1.5 ELECTRON CONFINEMENT

As briefly mentioned in the introduction of this chapter, nano structured materials have at least one of the dimensions in the range of 1 to 100 nm. In such cases properties of materials can be understood using quantum mechanics rather than classical mechanics. Even the properties of atoms, molecules or extended solids can be understood using quantum mechanics because in order to understand various properties even in case of bulk solids we need to understand the electron properties which are subatomic particles. For detailed descriptions it is necessary to refer to books devoted to Atoms and Molecules and Solid State Physics. Here we shall outline the essential features by which one can understand the methodology.

We shall discuss in this section confinement of a particle in one dimension (freedom in 2D), confinement in two dimensions (freedom in 1D) and confinement in all three dimensions (no freedom in any direction or 0D material). These confinements when referred to practical cases are often known as essentially 2D quantum wells (thin film), 1-D wire (wire) and 0D Quantum Dot (nanoparticles). These confinements in quantum mechanics are better discussed as particle in a 1D, 2D and 3D potential box.

1.5.2 Density of States

Density of states $D(E)$ is an important quantity. It enables to gain understanding of various spectroscopic and transport properties of materials. It is defined as the number of states per unit energy range and in general can be obtained as follows. Consider energy as is given for a particle in a 1-D box.

$$E_n = n^2 \frac{h^2}{8ma^2} ,$$ (Henceforth we drop suffix of E)

$$dE = \frac{h^2}{8ma^2} . 2n. dn$$ (1.42)

$$\frac{dn}{dE} = \frac{8ma^2}{h^2} . \frac{1}{2n} = \frac{a}{h} \sqrt{\frac{2m}{E}}$$ (1.43)

$$D(E) = \frac{dn}{dE} \propto E^{-\frac{1}{2}}$$ (1.44)

The equation (1.44) shows how the density of states will vary with change of energy. Depending upon the energy state's function, density of states would take form as briefly stated below.

Density of States for a Zero Dimensional (0–D) Solid

Neglecting the periodic potential existing in solids, we can imagine a zero dimensional solid in which electron is confined in a three dimensional potential box with extremely small (<100 nm) length, breadth and height as a 0-D solid. This will have the discrete energy levels as discussed above with density of states given as

$$D(E) = \frac{dN}{dE} = \sum_{\varepsilon_i} \delta(E - \varepsilon_i)$$ (1.45)

where ε_i are discrete energy levels and δ is Dirac function. The density of states as a function of energy would appear as illustrated in Fig. 1.9.
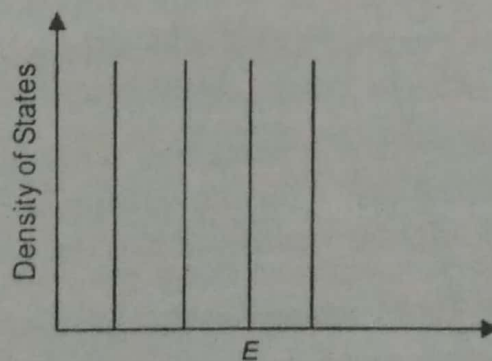

Fig. 1.9: Density of states for a particle in a zero dimensional solid.

Density of States in a One Dimensional (1–D) Potential Box, Quantum Wire

A particle confined in a one dimension is like a particle in a one dimensional potential well as in the previous case. However the potential in two directions is infinitely large but in the third direction it is zero. This gives rise to density of states as follows:

$$D(E) = \frac{dN}{dE} = \sum_{\varepsilon_i < E} \delta(E - \varepsilon_i)^{-1/2} \qquad \chi \qquad (1.46)$$

where ε_i are discrete energy levels. Figure 1.10 graphically illustrates nature of density of states for a one dimensional solid.
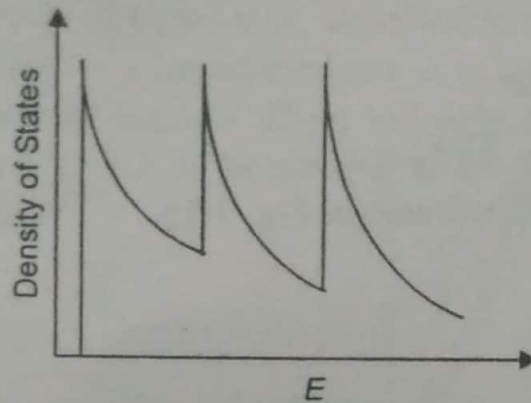

Fig. 1.10: Density of states for a particle in a one dimensional solid.

Density of States in a Two Dimensional (2-D) Potential Box, Thin Film

It can be shown that the density of states ($D(E)$) in the two dimensional solid which is nothing but the case of thin films, is given as

$$D(E) = \frac{dN}{dE} = \sum_{\varepsilon_i < E} 1 \qquad \chi \qquad (1.47)$$
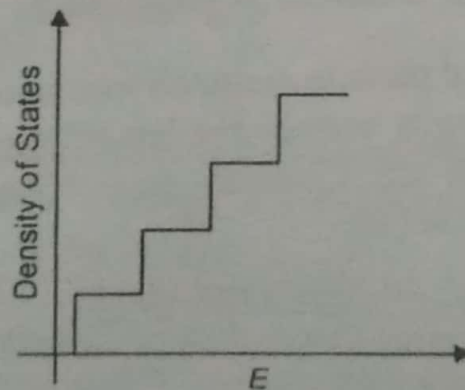

Fig. 1.11: Density of States for a 2-D potential box.

