BHARATHIDASAN UNIVERSITY

Tiruchirappalli- 620024
Tamil Nadu, India

Programme: M.Sc., Physics

Course Title : Thermodynamics and Statistical Physics
Course Code : 22PH202

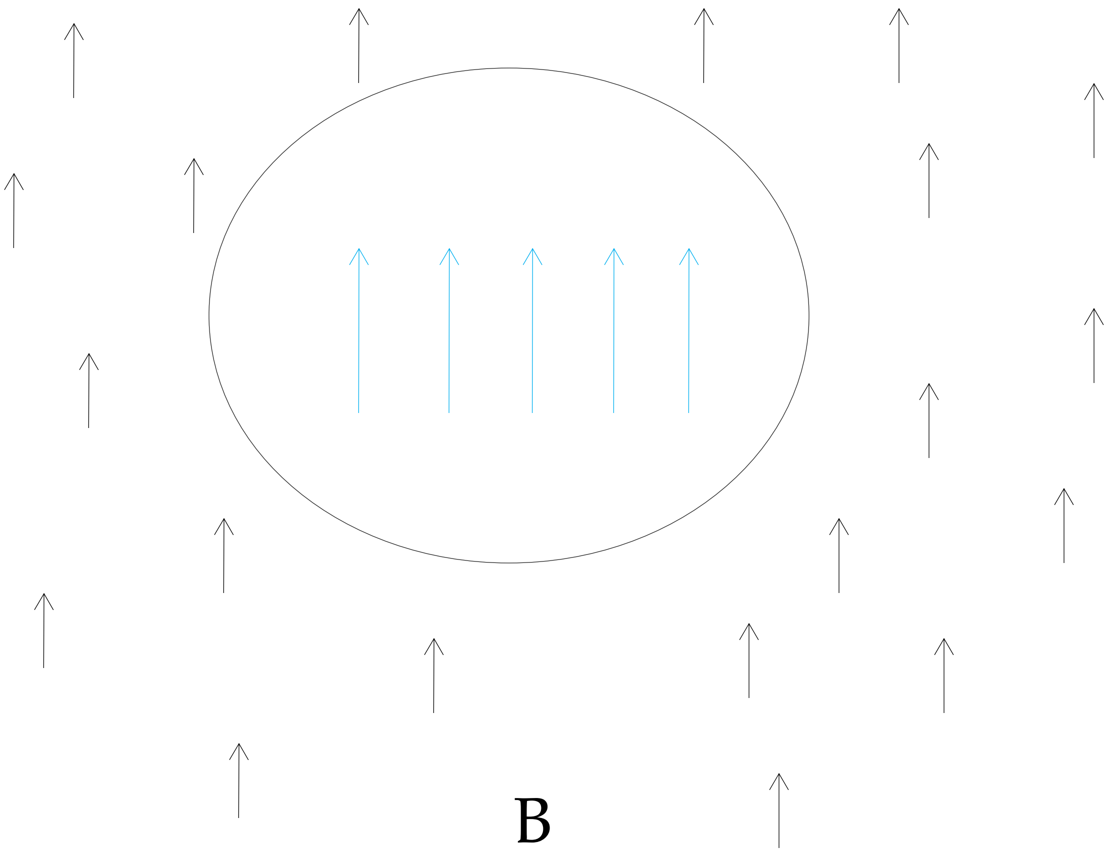
Dr. M. Senthilvelan
Professor
Department of Nonlinear Dynamics

UNIT - II

ENSEMBLE APPROACH

Introduction to Ensembles

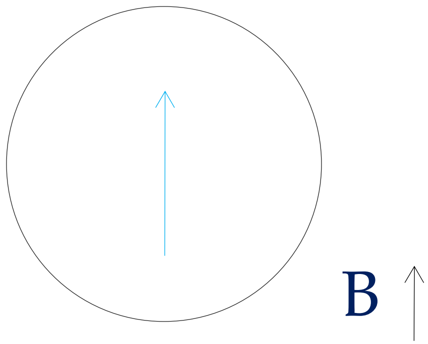
- Consider five non interacting *spins* or ***magnetic dipole***
- They are placed in a magnetic field **'B'**



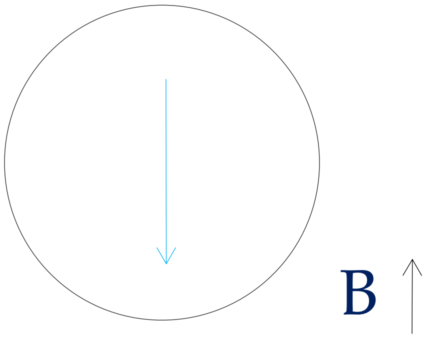
$$E = -\vec{\mu}.\vec{B} = -\mu B \cos\theta$$

$\theta = 0^{o}$ (parallel)

$\theta = 180^{o}$ (anti - parallel)



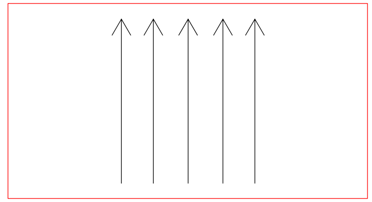
Energy of spin parallel to the magnetic field 'E' = $-\mu B$



Energy of spin anti-parallel to the magnetic field 'E' = $+\mu B$

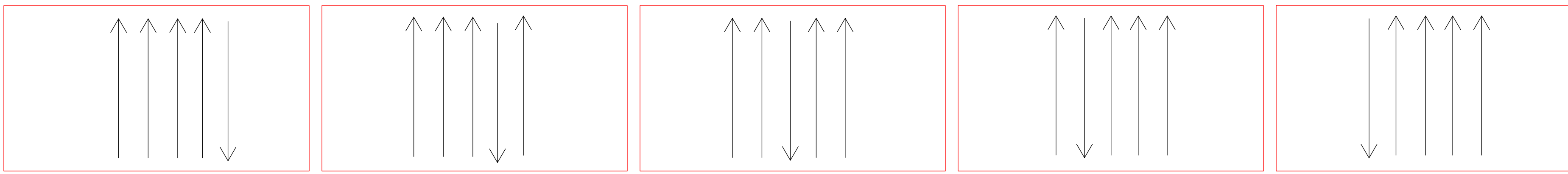
<u>**Question:**</u> Calculate the number of possible states having total energy = $-\mu B$

All Spins Up

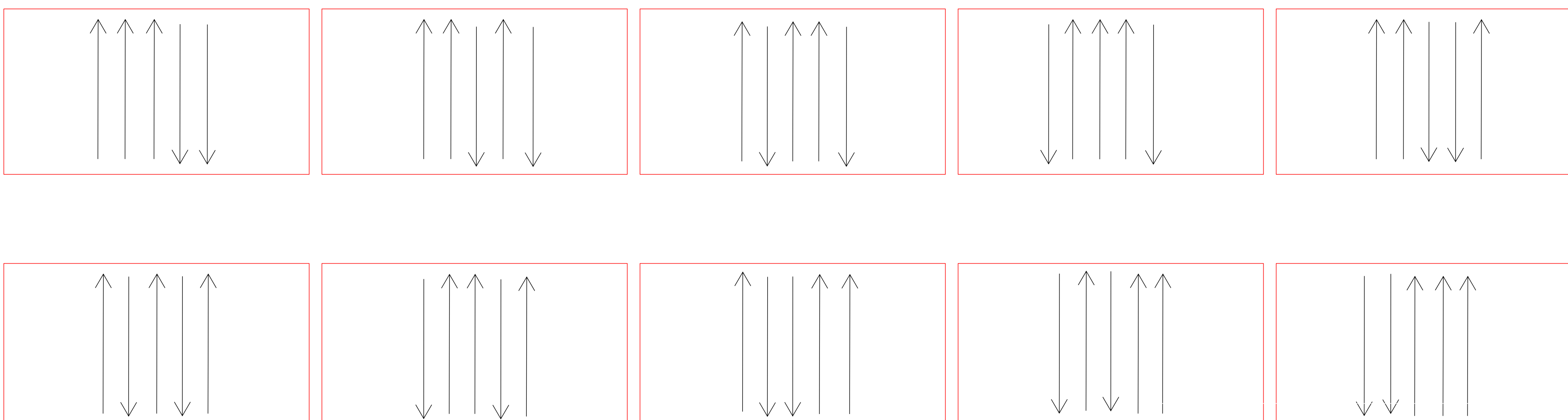


(-5μB) → 1 Microstate

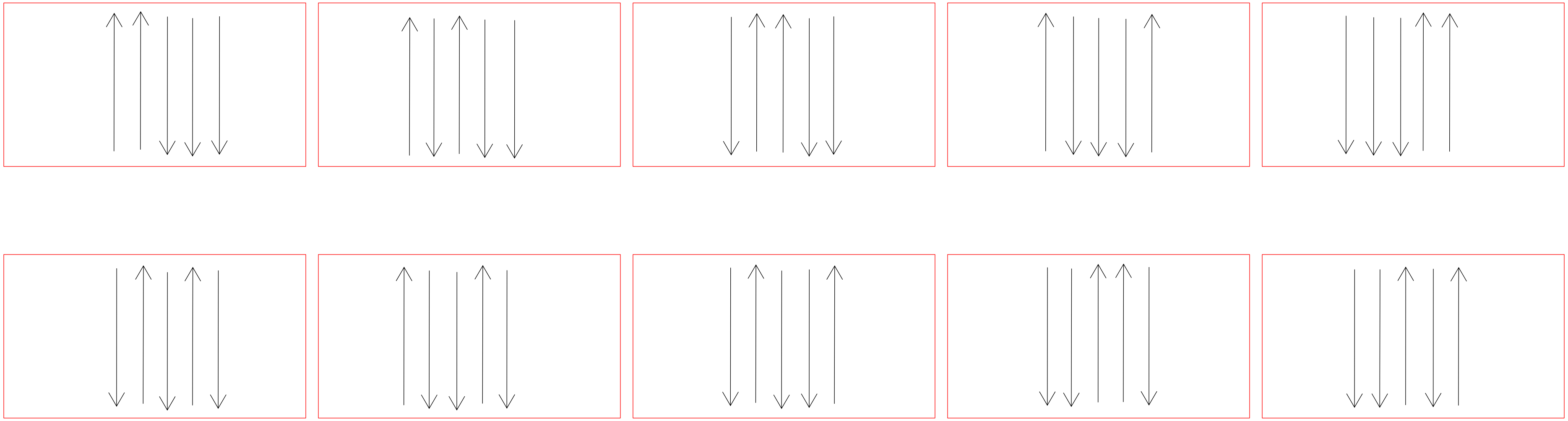
One Spin Down (-3μB) → 5 Microstates



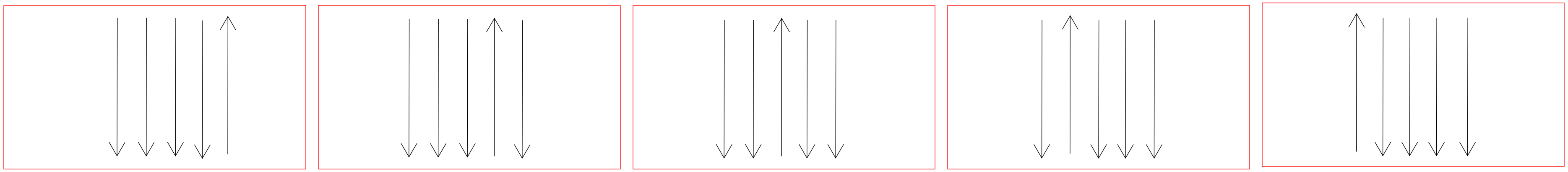
Two Spins Down (-μB) → 10 Microstates



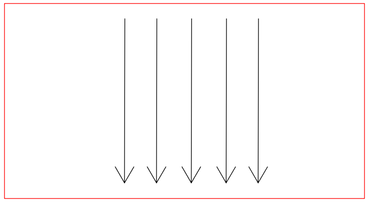
Three Spins Down (μB) → 10 Microstates



Four Spins Down ($3\mu B$) → 5 Microstates



All Spins Down ($5\mu B$) → 1 Microstates

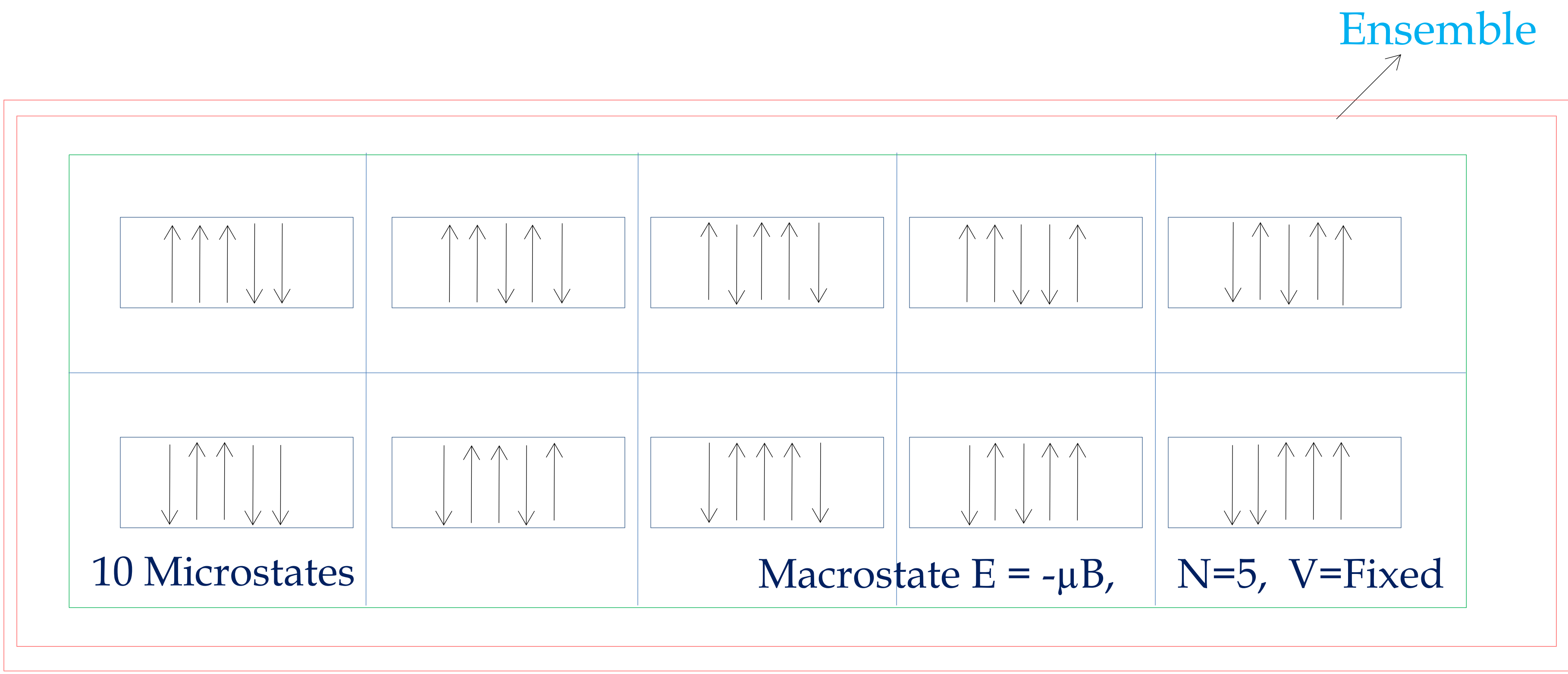


Totally 32 Microstates

1 + 5 + 10 + 10 + 5 + 1

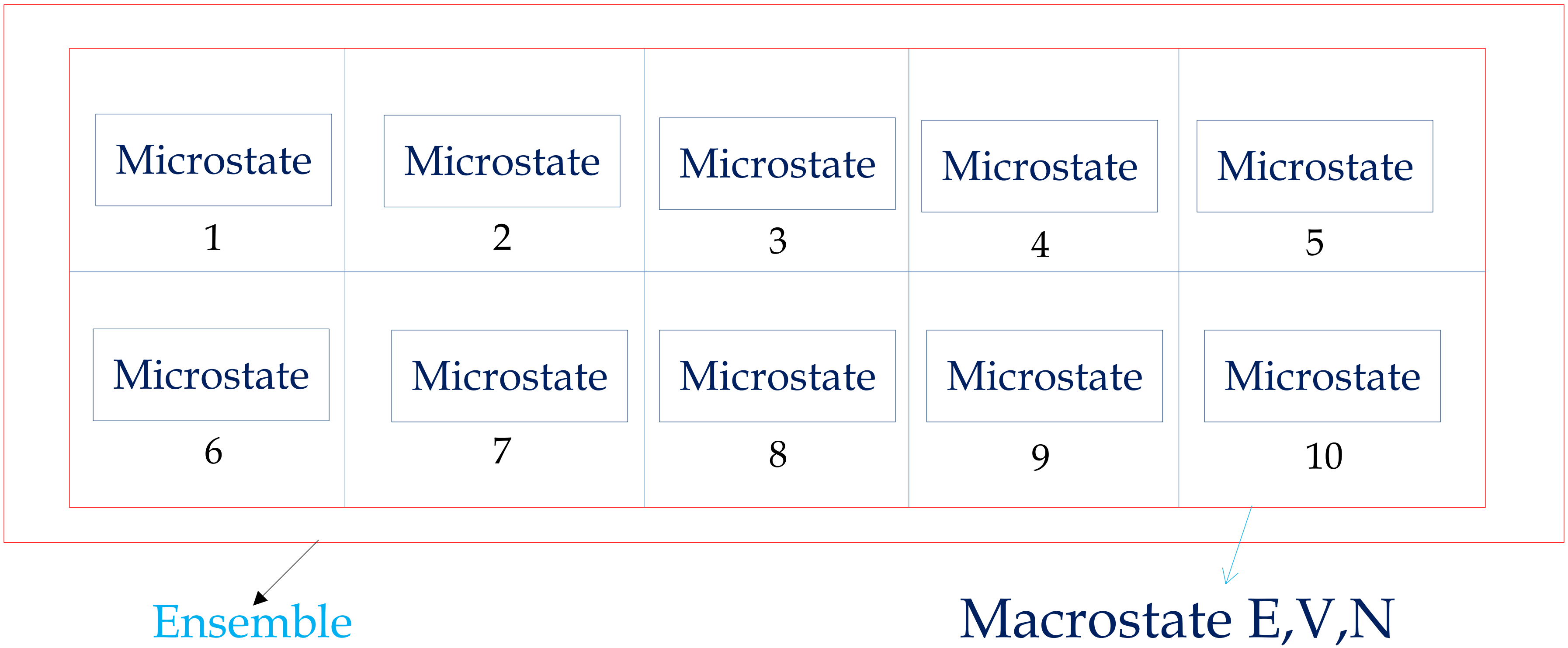
In this problem we are interested in finding the number of possible states having total energy = -μB.

