THERMAL & STATISTICAL PHYSICS
SSP3133

INTERNAL ENERGY STATES OF A SYSTEM

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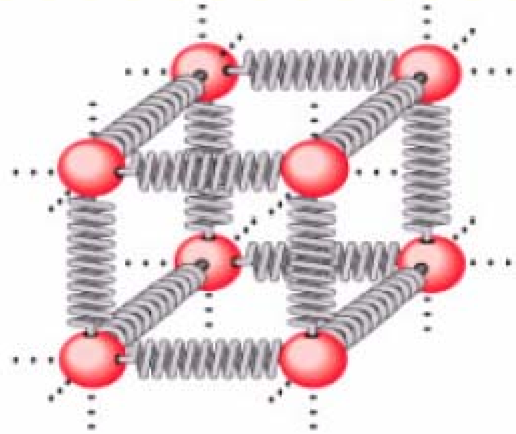
Acknowledgement : PROFESSOR DR RAMLI ABU HASSAN

Consider the atom of a solid



Energy of each atom = PE + KE

Vibration in 3-D

Potential energy: $E_P = \frac{1}{2} kx^2 + \frac{1}{2} ky^2 + \frac{1}{2} kz^2$

Kinetic energy: $E_K = \frac{1}{2} mv_x^2 + \frac{1}{2} mv_y^2 + 1/2\ mv_z^2$

$= \frac{1}{2} (mv_x)^2 /m + \frac{1}{2} (mv_y)^2/m + 1/2\ (mv_z)^2/m$

$$= \frac{1}{2m} P_X^2 + \frac{1}{2m} P_Y^2 + \frac{1}{2m} P_Z^2$$

P: momentum

PE & KE in the form $E = b\,q^2$ for energy of the form $E = bq^2$

b: constant

The energy stored in the motions and interactions of the elements (e.g: atoms, molecules, electrons, etc) of a system.

Degree of freedom – ways each elements can store energy.

Each particle has 6 degrees of freedom

Therefore if there is N particles – 6N degrees of freedom

EQUIPARTITION THEOREM

- The Internal energy will be distributed equally among all those degrees of freedom with energy in the form **E = bq^2**
- e.g: Ideal Gas PV = mRT
- In terms of Boltzmann's Constant PV =NkT
- From molecular theory

$$PV = \frac{1}{3} Nm \langle v^2 \rangle$$

$$\text{KE: } \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m \langle v_x^2 \rangle + \frac{1}{2} m \langle v_y^2 \rangle + \frac{1}{2} m \langle v_z^2 \rangle \qquad \langle v^2 \rangle\text{: Average velocity}$$

$$\text{Equip. theorem: } \langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

By assumptions, there are no preferred directions

Equip. theorem: $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$

$$\frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}m\langle v_x^2 \rangle + \frac{1}{2}m\langle v_x^2 \rangle + \frac{1}{2}m\langle v_x^2 \rangle$$

$$\frac{1}{2}m\langle v^2 \rangle = 3(\frac{1}{2}m\langle v_x^2 \rangle)$$

$$\boxed{\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}kT}$$

The average energy per degree of freedom $\langle E \rangle = \frac{1}{2}kT$

k = 1.381 x 10^{-23} JK^{-1} (Boltzmann's constant)

KE is related to temperature; higher KE, Higher Temperature

Note: when heat is added, but temperature remains constant
→new degrees of freedom, where the added energy is stored

Changing the internal energy - 3 ways / interactions

i. thermal interaction

-adding / removing heat from the system

ii. mechanical interactions

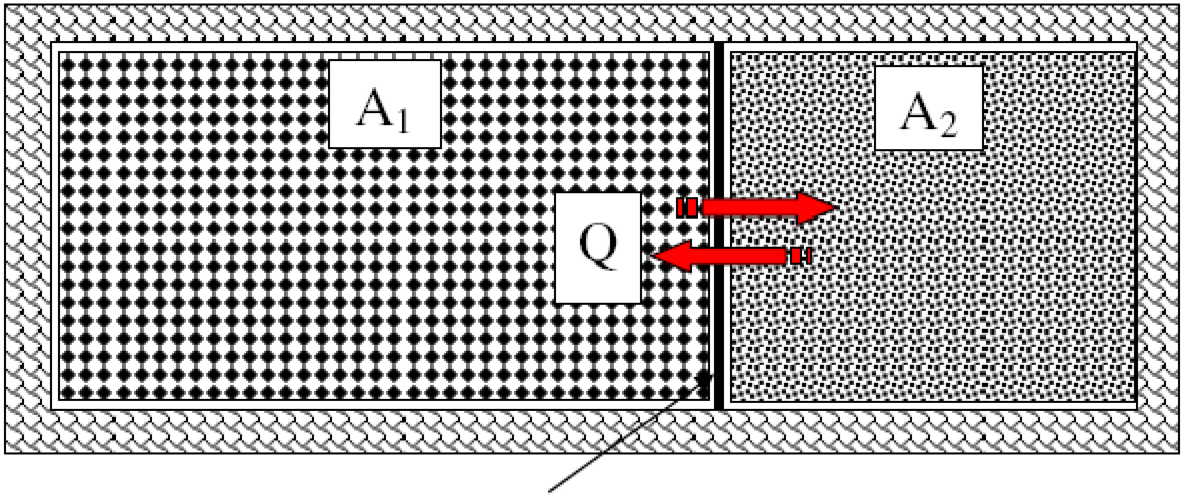
-doing work on the system or letting system doing work on something else

iii. diffusive interaction

-adding or removing particles that undergo reactions with the particles of the system

