BHARATHIDASAN UNIVERSITY

Tiruchirappalli- 620024

Tamil Nadu, India

Programme: M.Sc., Physics

Course Title : Thermodynamics and Statistical Physics

Course Code : 22PH202

Dr. M. Senthilvelan

Professor

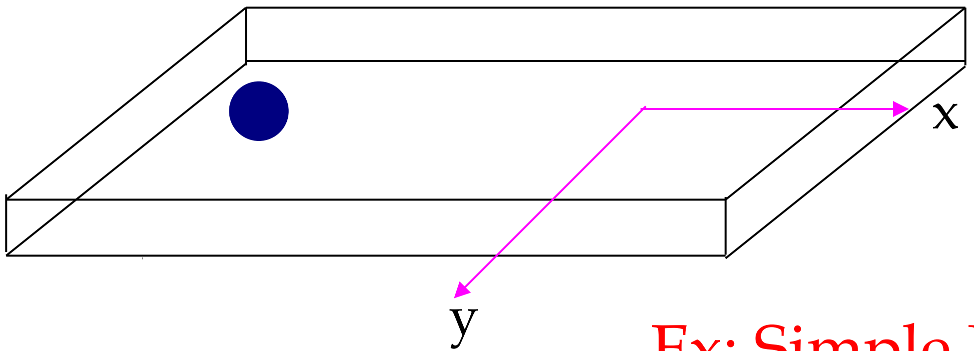
Department of Nonlinear Dynamics

UNIT - I

EQUILIBRIUM THERMODYNAMICS

Newton's Second Law

One Particle – 1 Dimension



Equation of Motion

$$\frac{d^2x}{dt^2} = F\left(t, x, \frac{dx}{dt}\right)$$

Solution

$$x(t) = f(t, c_1, c_2)$$

c_1, c_2 are constants

I.C Needed 2

Ex: Simple Harmonic Oscillator

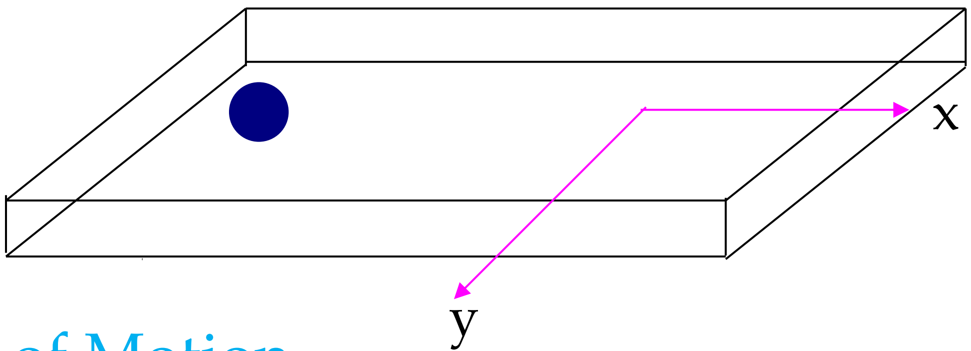
$$\frac{d^2x}{dt^2} = -\frac{k}{m}x$$

Solution

$$x(t) = A\sin\left(\sqrt{\frac{\mathrm{k}}{\mathrm{m}}}\,t + \delta\right)$$

A, δ; constants

One Particle – 2 Dimension



<u>Equations of Motion</u>

$$\frac{d^2x}{dt^2} = F(t, x, y, \dot{x}, \dot{y})$$

$$\frac{d^2y}{dt^2} = G(t, x, y, \dot{x}, \dot{y})$$

<u>Solution</u>

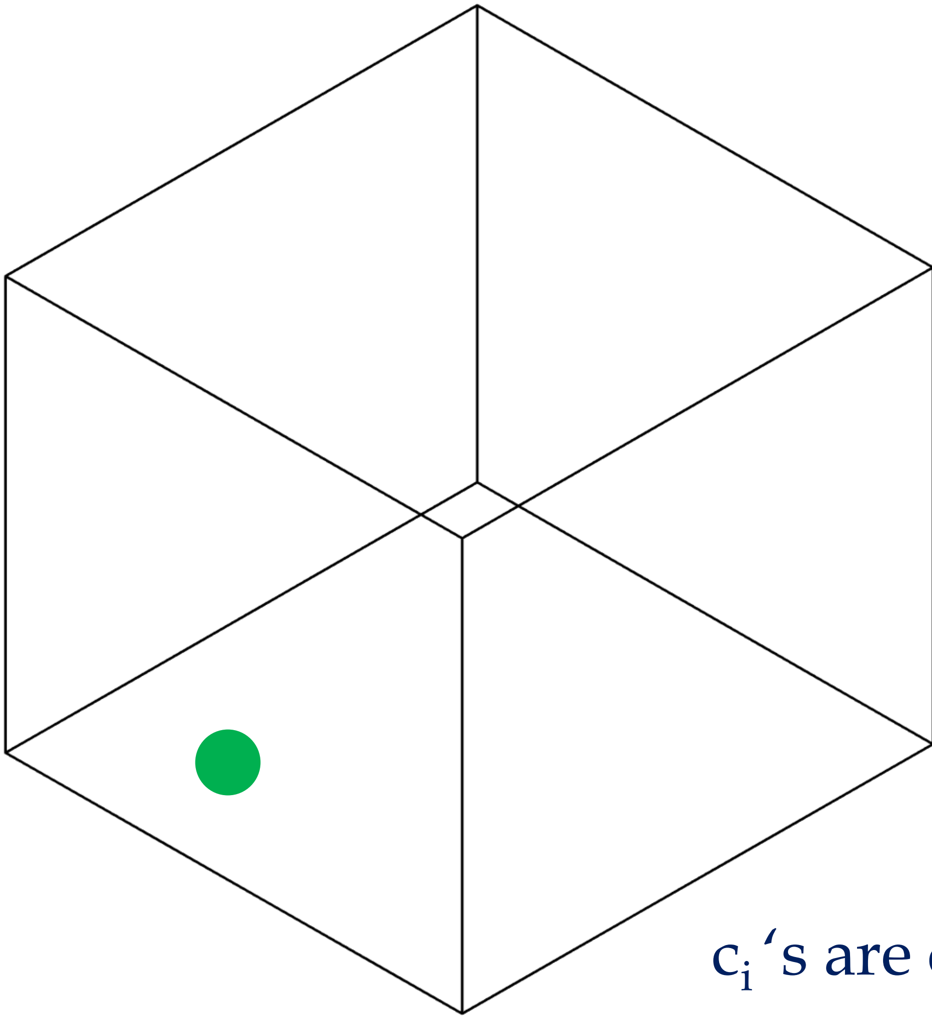
$$\mathrm{x(t)} = \mathrm{f_1(t, c_1, c_2, c_3, c_4)}$$

$$\mathrm{y(t)} = \mathrm{f_2(t, c_1, c_2, c_3, c_4)}$$

c_i ‘s are constants (4)

I.C Needed 4

One Particle – 3 Dimension



Equation of Motion

$$\frac{d^2x}{dt^2} = F(t, x, y, z, \dot{x}, \dot{y}, \dot{z})$$

$$\frac{d^2y}{dt^2} = G(t, x, y, z, \dot{x}, \dot{y}, \dot{z})$$

$$\frac{d^2z}{dt^2} = H(t, x, y, z, \dot{x}, \dot{y}, \dot{z})$$

Solution

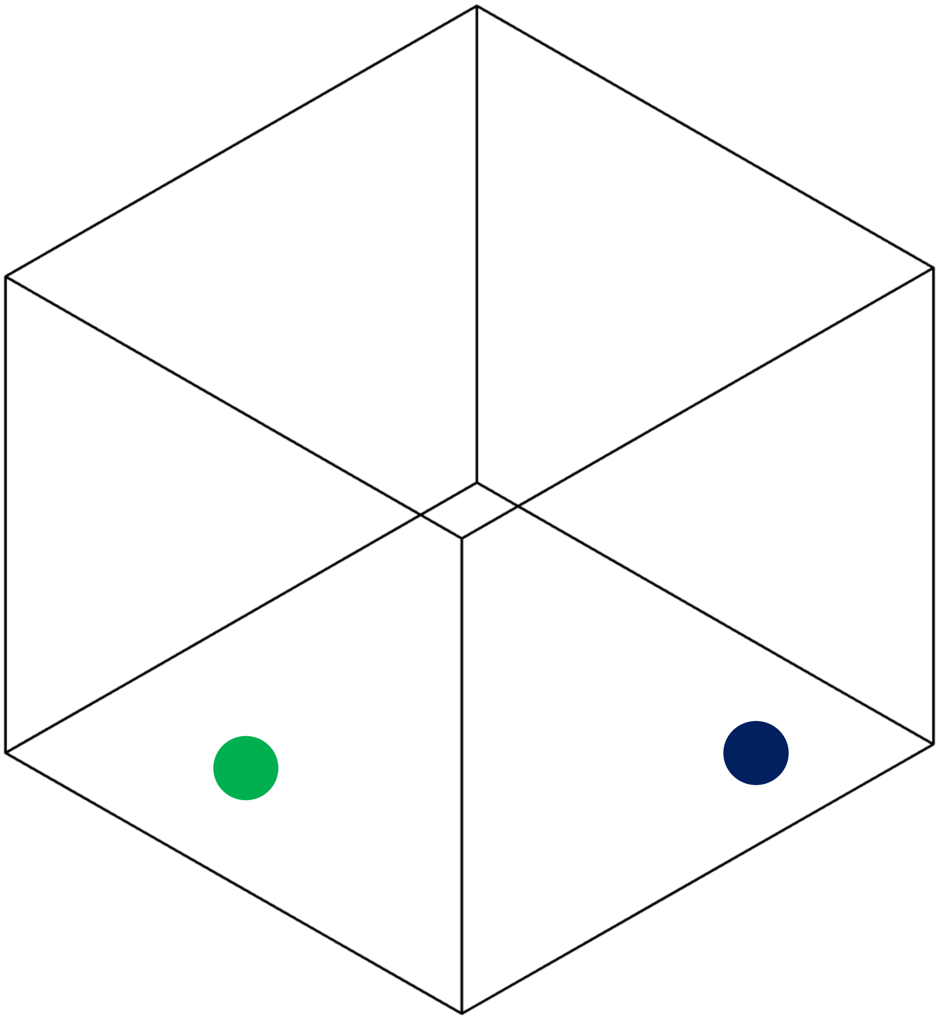
$$x(t) = f_1(t, c_1, c_2, c_3, c_4, c_5, c_6)$$

$$y(t) = f_2(t, c_1, c_2, c_3, c_4, c_5, c_6)$$

$$z(t) = f_2(t, c_1, c_2, c_3, c_4, c_5, c_6)$$

c_i's are constants (6)   I.C Needed 6

Two Particles – 3 Dimension



Equation of Motion

1st Particle

$$\begin{cases} \dfrac{d^2 x_1}{dt^2} = F_1(t, x_1, y_1, z_1, x_2, y_2, z_2, \dot{x}_1, \dot{y}_1, \dot{z}_1, \dot{x}_2, \dot{y}_2, \dot{z}_2) \\ \dfrac{d^2 y_1}{dt^2} = F_2(t, x_1, y_1, z_1, x_2, y_2, z_2, \dot{x}_1, \dot{y}_1, \dot{z}_1, \dot{x}_2, \dot{y}_2, \dot{z}_2) \\ \dfrac{d^2 z_1}{dt^2} = F_3(t, x_1, y_1, z_1, x_2, y_2, z_2, \dot{x}_1, \dot{y}_1, \dot{z}_1, \dot{x}_2, \dot{y}_2, \dot{z}_2) \end{cases}$$

$$\begin{cases} \dfrac{d^2 x_2}{dt^2} = F_4(t, x_1, y_1, z_1, x_2, y_2, z_2, \dot{x}_1, \dot{y}_1, \dot{z}_1, \dot{x}_2, \dot{y}_2, \dot{z}_2) \\ \dfrac{d^2 y_2}{dt^2} = F_5(t, x_1, y_1, z_1, x_2, y_2, z_2, \dot{x}_1, \dot{y}_1, \dot{z}_1, \dot{x}_2, \dot{y}_2, \dot{z}_2) \\ \dfrac{d^2 z_2}{dt^2} = F_6(t, x_1, y_1, z_1, x_2, y_2, z_2, \dot{x}_1, \dot{y}_1, \dot{z}_1, \dot{x}_2, \dot{y}_2, \dot{z}_2) \end{cases}$$

2nd Particle

Solution

$$x_1 = f_1(t, c_1, c_2, c_3, c_4, c_5, c_6, c_7, c_8, c_9, c_{10}, c_{11}, c_{12})$$

$$y_1 = f_2(t, c_1, c_2, c_3, c_4, c_5, c_6, c_7, c_8, c_9, c_{10}, c_{11}, c_{12})$$

$$z_1 = f_3(t, c_1, c_2, c_3, c_4, c_5, c_6, c_7, c_8, c_9, c_{10}, c_{11}, c_{12})$$

$$x_2 = f_4(t, c_1, c_2, c_3, c_4, c_5, c_6, c_7, c_8, c_9, c_{10}, c_{11}, c_{12})$$

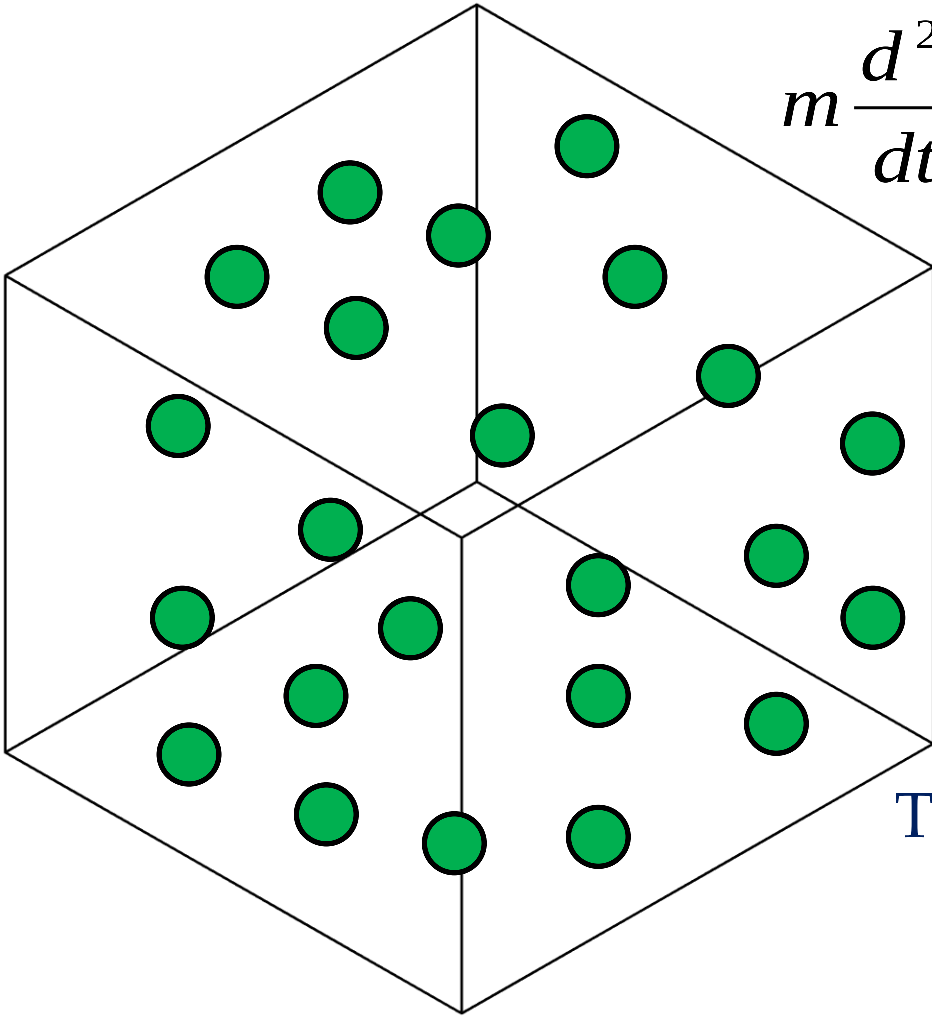
$$y_2 = f_5(t, c_1, c_2, c_3, c_4, c_5, c_6, c_7, c_8, c_9, c_{10}, c_{11}, c_{12})$$

$$z_2 = f_6(t, c_1, c_2, c_3, c_4, c_5, c_6, c_7, c_8, c_9, c_{10}, c_{11}, c_{12})$$

c_i's are constants (12)

I.C Needed 12

‘N’ Particles – 3 Dimension



$$m\frac{d^2\vec{r}_i}{dt^2} = \vec{F}_i(t, \vec{r}_i, \dot{\vec{r}}_i), i = 1,2,..N$$

Total Number of Equations = 3N

Initial Conditions Needed = 6N

N is of the order of 10^{23}

- As the particles/systems increases, the complexity also increases.
- It is difficult to specify the Initial Conditions and hence difficult to solve the Newton's equations.
- At the quantum level, difficulties arise while solving the Schrödinger equation in the *N* particle case.
- Need an alternate formalism.

