[(N)! \left(\Pi_i \frac{g_i^{N_i}}{N_i!} \right) \right]$$

$$= \ln N! + \sum_i (N_i \ln g_i - \ln N_i!)$$

Reference: K.L Kapoor

For a large value of x, one can simplify $\ln x!$ by using Stirling approximation

$$\ln x ! = x \ln x - x$$

Hence, $$\ln W = (N \ln N - N) + \sum_i [N_i \ln g_i - (N_i \ln N_i - N_i)]$$

The condition of maximizing $\ln W$ is

$$\mathrm{d} \ln W = \sum_i \left(\frac{\partial \ln W}{\partial N_i} \right) \mathrm{d}N_i = 0 \qquad (4.2.9)$$

Now $$\frac{\partial \ln W}{\partial N_i} = \left[\left(\frac{\partial N}{\partial N_i} \right) \ln N + N \cdot \frac{1}{N} \frac{\partial N}{\partial N_i} - \frac{\partial N}{\partial N_i} \right]$$

$$+ \left[\ln g_i - \ln N_i - N_i \frac{1}{N_i} + 1 \right]$$

Since $$\frac{\partial N}{\partial N_i} = \frac{\partial \sum_i N_i}{\partial N_i} = 1,$$ we have

$$\frac{\partial \ln W}{\partial N_i} = \ln N + \ln g_i - \ln N_i = - \ln \left(\frac{N_i}{N g_i} \right)$$

Reference: K.L Kapoor

With this, Eq. (4.2.9) becomes

$$\sum_i -\ln\left(\frac{N_i}{Ng_i}\right) dN_i = 0 \tag{4.2.10}$$

The constancy of number of particles (Eq. 4.2.6) and energy of the system (Eq. 4.2.8) are introduced in Eq. (4.2.10) by the method of Lagrange multipliers. In this method, Eqs (4.2.6) and (4.2.8) are multiplied by undetermined multipliers and added in Eq. (4.2.10). Hence, we can write

$$\sum_i \left[-\ln\left(\frac{N_i}{Ng_i}\right) + \alpha - \beta\varepsilon_i\right] dN_i = 0 \tag{4.2.11}$$

where α and $-\beta$ are the undetermined multipliers. For the sum to be equal to zero, each coefficient of dN_i is set equal to zero. Hence, we write

$$-\ln\left(\frac{N_i}{N g_i}\right) + \alpha - \beta\varepsilon_i = 0 \tag{4.2.12}$$

or
$$N_i = Ng_i e^{\alpha} e^{-\beta\varepsilon_i} \tag{4.2.13}$$

Equation (4.2.13) is known as *Boltzmann distribution law*. This specifies the most probable distribution of particles among the energy levels.

Identification of the Constant α

The constant α may be eliminated by using the relation

$$N = \sum_i N_i$$

Substituting N_i from Eq. (4.2.13), we get

$$N = \sum_i Ng_i e^{\alpha} e^{-\beta\varepsilon_i}$$

Reference: K.L Kapoor

This gives

$$e^{\alpha} = \frac{1}{\sum_i g_i e^{-\beta\epsilon_i}}$$

With this, Eq. (4.2.13) becomes

$$N_i = N \frac{g_i e^{-\beta\epsilon_i}}{\sum_i g_i e^{-\beta\epsilon_i}} = \frac{N}{q} g_i e^{-\beta\epsilon_i} \tag{4.2.14}$$

where q, known as *molecular partition function,* is given by

$$q = \sum_i g_i e^{-\beta\epsilon_i} \tag{4.2.15}$$

The degeneracy of the energy levels is taken care of by the term g_i. However, if we take summation over quantum states, Eq. (4.2.15) may be written as

$$q = \sum_{\text{(states)}} e^{-\beta\epsilon_i}$$

It is for this reason, the molecular partition function is sometimes referred to as a 'sum over states'.

