WELCOME

Atomic and molecular Physics

- study of the spectroscopy

T.Y. B.Sc- 2018-19

Prof. Ghule N.B.

SPECTROSCOPY

- Spectroscopy is that branch of science which deals with the study of interaction of electromagnetic radiations with matter

Raman spectra

- This is based on scattering of radiation and not on the absorption of radiation by the sample.

RAMAN SPECTRA

GENERAL INTRODUCTION

- It is a type of spectroscopy which deals not with the absorption of electromagnetic radiation but deals with the **scattering of light** by the molecules. When a substance which may be gaseous, liquid or even solid is irradiated with monochromatic light of a definite frequency v, a small fraction of the light is scattered. Rayleigh found that if the scattered light is observed at right angles to the direction of the incident light, the scattered light is found to have the same frequency as that of the incident light. This type of scattering is called **Rayleigh scattering.**

- When a substance is irradiated with monochromatic light of a definite frequency v, the light scattered at right angles to the incident light contained lines not only of the incident frequency but also of lower frequency and sometimes of higher frequency as well. The lines with lower frequency are called **Stokes' lines** whereas lines with higher frequency are called **anti-Stokes' lines.**

- Raman further observed that the difference between the frequency of the incident light and that of a particular scattered line was constant depending only upon the nature of the substance being irradiated and was completely independent of the frequency of the incident light. If vi is the frequency of the incident light and vs' that of particular scattered line, the difference v = vi - vs is called **Raman frequency** or **Raman shift.**

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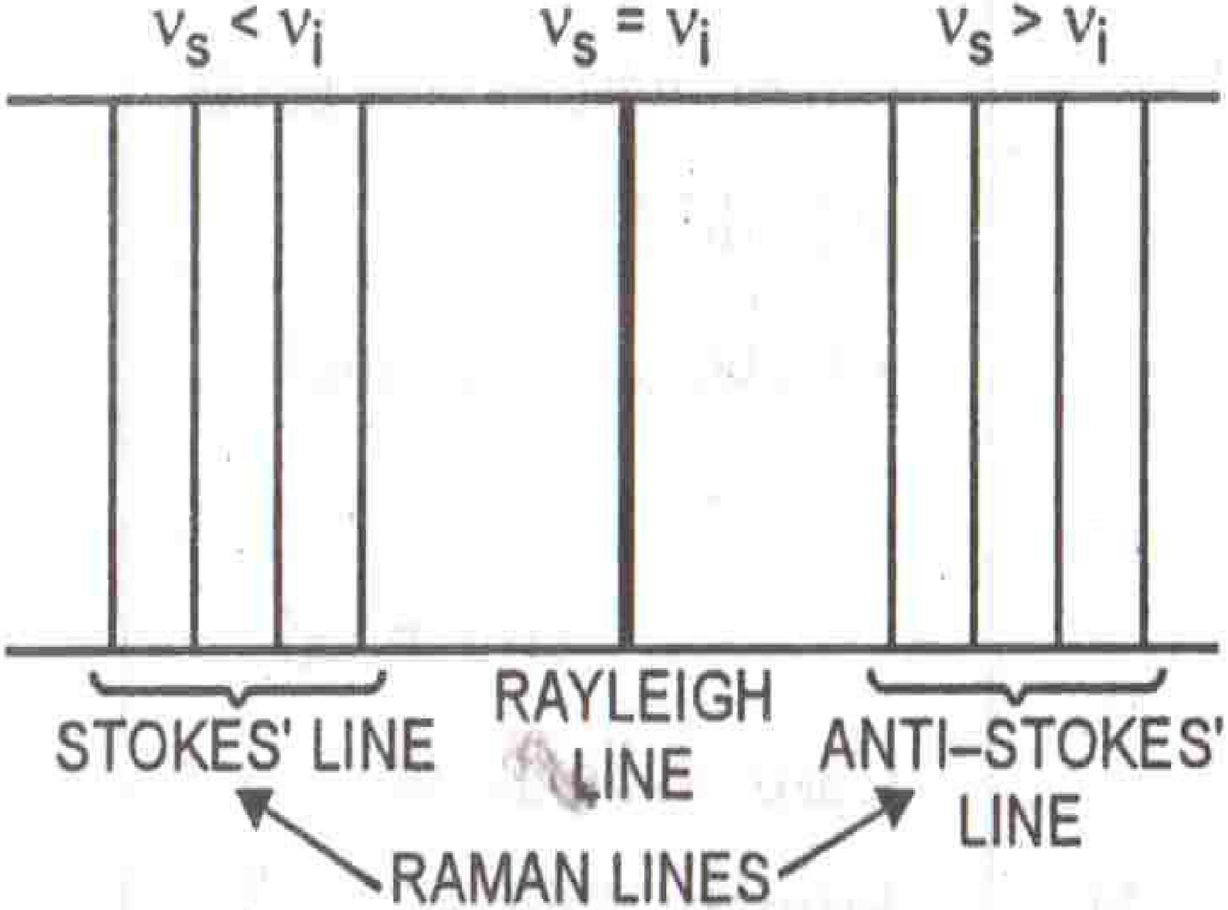

FIGURE 3.29

A simplified representation of Raman spectrum

EXPLANATION FOR OBSERVING RAYLEIGH LINE AND RAMAN LINES

- Elastic and inelastic collisions between the radiations and interacting molecules results in the formation of Rayleigh and Raman lines.
- In terms of excitation of electrons
- $v_{abs} = v_e$ Rayleigh line
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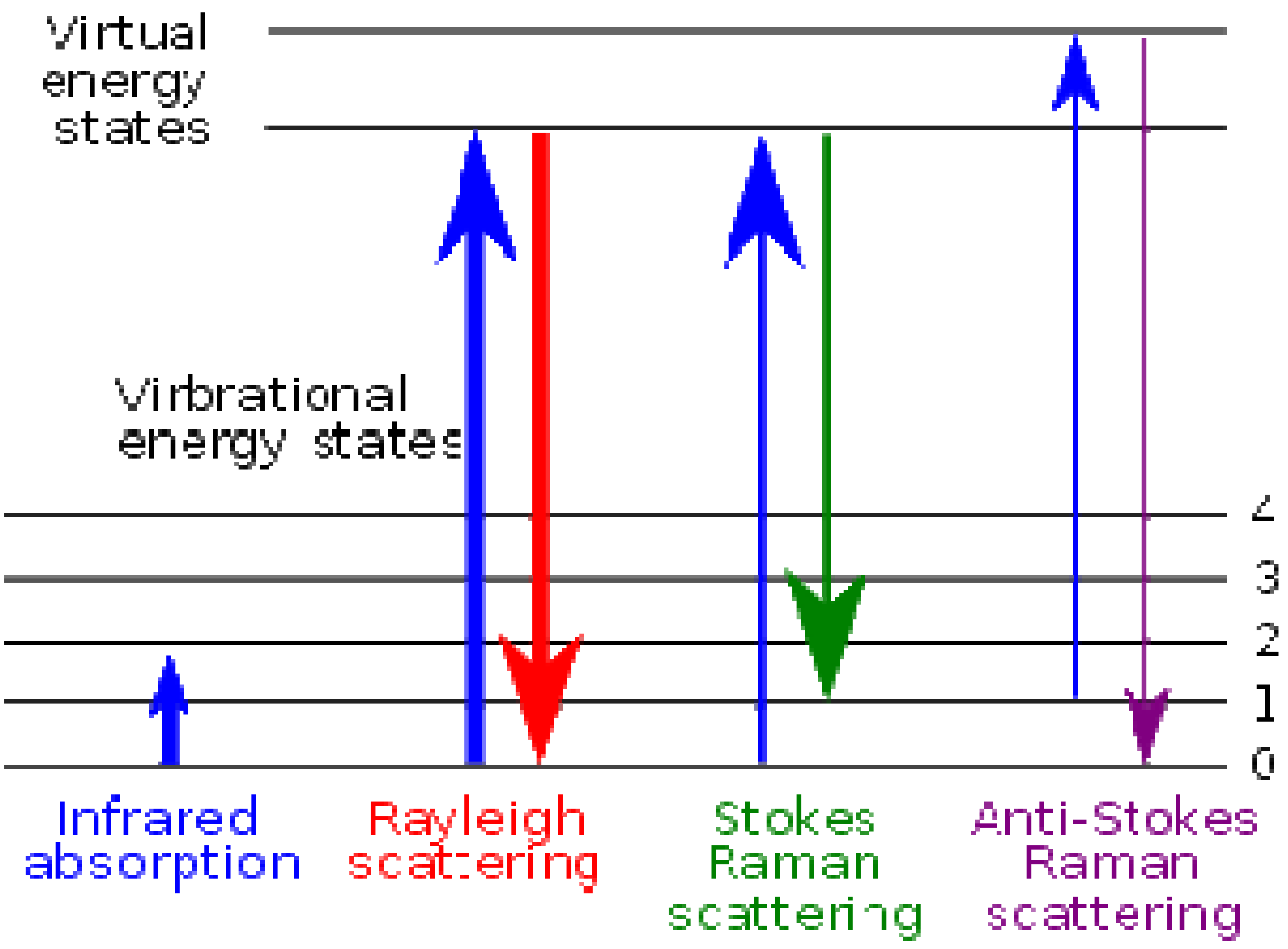
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POLARIZABILITY OF MOLECULES AND RAMAN SPECTRA

- The Raman effect arises on account of the polarization (distortion of the electron cloud) of the scattering molecules that is caused by the electric vector of the electromagnetic radiation. The induced dipole moment depends upon the strength of the electric field E and the nature of the molecules represented by α
- $\mu = \alpha E$

- In case of atoms or spherically symmetrical molecules (spherical rotors) such as CH4' SF6 etc same polarizability is induced whatever be the direction of the applied electric field. They are said to be *isotropically polarizable.* Such molecules are said to be isotropic molecules.

- In case of all diatomic molecules (homonuclear or heteronuclear) or non-spherical molecules (non-spherical rotors), the polarizability depends upon the direction of the electric field.
- Such molecules are, therefore, said to anisotropically polarizable.

Types of molecules showing Rotational Raman Spectra.

- A molecule scatters light because it is polarizable. Hence the *gross selection rule for a molecule to give a rotational Raman spectrum is that the polarizability of the molecule must be anisotropic i.e. the polarizability of the molecule must depend upon the orientation of the molecule with respect to the direction of the electric field.*

- Hence all diatomic molecules, linear molecules and non-spherical molecules give Raman spectra i.e. they are rotationally Raman active. On the other hand, spherically symmetric molecules such as CH4' SF6 etc. do not give rotational Raman spectrum i.e. they are rotationally Raman inactive. (These molecules are also rotationally microwave inactive).

PURE ROTATIONAL RAMAN SPECTRA OF DIATOMIC MOLECULES

- The selection rules for pure rotational Raman spectra of diatomic molecules are
- $\Delta J = 0 , \pm 2$
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- The selection rule $\Delta J = 0$ corresponds to Rayleigh scattering whereas selection rule
- $\Delta J = \pm 2$ gives rise to Raman lines as explained .

INTENSITIES OF LINES OF THE PURE ROTATIONAL RAMAN SPECTRA

- As explained earlier, the intensities of lines depend upon the population of initial level from where the molecules are excited or de-excited to the final level. Since the population of rotational energy levels is as shown in Fig. therefore the intensities of the Stokes' and anti-Stokes' lines vary in a similar manner.

