Chapter#1

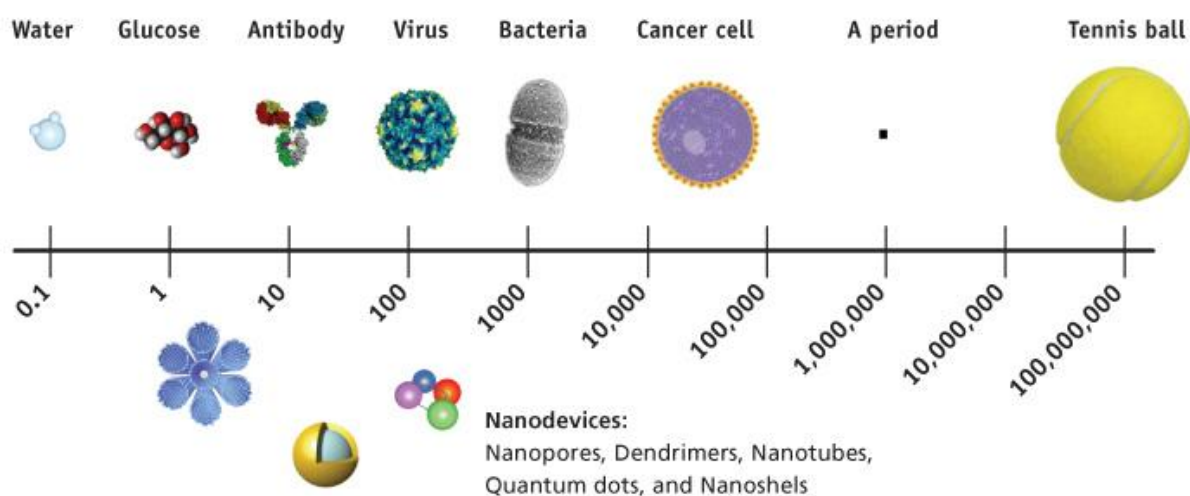## *Introduction to Nanotechnologies*

1.1: What is nanotechnology

Nanotechnology is the creation of useful/functional materials, devices, systems through control of matter on nanometer length scale and exploitation of useful novel phenomenon and properties (Physical, Chemical & Biological) on that length scale.

1.2: Types of Nano-structured materials with respect to dimensions

Zero dimensional - 0D

All three dimensions are in nanometer length scale

e.g, Isolated nanoparticles, Nanodots etc.

One dimensional - 1D

Two dimensions are in nanometer length scale

e.g, Nanorods, nanowires, nanostripes etc.

Two dimensional - 2D

One dimension in nanometer length scale

e.g, Thin films

1.3: History of Nanotechnology

History of Nanotechnology

- ~ 2000 Years Ago – Sulfide nanocrystals used by Greeks and Romans to dye hair
- ~ 1000 Years Ago (Middle Ages) – Gold nanoparticles of different sizes used to produce different colors in stained glass windows
- 1959 – "There is plenty of room at the bottom" by R. Feynman
- 1974 – "Nanotechnology" - Taniguchi uses the term nanotechnology for the first time
- 1981 – IBM develops Scanning Tunneling Microscope
- 1985 – "Buckyball" - Scientists at Rice University and University of Sussex discover C_{60}
- 1986 – "Engines of Creation" - First book on nanotechnology by K. Eric Drexler. Atomic Force Microscope invented by Binnig, Quate and Gerbe
- 1989 – IBM logo made with individual atoms
- 1991 – Carbon nanotube discovered by S. Iijima
- 1999 – "Nanomedicine" – 1st nanomedicine book by R. Freitas
- 2000 – "National Nanotechnology Initiative" launched
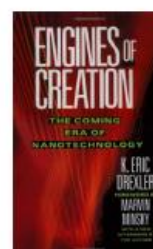
1.4: Importance of length Scale

At nanoscale both physical and chemical properties of materials change. Below are examples:

Chemical property

One of the size-dependent property of nanoparticles is their chemical reactivity. This is demonstrated most dramatically by gold, which in the bulk is inert material. It would therefore seem that gold, would be useless as a catalyst to speed up chemical reactions, but this is not so for gold nanoparticles. In fact, most catalysts are in the form of nanoparticles; and bearing in mind everything that has been said so far about how material properties change with size in the nanoworld, the same is true of gold. When gold is in the form of nanoparticles with diameters less than about 5 nm, it becomes a powerful catalyst, especially for the oxidation of carbon monoxide (CO). The full story is quite complicated because the reactivity of gold nanoparticles appears to depend not only on their size but also on the material on which they are supported.