We found that 10 microstates have total energy = -μB



All States are equally probable

$$P_s = \frac{1}{\Omega} = \frac{1}{\text{Number of Microstates}}$$

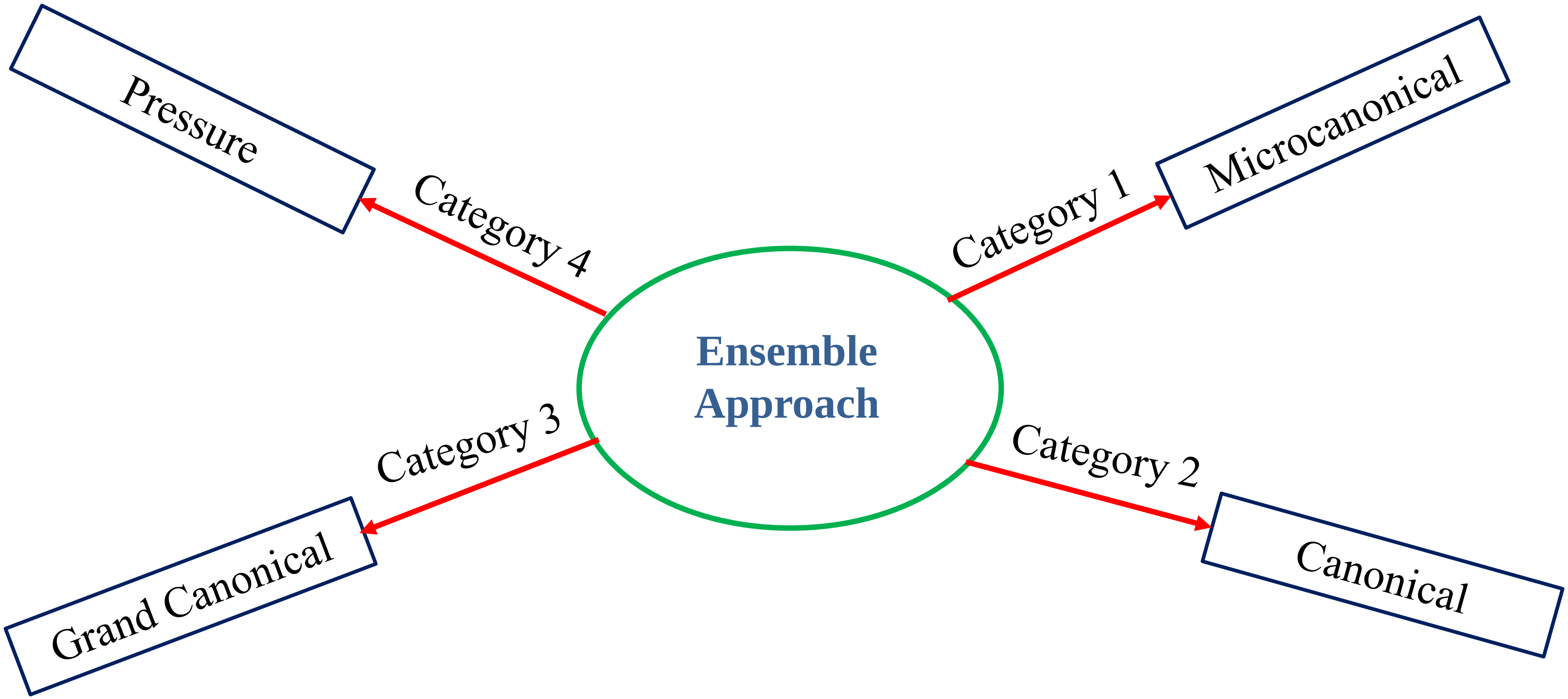


In this example, the Ensemble consists of *Ten* systems each of which is in one of the *Ten* accessible Microstates.

Isolated system, all accessible microstates have the same probability

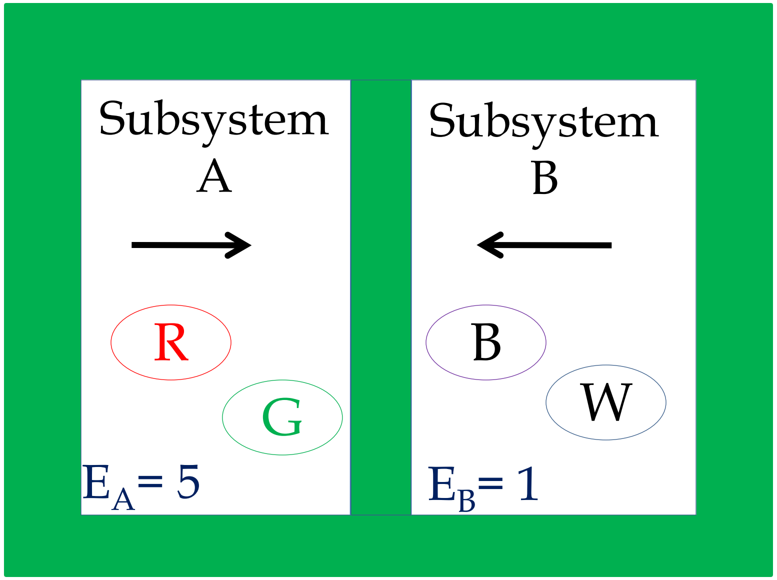
Microcanonical Ensemble

Ensemble Approach



Microcanonical Ensemble: Counting the Number of Microstates

Toy Model



Insulating rigid Impermeable

Energy, Volume and number of particles is fixed.

Subsystem *'A'* consists of two particles-> *Red* & *Green* .

Energy of the system A : $E_A = 5$.

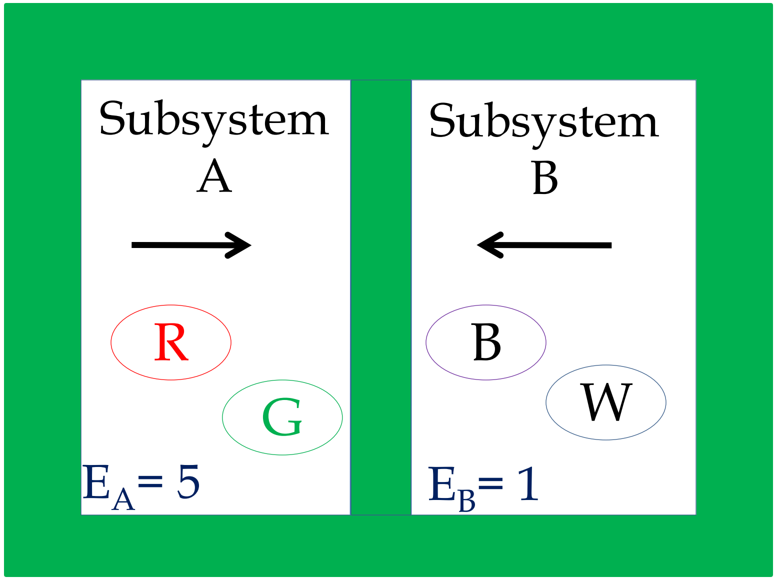
Subsystem *'B'* consists of two particles-> *Black* & White .

Energy of the system B : $E_B = 1$.

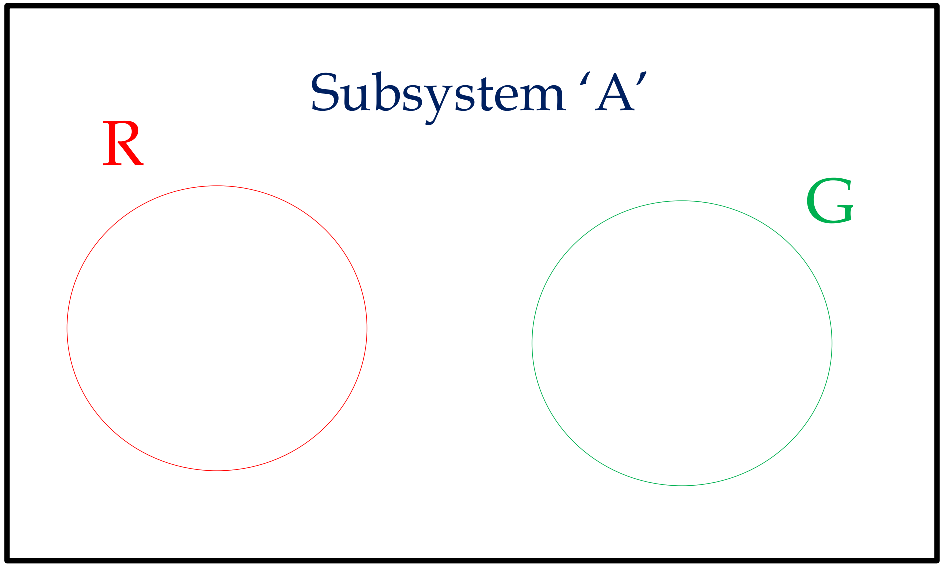
$$E_{tot} = E_A + E_B = 5+1 = 6$$

Let us calculate the number of accessible microstates

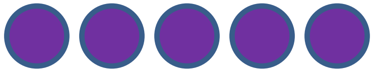
First we consider accessible microstates of **'A'**.



E_A	Accessible Microstates of A
5	(5,0)



Energy E_A

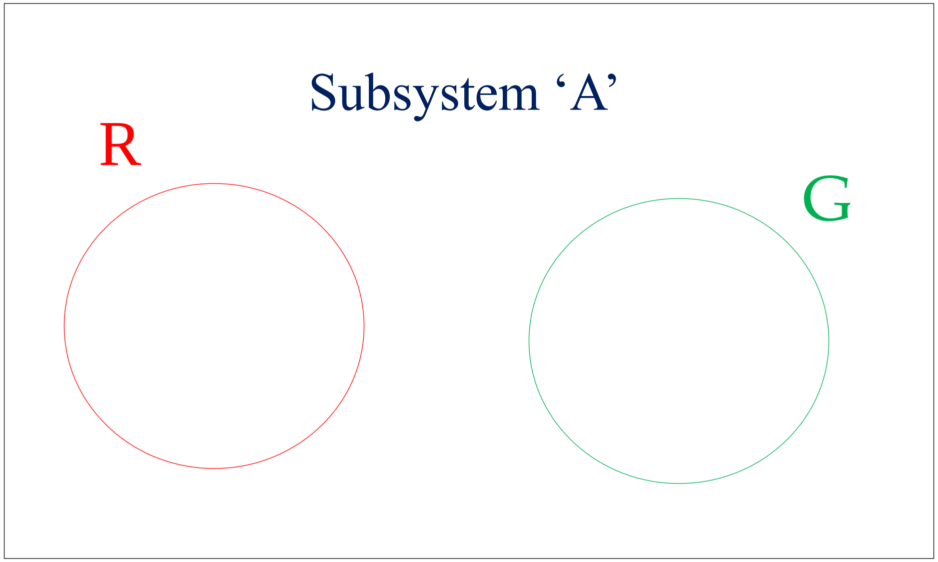


Let us calculate the number of accessible microstates

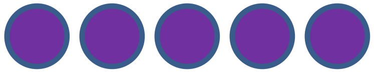
First we consider accessible microstates of 'A'.

•

E_A	Accessible Microstates of A
5	(5,0) (4,1)



Energy E_A

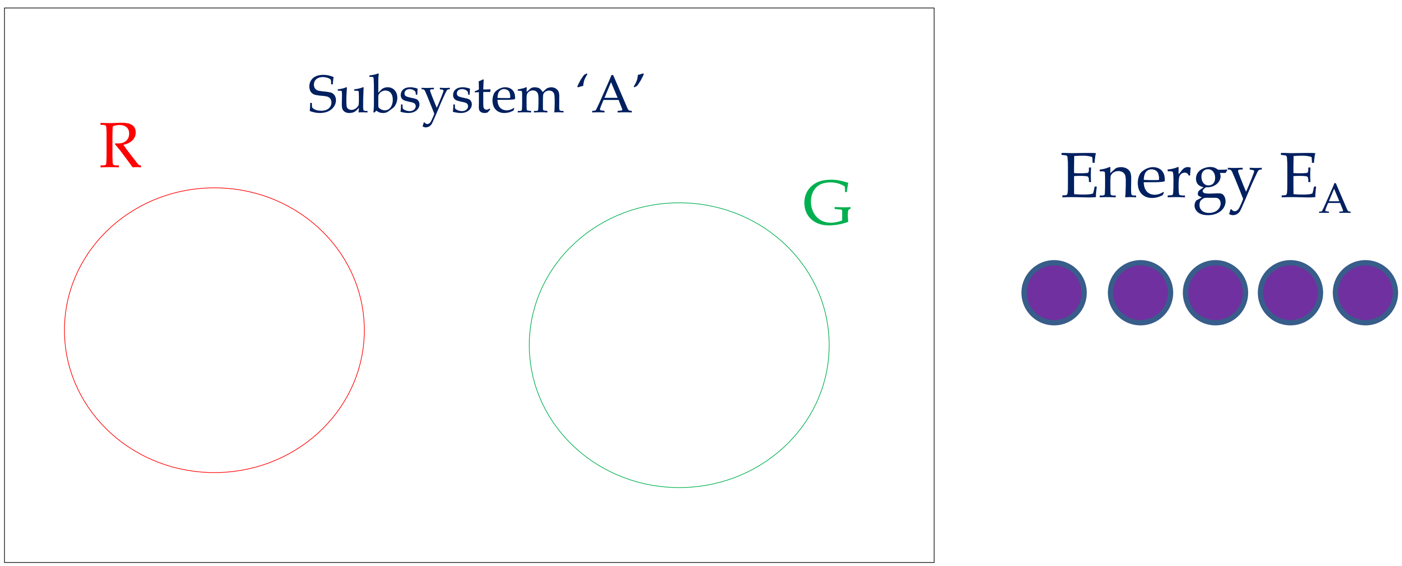


Let us calculate the number of accessible microstates

First we consider accessible microstates of ‘A’.

