Lecture
Introduction to Ensembles

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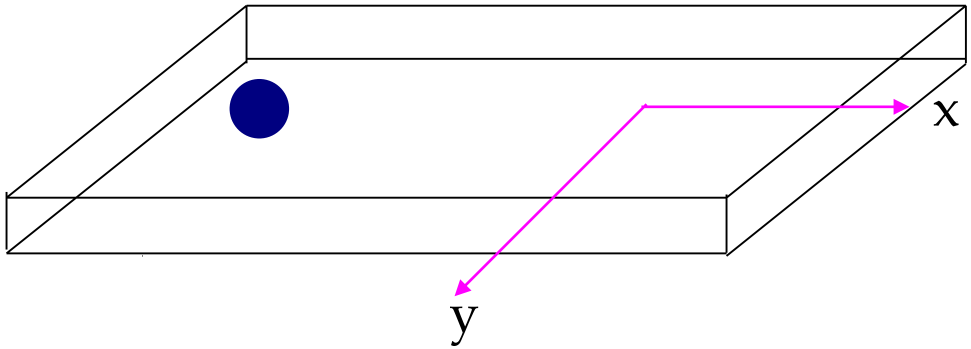
Classical Mechanics: Some Basic Facts

Newton's Second Law

One Particle – 1 Dimension



Equation of Motion

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

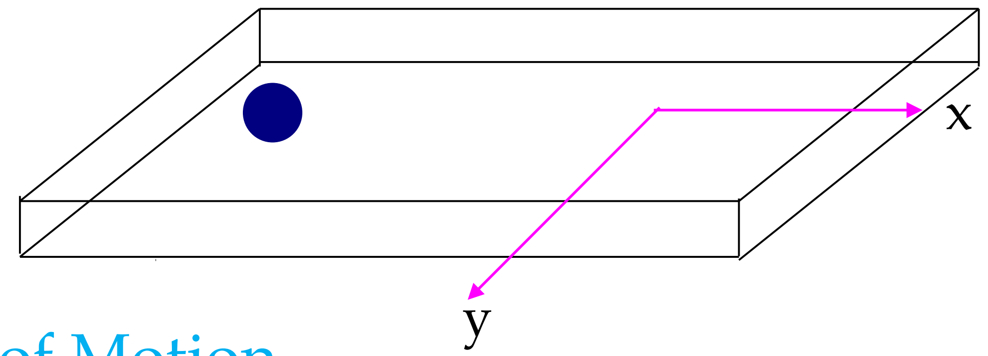
Solution

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

c_1, c_2 are constants

I.C Needed 2

One Particle – 2 Dimension