Physical property

When we reach the nanoscale, physical properties of gold also changes, e.g, gold's color, melting point etc. The reason for this change has to do with the nature of the interactions among the atoms that make up the gold, interactions that are averaged out of existence in the bulk material. Nano gold doesn't act like bulk gold.

The process of nanofabrication, in particular the making of gold nanoparticles, is not new. Much of the color in the stained glass windows found in medieval and Victorian churches and some of the glazes found in ancient pottery depend on the fact that nanoscale properties of materials are different from macroscale properties. In particular, nanoscale gold particles can be orange, purple, red, or greenish, depending on their size. In some senses, the first nanotechnologists were actually glass workers in medieval forges rather than the bunny-suited workers in a modern semiconductor plant. Clearly the glaziers did not understand what they did to gold that produced its different colors, but now we know.

Materials scientists and electrical, chemical, and mechanical engineers all deal with the unique properties of nanostructures and with how those special properties can be utilized in the manufacturing of entirely new materials that could provide new capabilities in medicine, industry, recreation, and the environment.

1.5: Moore's law

Moore's empirical law summarizes the "economy of scale" in getting the same function by making the working elements ever smaller. "The number of transistors in successive generations of computer chips has risen exponentially, doubling every 1.5 years or so".

Gordon Moore, co-founder of Intel, Inc. predicted this growth pattern in 1965, when a silicon chip contained only 30 transistors! The number of Dynamic Random Access Memory (DRAM) cells follows a similar growth pattern. The growth is largely due to continuous reduction in the size of key elements (Transistors & connecting wires) in the devices, to about 10 nm, with improvements in optical photolithography. Clock speeds have similarly increased, presently around 3 GHz.

There are some challenge to the continuation of this trend (Moore's Law)

Firstly, from the economic reality of steeply increasing plant cost to realize further reduced line widths and smaller transistors as we are continuosly decreasing transistor size.

Secondly, the granular nature of matter is the fundamental limit to making anything arbitrarily small. No transistor smaller than an atom, about 0.1 nm, is possible.

1.6: Origin of observed differences in properties of nanoscopic and macroscopic samples

❖ Broken translational symmetry in nanoscopic samples at surface (atoms here have reduced numbers of neighbors). The surface atoms may be at plane surface, at corner of step or inside the step having different coordination numbers.

❖ Nanoscopic objects: Higher proportion of surface or interface atoms or greater surface to volume ratio, making them ideal for use in composite materials, reacting systems, catalysts, drug delivery, and chemical energy storage (such as hydrogen and natural gas).

❖ Close contact with other physical systems: e.g with substrate or capping layer in case of thin films or multilayers, which can result strain in thin films and modification of lattice constant.

❖ Sizes of nanometric objects ~ fundamental or characteristics lengths of constituent material (exchange length, spin diffusion length, magnetic domain wall width, which are more relevant to magnetic properties)

❖ Different shape of density of electronic states and band structures. The quantum mechanical (wavelike) properties of electrons inside matter are influenced by variations on the nanoscale.

Explanation of Origin of observed differences in properties of nanoscopic materials

1.7: Nano Dimensionality and Density of Electronic States

The electronic band structure of a solid depends on its dimensionality. This can be exemplified in the simplest description of a conducting solid, the free electron model, in which the electrons are treated as a gas (called a Fermi gas) only subject to the infinite potentials at the walls of the container. An electron gas in a limited spatial region will show an availability of electronic states (measured by its density of states $D(E)$ that depends on the dimensionality of this region: if it is in one dimension or two dimensions, $D(E)$ will differ from the three-dimensional case. The effects of the difference in dimensionality may be shown through the differences in $D(E)$.