•

E_A	Accessible Microstates of A
5	(5,0) (4,1) (3,2)

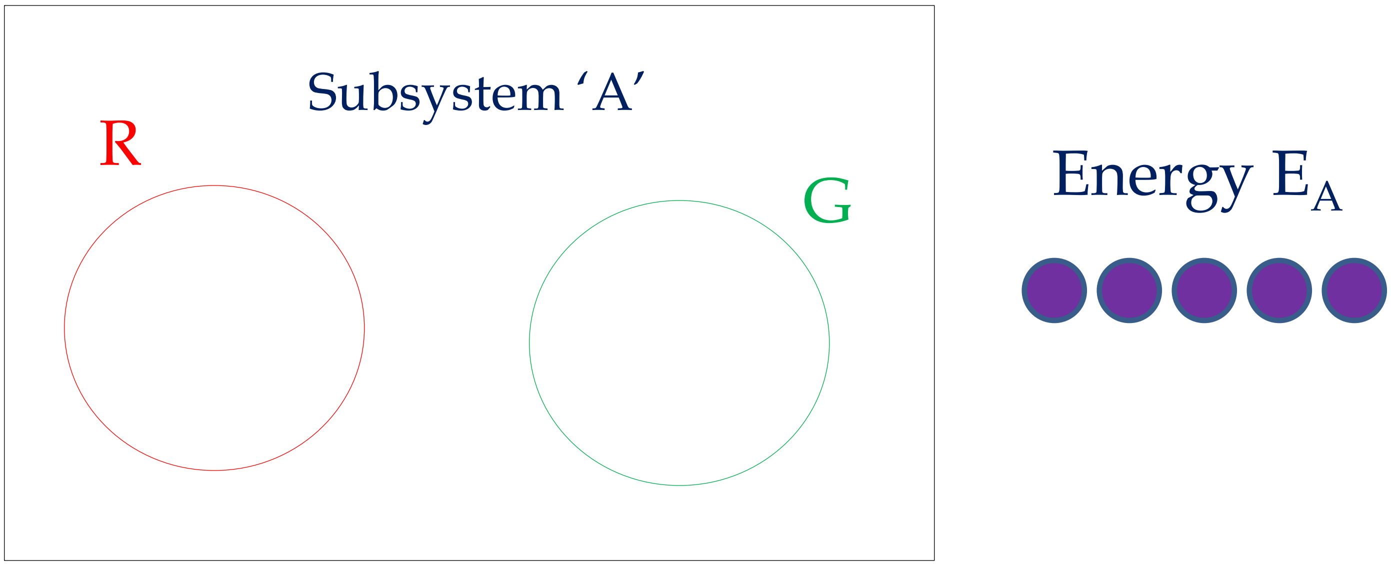


Let us calculate the number of accessible microstates

First we consider accessible microstates of 'A'.

•

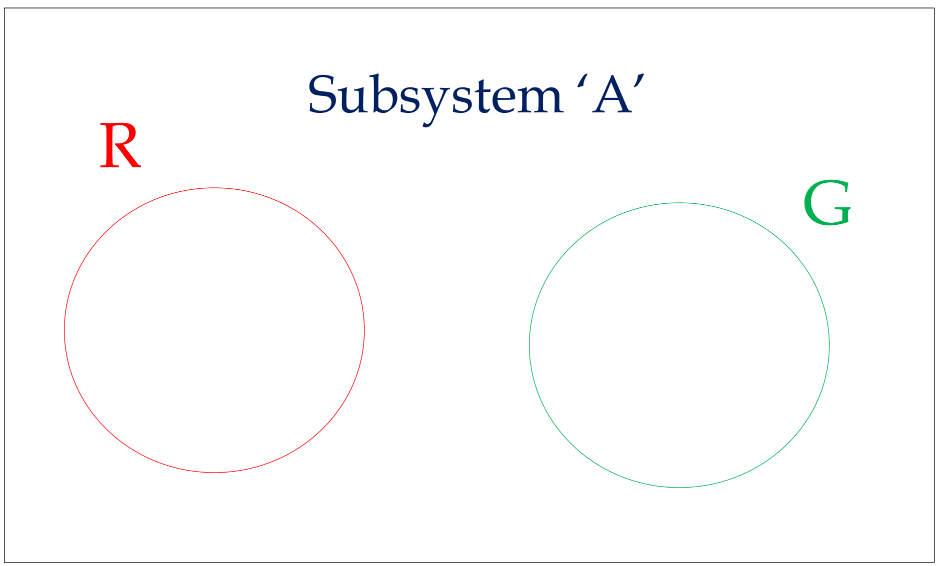
E_A	Accessible Microstates of A
5	(5,0) (4,1) (3,2) (2,3)



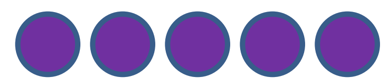
Let us calculate the number of accessible microstates

First we consider accessible microstates of 'A'.

E_A	Accessible Microstates of A
5	(5,0) (4,1) (3,2) (2,3) (1,4)



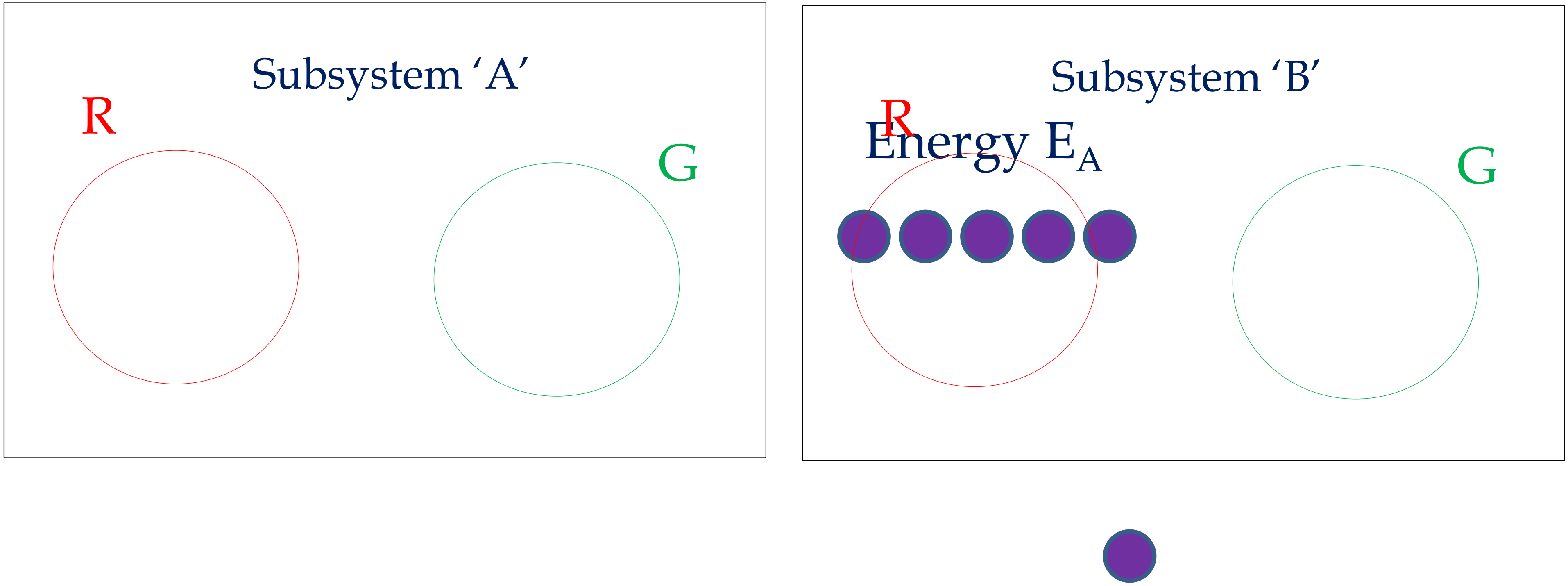
Energy E_A



Let us calculate the number of accessible microstates

First we consider accessible microstates of 'A'

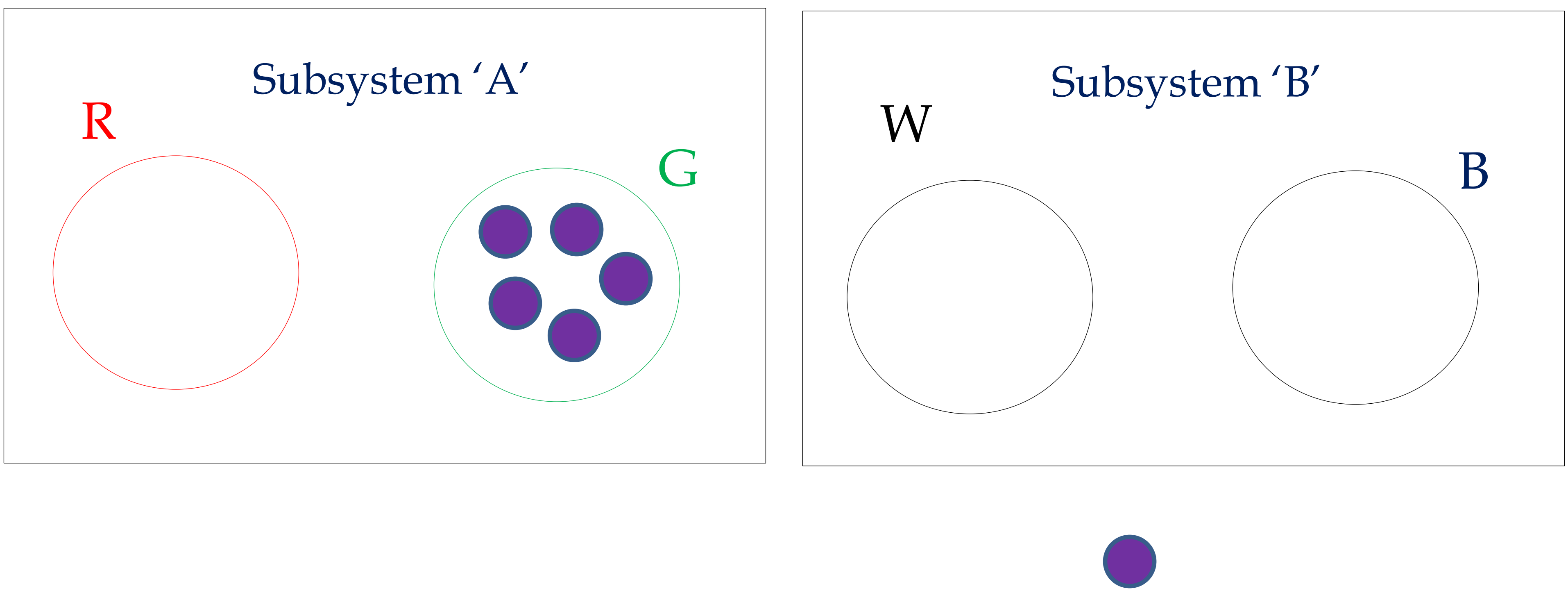
E_A	Accessible Microstates of A	E_B	Accessible Microstates of B
5	(5,0) (4,1) (3,2) (2,3) (1,4) (0,5)	1	(1,0)



Let us calculate the number of accessible microstates

First we consider accessible microstates of A

E_A	Accessible Microstates of A	E_B	Accessible Microstates of B
5	(5,0) (4,1) (3,2) (2,3) (1,4) (0,5)	1	(1,0) (0,1)



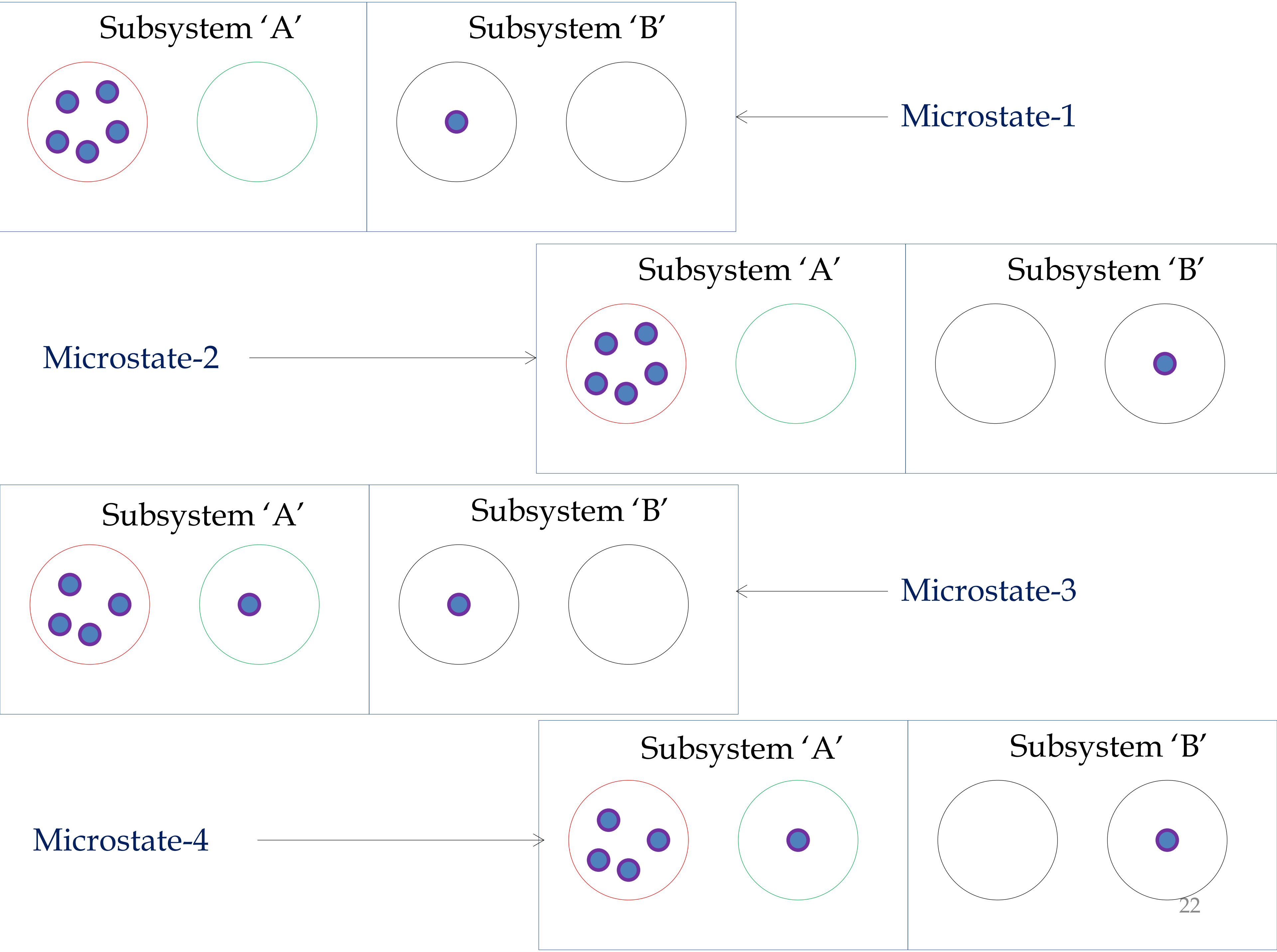
Counting Total Number of Microstates of the Combined System in the Microcanonical Ensemble

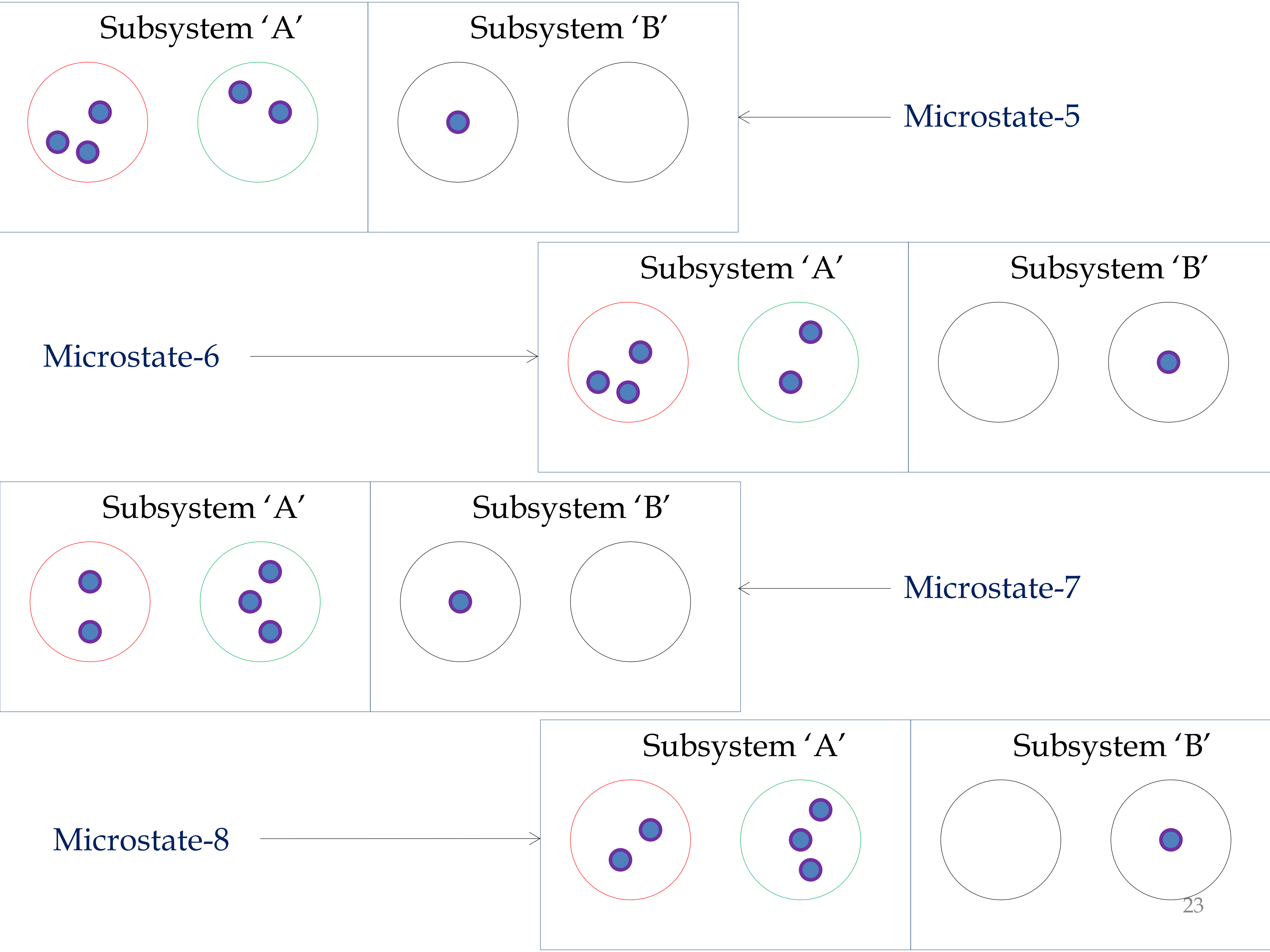
Two Isolated Systems:

