X-ray Diffraction
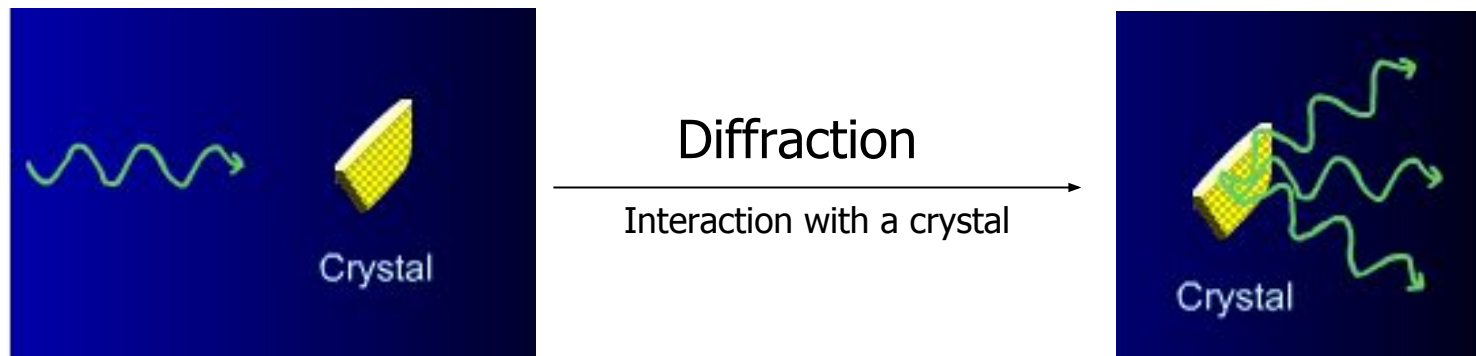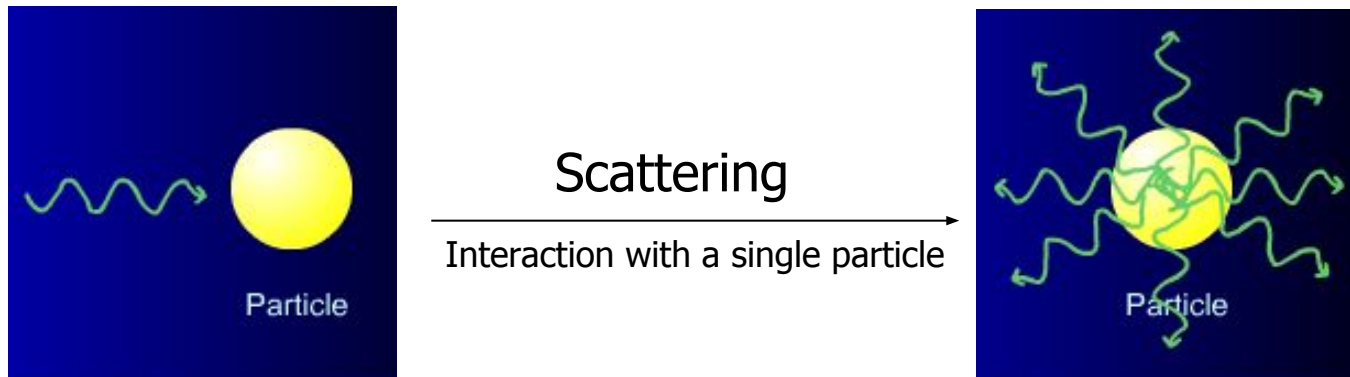
Points to discuss

1. Reflection vs. Diffraction

2. Bragg's law of Diffraction

3. Instrumentation

4. Applications

Diffraction

A diffracted beam may be defined as a beam composed of a large number of scattered rays mutually reinforcing each other

Scattering Modes

❖ **Random arrangement of atoms in space gives rise to scattering in all directions: weak effect and intensities add**

❖ **By atoms arranged periodically in space**

❑ In a few specific directions satisfying Bragg's law: strong intensities of the scattered beam :Diffraction

❑ No scattering along directions: not satisfying Bragg's law

How Diffraction Works
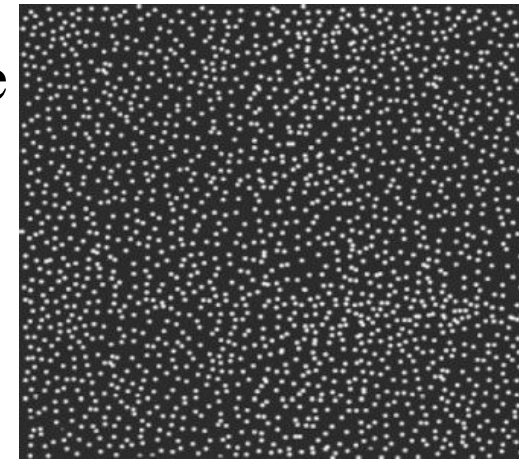
1) Wave Interacting with a Single Particle

Incident beams scattered uniformly in all directions
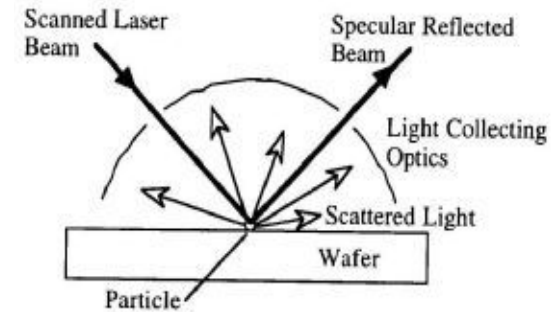
2) Wave Interacting with a Solid

Scattered beams interfere constructively in some directions, producing diffracted beams
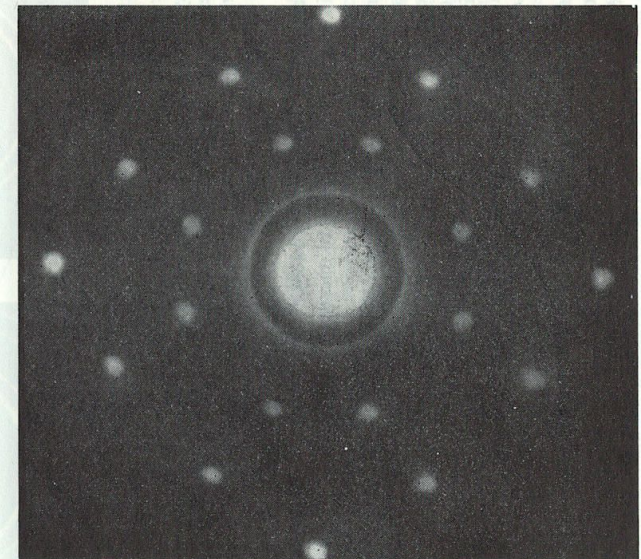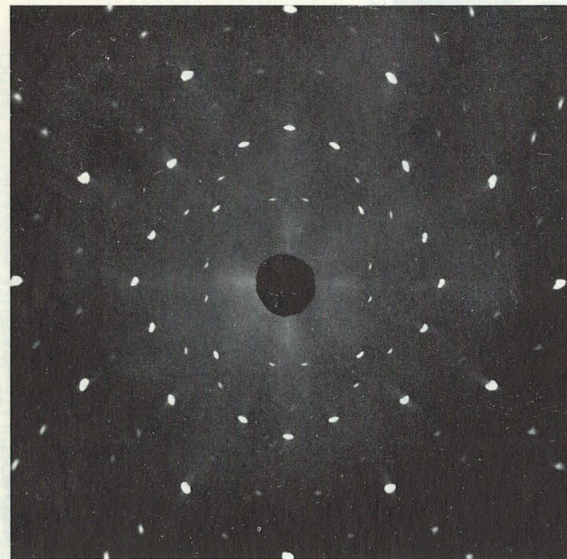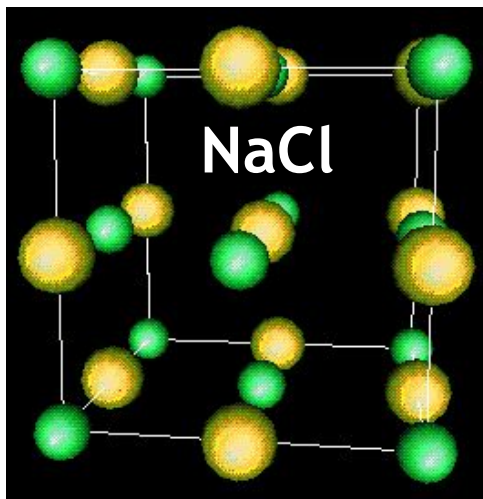Random arrangements cause beams to randomly interfere and no distinctive pattern is produced
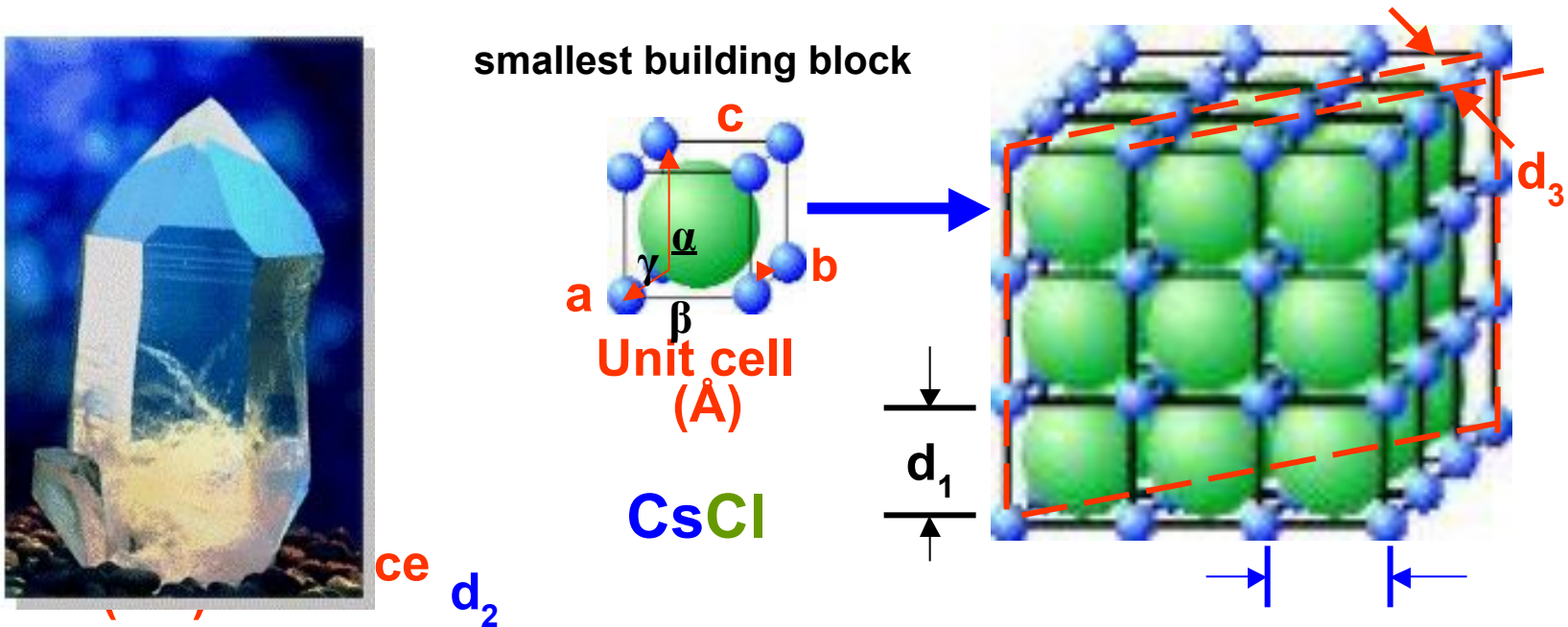
3) Wave Interacting with a Crystalline Material