A Recollection on Probability

Average Value

❖ The Average Value (or Mean Value) of a set of **'N'** values **x_1, x_2,....x_n** of **'x'** is denoted by either **$\bar{x}$** or **<x>** and is given by

$$\bar{x} = \langle x \rangle = \frac{x_1 + x_2 + \dots\dots + x_N}{N} = \frac{1}{N}\sum_{j=1}^{N} x_j$$

❖ The Summation is over all the **'N'** values of x_j's.

- For example, if the values x_j, are 6,7,6,7,7,8,9,7,5,8 the average value of **'x'** is

$$\bar{x} = \langle x \rangle = \frac{(6+7+6+7+7+8+9+7+5+8)}{10} = 7$$

- Since there are **five, two sixes, four sevens, two eights** and ***one nine***, the expression for **'x'** can be written in the form

$$\bar{x} = \frac{(1\times5+2\times6+4\times7+2\times8+1\times9)}{10}$$

$$= \frac{1}{10}\times5+\frac{2}{10}\times6+\frac{4}{10}\times7+\frac{2}{10}\times8+\frac{1}{10}\times9$$

$$\text{Probability of getting a } 5 = \frac{1}{10}$$

$$\text{Probability of getting a } 6 = \frac{2}{10} \text{.....} \textit{and so on}$$

$$\therefore \bar{x} = \langle x \rangle = \sum_i x_i P_i$$

P_i → Probability of getting the value of x_i

Microstates and Macrostates

MACROSTATES AND MICROSTATES
Another Example

Distribution of 4 distinguishable particles {a,b,c,d} in 2 similar compartments.

Possibilities

Compartment	
1	**2**
0	4
1	3
2	2
3	1
4	0

We have 5 different distributions

(0,4), (1,3), (2,2), (3,1) and (4,0)

⇩

Macrostates

Microstates

⇩

The number of different possible arrangements.

Macrostates	Possible arrangement in compartment 1	Possible arrangement in compartment 2	No. of Microstates
(0,4)	0	abcd	1
(1,3)	a b c d	bcd acd abd abc	4
(2,2)	ab ac ad bc db cd	cd bd bc ad ac ab	6

One Macrostate

Six different Microstates

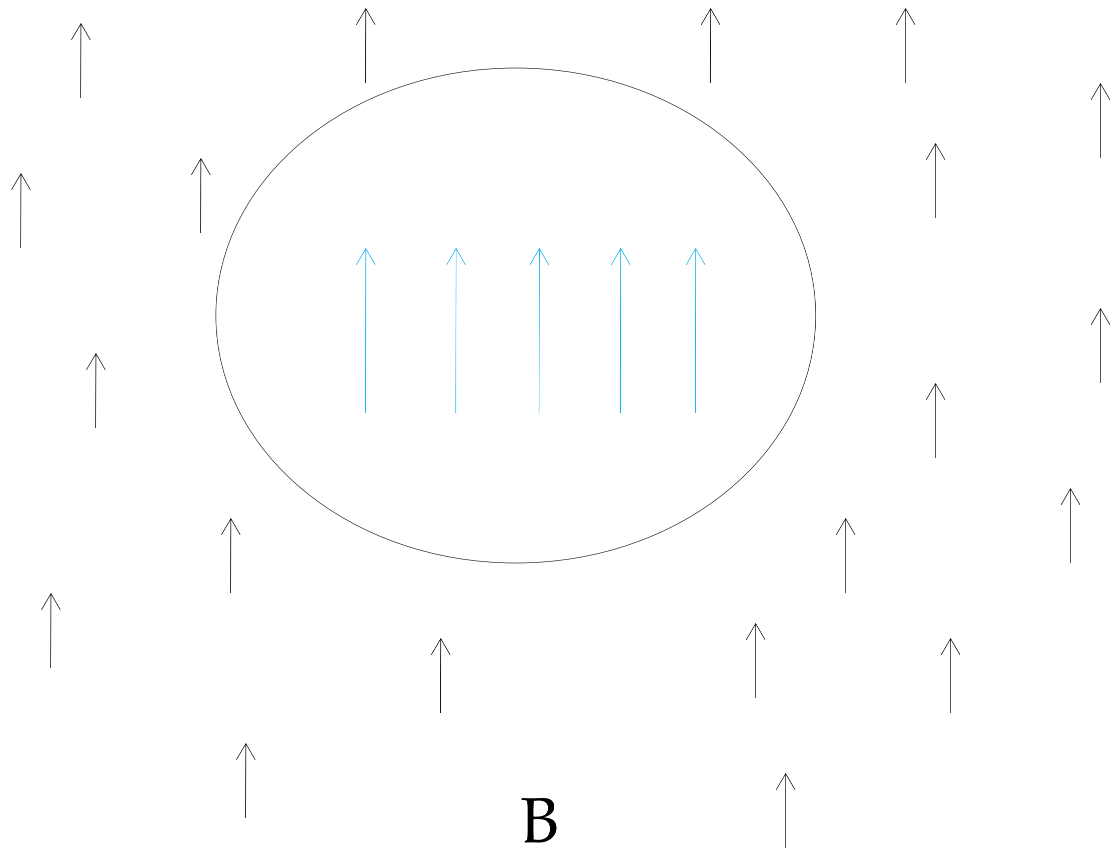
Some more examples:

Microstates: Position, Momentum, Spin,....

Macrostates: Pressure, Volume, Magnetic field,...

❖ Consider five non interacting *spins* or ***magnetic dipole***

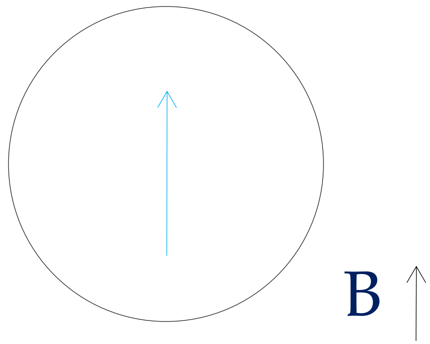
❖ They are placed in a magnetic field **'B'**



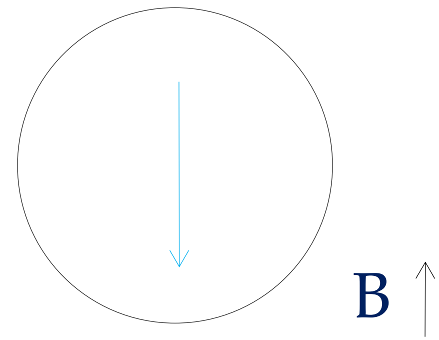
$$E = -\vec{\mu}.\vec{B} = -\mu B \cos\theta$$

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

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



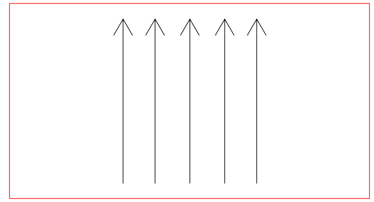
Energy of spin parallel to the magnetic field 'E' = $-\mu B$



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

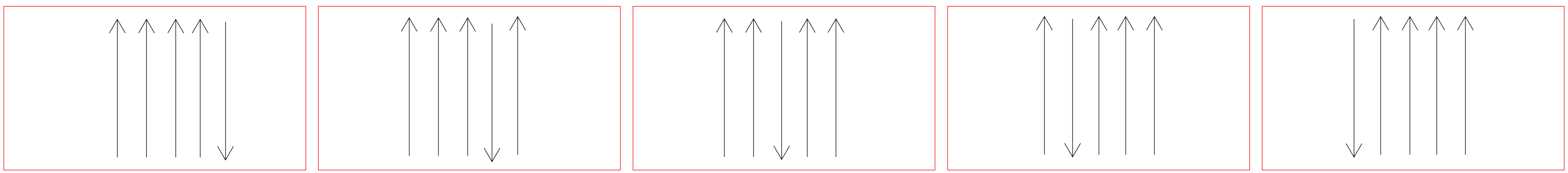
Question: Calculate the number of possible states having total energy = $-\mu B$

