

Physical chemistry of surfaces

Nanostructures possess a large fraction of surface atoms per unit volume. The physical and chemical properties of surfaces have great importance when describing general properties of nanostructured materials. To illustrate this let us consider 1 cm^3 of iron. The percentage of surface atoms will be approximately $10^{-5} \%$. When the volume is broken into smaller cubes with side 10 nm the percentage of the surface atoms would increase to 10% . To illustrate that Figure 1 shows the percentage of surface atoms changes with the cluster size for the case of Palladium clusters.

The total surface energy increases with the overall surface area, which is in turn strongly dependant on the dimension of the material. One challenge in nanomaterial fabrication is to overcome the surface energy, and to prevent the nanostructure from growth in size driven by the reduction on overall surface energy. In order to stabilize the nanomaterial structures it will be necessary to understand the chemistry and physics of the surface, which represents a large percentage of the nanostructures.

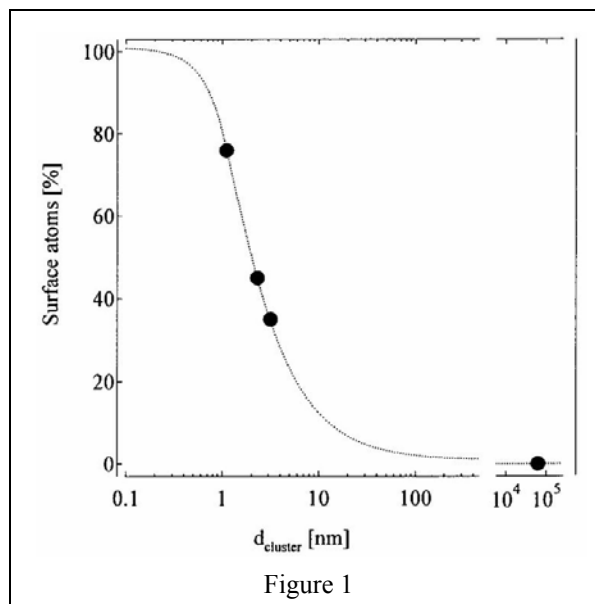


Figure 1

Surface Energy

Atoms or molecules in the surface has fewer nearest neighbors and thus have dangling bonds exposed to the surface. These surface dangling bonds produce a inwardly directed force and the distance between the surface atoms/molecules and the sub-surface atoms is smaller than the distance between atoms in the bulk (interior atoms). When the particles are very small this difference in distance becomes significant and the lattice constant of the solid shows an appreciable reduction. The extra energy possessed by the surface atoms is described as the surface free energy or surface tension.

The surface energy γ is by definition the required energy to create a unit area of “new” surface. For example, consider the case of figure 2. A rectangular solid is separated into two pieces. On the new created surfaces the atoms will be located in an asymmetric environment and will move towards the interior due to the breaking of the bonds at the surface. An additional force will be necessary to move the surface atoms back to its original position. The energy required per atom will be equal to the number of broken bonds N_b multiplying by