Regular pattern of crystalline atoms produces regular diffraction pattern. Diffraction pattern gives information on crystal structure

X-ray and neutron diffraction patterns of NaCl

NaCl

Basics of Crystallography

smallest building block

Unit cell
(Å)

CsCl

ce

d_1 d_2 d_3

A <u>crystal</u> consists of a <u>periodic</u> arrangement of the <u>unit cell</u> into a <u>lattice</u>. The unit cell can contain a single atom or atoms in a fixed arrangement.

Crystals consist of planes of atoms that are spaced at distance d apart, but can be resolved into many atomic planes, each with a different d spacing.

a,b and c (length) and α, β and γ angles between a,b and c are lattice constants or parameters which can be determined by XRD

Seven Crystal Systems

Crystal class	Axis system
Cubic	$a = b = c, \ \alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c, \ \alpha = \beta = \gamma = 90°$
Hexagonal	$a = b \neq c, \ \alpha = \beta = 90°, \ \gamma = 120°$
Rhombohedral	$a = b = c, \ \alpha = \beta = \gamma \neq 90°$
Orthorhombic	$a \neq b \neq c, \ \alpha = \beta = \gamma = 90°$
Monoclinic	$a \neq b \neq c, \ \alpha = \gamma = 90°, \ \beta \neq 90°$
Triclinic	$a \neq b \neq c, \ \alpha \neq \beta \neq \gamma \neq 90°$

Bragg's Law

$$n\lambda = 2d\sin\theta$$

The Braggs (first father-son duo) were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond.

Sir William Henry Bragg
1/2 of the prize
United Kingdom
London University
London, United Kingdom
b. 1862
d. 1942

William Lawrence Bragg
1/2 of the prize
United Kingdom
Victoria University
Manchester, United Kingdom
b. 1890
(in Adelaide, Australia)
d. 1971

Later, Bragg's law has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with the condition that the wavelength is similar to the inter-atomic/molecular distance.

Derivation of Bragg's Law

Constructive interference occurs only when AB+BC = multiples of λ
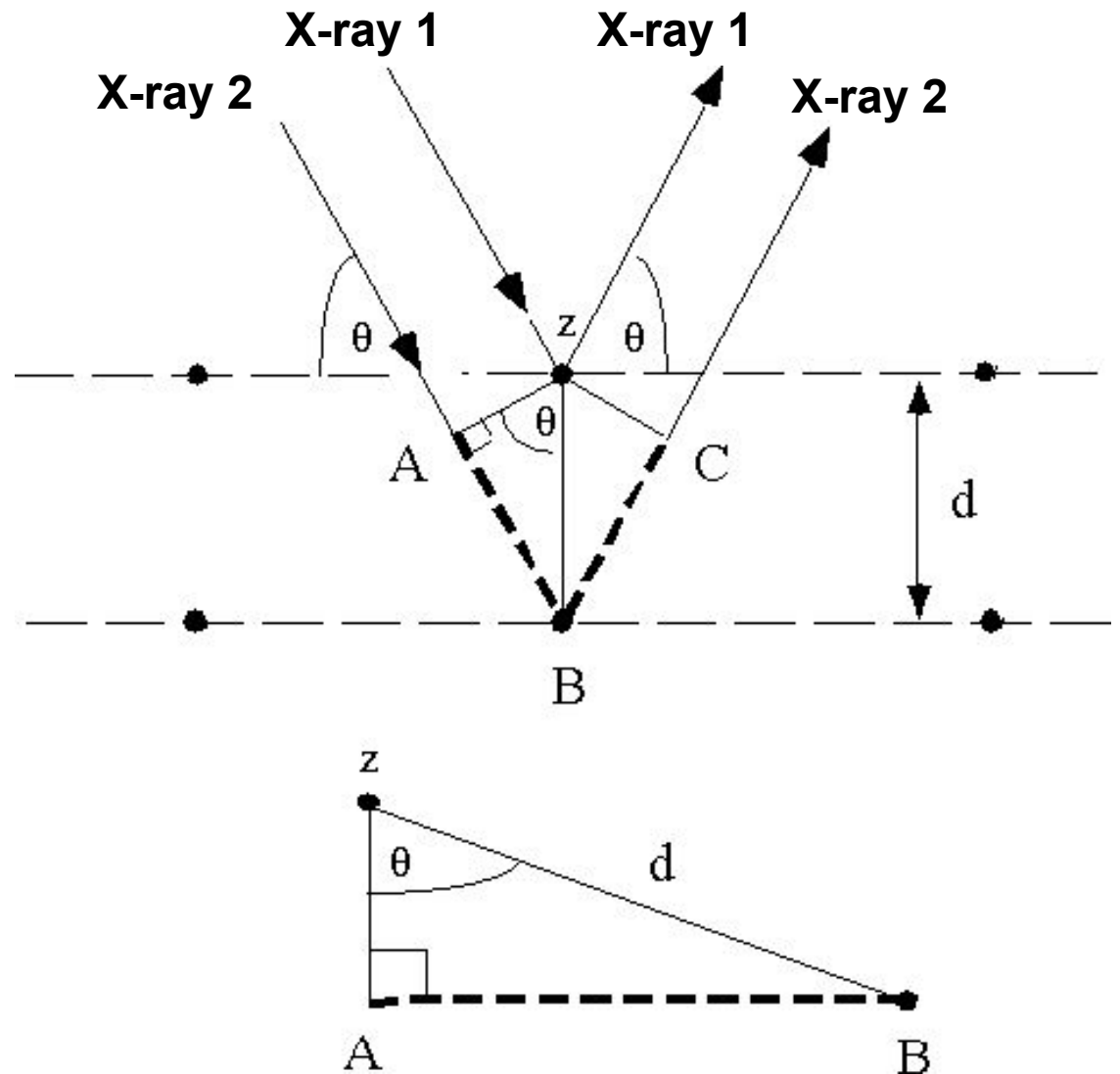
$n\lambda$ = AB + BC