Equation of Motion

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

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

Solution

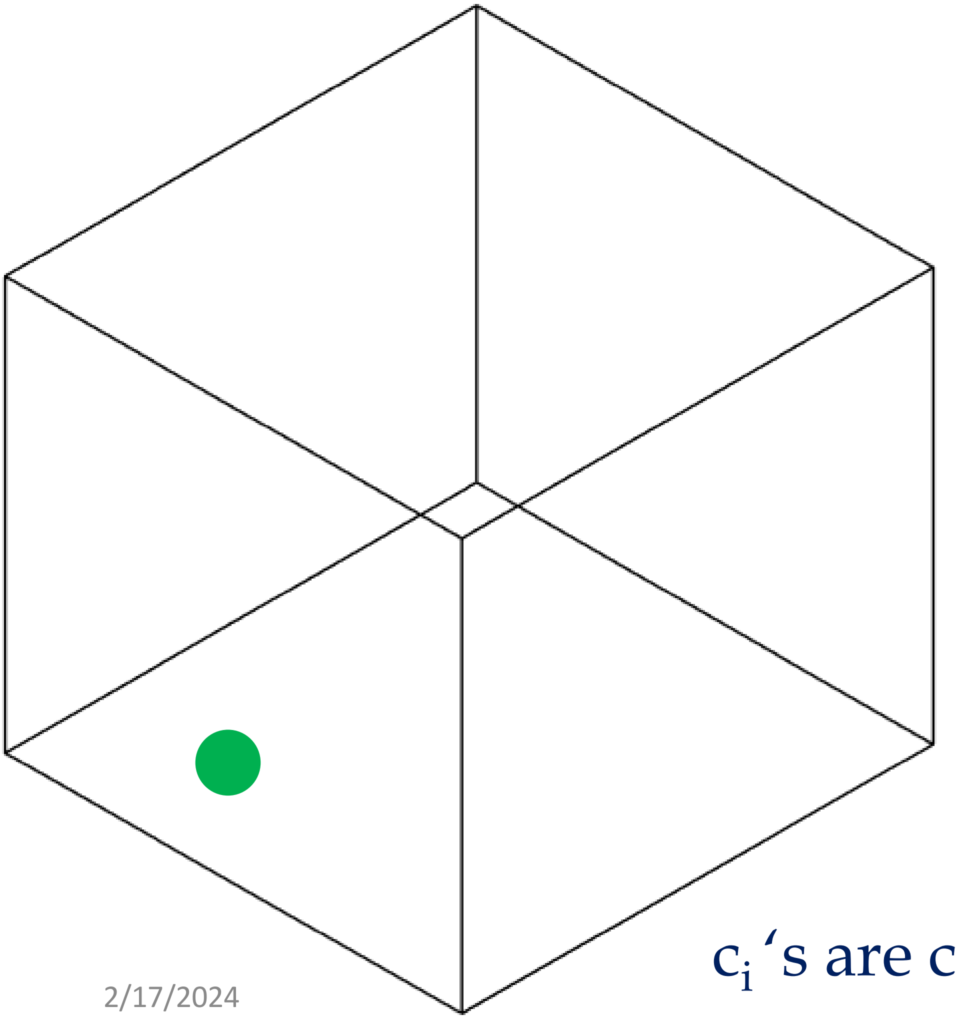
$$x(t) = f_1(t, c_1, c_2, c_3, c_4)$$

c_i's are constants (4)

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

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

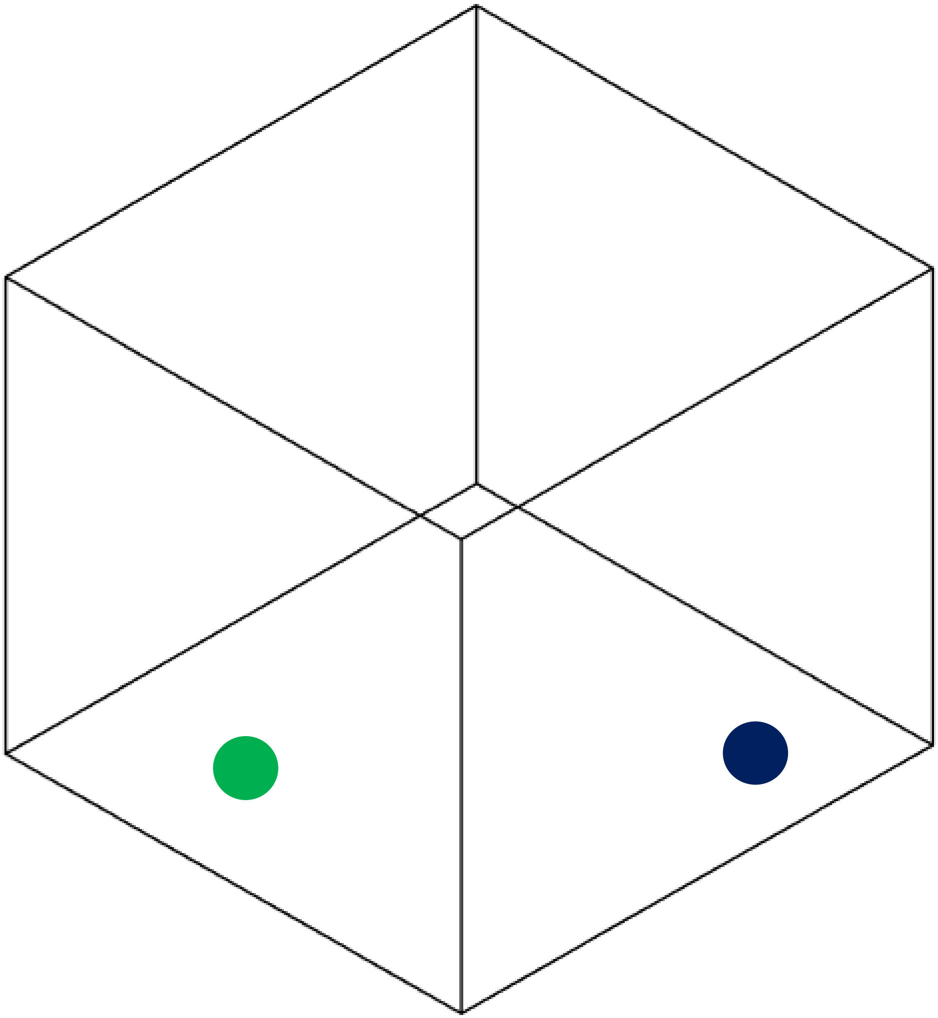
$$x(t) = f_1(t, c_1, c_2, c_3, c_4, c_5, c_6)$$

