

## Lecture 10. Common size and surface-related properties of nanoparticles

**The purpose of the lecture:** to familiarize students with common size and surface-related properties of nanoparticles.

**Expected results:** students getting information about common size and surface-related properties of nanoparticles.

All nanoparticles, irrespective of their chemistry, exhibit comparable surface reactivity and thermodynamic, electronic, mechanical, and magnetic properties. This lecture provides a detailed review of the size-related effects of nanoparticles.

### Surface Atoms

Nanoparticles exhibit exceptionally high surface area to volume (S/V) ratios compared to their bulk counterparts. The bulk particles (>500 nm) and mesoparticles (>100 nm but <500 nm) have less than 1% of total atoms on the surface. As the size decreases, there is a decrease in surface area and volume, but a significant increase in the S/V ratio. This is because surface area is  $4\pi r^2$  and volume is  $\frac{4}{3}\pi r^3$ . The surface area to volume ratio will be  $\frac{4\pi r^2}{(\frac{4}{3}\pi r^3)} = \frac{3}{r}$ . Because of this, an increase in radius reduces the S/V ratio, but increases the number of atoms at the surface.

In 1.0-nm (at least in one dimension) nanoparticles, greater than 80% of the total atoms reside at the surface. Spherical nanoparticles of 1.8 nm diameter have equal numbers of core and surface atoms (or molecules), while nanoparticles <1 nm in diameter may have all of their atoms facing the surface (may be unstable). As the percentage of surface atoms increase relative to the core atoms, surface atoms begin to play a greater role in determining the nanoparticles' physicochemical, electronic, mechanical, and magnetic properties. Contrarily, surface atoms play a minuscule role in determining the properties of bulk particles. Reduction in size from the micro (bulk particles) to nano (nanoparticle) range enhances the relative importance of surface atoms. As the diameter increases, the nanoparticles' melting temperature decreases, while the bandgap between the valence and the conduction bands increases. Thus, many metals may become semiconductors at the nanometer level.

To understand the surface effects, it is important to understand the characteristics of the core and the surface atoms. The core atoms form stable covalent bonds with the nearest neighboring atoms. Because the paired electrons spin in opposite directions, they are stable and relatively nonreactive. The surface atoms contain nonbonded electrons, exhibiting greater uncompensated spin. Therefore, the surface atoms exhibit relatively low nearest neighbor (NN) numbers and relatively great free energy, anisotropy, bond defects, surface strain, and narrowing of the band gap, which increase the density of electrons at the Fermi level that facilitates conduction of electrons (discussed later). These properties give the surface atoms many unique physicochemical and magnetic characteristics that are not present in the core atoms. In addition, the surface but not core atoms are in contact with oxygen, resulting in the formation of oxidized atoms, which further alters the properties of the surface atoms.

### Size-Dependent Thermodynamic Properties

An understanding of the thermodynamic properties (melting temperature, enthalpy and entropy of melting, elastic moduli, specific heat capacity, etc.) of nanoparticles is necessary to improve their applications by minimizing the adverse effects. Many studies have shown a close relationship between the Gibbs free energy of a particle and its thermodynamic properties. The Gibbs free energy of bulk particles ( $G_b$ ) is defined as  $G_b(p, T) = \Delta H - T\Delta S$ , where  $\Delta H$  is the change in enthalpy,  $T$  is temperature, and  $\Delta S$  is the entropy. Surface atoms have a minuscule role in determining the particle's  $G_b$ . However, as the particle size reaches the nanometer range, the surface free energy begins to dominate the core free energy; thus, the size becomes the key determinant of the nanoparticles' thermodynamic properties. The Gibbs free energy of

nanoparticles ( $G_n$ ) is sum of the Gibbs free energy of the surface ( $G_{\text{surface}}$ ) and that of the core ( $G_{\text{core}}$ ). For nanoparticles,  $G_{\text{surface}}$  is inversely related to diameter ( $D$ ).

#### Surface Free Energy

Considering the importance of the surface in nanoparticle properties, it is important to understand the surface free energy of nanoparticles ( $gG$ ) and its relationship with the nanoparticles' thermodynamic properties. Surface energy is defined as the energy required to produce a new surface by breaking the bonds of a nanoparticle core.

In all cases, the free energy in bulk particles was lower than that in nanoparticles. Nanoparticles capped with functional groups or embedded in another particle exhibited lower free energy. This suggests that the free surface energy of nanoparticles also

#### Thermodynamic Indices

This section describes characteristics of and relationship among cohesive energy, melting temperature, elastic moduli, specific heat capacity, evaporation, Curie temperature, and Debye temperature. Cohesive energy accounts for the strength of atomic bonds that is equal to the energy required to divide the nanoparticle into individual atoms. Consider a nanoparticle with diameter  $D$  composed of  $n$  atoms. If sufficient energy ( $E_n$ , also known as the cohesion energy) is applied, individual atoms will be separated and the cumulative surface area of  $n$  atoms will be  $S_j n \cdot d^2$  in which  $d$  is the individual atoms' diameter.

The core is an ensemble of bound atoms or molecules, while the surface has unsaturated bonds. Clusters or nanoparticles may contain greater density of the unpaired electrons (broken bonds) than the bulk particles. An increase in the particle size increases the cohesive energy. In nanoparticles greater than 100 nm, cohesive energy reaches the bulk size constant value. Because cohesive energy is directly related to the bond strength of a core, an increase in cohesive energy is associated with an increase in intermolecular bonds that cannot be broken easily, while a decrease in cohesive energy is associated with a decrease in intermolecular bonds (such as in wax) that can be broken easily. The surface of the nanoparticles, because of their dangling bonds, may have lowest level of cohesive energy, possibly because of the inverse relationship between the surface area of a nanoparticle and its cohesion energy.

In general, cohesive energy depends directly on the coordination number; thus, it affects the thermal stability that modulates the melting temperature of particles. The melting temperature of nanoparticles has a significant impact on other thermodynamic properties: they all decrease with a decrease in size. The size effect is more pronounced at diameters 10 nm or lower. For nanoparticles over 50 nm in size, some of the thermodynamic values may reach the bulk value.