All Spins Up

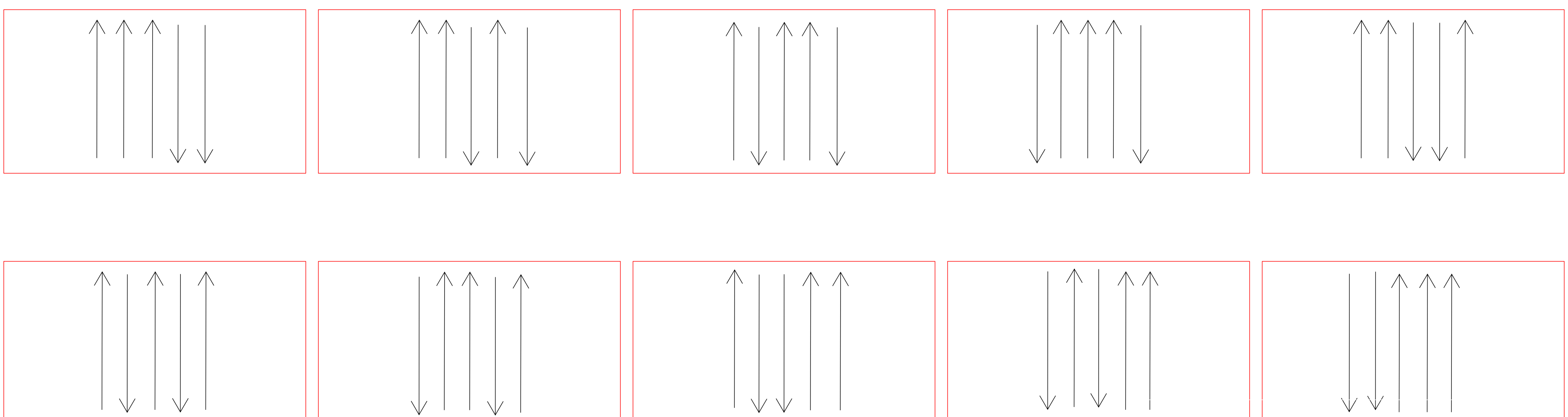


(-5μB) → 1 Microstate

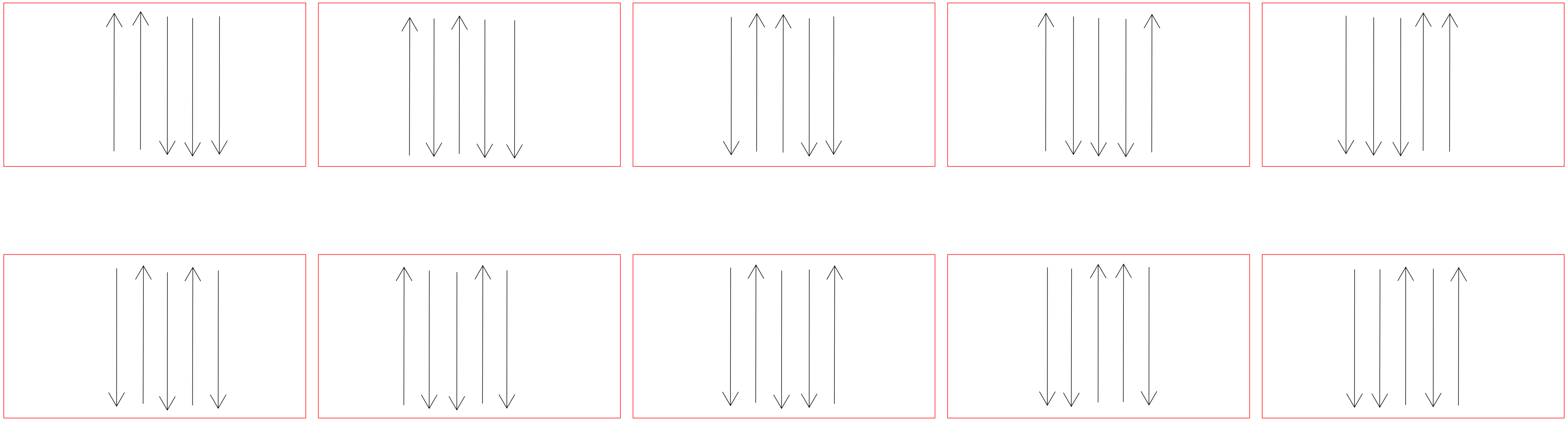
One Spin Down (-3μB) → 5 Microstates



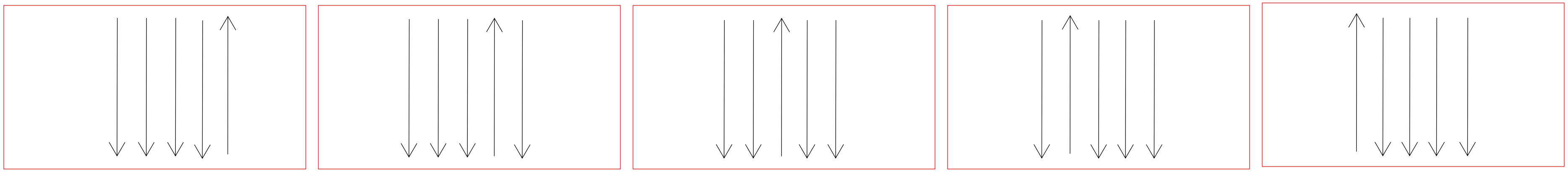
Two Spins Down (-μB) → 10 Microstates



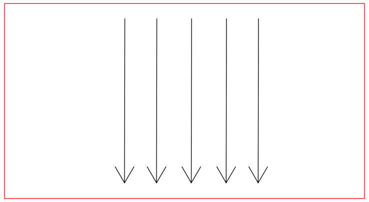
Three Spins Down (μB) → 10 Microstates



Four Spins Down (3μB) → 5 Microstates



All Spins Down (5μB) → 1 Microstates

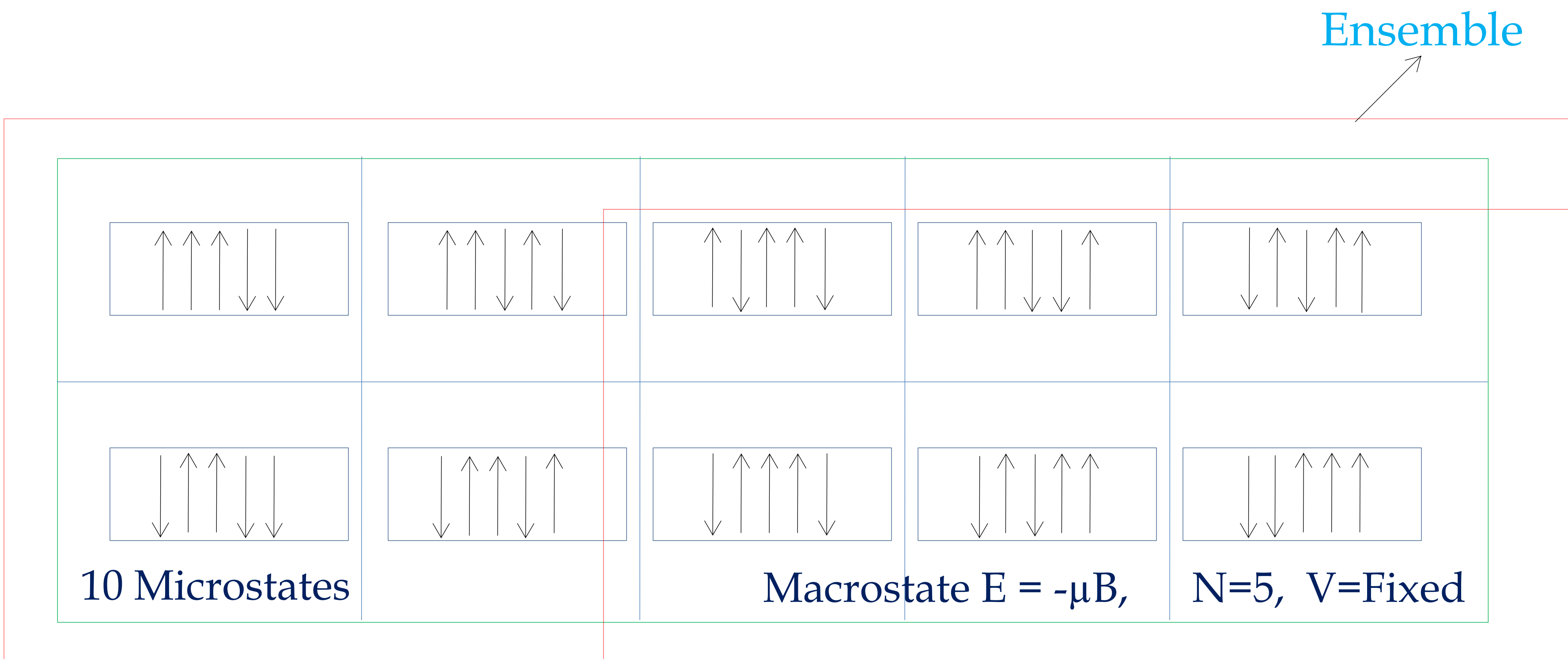


Totally 32 Microstates

1 + 5 + 10 + 10 + 5 + 1

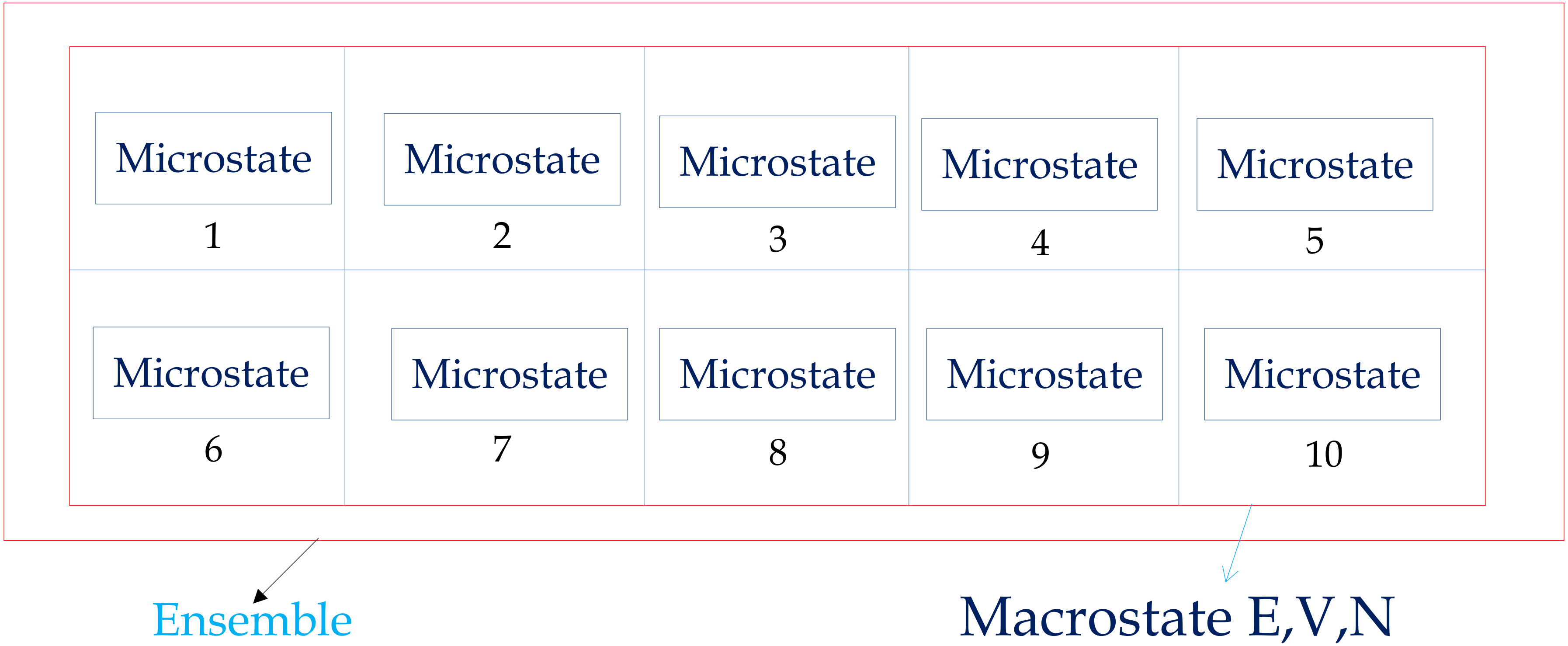
In this problem we are interested in finding the number of possible states having total energy = $-\mu B$.

We found that 10 microstates have total energy = $-\mu B$



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

Counting Number of Microstates

in

Simple Physical Models

Dynamics in Phase - Space

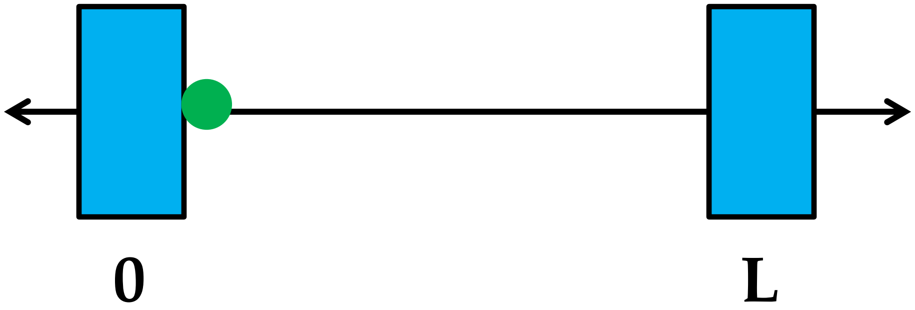
Ex.1 A Particle in a One-Dimensional Box (classical)

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

Equation of Motion

$$\dot{q} = \frac{p}{m} \qquad \dot{p} = 0 \Rightarrow p = const$$

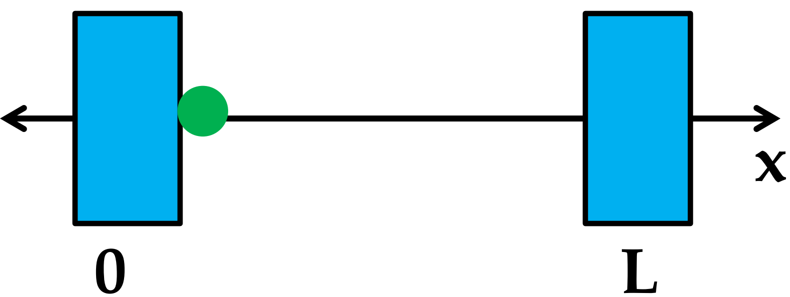
$$E = \frac{p^2}{2m} \qquad p = \pm\sqrt{2mE}$$

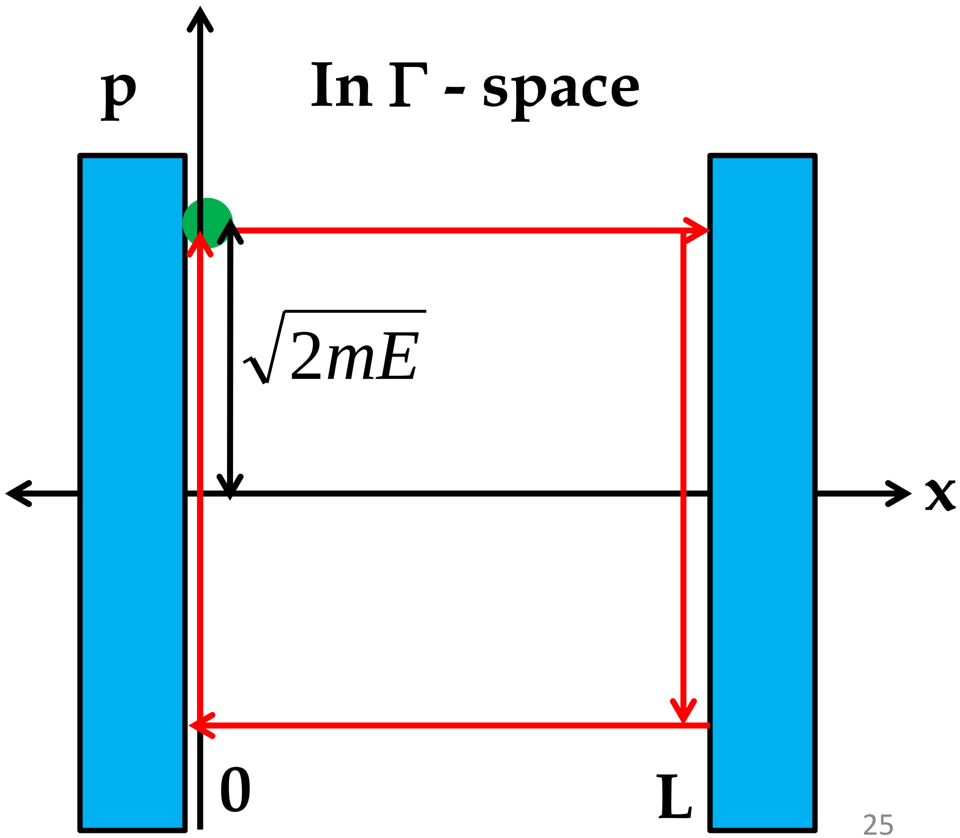


❖Say, at the initial time, the particle is at x = 0 (green dot) and has a +ve momentum. $p_x = p(E) = \sqrt{2mE}$

❖It will move towards right with constant momentum until it hits the wall.

❖At this time the momentum reverse sign and the particle starts moving towards the left until it hits the left wall and so on and so forth.

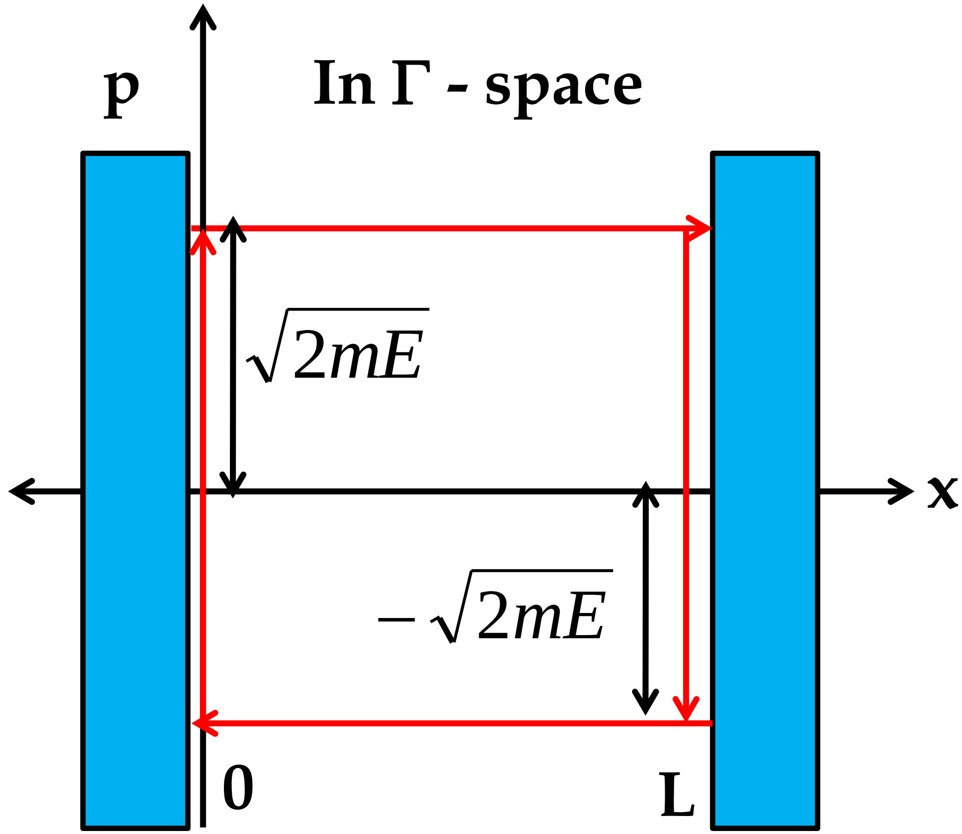


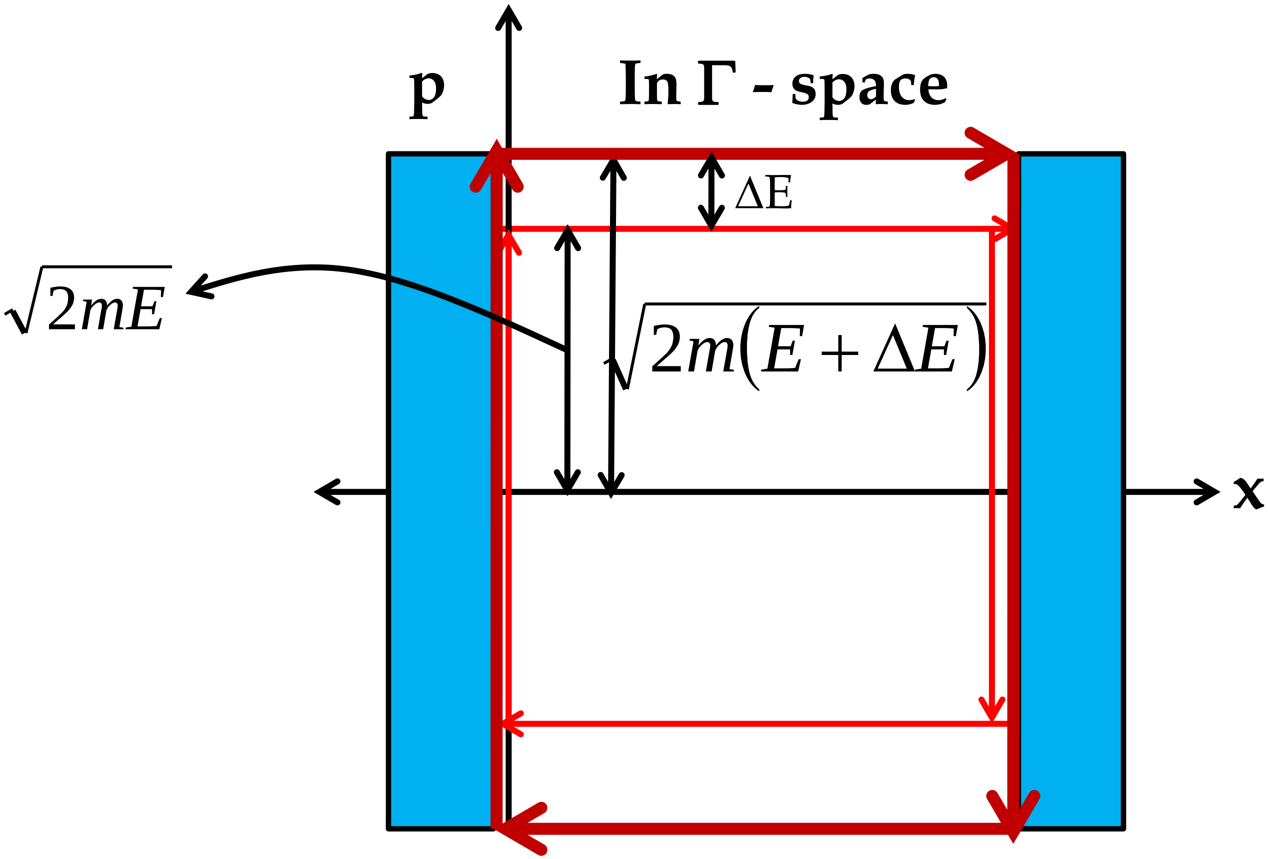


❖Each point on the trajectory (in Γ - space) is nothing but the microstate.