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

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

c_i ‘s are constants (6) I.C Needed 6

Two Particles – 3 Dimension



Equation of Motion

1st Particle

$$\left\{\begin{aligned}
\frac{d^2 x_1}{dt^2} &= F_1(t, x_1, y_1, z_1, x_2, y_2, z_2, \dot{x}_1, \dot{y}_1, \dot{z}_1, \dot{x}_2, \dot{y}_2, \dot{z}_2) \\
\frac{d^2 y_1}{dt^2} &= F_2(t, x_1, y_1, z_1, x_2, y_2, z_2, \dot{x}_1, \dot{y}_1, \dot{z}_1, \dot{x}_2, \dot{y}_2, \dot{z}_2) \\
\frac{d^2 z_1}{dt^2} &= F_3(t, x_1, y_1, z_1, x_2, y_2, z_2, \dot{x}_1, \dot{y}_1, \dot{z}_1, \dot{x}_2, \dot{y}_2, \dot{z}_2)
\end{aligned}\right.$$

$$\left\{\begin{aligned}
\frac{d^2 x_2}{dt^2} &= F_4(t, x_1, y_1, z_1, x_2, y_2, z_2, \dot{x}_1, \dot{y}_1, \dot{z}_1, \dot{x}_2, \dot{y}_2, \dot{z}_2) \\
\frac{d^2 y_2}{dt^2} &= F_5(t, x_1, y_1, z_1, x_2, y_2, z_2, \dot{x}_1, \dot{y}_1, \dot{z}_1, \dot{x}_2, \dot{y}_2, \dot{z}_2) \\
\frac{d^2 z_2}{dt^2} &= F_6(t, x_1, y_1, z_1, x_2, y_2, z_2, \dot{x}_1, \dot{y}_1, \dot{z}_1, \dot{x}_2, \dot{y}_2, \dot{z}_2)
\end{aligned}\right.$$