We will now discuss what happens if the object that contains the electrons is a solid of nanometric dimensions. There will be quantum confinement in any case where one or more dimensions of the volume that contains the electron gas are comparable to the Fermi wavelength $\lambda_F = 2\pi/k_F$ of the electron. In objects with dimensions comparable to this wavelength the wave character of the electrons will be dominant, and their energies will be quantized.

To obtain the densities of states in the confined systems, one has to take into consideration the boundary conditions. The electrons may be confined in the three dimensions, i.e., they may be contained in an object that is nanometric in the three dimensions – this is the case of a quantum dot. If the electrons are confined in two dimensions, i.e., if the third dimension is macroscopic, one has a quantum wire, or a nanowire. If the electrons are confined in one dimension, one has a quantum well, or a quantum film. If the electrons are not confined in any dimension, one has a macroscopic object.

I. **Object confined in three dimensional nanosystem (quantum dot):**
   The appearance of $D(E)$ for the 0D sample is similar to the same function for atoms: $D(E)$ has narrow peaks, corresponding to well-defined values of the kinetic energy of the conduction electrons. For this reason, quantum dots are often referred to as "artificial atoms."

II.   **Object confined in two dimensional nanosystem (thin film):**
The curve for a two-dimensional nanosystem shows some well-defined steps, and again there exists a quasi-continuum of states that may be occupied in the whole range of energies.

III.   **Object confined in one dimensional nanosystem (quantum wire):**
The curve $D(E)$ for quantum wires (one-dimensional) also has narrow peaks, but in this case there are electronic states that may be occupied for intermediate values of the energy E.

IV.   **Object confined in macroscopic system:**
The result of $D(E)$ for a macroscopic system in the free electron approximation is the well-known parabola, applicable in the simplest description of the metals.
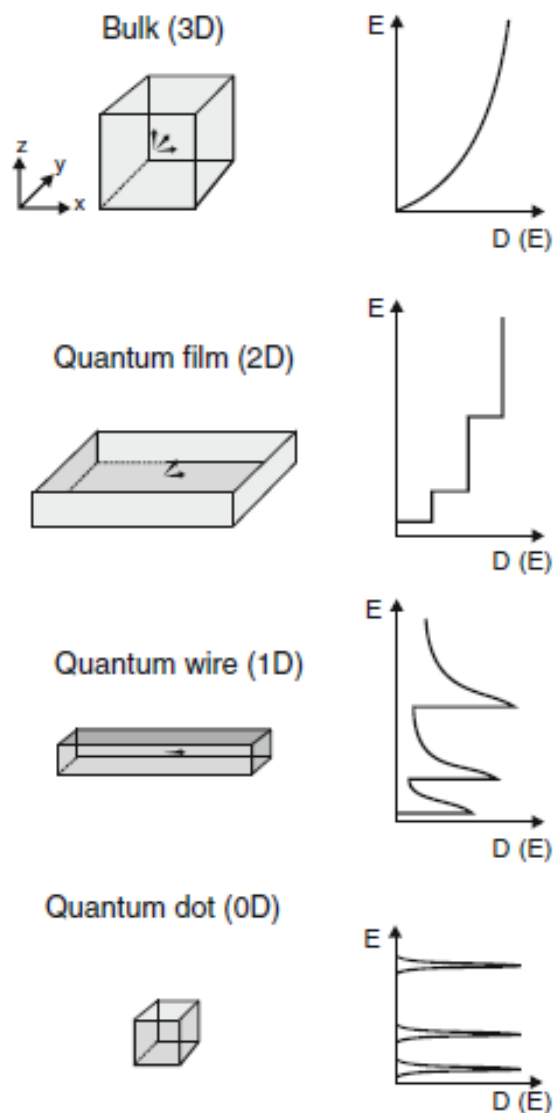
Fig. Density of electronic states $D(E)$ as a function of energy for electrons, from *bottom to top*, in zero dimension, in one dimension, two dimensions, and three dimensions.