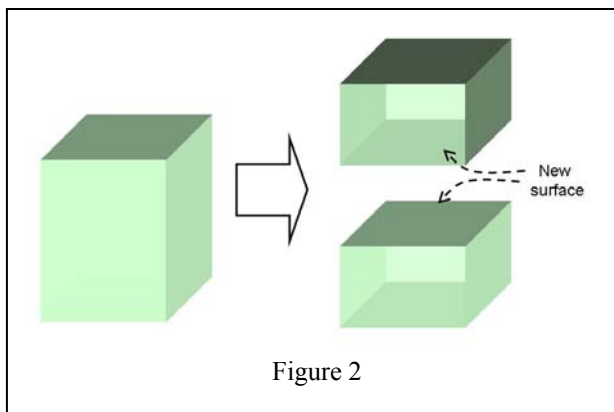
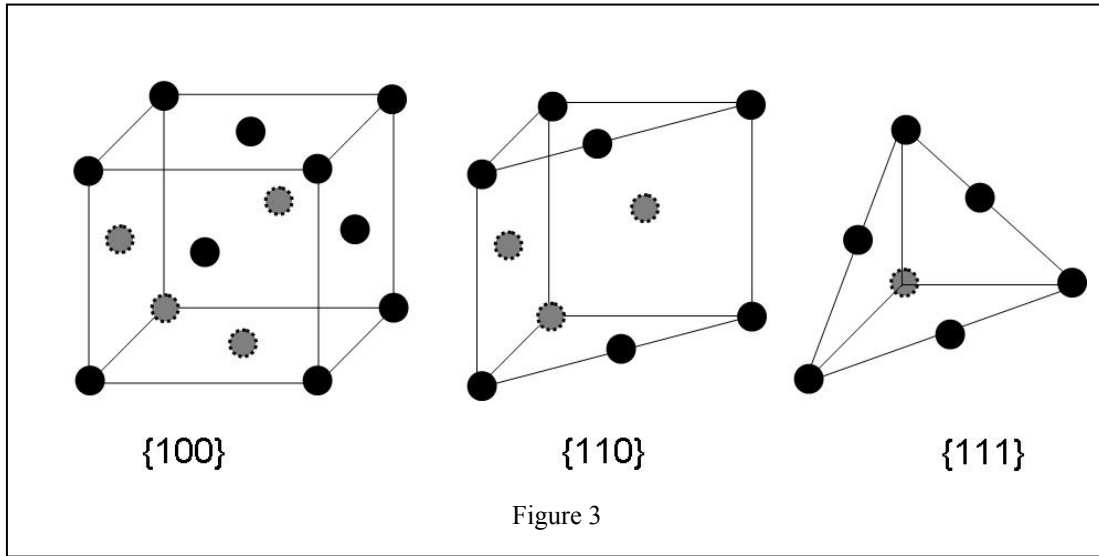


Figure 2



half of the bond strength ε . Therefore the surface energy is given by:

$$\gamma = \frac{1}{2} N_b \varepsilon \rho_a$$

where ρ_a is the surface atomic density. This is a crude model that gives a first approximation. It does not consider the interaction with higher order neighbors nor entropic or pressure-volume contributions. Nevertheless it gives in a first approximation a value for the surface energy. When there is a surface relaxation as atoms moving inwardly, or a surface restructuring surface energy will be smaller.

Let us take an elementary crystal with a facet centered cubic structure (FCC) as shown in figure 3. In the facet $\{100\}$ the atoms have a coordination number (this is the number of neighbors) equal to 12. Each surface atom in the $\{100\}$ facet will have 4 broken bonds and the surface energy for the $\{100\}$ surface will be

$$\gamma_{100} = \frac{1}{2} \frac{2}{a^2} 4 \varepsilon = \frac{4\varepsilon}{a^2}$$

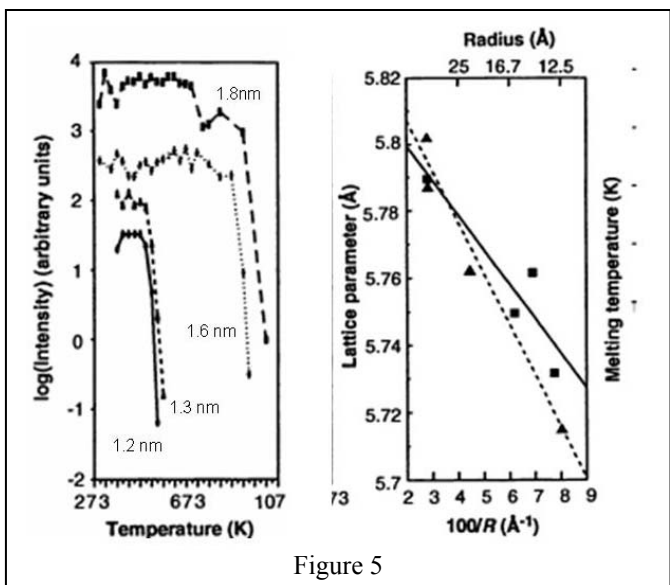
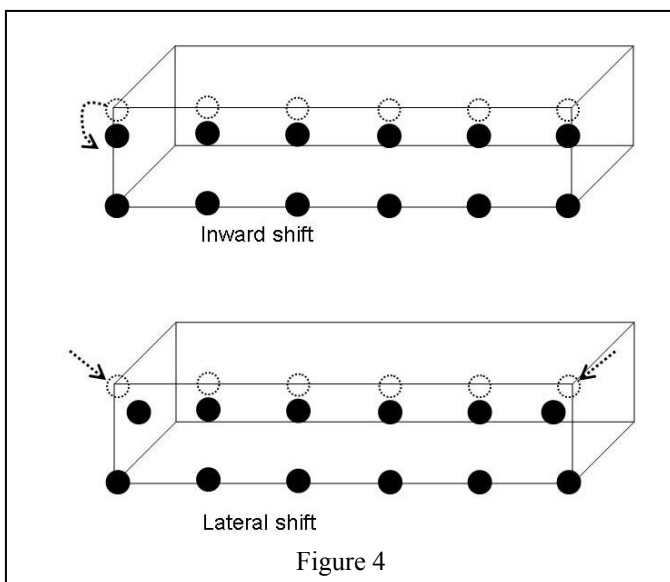
Similarly each atom in the $\{110\}$ surface has 5 broken chemical bonds and the atoms in the $\{111\}$ surface have 3. Thus