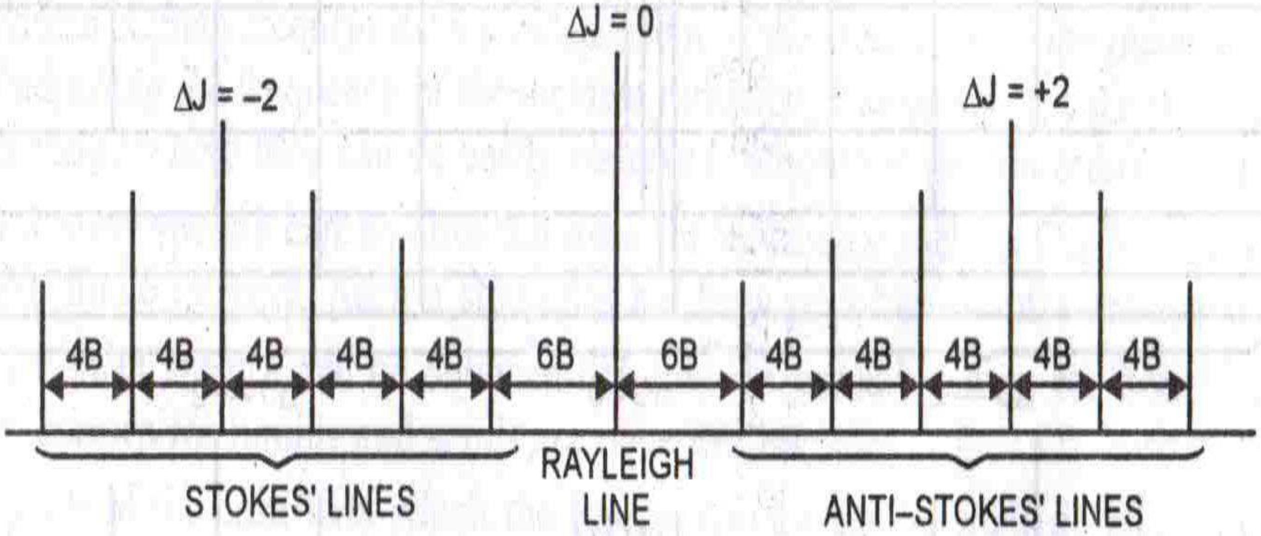

FIGURE 3.31

Pure rotational Raman spectrum expected for a diatomic molecule.

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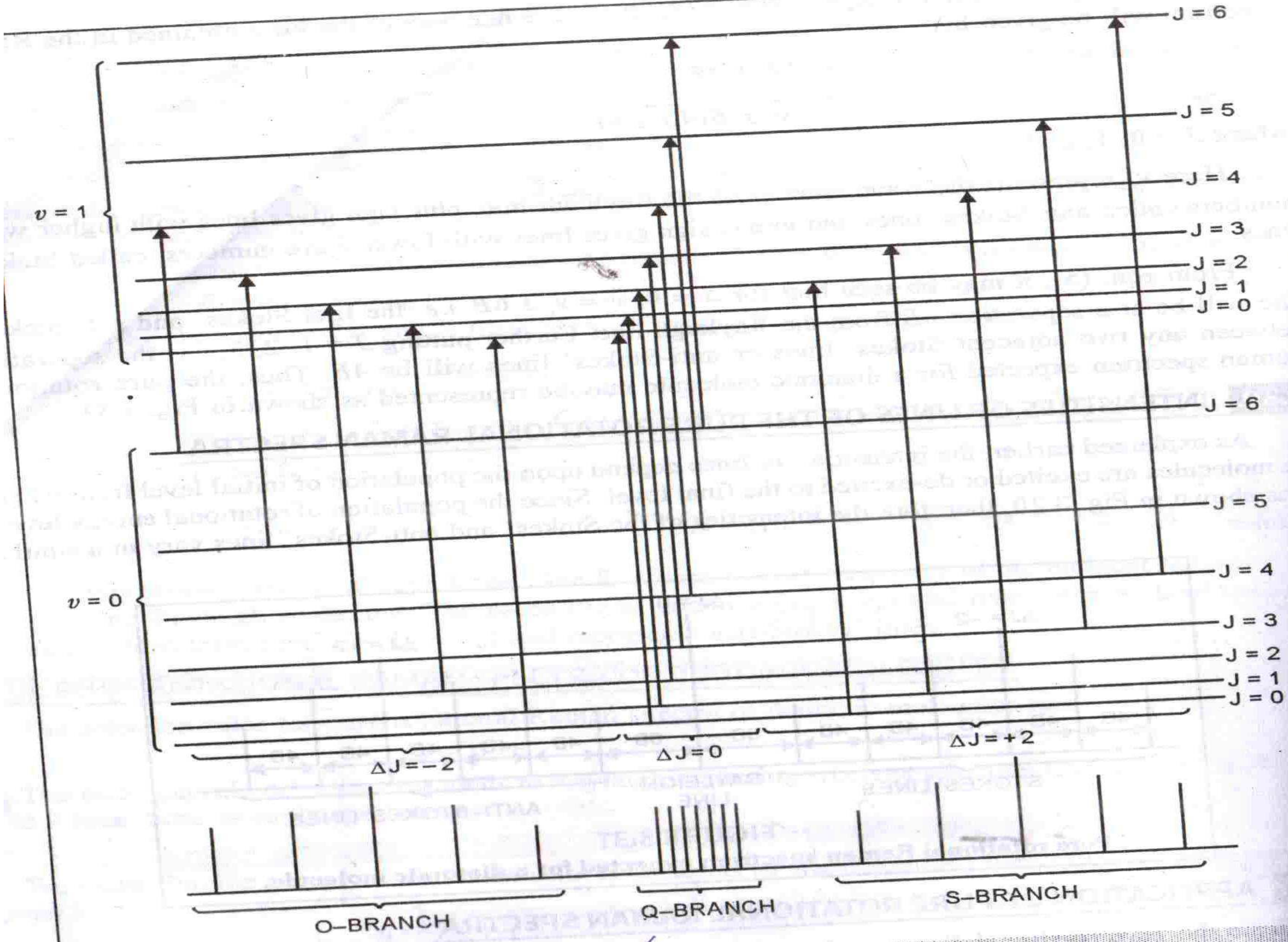
APPLICATION OF PURE ROTATIONAL RAMAN SPECTRA

- From the pure rotational Raman spectra, noting the separation between the lines, the value of B can be obtained from which the moment of inertia and the bond length of the diatomic molecules can be calculated



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Rotation-vibration Raman spectrum of a diatomic molecule.

ADVANTAGES OF RAMAN SPECTROSCOPY OVER INFRA-RED SPECTROSCOPY

- Raman frequencies are independent of the frequency of the incident radiation, hence by suitable adjusting the frequency of the incident radiation, Raman spectra can be obtained in the visible spectrum

- Raman spectra can be obtained even for molecules such as O2' N2' C12 etc. which have no permanent dipole moment. Such a study has not been possible by infra-red spectroscopy.

- Raman spectra can be obtained not only for gases but even for liquids and solids whereas infra-red spectra for liquids and solids are quite diffuse.

THANK YOU

Wel come

Element of Material Science

- Introduction of Material & Type of Material

T.Y. B.Sc- 2018-19

prof. Ghule N.B.

Introduction

What is material science?

Definition 1: A branch of science that focuses on materials; interdisciplinary field composed of physics and chemistry.

Definition 2: Relationship of material properties to its composition and structure.

What is a material scientist?

A person who uses his/her combined knowledge of physics, chemistry and metallurgy to exploit property-structure combinations for practical use.

What is materials ?

What do we mean when we say “materials”?

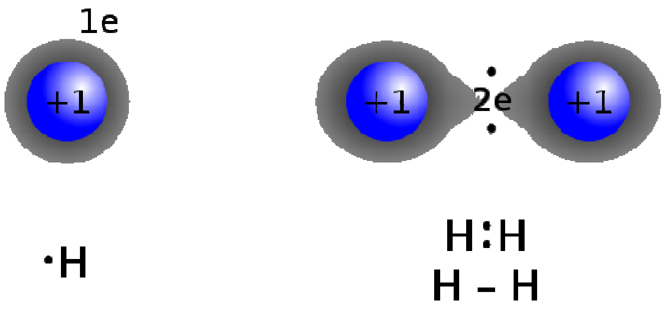
1. **Metals**
    - aluminum
    - copper
    - steel (iron alloy)
    - nickel
    - titanium
2. **Ceramics**
    - clay
    - silica glass
    - alumina
    - quartz
3. **Polymers**
    - polyvinyl chloride (PVC)
    - Teflon
    - various plastics
    - glue (adhesives)
    - Kevlar
4. **Composites**
    - wood
    - carbon fiber resins
    - concrete

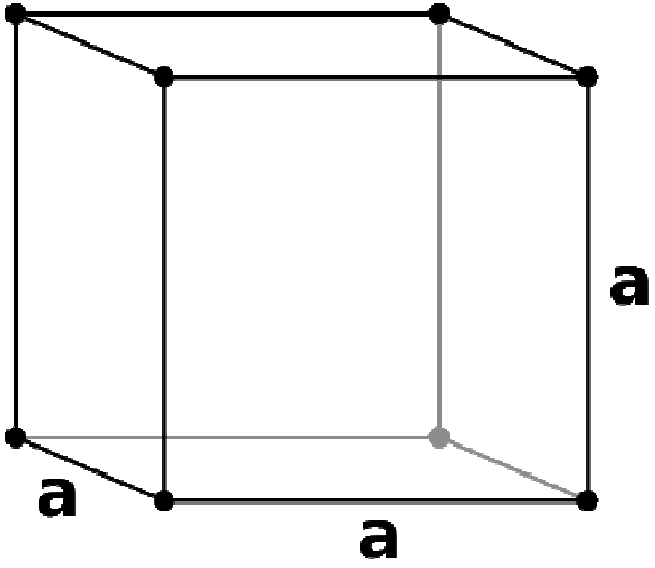
semiconductors (computer chips, etc.) = ceramics, composites

nanomaterials = ceramics, metals, polymers, composites

Atomic Structure

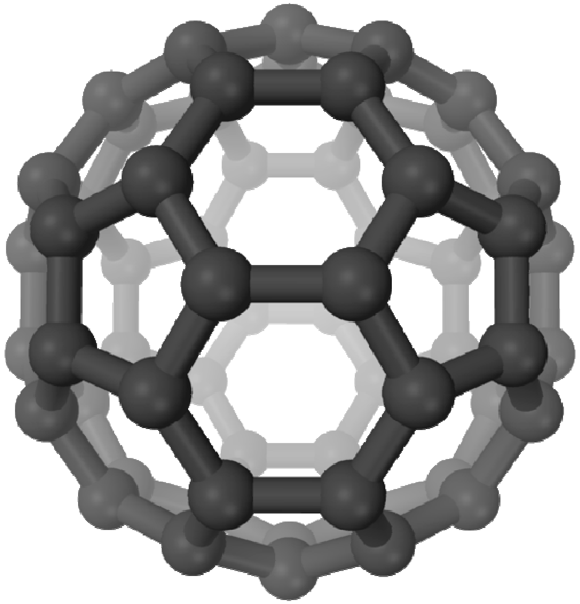
- Pertains to atom electron structure and atomic arrangement
- Atom length scale
  - Includes electron structure – atomic bonding
    - ionic
    - covalent
    - metallic
    - London dispersion forces (Van der Waals)
  - Atomic ordering – long range (metals), short range (glass)
    - 7 lattices – cubic, hexagonal among most prevalent for engineering metals and ceramics
    - Different packed structures include: Gives total of 14 different crystalline arrangements (Bravais Lattices).
      - Primitive, body-centered, face-centered