Thus it can be shown that the density of states in two dimensional case is a staircase (see Fig. 1.11). In this case $\frac{dN}{dE}$ would correspond to the states available in an area.

Density of States for a Particle in a Three Dimensional Box

Following the previous cases it is a straightforward task to show that in a box of length 'a', width 'b', and height 'c' with potential $V = 0$ inside the box and $V = \infty$ outside the box, the energy states can be obtained as

$$D(E) \propto E^{1/2} \qquad (1.50)$$

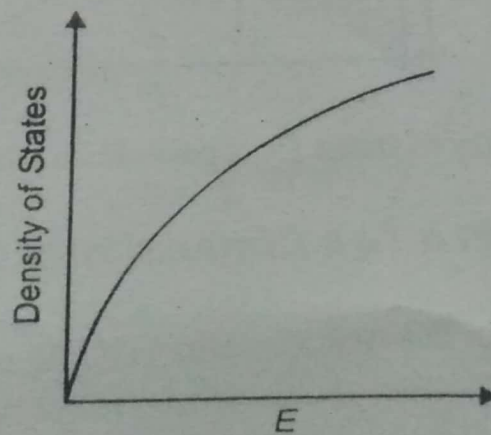This is graphically illustrated in Fig. 1.12.

Fig. 1.12: Density of states for a particle in a 3-D potential box.

4.2 COLLOIDS AND COLLOIDS IN SOLUTIONS

Colloids are known since very long time. A class of materials, in which two or more phases (solid, liquid or gas) of same or different materials co-exist with the dimensions of at least one of the phases less than a micrometre is known as colloids. Colloids may be particles, plates or fibres (see Fig. 4.1). Nanomaterials are a sub-class of colloids, in which one of the dimensions of colloids is in nanometre range.

spheres   rods   tubes   fibres

different shapes

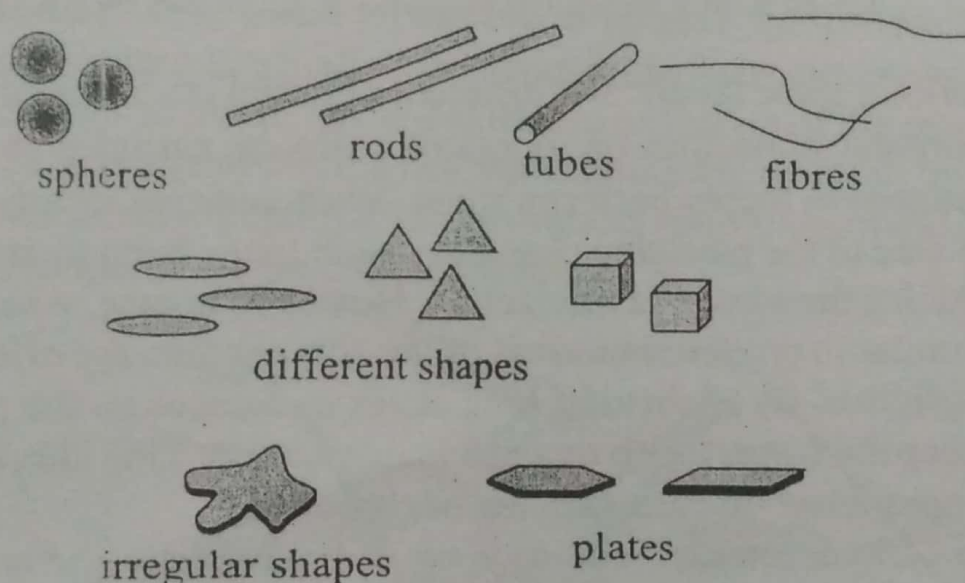irregular shapes   plates

Fig. 4.1: Different types of colloids. Spherical, lamellar, fibres etc.

There are several examples around us, having different combinations of phases, in the form of colloids like liquid in gas (fog), liquid in liquid (fat droplets in milk), solid in liquid (tooth paste), solid in solid (tinted glass), gas in liquid (foam) etc. There can be multiply existing colloids like water and oil bubbles in porous mineral rocks. Organic and inorganic materials can be dispersed into each other to form colloids. Several examples exist even of bio-colloids. Blood and bones are good examples of bio-colloids. Blood has corpuscles dispersed in serum and bone has colloids of calcium phosphate embedded in collagen.

Colloids may even form networks. For example aerogels (discussed in more details in Chapter 10) is a network of silica colloidal particles, pores of which are filled with air.

4.2.6 Synthesis of Colloids

Colloids are thus phase separated submicrometer particles in the form of spherical particles or particles of various shapes and sizes like rods, tubes, plates etc. They are the particles suspended in some host matrix. Metal, alloy, semiconductor and insulator particles of different shapes and sizes can be synthesized in aqueous or nonaqueous media. Colloidal particles in liquids are

stabilized as discussed above by Coulombic repulsion, which arises due to similar charges they may have acquired on their surfaces. In some cases surface passivating molecules may be used which provide sufficient stearic hindrance inhibiting coalescence or aggregation. Nanomaterials are a special class of colloidal particles which are few hundreds of nanometer or smaller in size.