$$\gamma_{110} = \frac{5}{\sqrt{2}} \frac{\varepsilon}{a^2} \quad \gamma_{111} = 2\sqrt{3} \frac{\varepsilon}{a^2}$$

For a given surface with a fixed surface area, the surface energy can be reduced through:

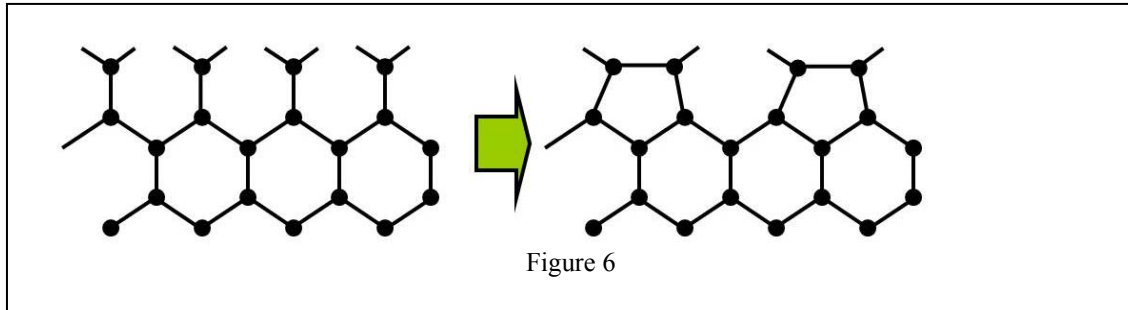
- i- Surface relaxation: surface atoms or ions move inwardly
- ii- Surface restructuring combining the dangling bonds into new chemical bonds
- iii- Surface adsorption (physical or chemical)
- iv- Segregation or impurity enrichment through solid state diffusion

Let us consider atoms located in the surface of an atomic flat $\{100\}$ surface in a cubic structure. The surface atoms are linked with one atom directly beneath and four surrounding in the surface. Each chemical bond acts as an attracting force so all the surface atoms are under the influence of a net inwardly force. Under this force the distance between the surface atoms and the sub-surface atomic layer will be smaller than



the distance between two atomic layers in the bulk. Furthermore, the surface atoms may also shift laterally relative to the surface atomic layer. Figure 4 shows schematically this effect. For bulk materials the effect of reduction in the dimension of the crystal lattice is very small and can be neglected, but in nanometer size structures can become important. This effect was observed in CdS nano-crystals through a significant decrease in the melting temperature relative to the bulk material. From these data it is possible to derive the corresponding decrease in the lattice parameter. Figure 5 shows plots revealing this effect. On the left the intensity of the electron diffraction of the {111} peak shows a sharp decay at decreasing temperatures for decreasing nanoparticle size, indicating the loss of the crystalline structure. On the right the lattice parameters for two different species of nanocrystals also decreases with the decreasing nanocrystal radius. Another possibility to minimize the surface energy is through a rearrangement of the surface. For example this restructuring of the surface is found in Si crystals. In Si and diamond, the restructured {100} surface has the minimum surface energy as compared with the other lower index structures. This restructuring of the free bonds in the surface can have a significant impact in crystal growth. Figure 6 is a scheme showing this effect.

