THERMAL & STATISTICAL PHYSICS
SSP3133

INTRODUCTION

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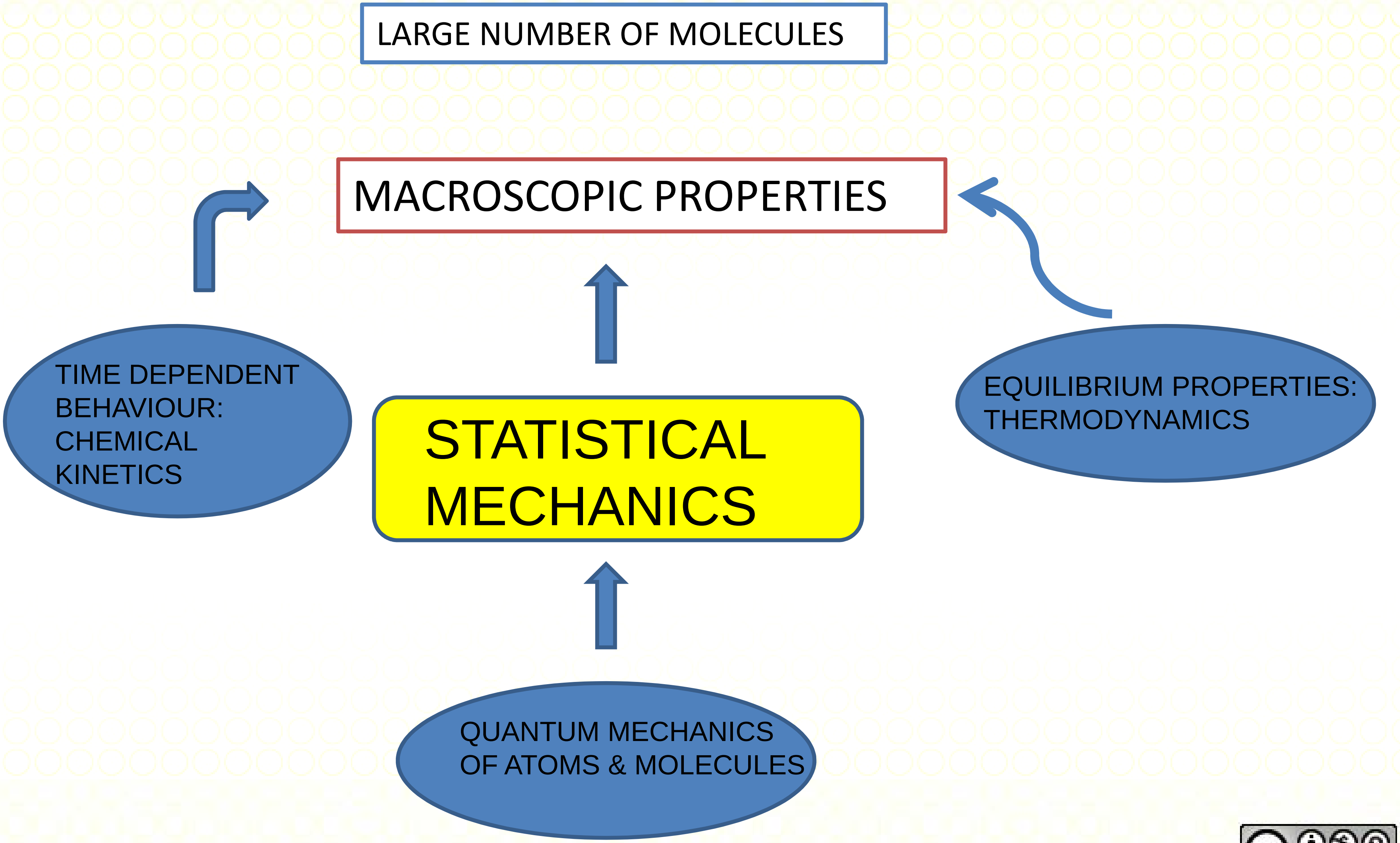
Acknowledgement : PROFESSOR DR RAMLI ABU HASSAN



LARGE NUMBER OF MOLECULES

MACROSCOPIC PROPERTIES

TIME DEPENDENT BEHAVIOUR: CHEMICAL KINETICS

STATISTICAL MECHANICS

EQUILIBRIUM PROPERTIES: THERMODYNAMICS

QUANTUM MECHANICS OF ATOMS & MOLECULES

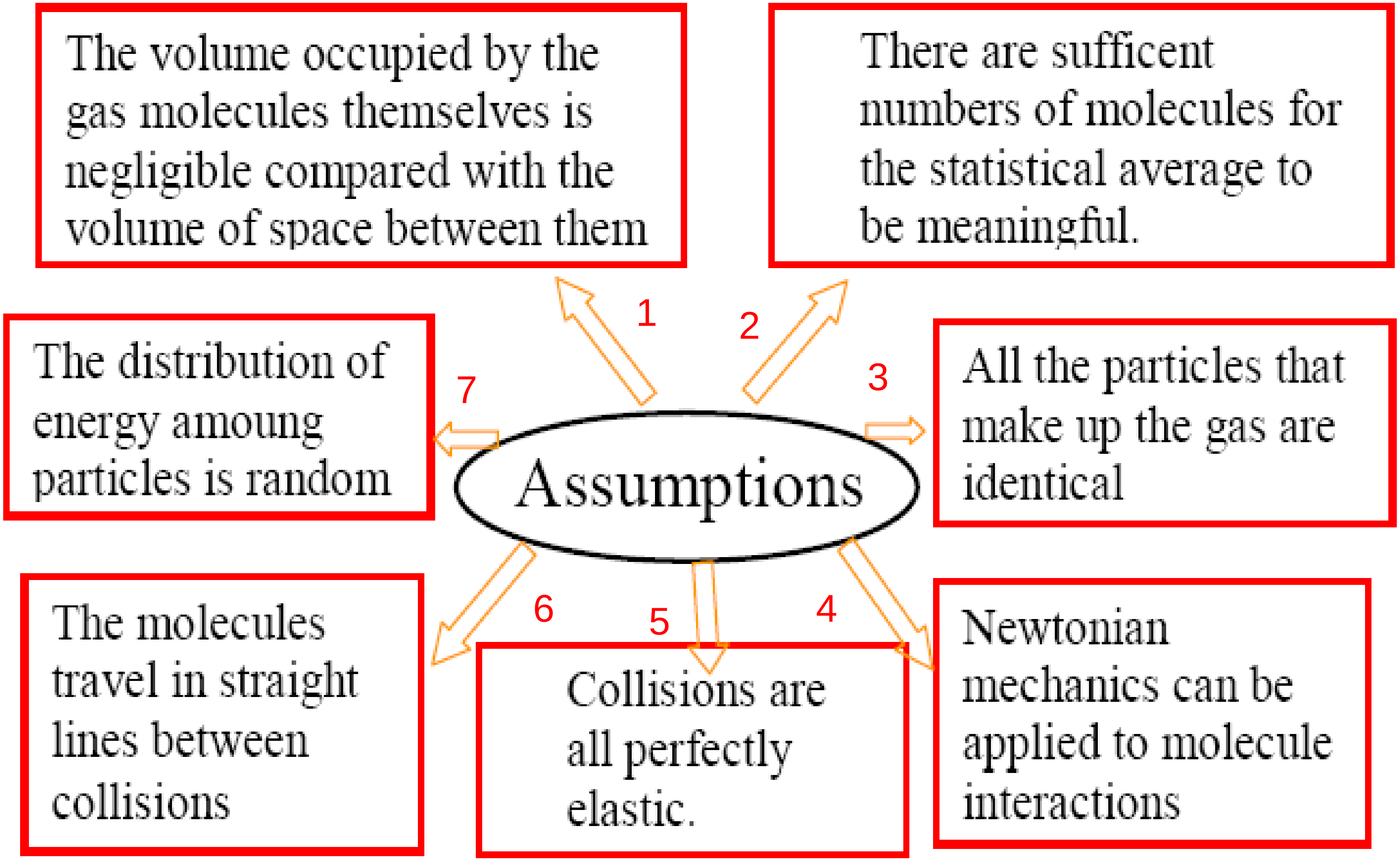
THE KINETIC THEORY OF GASES

Kinetic Theory or Kinetic theory of gases explains macroscopic properties of gases such as the pressure P, temperature T or volume V by considering their molecular composition and motion.