Synthesis of colloids is a very old method. Making nanoparticles using colloidal route goes back to 19th century when M. Faraday synthesized gold nanoparticles by wet chemical route. The particles are so stable that even today the colloidal solution made by him can be seen in British Museum in London.

Here we shall discuss some commonly used synthesis methods of metal, semiconductor and insulator nanoparticles with some examples.

Chemical reactions in which colloidal particles are obtained are carried out in some glass reactor of suitable size. Glass reactor usually has a provision to introduce some precursors, gases as well as measure temperature, pH etc. during the reaction. It is usually possible to remove the products at suitable time intervals. Reaction is usually carried out under inert atmosphere like argon or nitrogen gas so as to avoid any uncontrolled oxidation of the products. There is also a provision made to stir the reactants during the reaction by using teflon coated magnetic needle. Figure 4.13 illustrates a simple chemical synthesis set up to obtain nanoparticles by colloidal route.
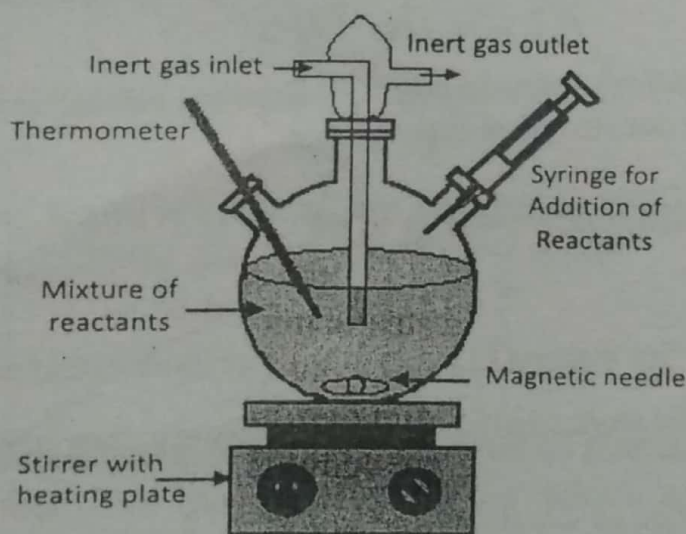

Fig. 4.13: A typical chemical reactor to synthesize nanoparticles.

4.3 GROWTH OF NANOPARTICLES

Although chemical synthesis of nanoparticles may appear as a complex process, by understanding how nucleation and growth of particles takes place, it is possible to control the various steps and try to achieve monodispersed (i.e. particles of nearly same size) nanoparticles. This can be done with the help of LaMer diagram shown in Fig. 4.14. As we keep on increasing the concentration of the reactants in the solution, at certain concentration say C_0, the formation of nuclei begins. There is no precipitate at this concentration. Further increase in concentration increases nuclei formation up to a concentration C_N, above which there is a 'super saturation' between C_N and C_S. Concentration C_N denotes

the maximum rate of nuclei formation. When nuclei formation reduces, again C_0 the minimum concentration for nucleation is reached. No new nuclei can be formed and crystal growth reduces the concentration. At this concentration C_S, an equilibrium is obtained. If new nuclei are formed during the growth of particles then particles with large size distribution are obtained. Therefore it is very important that concentration of solute and its diffusion be adjusted properly in order that no fresh nuclei are formed once the concentration has reached C_N. Particles can grow even at the expense of smaller particles. Larger particles are more stable and grow at the expense of smaller particles. This growth mode is known as *Ostwald ripening*. The driving force for larger particles is the reduction in surface-free energy.
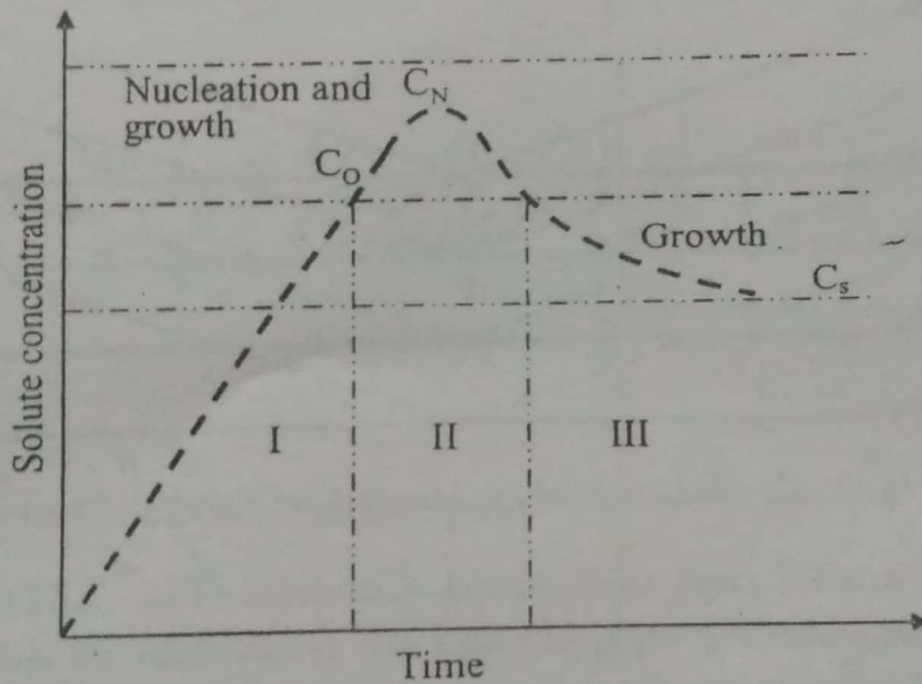

Fig. 4.14: LaMer diagram. Regions I, II, and III are for concentration increase, nucleation and growth respectively.