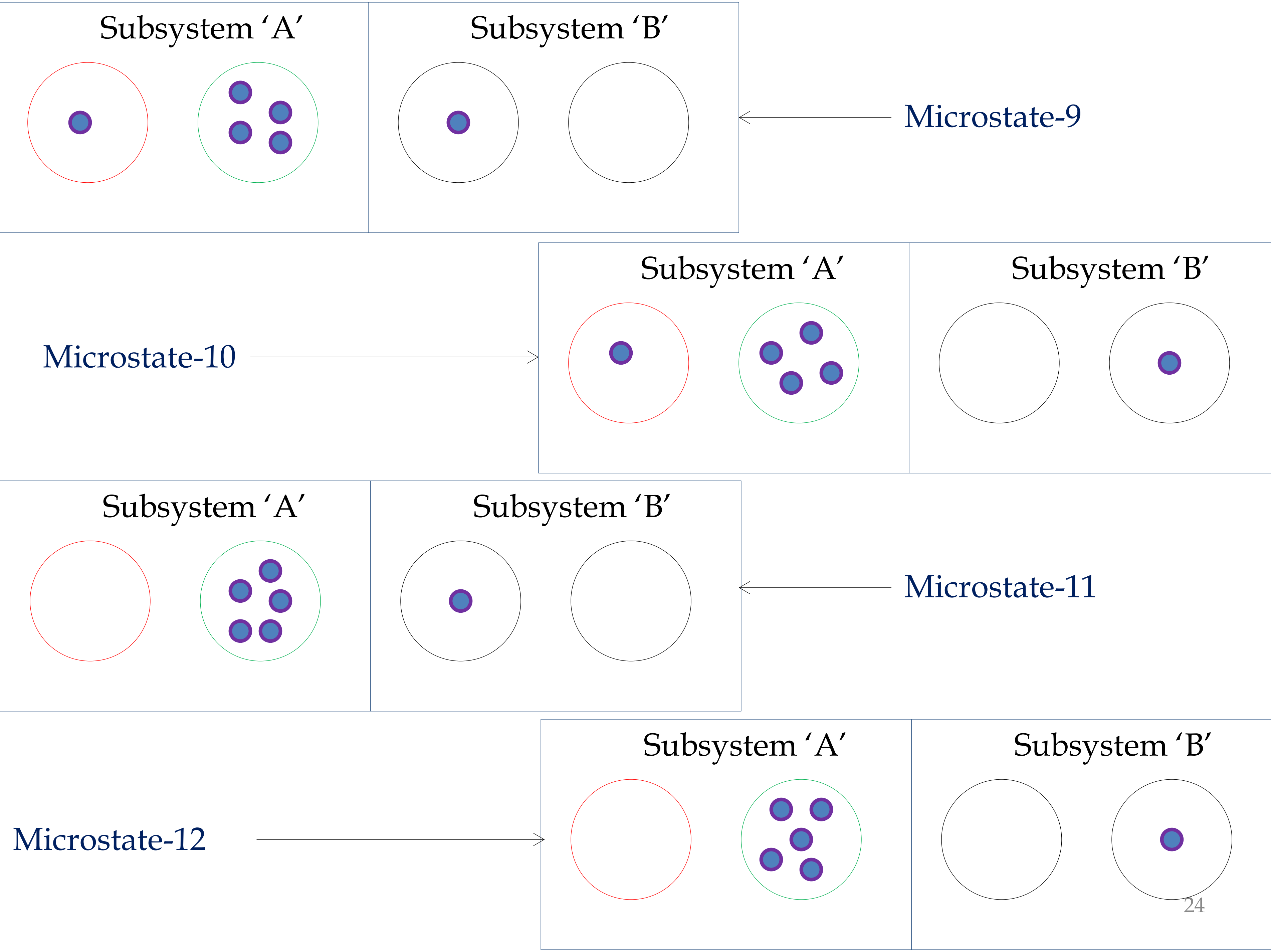
- The total system consisting of A plus B is characterized by the macroscopic quantities E_A, E_B, V_A, V_B, N_A *and* N_B.

- The number of microstates corresponding to this microstate is

$$\Omega_T(E_A, E_B, V_A, V_B, N_A, N_B) = \Omega_A(E_A, U_A, N_A) \times \Omega_B(E_B, U_B, N_B)$$


Subsystem 'A'
Subsystem 'B'
Microstate-1
Subsystem 'A'
Subsystem 'B'
Microstate-2
Subsystem 'A'
Subsystem 'B'
Microstate-3
Subsystem 'A'
Subsystem 'B'
Microstate-4


Subsystem 'A'
Subsystem 'B'
Microstate-5
Subsystem 'A'
Subsystem 'B'
Microstate-6
Subsystem 'A'
Subsystem 'B'
Microstate-7
Subsystem 'A'
Subsystem 'B'
Microstate-8


Subsystem ‘A’
Subsystem ‘B’
Microstate-9
Subsystem ‘A’
Subsystem ‘B’
Microstate-10
Subsystem ‘A’
Subsystem ‘B’
Microstate-11
Subsystem ‘A’
Subsystem ‘B’
Microstate-12

The Subsystem 'A' has $\Omega_A = 6$ accessible *Microstates*.

The Subsystem 'B' has $\Omega_B = 2$ accessible *Microstates*.

Total No of *Microstates* Ω_{tot} of the composite system.

$$\Omega_{tot} = \Omega_A x\ \Omega_B = 12$$

The Partition prevents the transfer of energy from one subsystem to another and in this case keeps $E_A = 5$ and $E_B = 1$.

Partition Function

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

Macrostate

Microstate

Entropy

Boltzmann Constant

Accessible Microstates

For historical reasons, it was chosen to have the value

$$k = 1.38 \times 10^{-23}\ J/K$$

It has no particular significance.

It is analogous to
1) 1 inch = 2.5 cm
2) 1 calorie = 4.186 J
3) 1 kelvin = 1.38×10^{-23} J

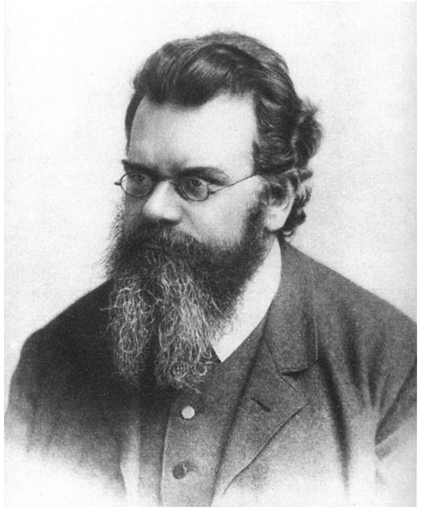
Thermodynamic quantities from Partition Function

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

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

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

In the Remembrance of Boltzmann



Boltzmann

Micro Canonical Ensemble: An Overview

- We begin with determining Partition Function

- Its connection to the entropy via Boltzmann Relation

- Thermodynamics and equilibrium properties it equated

- Micro canonical ensemble provides a starting point from which all other equilibrium ensembles are derived.

Micro-canonical Ensemble

Applications to Classical Systems

Example 1

Classical Ideal Gas

Ideal Gas

Ideal means – the particles do not interact with each other.

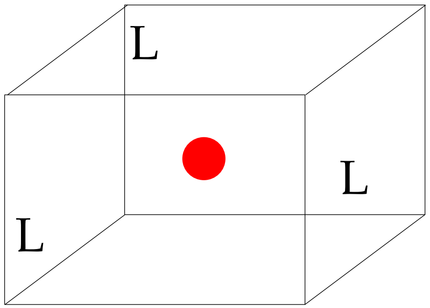
We assume Classical Mechanics provides adequate description.

Hamiltonian

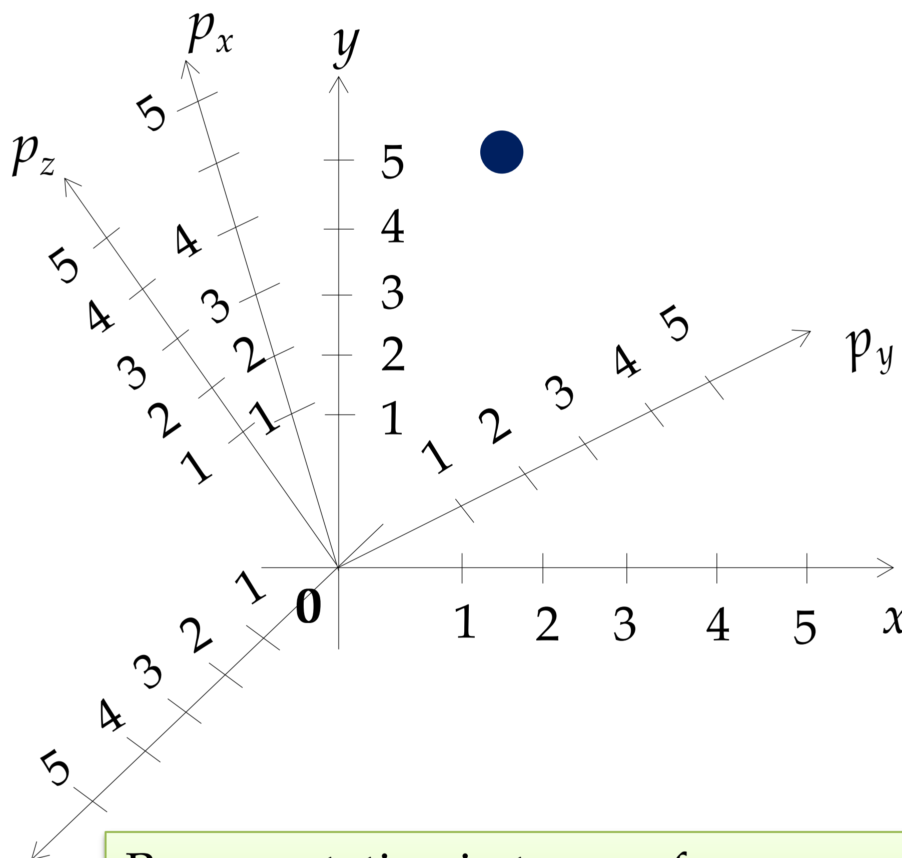
$$H = T + \cancel{V}$$

$$= \frac{p^2}{2m}$$

1 Particle in 3D



Phase – Space



Hamiltonian

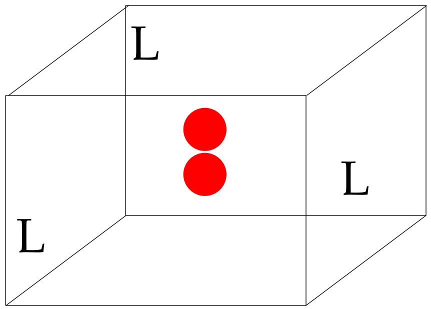
$$H = \frac{1}{2m}\left(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2\right)$$

→ Representation in terms of Coordinates (1 particle – 3 coordinates)

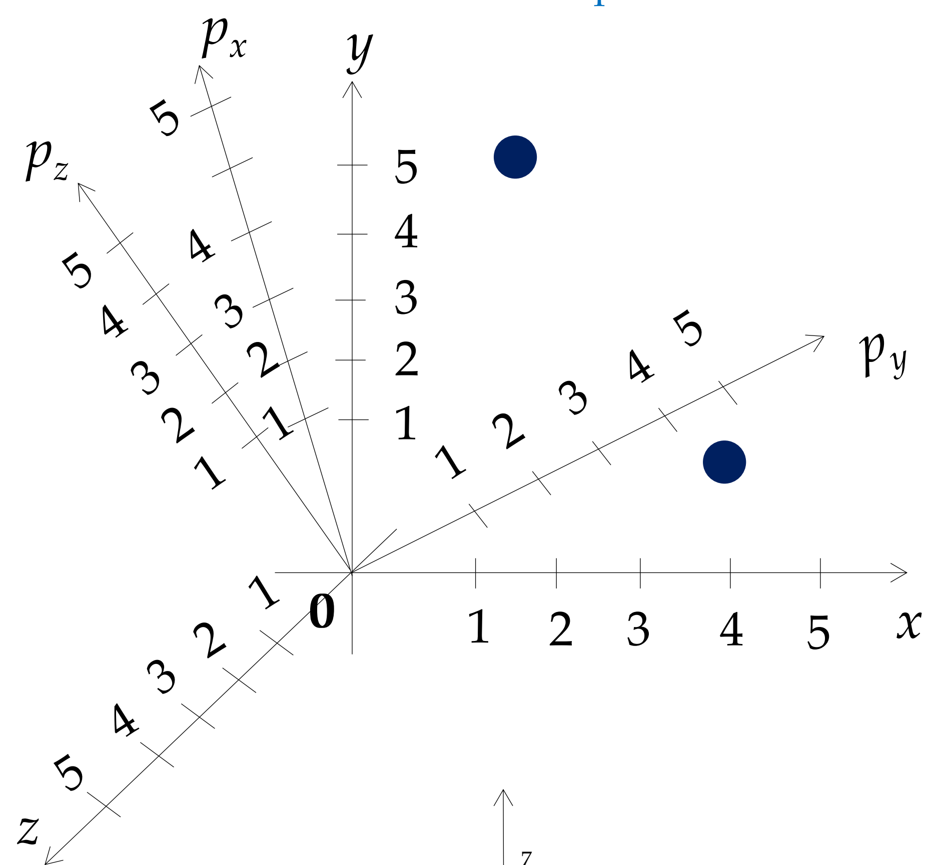
$$= \frac{1}{2m} p_1^2$$

→ Representation in terms of particle

2 Particles in 3D



Phase – Space – 6D



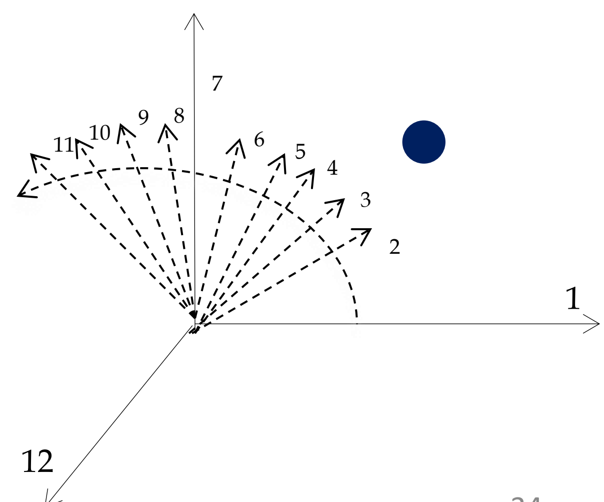
Hamiltonian

$$K.E = \frac{1}{2m}\left\{\begin{array}{l}(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2) \\ +(p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2)\end{array}\right\}$$

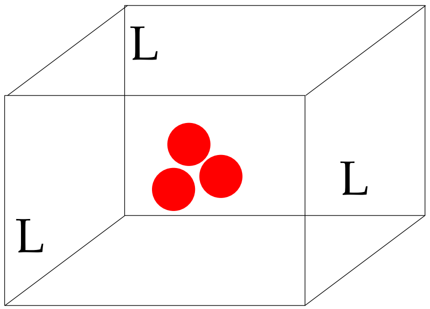
$$= \frac{1}{2m}\left(p_1^2 + p_2^2\right)$$