Reference: K.L Kapoor

i.e.
$$U = \frac{1}{2}mN\left[\frac{\int_{-\infty}^{+\infty} v_x^2 \exp(-\beta m v_x^2/2)\,dv_x}{\int_{-\infty}^{+\infty} \exp(-\beta m v_x^2/2)\,dv_x} + \frac{\int_{-\infty}^{+\infty} v_y^2 \exp(-\beta m v_y^2/2)\,dv_y}{\int_{-\infty}^{+\infty} \exp(-\beta m v_y^2/2)\,dv_y} + \frac{\int_{-\infty}^{+\infty} v_z^2 \exp(-\beta m v_z^2/2)\,dv_z}{\int_{-\infty}^{+\infty} \exp(-\beta m v_z^2/2)\,dv_z}\right]$$

Since v_x, v_y and v_z are independent, and each of the three terms has the same form, we can write

$$U = \frac{3}{2}mN\,\frac{\int_{-\infty}^{+\infty} v^2 \exp(-\beta m v^2/2)\,dv}{\int_{-\infty}^{+\infty} \exp(-\beta m v^2/2)\,dv} = \frac{3}{2}mN\left[\frac{(1/2)\sqrt{8\pi/\beta^3 m^3}}{\sqrt{2\pi/\beta m}}\right]$$

$$= \frac{3N}{2\beta}$$

The expression of average kinetic energy becomes

$$\overline{U} = \frac{U}{N} = \frac{3}{2\beta} \qquad (4.2.21)$$

Reference: K.L Kapoor

From the kinetic theory of gases, we have

$$\overline{U} = \frac{3}{2}kT$$

Hence, $$\frac{3}{2\beta} = \frac{3}{2}\,kT$$

This gives

$$\beta = \frac{1}{kT} \qquad (4.2.22)$$

Although, the above expression has been derived for a monatomic gas, it is valid for all types of system.

Reference: K.L Kapoor

Comment on the Molecular Partition Function .

The expression of molecular partition function is

$$q = \sum_i g_i \exp(-\varepsilon_i / kT)$$

At temperature T close to zero, the value of each of the term $\exp(-\varepsilon_i/kT)$ will be close to zero. If $\varepsilon_0 = 0$, then leaving the first term, for which $\exp(-\varepsilon_0/kT)$ will have a value of one, the partition function will have a value close to g_0, i.e.

$$\lim_{T \to 0} q = g_0$$

At very high temperature, the value of each of the term $\exp(-\varepsilon_i/kT)$ will be close to one, and the value of partition function will be close to the number of available energy states.

Thus, the molecular partition function gives an idea about the average number of states that are thermally accessible to a particle at the temperature of the system. At $T = 0$ K, only the lowest energy state will be accessible while at very high temperature, a large number of higher energy states are accessible.

Thermodynamic properties in terms of molecular partition function

Internal Energy

The expression of internal energy is

$$U = \sum_i N_i \varepsilon_i$$

From the Boltzmann expression, we have

$$N_i = \frac{N}{q} g_i e^{-\beta\varepsilon_i}; \qquad \text{(where } \beta = 1/kT\text{)}$$

Hence, $$U = \left(\sum_i \frac{N}{q} g_i e^{-\beta\varepsilon_i}\right)\varepsilon_i$$

From the fact that

$$\left(\frac{\partial e^{-\beta\varepsilon_i}}{\partial\beta}\right)_V = -\varepsilon_i e^{-\beta\varepsilon_i}$$

we can write the above expression as

$$U = -\frac{N}{q}\sum_i g_i\left(\frac{\partial e^{-\beta\varepsilon_i}}{\partial\beta}\right)_V = -\frac{N}{q}\frac{\partial}{\partial\beta}\left(\sum_i g_i e^{-\beta\varepsilon_i}\right)_V = -\frac{N}{q}\left(\frac{\partial q}{\partial\beta}\right)_V$$

$$= -N\left(\frac{\partial \ln q}{\partial\beta}\right)_V \qquad (4.5.1)$$

In terms of T, we have

$$U = -N\left(\frac{\partial \ln q}{\partial T}\right)_V\left(\frac{dT}{d\beta}\right)$$

Since $T = 1/k\beta$, we have

$$\frac{dT}{d\beta} = -\frac{1}{k\beta^2} = -\frac{1}{k(1/kT)^2} = -kT^2$$

Thus $$U = NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V$$

First Law of Thermodynamics

From the first law of thermodynamics, we have

$$dU = dq' + dw \tag{4.5.3}$$

where q' and w stand for heat and work, respectively.