Ideal Gases:

- modeling the gas as molecules (or atoms) in constant motion in space.
- as a mathematical explanation of the behaviour of gas.
- the kinetic energy, KE depends on the temperature of the gas.

The kinetc theory makes seven assumptions:



Assumptions

1 The volume occupied by the gas molecules themselves is negligible compared with the volume of space between them

2 There are sufficent numbers of molecules for the statistical average to be meaningful.

3 All the particles that make up the gas are identical

4 Newtonian mechanics can be applied to molecule interactions

5 Collisions are all perfectly elastic.

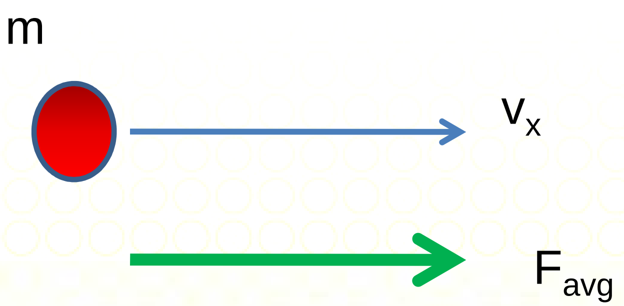
6 The molecules travel in straight lines between collisions

7 The distribution of energy amoung particles is random

The kinetic theory of gases -- deduced equations that related the easily observable properties such as P, ρ, V and T to properties not easily or directly observable -such as the sizes and speeds of molecules.

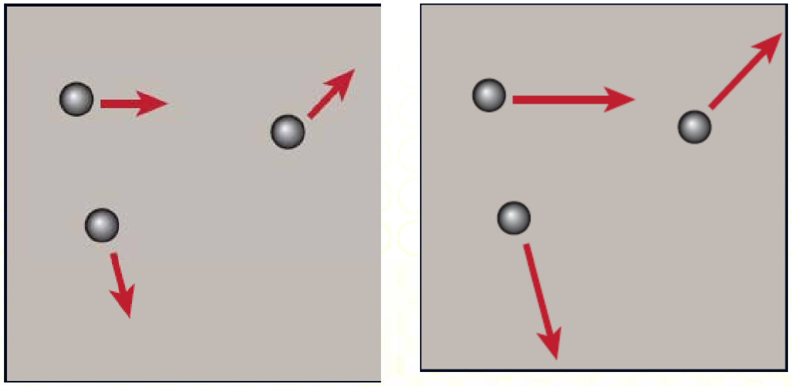
Pressure

- The pressure of a gas is caused by collisions of the molecules of the gas with the walls of the container.
- The magnitude of the pressure is related to how hard and how often the molecules strike the wall



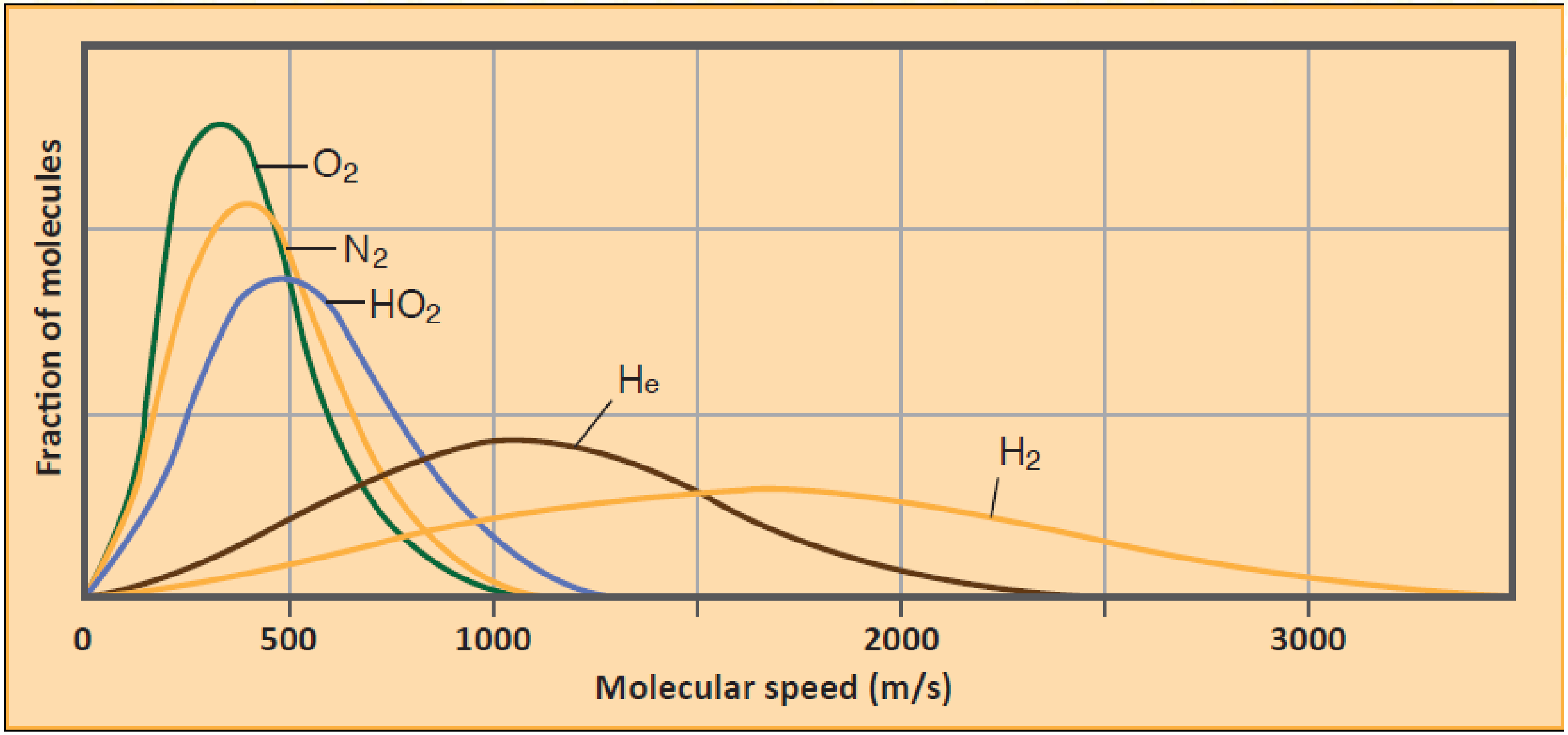
Absolute Temperature

- The absolute temperature of a gas is a measure of the average kinetic energy of its' molecules
- If two different gases are at the same temperature, their molecules have the same average kinetic energy
- If the temperature of a gas is ***doubled***, the average kinetic energy of its molecules is ***doubled***



Molecular Speed

- All the molecules ⇒average kinetic energy (and therefore an average speed)
- the individual molecules move at various speeds, →exhibit a DISTRIBUTION of speeds
- Collisions can change individual molecular speeds but the distribution of speeds remains the same.
- At the same temperature, lighter gases move on average faster than heavier gases.