Heat Transfer

-heat transfer between A_1 and A_2 only

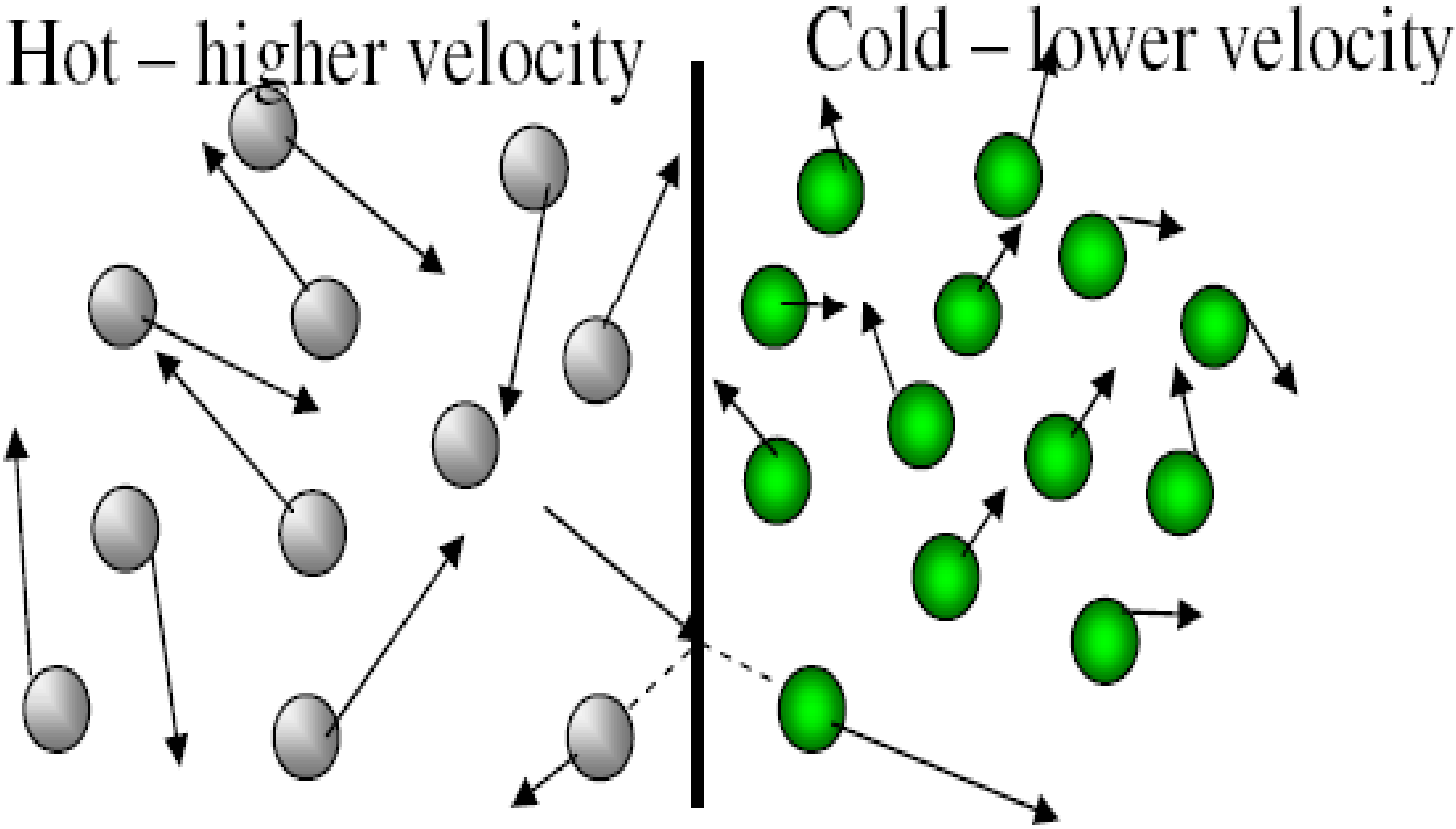


Rigid, thermally conducting membrane

heat in: increase particles velocity → increase temperature

heat out: lower the velocity → lower the temperature

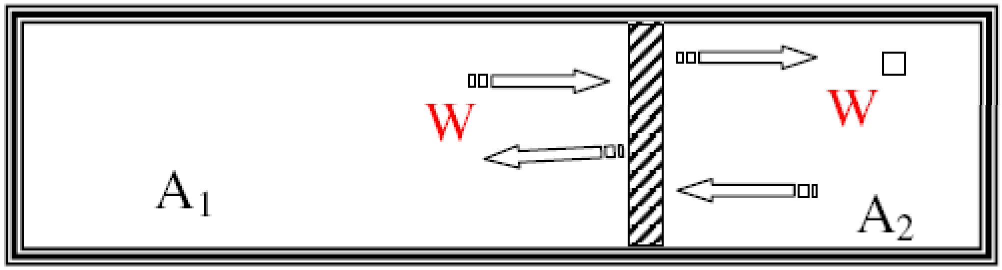
→ changing the internal energy



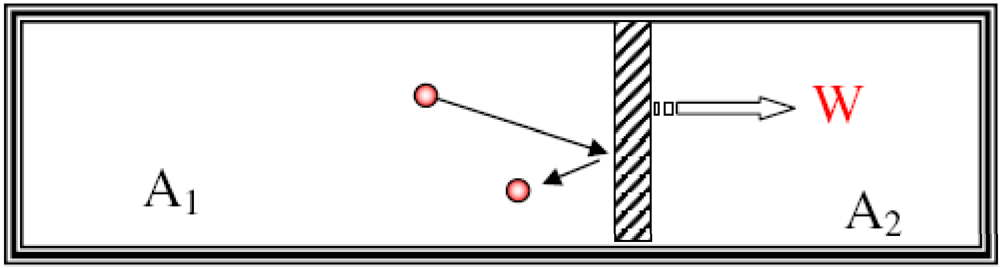
Hot – higher velocity

Cold – lower velocity

Work (mechanical interactions)

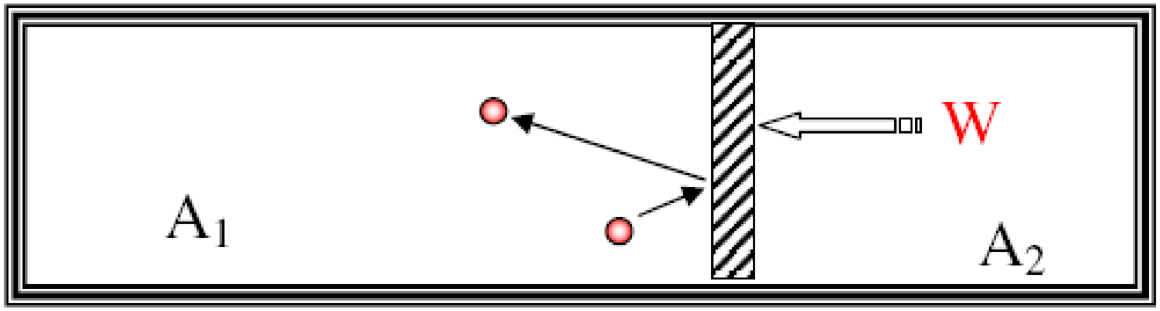


Expansion – molecules strike a receding piston, loosing KE
-system does work – loosing energy



Compression – molecules strike on incoming piston – gain KE
-work done on the system – increases energy

Particle transfer



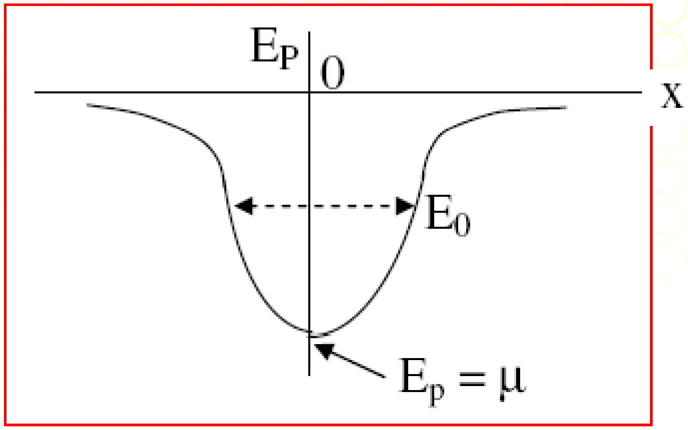
PE: interactions of an element with its neighbours