At the level of individual nanostructure there are two approaches to the reduction of the total surface energy. One is to reduce the overall surface assuming that the material is isotropic. Water on a hydrophobic surface always forms spherical droplets. Amorphous materials with isotropic surface energy always reduce the overall surface energy by reducing the total surface. However for crystalline materials different facets have different energies and a crystalline particle normally forms facets instead of having an spherical shape. The thermodynamically equilibrium shape of a crystal can be determined by considering the surface energies of all facets. The final surface shape corresponding to



the minimum surface energy is obtained when different facets are combined to have an overall minimum value of the surface energy. A systematic way to determine this minimum energy surface is considering a Wulff plot. For an equilibrium crystal, ie the total energy reaches minimum, there exists a point in the interior such that its perpendicular distance h_i from the i th face is proportional to the surface energy γ_i .

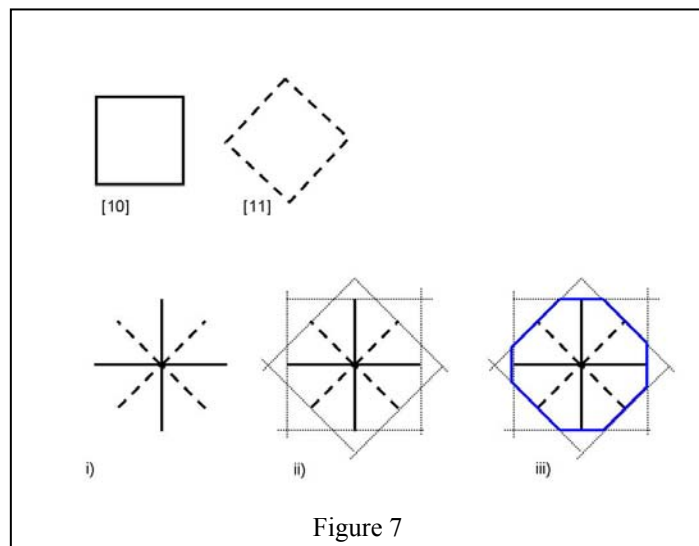
$$\gamma_i = C h_i$$

where C is a constant equal for all the surfaces. Considering this, a Wulff plot can be constructed with following steps:

- i) given a set of surface energies for the various crystal faces, draw a set of vectors from a common point of length proportional to the surface energy and direction normal to that the crystal face.
- ii) construct the set of faces normal to each vectors and positioned at its end, and
- iii) find a geometric figure whose sides are made up entirely from a particular set of such faces that do not intersect any of the other planes

Figure 7 schematically shows a hypothetical 2 dimensional crystal with (10) and (11) planes and the final crystal surface obtained with this construction method. The three steps indicated above correspond to the three steps in the construction shown in the lower part of the figure.

It should be pointed out that this type of constructions



corresponds to a mathematical ideal situation, i.e. the crystal reaches the minimal surface energy level thermodynamically. In practice however the geometric figure of a crystal depends on the dynamics in the synthesis or growth conditions. Different morphologies are obtained for different processing conditions.

Chemical potential as a function of the surface curvature

The properties of surface atoms or molecules are different from that of interior atoms, due to the fewer number of bonds in the surface. The chemical potential is also dependent on the curvature of the surface, so it is an important aspect to consider in nanoparticles where the radius of curvature of the surfaces are extremely small. To see that let us consider the example of figure 8. Suppose we transfer material from an infinite flat surface to a spherical solid particle. This amount of material transferred is composed by dn atoms, and the radius of the solid particle is R . The volume change of the spherical particle, dV , is equal to the atomic volume Ω times dn . That is

$$dV = 4\pi R^2 dR = \Omega dn$$

The work per atom transferred, $\Delta\mu$, equals to the change of the chemical potential, and is given by

$$\Delta\mu = \mu_c - \mu_\infty = \gamma \frac{dA}{dn} = 8\pi R dR \frac{\Omega}{dV}$$

μ_c and μ_∞ are the chemical potential on the particle surface and on the flat surface respectively. Combining the two former equations