- The average kinetic energy, ν, is related to the ***root mean square*** (rms) speed **u**

$$\boxed{\upsilon = \frac{1}{2} m u^2}$$

Statistical mechanics

Statistical mechanics is the application of probability theory to the field of mechanics, which is concerned with the motion of particles or objects when subjected to a force.

-relating the microscopic properties of individual atoms and molecules to the macroscopic or bulk properties of materials that can be observed in everyday life

-it can be used to calculate the thermodynamic properties of bulk materials from the spectroscopic data of individual molecules.

The fundamental Postulate in Statistical Mechanics:

Given an isolated system in equilibrium, it is found with equal probability in each of its accessible microstates.

This postulate is necessary because it allows one to conclude that for a system at equilibrium, the thermodynamic state (macrostate) which could result from the largest number of microstates is also the most probable macrostate of the system.

- Fundamental concepts: microstate, macrostates, accessible states, ensemble, the fundamentals postulate

- Microcanonical and canonical ensembles and their applications

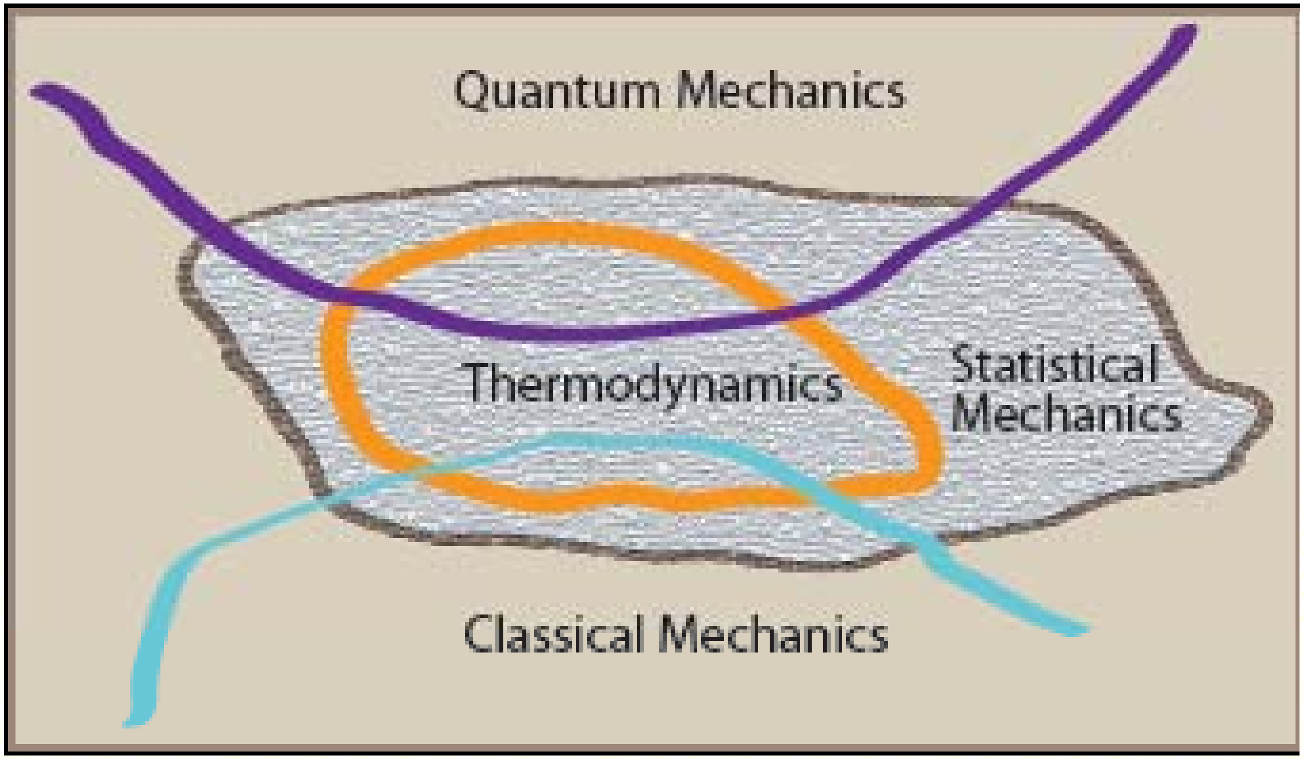
- Open systems, chemical potential. Grand canonical ensemble

- Distinguishable and indistinguishable particles

- Bose-Einstein and Fermi-Dirac statistics and their applications

Thermal Physics

Thermal physics is the study of the statistical nature of physical systems from an energetic perspective.



It include,

i. Thermodynamics – macroscopic theory, essentially completed by Carnot 1824

ii. Kinetic theory – microscopic theory of molecular distribution
   i. Maxwell
   ii. Boltzmann

iii. Ensemble theory of statistical mechanics – all thermodynamics informations can be derived from the partition function – formulated by Gibbs in 1902

Macroscopic & Microscopic systems

-*macroscopic* when it is large enough to be visible in the ordinary sense

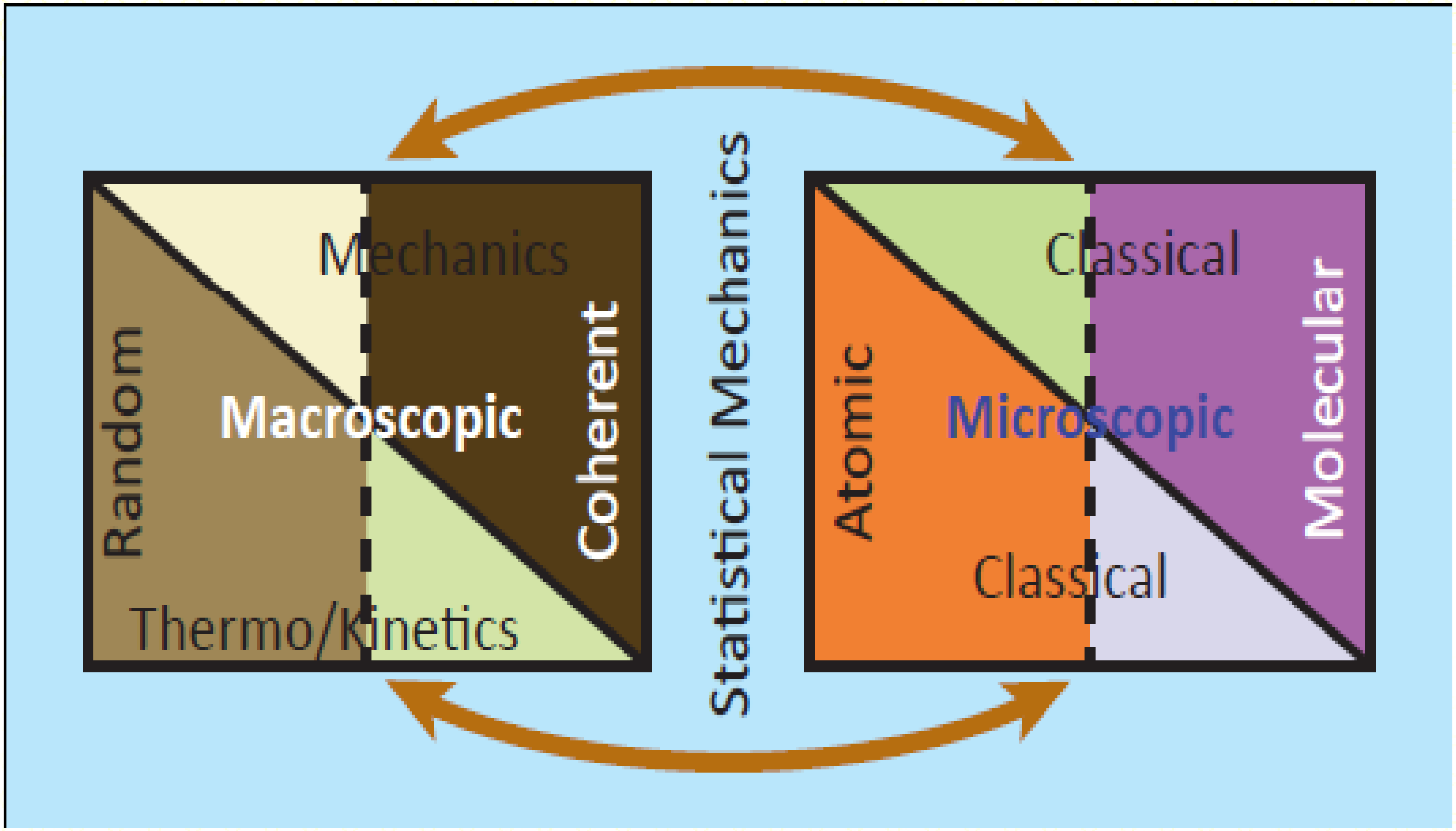
-*microscopic* if it is roughly of atomic dimensions, or smaller