-measured relative to a reference

-- known as zero-energy reference level

zero energy ref. level – the PE of an isolated particle

Consider: a particle trapped in a harmonic oscillator potential well



$E_P = \mu + ½\, kr^2$
Total energy
$E = E_P + E_K$
$= \mu + ½\, kr^2 + ½\, mv^2$
$= \mu + E_{TH}$

E_{TH}: thermal energy

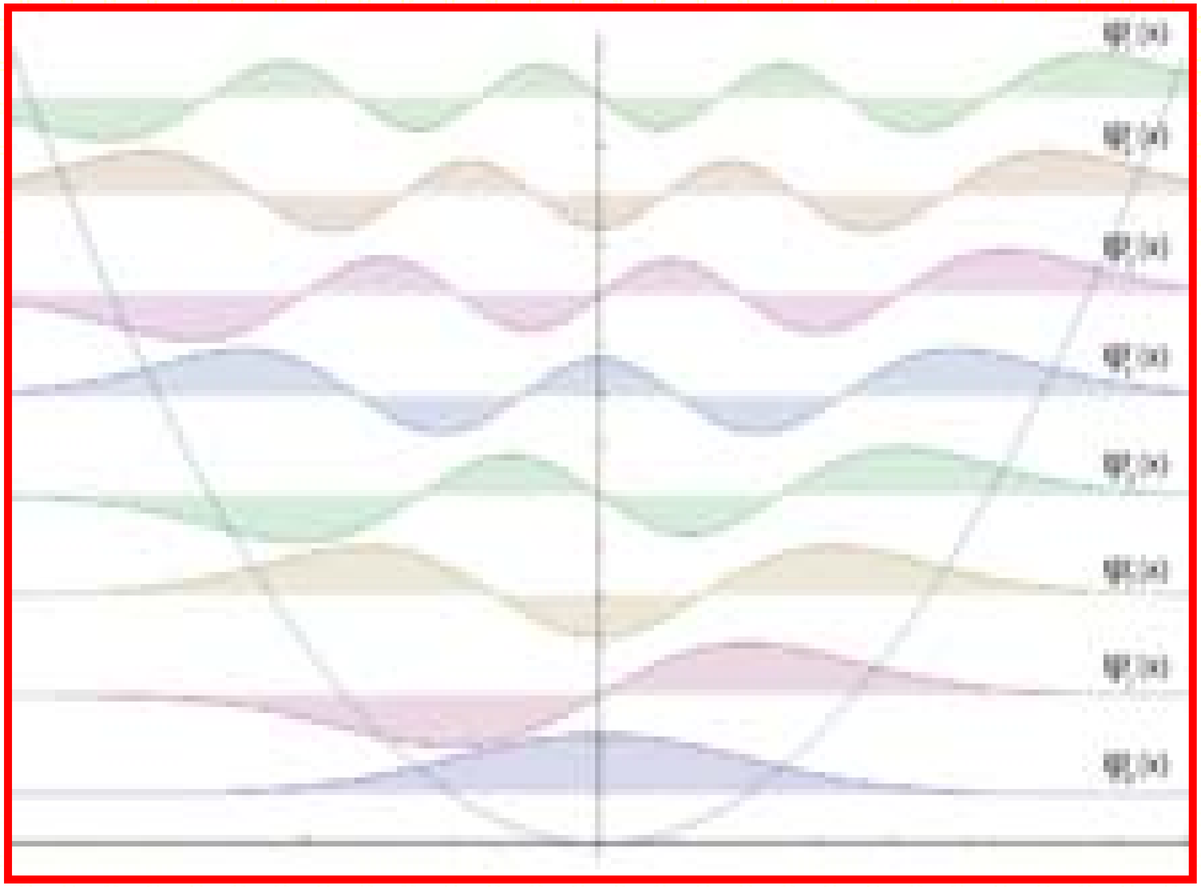
A particle with energy E_0 ossilates in a potential well -