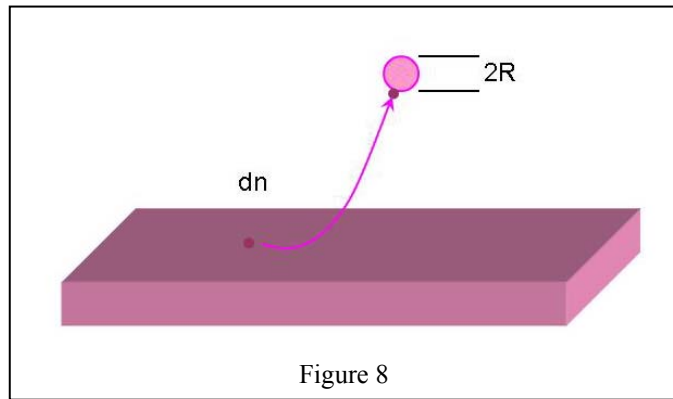
$$\Delta\mu = 2\gamma \frac{\Omega}{R}$$

This is also called the Young-Laplace equation and describes the chemical potential of an atom in a spherical surface with respect to a flat reference surface. This equation can be readily generalized for any type of curved surfaces.

The last equation indicates that the chemical potential of an atom in a convex surface (positive curvature) is higher than that on a flat surface. Mass transfer from a flat surface to a convex surface results in an increase in surface chemical potential. Thermodynamically an atom on a convex surface has the highest chemical potential, whereas an atom in a concave surface has the lowest. Such relationship is also reflected the difference in the vapor pressure and the solubility of a solid.

An interesting effect occurs when two particles with different radii, assuming $R_1 \gg R_2$ are put together into a solvent. Each particle will develop an equilibrium with the surrounding solvent. The solubility of the smaller particle will be larger than that of the large particle, so to maintain the equilibrium, solute will deposit onto the surface of the larger particle while the small particle has to continue to dissolve to compensate for amount of solute diffused away. The result is that the small particle gets smaller and the large particle larger. This phenomenon is called Ostwald ripening, which also occurs in solid state diffusion and evaporation/condensation.

Ostwald ripening has been used to narrow the size distribution of nanoparticles by eliminating small particles. Many relatively large particles grow at the expense of smaller



particles. The result is the elimination of the smaller particles thus the size distribution of the particles becomes narrower.

The reduction of the surface energy is the driving force for the surface restructuring, formation of faceted crystals, sintering and Ostwald ripening. These are the mechanisms for individual nanostructures and individual surfaces. The system can have another mechanism to reduce the overall surface energy. This is agglomeration. When nanostructures form agglomerates it is very difficult to disperse them. As the size of the nanostructure decreases, van der Waals forces become increasingly important. Without an appropriate stabilization mechanism the nanostructures are more likely to form agglomerates.

The following section will discuss stabilization mechanisms. There are two major stabilization mechanisms: electrostatic stabilization and steric stabilization.

Electrostatic stabilization

When a solid emerges in a polar solvent or an electrolyte solution, a surface charge will be developed through one or more of the following mechanisms:

- i) Preferential adsorption of ions
- ii) Dislocation of surface charged species
- iii) Isomorphic substitution of ions
- iv) Accumulation or depletion of electrons at the surface
- v) Physical adsorption of charged species onto the surface.

For a given surface in a given liquid medium, a fixed surface electrical charge density or electrode potential E will be established. The electrode potential E is given by the Nernst equation.

$$E = E_0 + \frac{R_g T}{n_i F} \ln a_i$$

where E_0 is the standard electrode potential when the concentration of ions is unity, n_i is the valence state of ions, a_i is the activity of ions, R_g is the gas constant ($R = 8.314472 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), T the temperature and F the Faraday's constant ($F = 96,485.3383 \text{ coulomb/mole}$). This equation indicates that the surface potential of a solid varies with the concentration of ions in the surrounding solution, and can be either positive or negative.

Let us concentrate in the case of oxides. The surface charge in oxides is mainly derived from preferential dissolution or deposition of ions. Ions adsorbed on the solid surface determine the surface charge and is referred as charge determining ions, also known as co-ions or "coions". In the oxide systems typical charge determining ions are protons and hydroxyl groups and their concentrations are described by pH ($\text{pH} = -\log[\text{H}^+]$). As the concentration of charge determining ions varies the surface charge density changes. The concentration of coions corresponding to a zero-charged surface is defined as "point zero charge" (p.z.c.). The following table gives the p.z.c. values for various oxides.