First Particle   Second Particle

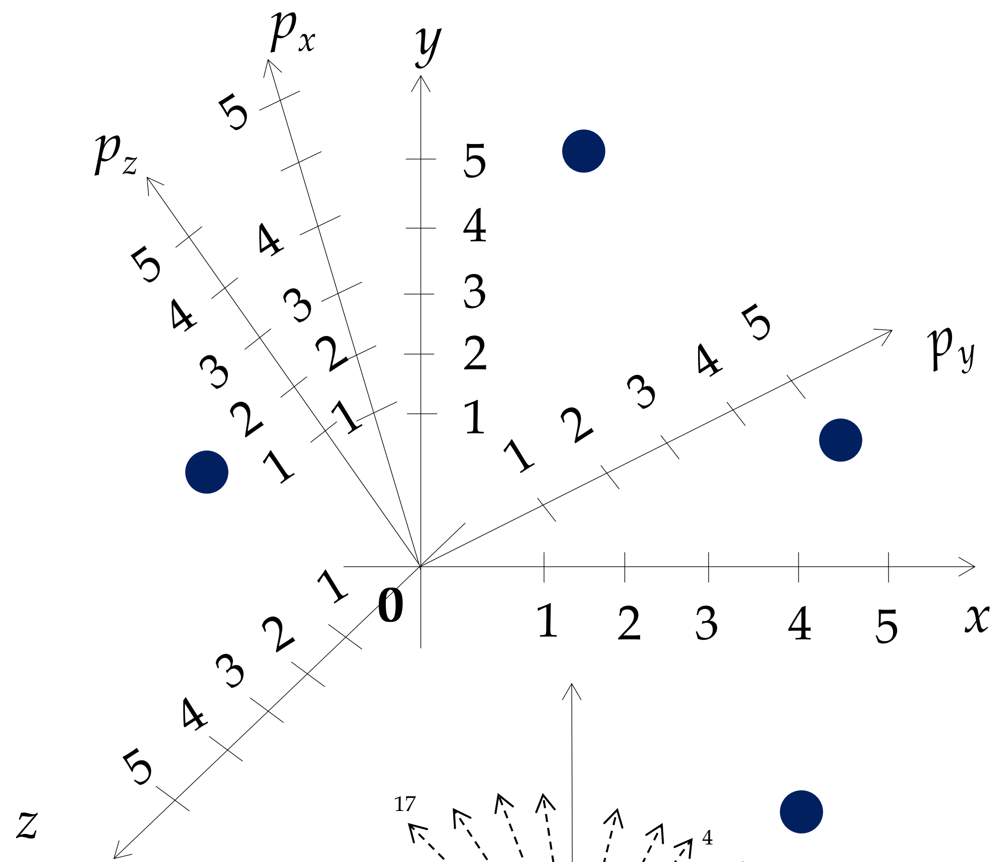
Γ - space – 12D →



3 Particles in 3D



Phase – Space – 6D

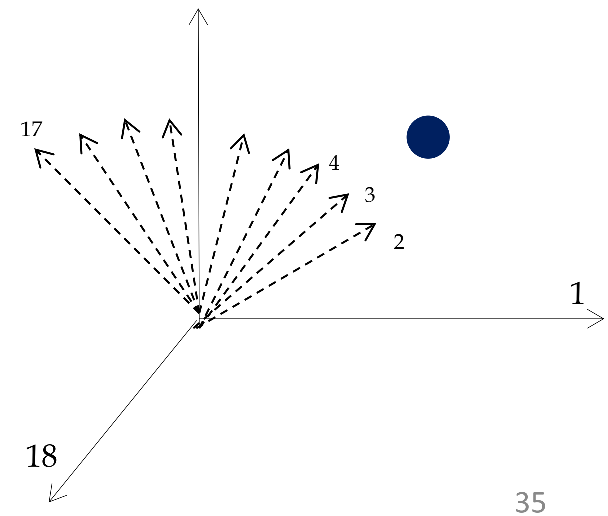


Hamiltonian

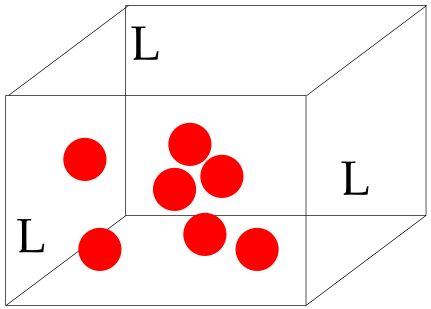
$$K.E = \frac{1}{2m}\left\{\begin{array}{l}(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2) \\ +(p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2) \\ +({p_{x_3}}^2 + {p_{y_3}}^2 + {p_{z_3}}^2)\end{array}\right\}$$

$$= \frac{1}{2m}\left(p_1^2 + p_2^2 + p_3^2\right)$$

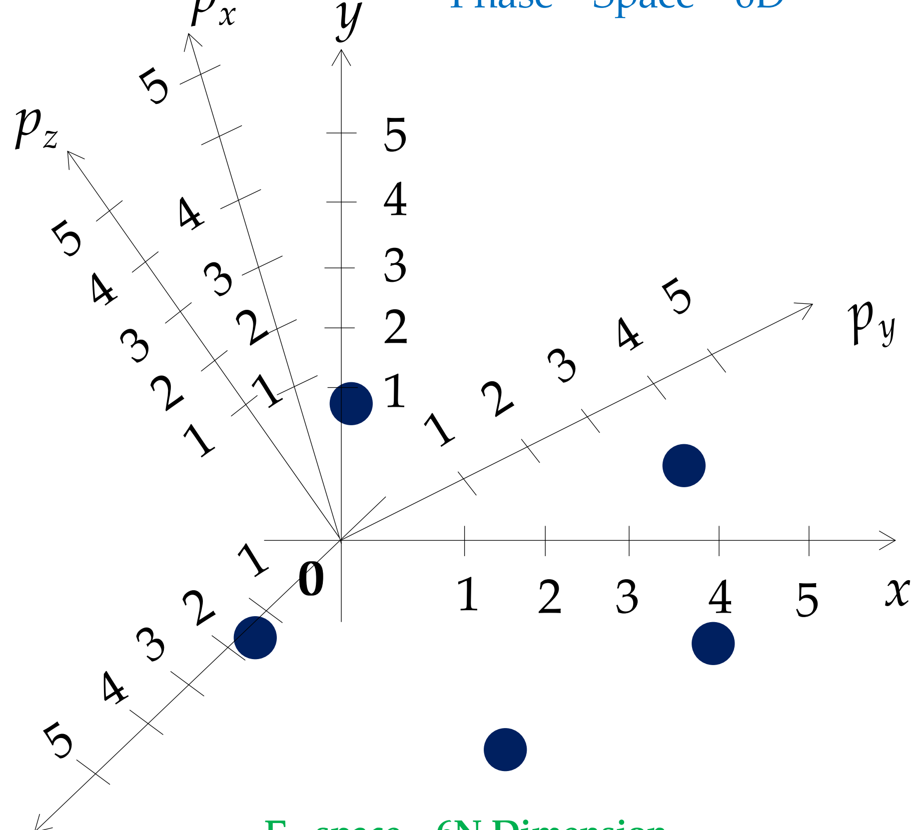
Γ - space – 18D



N Particles in 3D



Phase – Space – 6D



Hamiltonian

$$K.E = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{p_3^2}{2m} + \ldots\ldots + \frac{p_N^2}{2m}$$

$$= \frac{1}{2m}(p_1^2 + p_2^2 + p_3^2 + \ldots.. p_N^2)$$

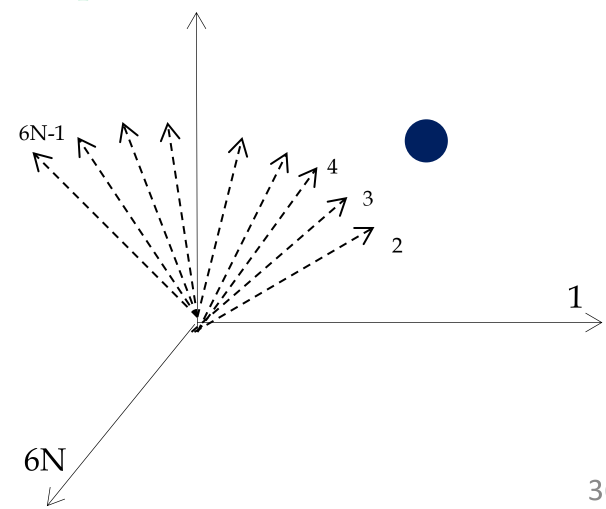
$$= \frac{1}{2m}\sum_{r=1}^{N} p_r^2$$

Representation in terms of particle

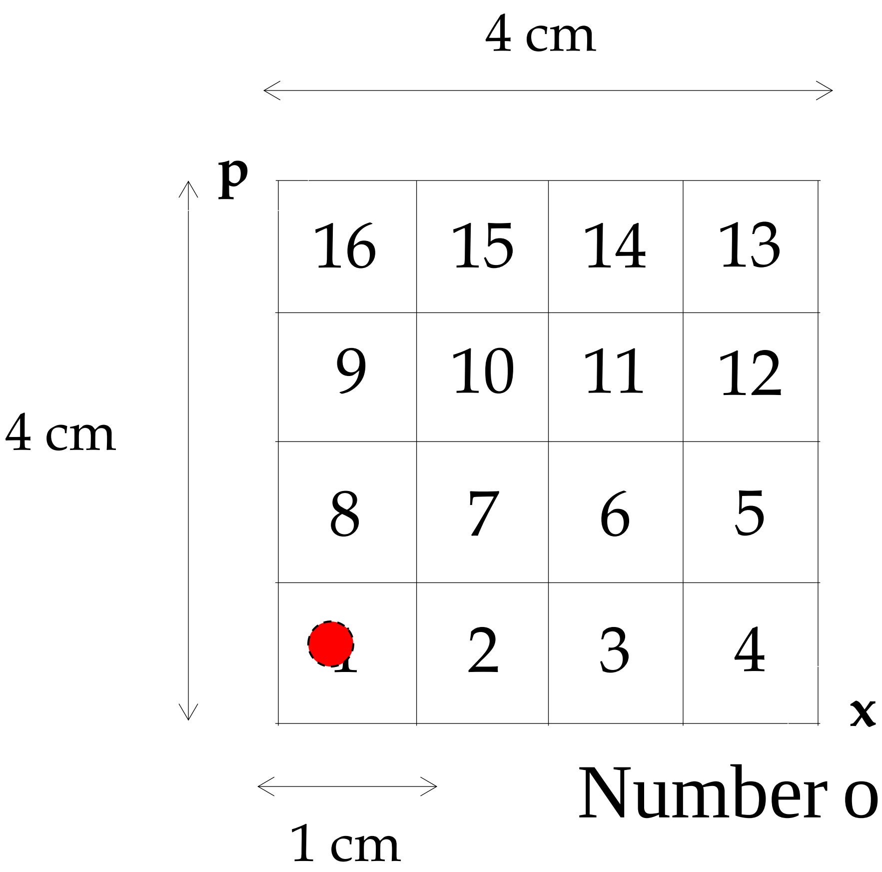
$$= \frac{1}{2m}\sum_{i=1}^{3N} p_i^2$$

Representation in terms of Coordinates (1 particle – 3 coordinates)

Γ - space – 6N Dimension



Counting Number of microstates in 1 Particle case in 1D



$$\text{Number of Cells} = \frac{\text{Total Area}}{\text{Area of a single cell}}$$

$$= \frac{4\,\text{cm} \times 4\,\text{cm}}{1\,\text{cm} \times 1\,\text{cm}}$$

$$= 16$$

❖ In the case *N*-particle ideal gas, finding the area is very difficult.

❖ Practically, it is easier to calculate volume rather than area.

❖ We can calculate area from the volume using Cavalieri's theorem

$$\underbrace{\sigma}_{\text{Area}}(E) = \frac{\partial \omega \;(\rightarrow \text{Volume})}{\partial E \;(\rightarrow \text{Parameter})}$$

Example: Volume of a 3d sphere, $\omega = \frac{4}{3}\pi R^3$ → Parameter (R)

$$\text{Area} \quad \sigma = \frac{\partial \omega}{\partial R} = 4\pi R^2$$

❖How to calculate the volume for the ideal gas problem?

Suppose we have 3N spatial coordinates and 3N momentum coordinates.

Volume of Γ Space

$$= \iint d^{3N}q \, d^{3N}p$$

3N integrals 3N integrals

Γ Space

N = 1 we have 6 dimensions (3 Spatial 3 Momentum).

N = 2 we have 12 dimensions (6 Spatial 6 Momentum).

N = 3 we have 18 dimensions (9 Spatial 9 Momentum).

For N particle 6N dimensions (3N Spatial 3N Momentum).

The volume of the accessible region of phase space is

$$\omega(E,V,N) = \int_{\mu(p_i,q_i)\leq E} d\,\Gamma$$

$$= \iint d^{3N}q\, d^{3N}p$$

$$= V^N \times \frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}\Gamma\frac{3N}{2}}(2mE)^{\frac{3N}{2}}$$

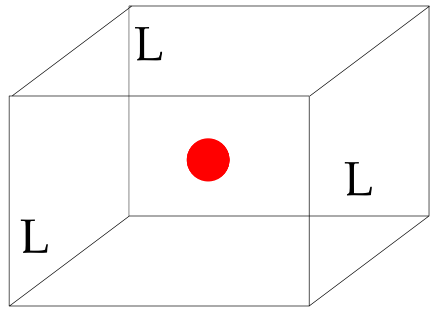
$$\Omega(E,V,N) = \frac{\partial\omega}{\partial E} = V^N \frac{\pi^{\frac{3N}{2}}}{\Gamma\frac{3N}{2}}(2m)^{\frac{3N}{2}} E^{\frac{3N}{2}-1}$$

Let us evaluate the integral $\int\int d^{3N}q\, d^{3N}p$

Since there are no product terms in q and p, we can separate the integrals

$$\int d^{3N}q \int d^{3N}p$$

Case (i) $N = 1$



$$\int d^3q \int d^3p = \underbrace{\int\int\int dx\, dy\, dz}_{\text{Coordinates}} \times \underbrace{\int\int\int d\mathrm{p}_x dp_y dp_z}_{\text{Momentum}}$$

Coordinates

Momentum

INTEGRALS INVOLVING COORDINATES

- The first integral is nothing but the volume available for a single particle.
- Which is nothing but V.

INTEGRALS INVOLVING MOMENTUM $\iiint dp_x dp_y dp_z$

- The integral is nothing but the volume available for a single particle in p space.
- Unlike the coordinates all the momentum coordinates are not independent.
- They are connected by the relation. $\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) = E$

$$p_x^2 + p_y^2 + p_z^2 = (\sqrt{2mE})^2$$

- The above equation represents equation of a sphere in 3 dimension with radius $\sqrt{2mE}$

$$\iiint dp_x dp_y dp_z = \frac{4}{3}\pi(2mE)^{3/2}$$

Hence $\iiint dx\, dy\, dz \times \iiint dp_x dp_y dp_z = V \times \frac{4}{3}\pi(2mE)^{3/2}$

TWO DIMENSIONAL CASE

$$\int d^6 q \int d^6 p$$

$$\int d^6 q = \int d^3 q_1 \int d^3 q_2 = (\int\int\int dx_1 dy_1 dz_1) \times (\int\int\int dx_2 dy_2 dz_2)$$

Vol. available for 1st particle

Vol.available for 2nd particle

$$= V \times V = V^2$$

$$\int d^6 p = \int d^3 p_1 \int d^3 p_2 = (\int\int\int dp_{x_1} dp_{y_1} dp_{z_1}) \times (\int\int\int dp_{x_2} dp_{y_2} dp_{z_2})$$

Vol. Available for 1st particle in the momentum coordinate

Vol.available for 2nd particle in the momentum coordinates

- The momentum coordinates are not independent.

- They are connected by the relation

$$\frac{1}{2m}(\underbrace{p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2}_{\text{1}^{\text{st}}\text{ particle in the momentum coordinates}} + \underbrace{p_{x_2}^2 + p_{y_2}^2 + p_{y_2}^2}_{\text{2}^{\text{nd}}\text{ particle in the momentum coordinates}}) = E$$

$$\underbrace{p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2}_{\text{1}^{\text{st}}\text{ particle in the momentum coordinates}} + \underbrace{p_{x_2}^2 + p_{y_2}^2 + p_{y_2}^2}_{\text{2}^{\text{nd}}\text{ particle in the momentum coordinates}} = (\sqrt{2mE})^2$$

- The above expression is nothing but the 6 dimensional sphere with radius $\sqrt{2mE}$.