Dependance of materials properties on Density of States

Many physical and chemical properties of a solid may be directly related to the electronic density of states $D(E)$, such as the Pauli susceptibility, the conduction electron contribution to the specific heat, and so on.

I. **The Pauli susceptibility**, that measures the response of the free electron gas to an applied magnetic field, is given by

$$\chi_P = \mu_0 \mu_B^2 D(E_F)$$

where $D(E_F)$ is the density of states at the Fermi level.

II. **The magnetic moments of the transition element atoms** also depend on the dimensionality of the structures where they are found. This dependence is evident in the computed magnetic moments of Ni and Fe for different dimensionalities, given in Table 1.3. The iron magnetic moment, for example, varies from $2.27\mu_B$, for a three-dimensional solid, to $4.0\mu_B$ for 0D (free atom).

Element	Zero (0D)	One (1D)	Two (2D)	Three (3D)
Ni	2.0	1.1	0.68	0.56
Fe	4.0	3.3	2.96	2.27

Computed magnetic moments (in μB) and dimensionality for Ni and Fe samples

1.8: Nano Dimensionality and Reduced Coordination Number

An additional circumstance that modifies the properties of nanoscopic systems is the relevance of their immediate neighborhood, or physical systems in close contact. The charge and spin densities near surfaces and interfaces are significantly modified from the corresponding densities at the inner rows of atoms because atoms in these regions have a reduced number of neighbors, as compared to atoms in the bulk of the sample.

This is the case of magnetic thin films that are deposited on substrates or are covered with protective capping layers. For example, films of Co deposited on Cu(001) have Curie temperatures that vary a few degrees, in an oscillatory way, with the thickness of a Cu capping layer.

In general electronic structure of atoms with smaller coordination number is different from that of atoms in bulk. The density of states shows that reduction in coordination number results in narrowing of electronic bands.

The quantum mechanical (wavelike) properties of electrons inside matter are influenced by variations on nanoscale.
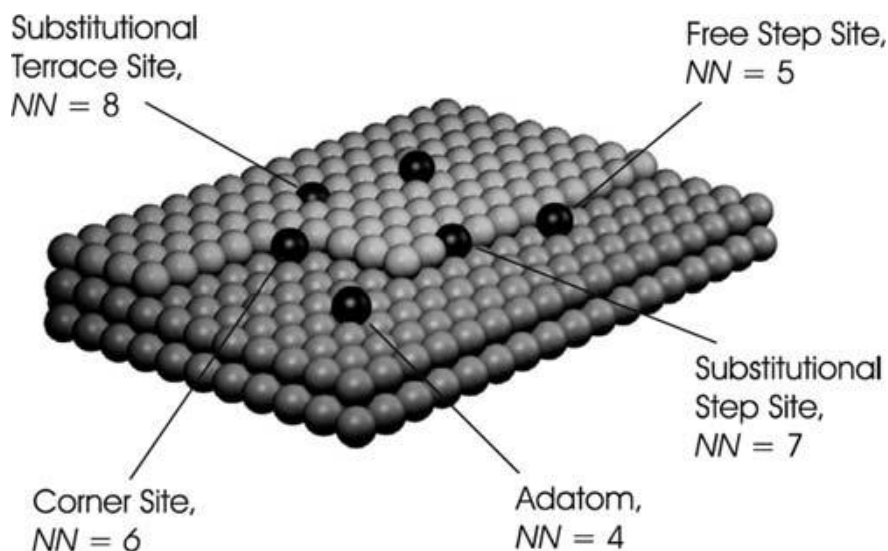
Fig. 1.7. Atomic sites on a thin film showing the different coordination numbers. The number NN of nearest neighbors of the atoms on the surface (adatom, NN = 4), atom near a step (NN =5), atom in the step (NN =7) and finally, a substitutional atom at the surface (NN

1.9: Nanoscopic Samples and Proportion of Surface Atoms

The role of surface atoms is widely utilized in catalysis. Catalysts are usually prepared in the form of finely divided powders, or porous matrices, since their activity relies on the contact of the substances that participate in the chemical reaction with atoms at their surface.