Solid	p.z.c.
WO_3	0.5
V_2O_5	1-2
SiO_2	2.5
Quartz	3.7

TiO ₂	6
SnO ₂	4.5
Al-O-Si	6
ZrO ₂	6.7
Mg)	12

At pH > p.z.c. the oxide surface is negatively charged since the surface is covered with hydroxyl groups (OH⁻) which is the electrical determining ion. At pH < p.z.c., H⁺ is the charge determining ion and the surface is positively charged. The surface charge density or surface potential E in volt can be simply related to the pH. The Nernst equation can be written as

$$E = \frac{2.303 R_g T [(p.z.c.) - pH]}{F}$$

At room temperature the former equation can be simplified to

$$E \approx 0.06 [(p.z.c.) - pH]$$

Electric potential at the proximity of a solid surface

When a surface charge is established there will be an electrostatic force between the surface and the charged species in the proximity of the surface. This electrostatic force will tend to segregate the charges in the region close to the surface. However there will be also Brownian motion and entropic forces that will homogenize the distribution of various species in the solution.

In the surface will always be surface charge determining ions and counter ions with opposite charge. Although neutral charge is maintained in a system, the distribution of charge determining ions and counter ions are very different and are inhomogeneous. the distribution of both ions are mainly controlled by a combination of the following forces:

- i- Coulombic forces
- ii- Entropic forces
- iii- Brownian motion

The result is that the concentration of counter ions is the highest near the solid surface and decreases as the distance from the surface increases, whereas the concentration of determining ions changes in the opposite way. This uneven concentration of charges generates what is called a “double layer” structure. Figure 9 is a scheme of this structure. The structure consists of two layers, the Stern layer and the diffuse layer also called Gouy layer. The two layers are separated by the Helmholtz plane.

In the Stern layer the electric potential drops linearly. Beyond the Helmholtz

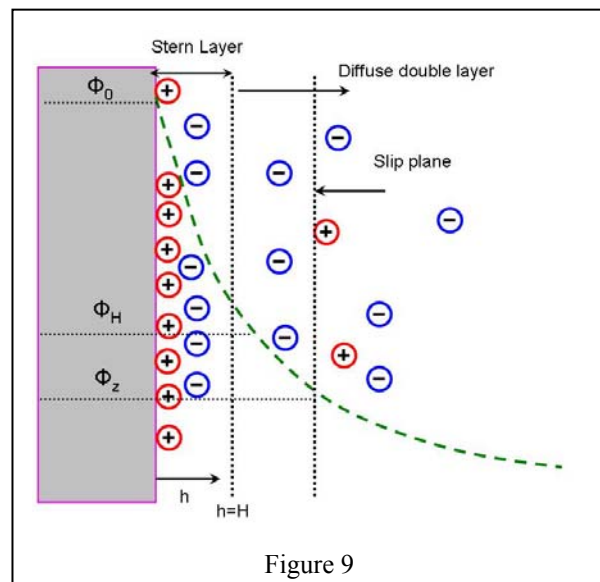


Figure 9

plane until the counter ions reach average concentration in the solvent is the Gouy layer or diffuse double layer. In the Gouy layer the counter ions diffuse freely and the electric potential does not reduce linearly. The electric potential drops approximately as

$$E \propto \exp[-K(h-H)]$$

with $h > H$, which is the thickness of the Stern layer. The constant $1/K$ is the Debye-Hückel screening strength. This constant has the expression:

$$K = \sqrt{\frac{F^2 \sum_i C_i Z_i^2}{\epsilon_r \epsilon_0 R_g T}}$$

where F is the Faraday constant, ϵ_0 is the permittivity of vacuum, ϵ_r is the dielectric constant of the solvent and C_i and Z_i are the concentrations and valence of the counter ions of type i .

Although this discussion was applied to flat surfaces in an electrolyte solution, the concepts are applicable to curved surfaces as well, assumed that the surface is smooth and the charges are distributed homogeneously. The two former equations are applicable for spherical particles where the surface charge is homogeneously distributed, and the particles are dispersed in an electrolyte solution and the distances between any two particles are large enough so that the charge distribution on the particle surface is not influenced by the other particles.