Sin θ=AB/d

AB=dsinθ

BC=dsinθ

$n\lambda$ =2dsinθ

$n\lambda$= 2d$_{hkl}$sinθ_{hkl}

n = integer, called order of reflection

How X-ray Diffraction works?
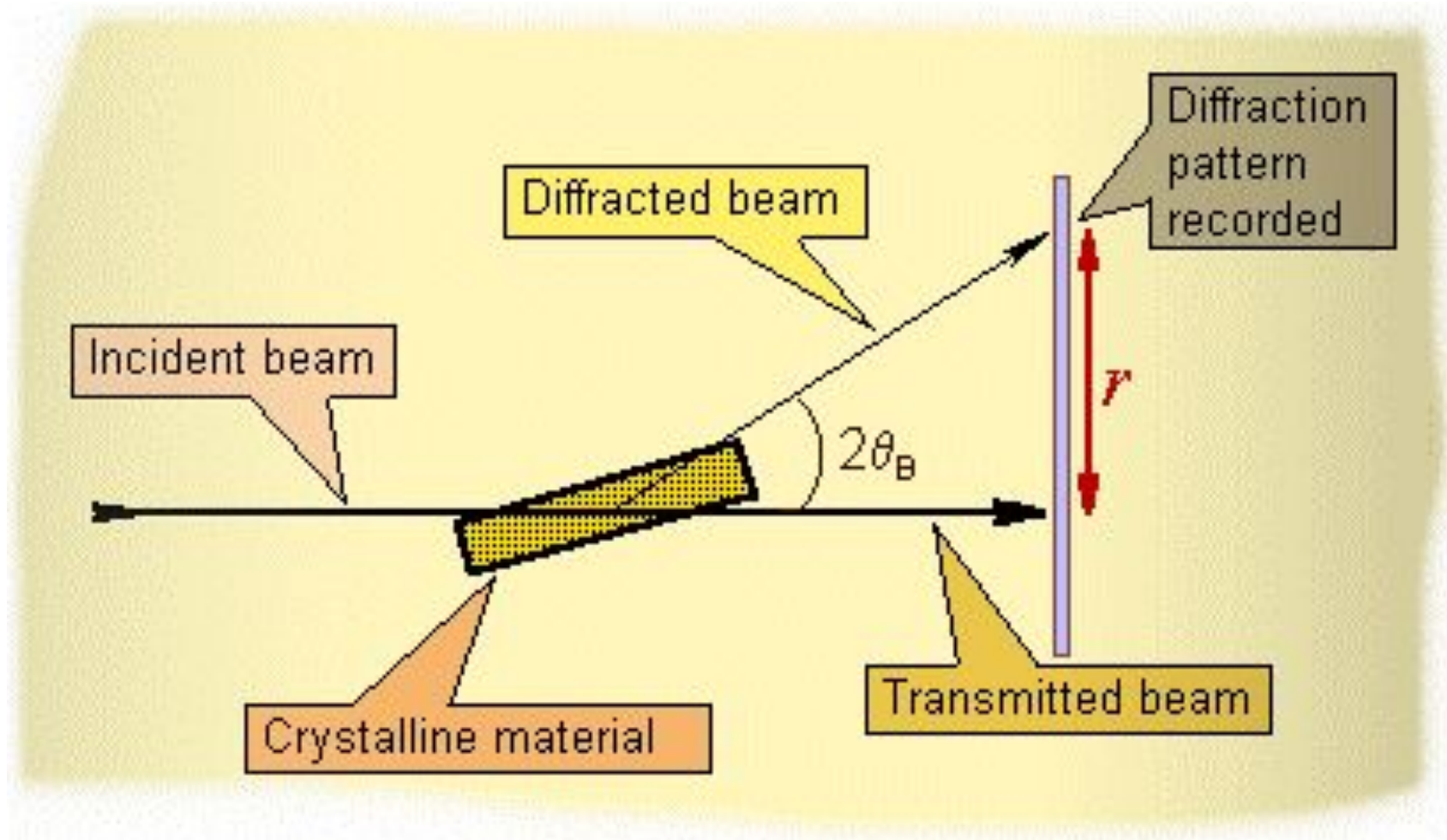
Diffraction Methods

$$\lambda = 2d\sin\theta$$

Method	Wavelength	Angle	Specimen
Laue	Variable	Fixed	Single Crystal
Rotating Crystal	Fixed	Variable	Single Crystal
Powder	Fixed	Variable	Powder

Planes in Crystals-2 dimension

Different planes have different spacings

$$\lambda = 2d_{hkl}\sin\theta_{hkl}$$

Square lattice

b(=a)

a
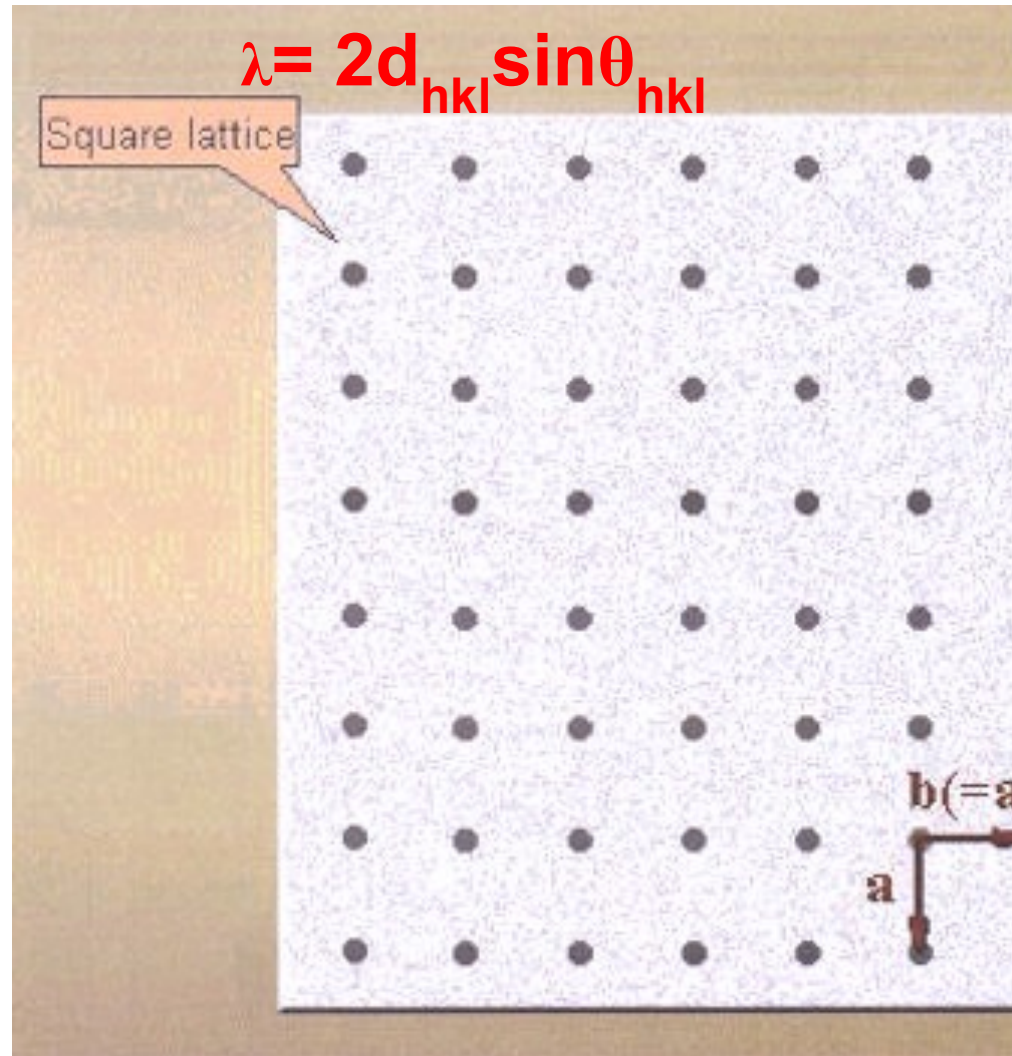
To satisfy Bragg's Law, θ must change as d changes e.g., θ decreases as d increases.

Current Setup

X-ray
Gun

Detector

Sample Holder
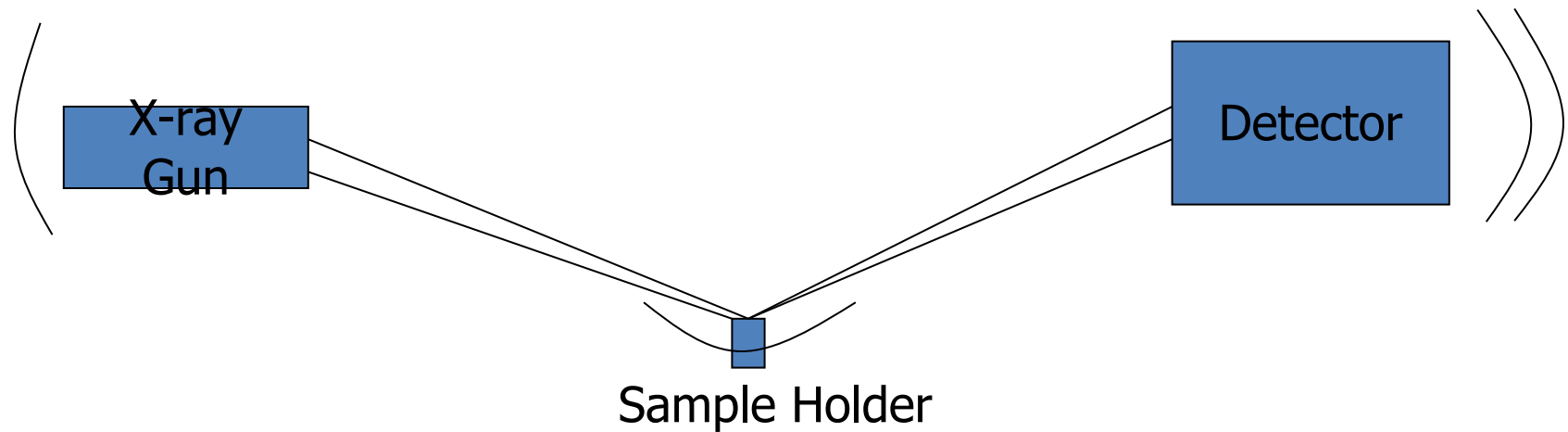
User can choose to move the sample and detector (fixed
source) or detector and source (sample stage fixed) at the
same time