If N is the number of particles in the system

- A system is macroscopic if

$$\sqrt{N} >> 1$$

- And is microscopic if the other way around.


Mechanics
Random
Macroscopic
Coherent
Thermo/Kinetics
Statistical Mechanics
Classical
Atomic
Microscopic
Molecular
Classical

Microscopic descriptions

Describes the system in highest degree of detail. (e.g. positions and velocities/momentums of all the atoms in the system).

Macroscopic descriptions

Overall state of the system: averaging over large number of entities (atoms or molecules). (e.g. pressure).

Instruments measure averages over a large number of atoms or molecules.

Understanding of a particular system: to relate macroscopic measurements to theoretical descriptions of the microscopic entities.

The Microscopic View

Thermodynamics properties like T & P can be related to microscopic quantities.

e.g T --in terms of a molecular velocity.

P --collisions of molecules with the walls of a container.

Levels of Description and Observation:

Mechanics: small number of particles (single molecule): single simulation --one single molecule experiment

Stochastisch: several particles (molecules): several simulations -- several single molecule Experiments

Statistics: huge number of particles and events: macroscopic measurement

Wave – particle duality

-light and matter exhibit properties of both waves and particles

Einstein: the electrons were knocked free of the metal by incident photons, with each photon carrying an amount of energy *E* that was related to the frequency, *v* of the light by

$$E = h\nu$$

h: Plank's constant (6.626 x 10^{-34} J seconds).

de Broglie: all matter has a wave-like nature; and related wavelength, λ and momentum, *p*:

$$\lambda = \frac{h}{p}$$

note: for photon; $p = E / c$ and $\lambda = c / \nu$.

where *c* is the speed of light in vacuum

Uncertainty principle

Heisenberg: certain specific pairs of variables cannot be measured simultaneously with high accuracy.

e.g: within an atom - possible to measure the position (Δx), or the momentum (Δp), of a subatomic particle (electron,..) but not possible to measure both of them at the same time.

-because the measuring process interferes to a substantial degree with what is being measured.

Formulation and characteristics

At atomic dimensions

–particle is not like a hard sphere

-the smaller the dimension→the more wave-like it becomes

Using light to identify the location or motion of an electron, the photon of light will influence the electron's motion and position.

Mathematically, the uncertainty principle looks like:

$$\Delta x \Delta p \geq h$$

Where Δx = the uncertainty in position
Δp = the uncertainty in momentum
h= Planck's constant

A sine wave:

λ - wavelength

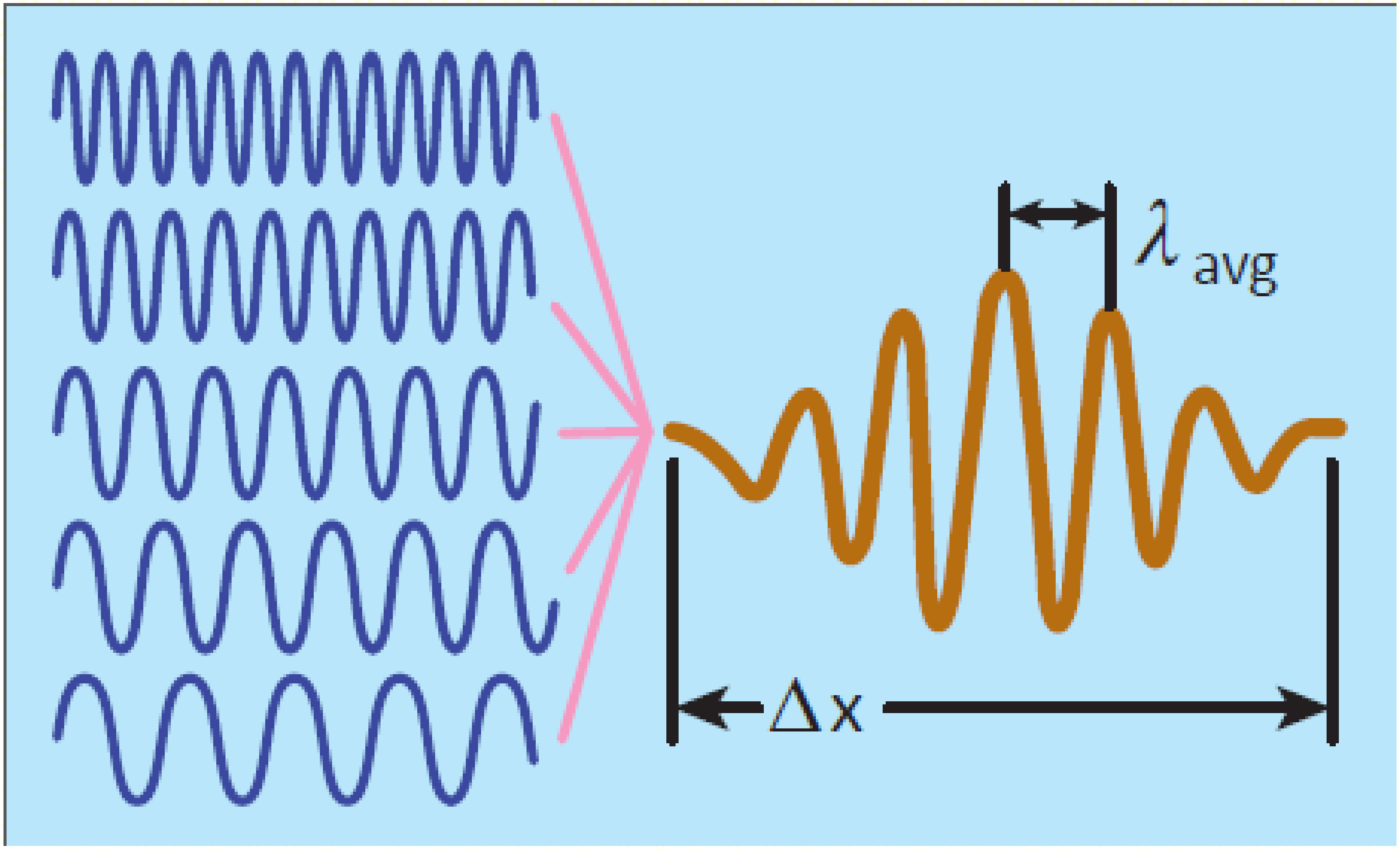
Momentum is precisely known, $p = h / \lambda$

The position, Δx is unknown

Adding several waves of different λ

-Localize the wave (position is certain)

-The momentum is uncertain (each different wavelength represents different momentum)


λ_{avg}
Δx

Application

-to caculate energy which would be required to keep a particle within a given volume.

