

# Introduction to Nanoscience

## Study Guide

### Chapter 5 - Introduction

With *chapter 5* we begin the study of nanomaterials in earnest. We begin with the surface, one of the most important phenomena in this universe.

#### Chapter Objectives

- Understand the importance of the surface not just to nanomaterials but to living things as well. Discuss with your group how the surface possibly played a role in the development of life itself
- Review all the engineering materials– they all come back in nanoform: metals and alloys, ceramics and glasses, semiconductors, carbon-based materials, polymers, composites and biological materials. Is there anything we missed?
- Understand the significance of particle shape– both of the exterior and interior variety
- Delve into the characteristics of collective surface area vs. specific surface area
- Understand the relationship of surface to volume and its significance, especially in living organisms
- Get a mathematical feel for surface-to-volume ratio of many kinds of shapes
- Get a mathematical feel for the limits of surface-to-volume ratio
- A brief review is provided about atomic structure. Please understand the basics of bulk material structure
- The unit cell is an important parameter in material structure. Be ready to understand why nanomaterials may differ from the standard structure of bulk materials
- A brief review of Miller indices, packing fraction, linear and planar density is presented
- Magic numbers! Learn why magic numbered clusters are more stable
- Understand the significance of particle orientation in an electric field

- Understand the significance of particle (inclusion) orientation in a composite

**5.1** There are a few classes of engineering materials. Please try and learn the salient features of each as they translate at the nanoscale— albeit with some altered properties. It is very important that you entrain your mind to absorb all of this information.

With **metals and alloys**, we are quite familiar. Metallic bonds are *delocalized* (non-directional) although they possess a high level of structure. Most metals crystallize into bcc, fcc or hcp structure. Please learn these basic types. Metals have high strength, are ductile and electrically and thermally conducting. The boundary between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUCO) is the Fermi level.

**Semiconductors** are held together with strong *directional covalent bonds*. The diamond tetragonal structure is common in many intrinsic and extrinsic semiconductors. Others show zinc-blende, rutile or anatase structures. Please refer to your inorganic chemistry or materials science text.

Extrinsic and compound semiconductors are ceramic-like and have high melting points, are brittle but chemically stable. The primary feature of semiconductors is their ability to conduct electricity— sort of. They "semi-conduct". Semiconductors are characterized by a phenomenon called a bandgap. The Fermi level in semiconductors (or more appropriately, the chemical potential boundary since a Fermi level implies occupied states) lies in the bandgap. This is an important aspect of semiconductor quantum dots due to the energy of the bandgap as a function of particle size.

**Ceramics** are truly amazing materials. They are of course the traditional hard, extremely brittle materials that serve as insulators but over the past decades, ceramics have shown utility as superconductors and composites. Ceramics are also considered to be ionic solids. Ionic bonds are non-directional but ceramics also are made of covalent bonds.

**Glasses** are technically ceramics but ones with noncrystalline short-range order. Glasses are lower melting, relatively soft and provide an insulating layer (mostly transparent) to many electrically conducting materials. The silicate glasses are the most common.

The kinds of **carbon-based materials** have burgeoned over the past decade. With the advent of fullerenes and carbon nanotubes, hundreds of new kinds of carbons have been synthesized. Learn the basic differences between graphite and diamond (more in *chapter 9*). All carbon allotropes are made with very strong covalent bonds— the differences among them are due to the type of bond (single, double or triple) and the structural details of their morphology. Diamond is  $sp^3$ , graphite  $sp^2$  and carbon nanotubes are conjugated.

Graphite, diamond and carbon nanotubes have the potential for extremely long-range order. Charcoal is made of tiny domains (micron to nano), carbon black as well (hence their excellent adsorptive ability). In terms of physical properties, graphite and diamond

are on the extremes of the opposite ends of the spectrum— one is hard, one is soft; one is black, one is transparent; one is an insulator, one is a conductor, and so on and so forth.

**Supramolecular structures** are actually a new kind of engineering material. They are held together with intermolecular bonds— bonds that we will go into more detail in *chapters 10 and 11*. Intermolecular interactions are hydrophobic interactions, hydrogen bonds, van der Waals forces, dative bonds, ion-ion attractions and a plethora of ion-dipole, dipole-dipole and induced dipole interactions. Supramolecular structures form materials that are commonly known as "soft matter".

**Polymers** are also considered to be soft matter but consist mainly of hydrocarbon and selected elements. Polymers have an extremely wide range of physical properties. they can be insulating or conducting, soft or hard, or elastic or hard.

**Composites** are combinations of engineering materials— usually a polymer, ceramic or metal as the host material (the matrix) and carbon or inorganic fibers, ceramics, metals or alloys as the filler. Composites combine the best features of two radically different materials to form one that has properties better than either one.

**5.2** Shape and the surface is important at any scale. At the nanoscale, it is very important. Let's reinforce a few definitions:

**Collective surface area** is the sum of surface area of all substituents. Surface area is an extensive (additive) property. The units of specific surface area are  $\text{m}^2$ . **Specific surface area** is an intensive property— e.g. no matter how many uniform particles are involved, the specific surface area always remains the same. The units of specific surface area are  $\text{m}^2 \cdot \text{g}^{-1}$ .

**Discussion Topic:** The sphere is the lowest surface energy configuration of any material. Why is this? Why does a sphere with the same volume as a cube have the lower surface-to-volume ratio? Why are the smallest drops and nanoparticles striving to attain the shape of a sphere? Is this always true?

The **interior surface** of a material, i.e. a porous material, also is able to contribute to large collective surface area. Porous materials such as the pore channels of anodically formed aluminas are able to contribute to a lot of surface. Any surface feature that is wider than it is deep is not a pore.