Experimentally it is often found that there is sometimes aggregation of particles (see Fig. 4.15). Aggregation also reduces the energy of the system. Thus Ostwald ripening and aggregation are competing processes and either of them may be responsible to reduce the surface-free energy.
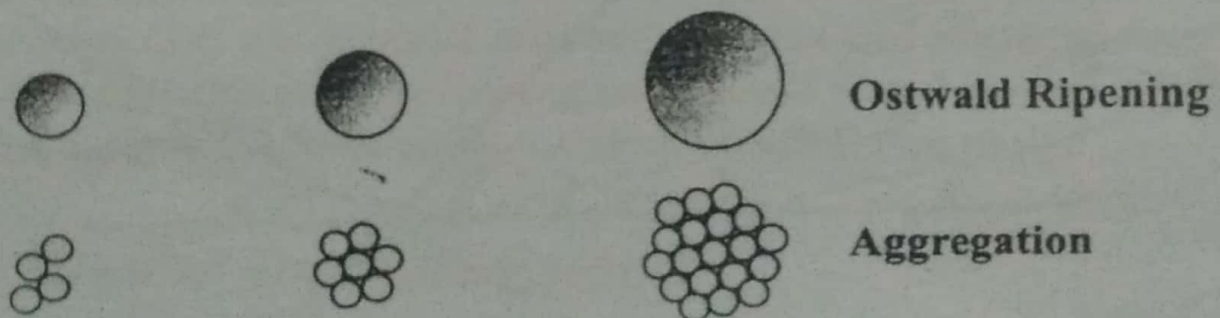

Fig. 4.15: Growth and aggregation of colloids.

(*i*) **Bottom-up technique** is a technique in which materials and devices are built up atom by atom. Bottom-up manufacturing would provide components made of single molecules, which are held together by covalent forces that are far stronger than the forces that hold together macro-scale components. Furthermore, the amount of information that could be stored in devices build from the bottom-up approach would be enormous.

(ii) Top-down technique is a technique in which devices are fabricated by removing existing material from larger entities. The current top-down method for manufacturing involves the construction of parts through methods such as cutting, carving and molding. Using these methods we have been able to fabricate a remarkable variety of machinery and electronic devices. However, the sizes at which we can make these devices are severely limited by our ability to cut, carve and mold. We describe here three different techniques used in making nanostructures.

39.13.3 Synthesis of Nanoparticles

There are a wide variety of methods to produce nanoparticles. A few commonly used methods are outlined here.

1. High-energy Ball milling: High energy ball milling is a *top-down approach* technique. Coarse grained materials are crushed mechanically in rotating drums by hard steel and tungsten carbide balls. The grain size in powder samples are reduced to nanometer range by mechanical deformation produced by ball milling process. Magnetic and catalytic nanoparticles are usually produced by this method.

In this method, a container is filled with stainless steel balls of a few millimeters in diameter (Fig. 39.25). The material to be crushed is added in the form of a powder of about 50 μm diameter grain size. After filling the container with liquid nitrogen, a rotating shaft grinds the material. The grinding periods are within the range of minutes to some 100 hours. This process is simple. However, the difficulty in this technique is that we cannot be sure that all the particles are broken down to the required particle size. Further, during mechanical attrition, contamination by the milling tools (Fe) and atmosphere (trace elements of O_2, N_2, in rare gases) can be a problem. The use of tungsten carbide component and inert atmosphere and /or high vacuum processes has reduced impurity levels to within acceptable limits. Common drawbacks include low surface, highly poly disperse size distribution, and partially amorphous state of the powder. The main advantage of this top-down approach is high production rates of nanopowders.
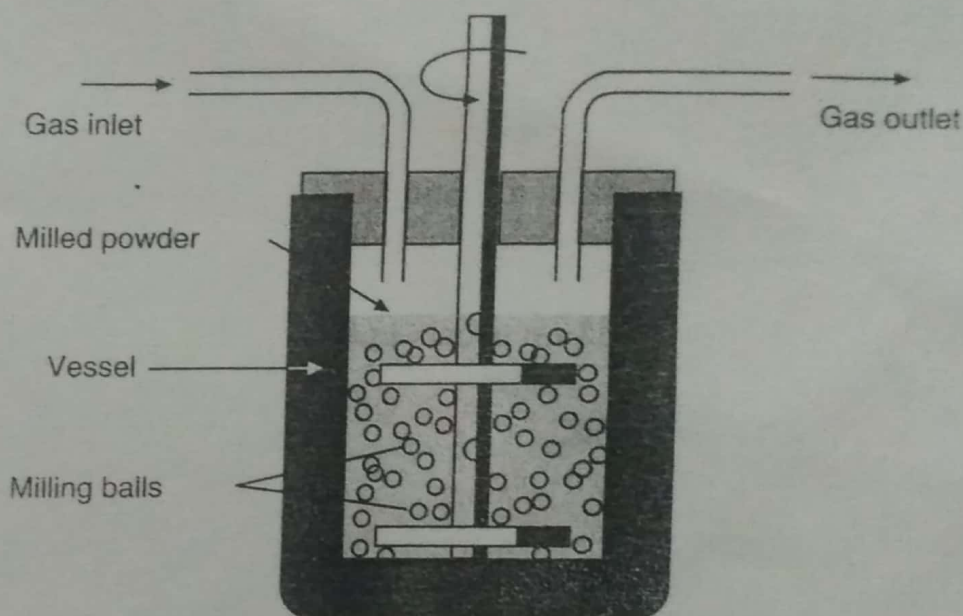
Gas inlet