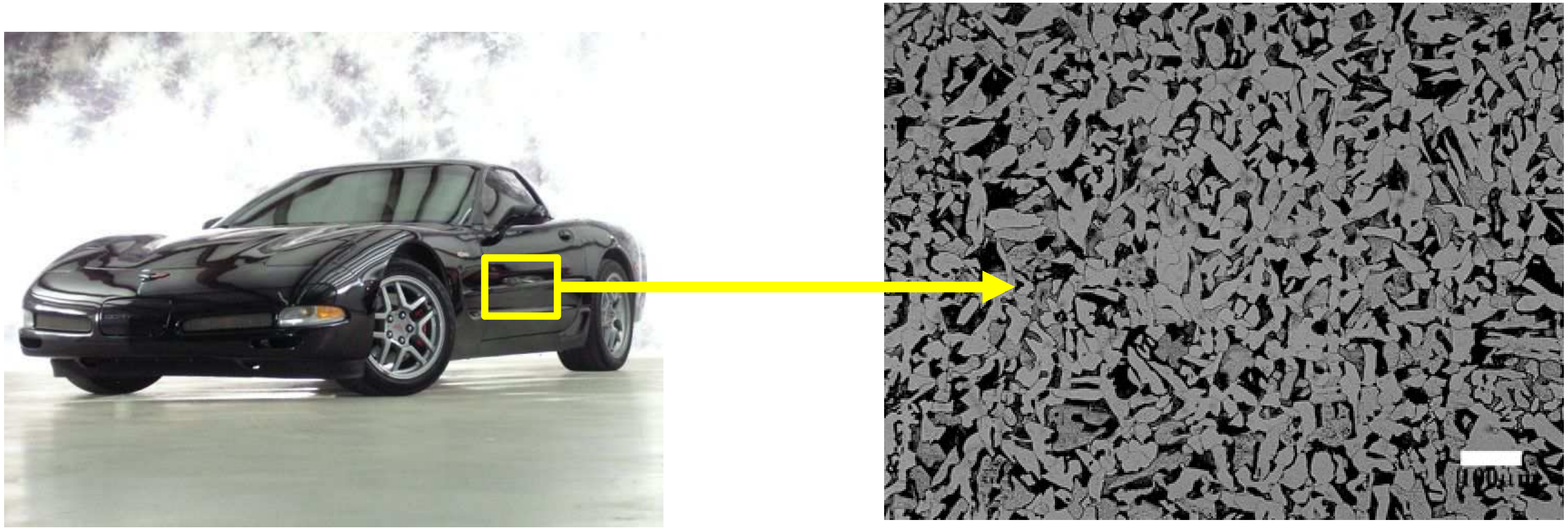
Nanostructure

- Length scale that pertains to clusters of atoms that make up small particles or material features
- Show interesting properties because increase surface area to volume ratio
    - More atoms on surface compared to bulk atoms
    - Optical, magnetic, mechanical and electrical properties change



Microstructure

- Larger features composed of either nanostructured materials or periodic arrangements of atoms known as crystals
- Features are visible with high magnification in light microscope.
  - Grains, inclusions other micro-features that make up material
  - These features are traditionally altered to improve material performance



Macrostructure

- Macrostructure pertains to collective features on microstructure level
- Grain flow, cracks, porosity are all examples of macrostructure features

Class of Materials

- metals
- polymers
- ceramics
- composites

Metals

- Metals consist of alkaline, alkaline earth, metalloids and transition metals
- Metal alloys are mixtures of two or more metal and nonmetal elements (for example, aluminum and copper, Cu-Ni alloy, steel)
- Bonding: Metallic
  - No particular sharing or donating occurs. Electron cloud is formed (that is, free electrons)
  - Strong bonds with no hybridization or directionality
- Properties:
  - Electrically conductive (free electrons)
  - Thermally conductive
  - High strength – large capacity to carry load over x-section area (stress)
  - Ductile – endure large amounts of deformation before breaking.
  - Magnetic – ferromagnetism, paramagnetic
  - Medium melting point

Metal Application

- Electrical wire: aluminum, copper, silver
- Heat transfer fins: aluminum, silver
- Plumbing: copper
- Construction beams (bridges, sky scrapers, rebar, etc.): steel (Fe-C alloys)
- Cars: steel (Fe-C alloys)
- Consumer goods:
  - soup cans
  - appliances (stainless steel sheet metal)
  - utensils
  - tools
  - Many, many, many more…

Polymers

- Polymers consist of various hydro-carbon (organic elements) with select additives to elucidate specific properties
- Polymers are typically disordered (amorphous) strands of hydrocarbon molecules.
- Bonding: Covalent-London Dispersion Forces
- Properties:
  - ductile: can be stretched up to 1000% of original length
  - lightweight: Low densities
  - medium strength: Depending on additives
  - chemical stability: inert to corrosive environments
  - low melting point

Polymer Applications

- Car tires: vulcanized polymer (added sulfur)
- Ziploc bags
- Food storage containers
- Plumbing: polyvinyl chloride (PVC)
- Kevlar
- Aerospace and energy applications: Teflon
- Consumer goods:
  - calculator casings
  - TV consuls
  - shoe soles
  - cell phone casings
  - Elmer’s Glue (adhesives)
  - contact lenses
  - Many, many. many more…

Ceramics

- Consist of metal and non metal elements
- Typically a mixture of elements in the form of a chemical compound , for example Al_2O_3 or glass
- Three types: composites, monolithic and amorphous ceramics
- Bonding covalent – ionic
  - Typically covalent. In some cases highly direction covalent bonding
  - Ionic in case of SiO_2 glasses and slags
- Properties:
  - wear resistant (hard)
  - chemical stability: corrosion resistant
  - high temperature strength: strength retention at very high temperatures
  - high melting points
  - good insulators (dielectrics)
  - adhesives
  - good optical properties

Ceramic Applications

- Window glass: Al_2O_3 – SiO_2 – MgO – CaO
- Aerospace, energy and automotive industry
  - heat shield tiles
  - engine components
  - reactor vessel and furnace linings
- Consumer products:
  - pottery
  - dishes (fine china, plates, bowls)
  - glassware (cups, mugs, etc.)
  - eye glass lenses

Composites

- A mixture of two different materials to create a new material with combined properties
- Types of composites:
  - Particulate reinforced – discontinuous type with low aspect ratio
  - Whisker/rod reinforced - discontinuous type with high aspect ratio
  - Fiber reinforced - continuous type with high aspect ratio (naturally)
  - Laminated composites - layered structures (surf boards, skate boards)
- Bonding: depends on type of composite (strong-covalent, medium-solid solution, weak-tertiary phase layer)
- Properties: Depends on composites
  - High melting points with improved high temperature strength: ceramic-ceramic
  - High strength and ductile with improved wear resistance: metal-ceramic
  - High strength and ductile: polymer-polymer

Composites Applications

- Wood: naturally occurring biological material consists of very strong fibers imbedded in a soft matrix
- Plywood: laminated wood for buildings
- Concrete: basements, bridges, sidewalks
- Fiberglass: boats
- Carbon fiber resins: bicycle frames

Other well Known materials

- Semiconductors – ceramics
  - computer chips
  - memory storage devices
  - solar cells
  - image screens
- Nanomaterials – ceramics, metals, polymers
  - gold nanoshells
  - quantum dots
  - ferrofluids
  - medical devices

Thank You

WELCOME

MECHANICS

Newtons law of Motion

F.Y.B.Sc 2018-19

Prof. Ghule N.B.

Newtons of Motion

Background

- Sir Isaac Newton (1643-1727) was an English scientist and mathematician famous for his discovery of the law of gravity also discovered the three *laws of motion*.

- Today these laws are known as *Newton's Laws of Motion* and describe the motion of all objects on the scale we experience in our everyday lives.

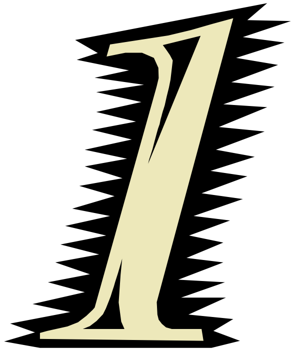
“If I have ever made any valuable discoveries, it has been owing more to patient attention, than to any other talent.”

-Sir Isaac Newton

Newton’s Laws of Motion

1. An object in motion tends to stay in motion and an object at rest tends to stay at rest unless acted upon by an unbalanced force.
2. Force equals mass times acceleration (F = ma).
3. For every action there is an equal and opposite reaction.

Newton’s First Law



An object at rest tends to stay at rest and an object in motion tends to stay in motion unless acted upon by an unbalanced force.

What does this mean?

Basically, an object will “keep doing what it was doing” unless acted on by an unbalanced force.

If the object was sitting still, it will *remain stationary*. If it was moving at a constant velocity, it will *keep moving*.

It takes *force* to change the motion of an object.

FORCE

A force is a push or pull upon an object resulting from the interaction with another object.

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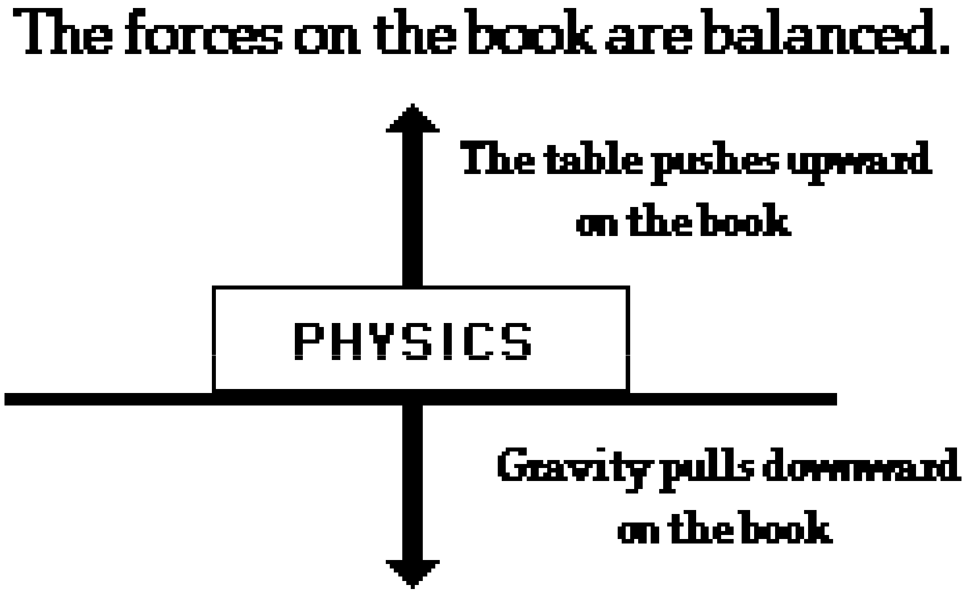
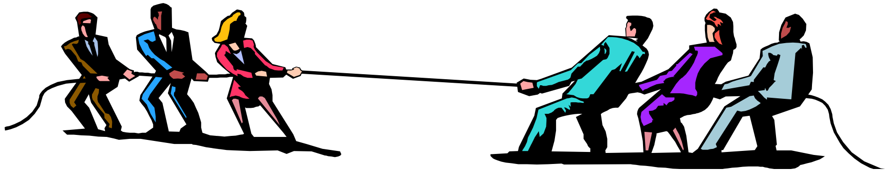
What is meant by *unbalanced force?*



If the forces on an object are equal and opposite, they are said to be balanced, and the object experiences no change in motion. If they are not equal and opposite, then the forces are unbalanced and the motion of the object changes.

Some Examples from Real Life

A soccer ball is sitting at rest. It takes an unbalanced force of a kick to change its motion.



Two teams are playing tug of war. They are both exerting equal force on the rope in opposite directions. This balanced force results in no change of motion.

Newton's First Law is also called the *Law of Inertia*

Inertia: the tendency of an object to resist changes in its state of motion

The First Law states that *all objects have inertia*. The more mass an object has, the more inertia it has (and the harder it is to change its motion).

Newton's Second Law

Force equals mass times acceleration.