2nd Particle

Solution

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

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

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

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

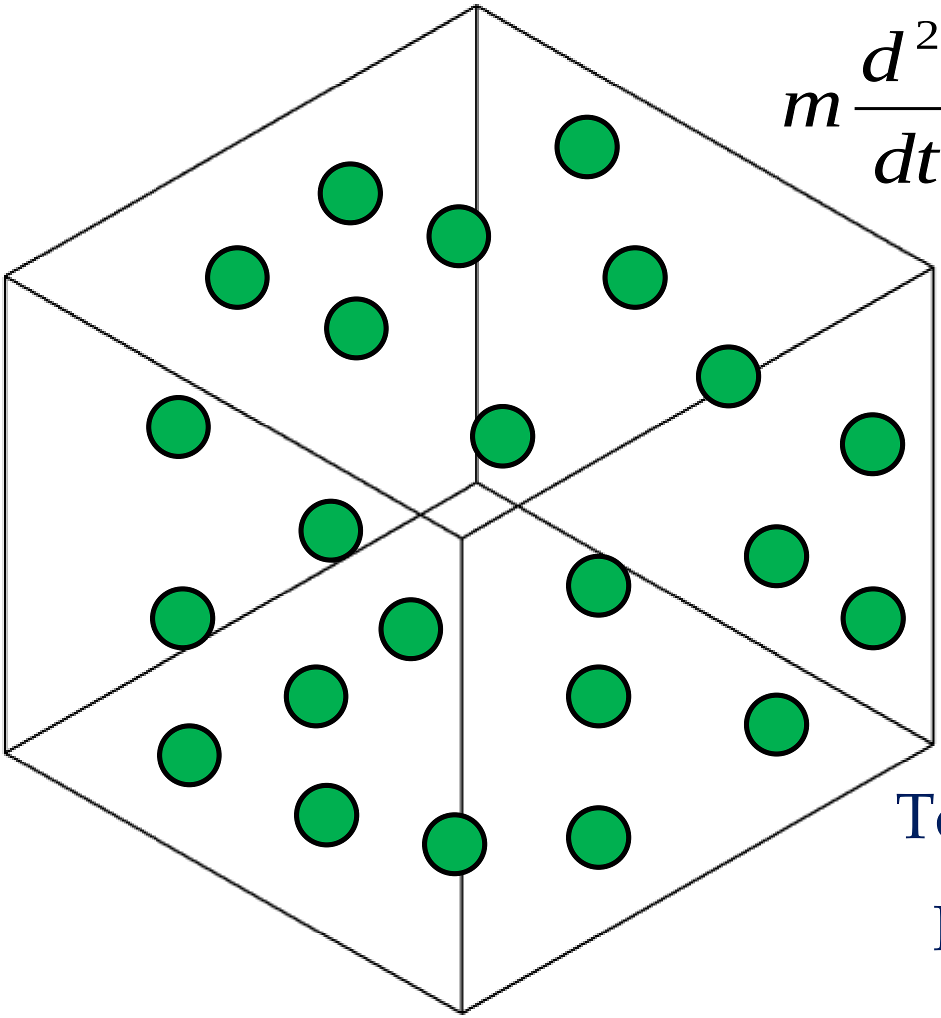
$$y_2 = f_5(t, c_1, c_2, c_3, c_4, c_5, c_6, c_7, c_8, c_9, c_{10}, c_{11}, c_{12})$$

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

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.

STATISTICAL MECHANICS

- By describing the individual microscopic states of a system and using statistical methods we derive the macroscopic properties from them.
- This approach received an additional impetus with the development of ***quantum theory*** which showed explicitly how to describe the microscopic quantum states.

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

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

- 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

$$\bar{x} = \frac{(1\times 5 + 2\times 6 + 4\times 7 + 2\times 8 + 1\times 9)}{10}$$

$$= \frac{1}{10}\times 5 + \frac{2}{10}\times 6 + \frac{4}{10}\times 7 + \frac{2}{10}\times 8 + \frac{1}{10}\times 9$$

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

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

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

P_i: Probability of getting the value of x_i

Microstates and Macrostates

Microstates	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
(3,1)	bcd acd abd abc	a b c d	4
(4,0)	abcd	0	1

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

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.

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

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

Macrostate Microstate

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

Entropy Boltzmann Constant Accessible Microstates

Thermodynamics

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

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

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

Canonical Ensemble: Counting the Number of Microstates

The Microstates are given in the table for all the possible values of E_A and E_B

E_A	E_B	Microstates of E_A	Microstates of E_B	$\Omega_A(E_A)$	$\Omega_A(E_B)$	$\Omega_A \Omega_B$	$P_A(E_A)$
6	0	(6,0) (5,1) (4,2) (3,3) (2,4) (1,5) (0,6)	(0,0)	7	1	7	7/84
5	1	(5,0) (4,1) (3,2) (2,3) (1,4) (0,5)	(1,0) (0,1)	6	2	12	12/84
4	2	(4,0) (3,1) (2,2) (1,3) (0,4)	(2,0) (1,1) (0,2)	5	3	15	15/84
3	3	(3,0) (0,3) (2,1) (1,2)	(3,0) (0,3) (2,1) (1,2)	4	4	16	16/84
2	4	(2,0) (1,1) (0,2)	(4,0) (3,1) (2,2) (1,3) (0,4)	3	5	15	15/84
1	5	(1,0) (0,1)	(5,0) (4,1) (3,2) (2,3) (1,4) (0,5)	2	6	12	12/84
0	6	(0,0)	(6,0) (5,1) (4,2) (3,3) (2,4) (1,5) (0,6)	1	7	7	7/84

$\boxed{\Omega_{tot} = 84}$

The Microstates are given in the table for all the possible values of E_A and E_B