Gas outlet

Milled powder

Vessel

Milling balls

Fig. 39.25

7.5.7 X-ray Diffractometer

There are different types of X-ray diffractometers available for crystal structure analysis. Same can be used for nanomaterials analysis. The most commonly used diffractometer is known as Powder Diffractometer or Debye-Scherrer Diffractometer after its inventors. This diffractometer is conceptually simple and allows quite an accurate determination of crystal structure of polycrystalline samples, thin films and nanoparticles.

As illustrated in Fig. 7.29, it consists of a monochromatic source of X-rays, usually from a copper target or anode giving CuK_α ($\lambda = 0.154$ nm after passing through nickel filter), sample holder and an X-ray detector. Both sample and the detector move around an axis passing through sample centre.

Samples in the form of powder, thin films etc. can be used. Some times sample heating/cooling facilities are provided.
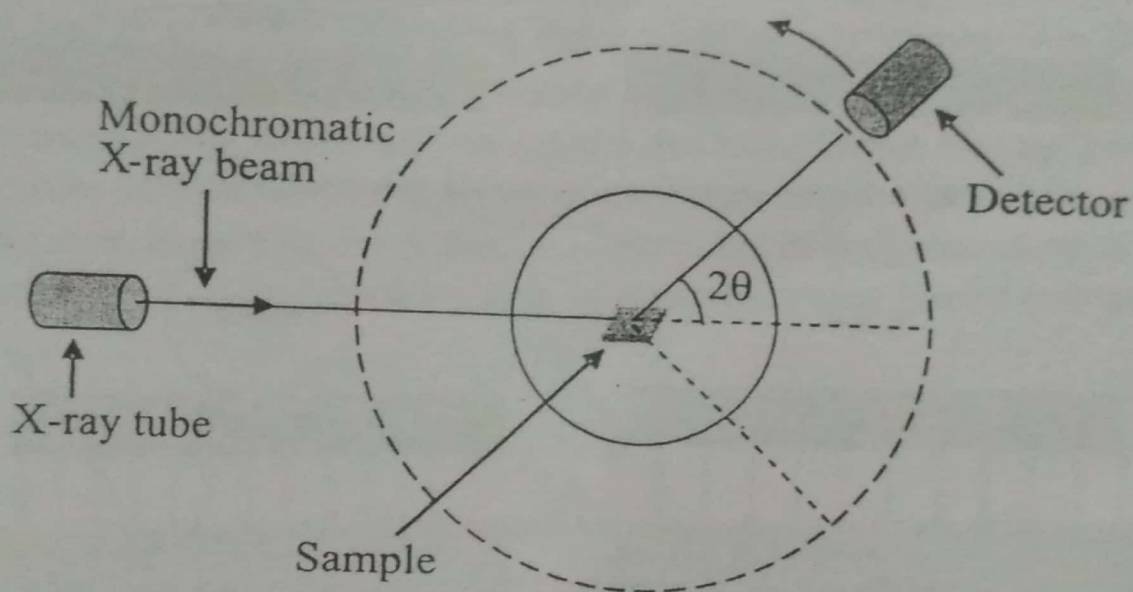
Fig. 7.29: Schematic of X-ray diffractometer.

The diffracted rays make an angle 2θ at the detector with respect to incident beam direction. A plot of intensity (counts) as a function of angle 2θ (usually $20°$ to $160°$) is a diffraction pattern ready for analysis. For most of the routine work this is quite sufficient. Detector is a suitable photon counter like Geiger Müller tube, proportional counter or scintillation counter. Usually, due to finite size of X-ray beam ~1-2 mm², smaller angles (<20°) are not accessible using these diffractometers. However for some detailed analysis of thin films or nanoparticles, where additional information can be obtained at as small as θ ~0.1-0.2°, modifications of Debye Scherrer Diffractometer or another diffractometer is needed.

7.5.4 Diffraction from Different Types of Samples

So far we considered the diffraction from a set of planes, assuming them to be infinite in number. We may have samples which are single crystalline, polycrystalline solids, liquids or even gases. Amorphous solids, liquids, gases and nanocrystalline materials do not have infinite ordered arrangement of atoms but have few atoms and few planes (small single crystals). Nanoparticles with disordered structure can be treated like amorphous bulk solids. In Fig. 7.26 the differences in scattering of X-rays by different materials are shown.