Diffraction from a variety of materials
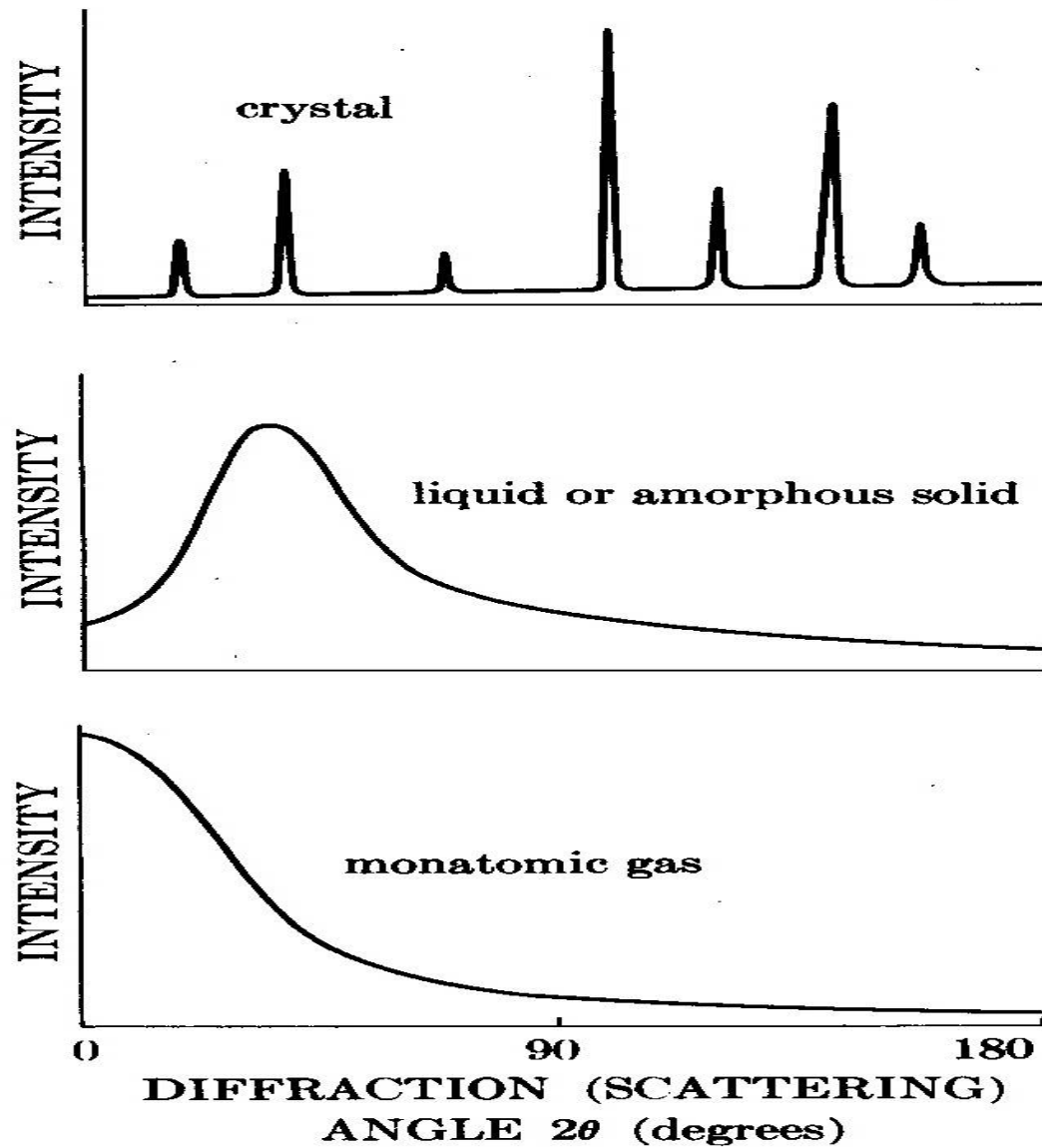
Particle size: Scherrer Formula
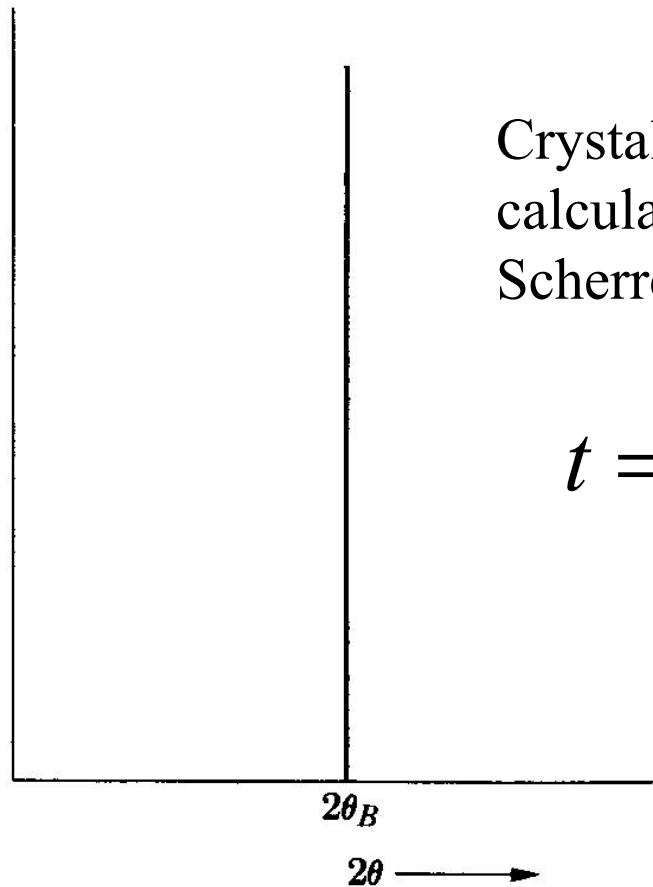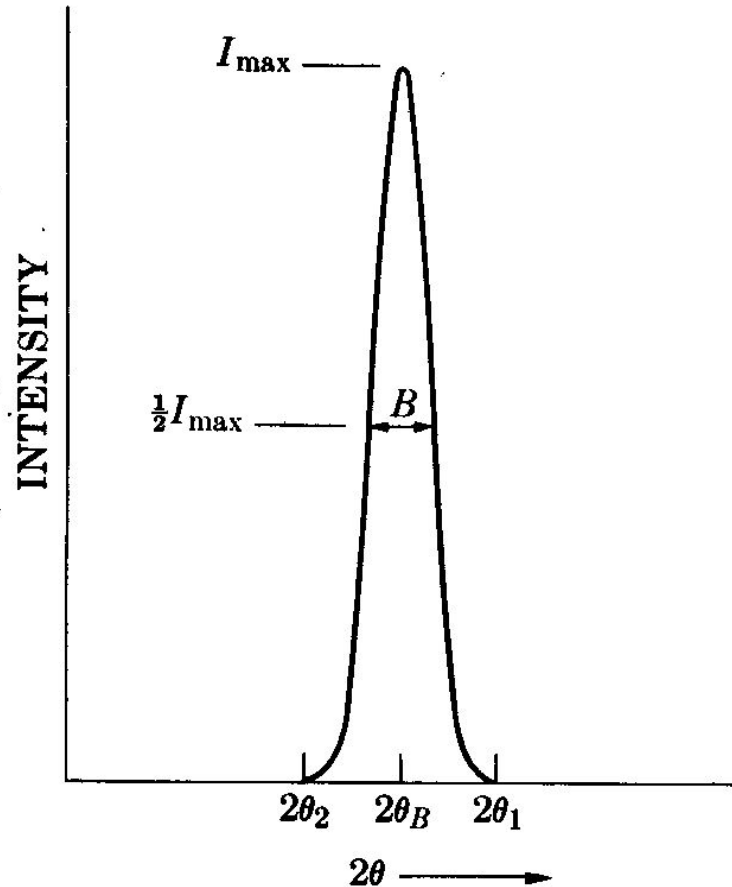
Crystallite size can be calculated using Scherrer Formula

$$t = \frac{0.9\lambda}{B\cos\theta_B}$$

Instrumental broadening must be subtracted

(From "Elements of X-ray Diffraction", B.D. Cullity, Addison Wesley)

Instrumentation:

- ## Production of X-rays:

     X-rays are produced whenever high-speed electrons collide with a metal target.
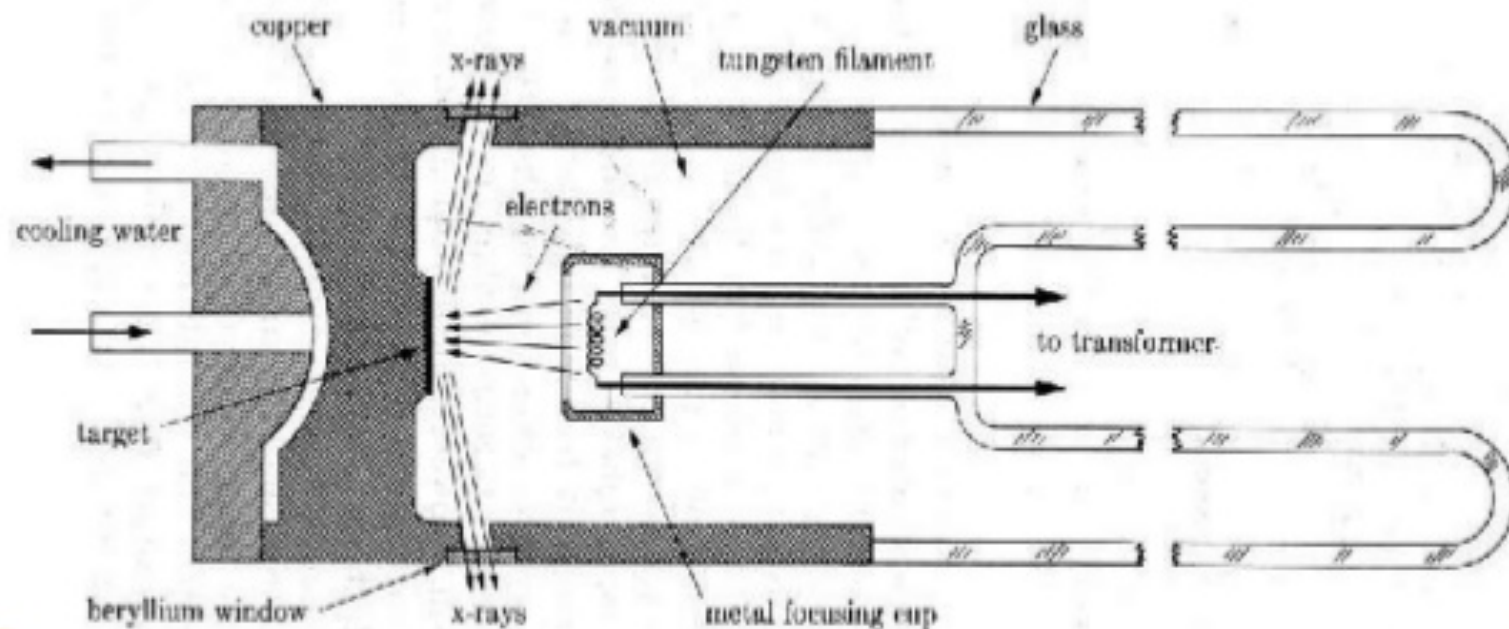
PRODUCTION OF X-RAYS:
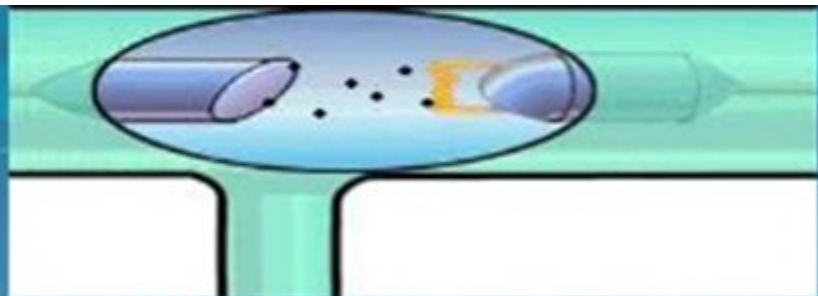
➢ X-rays are generated when high velocity electrons impinge on a metal target.