E_A	E_B	Microstates of E_A	Microstates of E_B	$\Omega_A(E_A)$	$\Omega_A(E_B)$	$\Omega_A\,\Omega_B$	**$P_B(E_B)$**
6	0	(6,0) (5,1) (4,2) (3,3) (2,4) (1,5) (0,6)	(0,0)	7	1	7	7/84
5	1	(5,0) (4,1) (3,2) (2,3) (1,4) (0,5)	(1,0) (0,1)	6	2	12	12/84
4	2	(4,0) (3,1) (2,2) (1,3) (0,4)	(2,0) (1,1) (0,2)	5	3	15	15/84
3	3	(3,0) (0,3) (2,1) (1,2)	(3,0) (0,3) (2,1) (1,2)	4	4	16	16/84
2	4	(2,0) (1,1) (0,2)	(4,0) (3,1) (2,2) (1,3) (0,4)	3	5	15	15/84
1	5	(1,0) (0,1)	(5,0) (4,1) (3,2) (2,3) (1,4) (0,5)	2	6	12	12/84
0	6	(0,0)	(6,0) (5,1) (4,2) (3,3) (2,4) (1,5) (0,6)	1	7	7	7/84

- The Total Number of Microstates $\Omega_{tot}(E_A + E_B)$ accessible to the isolated composite system whose subsystems have energy E_A and E_B is

  - $\Omega_{tot}(E_A + E_B) = \Omega_A(E_A)\,\Omega_B(E_B)$

- For example if $E_A = 4$ and $E_B = 2$, then 'A' can be any one of the 5 microstates and 'B' can be in an one of 3 microstates. There are two sets of microstates that can be combined to give 15 microstates.

- The Total Number of Microstates Ω_{tot} accessible to the composite system can be found by summing $\Omega_A(E_A)\,\Omega_B(E_B)$ for the possible ways of E_A and E_B consistent with the condition $E_A + E_B = 6$.

$$\Omega = \sum_{E_A} \Omega_A(E_A)\,\Omega_B(E_B)$$

$$= \Sigma\Omega_A(E_A)\,\Omega_B(E_{tot} - E_A)$$

From Table,

- Ω_{tot} = (7 x 1)+(6 x 2)+(5 x 3)+(4 x 4)+(3 x 5)+(2 x 6)+(1 x 7)

  = 84

The ***Composite System*** is isolated. So all accessible ***Microstates*** are equally probable.

That is the composite is equally likely to be in any of its 84 accessible ***Microstates***.

- Let $\mathbf{P_A(E_A)}$ = Probability that subsystem **'A'** has energy $\mathbf{E_A}$.

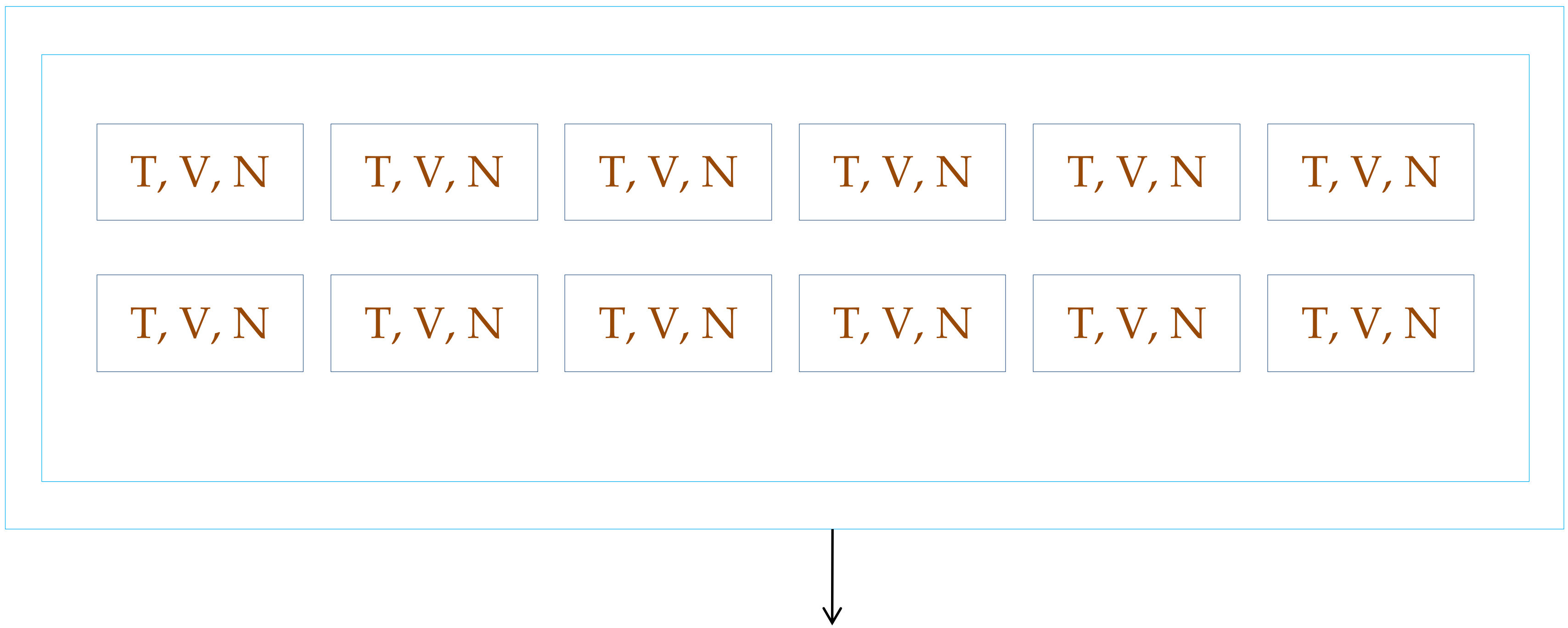
$$P_A(E_A) = \frac{\Sigma\Omega_A(E_A)\,\Omega_B(E_{tot} - E_B)}{\Omega_{tot}}$$