Since $U = \sum_i N_i \varepsilon_i$, we also have

$$dU = \sum_i \varepsilon_i \, dN_i + \sum_i N_i \, d\varepsilon_i \tag{4.5.4}$$

The first term of Eq. (4.5.4) expresses the change in internal energy due to the change in population of particles in the energy levels. This fact may be attributed to the term dq' of Eq. (4.5.3). Hence, we write

$$dq' = \sum_i \varepsilon_i \, dN_i \tag{4.5.5}$$

The second term of Eq. (4.5.4) expresses the change in internal energy due to the change in the magnitude of energy levels. This fact may be attributed to the term dw of Eq. (4.5.3) as the magnitude of energy level is affected by the change in the boundary parameters (say, volume) of the system. Hence, we write

$$dw = \sum_i N_i \, d\varepsilon_i \tag{4.5.6}$$

Expression of Pressure

The expression of mechanical work is

$$dw = -p\,dV$$

Using Eq. (4.5.6), this becomes

$$-p\,dV = \sum_i N_i\,d\varepsilon_i$$

Using the Boltzmann expression, we get

$$-p\,dV = \frac{N}{q}\sum_i (g_i\,e^{-\beta\varepsilon_i}\,d\varepsilon_i)\;; \qquad \text{(where } \beta = 1/kT\text{)} \tag{4.5.7}$$

The differential change in the molecular partition function q at fixed temperature is

$$dq = \sum_i g_i\,e^{-\beta\varepsilon_i}\,(-\beta)\,d\varepsilon_i$$

With this, Eq. (4.5.7) becomes

$$p\,dV = \frac{N}{q}\,\frac{1}{\beta}\,dq = \frac{N}{\beta}\,d\ln q$$

Hence, $$p = \frac{N}{\beta}\left(\frac{\partial \ln q}{\partial V}\right)_T \tag{4.5.8}$$

Since $\beta = 1/kT$, we have

$$p = NkT\left(\frac{\partial \ln q}{\partial V}\right)_T \tag{4.5.9}$$

Expression of Entropy

By definition,

$$dS = \frac{dq'_{rev}}{T} \tag{4.5.10}$$

Using Eq. (4.5.5), this becomes

$$dS = \frac{1}{T}\sum_i \varepsilon_i \, dN_i \tag{4.5.11}$$

Since $\beta = 1/kT$, we get

$$dS = \beta k \sum_i \varepsilon_i \, dN_i = k \sum_i (\beta\varepsilon_i) \, dN_i \tag{4.5.12}$$

From the Boltzmann expression

$$\frac{\partial \ln W}{\partial N_i} + \alpha - \beta\varepsilon_i = 0 \qquad \text{(Eq. 4.2.12)}$$

we get $\beta\varepsilon_i = \dfrac{\partial \ln W}{\partial N_i} + \alpha$

With this, Eq. (4.5.12) becomes

$$dS = k \sum_i \left(\frac{\partial \ln W}{\partial N_i} \right) dN_i + k\alpha \sum_i dN_i \qquad (4.5.13)$$