It can be seen from Fig. 7.26 that in case of a monoatomic gas (like He, Ar, Kr) forward scattering occurs without any diffraction peaks in any other direction. In case of liquids or amorphous solids one or two peaks at angles other than the angle of incidence appear due to short range order in these materials. For single crystals, diffraction peaks appear at various angles. Intensities of peaks depend upon atomic scattering factor as well as crystal structure (or form) factor which we shall consider in the following section. The diffraction peaks from ideal single crystals are sharp, and broadened to
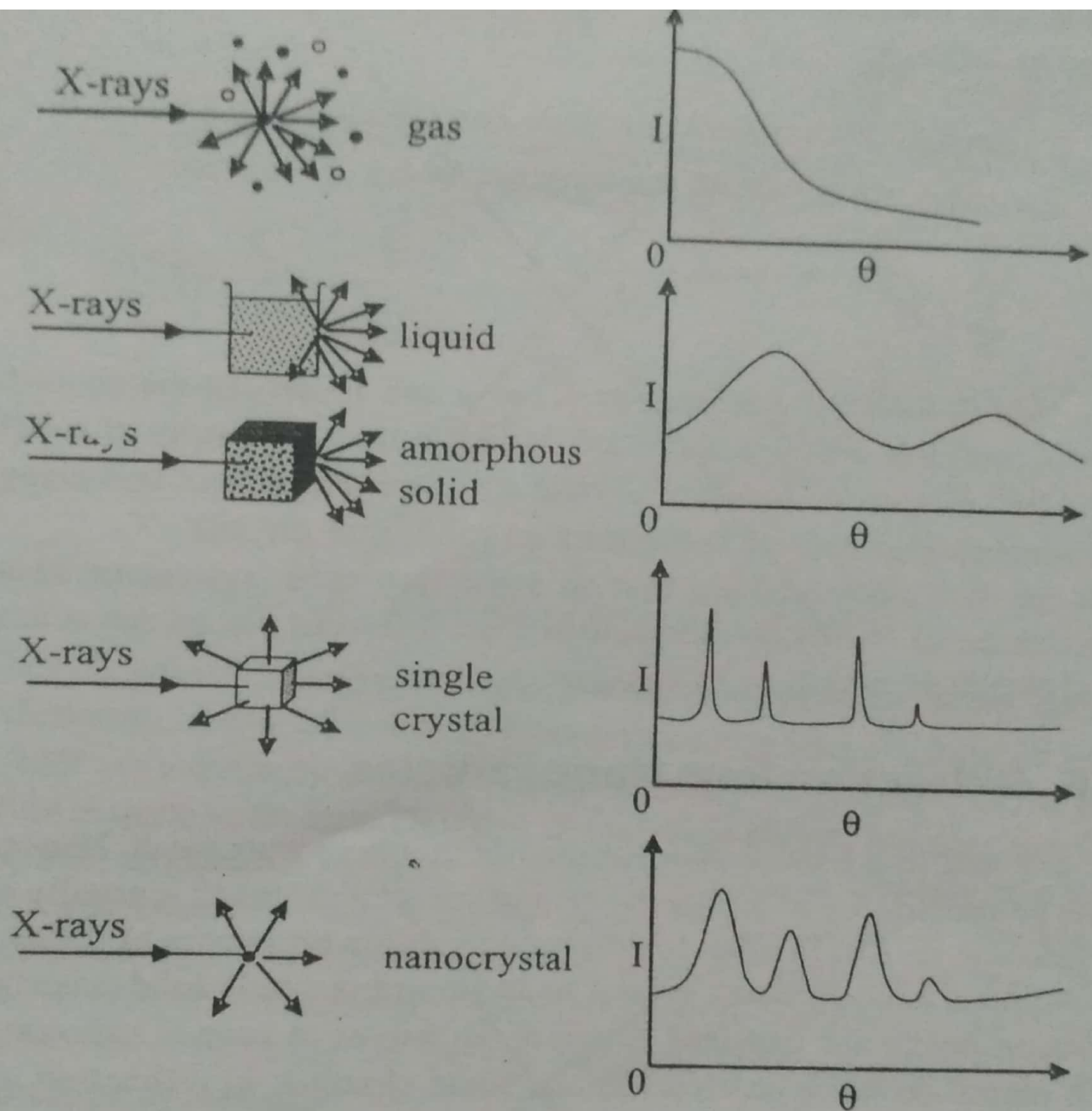
Fig. 7.26: Diffraction from gases, liquids, solids and nanocrystals.