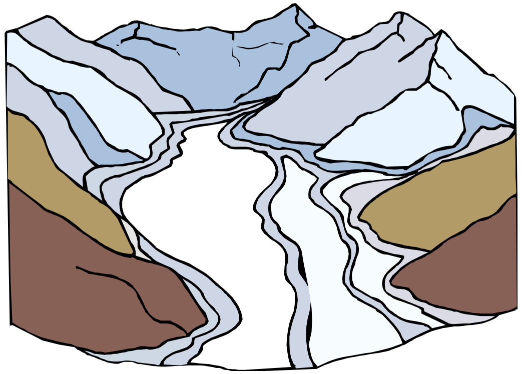
$F = ma$

<u>Acceleration</u>: a measurement of how quickly an object is changing speed.

What does F = ma say?

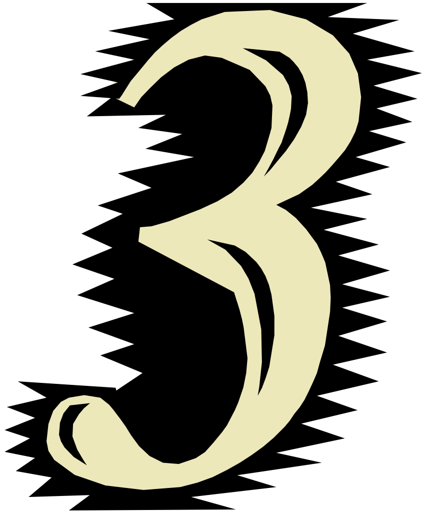
F = ma basically means that the force of an object comes from its mass and its acceleration.

Something very massive (high mass) that's changing speed very slowly (low acceleration), like a glacier, can still have great force.



Something very small (low mass) that's changing speed very quickly (high acceleration), like a bullet, can still have a great force. Something very small changing speed very slowly will have a very weak force.

Newton’s Third Law



For every action there is an equal and opposite reaction.

What does this mean?

For every force acting on an object, there is an equal force acting in the opposite direction. Right now, gravity is pulling you *down* in your seat, but Newton's Third Law says your seat is pushing *up* against you with *equal force*. This is why you are not moving. There is a *balanced force* acting on you– gravity pulling down, your seat pushing up.

What is momentum?

- the strength or force that something has when it is moving
- Product of mass and velocity

Newton’s Third Law and Momentum

“For every action there is an equal and opposite reaction.”

Momentum: a quantity defined as the product of mass and velocity of an object.

Momentum = mass x velocity

$p=mv$

THANK YOU

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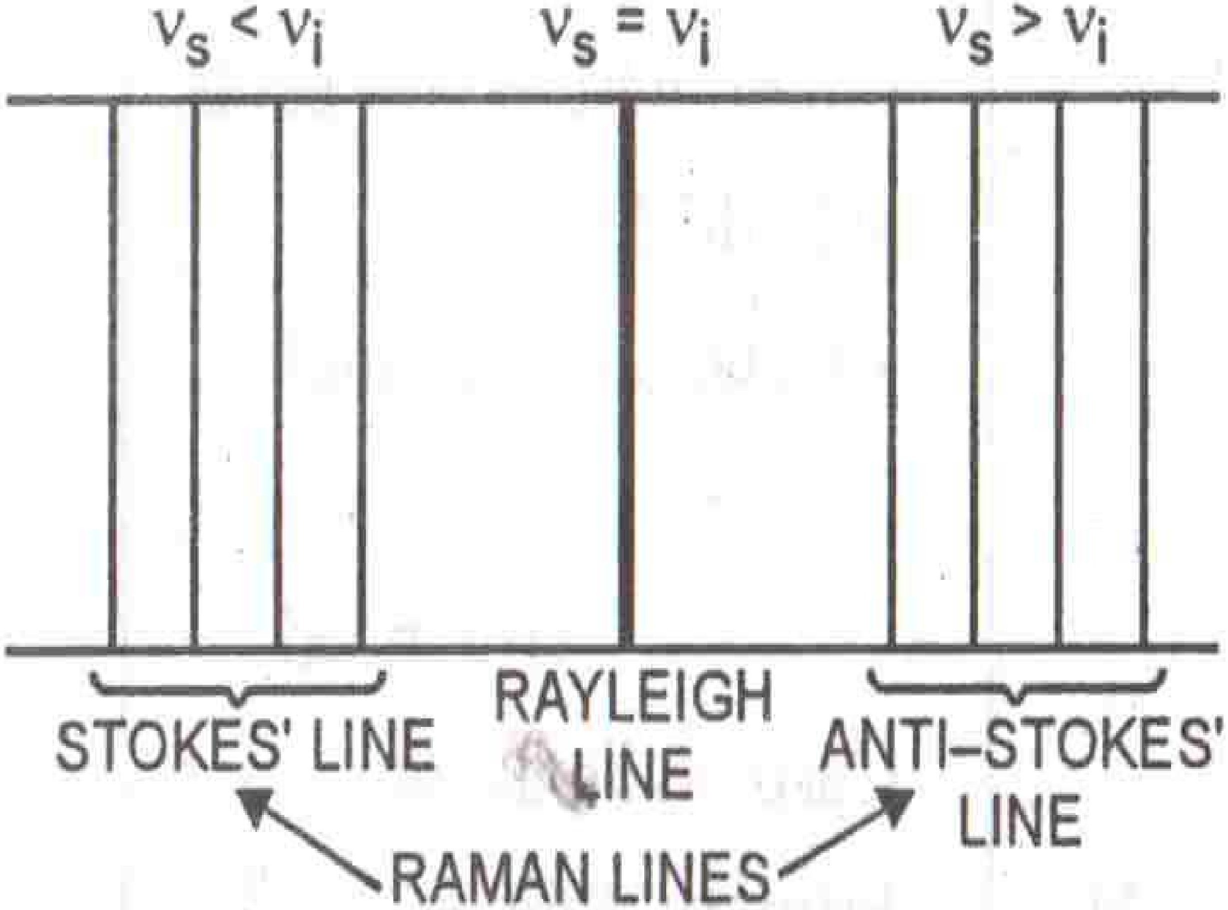

FIGURE 3.29

A simplified representation of Raman spectrum

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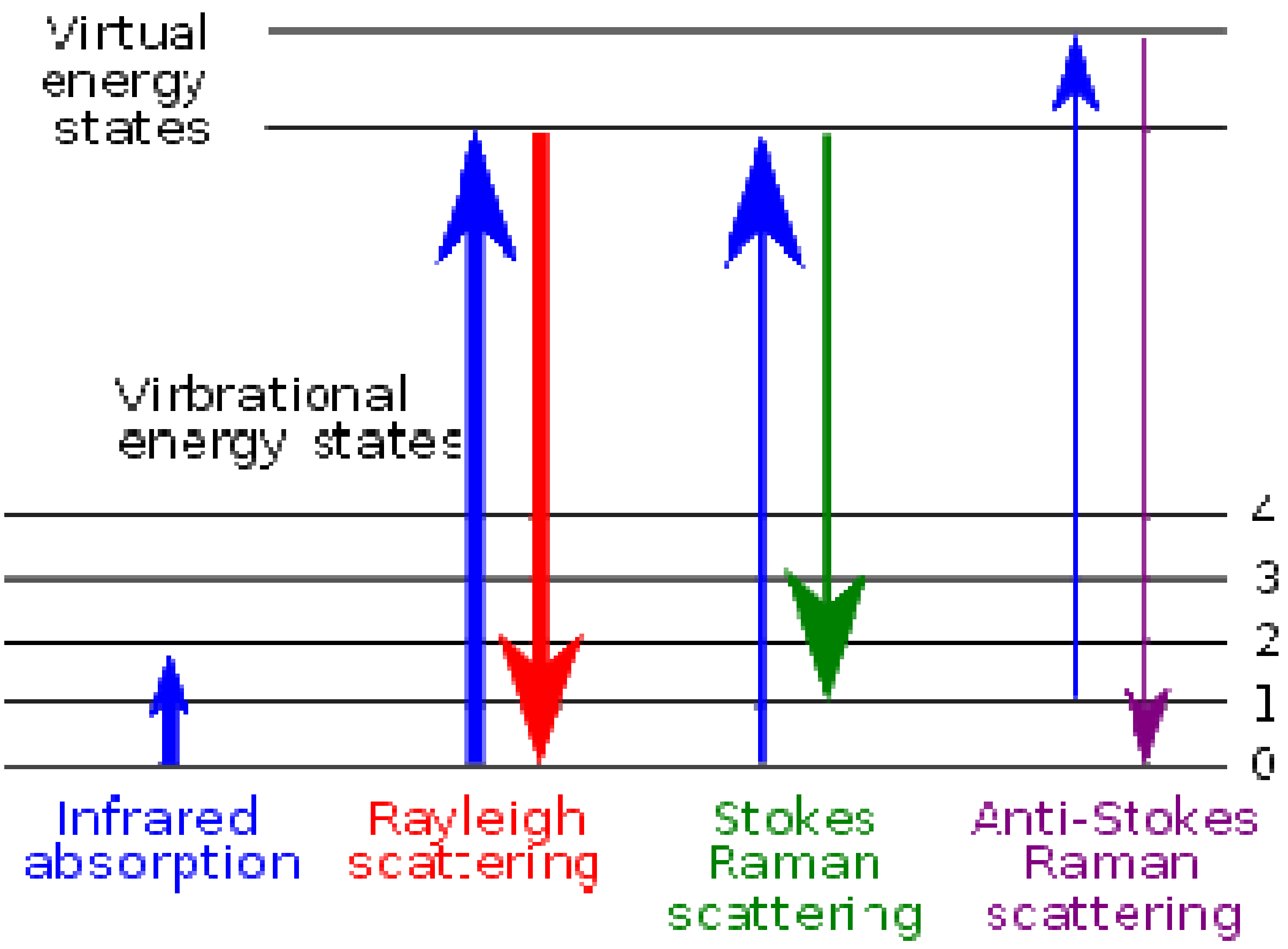
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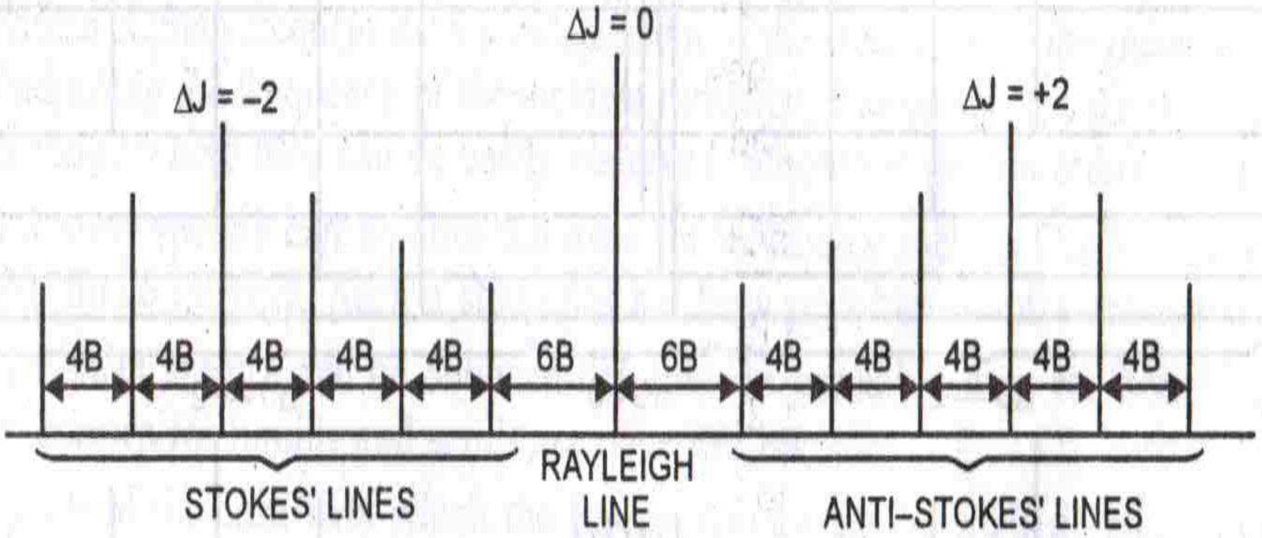