But $\sum_i dN_i = 0$. Hence

$$dS = k \sum_i \left(\frac{\partial \ln W}{\partial N_i} \right) dN_i = k \, (d \ln W)$$

or $$S = k \ln W \qquad (4.5.14)$$

Equation (4.5.14) is known as *Botlzmann-Planck equation.*

Entropy of Distinguishable Particles

Since $W = N!\,\Pi_i \frac{g_i^{N_i}}{N_i!}$, we get

$$\ln W = \ln N! + \sum_i N_i \ln g_i - \sum_i \ln N_i!$$

Using Stirling approximation, we get

$$\ln W = (N \ln N - N) + \sum_i N_i \ln g_i - \sum_i (N_i \ln N_i - N_i)$$

$$= N \ln N + \sum_i N_i \ln g_i - \sum_i N_i \ln N_i$$

$$= -\sum_i N_i \ln \left(\frac{N_i}{N g_i}\right) \tag{4.5.15}$$

From the Boltzmann expression $N_i = (N/q)\, g_i \exp(-\beta\varepsilon_i)$, we get

$$\frac{N_i}{N g_i} = \frac{e^{-\beta\varepsilon_i}}{q}$$

or $$\ln \left(\frac{N_i}{N g_i}\right) = -\beta\varepsilon_i - \ln q$$

With this, Eq. (4.5.15) becomes

$$\ln W = \sum_i N_i (\beta\varepsilon_i + \ln q) = \beta\left(\sum_i N_i \varepsilon_i\right) + \left(\sum_i N_i\right) \ln q$$

$$= \beta U + N \ln q \tag{4.5.16}$$

Hence, the expression of entropy is

$$S = k \ln W = k\beta U + kN \ln q$$

$$= \frac{U}{T} + kN \ln q \tag{4.5.17a}$$

Substituting the expression of U from Eq. (4.5.2), we get

$$S = NkT \left(\frac{\partial \ln q}{\partial T}\right)_V + Nk \ln q$$

$$= Nk \left[T \left(\frac{\partial \ln q}{\partial T}\right)_V + \ln q\right] \tag{4.5.18a}$$

Entropy of Indistinguishable Particles

For indistinguishable particles

$$W = \Pi_i \frac{g_i^{N_i}}{N_i !}$$

Hence, $\ln W = \sum_i (N_i \ln g_i - \ln N_i !)$

Using Stirling approximation, we get

$$\ln W = \sum_i (N_i \ln g_i - N_i \ln N_i + N_i)$$

$$= \sum_i N_i \ln \frac{g_i}{N_i} + N$$

From Boltzmann expression $N_i = (N/q)\, g_i \exp(-\beta\varepsilon_i)$, we get

$$\frac{g_i}{N_i} = \frac{q}{N} e^{\beta\varepsilon_i}$$

or $$\ln\left(\frac{g_i}{N_i}\right) = \ln\left(\frac{q}{N}\right) + \beta\varepsilon_i$$

Hence, $$\ln W = \sum_i N_i \left[\ln\left(\frac{q}{N}\right) + \beta\varepsilon_i\right] + N$$

$$= N \ln\left(\frac{q}{N}\right) + \beta\left(\sum_i N_i\varepsilon_i\right) + N$$

$$= N \ln\left(\frac{q}{N}\right) + \beta U + N$$

The expression of entropy is

$$S = k \ln W$$

$$= k\left[N \ln\left(\frac{q}{N}\right) + \beta U + N\right]$$

The expression of entropy is

$$S = k \ln W$$

$$= k\left[N \ln\left(\frac{q}{N}\right) + \beta U + N\right]$$

$$= Nk\left[\ln\left(\frac{q}{N}\right) + T\left(\frac{\partial \ln q}{\partial T}\right)_V + 1\right]$$

Enthalpy

Since $H = U + pV$, the expression of H is

$$H = NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V + pV$$

Heat Capacities

Since $C_V = (\partial U / \partial T)_V$, the expression of C_V is

$$C_V = \left[\frac{\partial}{\partial T} NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \right]_V = Nk \left[\frac{\partial}{\partial T} T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \right]_V$$

Since $C_p = (\partial H / \partial T)_p$, the expression of C_p is

$$C_p = \left[\frac{\partial}{\partial T} \left\{ NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V + pV \right\} \right]_p$$