- Let us find the volume of 12-dimensional sphere.

$$\int\int\int dx_1 dy_1 dz_1 \times \int\int\int dx_2 dy_2 dz_2 = V^2$$

$$\int\int\int dp_{x_1} dp_{y_1} dp_{z_1} \int\int\int dp_{x_2} dp_{y_2} dp_{z_2} = \frac{4}{3}\pi(2mE)^3$$

HIGHER DIMENSIONAL CASE $\int d^{3N}q \int d^{3N}p$

$$\int d^{3N}q = \int d^3q_1 \int d^3q_2 \int d^3q_3 \dots \int d^3q_N$$

$$= \underbrace{\left(\int\int\int dx_1 dy_1 dz_1\right)}_{\text{Vol. available for } 1^{st} \text{ particle}} \times \underbrace{\left(\int\int\int dx_2 dy_2 dz_2\right)}_{\text{Vol.available for } 2^{nd} \text{ particle}} \times \dots \times \underbrace{\left(\int\int\int dx_N dy_N dz_N\right)}_{\text{Vol.available for } N^{th} \text{ particle}}$$

$$= V \times V \times \dots \times V = V^N$$

$$\int d^{3N}p = \int d^3p_1 \int d^3p_2 \int d^3p_3 \dots \int d^3p_N$$

$$= \underbrace{\left(\int\int\int dp_{x_1} dp_{y_1} dp_{z_1}\right)}_{\text{Vol. Available for } 1^{st} \text{ particle in the momentum coordinate}} \times \underbrace{\left(\int\int\int dp_{x_2} dp_{y_2} dp_{z_2}\right)}_{\text{Vol.available for } 2^{nd} \text{ particle in the momentum coordinates}} \times \dots \underbrace{\left(\int\int\int dp_{x_N} dp_{y_N} dp_{z_N}\right)}_{\text{Vol.available for } N^{th} \text{ particle in the momentum coordinates}}$$

- The momentum coordinates are not independent.

- They are connected by the relation

$$\frac{1}{2m}\Big(\underbrace{p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2}_{\text{1st particle in the momentum coordinates}} + \underbrace{p_{x_2}^2 + p_{y_2}^2 + p_{y_2}^2}_{\text{2nd particle in the momentum coordinates}} + \ldots + \underbrace{p_{x_N}^2 + p_{y_N}^2 + p_{z_N}^2}_{N\text{th particle in the momentum coordinates}}\Big) = E$$

$$\underbrace{p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2}_{\text{1st particle in the momentum coordinates}} + \underbrace{p_{x_2}^2 + p_{y_2}^2 + p_{y_2}^2}_{\text{2nd particle in the momentum coordinates}} \ldots + \underbrace{p_{x_N}^2 + p_{y_N}^2 + p_{z_N}^2}_{N^{th}\text{ particle in the momentum coordinates}} = (\sqrt{2mE})^2$$

- The above expression is nothing but the 3N dimensional sphere with radius $\sqrt{2mE}$.

- We are calculating the volume of 3N-dimensional sphere.

VOLUME OF A 3N DIMENSIONAL SPHERE

- Volume of a 3N dimensional sphere.

$$\frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)}(2mE)^{\frac{3N}{2}}$$

- Cross-check N=1 V= $\dfrac{\pi^{\frac{3}{2}}}{\frac{3}{2}\times\frac{1}{2}\times\sqrt{\pi}}(2mE)^{\frac{3}{2}} = \dfrac{4}{3}\pi(2mE)^{\frac{3}{2}}$

- The volume of the accessible region is

$$V^{N}\times\frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)}(2mE)^{\frac{3N}{2}}$$

❖ Entropy of the ideal gas is S=k log Ω

$$S(E,V,N) = k \ln\left\{ \frac{1}{\mathrm{h}^{3\mathrm{N}}} V^{N} \frac{\pi^{\frac{3N}{2}}}{\Gamma\frac{3N}{2}} (2m)^{\frac{3N}{2}} E^{\frac{3N}{2}} \right\}$$

$$= Nk\left[\ln\left\{ V\left(\frac{4\pi mE}{3Nh^2}\right)^{\frac{3}{2}} \right\} + \frac{3}{2} \right]$$

❖ Energy of the ideal gas is

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3}{2}\frac{Nk}{E} \Rightarrow E = \frac{3}{2}NkT \longrightarrow \text{Average Energy}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{V,N} = \frac{Nk}{V} \Rightarrow PV = NkT \longrightarrow \text{Equation of State}$$

Validity of the Obtained Expressions

- All expressions agree with the classical thermodynamics results.

- But entropy expression does not satisfy additive property.

- That is,

$$S + S \neq 2S$$

Intensive parameters

Thermodynamics variable which do not vary when the system volume increases.

Ex: Temperature, pressure, difference in electric potential.

Extensive parameters

Thermodynamic variables which vary when the system volume increase.

Ex: Volume, internal energy, electrical charge.

Intensive parameters:

Thermodynamics variable which do not vary when the system volume increases.

Ex: Temperature, pressure, difference in electric potential.

Extensive parameters:

Thermodynamic variables which vary when the system volume increase.

Ex: Volume, internal energy, electrical charge.

Gibbs Paradox

❖ Gibbs Paradox

❖ We obtained the following expression for entropy of an ideal gas in the microcanonical picture.

$$S = Nk\log\left[V\left(\frac{E}{N}\right)^{\frac{3}{2}}\left(\frac{4\pi M}{3h^2}\right)^{\frac{3}{2}}\right] + \frac{3}{2}Nk$$

❖ The entropy given by the above expression does not satisfy the additive property.

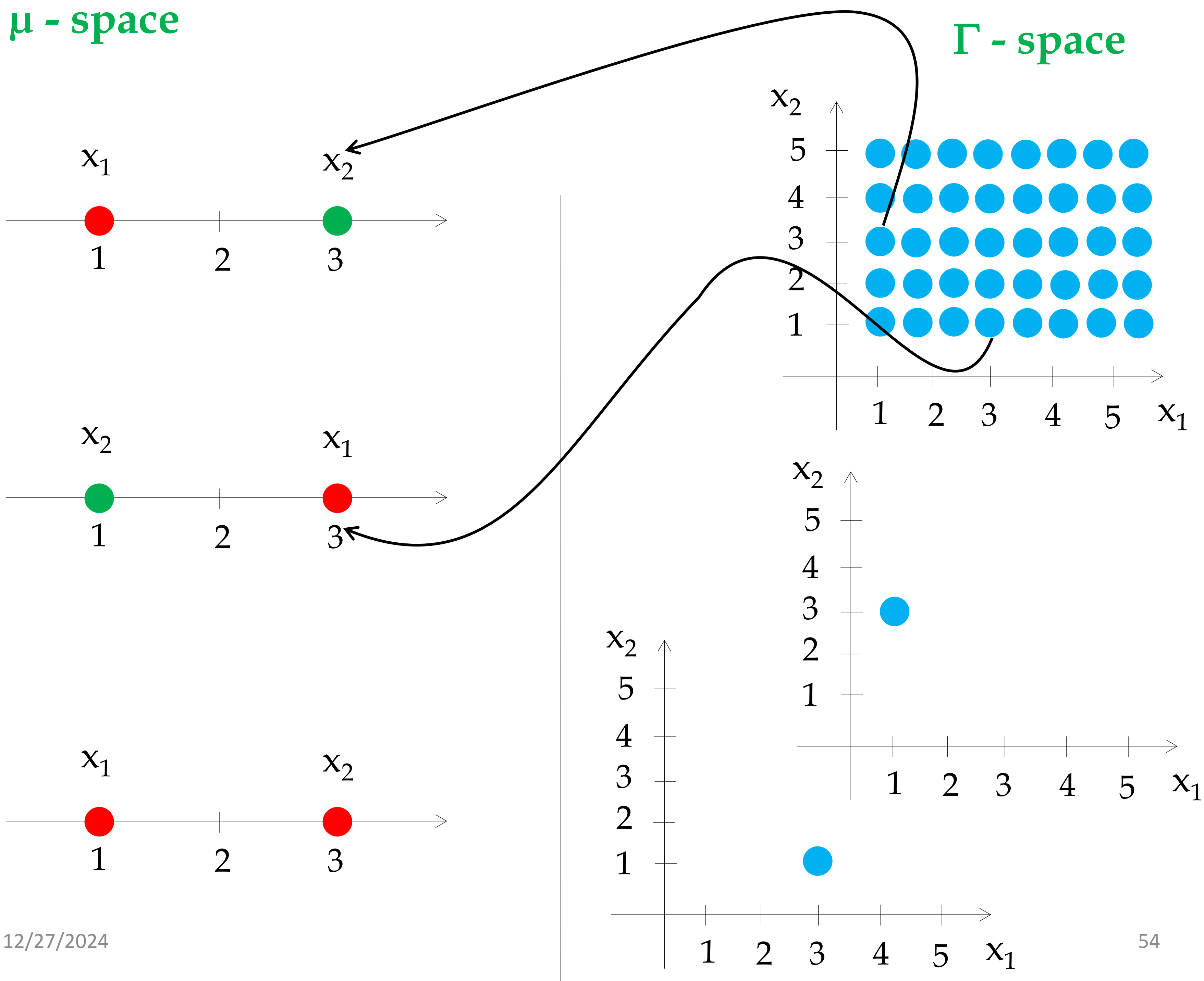
❖ According to the above relation, the entropy of new system is

$$S + S = S' = 2Nk\log\left[2V\left(\frac{E}{N}\right)^{\frac{3}{2}}\left(\frac{4\pi M}{3h^2}\right)^{\frac{3}{2}}\right] + 3Nk$$

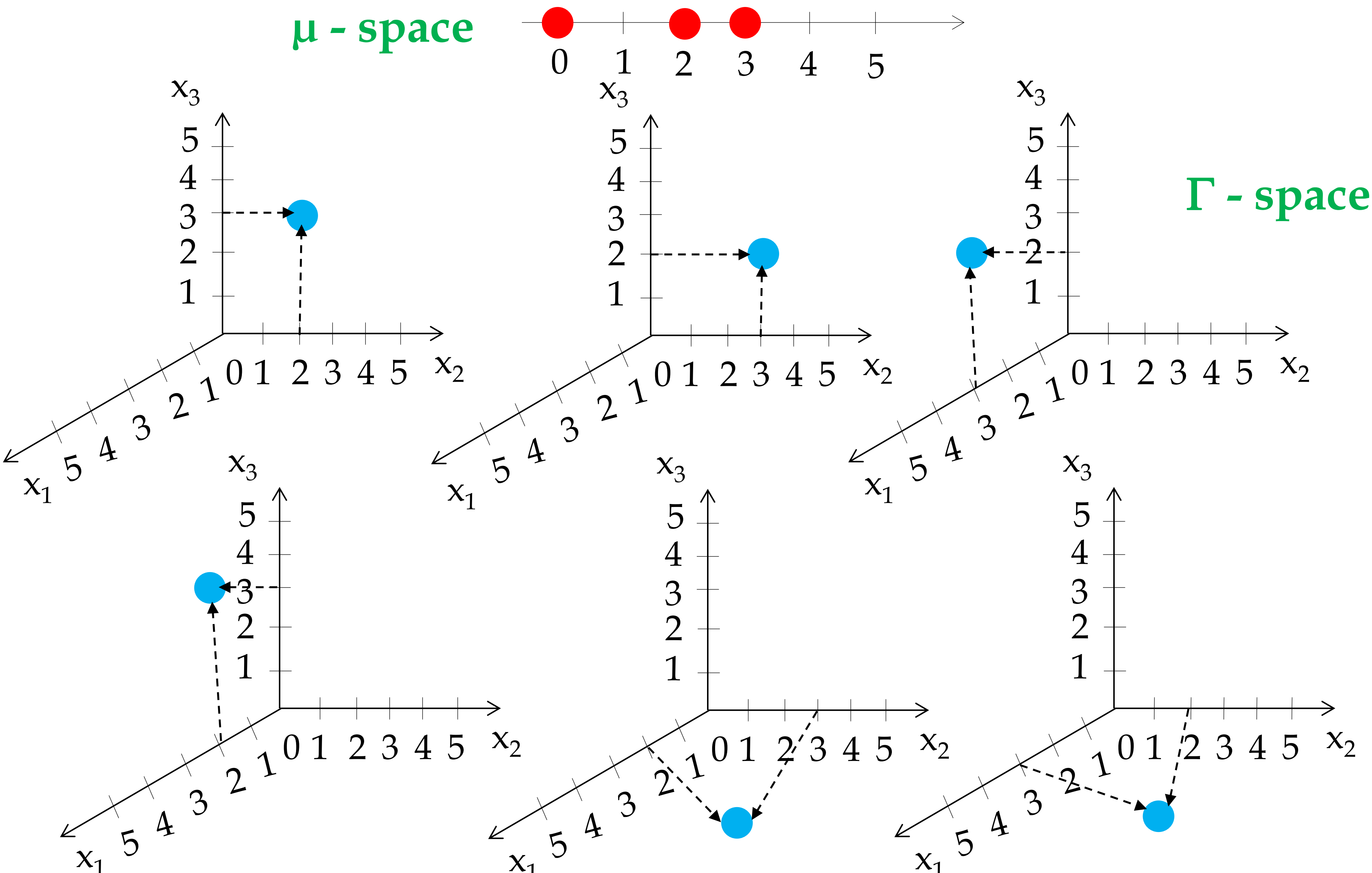
$$= 2S + \underbrace{2Nk\log 2}_{\text{Extra Constant}}$$

Why this extra constant arise???

- The expression for entropy fails to satisfy the extensive property.
- This is called **Gibbs Paradox**.
- Gibbs solved this buffling paradox by considering two systems are the same, hence the gas molecules are completely identical and indistinguishable.
- In this case one cannot observe or label the individual particles.
- So we must apply here the idea of indistinguishability.
- Hence if two systems containing the same Number ‘N’ of identical particles are diffusion takes place unnoticeably.



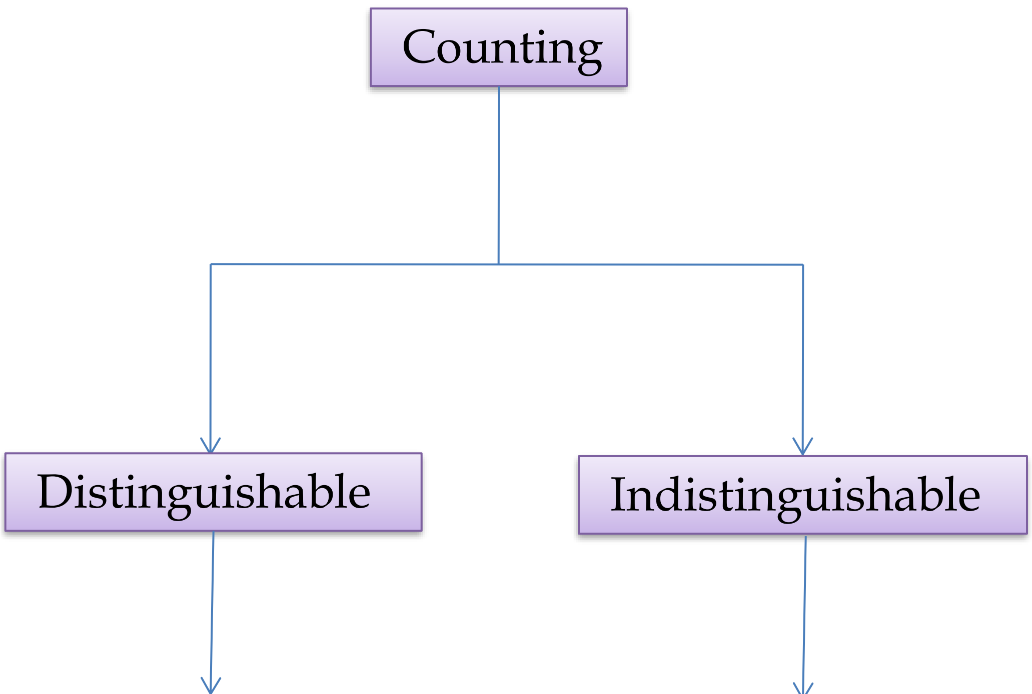
μ - space
Γ - space
x1
x2
1
2
3
x2
x1
1
2
3
x1
x2
1
2
3
x2
5
4
3
2
1
1
2
3
4
5
x1
x2
5
4
3
2
1
1
2
3
4
5
x1
x2
5
4
3
2
1
1
2
3
4
5
x1



Instead of one count, six counting has been made

$$\textbf{Correct Counting} = \frac{\text{Total Counting}}{(\text{No. of particles})!} = \frac{6}{3!} = 1$$

Distinguishability v/s Indistinguishability



Particles	Ways
2	2
3	6
4	24
N	N!

Particles	Ways
2	1
3	1
4	1
N	1

Lesson

1. Indistinguishable particles

$$\text{Correct Counting} = \frac{\Omega}{N!}$$

2. Distinguishable particles

No need to Divide

Correct Formula for Entropy

$$S = k \log\left(\frac{\Omega}{N!}\right) = k \log\left[\frac{V^N}{N!(3N)!}\left(\frac{2\pi mE}{h^2}\right)^{\frac{3N}{2}}\right]$$

$$= Nk \log\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] + \frac{5}{2}Nk$$

❖ The above entropy expression satisfies the extensive property.

❖ All other expressions turned out exactly the same.