Example: energy to keep an electron inside an atom.

Assume: the diameter of the atom = 4 A = Δx

$\Delta p = h / \Delta x$

$h = 6.626 \times 10^{-34}$ J-s

$\Delta p = h / \Delta x = 6.626 \times 10^{-34}$ J-s / 4×10^{-10} m

$= 1.\ 6565 \times 10^{-24}$ kgm/s

$E = \frac{1}{2} mV^2 = (mV)^2/(2m) = p^2/(2m)$

$m = 9.11 \times 10^{-31}$ kg (electron mass)

$1\ ev = 1.6 \times 10^{-19}$ J

$$E = \frac{1.6565\mathrm{x}10^{-24} \quad \mathrm{kgm/s}}{2\left(9.11\mathrm{x}10^{-31}\ \mathrm{kg}\right)\left(1.6\mathrm{x}10^{-19} \quad \mathrm{J/ev}\right)}$$

$= 9.4$ ev

Quantized Energy States

Max Planck suggested that energy is transferred in "packets" called quanta (plural).

Quantum: the smallest quantity of energy that can be emitted or absorbed as electromagnetic energy

Bohr model (1913)

-electrons were orbiting the nucleus

-when a charge traveling in a circular path should lose energy by emitting electromagnetic radiation

-it should end up spiraling into the nucleus (which it does not).

Classical physical laws inadequate to explain the inner workings of the atom

-idea of quantized energy from Planck

-only orbits of certain radii, corresponding to defined energies, are "permitted"

-An electron orbiting in one of these "allowed" orbits:

- Has a defined energy state
- Will not radiate energy
- Will not spiral into the nucleus

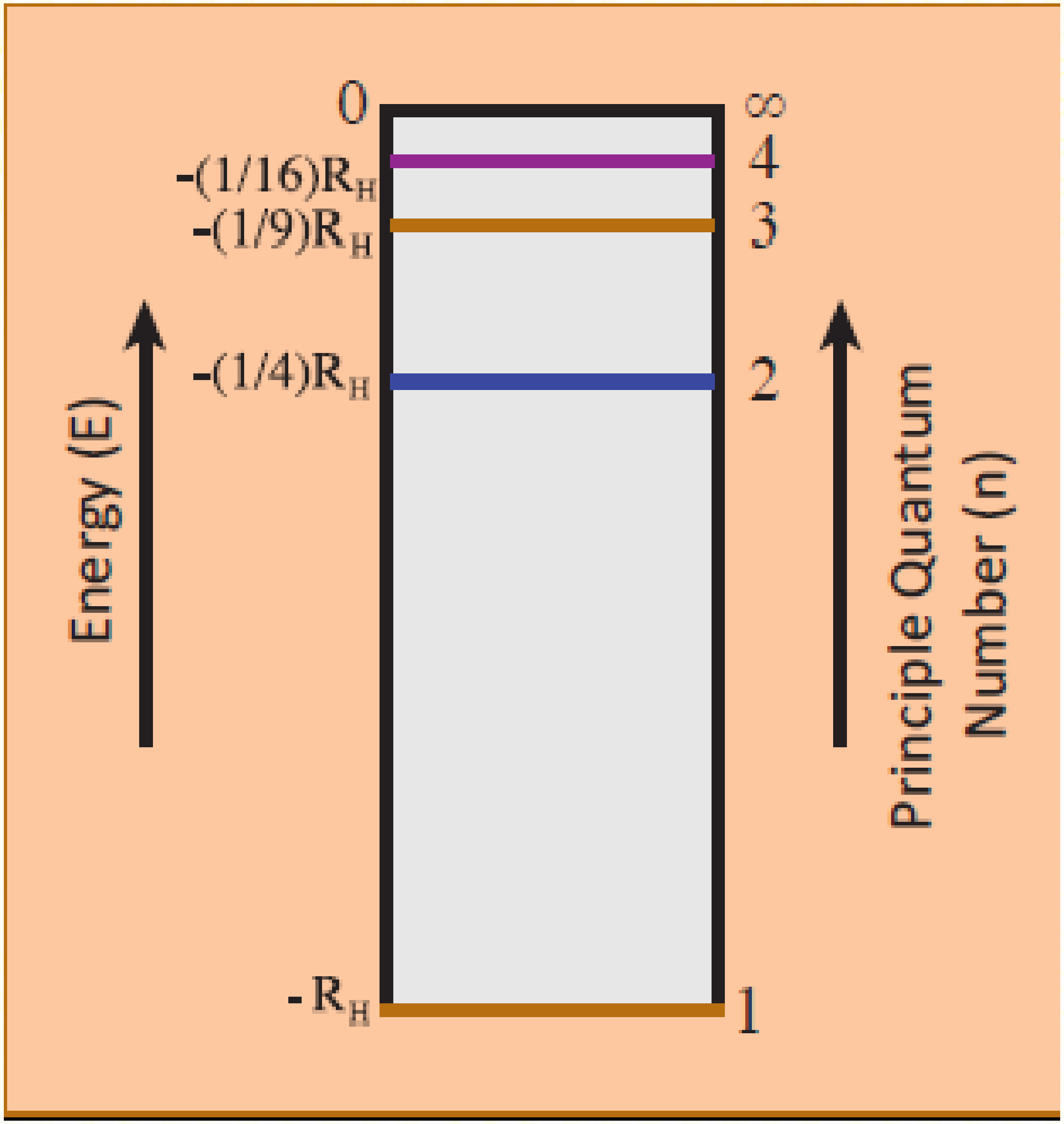
Electron energy:

$$E_n = (-R_H)\left(\frac{1}{n^2}\right)$$

$R_H = 2.18 \times 10^{-18}$ J ***Rydberg constant***

n: the ***principle quantum number***, ***$n = 1, 2, 3, \ldots$..***

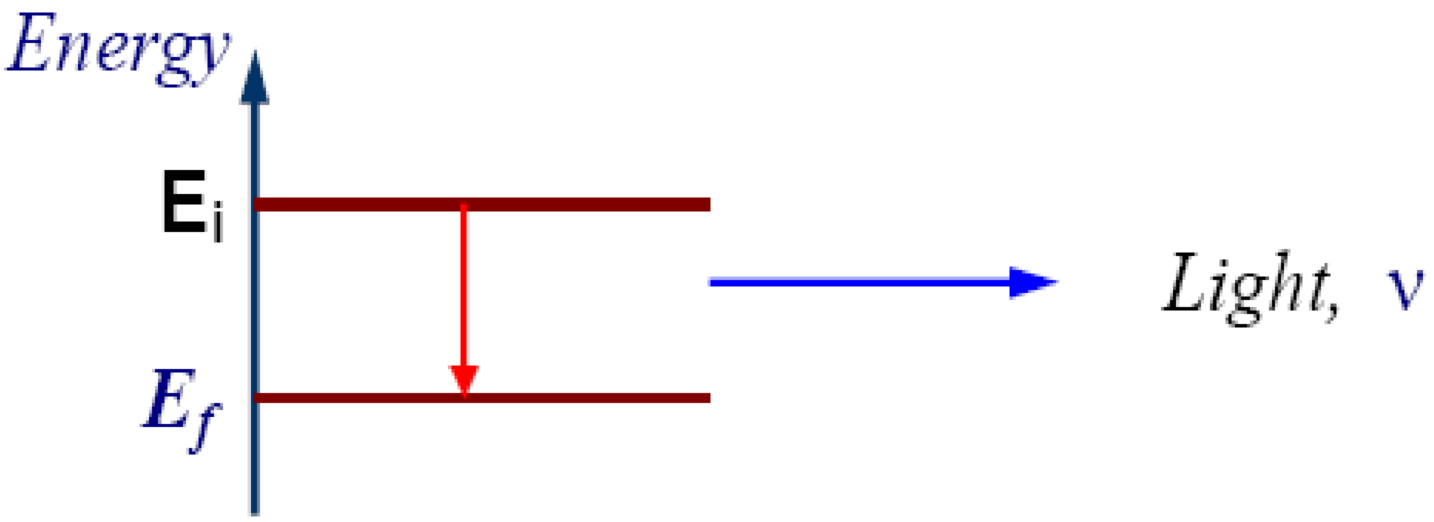
n --corresponds to the different allowed orbits for the electron.