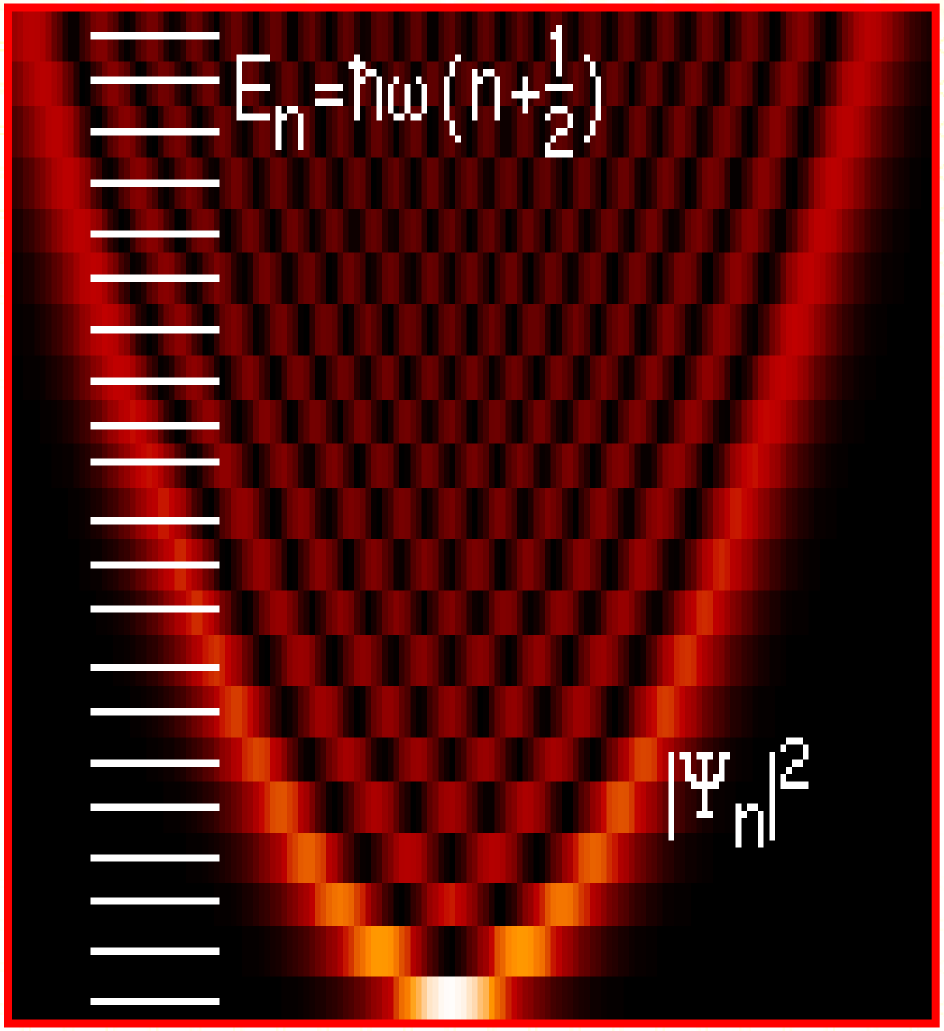
$E_{TH} = E_0 - \mu$

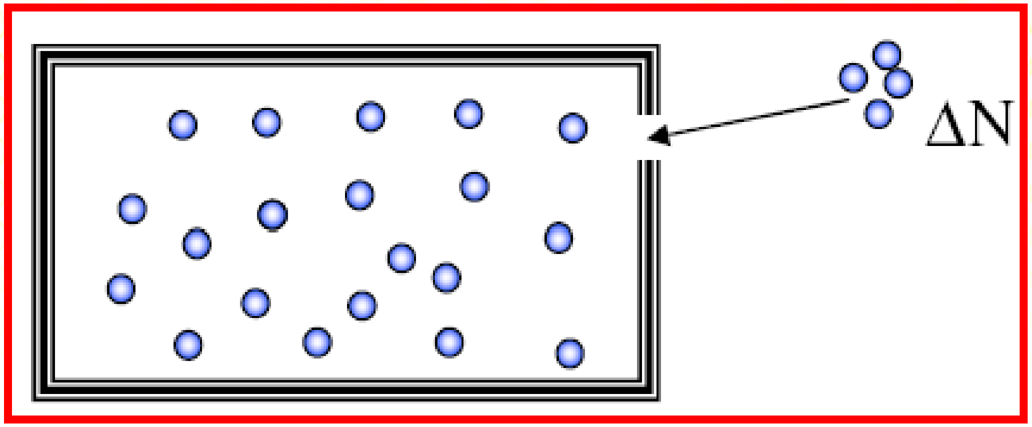
For N particles:

$E_{TH} = E_0 - \mu N$

Chemical potential, μ: the energy of the very lowest point in the particle's potential well.


$\psi_7(x)$
$\psi_6(x)$
$\psi_5(x)$
$\psi_4(x)$
$\psi_3(x)$
$\psi_2(x)$
$\psi_1(x)$
$\psi_0(x)$


$E_n = \hbar\omega(n+\frac{1}{2})$
$|\Psi_n|^2$



Adding ΔN particles without adding thermal energy (constant T and S), the internal energy of the system

$$\Delta E = (\mu \Delta N)_{T,S} \qquad or \qquad \mu = \left(\frac{\Delta E}{\Delta N}\right)_{T,S}$$

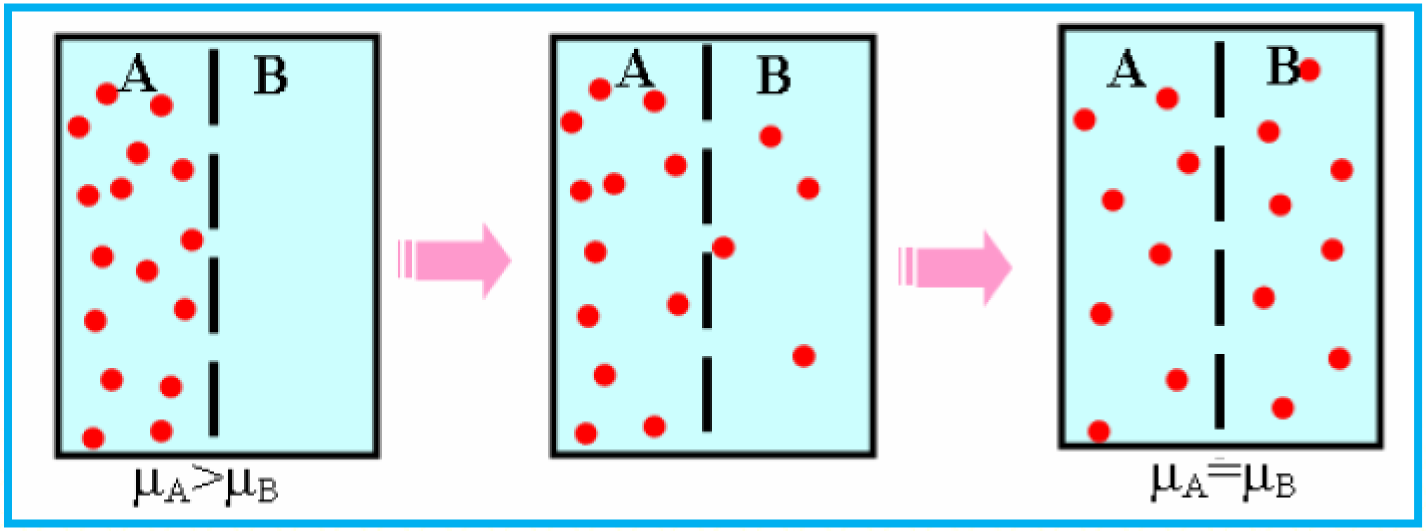
-introduced in 1876 by the American mathematical physicist Willard Gibbs

If to any homogeneous mass in a state of hydrostatic stress we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass divided by the quantity of the substance added is the potential for that substance in the mass considered

Note: Chemical potential energy is a form of potential energy related to the structural arrangement of atoms or molecules --the breaking and forming of chemical bond.

The **chemical potential** μ of a thermodynamic system is the amount by which the energy of the system would change if an additional particle were introduced, with the entropy and volume held fixed.

Chemical potential μ is a measure of the free energy available to do the work of moving a mole of molecules from one location to another or through a barrier such as a cell membrane…



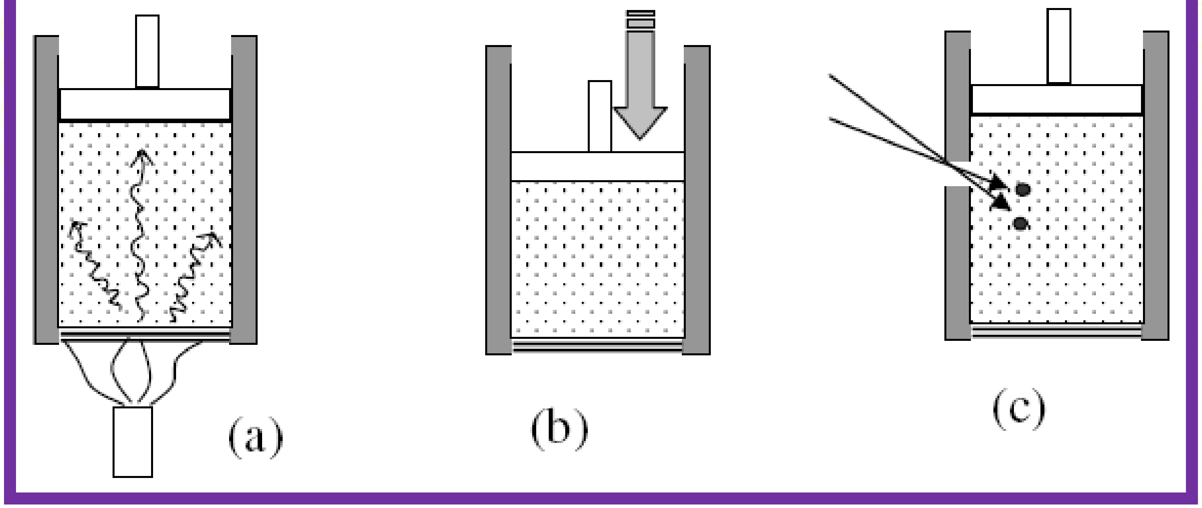
Molecules tend to spontaneously move from areas of higher μ (higher concentration) to areas of lower μ (lower concentration), thus increasing the entropy of the universe

$\mu_A > \mu_B$**:** transformation of substance A into substance B, or transport from place A to place B

$\mu_A = \mu_B$**:** no transformation, no transport, chemical equilibrium

$\mu_A < \mu_B$**:** transformation of substance B into substance A, or transport from place B to place A.