certain extent only by instrumentation factor. However in case of polycrystalline sample the peaks are broadened due to the size of the grains. All the grains in crystal may not be of the same size. Therefore the width of the diffraction peaks can be considered as the effect of convolution of different peaks giving the average grain size. The diffraction peaks are broadened in case of nanoparticles also due to small number of atoms and planes present in them. We shall discuss this in the following section and show how one can determine the average particle size using the widths of diffraction peaks.
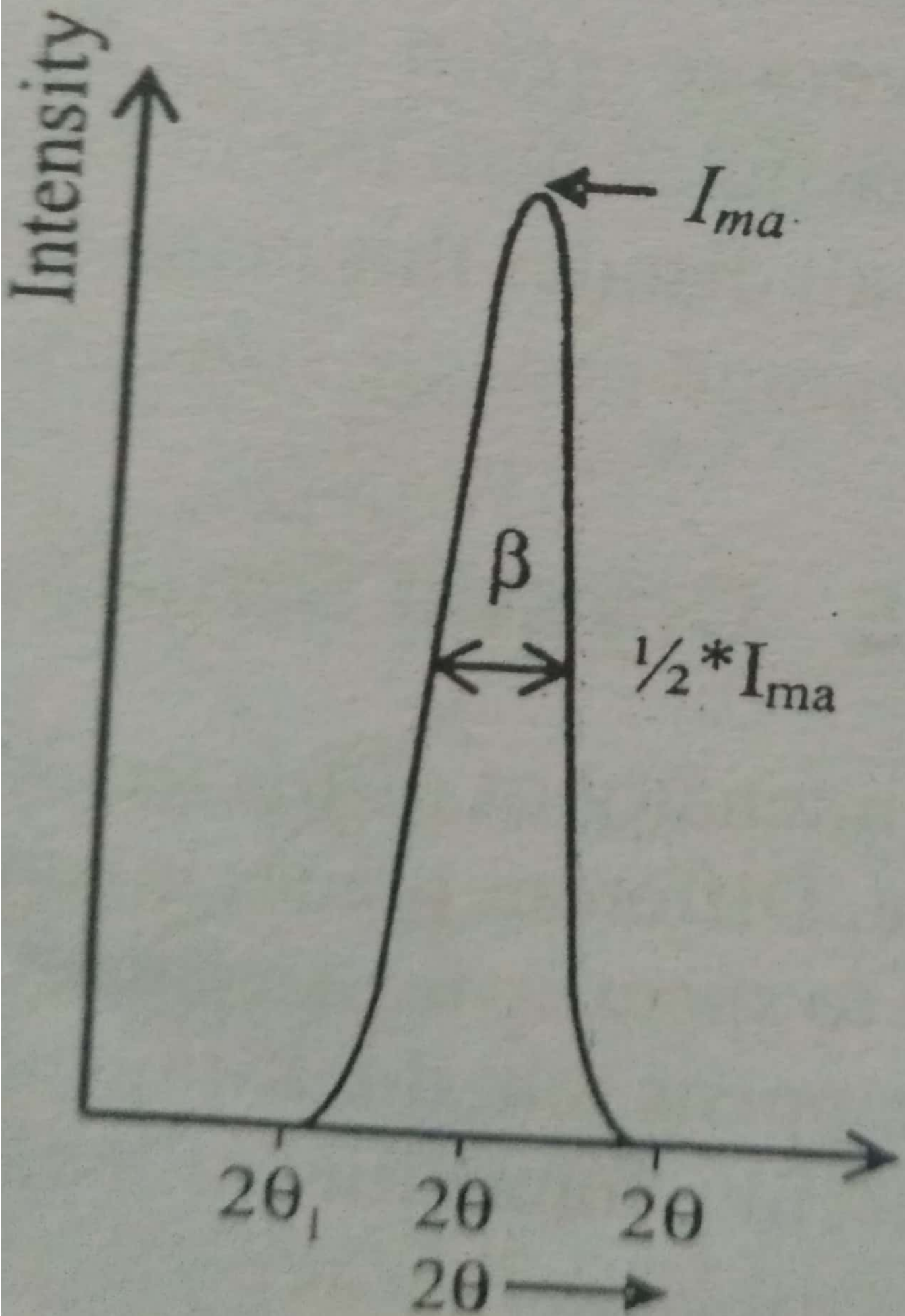
$$T = \frac{0.9\lambda}{\beta \cos\theta_B}$$

(7.29)

This is known as Scherrer equation. The width β is the broadening caused by nanoparticle size. Scherrer formula can be used to evaluate the average particle size smaller than ~100 nm which is just what is needed in Nanoscience. However for extremely small particles (<2 nm) the broadening of diffraction

7.3.1 Scanning Electron Microscope

In Fig. 7.7, essential parts of a scanning electron microscope are shown. In an electron microscope, electrons emitted from a hot filament are usually used.
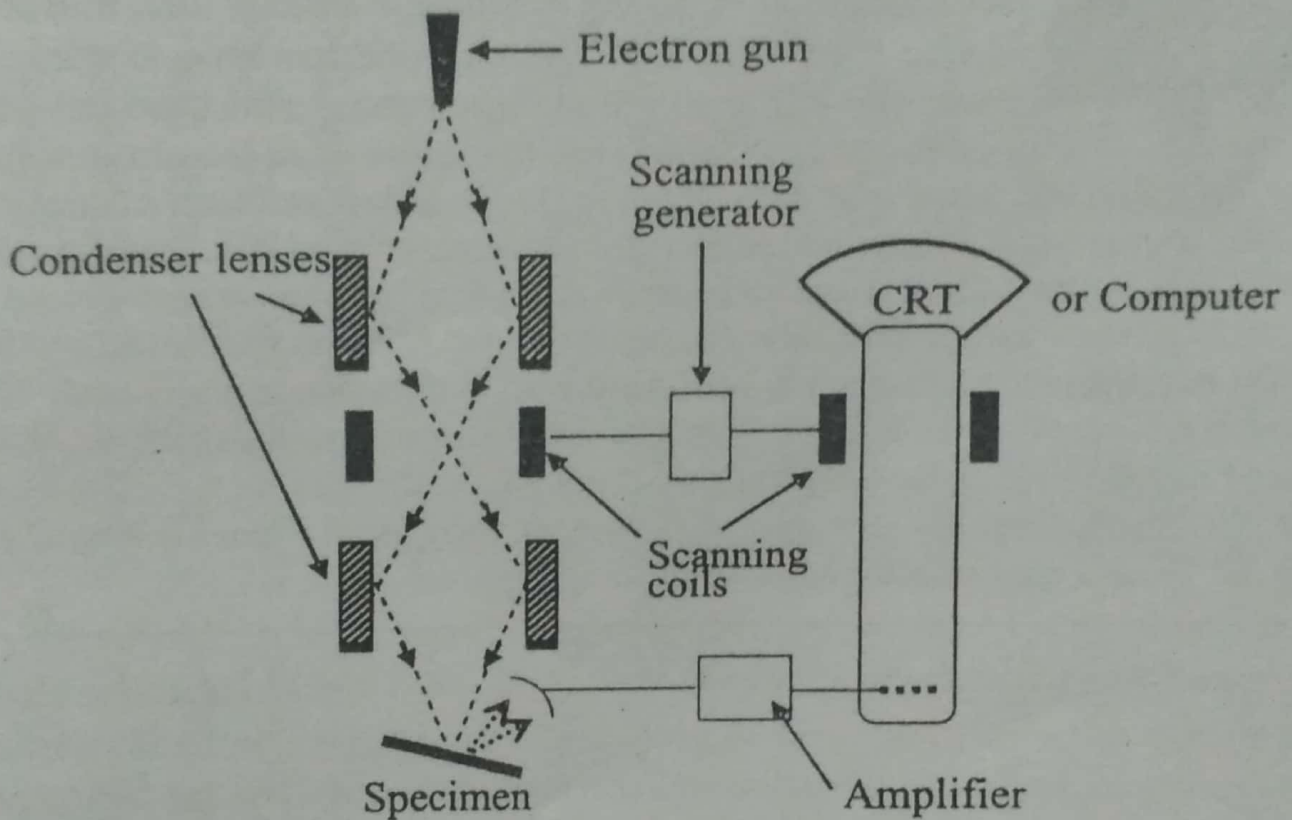