0
-(1/16)R_H
-(1/9)R_H
-(1/4)R_H
- R_H
∞
4
3
2
1
Energy (E)
Principle Quantum Number (n)

Emission of light corresponds to a ***transition*** of the atoms between two states

Frequency of emitted light

$$h\upsilon = \Delta E = E_i - E_f \qquad \& \qquad \upsilon = \frac{E_i - E_f}{h}$$



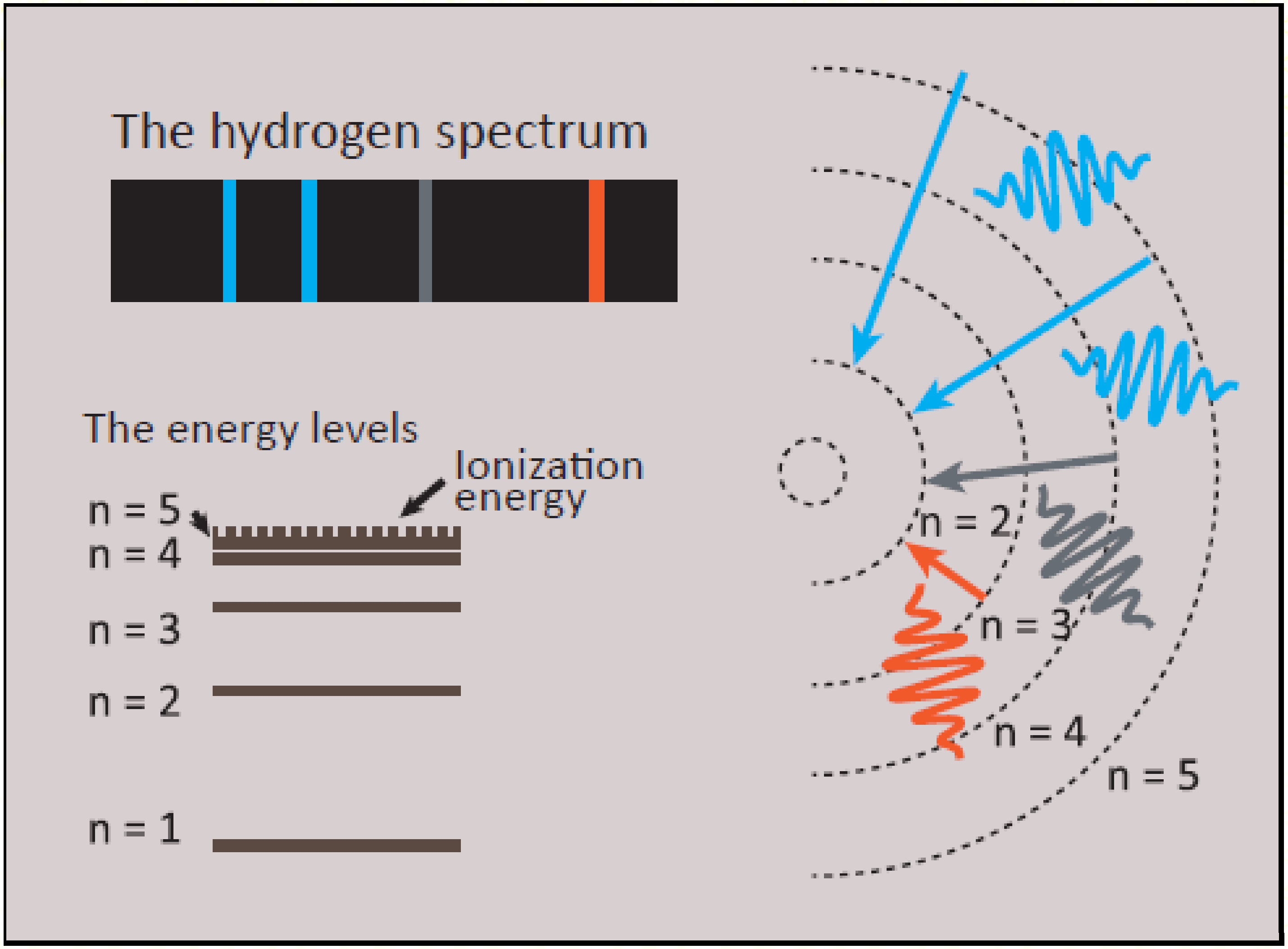
Consequence of Bohr's deduction

1. Each atom can be represented by an energy diagram
2. Distance between two energy levels gives a particular

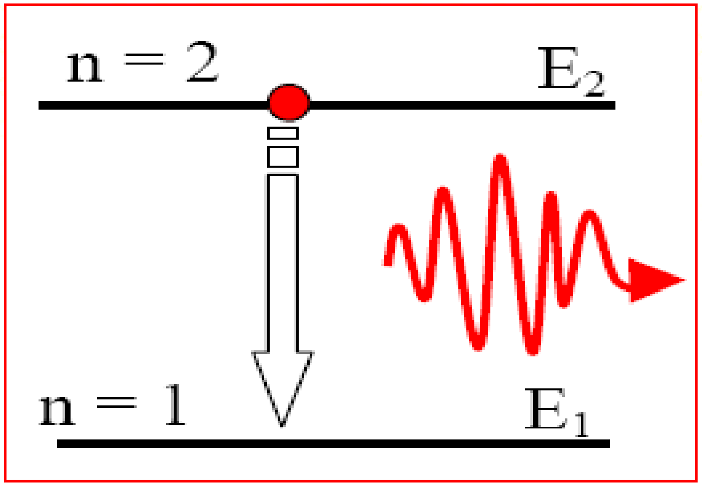
ν → *the energy of atoms is quantized*

The implications --only certain photon energies are allowed when electrons jump down from higher levels to lower levels

→ producing the spectrum.


The hydrogen spectrum
The energy levels
Ionization energy
n = 5
n = 4
n = 3
n = 2
n = 1
n = 2
n = 3
n = 4
n = 5

An electron transition between quantized energy levels with different quantum numbers n yields a photon by emission with quantum energy E_{photon}.



$$E_{photon} = h\nu = E_2 - E_1$$

$$h\nu = \frac{2\pi^2 me^4}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = 13.6\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ eV}$$

for transition from n = 2 to n = 1

$$h\nu = 13.6\left[1 - \frac{1}{4}\right] = 10.2 \quad \text{eV}$$

$$\nu = 10.2 \text{ eV} / h$$

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J} \qquad h = 6.626 \times 10^{-34} \text{ J.s}$$

$$\nu = (10.2 \times 1.6 \times 10^{-19} \text{ J}) / (6.626 \times 10^{-34} \text{ J.s})$$

$$= 121.95 \text{ nm (UV)}$$

Planck's theory:

- Energy is always emitted or absorbed in whole number multiples of hν (i.e hν, 2hν, 3hν)

-the energy levels that are allowed are 'quantized.'