- The mean energy of subsystem **'A'** is found by calculating the ***Ensemble*** average over the 84 ***Microstates*** of the ***Composite System***.

$$\begin{aligned}
< E_A > = \bar{E}_A &= \sum E_{A,i} P(E_{A,i}) \\
&= \left(6 \text{ x } \frac{7}{84}\right) + \left(5 \text{ x } \frac{12}{84}\right) + \left(4 \text{ x } \frac{15}{84}\right) + \left(3 \text{ x } \frac{16}{84}\right) + \left(2 \text{ x } \frac{15}{84}\right) \\
&\quad + \left(1 \text{ x } \frac{12}{84}\right) + \left(0 \text{ x } \frac{7}{84}\right) \\
&= 3
\end{aligned}$$

Hence, it is reasonable to assume that when a closed isolated system had time to reach internal ***Thermodynamic Equilibrium***, we are likely to find the closed system in any one of the microstates.

At ***Thermal Equilibrium***, the probability of finding the ***Composite System*** in any one of the **84** accessible ***Microstates*** of the ***Composite System*** is **1/84**.



Canonical Ensemble

In this example, the Ensemble consists of *84* systems each of which is in one of the *84* accessible Microstates.

Probability of finding the particle in a particular microstate

$$p_i = \frac{e^{-\beta\varepsilon_i}}{\Sigma e^{-\beta\varepsilon_i}} = \frac{e^{-\beta\varepsilon_i}}{z}$$

$$z = \Sigma e^{-\beta\varepsilon_i} \longrightarrow \text{Partition function}$$

- The partition function 'Z' contains all the information about the energies of the states of the system.
- All thermodynamical quantities can be obtained from it.
- From 'Z', we can get thermodynamics functions energy, entropy, Helmholtz function, or heat capacity to simply drop out.

Thermodynamic quantities derived from the partition function Z

Function of states	Statistical mechanical expression
U	$-\dfrac{d \ln Z}{d\beta}$
F	$-k_B T \log Z$
$S = -\left(\dfrac{\partial F}{\partial T}\right)_v = \dfrac{U - F}{T}$	$k_B \ln Z + k_B T\left(\dfrac{\partial \ln Z}{\partial T}\right)_V$
$p = -\left(\dfrac{\partial F}{\partial V}\right)_T$	$k_B T\left(\dfrac{\partial \ln Z}{\partial V}\right)_T$
$H = U + pV$	$k_B T\left[T\left(\dfrac{\partial \ln Z}{\partial V}\right)_V + V\left(\dfrac{\partial \ln Z}{\partial V}\right)_T\right]$
$G = F + pV = H - TS$	$k_B T\left[-\ln Z + V\left(\dfrac{\partial \ln Z}{\partial V}\right)_T\right]$
$C_V = \left(\dfrac{\partial U}{\partial V}\right)_V$	$k_B T\left[2\left(\dfrac{\partial \ln Z}{\partial T}\right)_V + T\left(\dfrac{\partial^2 \ln Z}{\partial T^2}\right)_V\right]$