First law of thermodynamics



Changing the internal energy
- (a) adding heat (ΔQ)
- (b) doing work (ΔW)
- (c) adding particles (ΔN)

$\Delta U = \Delta Q - \Delta W + \mu \Delta N$ --- The First Law of Therm.

Note: $-\Delta W$: work is done on the system

Note: U – property of a system, determined by the two end points (initial & final)

Q, W – interactions, determined by the routes taken. **Cannot** be determined from the end points alone.

$$\boxed{dU = \delta Q - \delta W + \mu dN}$$

Or

$$\boxed{dU = \delta Q - \delta W}$$ for non diffusive int.

To differentiate between properties and interactions;

-exact differential- property functions

-inexacct diff. – non-property functions (Interactions)

Let $F = f(x, y)$
Initial state: (x_i, y_i)
Final state: (x_f, y_f)

x, y: variables $\Delta F = f(x_f, y_f) - f(x_i, y_i)$

F is determined by the two end points

Diff. form $dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy$

Let a diff. eq. $g(x,y)dx + h(x,y)dy$ -- exact or not?

EXACT – if there is a F(x, y) function which satisfy

$$\frac{\partial F}{\partial x} = g \quad \text{and} \quad \frac{\partial F}{\partial y} = h$$

Alternatively, use the identity $\frac{\partial^2 F}{\partial y \partial x} = \frac{\partial^2 F}{\partial x \partial y}$

Note: dependent & independent variables

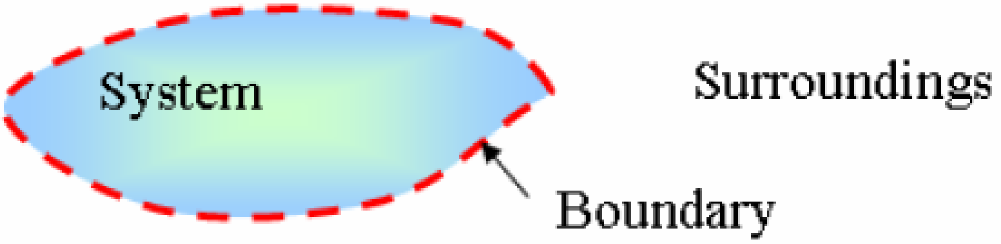
$$F = F(x, y) \qquad \frac{\partial F(x, y)}{\partial x}$$

y is held constant.

Or $\left(\frac{\partial F}{\partial x}\right)_y$ y is held constant

Note:

The system



Universe = System + Surroundings

Definite boundaries in space
May be open or closed (respect to transfer of matter)
May or may not be thermally insulated

Thermodynamics state of a system

System characteristics

- at equilibrium, system assumed to occupy one of a set of abstract, thermodynamics states
- each state is defined by the values of state variables
  - e.g: at least two of the variables (T, V, P….)
- system state determines system properties
- two types properties
  - Extensive (e.g volume, mass..)
  - Intensive (e.g T, P, density…..)

Change of System State

- System traverses from initial to final state.
-Resulting change in some macroscopic system property.
-Reversible or Irreversible.

- Reversible – change take a path near to equilibrium – system changes can be accurately predicted.
- Irreversible – changes deviate from equilibrium – system changes cannot be accurately predicted.

Statistical Thermodynamics

-concern ; behaviour of a large number of particles

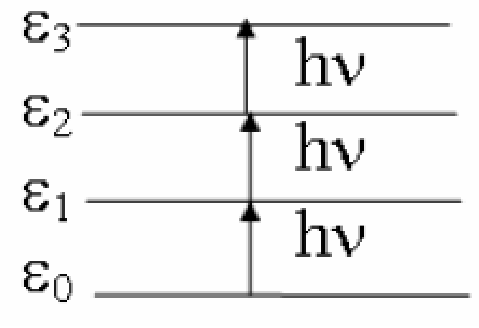
- take a statistical view

-Thermodynamic state – the state of a system for N particles

The states of a system

-A microstate is the state defined by specifying in detail the location and momentum of each particle

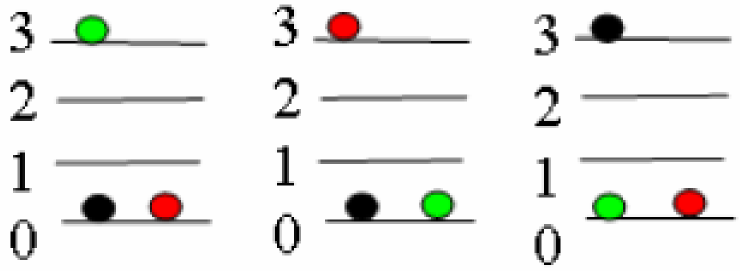
-Each atom is an **oscillator** that contains equally spaced energy levels. Atoms may be in any of these quantum states



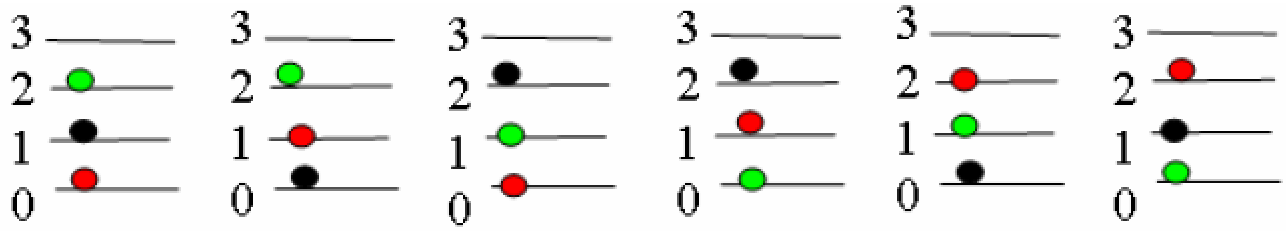
The total number of atoms, *N* $$\sum_i n_i = N$$

The total energy the system E $$\sum_i n_i \varepsilon_i = E$$

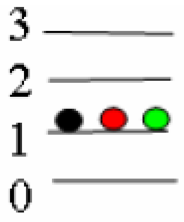
-Consider 3 atoms with a total energy of 3 units.