➢ Approximately 1% of the total energy of the electron beam is converted into x-radiation.

➢ The remainder being dissipated as heat.

➢ Many types of x-ray tubes are available which are used for producing x-rays.

COLLIMATOR:
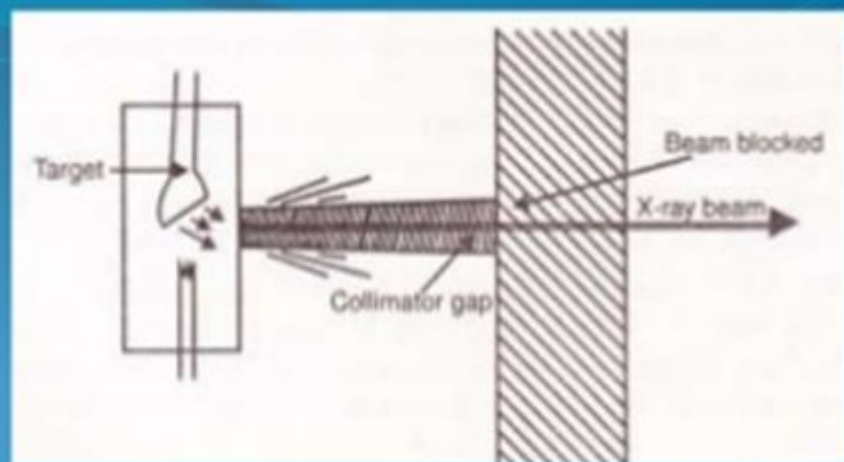
➤ In order to get a narrow beam of x-rays, the x-rays generated by the target material are allowed to pass through a collimator which consists of two sets of closely packed metal plates separated by a small gap.

➤ The collimator absorbs all the x-rays except the narrow beam that passes between the gap.

TYPES OF MONOCHROMATORS

In order to do monochromatization,2 methods are available

1.Filter

2.Crystal monochromator

a)Flat crystal monochromator

b)Curved crystal monochromator

Materials used-Nacl,quartz etc,.

- A.FILTER: X-ray beam may be partly monochromatized by insertion of a suitable filter

- A filter is a window of material that absorbs undesirable radiation but allows the radiation of required wavelength to pass

- 2)CRYSTAL MONOCHROMATOR : Crystal monochromators is made up of suitable crystalline material positioned in the x-ray beam so that the angle of reflecting planes satisfied the Bragg's equation for the required wavelength
the beam is split up into component wavelengths
crystals used in monochromators are made up of materials like Nacl, lithium fluoride , quartz etc.

(a) Flat crystal monochromator and, (b) Curved crystal monochromator.
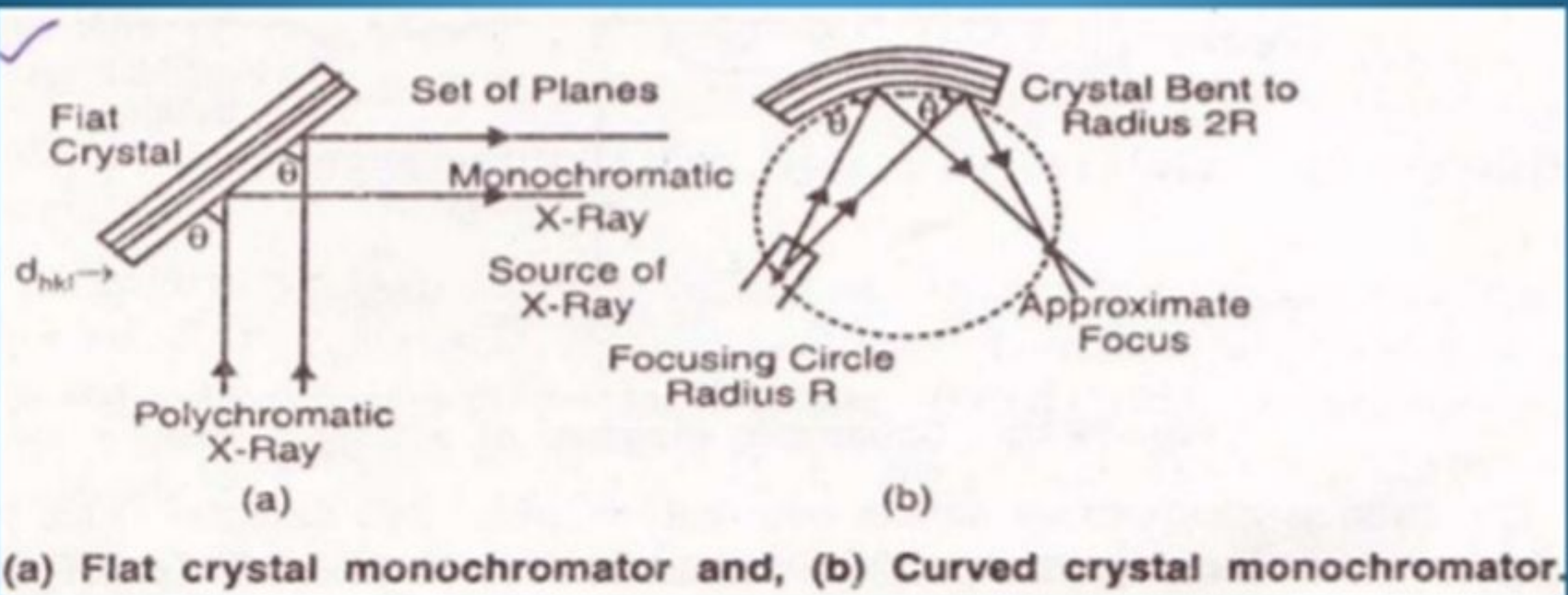
DETECTORS

- The x-ray intensities can be measured and recorded either by
- 1)Photographic methods

- 2)Counter methods
  - a) Geiger - Muller tube counter
  - b) Proportional counter
  - c) Scintillation detector
  - d) Solid state semi conductor detector
  - e) Semi conductor detectors

- Both these types of methods depends upon ability of x-rays to ionize matter and differ only in the subsequent fate of electrons produced by the ionizing process.