❖ For a given energy ‘E’ and length ‘L’ the particle can be in any of the microstates on the directed line shown.

❖ If we want wait long enough, the particle will go through all the possible microstates associated with the macrostate E, L.





❖ How to count the number of microstates within E + ΔE?

Calculating Number of Microstates

We have seen $S = k \log \Omega\ (E, V, N)$

Ω = Number of Microstates

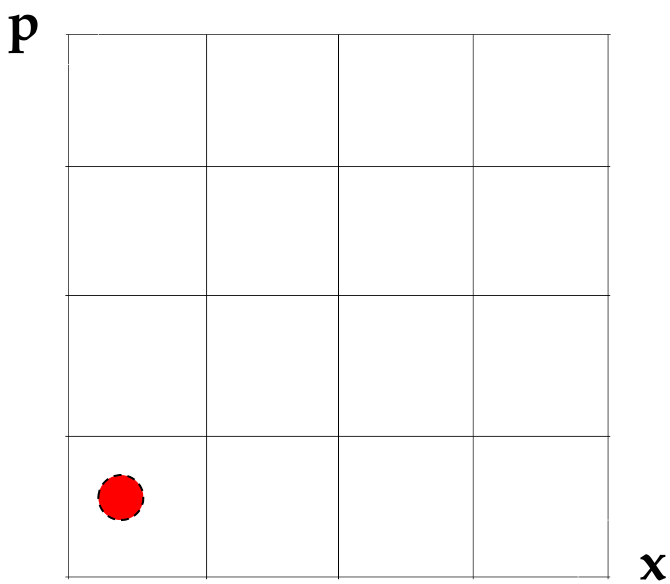
How to calculate Ω?

Classical:

Assume that a particle is moving in 1 dimension.

The phase space is described in the following figure.

Counting Number of States in 2D

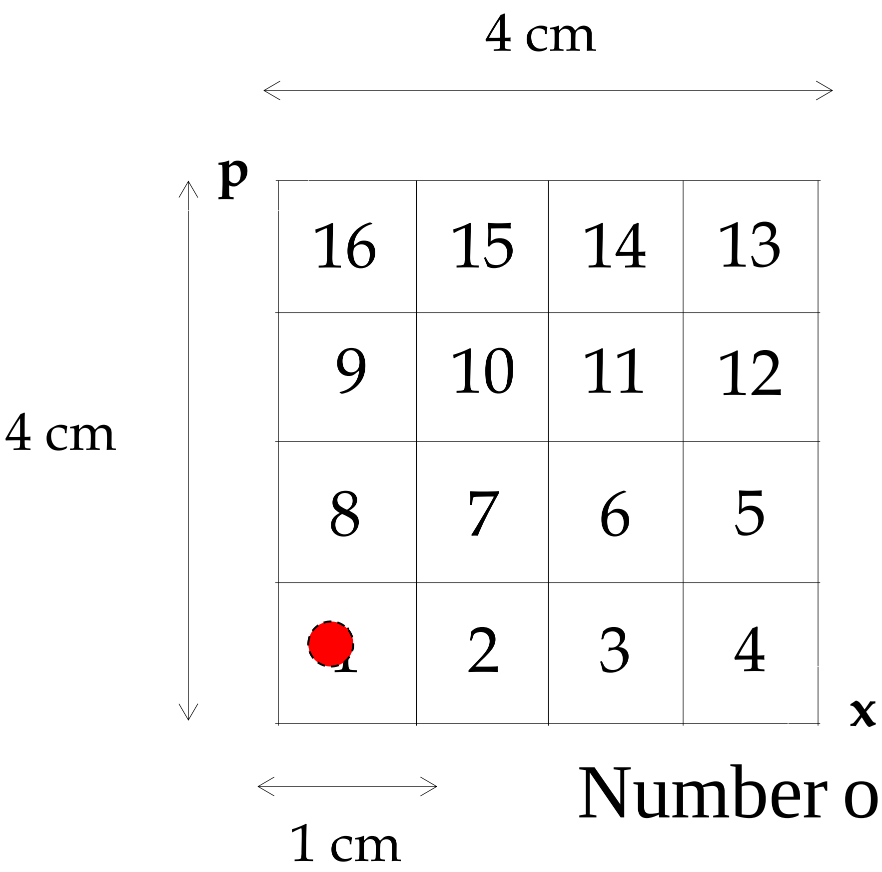


- ❖ Each point in this space gives the position and velocity of a particle.
- ❖ The position and velocity of the particles changes with time.
- ❖ The more off the region and so to new cells or new microstates.
- ❖ The number of microstates are so large. Hence we have to make some assumptions about their probabilities.

Let us raise the question

- ❖ " which microstates do we feel are equally likely to occur ?"
- ❖ The answer to this question depends on what we know.
- ❖ If we know nothing about the system then all microstate are equally likely to occur.

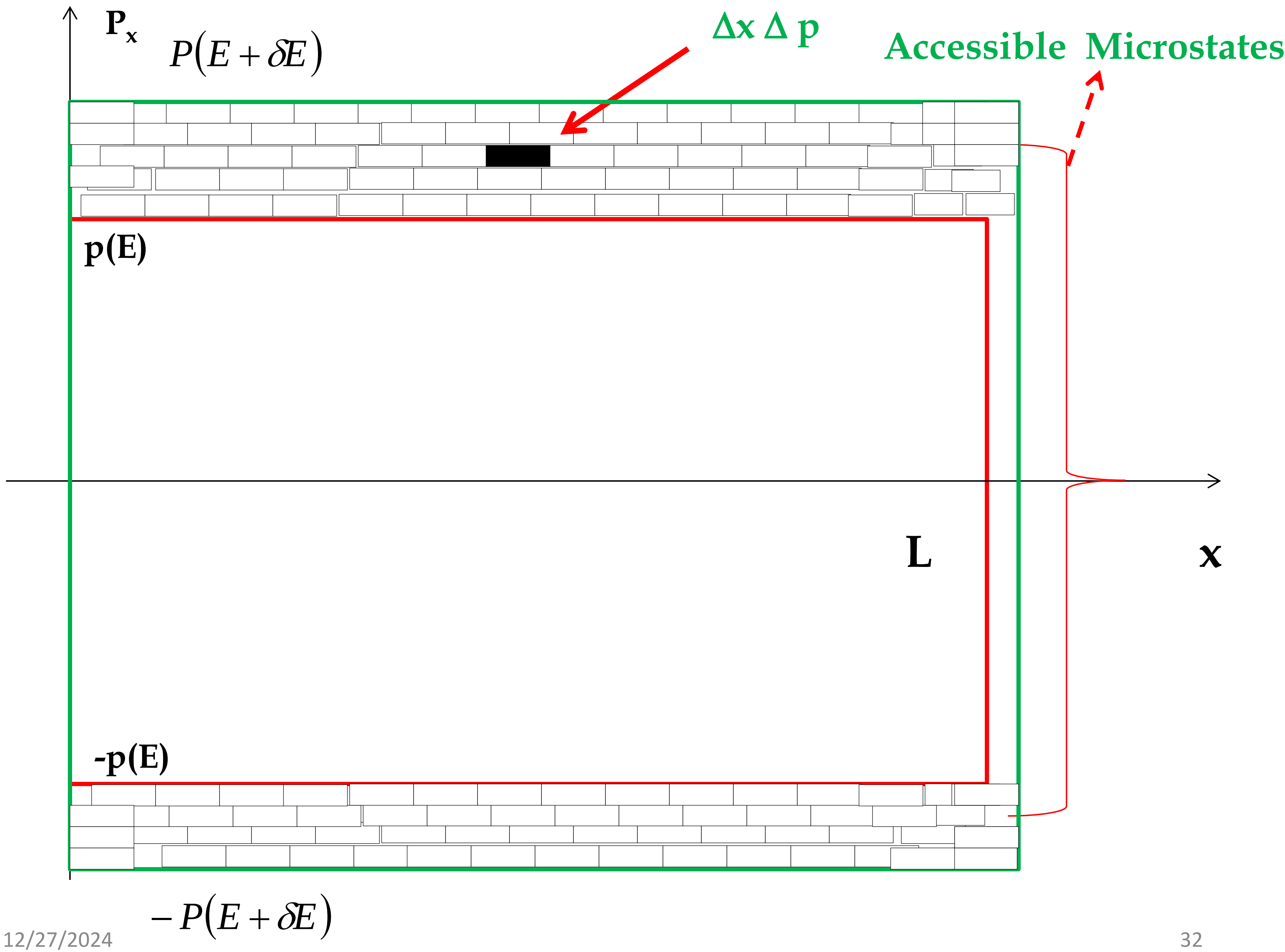
Counting Number of States in 2D



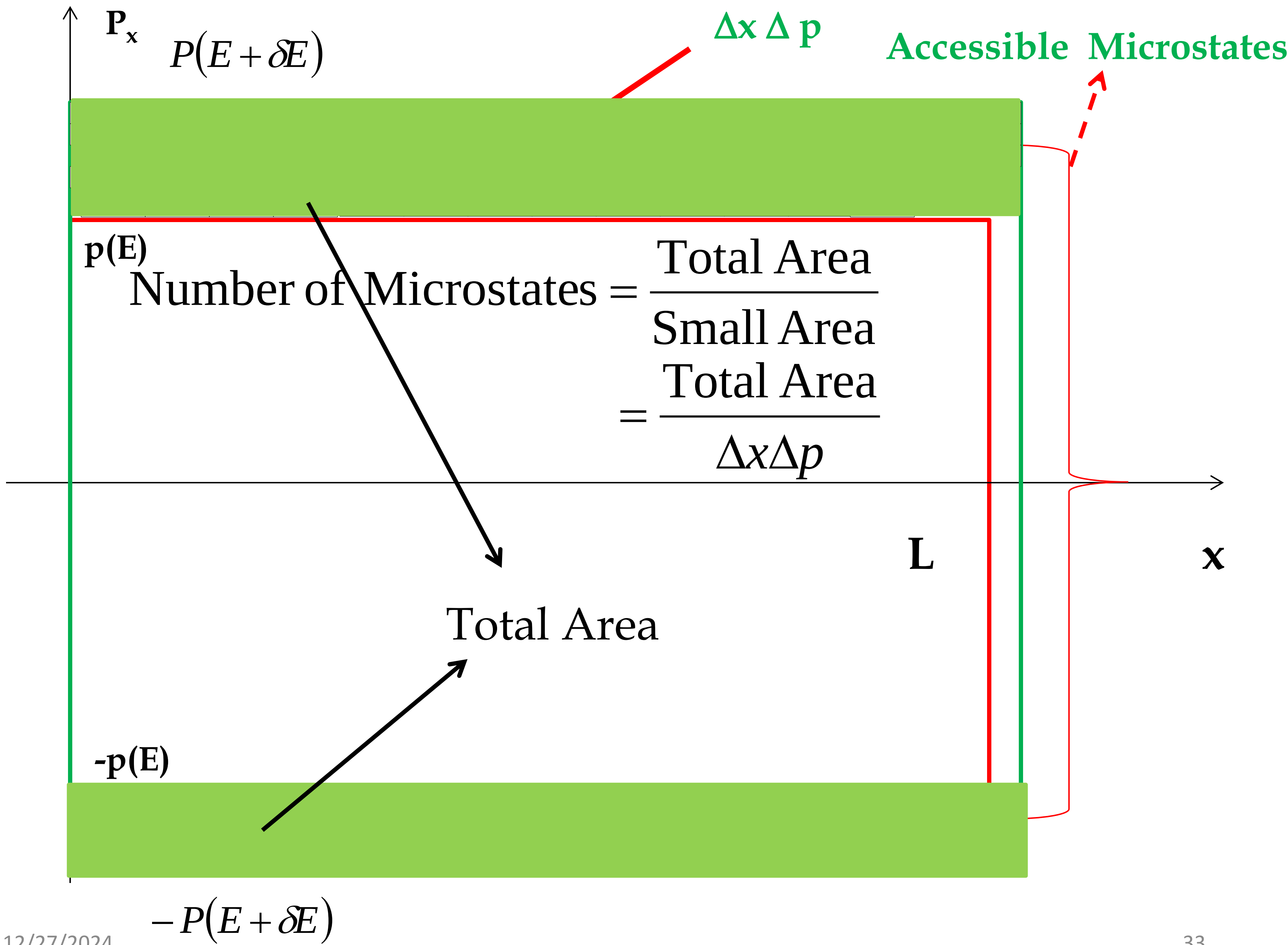
$$\text{Number of Cells} = \frac{\text{Total Area}}{\text{Area of a single cell}}$$

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

$$= 16$$



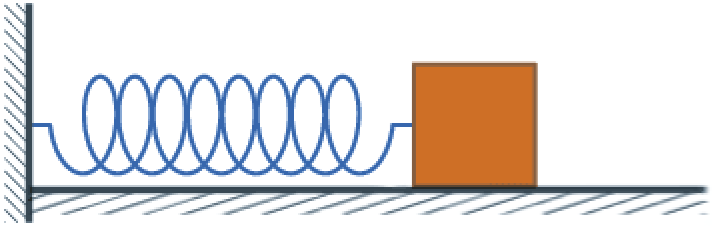
P_x
$P(E + \delta E)$
$\Delta x \, \Delta p$
Accessible Microstates
p(E)
L
x
-p(E)
$-P(E + \delta E)$



$$\text{Number of Microstates} = \frac{\text{Total Area}}{\text{Small Area}} = \frac{\text{Total Area}}{\Delta x \Delta p}$$