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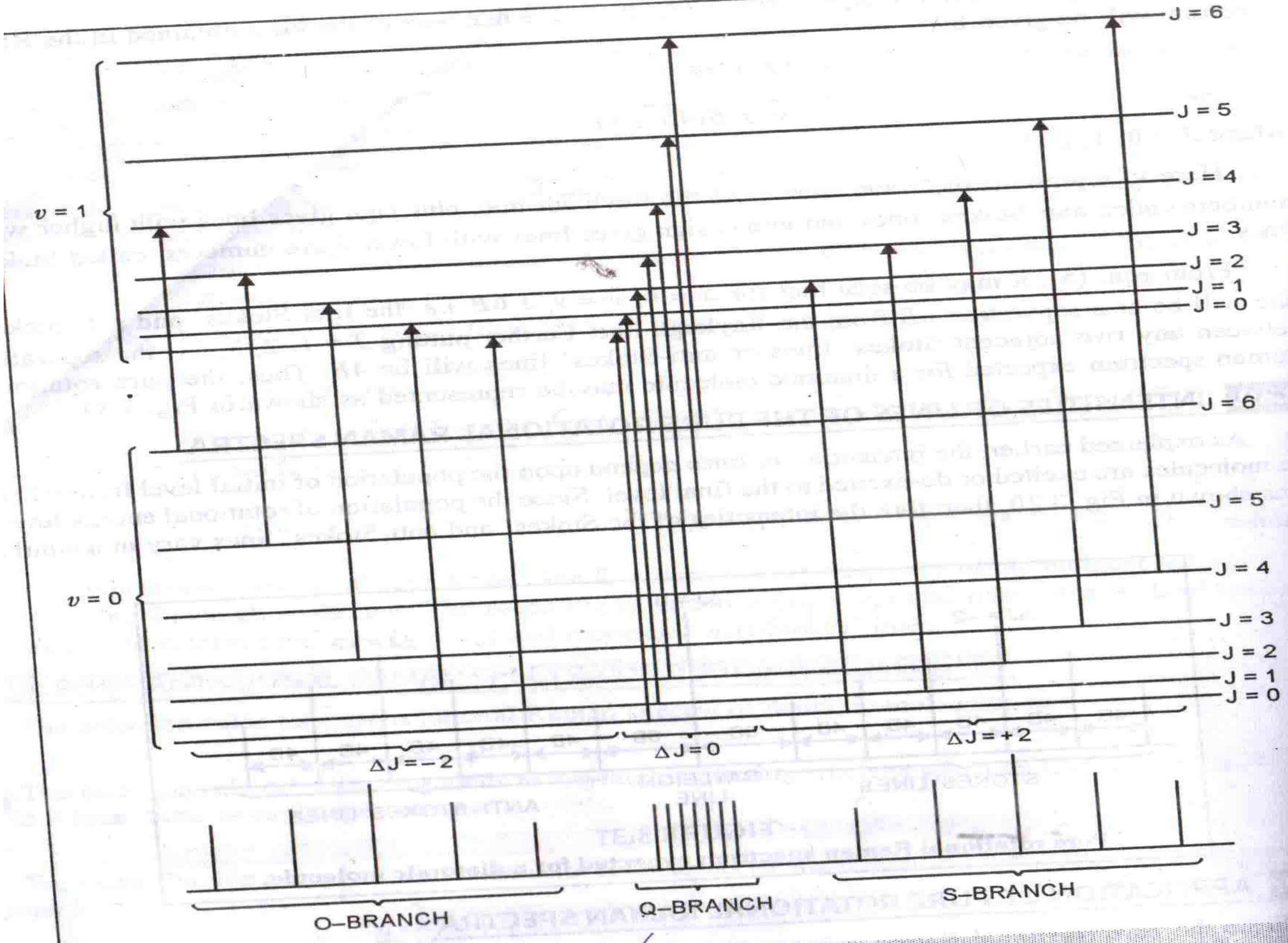

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THANK YOU

Thermodynamics
GHULE N B

Temperature, Heat, Work

Heat Engines

Introduction

- In mechanics we deal with quantities such as mass, position, velocity, acceleration, energy, momentum, etc.
- Question: What happens to the energy of a ball when we drop it on the floor?
- Answer: It goes into heat energy.

- In *Thermodynamics* we deal with quantities which describe our system, usually (but not always) a gas.
- Volume, Temperature, Pressure, Heat Energy, Work.

- We all know about Volume.
- Pressure:

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

Demonstrations: Balloons, Bed of Nails, Magdeburg hemispheres.

Temperature and Heat

- Everyone has a qualitative understanding of temperature, but it is not very exact.
- Question: Why can you put your hand in a 400° F oven and not get instantly burned, but if you touch the metal rack, you do?
- Answer: Even though the air and the rack are at the same temperature, they have very different energy contents.

Construction of a Temperature Scale

- Choose fixed point temperatures that are easy to reconstruct in any lab, e.g. freezing point of water, boiling point of water, or anything else you can think of.
- Fahrenheit: Original idea:

0°F Freezing point of Salt/ice

100°F Body Temperature

Using this ice melts at 32°F and water boils at 212°F (Not overly convenient) Note: 180°F between boiling an freezing.

- Celsius (Centigrade) Scale:

  0°C - Ice Melts

  100°C - Water Boils

Note a change of 1°C = a change of 1.8°F.

Conversion between Fahrenheit and Celsius

If we know Celsius and want Fahrenheit

$$F = \frac{9}{5}C + 32$$

If we know Fahrenheit and want Celsius

$$\mathrm{C} = \frac{5}{9}\left(F - 32\right)$$

Absolute or Kelvin Scale

- The lowest possible temperature on the Celsius Scale is -273°C.
- The Kelvin Scale just takes this value and calls it 0K, or absolute zero.
- Note: the “size” of 1K is the same as 1°C.
- To convert from C to K just add 273.

$$K=C+273$$

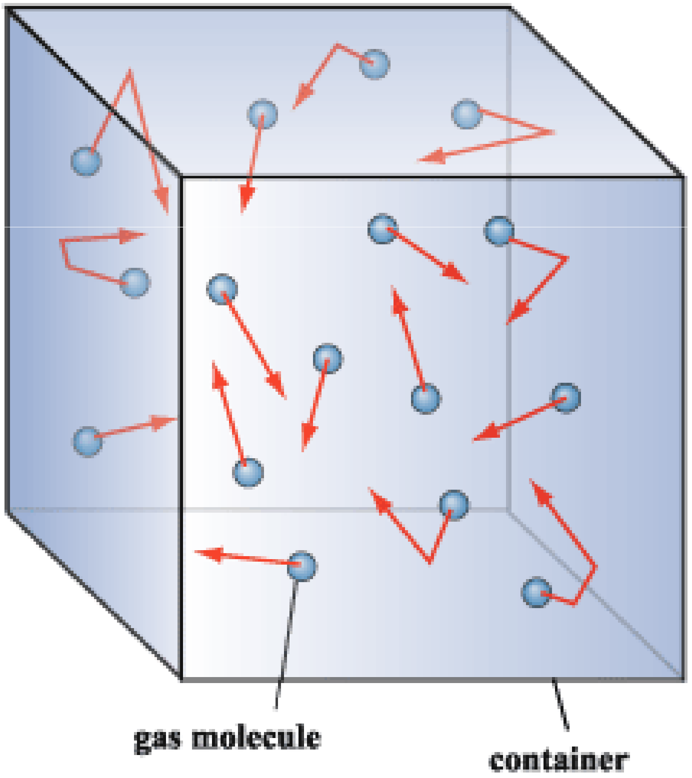
When do you use which scale.

- Never use Fahrenheit, except for the weather.
- You can always use Kelvin and you must use Kelvin when doing absolute temperature measurements.
- You can use either Kelvin or Celsius when measuring differences in temperature.

Heat

- Heat is the random motion of the particles in the gas, i.e. a "degraded" from of kinetic energy.

- Nice web simulation
- gas simulation



Specific Heat

- Observational Fact: It is easy to change the temperature of some things (e.g. air) and hard to change the temperature of others (e.g. water)
- The amount of heat (*Q*) added into a body of mass *m* to change its temperature an amount ΔT is given by

$$Q=m\,C\,\Delta T$$

- C is called the specific heat and depends on the material and the units used.
- Note: since we are looking at changes in temperature, either Kelvin or Celsius will do.

Units of Heat

- Heat is a form of energy so we can always use Joules.
- More common in thermodynamics is the calorie: By definition 1 calorie is the amount of heat required to change the temperature of 1 gram of water 1°C.
- 1 Cal = 1 food calorie = 1000 cal.

Units of Specific Heat

$$C = \frac{Q}{m\Delta T} = \left(\frac{cal}{g^{o}C}\right) = \left(\frac{J}{kg^{o}C}\right)$$

Note that by definition, the specific heat of water is 1 cal/g°C.

Heat Transfer Mechanisms

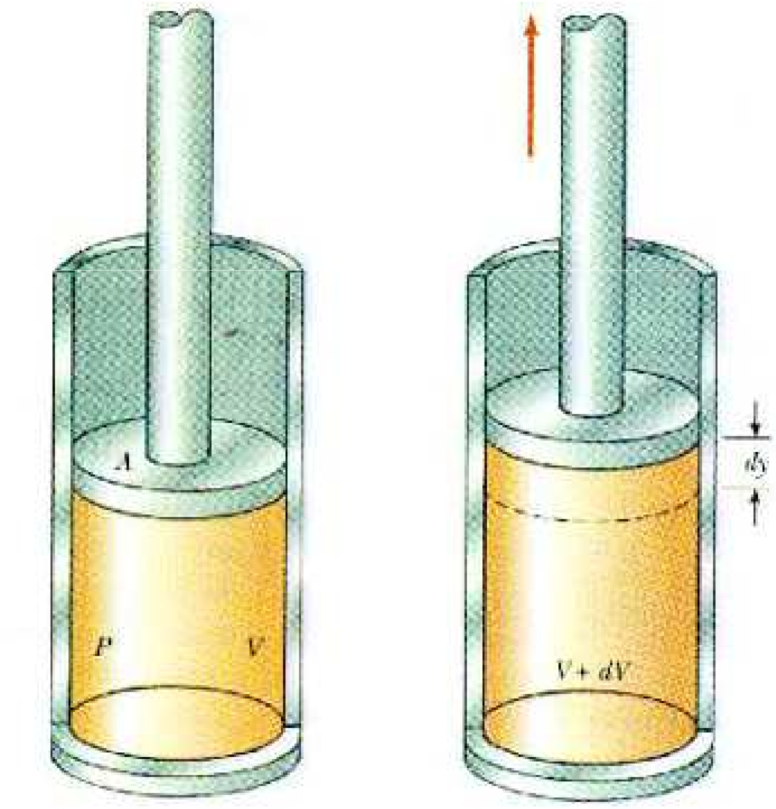
1. Conduction: (solids--mostly) Heat transfer without mass transfer.
2. Convection: (liquids/gas) Heat transfer with mass transfer.
3. Radiation: Takes place even in a vacuum.

Work Done by a Gas

- Work=(Force)x(distance)

  $=F\Delta y$
- Force=(Presssure)x(Area)
- $W=P(A\Delta y)$

  $=P\Delta V$



First Law of Thermodynamics
Conservation of energy

- When heat is added into a system it can either 1) change the internal energy of the system (i.e. make it hotter) or 2) go into doing work.