From Microstates to Macrostates in MCE

- Gateway $S = \mathrm{k} \log \Omega$

- $\Omega = \dfrac{\text{Total Volume}}{\text{Small Volume}} = \iint \dfrac{d^{3N}q\, d^{3N}p}{h^{3N}}$

$$\text{Indistinguishable Particles} = \frac{\Omega}{N!}; \quad \text{Distinguishable Particles} = \Omega$$

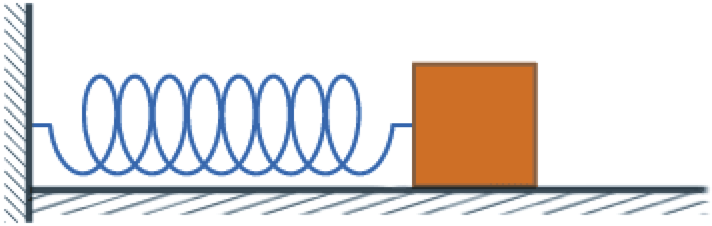
- S $\longrightarrow$ **E, P, C_v , ………**

Example 2

N one dimensional distinguishable Classical Harmonic Oscillators

One dimensional Harmonic Oscillator

$$F = -kx$$



Newton's Equation

$$m\frac{d^2x}{dt^2} = -kx$$

Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 \qquad \omega = \sqrt{\frac{k}{m}}$$

Hamiltonian Equation

$$\dot{x} = \frac{p}{m} \qquad \dot{p} = -kx$$

Solution

$$x = A\sin(\omega t + \delta) \qquad p = A\cos(\omega t + \delta)$$

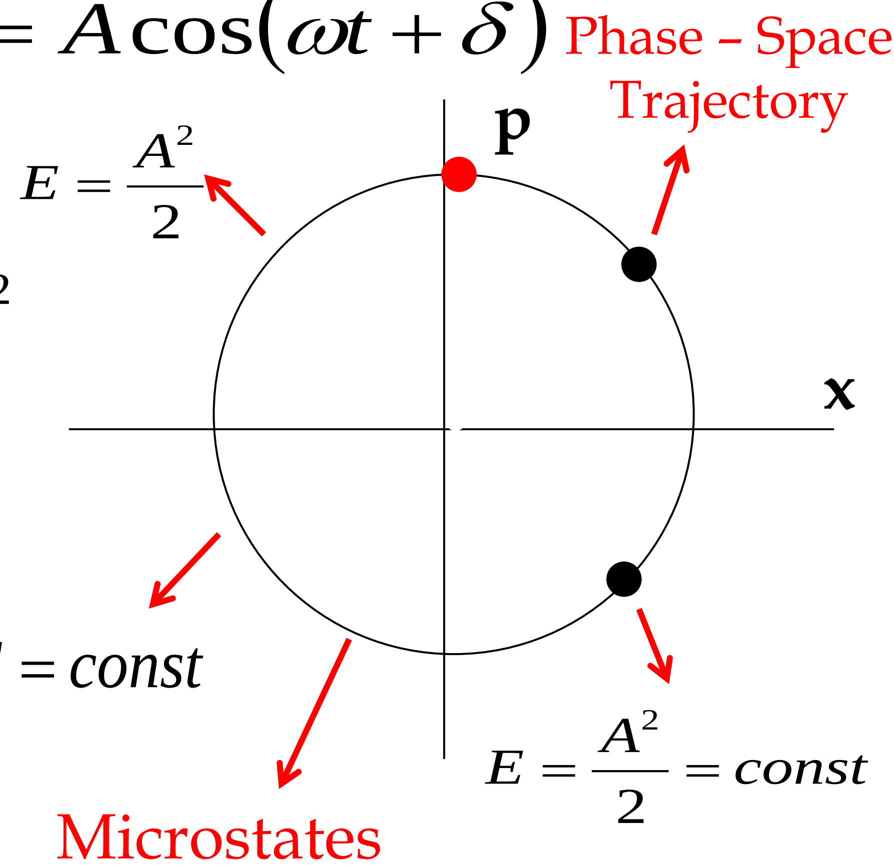
Phase - Space

$$x(t) = A\sin(\omega t + \delta) \quad p(t) = A\cos(\omega t + \delta)$$

$$E = K.E + P.E = \frac{p^2}{2m} + \frac{k}{2}x^2$$

$$= \frac{1}{2}\left(\sin^2 t + \cos^2 t\right) = \frac{A^2}{2}$$

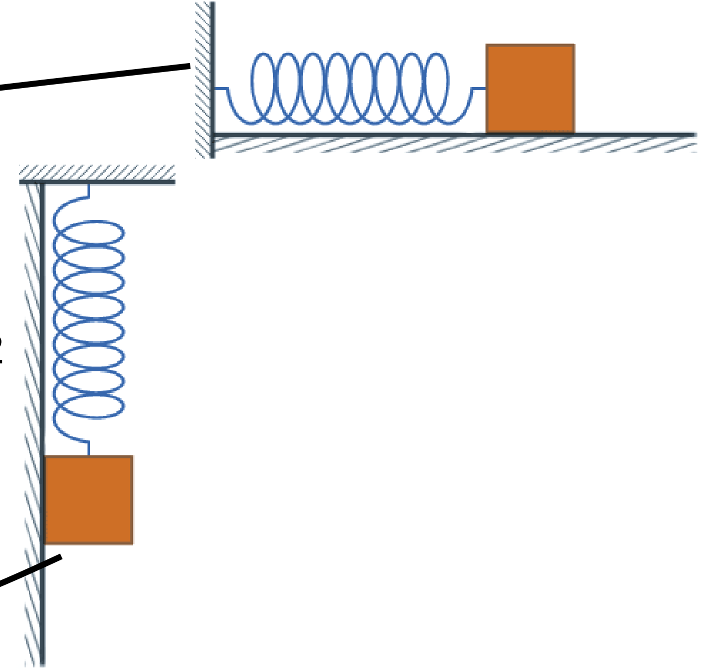
$$E = \frac{A^2}{2} = \text{constant}$$



Each pt on phase – space trajectory is a microstates.

$\therefore$ We have to count number of microstates on the circle.

Two One dimensional harmonic oscillators

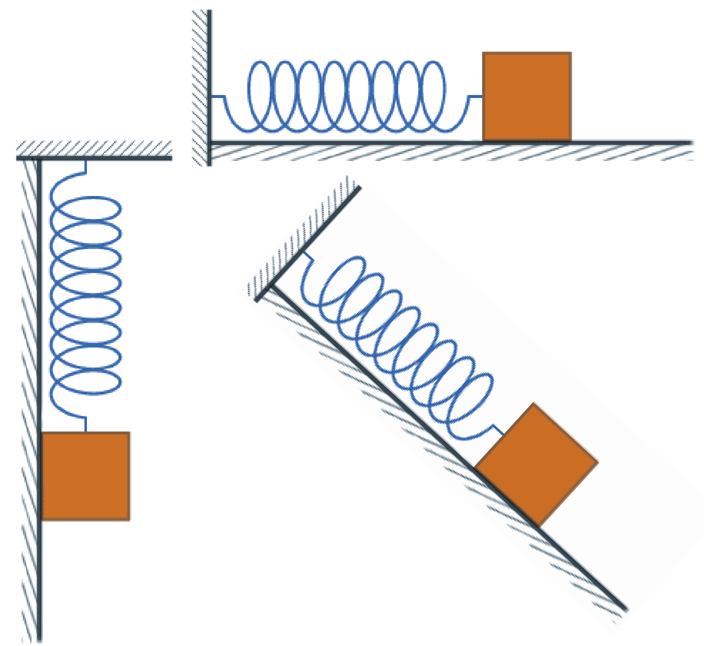


$$H = H_1 + H_2$$

$$= \frac{p_1^{\,2}}{2m} + \frac{1}{2}kq_1^{\,2} + \frac{p_2^{\,2}}{2m} + \frac{1}{2}kq_2^{\,2}$$

$$= \sum_{i=1}^{2} \frac{p_i^{\,2}}{2m} + \frac{1}{2}kq_i^{\,2}$$

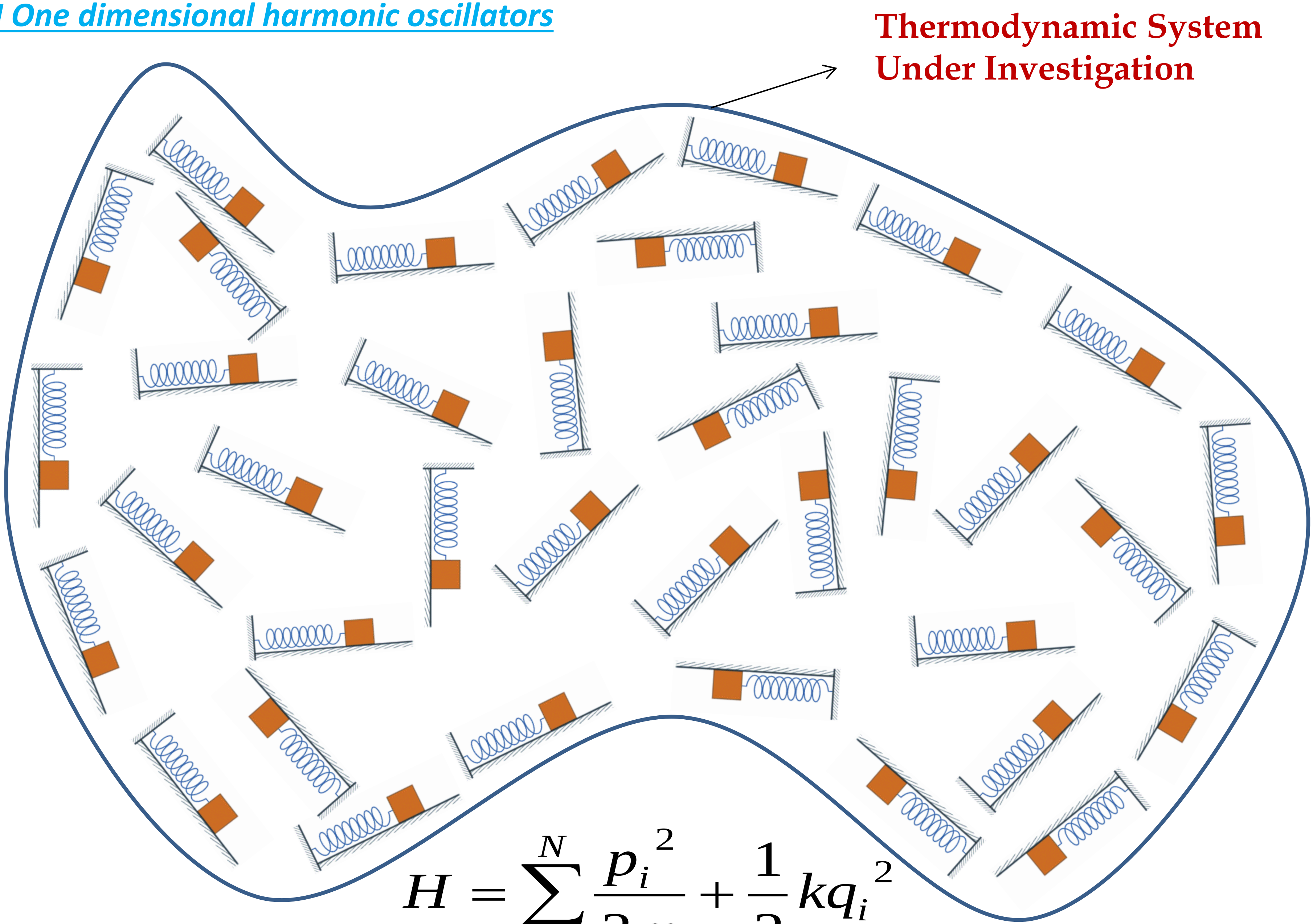
Three One dimensional harmonic oscillators



$$H = H_1 + H_2 + H_3$$

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

N One dimensional harmonic oscillators



$$H = \sum_{i=1}^{N} \frac{p_i^{\ 2}}{2m} + \frac{1}{2} k q_i^{\ 2}$$

Rewriting Hamiltonian in the standard form

$$H = \sum_{i=1}^{N} \frac{p_i^{\ 2}}{2m} + \frac{1}{2} m\omega^2 q_i^{\ 2}$$

Substituting $x_i = m\omega\, q_i$

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

Expanding

$$= (p_1^{\ 2} + p_2^{\ 2} + \ldots\ldots + p_N^{\ 2}) + (x_1^{\ 2} + x_2^{\ 2} + \ldots\ldots + x_N^{\ 2}) = (\sqrt{2mE})^2$$

Equation represents 2N dimensional sphere of radius $\sqrt{2mE}$

➢Number of accessible micro states for N classical distinguishable harmonic oscillators with frequency (ω) is

$$\Omega(E,V,N)=\frac{1}{h^N}\left(\frac{1}{m\omega}\right)^N\iint d^N x\, d^N p$$

A Word about Integration

➢ Unlike ideal gas, here spatial integrals and momentum integrals cannot be separated since the given energy is distributed equally to all coordinates and momenta by the following expression

$$(p_1{}^2+p_2{}^2+.....+p_N{}^2)+(x_1{}^2+x_2{}^2+.....+x_N{}^2)=(\sqrt{2mE})^2$$

➢So we have to evaluate the integral $\iint d^N x\, d^N p$ together

➢The Integral gives the volume of a 2N dimensional sphere.

$$V=\frac{\pi^N}{N\,\Gamma(N)}(2mE)^N$$

No. of microstates $\Omega(E,V,N) = \frac{1}{h^N}\left(\frac{1}{m\omega}\right)^N \iint d^N x \, d^N p$

$$\Omega(E,V,N) = \frac{1}{h^N}\left(\frac{1}{m\omega}\right)^N \frac{\pi^N}{N\,\Gamma(N)}(2mE)^N = \frac{1}{N\,\Gamma(N)}\left(\frac{E}{\hbar\omega}\right)^N$$

Entering into the Gateway S = k log Ω, we find

$$S(E,V,N) = Nk\left[1 + \ln\left\{\frac{E}{N\hbar\omega}\right\}\right]$$

Thermodynamics

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N} = Nk\frac{1}{E}, \quad E = NkT$$

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{E,N} = 0, \quad P = 0$$

Energy agrees with the classical result

Micro-canonical Ensemble

Applications to Quantum Systems

Example 3

Quantum Ideal Gas

One Particle in 1D

$$E_n = \frac{h^2}{8ma^2} n^2$$

One Particle in 2D

$$E_{n_x, n_y} = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2\right)$$

One Particle in 3D

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

Where

$$n_1, n_2, n_3 = 1,2,3,.......$$

Two Particles in 3D

$$E_{n_{x_1},n_{y_1},n_{z_1}} + E_{n_{x_2},n_{y_2},n_{z_2}} = \frac{h^2}{8ma^2}\left(n_{x_1}^2 + n_{y_1}^2 + n_{z_1}^2\right) + \frac{h^2}{8ma^2}\left(n_{x_2}^2 + n_{y_2}^2 + n_{z_2}^2\right)$$

Three Particles in 3D

$$\left.\begin{aligned} &E_{n_{x_1},n_{y_1},n_{z_1}} + E_{n_{x_2},n_{y_2},n_{z_2}} \\ &+ E_{n_{x_3},n_{y_3},n_{z_3}} \end{aligned}\right\} = \frac{h^2}{8ma^2}\left(n_{x_1}^2 + n_{y_1}^2 + n_{z_1}^2\right) + \frac{h^2}{8ma^2}\left(n_{x_2}^2 + n_{y_2}^2 + n_{z_2}^2\right) + \frac{h^2}{8ma^2}\left(n_{x_3}^2 + n_{y_3}^2 + n_{z_3}^2\right)$$

N Particles in 3D

$$E_{n_{x_i},n_{y_i},n_{z_i}} = \frac{h^2}{8ma^2}\left(n_{x_1}^2 + n_{y_1}^2 + n_{z_1}^2\right) + \frac{h^2}{8ma^2}\left(n_{x_2}^2 + n_{y_2}^2 + n_{z_2}^2\right) + \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots + \frac{h^2}{8ma^2}\left(n_{x_N}^2 + n_{y_N}^2 + n_{z_N}^2\right)$$

$$\rightarrow E_{n_{x_1},n_{y_1},n_{z_1}} + E_{n_{x_2},n_{y_2},n_{z_2}} + \ldots\ldots\ldots + E_{n_{x_N},n_{y_N},n_{z_N}} = E$$

$$E = \frac{h^2}{8ma^2}\left(n_{x_1}^2 + n_{y_1}^2 + n_{z_1}^2 + n_{x_2}^2 + n_{y_2}^2 + n_{z_2}^2 + \ldots. + n_{x_N}^2 + n_{y_N}^2 + n_{z_N}^2\right)$$

$$a^3 = V$$

$$n_{x_1}^2 + n_{y_1}^2 + n_{z_1}^2 + n_{x_1}^2 + n_{y_2}^2 + n_{z_2}^2 + \ldots. + n_{x_N}^2 + n_{y_N}^2 + n_{z_N}^2 = \frac{8mV^{\frac{2}{3}}E}{h^2} \rightarrow R^2$$

Expression represents 3N dimensional sphere

Recalling the number of allowed states

No. of allowed states in 3d

$$\Gamma(E) = \left(\frac{1}{8} \times \frac{4}{3}\pi R^3\right)^N = \left(\frac{1}{2^3}\right)^N \frac{\left(\frac{8m\pi EV^{\frac{2}{3}}}{h^2}\right)^{\frac{3N}{2}}}{\frac{3N}{2}!}$$

Rearranging

$$\Gamma = \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{\frac{3N}{2}}}{\frac{3N}{2}!} \Rightarrow \ln\Gamma = N\ln\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right] + \frac{3}{2}N$$

Entropy $S = k\ln\Gamma = Nk\ln\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right] + \frac{3}{2}Nk$

Rewriting E in terms of S

$$\left(\frac{1}{T} = \frac{\partial S}{\partial E}\right)$$

$$E = \frac{3h^2N}{4\pi\, mV^{\frac{2}{3}}} e^{\left(\frac{2S}{3Nk} - 1\right)} \Rightarrow \quad E = \frac{3}{2}NkT$$

$$p = \frac{NkT}{V}$$

The above two equations gives the Equation of State for non relativistic particles in a box which is same for the non Relativistic ideal gas.