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

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

Parametric representation of curves **Circle**

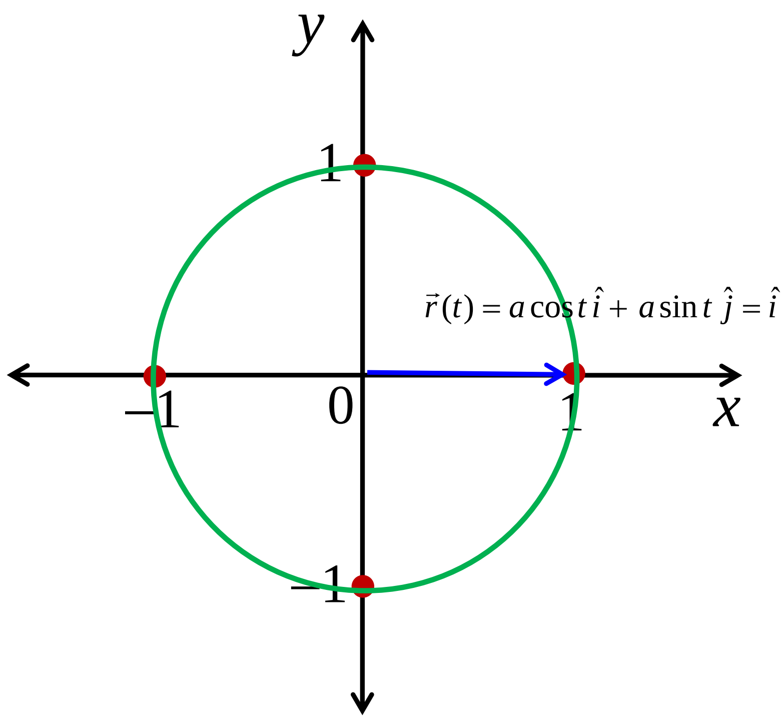
A circle $x^2 + y^2 = a^2$ can also be represented in the form

$$\vec{r}(t) = x(t)\,\hat{i} + y(t)\,\hat{j} = a\cos t\,\hat{i} + a\sin t\,\hat{j}$$

with $x = a\cos t,\ y = a\sin t,\ 0 \le t \le 2\pi.$

Unit radius $a = 1$

$x = \cos t,\ y = \sin t,\ 0 \le t \le 2\pi$



t	$x = \cos t$	$y = \sin t$
0	1	0
$\frac{\pi}{2}$	0	1
π	-1	0
$\frac{3\pi}{2}$	0	-1
2π	1	0

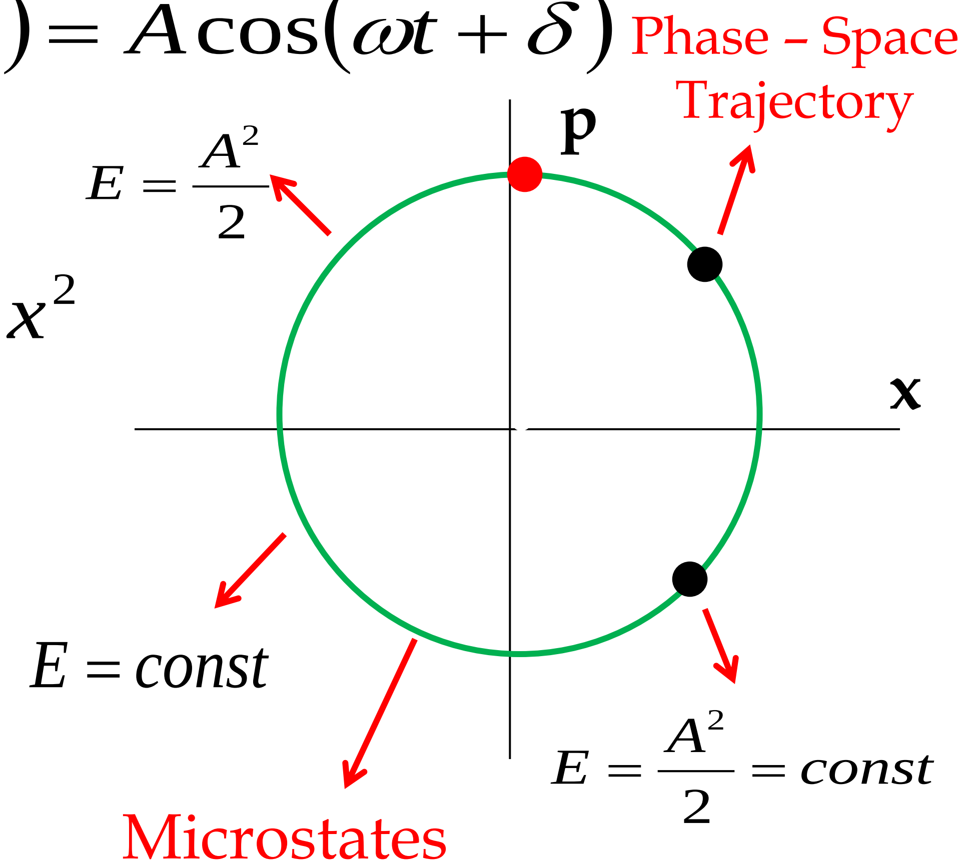
Phase - Space

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

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

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

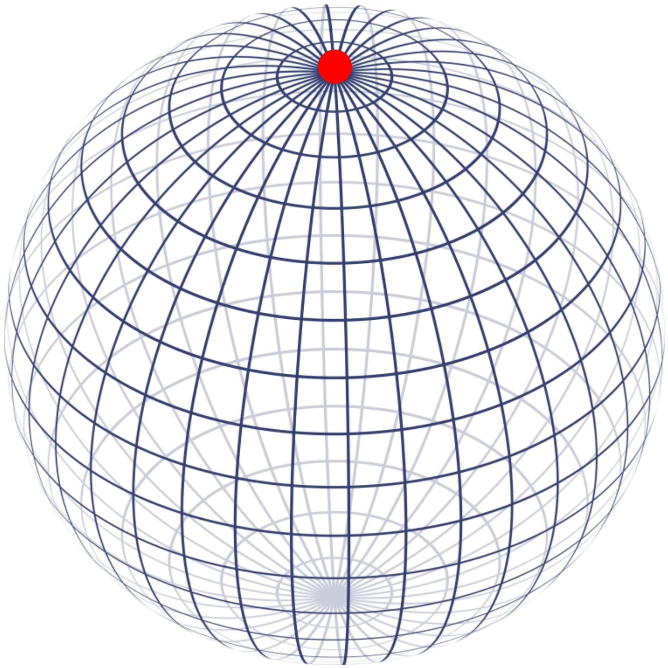
$$E = \frac{A^2}{2} = \text{constant}$$

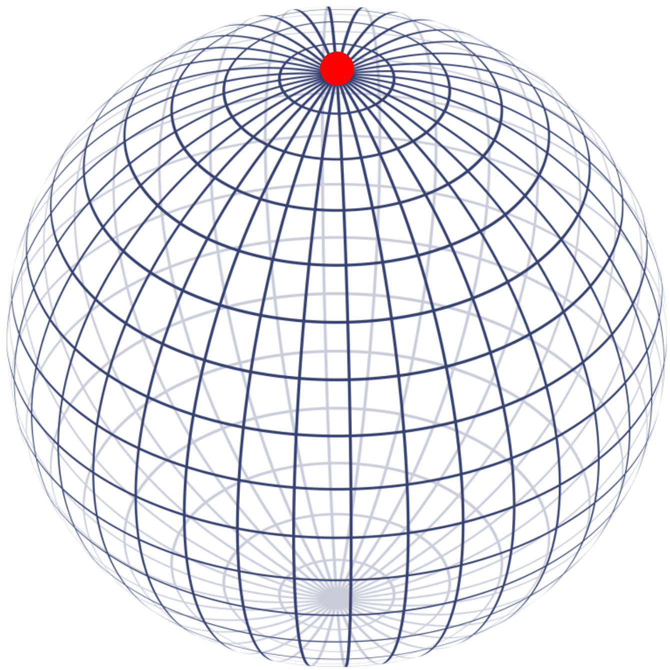


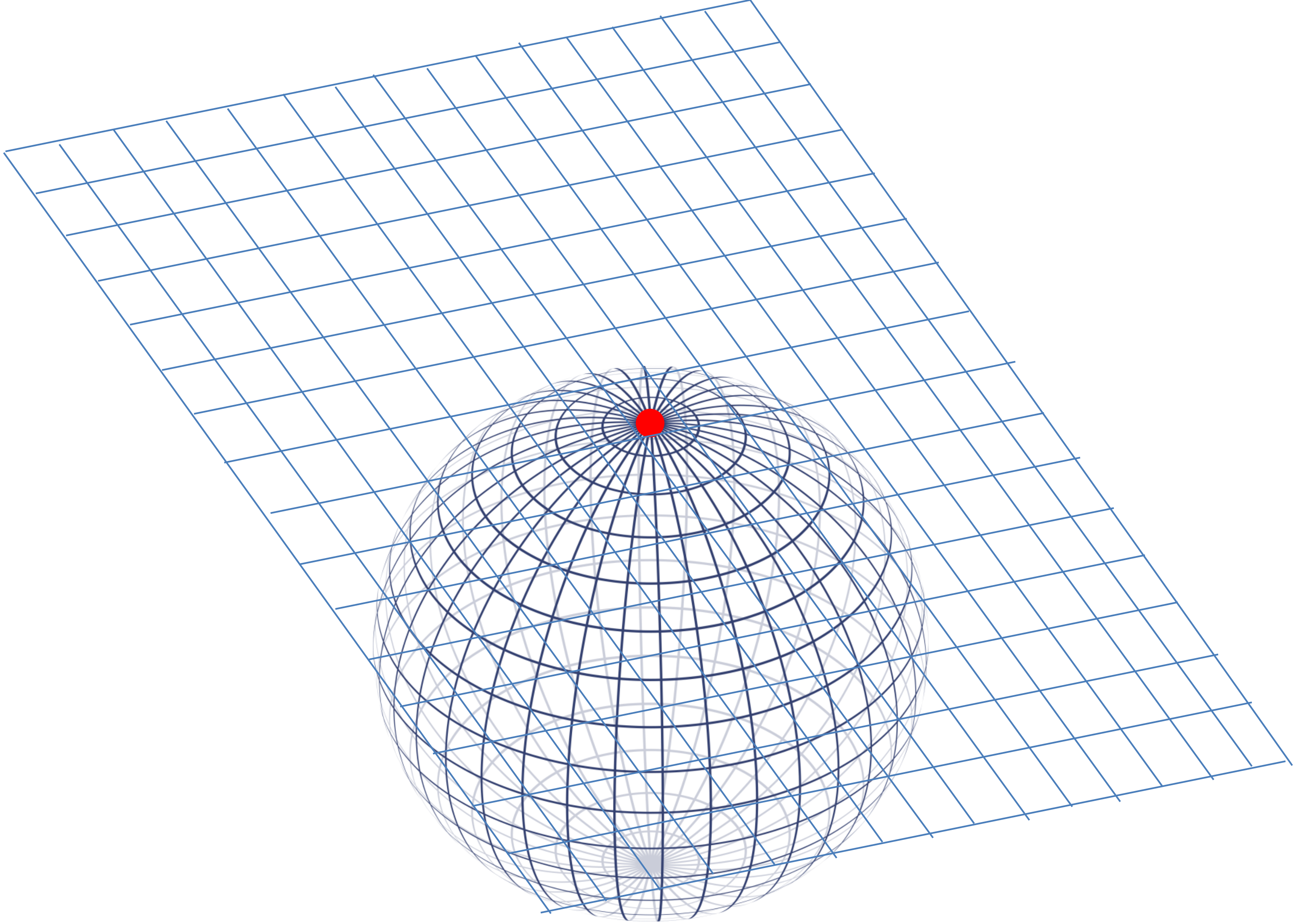
Each pt on phase – space trajectory is a microstates.

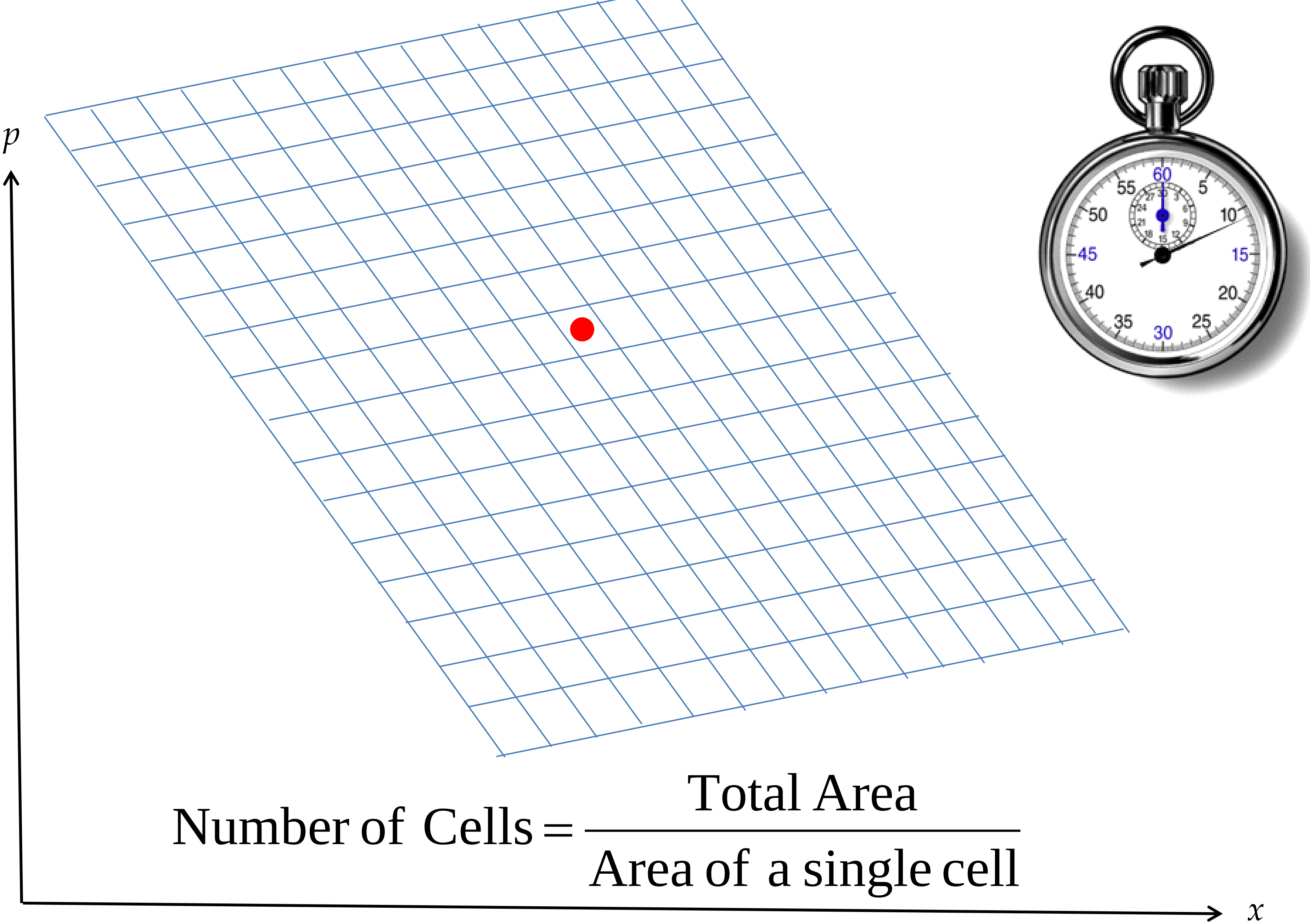
$\therefore$ We have to count number of microstates on the circle.