Microstates 1, 2 & 3



Microstates 4, 5, 6, 7, 8, & 9



Microstate 10

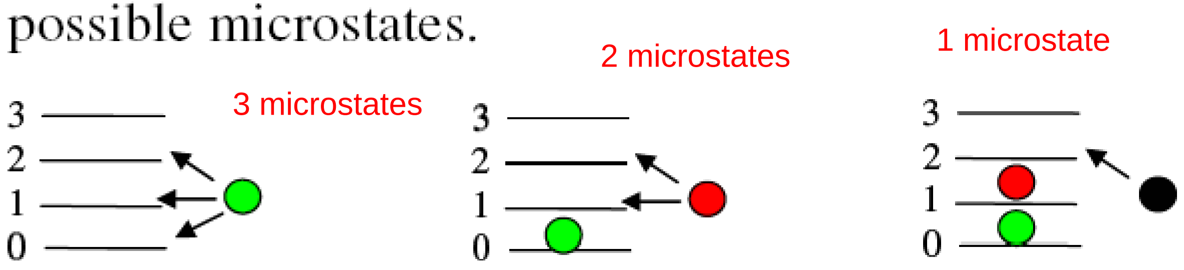
For **3 atoms** with E = **3 units** → **10 possible microstates**

To predicts the number of microstates

(Case: 3 atoms with E = 3 units)

STEP 1

1. The 1st oscillator can be in any one of three states → 3 possible microstates.



2. The 2nd oscillator →in any one of the two states→ 2 additional microstates

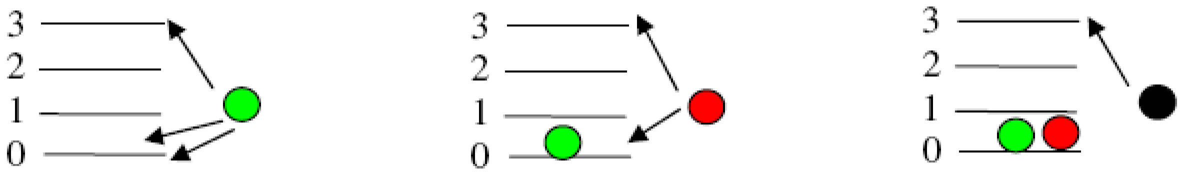
3. The 3rd oscillator→only one state→ 1 additional microstate.

The total number of microstates Ω is

$$\Omega = 3\cdot 2\cdot 1 = 3! = 6$$ [(3+2+1) microstates]

STEP 2:

-One oscillator in state 3 and the other two in state 0.

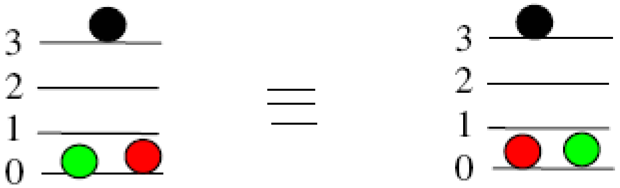


1. The 1st oscillator → 3 possible microstates.
2. The 2nd oscillator → 2 additional microstates
3. The 3rd oscillator → 1 additional microstate.

→ Total of 6 microstates

Note: but

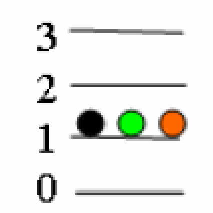
Same microstate



-reduces the configuration to 3 microstates.

$$\Omega = \frac{3 \cdot 2 \cdot 1}{2} = \frac{3!}{2!} = 3$$

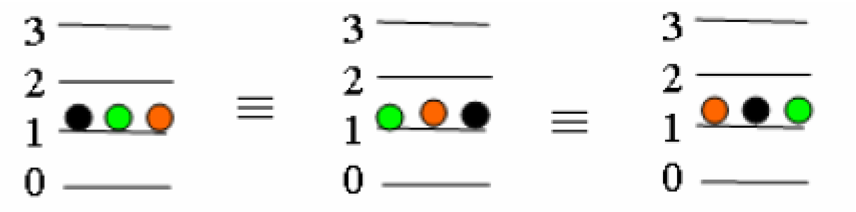
STEP 3 -all three oscillators are in the same state



1. The 1st oscillator → 3 possible microstates.
2. The 2nd oscillator → 2 additional microstates
3. The 3rd oscillator → 1 aditional microstate.

→ Total of 6 microstates

Note: But



etc

-reduces this configuration to 1 microstates

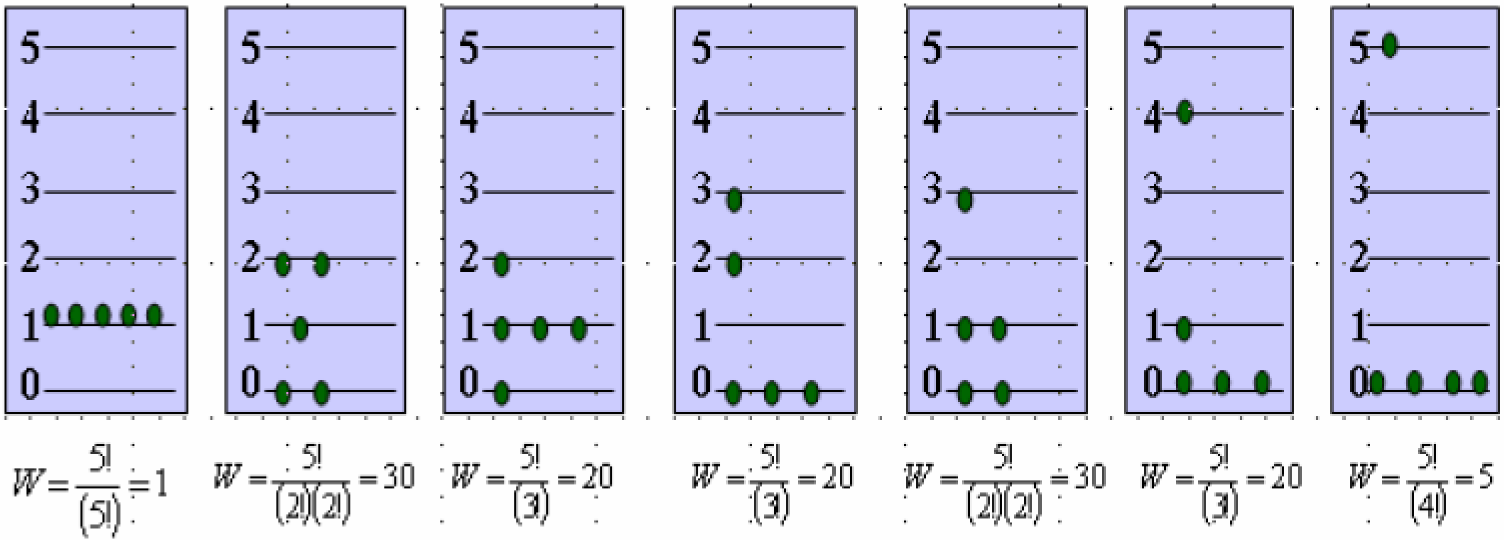
$$\Omega = \frac{3 \cdot 2 \cdot 1}{6} = \frac{3!}{3!} = 1$$

Then, in general, the number of microstates for any given configuration is

$$\boxed{\Omega = \frac{N!}{(n_o!)(n_1!)(n_2!)(n_3!)} = \frac{N!}{\prod(n_i!)}}$$