Grand-Canonical Ensemble: Counting the Number of Microstates

N_A	N_B	(E_A, E_B)	(Ω_A, Ω_B)	$\Omega_A \Omega_B$	$P_{E_A} \times N_A$	$P_{E_A} \times E_A$
0	4	(0,6)	(1, 84)	84	$\left(\frac{84}{420}\right) \times 0$	(84/420) x 0
		(0,6)	(0, 28)	28		(28/420) x 0
		(1,5)	(1, 21)	21		(21/420) x 1
		(2, 4)	(1, 15)	15		(15/420) x 2
1	3	(3, 3)	(1, 10)	10	$\left(\frac{84}{420}\right) \times 1$	(10/420) x 3
		(4, 2)	(1, 6)	6		(6/420) x 4
		(5, 1)	(1, 3)	3		(3/420) x 5
		(6, 0)	(1, 1)	1		(3/420) x 6
		(6, 0)	(7, 1)	7		(7/420) x 6
		(5, 1)	(6, 2)	12		(12/420) x 5
		(4, 2)	(5, 3)	15		(15/420) x 4
2	2	(3, 3)	(4, 4)	16	$\left(\frac{84}{420}\right) \times 2$	(16/420) x 3
		(2, 4)	(3, 5)	15		(15/420) x 2
		(1, 5)	(2, 6)	12		(12/420) x 1
		(0, 6)	(1, 7)	7		(7/420) x 0

N_A	N_B	(E_A, E_B)	(Ω_A, Ω_B)	$\Omega_A\Omega_B$	$P_{E_A} \times N_A$	$P_{E_A} \times E_A$
		(0, 6)	(1, 1)	1		(1/420) x 0
		(1, 5)	(3, 1)	3		(3/420) x1
		(2, 4)	(6, 1)	6		(6/420) x 2
3	1	(3, 3)	(0, 1)	10	$\left(\frac{84}{420}\right) \times 3$	(10/420) x 3
		(4, 2)	(15, 1)	15		(15/420) x 4
		(5, 1)	(21, 1)	21		(21/420) x 5
		(6, 0)	(28, 1)	28		(28/420) x 6
4	0	(6, 0)	(1, 84)	84	$\left(\frac{84}{420}\right) \times 4$	(7/420) x 6
				The picture can't be displayed.	$\overline{N}_A = 2$	$\overline{E}_A = 3$

T,V μ	T,V μ	T,V μ	T,V μ	T,V μ	T,V μ
T,V μ	T,V μ	T,V μ	T,V μ	T,V μ	T,V μ
T,V μ	T,V μ	T,V μ	T,V μ	T,V μ	T,V μ
T,V μ	T,V μ	T,V μ	T,V μ	T,V μ	T,V μ
T,V μ	T,V μ	T,V μ	T,V μ	T,V μ	T,V μ
T,V μ	T,V μ	T,V μ	T,V μ	T,V μ	T,V μ
T,V μ	T,V μ	T,V μ	T,V μ	T,V μ	T,V μ

Grand Canonical Ensemble

Microstate
($E_A + E_B = E_T$ $N_A + N_B = N_T$)

In this example, the ***Ensemble*** consists of ***420*** systems each of which is in one of the ***420*** accessible ***Microstates***.

Probability of finding the particle in a particular microstate

$$p_i = \frac{e^{-\beta(E_A - \mu N_A)}}{\sum e^{-\beta E_i - \mu \beta N_i}}$$

$$\Xi = \sum_i e^{-\beta E_i - \mu \beta N_i} \longrightarrow \text{Grand Partition function}$$

- ❖ The grand partition function 'Ξ' contains all the information about the energies of the states of the system.
- ❖ All thermodynamical quantities can be obtained from it.
- ❖ From 'Ξ', we can get thermodynamics functions energy, entropy, Helmholtz function, or heat capacity.

Gateway to Thermodynamics

$$\Phi_G = -k_B T \ln \mathrm{Z}$$

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

$$p = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu}$$

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

END