Fig. 7.7: A typical sketch of a scanning electron microscope. Electron gun, specimen and various electrodes or coils need to be mounted in a vacuum chamber.

Typically electrons are accelerated upto ~30 keV and resolution upto 3-5 nm can be achieved. However, sometimes cold cathode (a cathode that emits electrons without heating it) is also used. A cold cathode emits electrons under the application of a very high electric field. It is also known as a field emitter. Such SEMs are known as FE-SEM and are able to give better images than hot filament SEM. However, such FE-SEM is less common than hot cathode SEM. FE-SEM are operated at energies between 0.1 to 30 keV and resolution from 1 nm-2 nm is possible.

In a scanning electron microscope, backscattered electrons or secondary electrons are detected (in some cases it is also possible to use sample current). Due to interaction of focussed beam with solid, the backscattered electrons are somewhat defocussed resulting into lowered resolution than one would expect.

In an electron microscope, the electron beam can be focussed to a very small spot size using electrostatic or magnetic lenses. Usually the electrostatic lenses are used for an SEM. The fine beam is scanned or rastered on the sample surface using a scan generator and backscattered electrons are collected by an appropriate detector.

Signal from scan generator along with amplified signal from the electron collector generates the image of sample surface. In order to avoid the oxidation and contamination of filament as well as reduce the collisions between air molecules and electrons, filament and sample have to be housed in a vacuum chamber. Usually vacuum $\sim 10^{-2}$ to 10^{-3} Pa or better is necessary for a normal operation of scanning electron microscope. This makes electron microscopes

rather inconvenient. However some manufacturers have been successful in marketing electron microscopes known as *environmental microscopes*, which operate at rather high pressure of few Pa. No sample preparation is necessary. Electrons are accelerated as usual in a vacuum system but they enter the sample chamber through a thin foil or aperture so that a large pressure difference can be maintained. This helps to analyze biological samples without dehydrating them. Change of samples also becomes easy.

One disadvantage of electron microscopes is that insulating samples cannot be analyzed directly as they get charged due to incident electrons and images become blurred/faulty. Therefore insulating solids are coated with a very thin metal film like gold or platinum (<10 nm) making them conducting without altering any essential details of the sample. The metal film is usually sputter-coated on the sample to be investigated prior to the introduction into the electron microscope. This enables even biological samples to be analyzed using an electron microscope.

Electron microscope can also be used to obtain the composition of sample using a technique known as Energy Dispersive Analysis of X-rays (EDAX). The high energy electrons striking the sample produce characteristic X-rays of atoms with which they interact. When intensities of such characteristic X-rays are compared one can obtain the composition analysis of the sample under investigation.
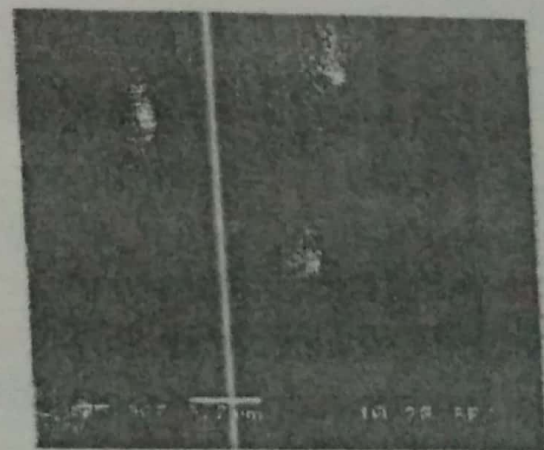

Fig. 7.8: Scanning Electron Microscopy images of ZnO with flower like morphology and belt like morphology. The chemical co-precipitation synthesis method has been used to obtain various morphologies by varying the synthesis parameters.