

# Introduction to Nanoscience

## Study Guide

### Chapter 7 - Introduction

We are all familiar with bulk materials and their properties. Chapter 7 presents a discussion about the quantum domain and the nanodomain and how they link with the smooth curves of the macroscopic. Materials also form a continuum— similar in sense to energy and electrostatic interactions between atoms and molecules. Or are there abrupt boundaries between the quantum domain and nanoparticles or between nanoparticles and the micro- macroscopic?

We believe there is actually a smooth continuum between and among all the different size classifications of materials. The designation is simply a function of how much material exists within. Starting with an atom with specified quantum states, one adds another atomic. All of a sudden, there is a molecule in which molecular orbitals replace atomic orbitals. There is the highest occupied orbital (HOMO made of bonding electrons) and the lowest unoccupied orbital (LUMO consisting of antibonding orbitals). We keep on adding more atoms or molecules and a cluster is formed that now has highest occupied cluster orbitals (HOCO) and lowest unoccupied cluster orbitals (LUCO). We keep on adding and get bands— insulators with a wide band gap, semiconductors with a reasonable bandgap and metals with the Fermi level with no band gap. A continuum? Yes, but with clearly definable distinct regions.

### Chapter Objectives

- Observe how properties change from the bulk to the nanoscale in areas such as confinement, surface area ratio, lattice spacing, coordination, quantum mechanics, classical physics, optical response, bandgap, conduction, reactivity and many more traits and scaling laws
- The de Broglie relationship rears its head again
- Understand confinement (of what? electrons) by 0-D, 1-D and 2-D nanomaterials.
- The bathtub is the basis of quantum mechanics
- The ubiquitous "particle in box". Learn it. It is fundamental to QM and also nanoscience
- Understand the fundamental importance of scaling laws

We will not review QM here in this study guide but we will review the relevant aspects of 0-D, 1-D and 2-D materials.

**0-D Materials** are materials that confine electrons in three dimensions. A good way to visualize this is to stick your head inside a basketball (or more practically, a diver's helmet). You will realize that the sound of your voice is very different in the bell from that in our regular environment— e.g. the unconfined space. The energy of your voice has been altered. In a quantum dot (a 0-D material), the energy of an electron loses all its continuity and considered to be quantized. One thing you realize is that there is no resonance of your voice, no echo, no nothing.

**Figure 7.15** shows how the energy levels of electrons in a ligand-stabilized gold-55 QD behave as if in a "box" that is 2.1-nm in diameter along x,y and z spatial dimensions.

If the cluster size is on the order of the de Broglie wavelength  $\lambda_{\text{deBroglie}}$  of the electron in the ground state, then quantum effects begin to emerge. If the size is reduced to  $\lambda_{\text{deBroglie}}/2$ , the electron levels in clusters become quantized.

For larger clusters (more like colloids), a **dipolar plasmon resonance** (a phenomenon introduced in earlier chapters) requires many more electrons, hence more atoms. As clusters get smaller, the plasmon disappears. So, going from the bulk where surface plasmon resonance is exploited for surface analysis, to colloidal sizes in which the localized surface plasmon is in effect to the case of the dipolar plasmon and finally to small clusters in which only 2 electrons contribute to the optical properties, optical response is expected to be quite varied.

**Melting point** is related to the radius of the particle: the larger the particle, the higher the melting point.

**Discussion Topic:** Why do you think that melting point behaves in this way? Please include atomic structure in your discussion. What do you think happens to the coordination number of surface atoms, or that of volume atoms?

**Electrical conductivity** through 0-D materials is not like that of the bulk. Bulk conductivity is relatively continuous, if not outright linear in nature: the more voltage that is applied induces more current to flow in a relatively predictable manner. However, at the scale of a nanocluster, single electron transport is a reality. The Coulomb staircase (or blockade) demonstrates how there seem to be "quantum jumps" in current as voltage is applied. One reason for this is the tunneling current threshold (or the tunneling current resistance).

**Catalytic behavior** of nanoparticles is a well-researched field. The most remarkable of nanocatalysts is that of gold nanoparticles. Gold is not a catalyst. It is relatively inert. However, by assuming nanoscale proportions, gold becomes an extremely active and effective catalyst.

**Discussion Topic:** Why is nanogold catalytically active?

**1-D Materials** are those that are confined in two dimensions. In other words, one dimension is still open and available for bulk like phenomena. A good way to visualize a 1-D material is to stick your head in a pipe. You will notice confinement on either side of your head and up and down but not along your nose. If you were to speak into the pipe, you may hear echoes and resonance along the length of the pipe. 1-D materials are commonly referred to as *quantum wires*.

**Discussion Topic:** How do you expect properties to behave along the confined or unconfined directions?

**Carbon nanotubes** are some of the best examples of a 1-dimensional material. A more complete discussion of CNTs is given in *chapter 9*.

**2-D Materials** are thin films—very thin films. In these materials, confinement exists only in one dimension but not in the other two. Perhaps a weak analogy could be fabricated by considering a crawl space underneath the ground floor of a house. One is able to crawl freely within a plane defined by  $x$  and  $y$  but would most certainly bump his head in the  $z$ -direction.

A 2-D material is one in which the crystal size is negligible in one direction but unrestricted in the other two. These are commonly referred to as *quantum wells*.

Optical properties of thin films are a function of thickness. Perhaps the phenomenon we are most familiar with is that of interference. The thickness of such films, however, is actually quite large—on the order of the wavelength of the light (and of course the interference color is also dependent on the angle of incidence). Many thin films act as gates—providing just enough resistance in one direction to prevent backflow of current.

**Scaling Laws** (or power laws) are fundamental to nature. Scaling laws are mathematical laws that predict how variation in one quantity affects variations in other quantities. Scaling laws are commonly referred to as power laws. The Stefan-Boltzmann law is a power law. Scaling laws relate one function to that function at different size regimes. For example, ants are able to lift ca. 20x times their own weight in mass while humans are not quite able to achieve that level of perfection. Put another way, if there were no scaling laws, then we should be able to lift 2 tons of weight (assuming a 200 lb person) in proportion to what an ant is able to lift (e.g. a linear transposition).

The simplest way to get a feel for scaling laws is to study mechanical systems. In mechanical systems, mass is proportional to volume however if the linear dimension of an object is reduced by a factor of  $x$ , then the volume of that object is reduced by a factor of  $x^3$ .

## Chapter Summary

- The concept of the material continuum is a valid one although its divisions may seem disjointed.
- With more and more material, quantum atomic orbitals merge into molecular orbitals (HOMO and LUMO), into cluster orbitals (HOCO and LUCO) and into bands at the bulk stage
- Zero-dimensional materials exhibit confinement of electrons in all three spatial dimensions
- 0-D materials are quantum dots
- One -dimensional materials exhibit confinement of electrons in two dimensions
- 1-D materials are represented by quantum wires
- Two-dimensional materials exhibit confinement of electrons in one dimension
- 2-D materials are represented by quantum wells (thin films)
- Scaling laws apply to nanomaterials but the fit of scaling laws depends on the physical phenomena
- Electromagnetic phenomena with low time constraints have poor accuracy
- Thermal systems and slowly varying electromagnetic systems show good accuracy
- Mechanical systems with dimensions exceeding that of the atomic show excellent accuracy with continuum models