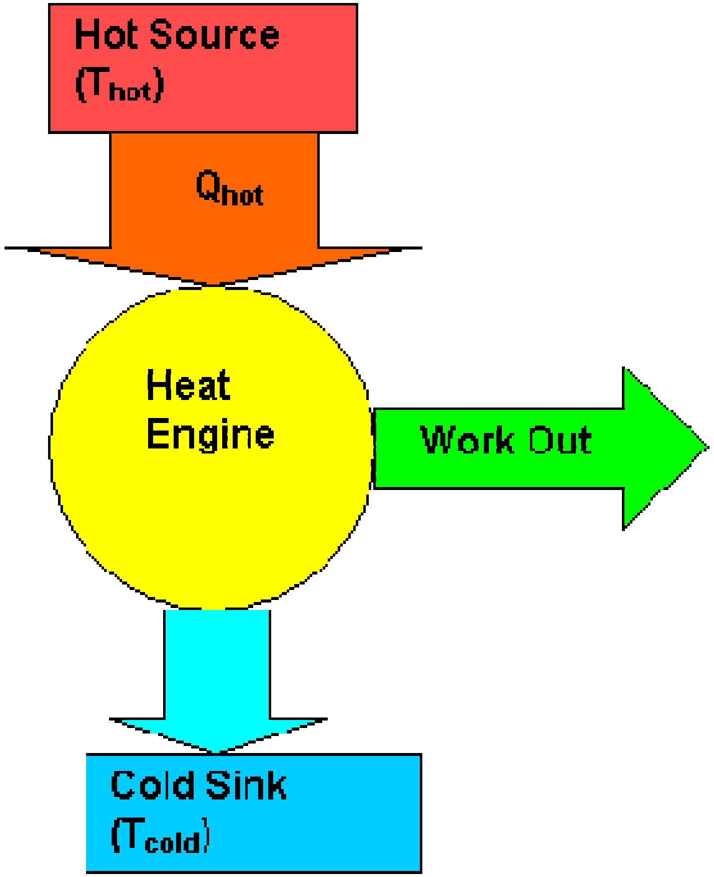
$$Q=W+\Delta U.$$

Heat Engines

- If we can create an “engine” that operates in a cycle, we return to our starting point each time and therefore have the same internal energy. Thus, for a complete cycle

$$Q=W$$

Model Heat Engine



- $Q_{hot} = W + Q_{cold}$

  or

- $Q_{hot} - Q_{cold} = W$

Efficiency

- We want to write an expression that describes how well our heat engine works.
- Q_{hot}=energy that you pay for.
- W=work done (what you want.)
- Q_{cold}= Waste energy (money).

$$\text{Efficiency} = e = W/Q_{hot}$$

- If we had a perfect engine, all of the input heat would be converted into work and the efficiency would be 1.
- The worst possible engine is one that does no work and the efficiency would be zero.
- Real engines are between 0 and 1

$$e=\frac{W}{Q_{hot}}=\frac{Q_{hot}-Q_{cold}}{Q_{hot}}=1-\frac{Q_{cold}}{Q_{hot}}$$

WELCOME

GHULE N B

Thermodynamics and statistical physics

Introduction of statistical physics

T.Y.B.Sc 2018-19

Prof. Ghule N.B.

*Introduction to statistical Mechanics

From the seventeenth century onward it was realized that *material systems* could often be described by a *small number of descriptive parameters* that were related to one another in simple lawlike ways.

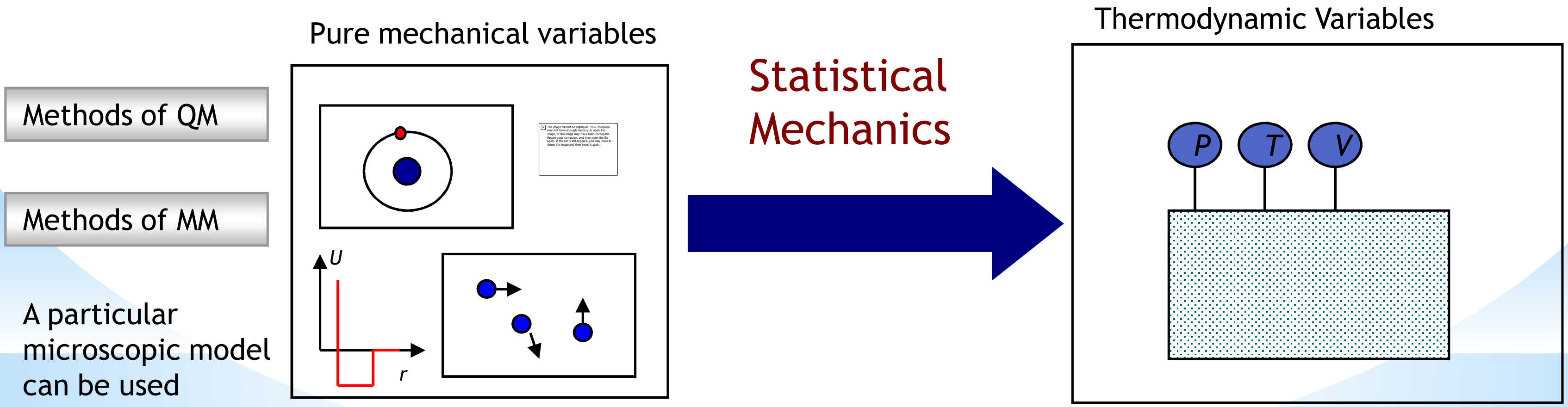
These parameters referred to *geometric, dynamical and thermal properties* of matter.

Typical of the laws was the *ideal gas law* that related product of *pressure* and *volume* of a gas to the *temperature* of the gas.

Microscopic and Macroscopic state

- The main aim of this course is the investigation of general properties of the macroscopic systems with a large number of degrees of dynamically freedom (with $N \sim 10^{20}$ particles for example).
- From the mechanical point of view, such systems are very complicated. But in the usual case only a few physical parameters, say temperature, the pressure and the density, are measured, by means of which the ”state” of the system is specified.
- A state defined in this cruder manner is called a macroscopic state or thermodynamic state. On the other hand, from a dynamical point of view, each state of a system can be defined, at least in principle, as precisely as possible by specifying all of the dynamical variables of the system. Such a state is called a microscopic state.

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



Methods of QM

Methods of MM

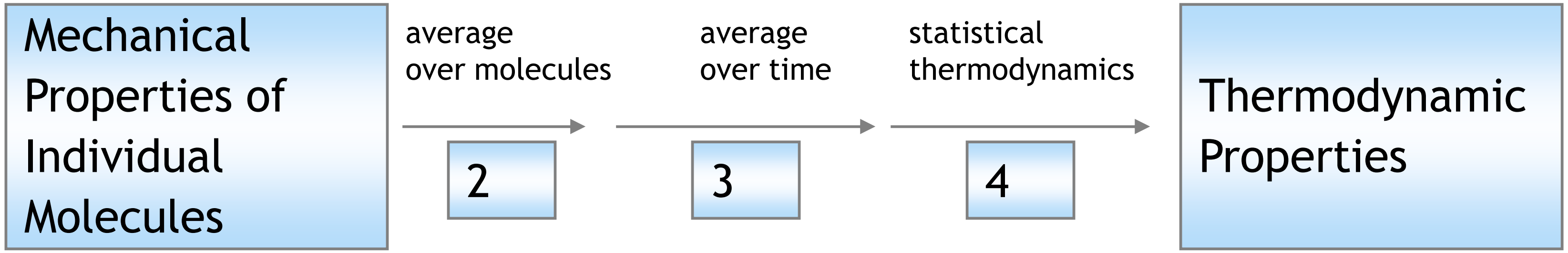
A particular microscopic model can be used

Pure mechanical variables

Statistical Mechanics

Thermodynamic Variables

- Equilibrium Macroscopic Properties
  - Properties are consequence of average of individual molecules
  - Properties are invariant with time → Time average



Mechanical Properties of Individual Molecules

average over molecules

2

average over time

3

statistical thermodynamics

4

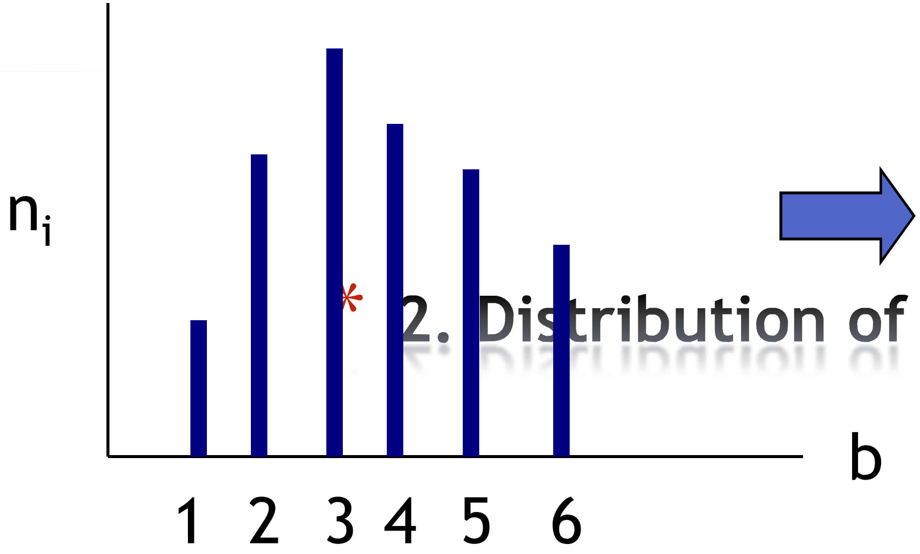
Thermodynamic Properties

position, velocity
energy, ...

temperature, pressure
internal energy, enthalpy,.

- Description of States
  - *Macrostates* : T, P, V, … (fewer variables)
  - *Microstates* : position, momentum of each particles (~10^{23} variables)
- Fundamental methodology of statistical mechanics
  - Probabilistic approach : statistical average
    - Most probable value
  - Is it reasonable ?
    - As N approaches very large number, then fluctuations are negligible
    - “Central Limit Theorem” (from statistics)

- Statistical Distribution
  - n : number of occurrences
  - b : a property

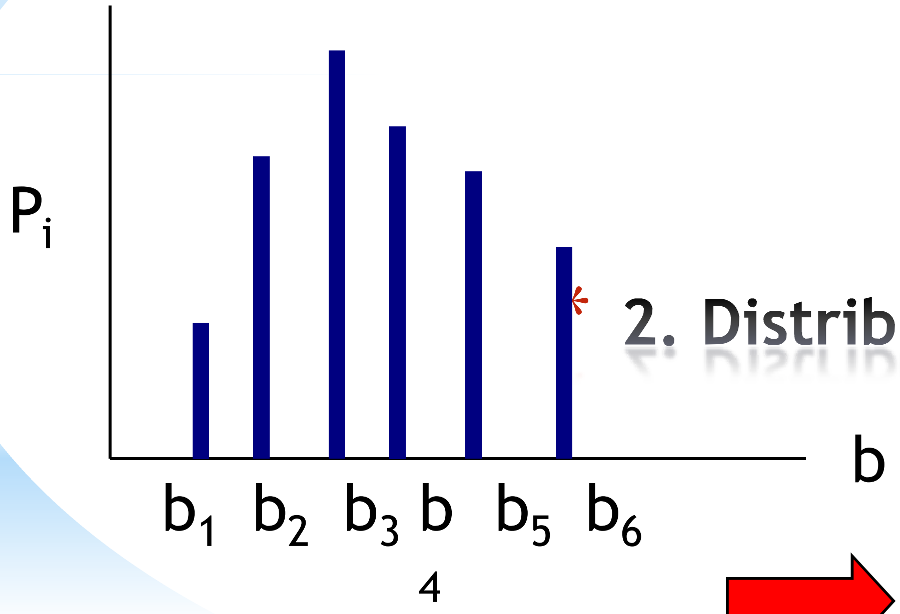


if we know “distribution”
we can calculate the average
value of the property b

- **2. Distribution of Molecular States**

*Normalized Distribution Function

→ Probability Distribution Function



$$P_i(b_i) = \frac{n_i(b_i)}{n} = \frac{n_i(b_i)}{\sum_i n_i(b_i)}$$

$$\sum_i P_i(b_i) = 1$$

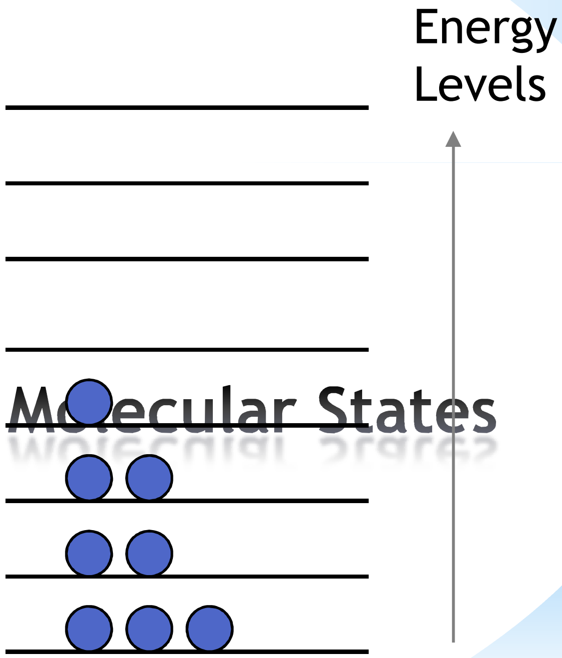
*2. Distributio r States

$$< b >= \sum_i b_i P_i$$

$$< F(b) >= \sum_i F(b_i) P_i$$

Finding probability (distribution) function i
the main task in statistical thermodynam