How to detect diffracted X-rays

by Photographic film

sample

film

X-ray

Point where incident beam enters

Film

Beam entry

Beam exit
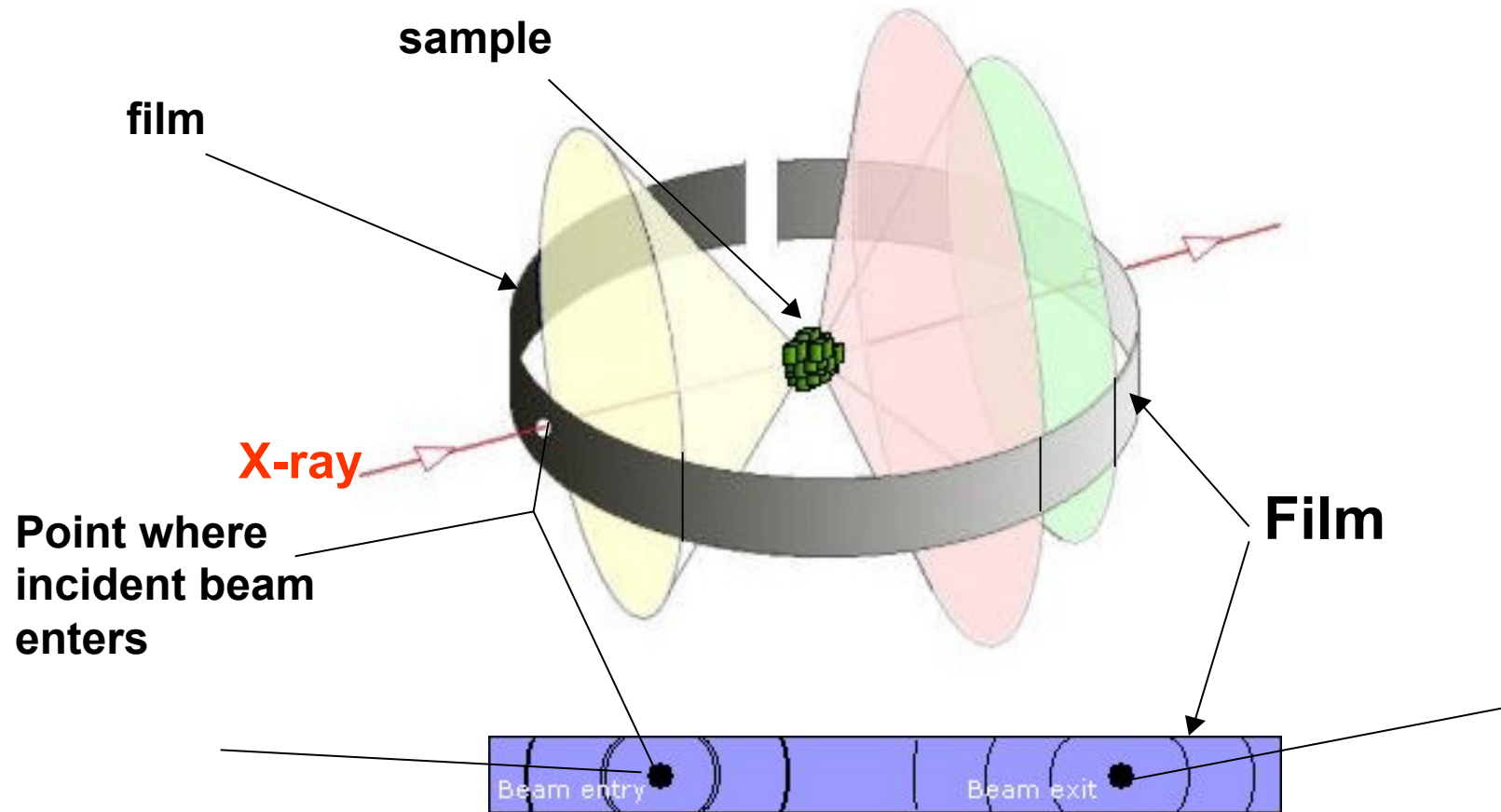
Applications of XRD

- XRD is a nondestructive technique
- To identify crystalline phases and orientation
- To determine structural properties:

  Lattice parameters (10^{-4}Å resolution), strain, grain size, expitaxy, phase composition, preferred orientation (Laue) order-disorder transformation, thermal expansion etc.
- To measure thickness of thin films and multi-layers
- To determine atomic arrangement
- Detection limits: ~3% in a two phase mixture; can be ~0.1% with synchrotron radiation

XRD Pattern of NaCl Powder

Miller indices: The peak is due to X-ray diffraction from the {220} planes.

NaCl   (Cu $K\alpha$)

Diffraction angle 2θ (degrees)
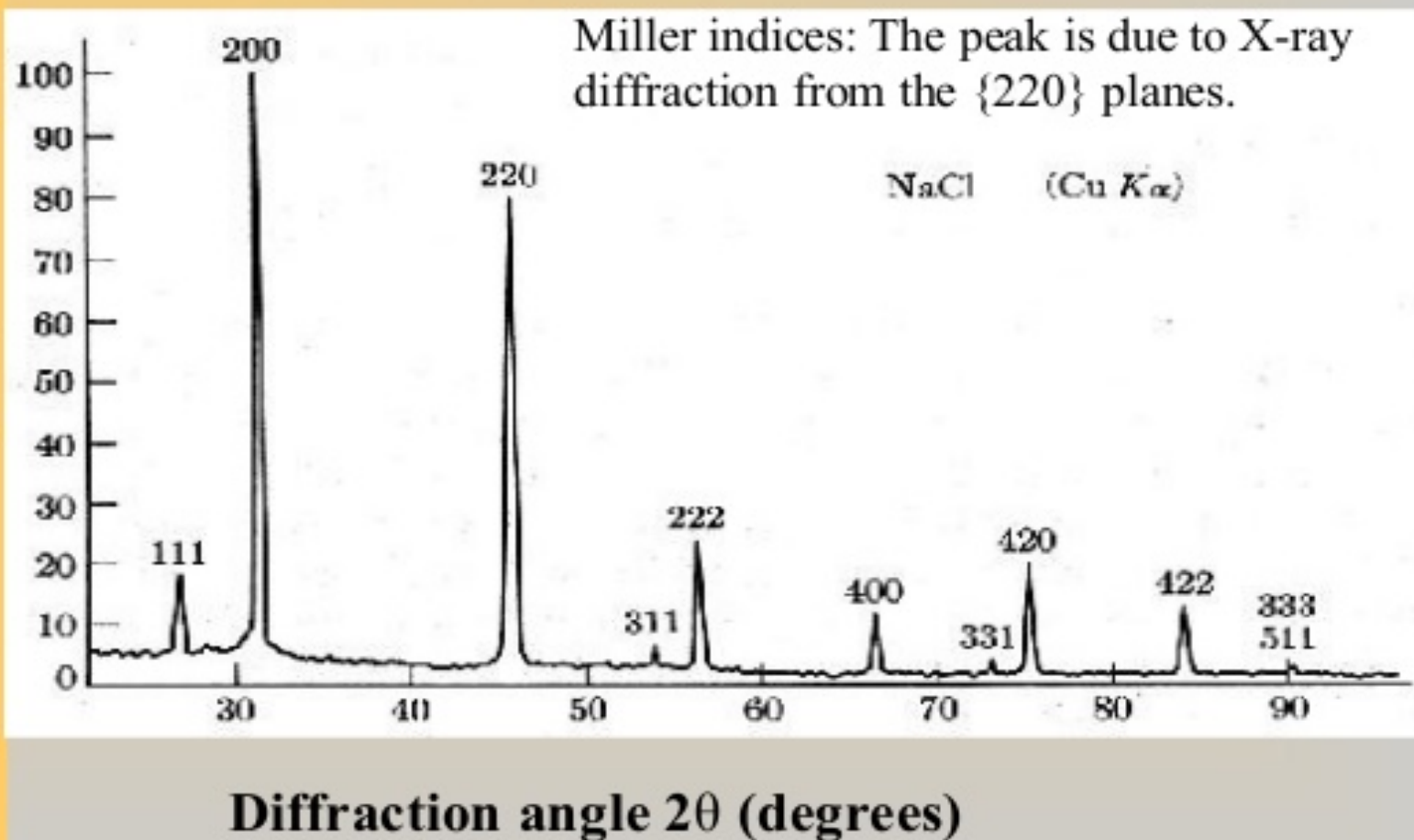
Several Atomic Planes and Their d-spacings in a Simple Cubic system

a	b
	c
1	0
	0
1	0
	0

(100)

Cubic
$a=b=c=a_0$

a	b
	c
1	1
	0
1	1
	0

(110)

a	b
	c
1	1
	1
1	1
	1

(111)

a	b
	c
0 1 ½	
0	1
	2

(012)
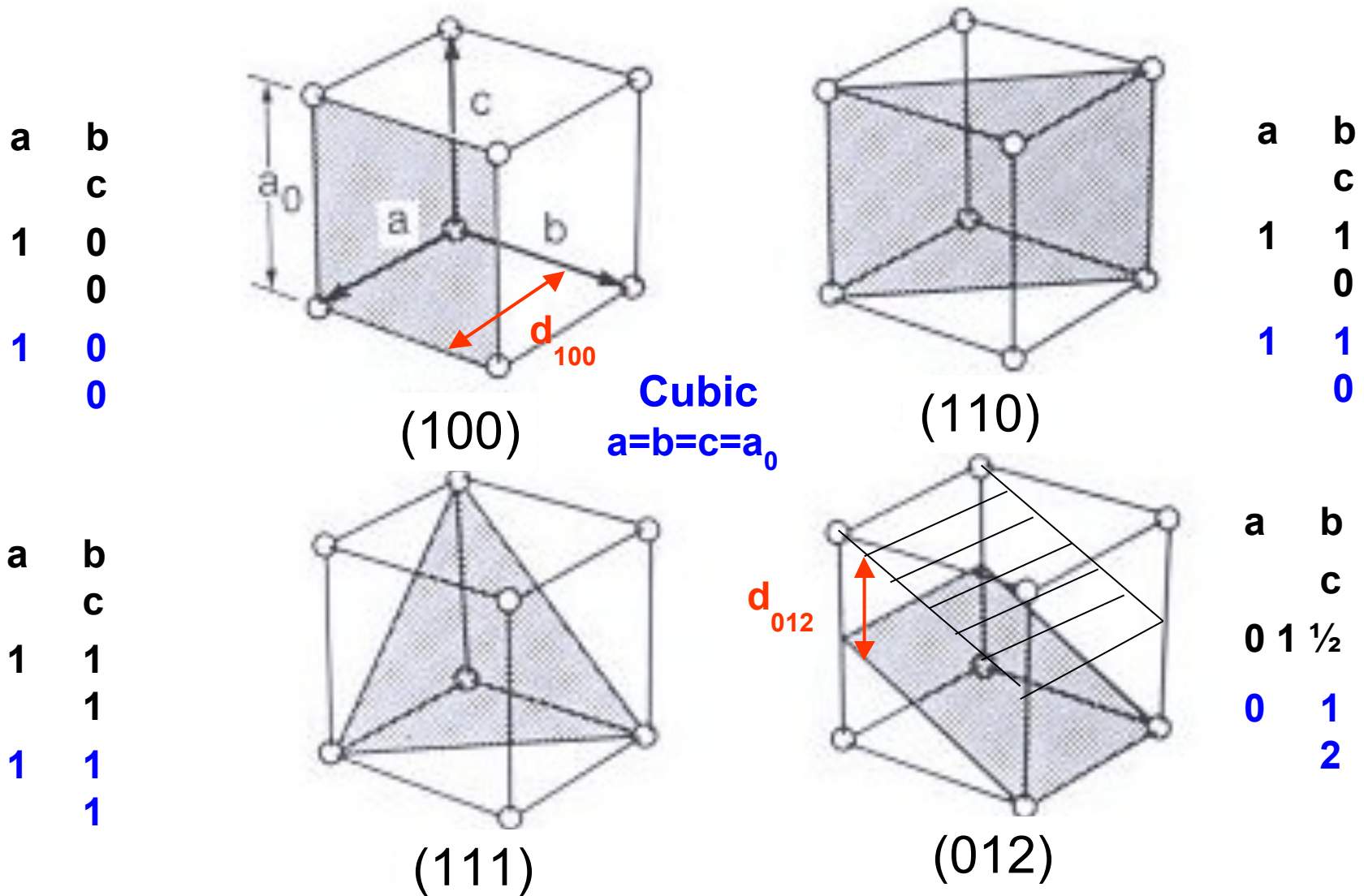
Black numbers-fractional intercepts, Blue numbers-Miller indices

Qn. Calculate the Miller indices of crystal plane which cut through the crystal axes at (2a,3b,c)?