Example: -the number of microstates for N = 5 & E= 5

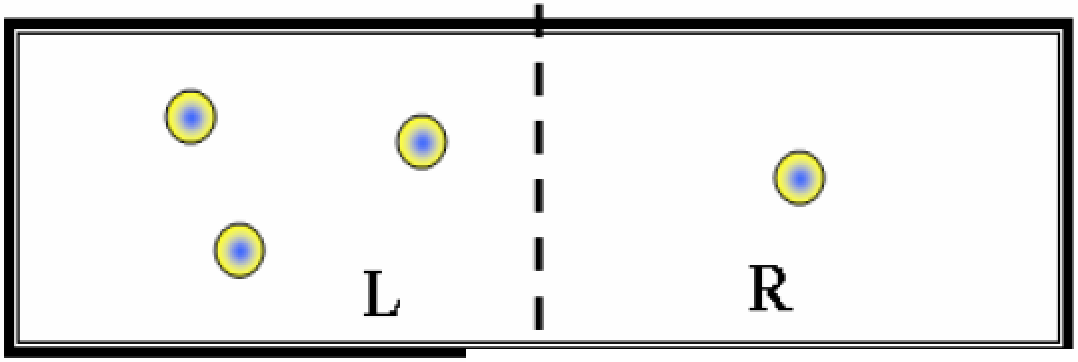
-possible configurations



-the total number of microstates is

$$\Omega = \frac{5!}{5!} + \frac{5!}{4!} + \frac{5!}{3!} + \frac{5!}{2!} + \frac{5!}{1!} = 1 + 5 + 20 + 60 + 120$$
$$= 206$$

Example:
4 molecules in a box



How many ways are there?

-to place 0 in L and 4 in R: $\frac{4!}{0!4!} = 1$

-to place 1 in L and 3 in R: $\frac{4!}{1!3!} = 4$

-to place 3 in L and 1 in R: $\frac{4!}{3!1!} = 4$

-to place 2 in L and 2 in R: $\frac{4!}{2!2!} = 6$

-to place 4 in L and 0 in R: $\frac{4!}{4!0!} = 1$

MICROSTATE	MACROSTATE	DEGENERACY
LLLL	I	1
RLLL	II	4
LRLL		
LLRL		
LLLR		
LLRR	III	6
LRLR		
RLLR		
LRRL		
RLRL		
RRLL		
LRRR	IV	4
RLRR		
RRLR		
RRRL		
RRRR	V	1
	∑5	∑16

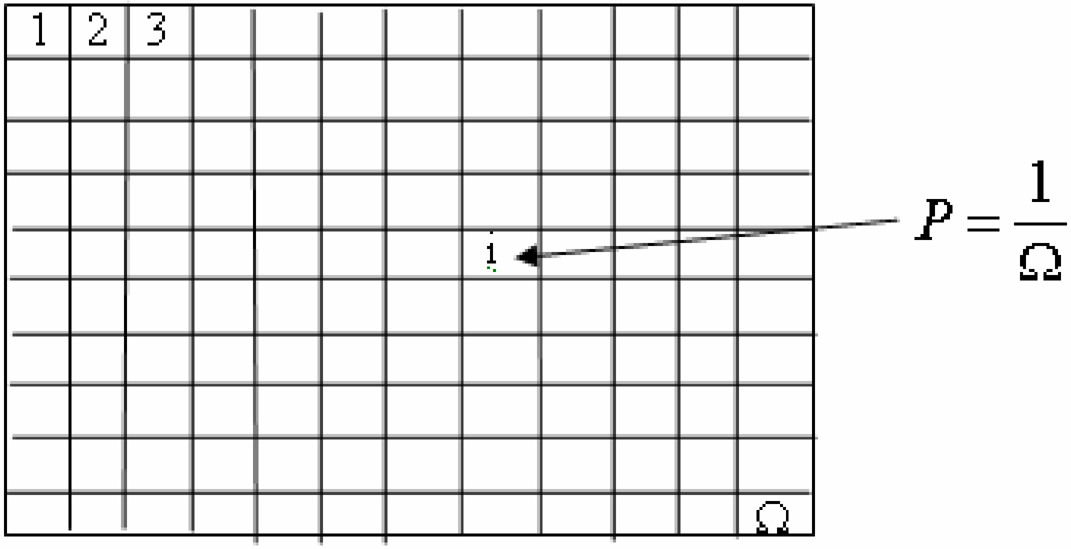
Fundamental Postulate

An isolated system in equilibrium is equally likely to be in any of its accessible state

Let Ω_o: the number of states accessible to the entire system

The probability it will be found in any one of them,

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



Calculate all the possible microstates for a lattice of 3 non-interacting particles:

microstates	magnetization
↑ ↑ ↑	+3μ
↑ ↑ ↓	+1μ
↑ ↓ ↑	+1μ
↓ ↑ ↑	+1μ
↓ ↓ ↑	-1μ
↓ ↓ ↑	-1μ
↓ ↑ ↓	-1μ
↓ ↓ ↓	-3μ
$\sum =$ 8 microstates	

How many microstates are there for a total magnetization of +1μ and the first particle's magnetic moment is + ?

ii) What is the probability that the orientation of the first particle's magnetic moment is + and the total magnetization is +μ?

Ans

$$P(+\mu \ of \ \ state\,1\, is\, +\,) = \frac{number\ states\ with\ \mu\ of\ 1\ being\ +}{total\ number\ of\ \ state} = \frac{2}{3}$$

The spacing of states

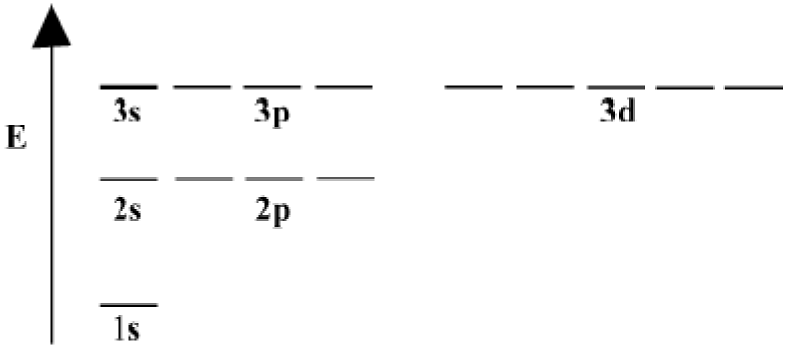
- identify the state of a system by its internal energy, U
- several different states have the same energy –
  The state is degenerate or
  The energy level is degenerate

E.g three spins ½ particles in magnetic field B

microstate		energy
↑ ↑ ↑	(+++)	$+3\mu B$
↑ ↑ ↓	(++ -)	$+1\mu B$
↑ ↓ ↑	(+- +)	$+1\mu B$
↓ ↑ ↑	(-++)	$+1\mu B$
↑ ↓ ↓	(+- -)	$-1\mu B$
↓ ↑ ↓	(-+ -)	$-1\mu B$
↓ ↓ ↑	(- -+)	$-1\mu B$
↓ ↓ ↓	(- - -)	$-3\mu B$