The study of the surface in this chapter is simply a study of simple geometry. The wire ( $h \gg d$ ), the disc ( $h \ll d$ ), the sphere (the dot), the cube and the extended rectangle (the 2-dimensional film where  $l$  and  $w \gg d$ ) are all shapes with differing surface-volume relationships. The thin film, for example, essentially is all surface.

**5.3** **Surface atoms** are the key to unlocking the properties of nanomaterials. This is a fundamental concept in any course in nanoscience. We are starting to pry open the door

slightly to the relevance of physical properties to the nanoscale. All physical and chemical parameters interact with the surface first and foremost.

The previous statement was just a tease, however. Let's get into methods to estimate the number of surface atoms, the number of volume atoms and their ratio first.

The first method is the method of *brute force*. If we know the atomic radius (by various means) and the size of the cluster, we can calculate the number of surface atoms— at least to make an estimate. The simplest method is shown in **Exercise 5.6** and **Table 5.2**.

The *spherical cluster approximation* (SCA) does not consider packing fraction and assumes that all atoms act like incompressible hard spheres. Coordination number is also neglected. In other words, volume atoms can be calculated by simply dividing the number of atoms into the geometrical volume of the cluster. Please review **Example 5.8** with great concentration.

Many assume that the surface layer consists of atoms in a layer 2-Å in thickness— certainly not a bad approximation. In this case, we just take the volume of the shell and divide it by the volume of the sphere to get our surface-to-volume ratio.

**5.4** This section on atomic structure is a generalized review of crystal systems, packing schemes and Miller indices. The major crystal systems are shown in **Figure 5.9**. For the purposes of this text, we only focus on the three cubic systems: simple, face-centered and body-centered cubic. The best way to review this material is to consult your inorganic chemistry or materials science textbook.

Consideration of *packing fraction* is required to understand real world materials. Packing fraction depends on the crystal structure. Once again, we will not review these topics in this section. Please consult any inorganic chemistry or inorganic text.

A structural magic numbered cluster possesses unusual stability. Why is this? Starting with the first magic numbered cluster, one atom surrounded by 12. This gives the first magic number = 13. This cluster is expected to be more stable than a cluster with 12 atoms or 14 atoms. Where would the 14th atom be placed in this structure? For the 13-atom cluster, there is only one true volume atom— the rest are surface atoms. The surface-to-volume ratio is then 12/13 or 92.3%.

Each type of crystal is able to generate a series for calculation of magic number clusters.

Miller indices are reviewed in several inorganic, chemistry, materials science or texts explaining x-ray diffraction.

**5.5** *Particle orientation* is particularly important when external electric fields, i.e. from an electromagnetic source such as light, are applied to an array of nanoparticles.

A key point to remember is this one: "If a particle is much smaller than the wavelength of the impinging EM-radiation (e.g.  $r \leq 0.01\lambda$ ) then the mathematical treatment of the optical response reduces to one of electrostatics". This is also known as the quasi-static limit.

The surface plasmon is both a macroscopic and a microscopic phenomenon (and nanoscopic). Metals possess a cloud or "sea" of free electrons on their surface. These electrons act in unison, are quantized and characterized by a characteristic resonance when stimulated by energy with the proper wavelength. There are few terms to recall:

**Eccentricity** is simply the deviation of an ellipsoid from an ideal spherical shape

**Depolarization factor** is the ratio of the internal electric field induced by the charges on the surface when an external field is applied. Another way to look at it is via the ratio between the half-axes of an ellipsoid. For a rods, the depolarization factor is  $0 \leq q \leq 1/3$  where  $q = 1$  is the case of the sphere. For a disc,  $1/3 \leq q \leq 1$ . In extreme cases,  $q = 0$  for parallel rods and  $q = 1$  for parallel discs. Obviously,  $q$  is related directly to the eccentricity.

Another way to look at the depolarization factor is to call it a **geometrical factor** that is dependent only on the aspect ratio determined by the ellipsoidal axes.  $q$  does not depend on the properties of the material— only its shape.

The **screening parameter**  $\kappa$  represents a simple relationship derived from the depolarization factor:  $\kappa = (1-q)/q$ . This is actually the form used in the Maxwell-Garnett equation. The 2 represents the case for the sphere: as  $(1 - 1/3)/(1/3) = 2$ .

### Chapter Summary:

- The importance of the surface plays a major role in nanomaterial properties
- There are a few classes of traditional engineering materials: metals and alloys, ceramics and glasses, semiconductors, polymers and composites
- For nanoscience, we add a few "new" classes: carbon and allotropes, biological materials
- Collective surface area is the sum of all the surface area of all the particles in an assembly and is an extensive property: e.g. depends on how many particles
- Specific surface area is an intensive property that relates surface area per gram of material. This parameter does not depend on how much material is present.
- Surface-to-volume ratio is specific to certain shapes. For example, the sphere has the lowest surface-to-volume ration of all geometric shapes. As we will learn

later, the sphere is also the lowest energy configuration of the basic geometric shaped nanoparticles.

- Particle shape is related to total surface area. Wires and discs (and infinitely thin films) have the highest Surface-to-volume ratio. A thin films can be construed as infinite discs.
- The number of surface atoms to volume atoms plays a major role in physical and chemical properties of nanomaterials
- Magic numbered clusters exhibit more stability than those with similar mass.
- Particle orientation matters especially in materials that host nanoparticles that are other than spherical.
- Orientation matters for particles in an electric field or in a composite that is designed for mechanical strength