Counting Number of Microstates on the Energy Surface









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

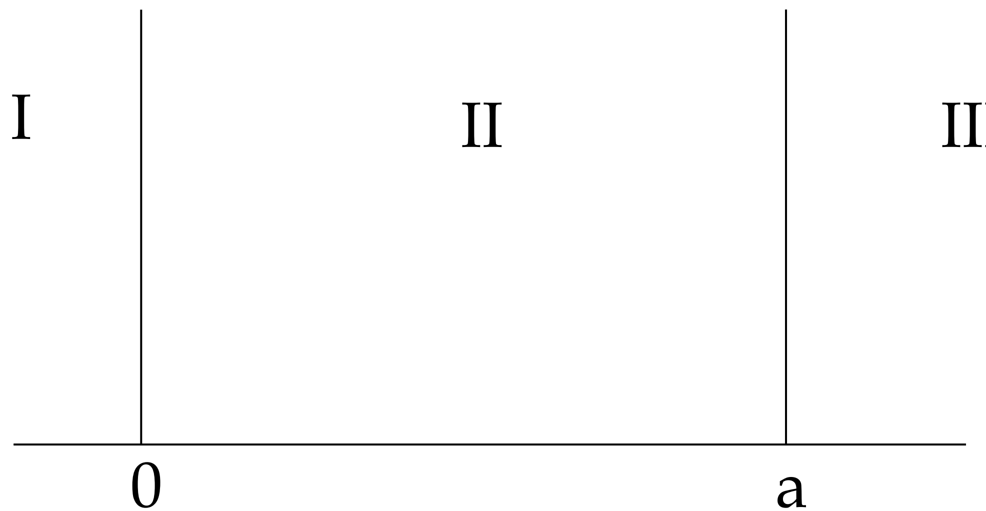
The Particle in a One Dimensional Box

(Quantum)

THE PARTICLE IN A ONE-DIMENSIONAL BOX

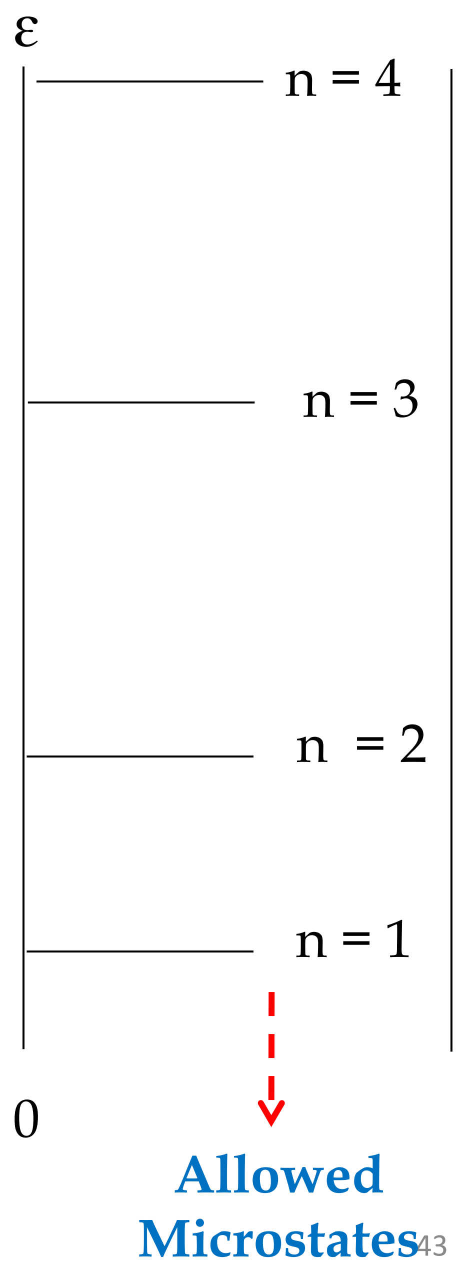
- Let us consider a single microscopic particle of mass 'M' moving in one-dimension 'x' and subject to the Potential Energy function of shown in fig.

$$V = \begin{cases} 0 & 0 \le x \le a \quad \text{Region II} \\ \infty & x < 0 \ \text{ and } x > a. \quad \text{Region I \& III} \end{cases}$$



❖ The Potential Energy combines the particle to move in the region between ‘o’ and ‘a’ as the ‘x’ axis.

❖ Time independent Schrodinger equation.

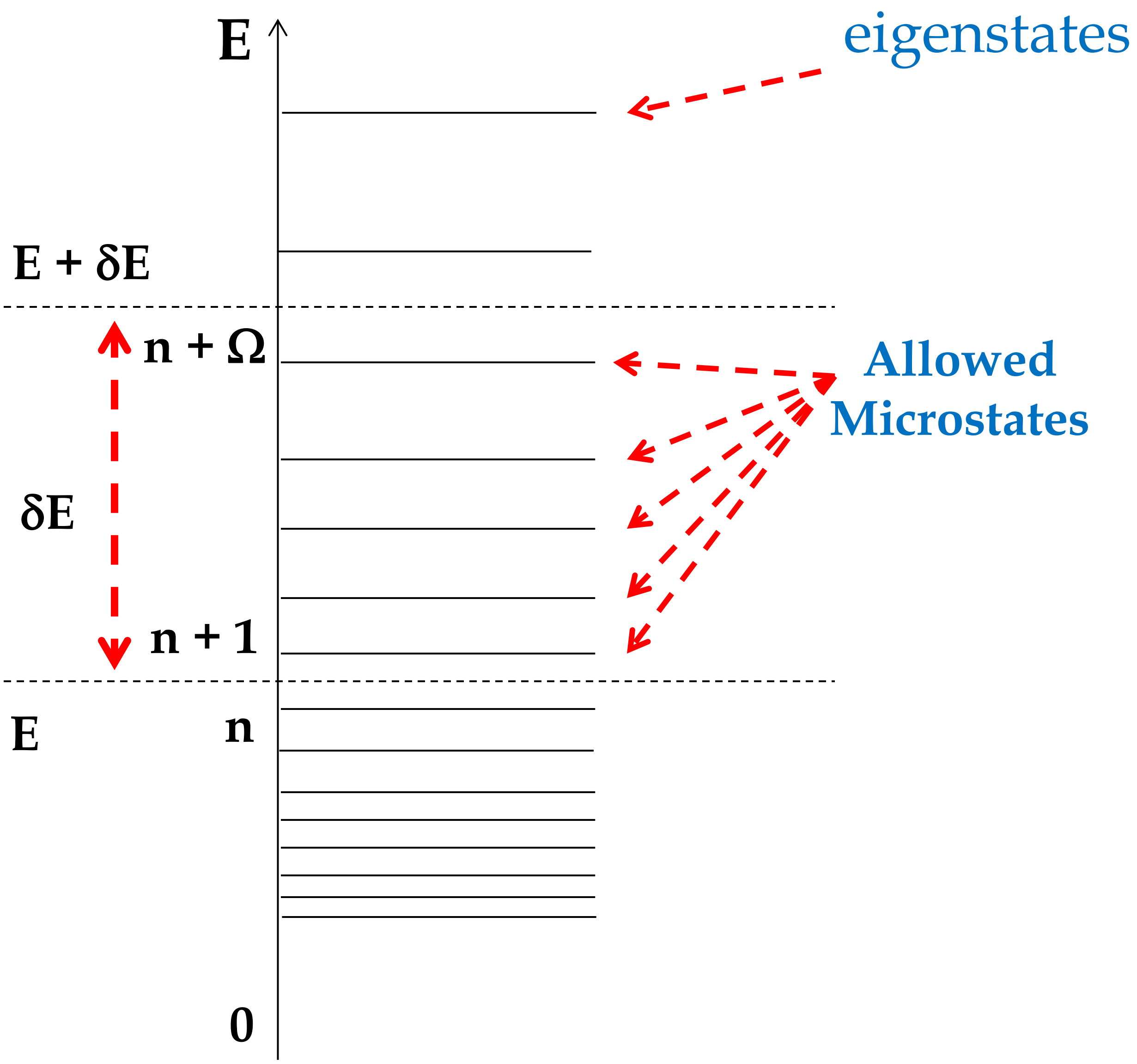


$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\Psi = 0 \qquad 0 \le x \le a$$

$$\frac{d^2\Psi}{dx^2} + \alpha^2\Psi = 0$$

$$\Rightarrow \Psi = A\sin\frac{n\pi}{a}x$$

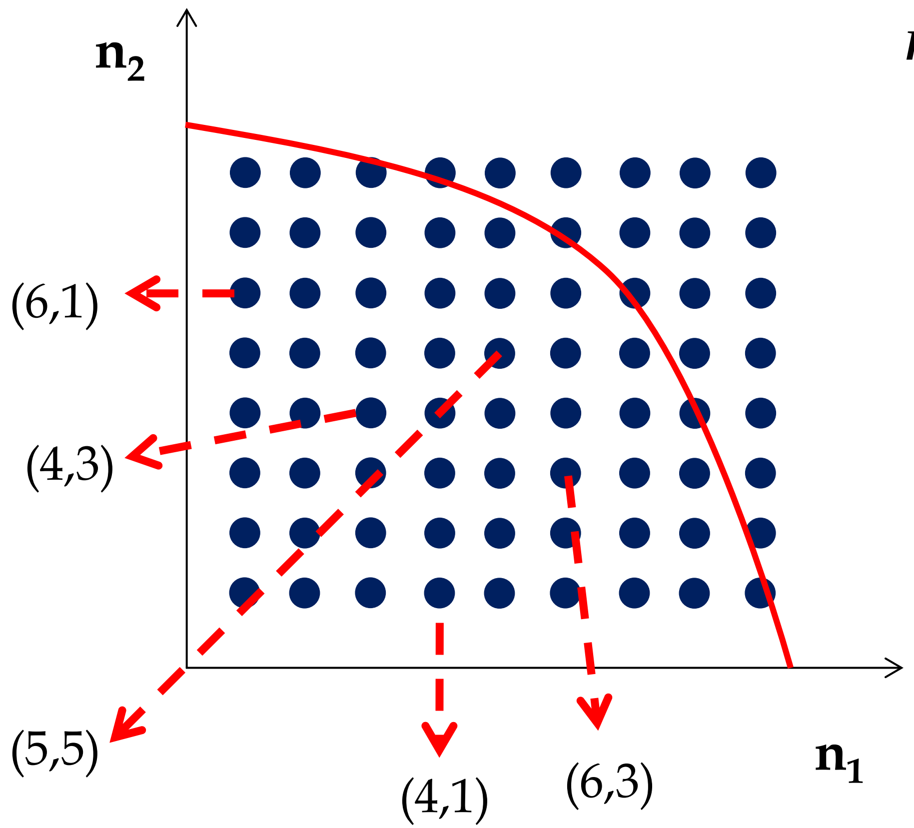
$$E_n = \frac{h^2}{8ma^2}n^2 \qquad n = 1,2,3,4$$


E
eigenstates
E + δE
n + Ω
Allowed
Microstates
δE
n + 1
E
n
0

One Particle in a 2^d Box

- The Schrodinger equation is $$\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{2m}{\hbar^2}E\Psi=0$$

$$E_{n_1,n_2}=\frac{h^2}{8mL^2}\left(n_1^2+n_2^2\right) \qquad n_1,n_2=1,2,3,.......$$



$$n_1^2+n_2^2=\left(\frac{2L}{h}\right)^2(2mE)$$

$$R^2=\left(\frac{2L}{h}\right)^2(2mE)$$

$$\Rightarrow R=\frac{2L}{h}(2mE)^{\frac{1}{2}}$$

No. of Energy States

$$\Gamma(E)=\frac{1}{4}\times\text{Total Area}$$

- Question: How to count the number of Microstates?

One Particle in a 3^{d} Box

❖ Schrodinger equation

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}+\frac{2m}{\hbar^2}E\Psi=0$$

$$\Rightarrow \Psi=\left(\frac{8}{V}\right)^{\frac{1}{2}}\sin\frac{n_1\pi x}{a}\sin\frac{n_2\pi y}{a}\sin\frac{n_3\pi z}{a}$$

$$E_{n_1,n_2,n_3}=\frac{h^2}{8ma^2}\left(n_1^2+n_2^2+n_3^2\right) \qquad n_1,n_2,n_3=1,2,3,\ldots\ldots$$

Example:

A Helium gas in a cubic box of volume 0.0024m^3 kept at 273 K is likely to be in a single particle quantum state having quantum numbers in the range 10^9 to 10^{10}

❖ Number of Microstates

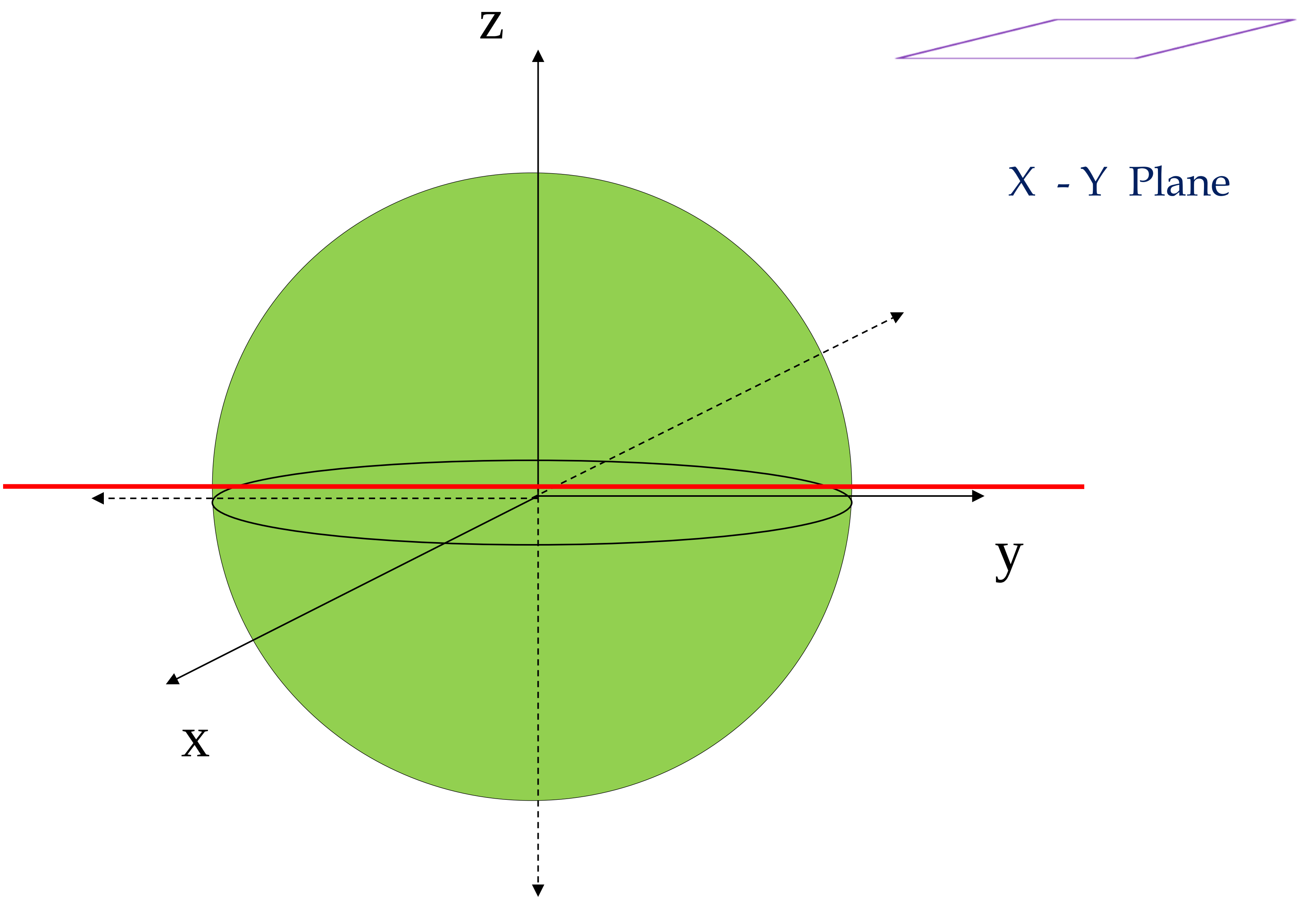
$$R^2 = n_1^2 + n_2^2 + n_3^2 = \frac{8ma^2}{h^2}E = \left(\frac{2a}{h}\right)^2 (2mE)$$