Ans:

	a	b	c	
	2	3	1	intercepts
	½	1/3	1	reciprocals
	3	2	6	clear fractions

Hence, the Miller indices are (326).

Peak Position: d-spacings and lattice parameters

$$\lambda = 2d_{hkl}\sin\theta_{hkl}$$

Fix λ (Cu kα) = 1.54Å
λ (Mo kα) = 0.71Å
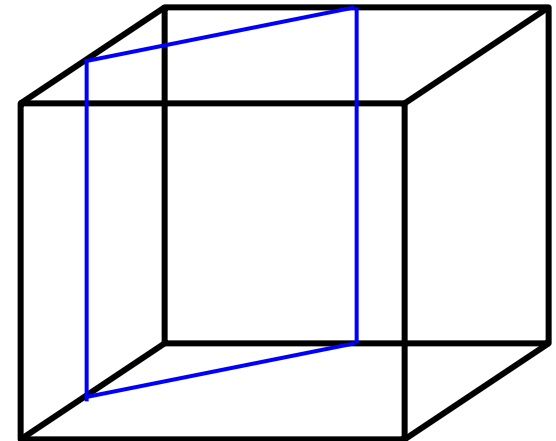
$$d_{hkl} = 1.54\text{Å}/2\sin\theta_{hkl}$$

(Most accurate d-spacings are those calculated from high-angle peaks)

$$\frac{1}{d^2_{hkl}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

For a simple cubic (a = b = c = a_0)

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

$$a_0 = d_{hkl}(h^2+k^2+l^2)^{\frac{1}{2}}$$

Ionic, dipolar Interactions

❑ Ionic, dipolar interactions is a kind of weak electrostatic interaction, where either a permanent charge or dipole attract the opposite charge (may be partial) in a dipolar molecule/ion or induce charge in a non-polar molecule.

❑ Such interactions become particularly important in explaining dissolution, gas phase interaction, liquefaction of inert gases etc.

| Bond type	Bond Strength
Ionic	>700 kJmol^{-1}
Covalent	>400 kJmol^{-1}
Hydrogen bonding	$\sim 8-40^*$ kJmol^{-1}
Ion-dipole Dipole-dipole	$1-8$ kJmol^{-1}

Ion-dipole Interactions

❏ Ion–dipole interactions is a kind of electrostatic interaction, where the permanent charge attract the opposite partial charge in the dipolar molecule.

❏ Such interactions become particularly important in dissolution of ionic salts in polar solvents.

Bond type	Bond Strength
Ionic	>700 kJmol^{-1}
Covalent	>400 kJmol^{-1}
Hydrogen bonding	~8-40* kJmol^{-1}
Ion-dipole Dipole-dipole	1-8 kJmol^{-1}

$+$ $\longleftrightarrow$ δ^- δ^+

Cation   **Polar molecule**

$-$ $\longleftrightarrow$ δ^+ δ^-

Anion   **Polar molecule**
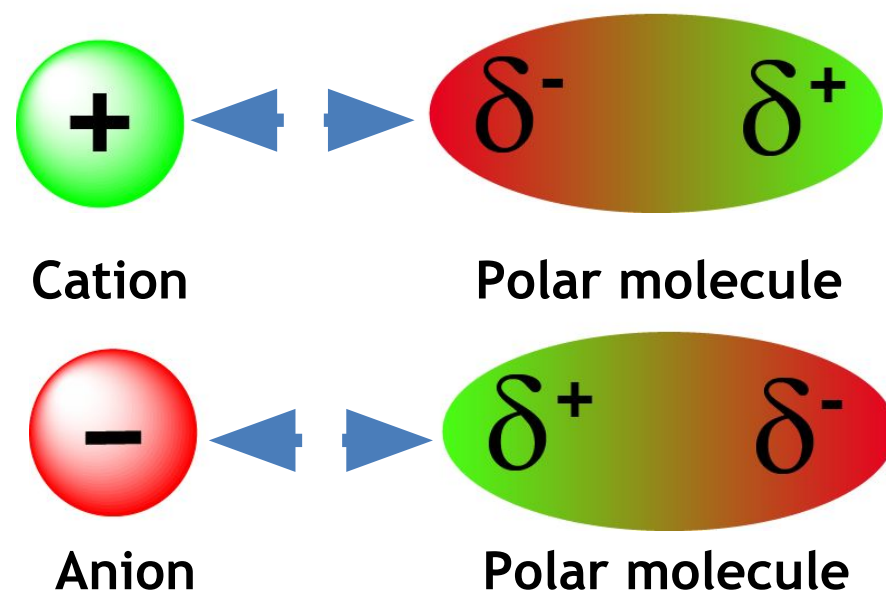
The intermolecular forces of attraction exist between polar as well as nonpolar molecules are called cohesive or vander Waals forces.

1.   Dipole-dipole interaction

The electrical interaction between the permanent dipoles of molecules is known as dipole-dipole interaction.

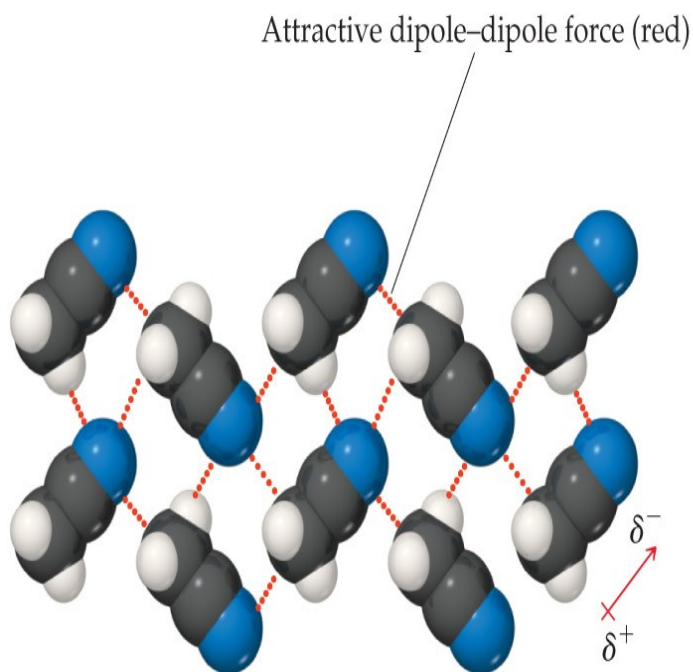**The magnitude of interaction depends upon the dipole moment of the molecules concerned.**

The interaction energy can be given by,
$\Phi(r) = -2\,C/\,r^6$

where $C = (2/3kT)(\mu_1\mu_2/4\pi\epsilon_0)^2$

Dipole–Dipole interactions

❑ Molecules that have permanent dipoles are attracted to each other.

❑ The partial positive end (d^+) of one molecule is attracted to the partial negative end (d^-) of the other molecule, and vice versa.

❑ These interactions are important only when the molecules are in close proximity.

Attractive dipole–dipole force (red)

Repulsive dipole–dipole force (blue)

δ^-

δ^+

(a) Solid CH_3CN
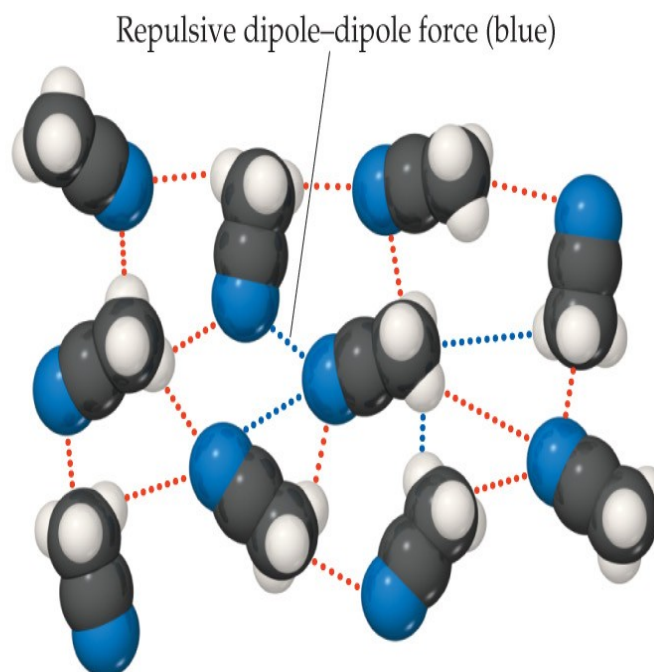
(b) Liquid CH_3CN

Dipole–Dipole interactions: Rules and consequences

The higher the polarity/dipole moment of the molecule, the higher is the interaction energy, and the higher is its boiling point.

Propane	Dimethyl ether	Acetaldehyde	Acetonitrile
$CH_3CH_2CH_3$	CH_3OCH_3	CH_3CHO	CH_3CN
MW = 44 amu	MW = 46 amu	MW = 44 amu	MW = 41 amu
$\mu = 0.1$ D	$\mu = 1.3$ D	$\mu = 2.7$ D	$\mu = 3.9$ D
bp = 231 K	bp = 248 K	bp = 294 K	bp = 355 K

Increasing polarity
Increasing strength of dipole–dipole forces

2. Dipole- induced dipole interaction

The electrical interaction between the permanent dipole and the induced dipole of molecules is known as dipole-dipole interaction.