- Quantum theory says ,
  - Each molecules can have only discrete values of energies
- Evidence
  - Black-body radiation
  - Planck distribution
  - Heat capacities
  - Atomic and molecular spectra
  - Wave-Particle duality

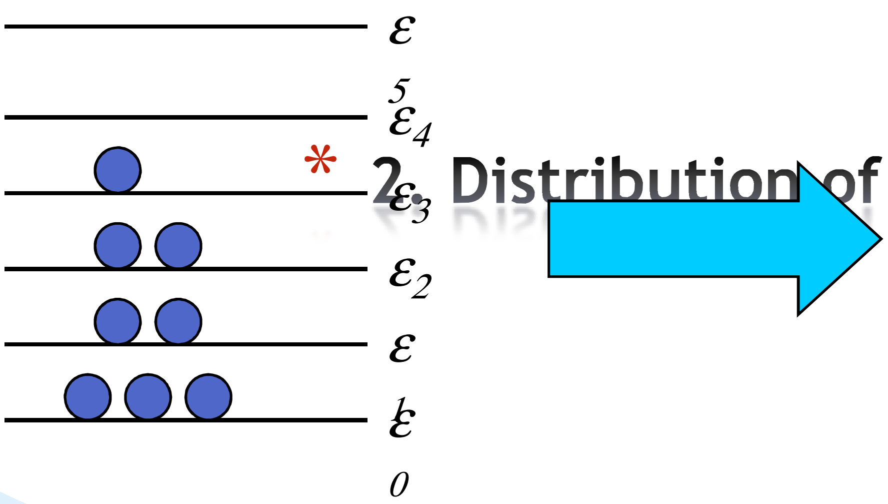


2. Distribution of Molecular States

Configuration ....

- At any instance, there may be n_o molecules at ε_0 , n_1 molecules at ε_1, n_2 molecules at ε_2 , ...

  → $\{n_0 , n_1 , n_2 ...\}$ configuration



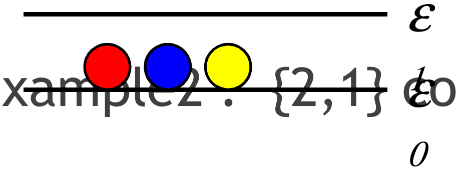
{ 3,2,2,1,0,0}

2. Distribution of Molecular States

Weight ....

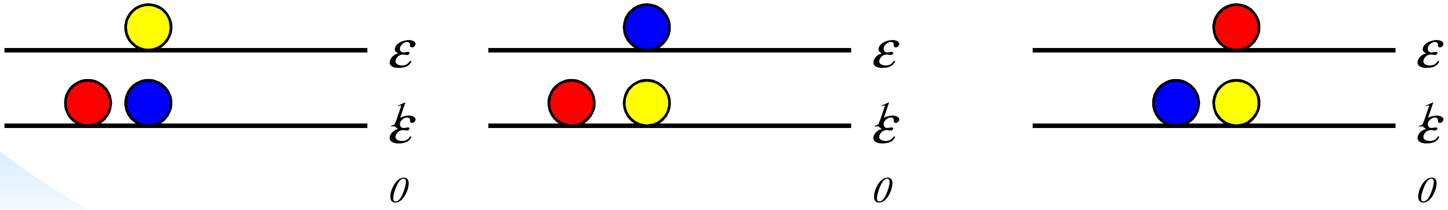
- Each configurations can be achieved in different ways

- Example1 : {3,0} configuration → 1

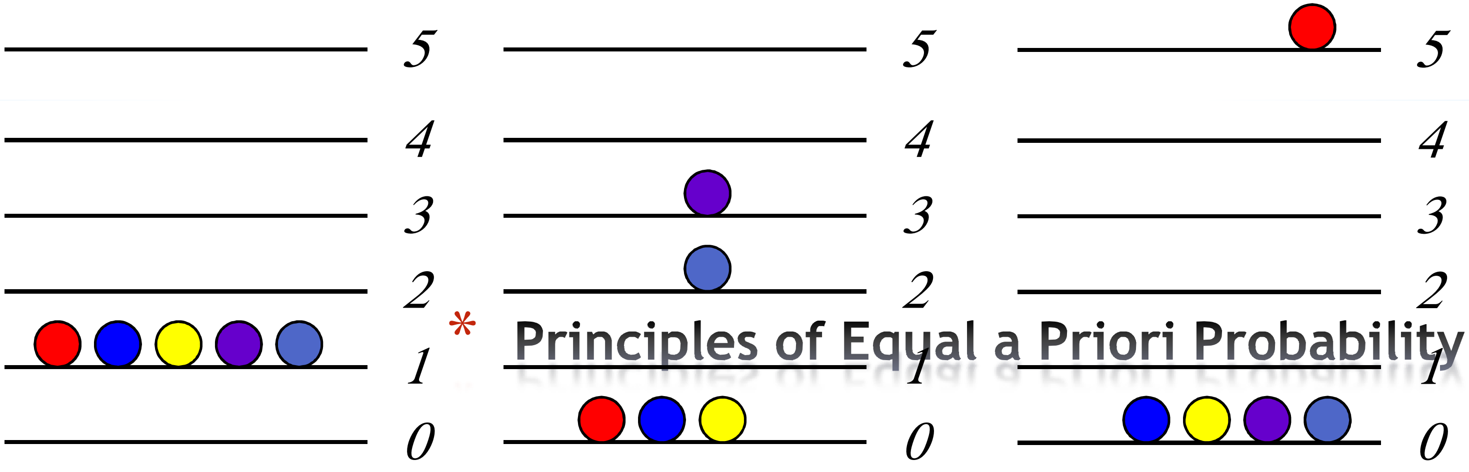


- Example2 : {2,1} configuration → 3

2. Distribution of Molecular States



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



- **Principles of Equal a Priori Probability**

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

- Boltzmann Distribution

- I n Function

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_j e^{-\beta\varepsilon_j}} = \frac{e^{-\beta\varepsilon_i}}{q}$$

- Degeneracies : Same energy value but d states (g_j-fold degenerate)

$$q = \sum_j e^{-\beta\varepsilon_j}$$

The Molecular Partition Function

$$q = \sum_{\substack{levels \\ j}} g_j e^{-\beta\varepsilon_j}$$

- Similar method (Section 2) can be used to get most probable distribution

$$P_i = \frac{n_i}{N} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}$$

$$P_i = \frac{n_i}{N} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_i}}{Q}$$

Canonical Partition Function

$$Q = \sum_j e^{-\beta E_j}$$ → Canonical Partition Function

How to obtain beta ? - Another interpretation

$$dU = d(\sum_i E_i P_i) = \sum_i E_i dP_i + \sum_i P_i dE_i$$

$$dU = \delta q_{rev} - \delta w_{rev} = TdS - pdV$$

$$\sum_i P_i dE_i = \sum_i P_i \left(\frac{\partial E_i}{\partial V}\right)_N dV = -PdV = -\delta w_{rev}$$

$$\sum_i E_i dP_i = -\frac{1}{\beta}(\sum_i \ln P_i dP_i + \ln Q \sum_i dP_i) = -\frac{1}{\beta}\sum_i \ln P_i dP_i = TdS = dq_{rev}$$

The only function that links heat (path integral) and state property is TEMPERATURE.

$$\beta = 1/kT$$

*Internal Energy

$$U =< E >= \sum_{i} E_i P_i == \frac{1}{Q} \sum_{i(qs)} E_i e^{-\beta E_i}$$

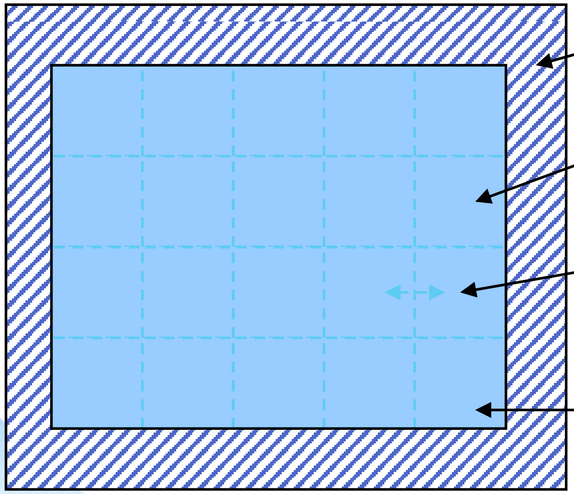
$$\left(\frac{\partial Q}{\partial \beta}\right)_{N,V} = -\sum_{i(qs)} E_i e^{-\beta E_i}$$

$$U = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{N,V} = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$$

Properties from Canonical Partition Function

Grand Canonical Ensemble

- Ensemble approach for open system
  - Useful for open systems and mixtures
  - Walls are replaced by permeable walls



Large reservoir (constant T)