In the study of nanoscopic samples the contribution of the surface atoms to the physical properties increases with decreasing sample sizes. This is obvious, since the area of the surface of the samples varies typically as r^2, while the volume of the samples varies as r^3. As a consequence, the ratio of surface to volume varies roughly speaking as r^{-1}, therefore increasing with decreasing sample size. This can be illustrated with the ratio of surface atoms to total number of atoms in cubic nano clusters. For example, a cube with 10 atoms of side has about half of the atoms on its surface. In some limiting cases, as for example, in a thin film formed of only one or two atomic layers, every atom of the sample is a surface atom.

The area per unit mass, or specific surface area of nanoscopic samples can be very large: for typical 2 nm spherical particles this may be in the range of hundreds of square meters per gram.

1.10: Nanoscopic Samples and Magnetization Reversal

The dynamic behavior of the magnetization of nanomagnets may also be very different from that of macroscopic objects. This arises because, under the usual experimental conditions, thermal fluctuations play in this case a more important role. For example, in nanoscopic magnetic particles it is observed the phenomenon of superparamagnetism: in such particles, the magnetization inverts spontaneously, since the thermal energy k_BT is comparable to their anisotropy energy.

A single-domain magnetic particle may spontaneously invert its magnetization, i.e., its direction may change from $+z$ to $-z$, if its temperature T is above a certain blocking temperature T_B. This effect has important implications, since if the magnetization of such particle were to be used for information storage, at $T = T_B$ the information would be lost. Therefore, in magnetic storage, with the reduction in physical size of the recorded bit, its thermal stability becomes more and more an important issue.

1.11: Sample Dimensions and Characteristic Lengths

When the size of materials is compareable to some fundamental or characteristics lengths e.g, Fermi wavelength, Electron mean free path, Interatomic distance etc., the properties of that materials changes a lot. Normally these charactersistic lengths ranges from fraction of nanometer to 100's of nanometers (nanoscale length)

Fermi wavelength can be computed from the expression relating N to k_F.

$$k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

Using the electronic density $n = N/V$, the Fermi wavelength becomes

$$\lambda_F = 2\pi \left(\frac{1}{3\pi^2 n} \right)^{1/3}$$

Therefore, the Fermi wavelength is inversely proportional to $n^{1/3}$, and consequently this wavelength is much larger in semiconductors (~100 nm) than in the metals (~0.1 nm). For example, in Fe, the Fermi wavelength is $\lambda_F = 0.37$ nm.

The simplest example of the effect of the characteristic lengths on the magnetic properties is the case of magnetic particles that have dimensions smaller than the critical magnetic single-domain diameter (Normally ranges from few to few tens of nanometer, depending upon nature of magnetic materials).These particles therefore becomes superparamagnet and have the single domain as their lowest energy configuration.

Some of these characteristic lengths, which include the exchange interaction length, the domain wall width and the spin diffusion length, are given in Table together with their typical values. From this table, it is evident that nanoobjects have dimensions in the range of many of these characteristic lengths.

Table 1.1. Some characteristic lengths in magnetism and their typical magnitudes

Symbol	Length	Typical magnitude (nm)
d_a	Interatomic distance (Fe)	2.5×10^{-1}
d_{ex}	Range of exchange interaction	$\sim 10^{-1} - \sim 1$
d_{RKKY}	Range of RKKY interaction	$\sim 10^{-1} - \sim 10$
d_c	Domain size	$10 - 10^4$
D_{cr}^{spm}	Superparamagnetic critical diameter	$\sim 1 - \sim 10^2$
D_{cr}	Critical single-domain size	$\sim 10 - \sim 10^3$
δ_0	Domain wall width	$\sim 1 - \sim 10^2$
l_{ex}	Exchange length	$\sim 1 - \sim 10^2$
l_{sd}	Spin diffusion length	$\sim 10 - 10^2$
λ_{mfp}	Electron mean free path	$\sim 1 - 10^2$
ζ	Superconducting coherence length	$\sim 1 - 10^3$
λ_F	Fermi wavelength/metal	$\sim 10^{-1}$
λ_F	Fermi wavelength/semiconductor	$\sim 10^2$