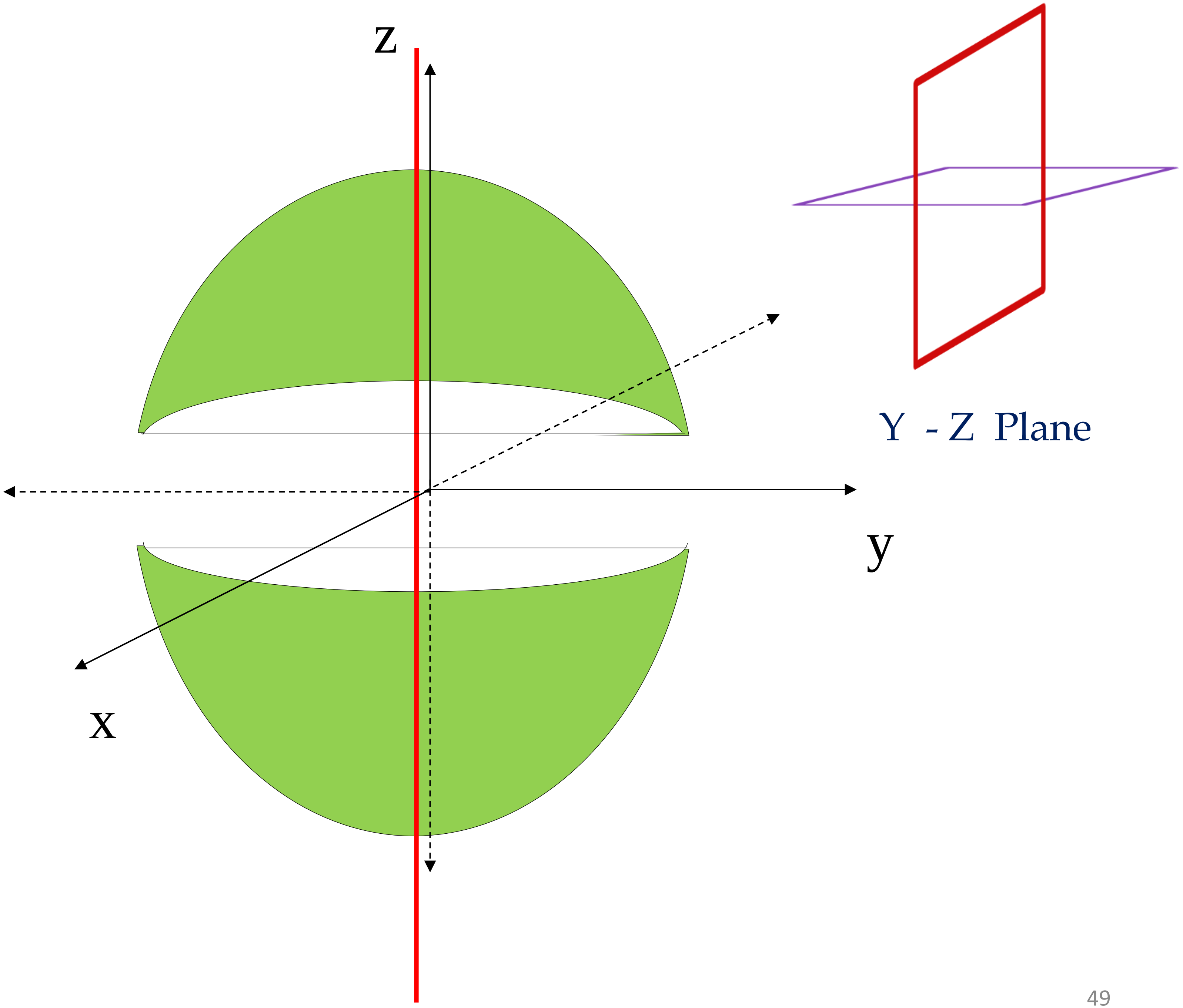
❖ Looks like $x^2 + y^2 + z^2 = r^2$ (equation of the sphere)

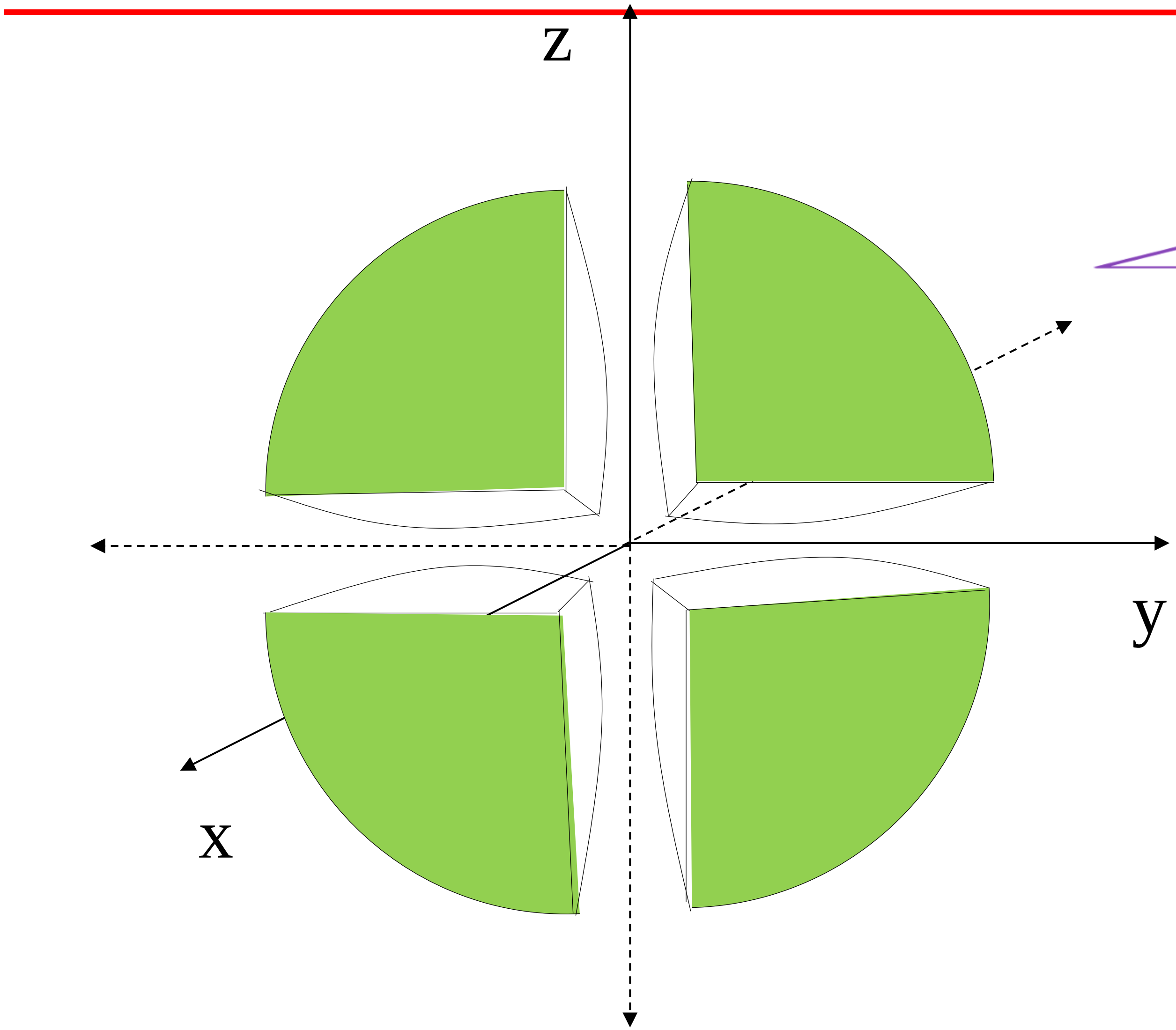
❖ Volume of the sphere $\frac{4}{3}\pi r^3$

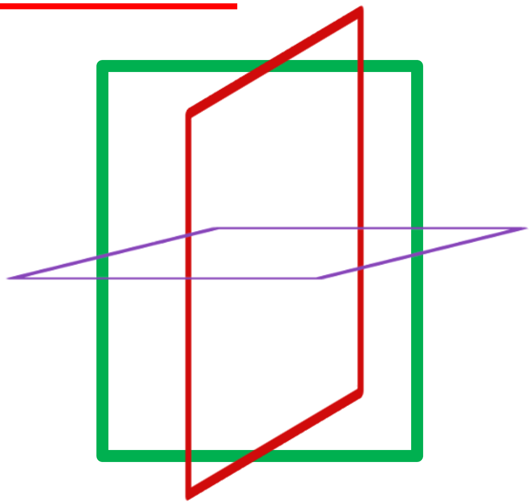
❖ In our case, we should not consider full volume since n_1,n_2 and n_3 are all positive integers.

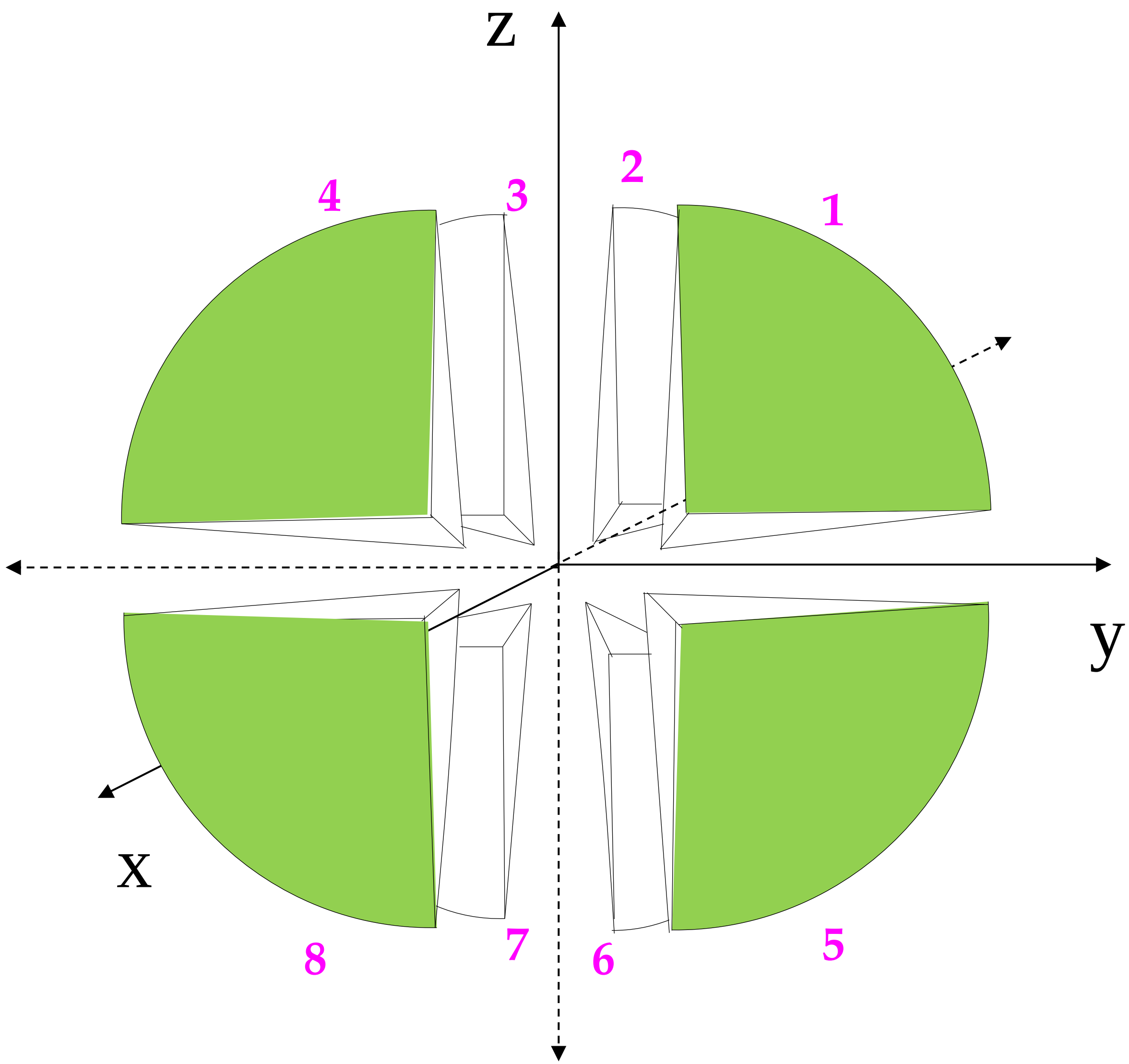
❖ So we have to consider the quadrant in which all are positive numbers.

