

# Introduction to Nanoscience

## Study Guide

### Chapter 6 - Introduction

*Chapter 6* brings on some explanation of nanomaterial properties— by way of investigating the energetics of nanomaterials and its relationship to the surface. A clear simplified example of the relationship between surface energy and volume is shown in **Example 6.1**.

### Chapter Objectives

- Understand the relationship between surface and energy and begin to develop a foundation for the physical and chemical ramifications of the surface energy.
- Get a feel for why surface atoms are different from volume atoms and how this difference accounts for physical and chemical behavior. This includes the phenomena of under-coordination, dangling bonds, nearest neighbors, melting points, reactivity and many more
- Understand why, then, that the formation of new surfaces requires energy
- One of the simplest tests for surface energy is to observe a drop of water on the surface of material. Understand why the drop assumes the shape that it does— e.g. between flat and spread out or very round.
- Learn the fundamental methods that materials undergo to stabilize the surface
- Derive the derivation of surface tension from classical principles
- Understand the definition of surface excess
- Understand the basics of the Kelvin equation, vapor pressure and particle radius
- Understand particle curvature and its relationship to material properties
- Everything is driven by chemical potential. Find out the deeper meaning of this phenomenon
- What is capillarity and how does it relate to the nanoscale
- Learn the distinction between cohesive energy and surface energy
- Surface energy of solids and liquids— be able to distinguish between the two

- The assumptions of the nearest neighbor model should be ingrained within your psyche
- Be able to derive the surface energy expressions of the low index crystals
- Understand the basics of DLVO theory

We arbitrarily designate the surface energy of each surface of the cube as  $\gamma$ . As we combine cubes, those  $\gamma$  combine into what we call cohesion energy. Since each surface loses one  $\gamma$  and two surfaces combine to form the solid, the cohesion energy is expected to be  $\gamma + \gamma = 2\gamma$ . The basic premise is just that simple. In this example, we do not consider structure, chemistry or forces— just simple geometry.

**Wettability** is the ability of a solid surface to break up the surface tension of water. Obviously that requires energy and that energy arises from the surface excess due to under-coordinated species existing there.

**Hydrophobic surfaces** do not have enough surface energy to break up water due to the completeness of their valencies. Hydrocarbons are for the most part saturated with hydrogens and do not require any more satisfaction. The contact angle of drops on this surface tend to be greater than  $90^\circ$  (e.g. the water is more spherical in shape).

**Hydrophilic surfaces**, on the other hand, do have enough energy to break the surface tension of water. For example, a metal like gold is wetted completely by water (e.g. contact angle =  $0^\circ$ ). This energy is the excess surface energy due to incompleteness of surface states.

## Chapter Summary

- Surface energy, although not unique to nanomaterials, is pronounced in nanomaterials and is responsible for many of their remarkable properties
- The energy required to create a new surface is equal to the 1/2 the cohesion energy between two atoms times the number of atoms at a newly cleaved surface plane
- The degree of wetting is an indication of the surface energy of a material. A droplet of water that spreads out on a surface is said to wet the surface. A drop that stays relatively round does not wet the surface.
- Cohesion energy for metals is often estimated from heats of sublimation
- Curvature is the measure of deviation from a straight line. It is, therefore, an analogous measure like eccentricity, that measures deviation from a spherical

shape for ellipsoids. The curvature is also a function of the particle radius. In other words, the smaller the radius becomes, the greater the extent of curvature. One more aspect to remember is that the radius of curvature for a sphere is the radius of the sphere.

- Chemical potential (e.g. a measure of "reactivity") is related to particle curvature. The smaller the radius (i.e. the higher the curvature), the more reactive a species is expected to become (Eqn. 6.20).
- Liquids contract (i.e. form droplets) due to surface tension. Surface water molecules, for example, have fewer nearest neighbors and therefore experiences lateral and inward forces. These factors are some of the reasons that water droplets are spherical.
- The energy of adhesion is the energy of cohesion between unlike materials.
- The Young-Laplace equation relates the surface energies that exist at the solid-vapor, solid-liquid and liquid-vapor boundaries. The result of this equation is an expression for the contact angle.
- Capillarity occurs at the nanoscale and is a well-known phenomenon that plays a major role in BJH measurements.
- The surface energy of low index crystals is straightforward to calculate if the planar face is known and the number of bonds that are broken to form a new surface.
- there are many mechanisms available to surfaces to effect stabilization: relaxation, restructuring, composition segregation, physisorption of other substances, sintering, Ostwald ripening, confinement, chemisorption, electrostatic stabilization, surfactants.... and many more.
- Nucleation is a well-known process to chemists. The thermodynamic expression for nucleation includes a volume term and a surface term.
- Ostwald ripening is a process by which larger clusters grow at the expense of smaller ones
- Sintering is the joining of similarly-sized particles to form larger aggregates.
- There are numerous kinds of structural stabilization: contraction, relaxation, reconstruction