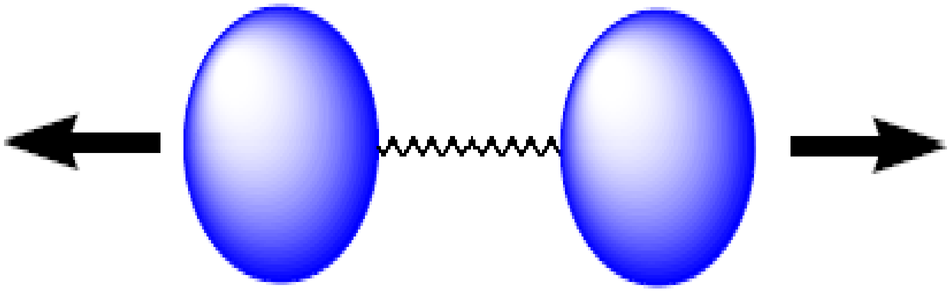
(restricted to certain quantities or values)

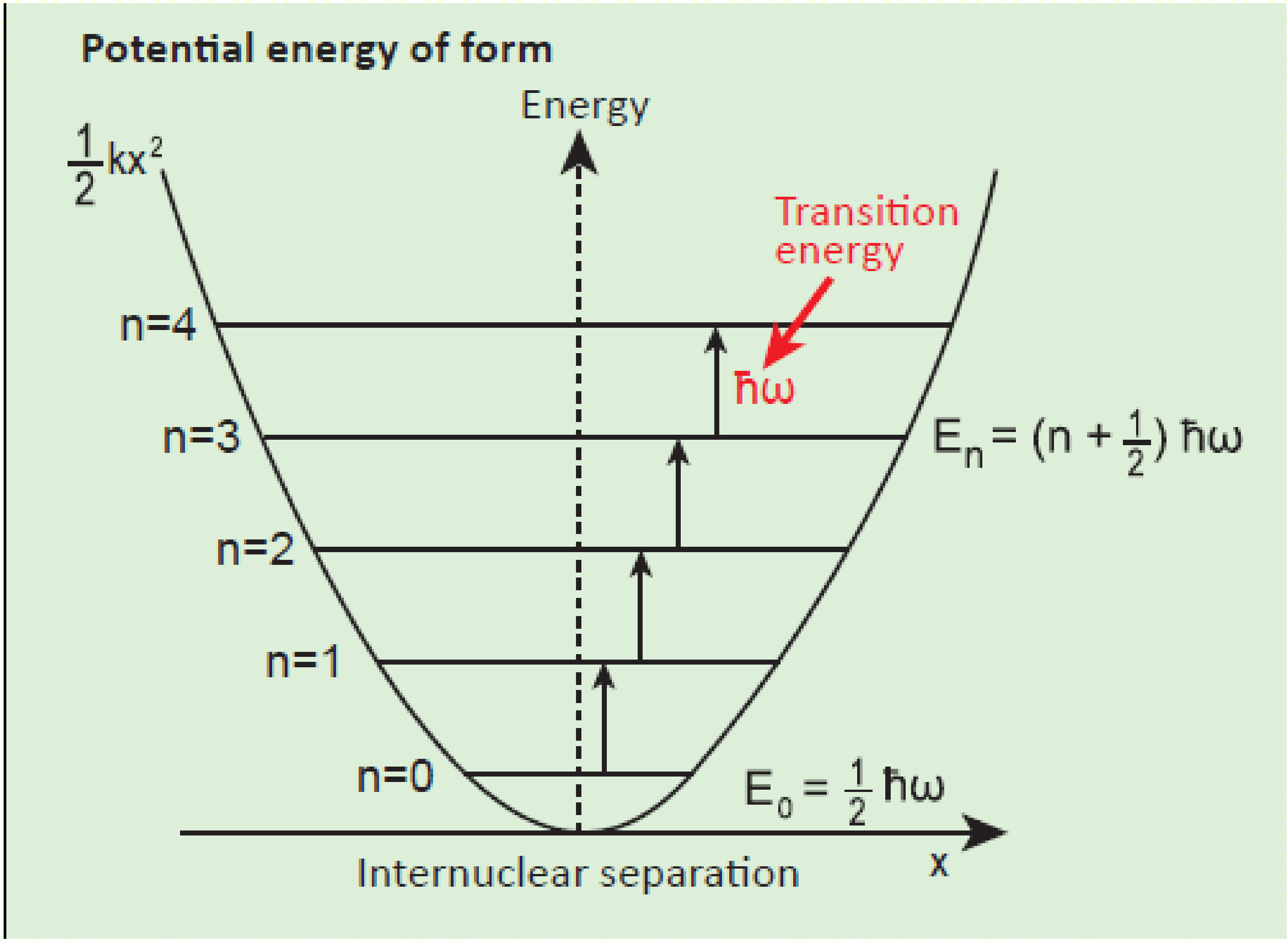
Quantum Harmonic Oscillator

A diatomic molecule vibrates;

- Potential energy that depends upon the square of the displacement from equilibrium.

-But the energy levels are quantized at equally spaced values.




Potential energy of form
$\frac{1}{2}kx^2$
Energy
Transition energy
$\hbar\omega$
n=4
n=3
n=2
n=1
n=0
$E_n = (n + \frac{1}{2})\hbar\omega$
$E_0 = \frac{1}{2}\hbar\omega$
Internuclear separation
x

The energy levels of the quantum harmonic oscillator are

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

$$\omega = 2\pi \quad (frequency)$$

$$\hbar = \frac{Planck's\ const.}{2\pi}$$

The quantum harmonic oscillator

-the foundation for the understanding of complex modes of vibration in larger molecules, the motion of atoms in a solid lattice, the theory of heat capacity, etc.

Statistical Mechanics
-relates the macroscopic thermodynamic properties of a system to the ensemble behaviour of its components.
-Each thermodynamic state of the system (represented by particular values of the state functions) is termed a macrostate.

-For each macrostate, there can be many corresponding microstates.
-requires a large number of particles (1 mol = 6.022×10^{23} particles)
-water = 55 mol/l, i.e. 3.3×10^{25} water molecules per liter