The Energy, $U = +1\mu B$ state is three-times degenerate

Note



Some orbits with the same *n* have the same energy
Orbits with identical energies are said to be ***degenerate***

Let ΔU = energy range of finite width
Expect: number of states $\propto \Delta U$

If $\Omega(U, \Delta U)$: number of states between U and $U+\Delta U$

$$\Omega(U, \Delta U) = g(U)\,\Delta U$$

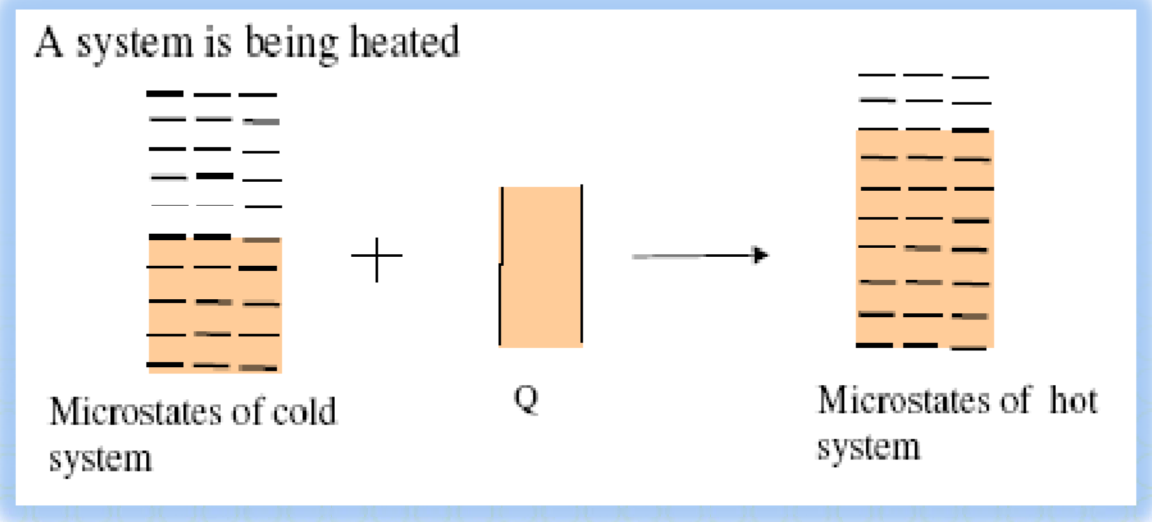
g (U): density of state

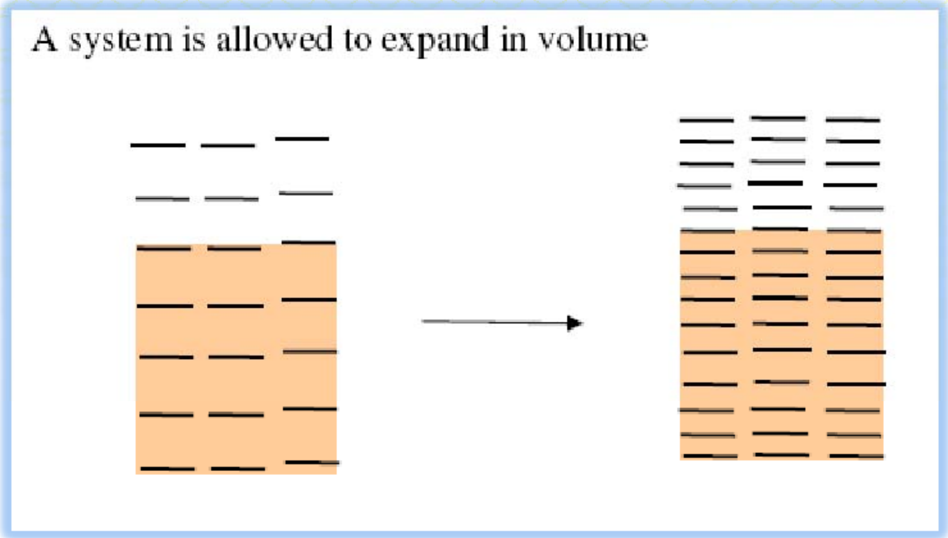
Changing the number microstates

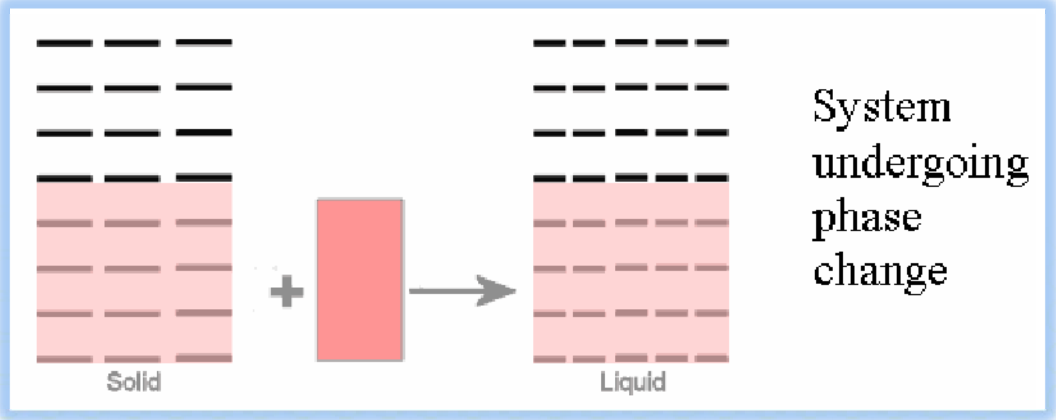
-by changing the internal energy

-Four ways to increase the number of quantum states of molecules

1-when a system is heated.
2-when a system expands into a vacuum of fluids mix.
3-when a solute is added to a solvent.
4-when a phase change occurs due to the input of energy as in the first







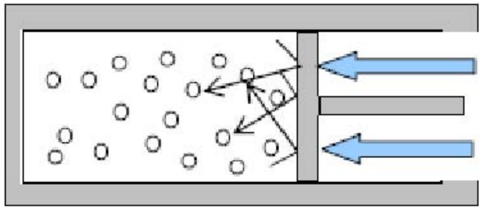
System undergoing phase change

Equilibrium

For an isolated system;

When the probability of it being in the various possible states do not vary with time.

Consider: changing the internal energy by compressing



-First the additional energy is given to particles near the boundary

–Then shared with the rest of the system – by mutual interaction

- When all possible states are equally probable – the system is in ***equilibrium***

Relaxation time – the time required for a system to reach equilibrium after being perturbed.

Quasi-static process – when system interact, the transfer of heat, work, or particles, the process must be slower compared to the relaxation time --- the system near equilibrium.

THAT'S ALL FOR NOW....

REFERENCES:

1. REAF, F : “Fundamentals Of Statistical And Thermal Physics”, McGraw-Hill.

2. KITTEL & KROMER: “Thermal Physics”, W.H. Freeman & Company.