All the ensemble members have the same (V,

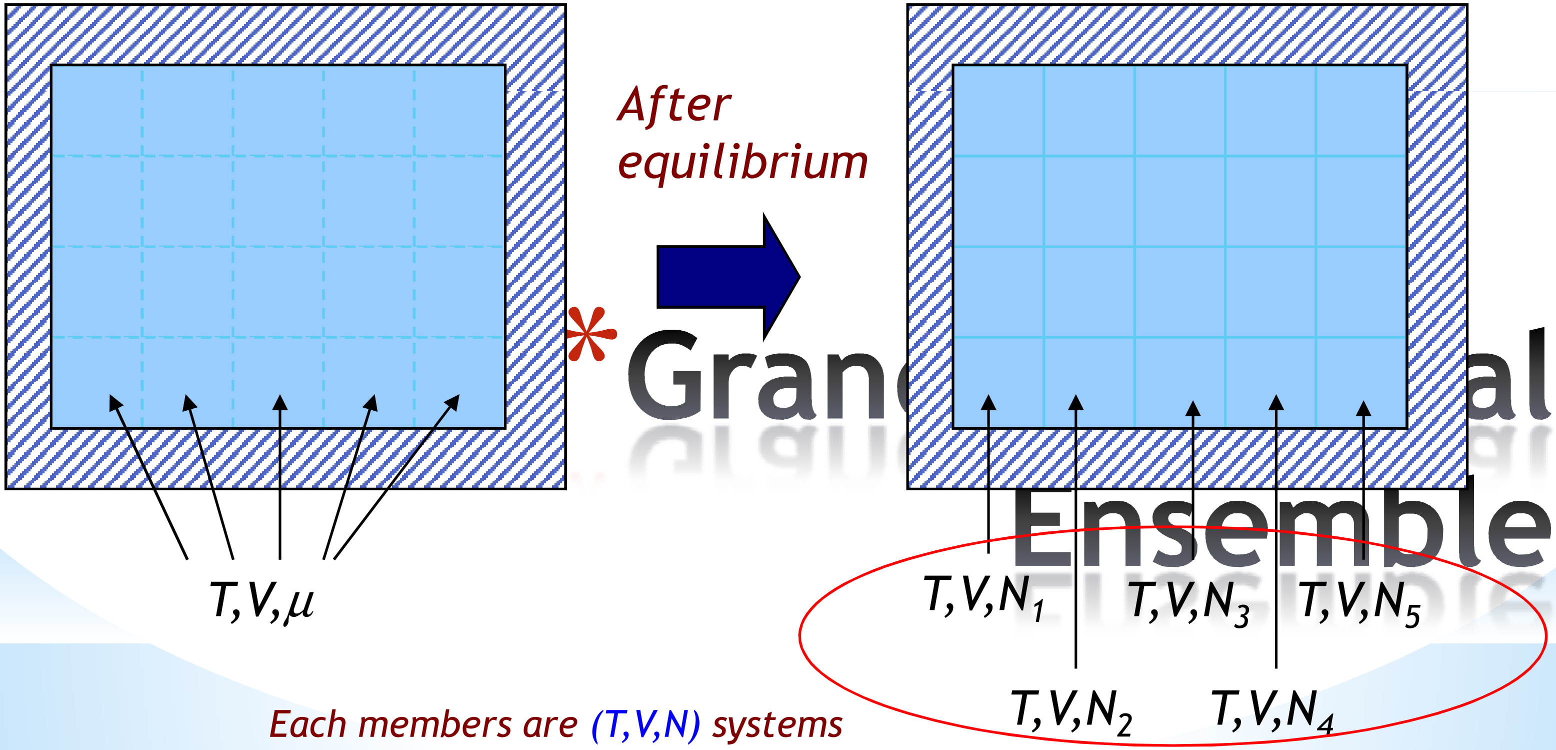
Energy and particles can be exchanged

Number of Systems : N

N → ∞

- Similar approach as Canonical Ensemble
  - We cannot use second postulate because *systems are not isolated*
  - After equilibrium is reached, we place walls around ensemble and treat each members the same method used in canonical ensemble

Gran al Ensemble



Each members are (T,V,N) systems
→ Apply canonical ensemble methods for each member

- The formalism of statistical mechanics relies very much at the microscopic states.
  - Number of states , sum over states
  - convenient for the framework of quantum mechanics
- What about “Classical Sates” ?
  - Classical states
    - We know *position* and *velocity* of all particles in the system
  - Comparison between Quantum Mechanics and Classical Mechanics

4. Classical Statistical Mechanics

QM Problem $H\psi = E\psi$ $\longrightarrow$ *Finding probability and discrete energy states*

CM Problem $F = ma$ $\longrightarrow$ *Finding position and momentum of individual m*

THANK YOU

WEL COME

Heat and Thermodynamics

Introduction of thermodynamics

F.Y.B.Sc – 2018-19

Prof. Ghule N.B.

Thermodynamics

Temperature, Heat, Work
Heat Engines

Introduction

- In mechanics we deal with quantities such as mass, position, velocity, acceleration, energy, momentum, etc.
- Question: What happens to the energy of a ball when we drop it on the floor?
- Answer: It goes into heat energy.

- In *Thermodynamics* we deal with quantities which describe our system, usually (but not always) a gas.
- Volume, Temperature, Pressure, Heat Energy, Work.

- We all know about Volume.
- Pressure:

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

Demonstrations: Balloons, Bed of Nails, Magdeburg hemispheres.

Temperature and Heat

- Everyone has a qualitative understanding of temperature, but it is not very exact.
- Question: Why can you put your hand in a 400° F oven and not get instantly burned, but if you touch the metal rack, you do?
- Answer: Even though the air and the rack are at the same temperature, they have very different energy contents.

Construction of a Temperature Scale

- Choose fixed point temperatures that are easy to reconstruct in any lab, e.g. freezing point of water, boiling point of water, or anything else you can think of.
- Fahrenheit: Original idea:

  0°F Freezing point of Salt/ice

  100°F Body Temperature

Using this ice melts at 32°F and water boils at 212°F (Not overly convenient) Note: 180°F between boiling an freezing.

- Celsius (Centigrade) Scale:

  0°C - Ice Melts

  100°C - Water Boils

Note a change of 1°C = a change of 1.8°F.

Conversion between Fahrenheit and Celsius

If we know Celsius and want Fahrenheit

$$F = \frac{9}{5}C + 32$$

If we know Fahrenheit and want Celsius

$$\mathrm{C} = \frac{5}{9}\left(F - 32\right)$$

Absolute or Kelvin Scale

- The lowest possible temperature on the Celsius Scale is -273°C.
- The Kelvin Scale just takes this value and calls it 0K, or absolute zero.
- Note: the "size" of 1K is the same as 1°C.
- To convert from C to K just add 273.

$$K=C+273$$

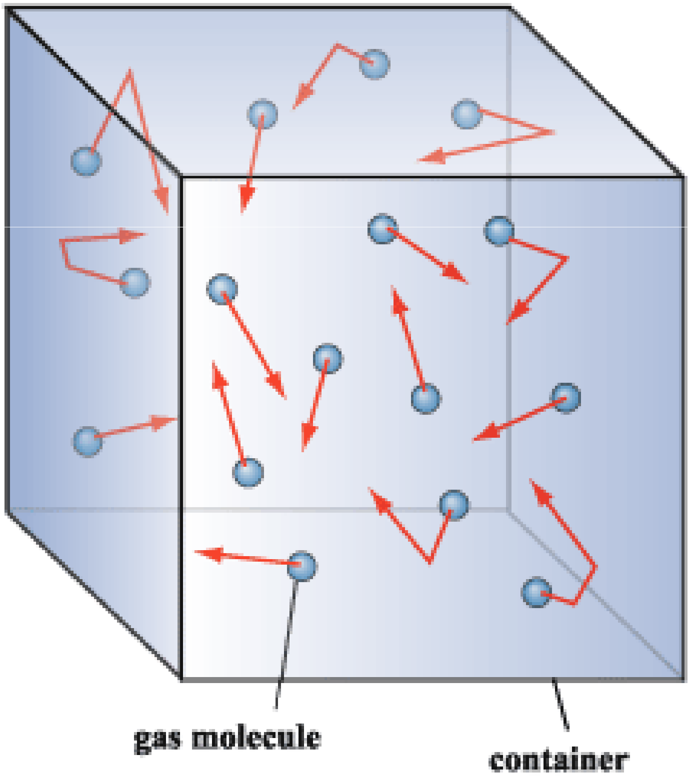
When do you use which scale.

- Never use Fahrenheit, except for the weather.
- You can always use Kelvin and you must use Kelvin when doing absolute temperature measurements.
- You can use either Kelvin or Celsius when measuring differences in temperature.

Heat

- Heat is the random motion of the particles in the gas, i.e. a “degraded” from of kinetic energy.

- Nice web simulation
- gas simulation



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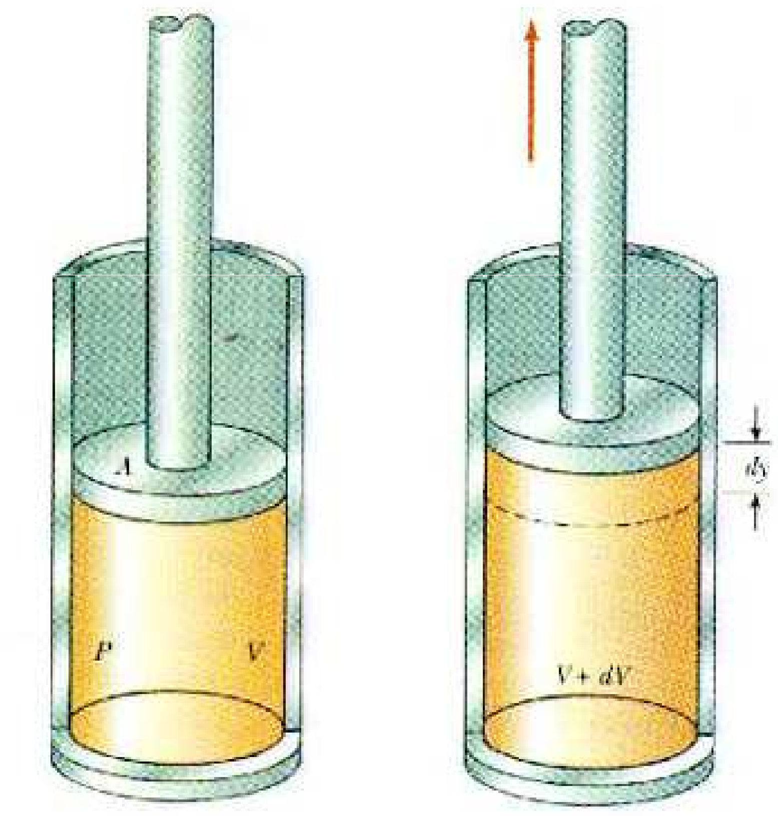

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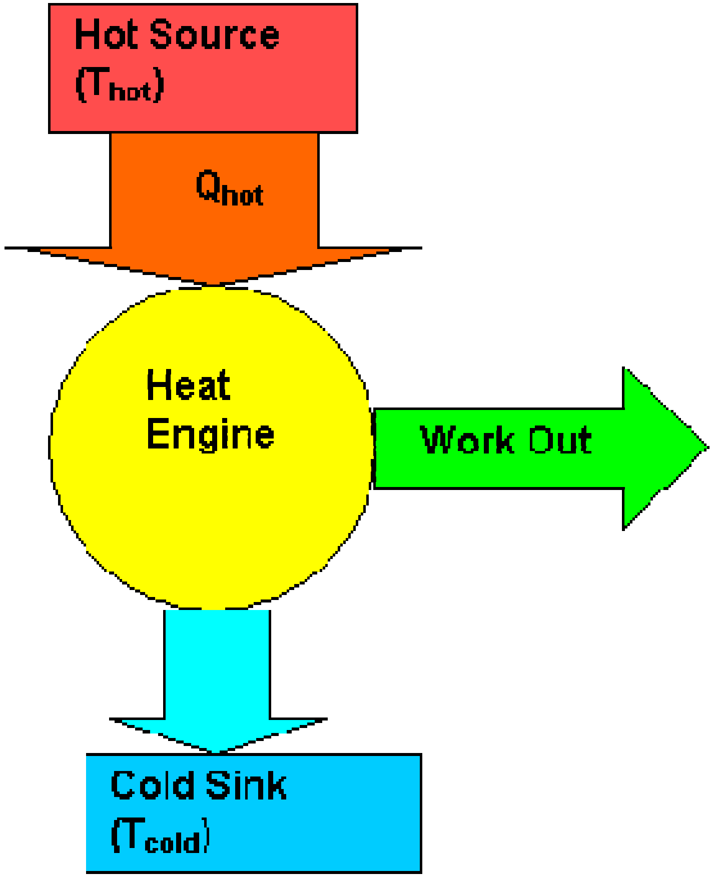

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$$e = \frac{W}{Q_{hot}} = \frac{Q_{hot} - Q_{cold}}{Q_{hot}} = 1 - \frac{Q_{cold}}{Q_{hot}}$$

Thank You