The magnitude of interaction depends upon the dipole moment of the molecule and the polarizability of the neutral molecule.
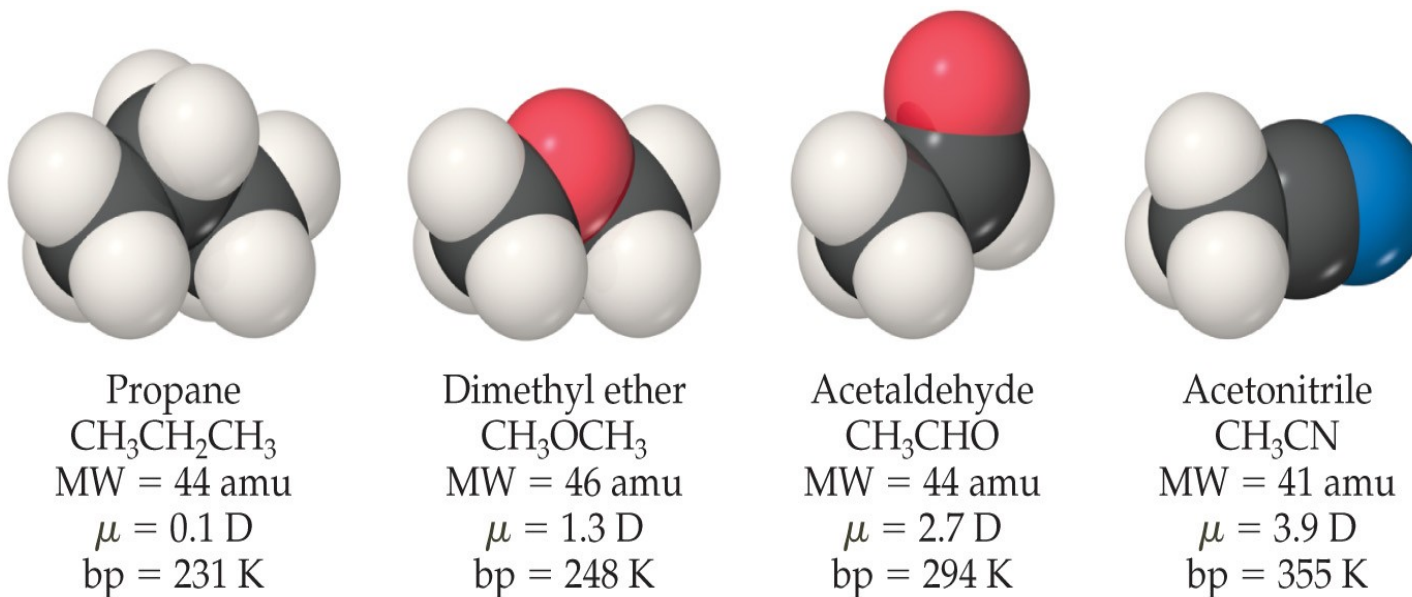
The interaction energy can be given by,
$$\Phi\,(r) = -\,C/\,r^6$$

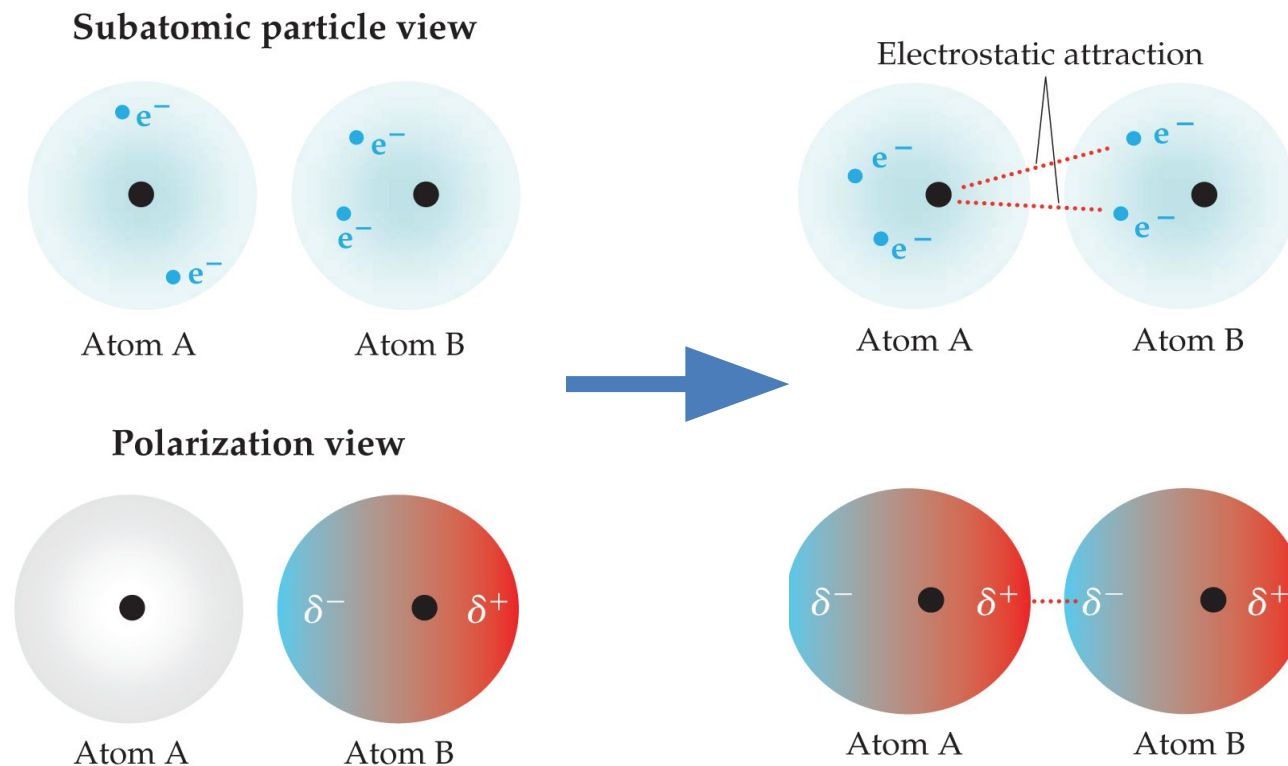where $C = \mu_1^2\alpha_2/4\pi\epsilon_0$

Dipole–Induced Dipole interactions

❑ **Molecules that have permanent dipoles can induce partial charge in an otherwise nonpolar molecule and thus attracted to each other.**

❑ **These interactions are important only when the molecules are in close proximity.**
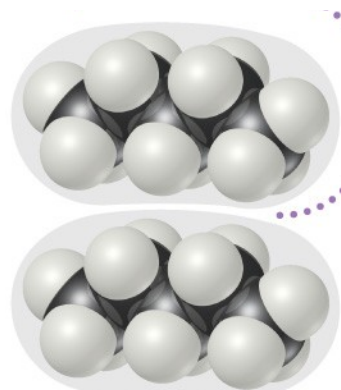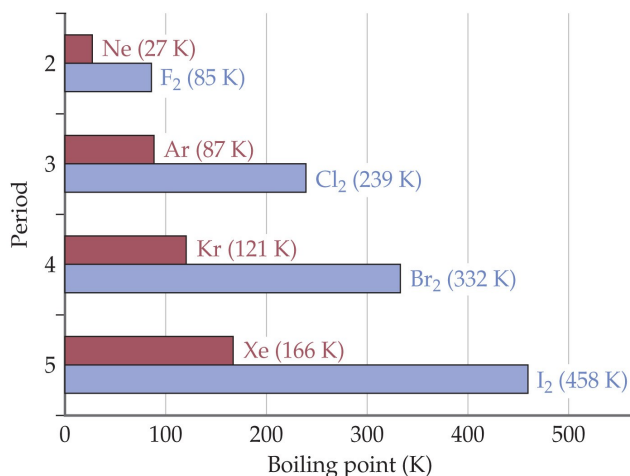
Cl-Cl……Cl-H

H-H……Cl-H

3. Induced dipole-induced dipole interaction: London Dispersion Force

❑ Attractive force between an instantaneous dipole and an induced dipole.

❑ Present in *all* molecules, whether polar or nonpolar.

❑ Short-lived, operate in very short distance.

❑ The average interaction energy, $\varphi(r) = -C/r6$

where $C = (3/2)\,\alpha_1\alpha_2\,(IE_1)\,(IE_2)\,/\,((IE_1) + (IE_2)$ (here IE is **ionization energy**)

Subatomic particle view

Atom A   Atom B

Electrostatic attraction

Atom A   Atom B

Polarization view

δ^- δ^+

Atom A   Atom B

δ^- δ^+ δ^- δ^+
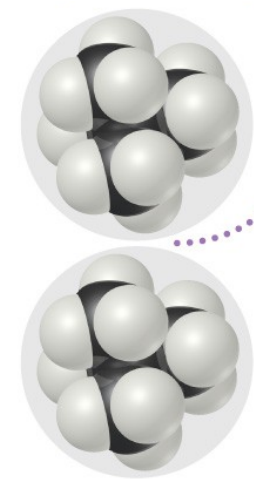
Atom A   Atom B

Factors affecting London Dispersion Forces

❏ **London Dispersion Force is proportional to molar mass/molecular weight.**

❏ **In case of same molecular weight (isomers), London Dispersion Force is proportional to the surface area.**

❏ **Higher dispersion force = higher boiling point and viscosity in nonpolar molecules.**

❏ **If two molecules are of comparable size/shape, dipole–dipole interactions will dominate over London force.**

❏ **For molecules with large size/shape difference, London force will determine physical properties.**

vs.

Period

Ne (27 K)
F$_2$ (85 K)
2

Ar (87 K)
Cl$_2$ (239 K)
3

Kr (121 K)
Br$_2$ (332 K)
4

Xe (166 K)
I$_2$ (458 K)
5

0   100   200   300   400   500
Boiling point (K)

n-Pentane (C$_5$H$_{12}$)
bp = 309.4 K

Neopentane (C$_5$H$_{12}$)
bp = 282.7 K

Flow chart for Intermolecular Forces