Thermal Concept

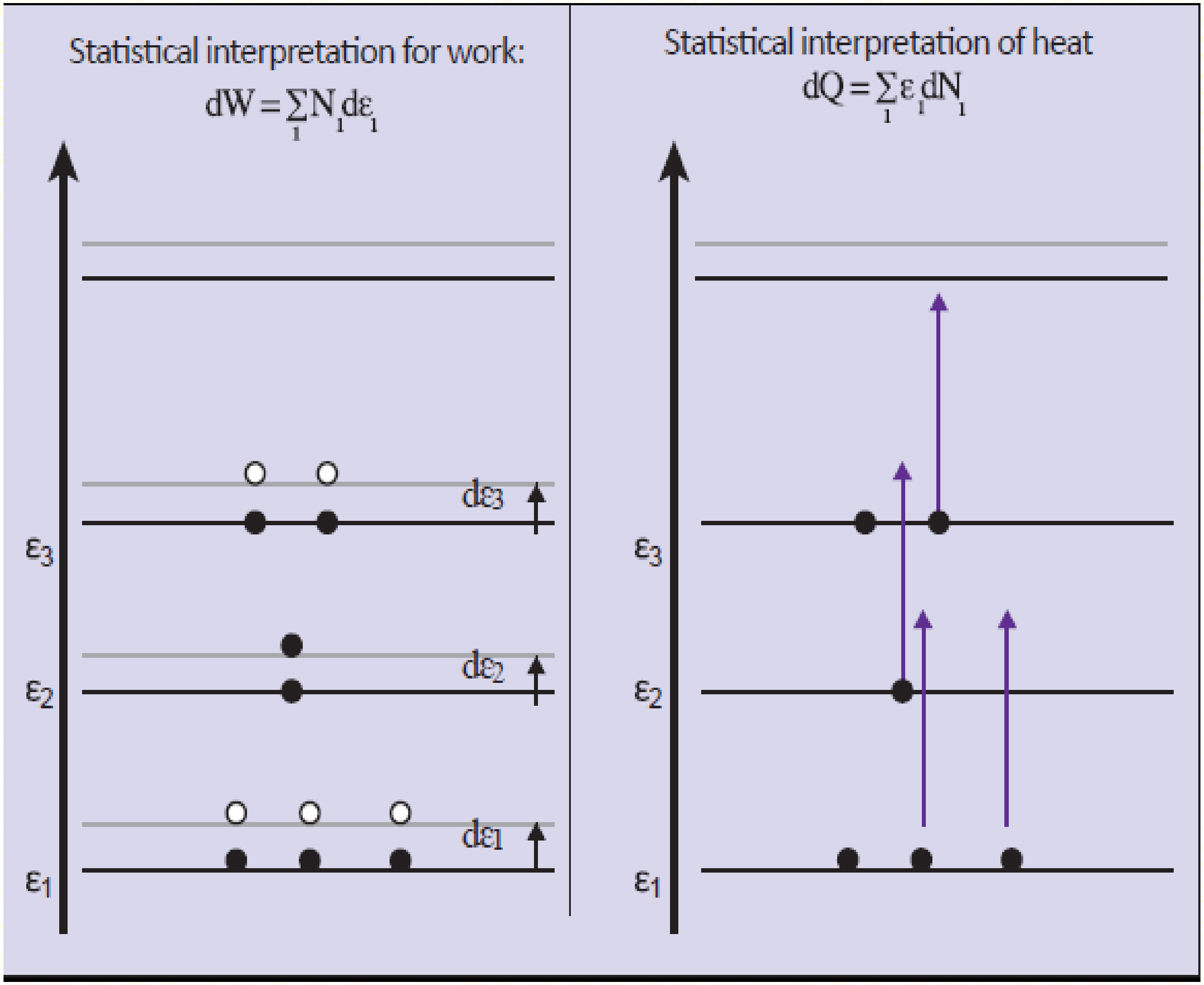
Temperature is the **average kinetic energy** per molecule of the molecules in the substance.

Heat is the **energy transferred** between objects when they change temperature, and moves from areas of high temperature to areas of low temperature

Internal energy is the **total energy** related to the thermal motion of the molecules in a substance --vibrational & translational

δW – all the levels are raised by $\delta\varepsilon_i$. No change in populations

$\delta\varepsilon_I$ –No change in the energy level ε_i. Populations are change by dN_i

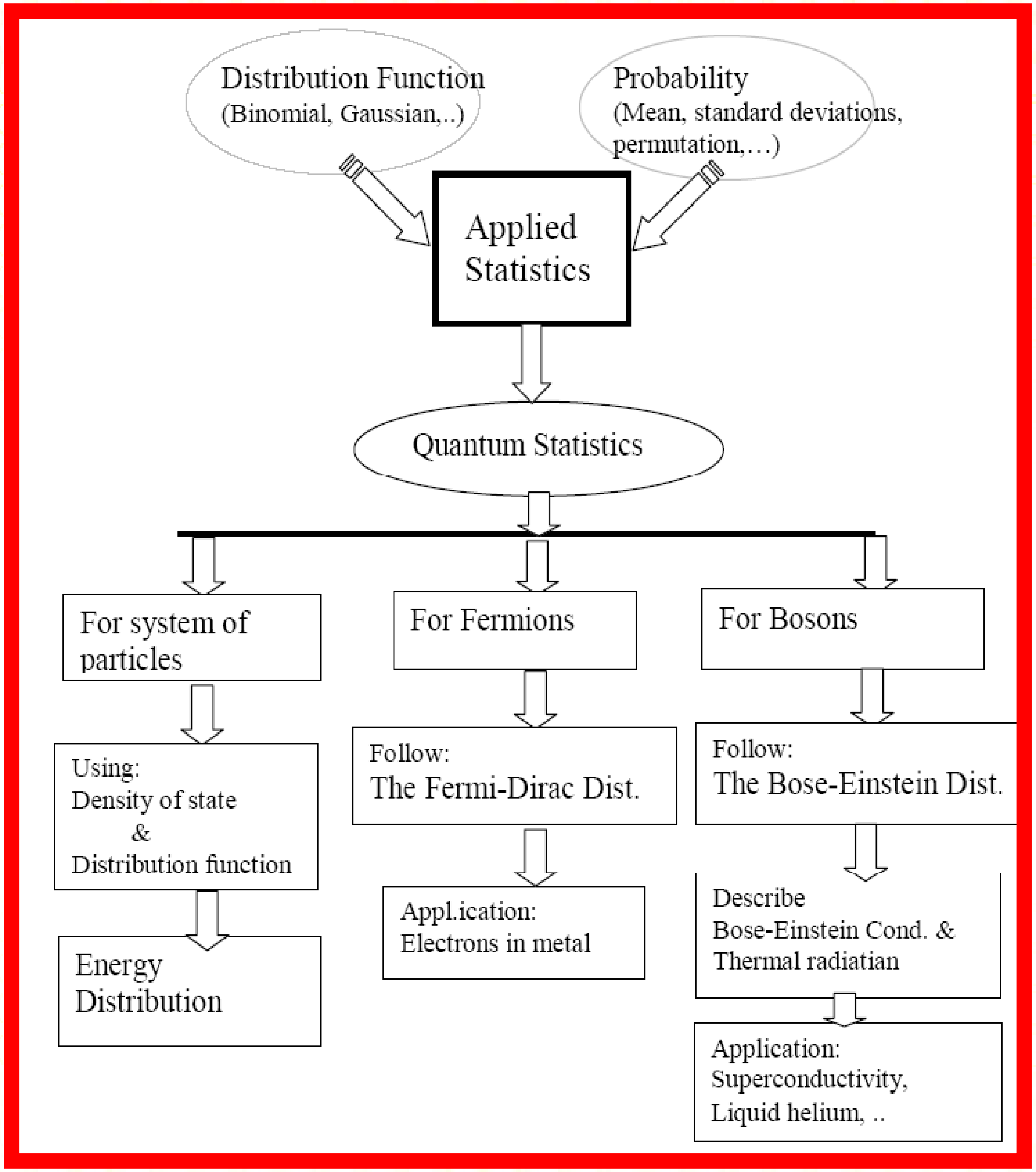


Statistical interpretation for work:

$$dW = \sum_i N_i d\varepsilon_i$$

Statistical interpretation of heat

$$dQ = \sum_i \varepsilon_i dN_i$$



Distribution Function
(Binomial, Gaussian,..)

Probability
(Mean, standard deviations, permutation,…)

Applied Statistics

Quantum Statistics

For system of particles

Using:
Density of state
&
Distribution function

Energy Distribution

For Fermions

Follow:
The Fermi-Dirac Dist.

Appl.ication:
Electrons in metal

For Bosons

Follow:
The Bose-Einstein Dist.

Describe
Bose-Einstein Cond. &
Thermal radiatian

Application:
Superconductivity,
Liquid helium, ..

Note

Alpha	A	α	*Beta*	B	β	*Gamma*	Γ	γ	*Delta*	Δ	δ
Epsilon	E	ε	*Zeta*	Z	ζ	*Eta*	H	η	*Theta*	Θ	θ
Iota	I	ι	*Kappa*	K	κ	*Lambda*	Λ	λ	*Mu*	M	μ
Nu	N	ν	*Xi*	Ξ	ξ	*Omicron*	O	o	*Pi*	Π	π
Rho	P	ρ	*Sigma*	Σ	σ	*Tau*	T	τ	*Upsilon*	Υ	υ
Phi	Φ	ϕ	*Chi*	X	χ	*Psi*	Ψ	ψ	*Omega*	Ω	ω

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

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