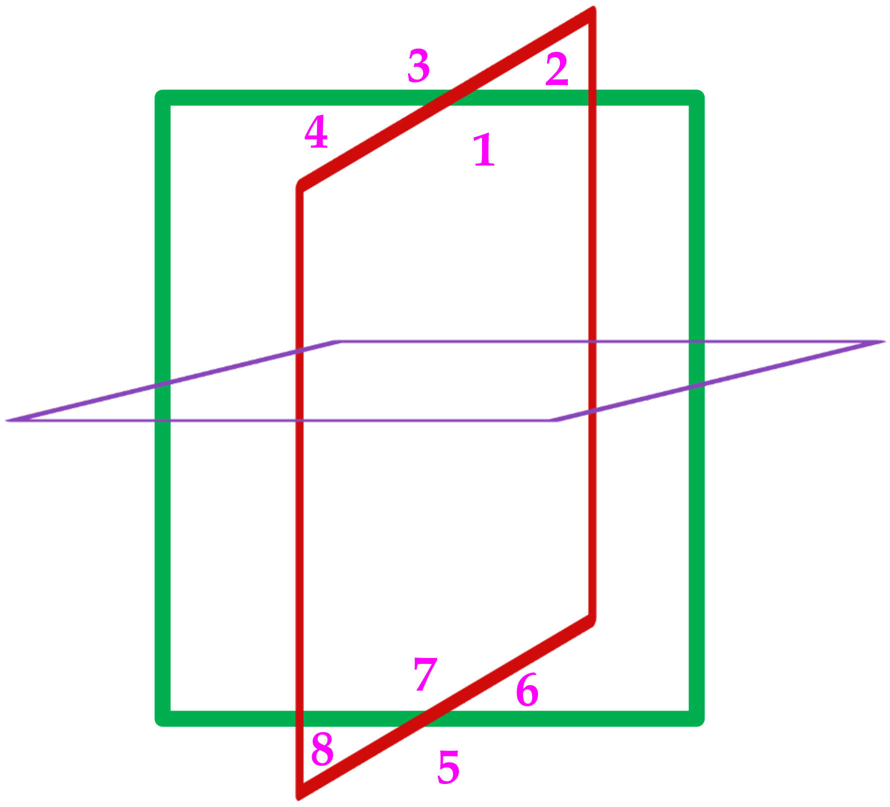

z
X - Y Plane
y
x

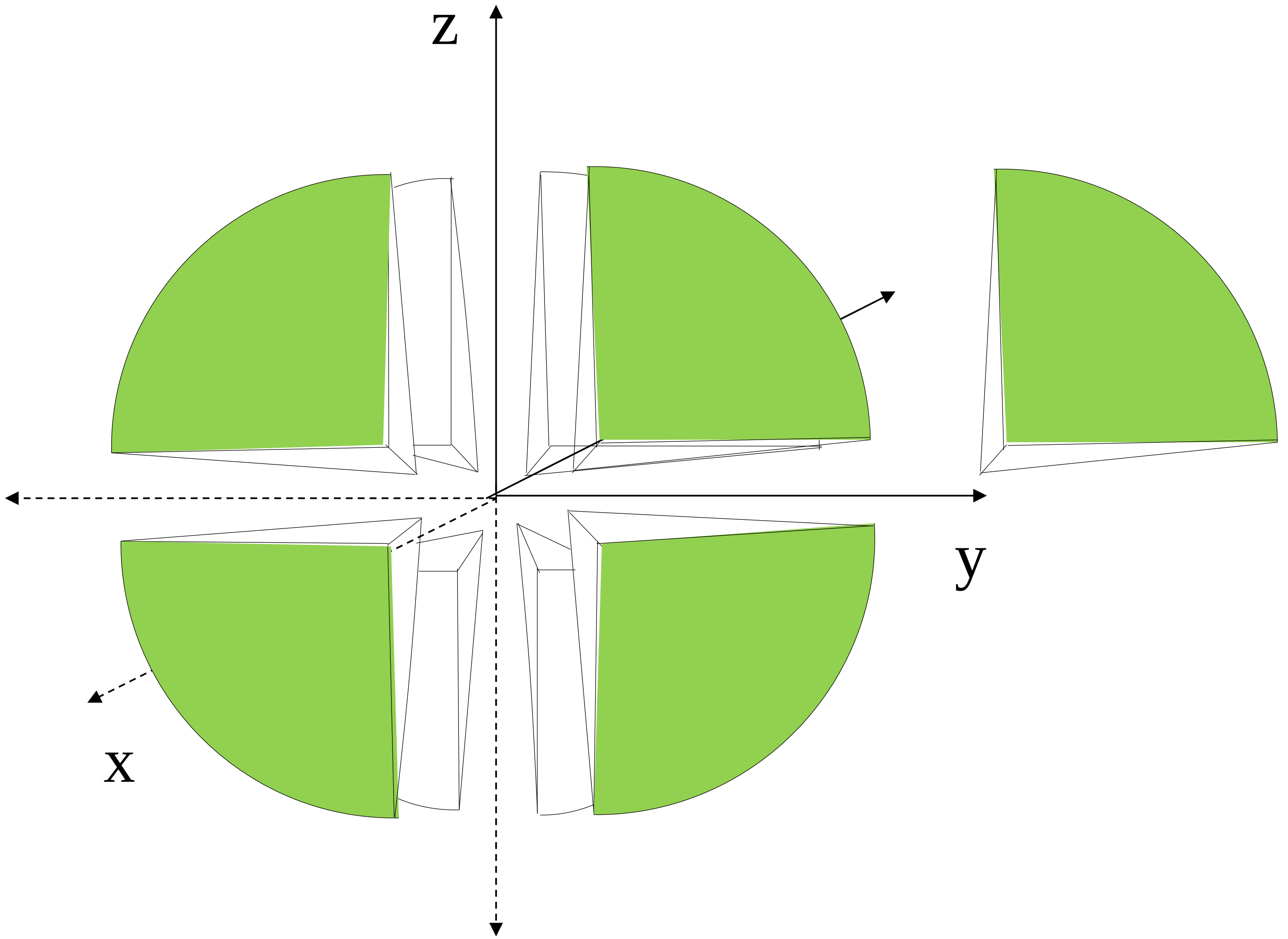

z
y
x
Y - Z Plane

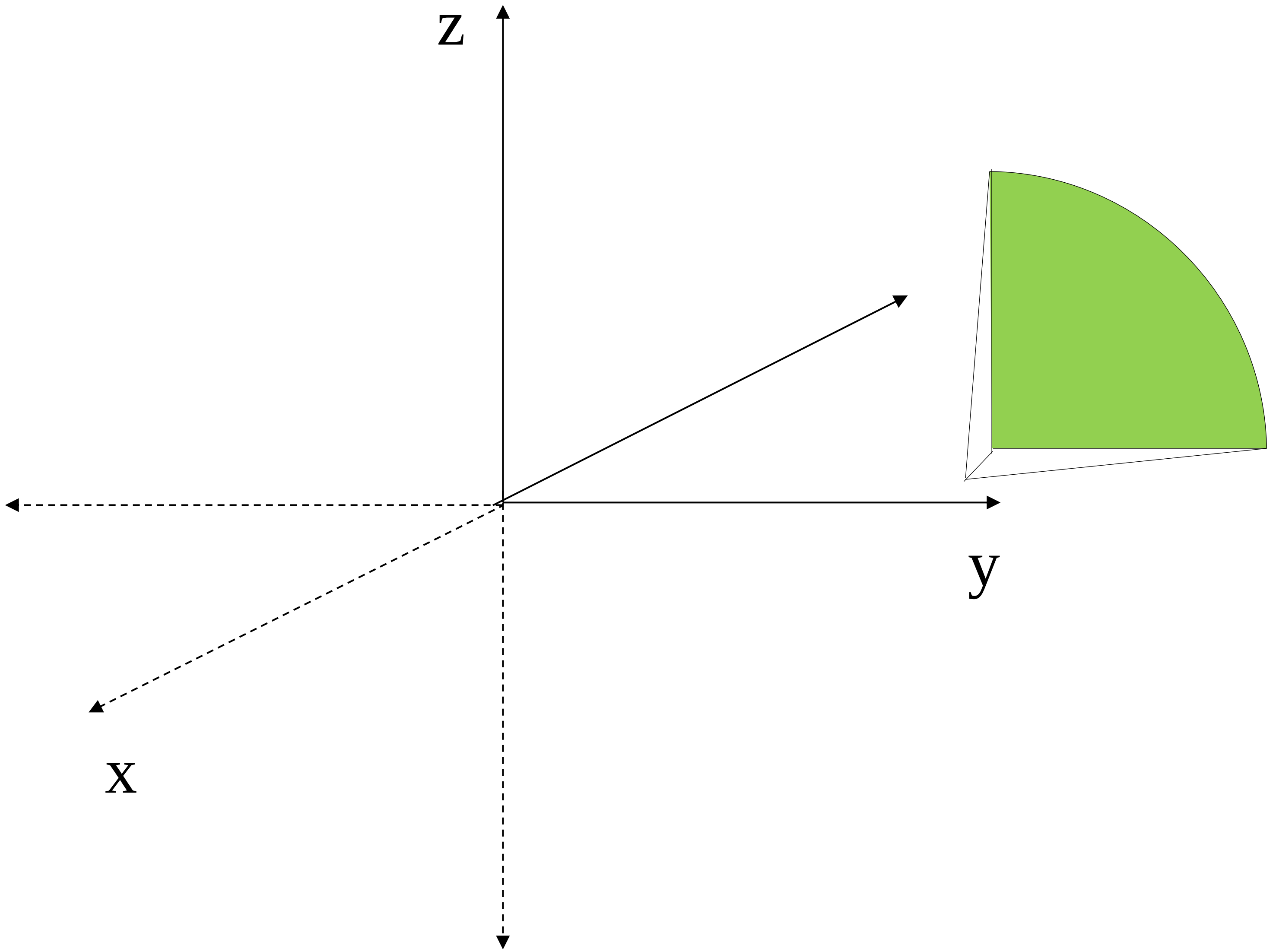

z
y
x

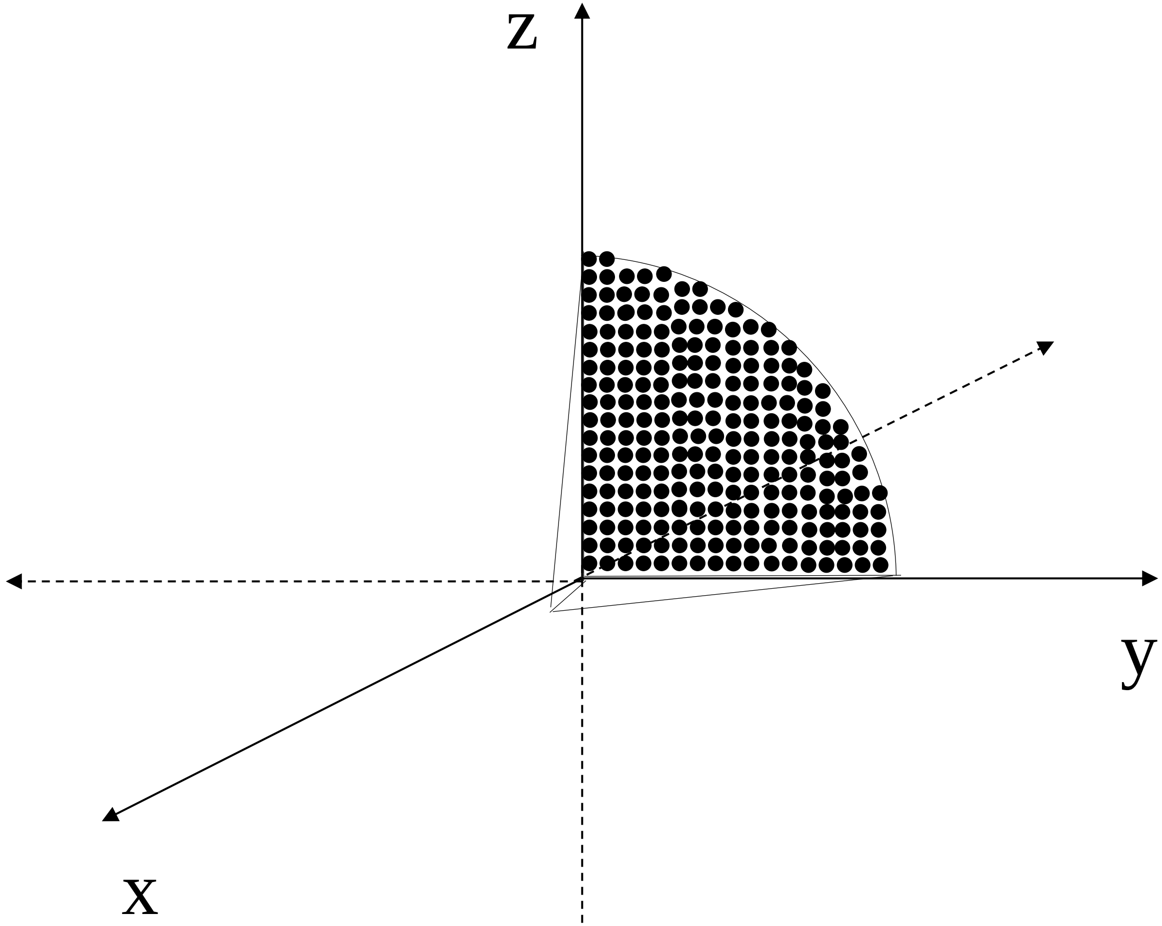

Z - X Plane


z
y
x
1
2
3
4
5
6
7
8


3
2
4
1
7
6
8
5


z
y
x

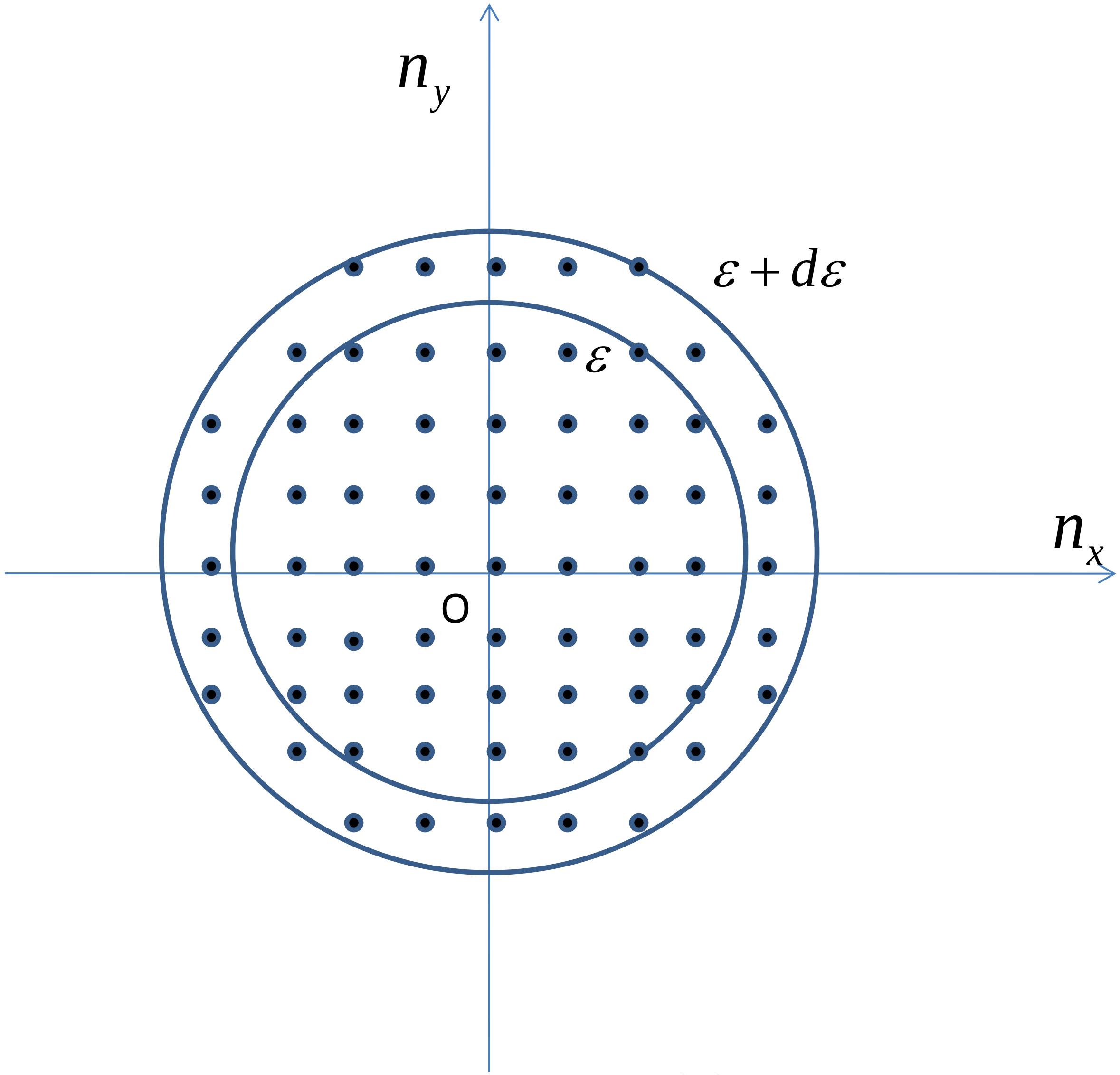

z
y
x



$$\Gamma(E) = \frac{1}{8} \times \frac{4}{3}\pi R^3 = \frac{\pi}{6}\left(\frac{2a}{h}\right)^3 (2mE)^{\frac{3}{2}}$$

$$= \frac{4\pi}{3}\left(\frac{v}{h^3}\right)(2mE)^{\frac{3}{2}}$$

The No of available states between the quantum No E and $E + dE$



$$\Omega(E)\,dE = 2\pi V \left(\frac{2M}{h^2}\right)^{3/2} E^{\frac{1}{2}} dE$$

Density of States

$$= \frac{1}{8} \times \frac{4}{3}\pi \times \left(\frac{8mL^2}{h^2}\right)^{3/2} E^{3/2}$$

$$= \frac{4}{3}\frac{\pi V}{L^3}(2m)^{3/2} E^{3/2}$$

$$= \frac{4}{3}\frac{\pi V}{L^3}(2m)^{3/2}\left[(E+\Delta E)^{3/2} - E^{3/2}\right]$$

$$= 2\pi V\left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE$$

Density of States
in Energy Space

$$= g(E)dE$$

In momentum space

$$g(E)dE = \frac{VK^2 dK}{2\pi^2}$$

Density of States
in Momentum Space

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).