Example 4

N one dimensional distinguishable Quantum Harmonic Oscillators

Energy Levels of a one dimensional harmonic oscillator is given by

$$E_N = \left(n + \frac{1}{2}\right)\hbar\omega, \qquad n = 0,1,2,3,......$$

Energy Levels of two one dimensional harmonic oscillator is given by

$$E_N = \left(n_1 + n_2 + 1\right)\hbar\omega, \qquad n_1, n_2 = 0,1,2,3,......$$

Energy Levels of three one dimensional harmonic oscillator is given by

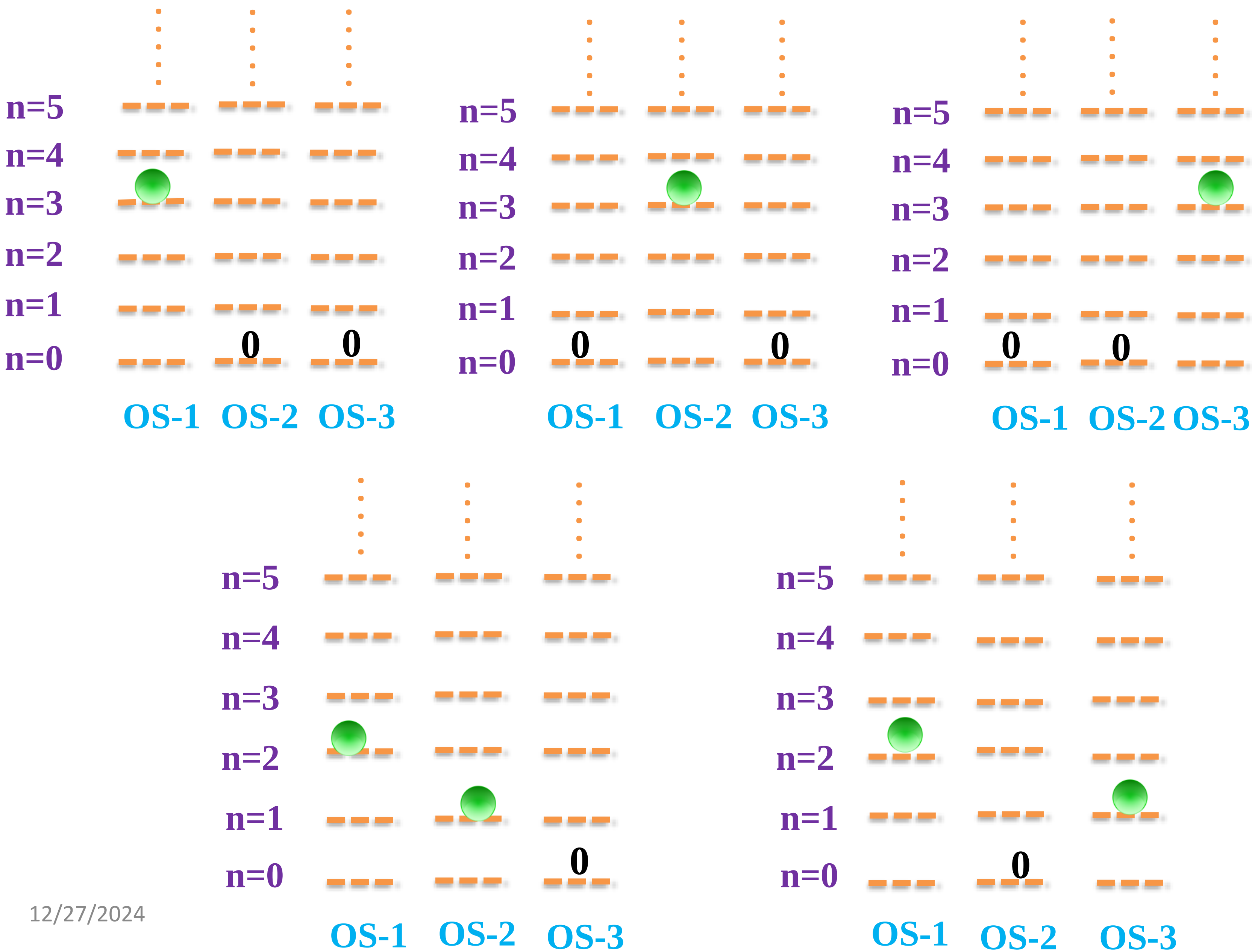
$$E_N = \left(n_1 + n_2 + n_3 + \frac{3}{2}\right)\hbar\omega, \qquad n_1, n_2, n_3 = 0,1,2,3,......$$

Energy Levels of N one dimensional harmonic oscillator is given by

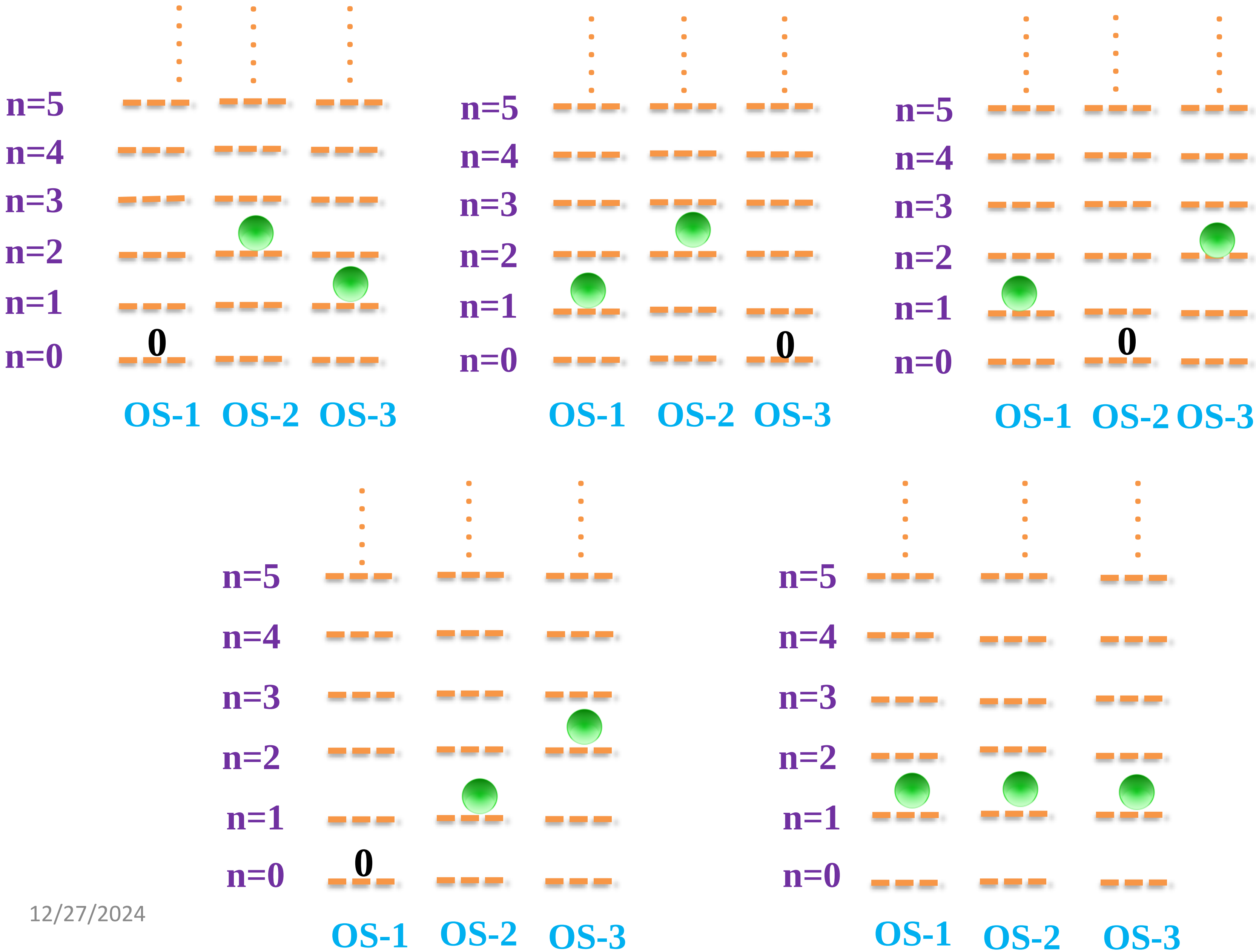
$$E_N = \left(n_1 + n_2 + n_3 + ... + n_N + \frac{N}{2}\right)\hbar\omega, \qquad n_1, n_2, n_3 = 0,1,2,3,......$$

$$E = (r + \frac{N}{2})\,\hbar\omega$$

The number of ways one can distribute 3 units of energy to 3 oscillators.



The number of ways one can distribute 3 units of energy to 3 oscillators.



Quantum Harmonic Oscillators

$$\Omega = \frac{(r+N-1)!}{r!(N-1)!} = \frac{(r+N)!}{r!(N)!}$$

Using Stirling's Approximation

$$\log \Omega = (r+N)\log(r+N) - (\cancel{r}+\cancel{N}) - r\log r + \cancel{r} - N\log N + \cancel{N}$$

$$= (r+N)\log(r+N) - r\log r - N\log N$$

Recall

$$E = (r + \frac{N}{2})\hbar\omega \Rightarrow r = \frac{E}{\hbar\omega} - \frac{N}{2}$$

Replacing $\boldsymbol{r}$ by E in **log Ω** and substituting it in $S = \mathrm{k}\log\Omega$

$$S = \mathrm{k}\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)\log\frac{\left(\frac{E}{\hbar\omega} + \frac{N}{2}\right)}{\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)} + \mathrm{k}\,N\log\frac{\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)}{N}$$

$$\frac{1}{T}=\frac{\partial S}{\partial E}=\frac{k}{\hbar\omega}\log\frac{\left(\frac{E}{\hbar\omega}+\frac{N}{2}\right)}{\left(\frac{E}{\hbar\omega}-\frac{N}{2}\right)}$$

Re-expressing E in terms of T

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

Ground State Energy (Independent of Temperature)

Term dependent of Temperature

At high T

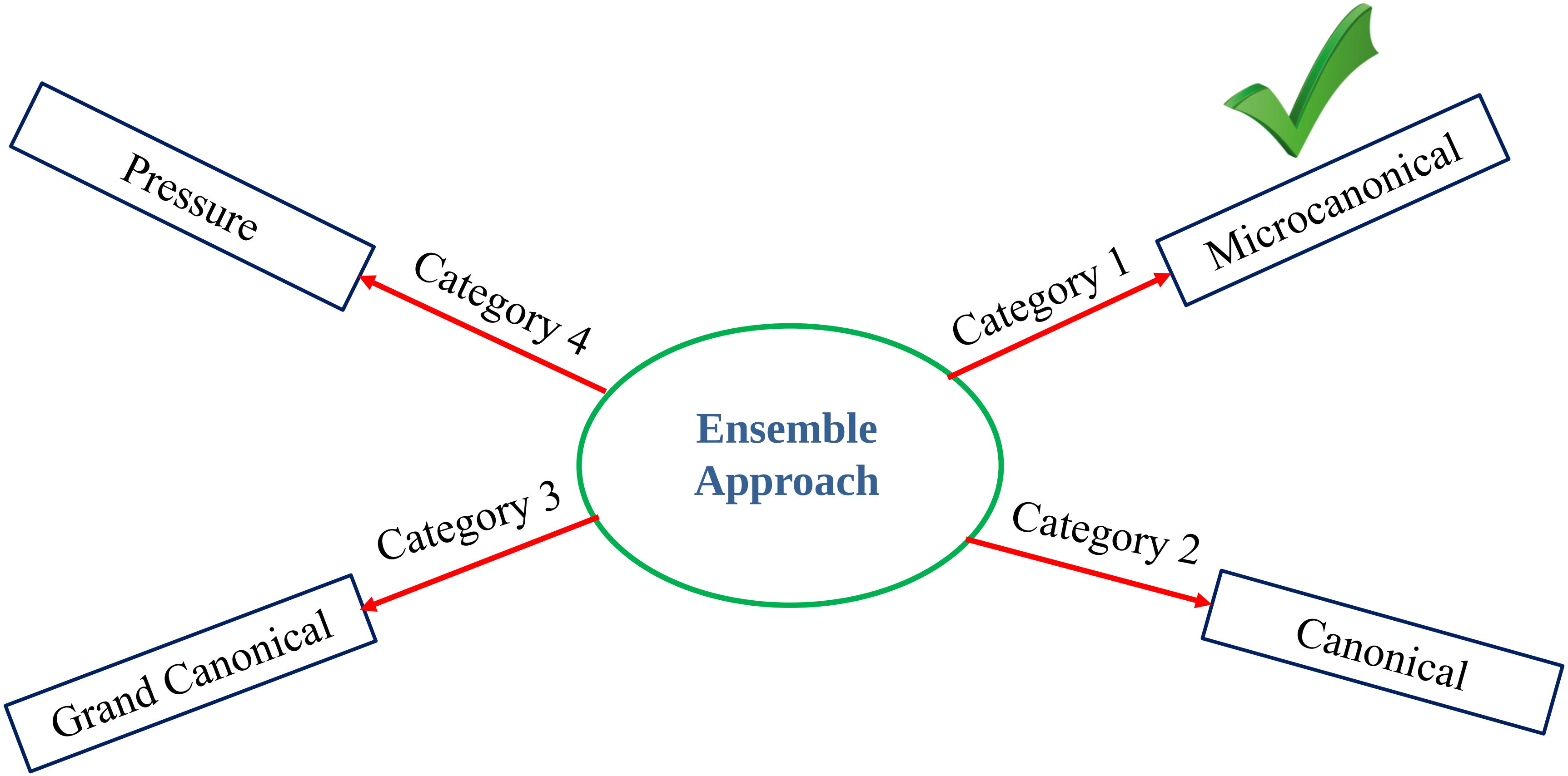
$$kT>>\hbar\omega,\quad \beta\hbar\omega<<1\Rightarrow\left(e^{\beta\hbar\omega}-1\right)\approx e^{\beta\hbar\omega}$$

$$E=\frac{N}{2}\hbar\omega+\frac{N\hbar\omega}{\beta\hbar\omega}=NkT$$

$$c_v=\frac{\partial E}{\partial T}=Nk$$

Coincides with well known results

Ensemble Approach



References:

1) B. K. Agarwal and M. Eisner, Statistical Mechanics(New Age International, New Delhi, 2020).
2) R. K. Pathria and P. D. Beale, Statistical Mechanics (Academic Press, Cambridge, 2021).
3) S. L. Kakani and C. Hemrajani, Statistical Mechanics (Viva Books Private Limited, New Delhi, 2017).
4) A. K. Saxena, An Introduction to Thermodynamics and Statistical Mechanics (Alpha Science International, New Delhi, 2010).
5) Satya Prakash, Statistical Mechanics(Kedar Nath Ram Nath, Meerut, 2008).
6) S. Chandra and M. K. Sharma, A Textbook on Statistical Mechanics(CBS Publisher, New Delhi, 2016).
7) S. C. Garg, R. M. Bansal and C. K. Ghosh, Thermal Physics: Kinetic Theory, Thermodynamics and Statistical Mechanics (McGraw Hill, New Delhi, 2013).
8) D.A. McQuarrie, Statistical Mechanics(Viva Books India, Viva Student Edition, 2018).
9) S. C. Garg, R. M. Bansal and C. K. Gosh, Thermal Physics: with Kinetic Theory, Thermodynamics and Statistical Mechanics (McGraw Hill Education, 2nd edition, 2017).
10) B. K. Agarwal and M. Eisner, Statistical Mechanics(New Age International Publishers, 3rd edition, 2013).
11) R. K. Pathria and P. D. Beale, Statistical Mechanics(Academic Press, 3rd edition, 2011).
12) F. Reif, Fundamentals of Statistical and Thermal Physics(Waveland Press, 2010).
13) W. Greiner, L. Neise and H. Stocker, Thermodynamics and Statistical Mechanics (Springer Verlag, New York, 1st edition, 1995).