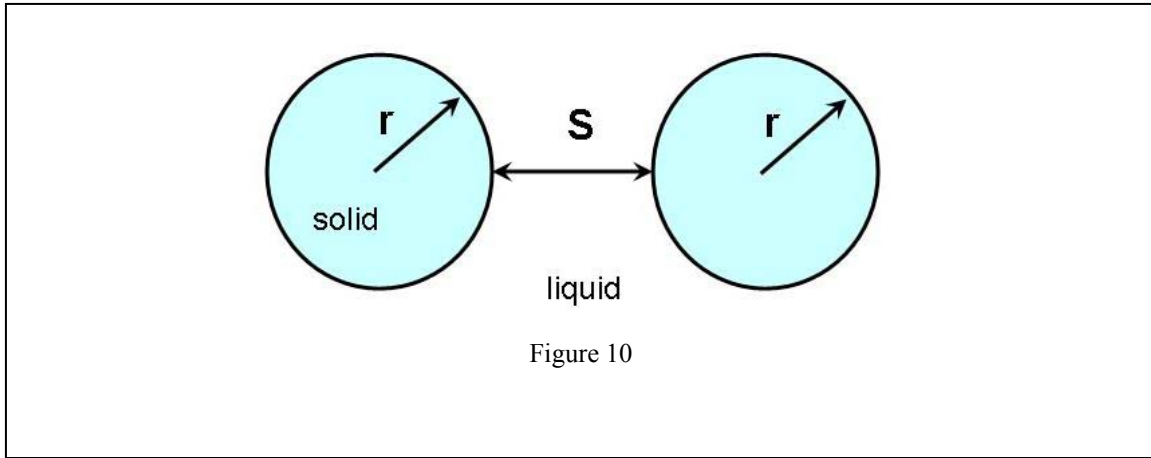
One of the interactions that occur between particles is directly associated with the surface charge and the electric potential adjacent to the interface. The electrostatic repulsion between two particles arises from the electric surface charges which are attenuated by the double layers structure. When two particles are far apart, there will be no overlap of two double layers and electrostatic repulsion between two particles is zero. When two particles approach each other, the double layers superpose and a repulsive force appear. The electrostatic repulsion between two equally sized spherical particles of radius r separated by a distance S is given by

$$\Phi_R = 2\pi \epsilon_0 \epsilon_r r E^2 e^{-KS}$$

Van der Waals attraction potential

When the particles are small, in the one micron size and below, the Van der Waals and the Brownian motion play important roles whereas the influence of the gravity becomes negligible. We will limit the discussion to spherical nanoparticles. Van der Waals force is a weak very short distance interaction force. Brownian motion assures that the particles are colliding with each other all the time. The combination of the Van der Waals force and the Brownian motion will produce the agglomeration of the nanoparticles.

The van der Waals interaction between two particles of radius r separated by a distance S (as schematically indicated in figure 10) is given by



$$\Phi_A = -\frac{A}{6} \left\{ \frac{2r^2}{S^2 + 4rS} + \frac{2r^2}{S^2 + 4rS + 4r^2} + \ln \left(\frac{S^2 + 4rS}{S^2 + 4rS + 4r^2} \right) \right\}$$

where the negative sign represents the attractive nature of the interaction and A is the Hamaker constant that depends on the material. The Hamaker constant are in the range of 10^{-19} to 10^{-20} J. The following table gives some Hamaker constant values for different materials. When the separation distance between two equal size spherical nanoparticles is significantly smaller than the particle radius, the simplest expression of the Van der Waals attraction could be obtained.

Material	A [10^{-20} J]
gold	45.3
Al ₂ O ₃	15.4
MgO	10.5
SiO ₂	6.5
CaF ₂	7.2
polymers	6.15-6.6
water	4.35
acetone	4.2
calcite	10.1
Ethyl acetate	4.17
toluene	5.4

$$\Phi_A = -\frac{A r}{12 S}$$

Other simplified expressions for the Van der Waals force are given in the following table for different cases

Particles	Φ_A
two spheres of equal radius	$-\frac{A r}{12 S}$
two spheres of unequal radius r_1 r_2	$-\frac{A r_1 r_2}{6 S (r_1 + r_2)}$
two parallel plates with thickness δ (per unit area)	$-\frac{A}{12\pi} \left[S^{-2} + (2\delta + S)^{-2} + (\delta + S)^{-2} \right]$

two blocks interaction per unit area	$-A r / 12\pi S^2$
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From this table it is notice that the van der Waals attraction potential between two particles are different from that between two flat surfaces. The attraction force between two particles decays much slowly and extend over distances of nanometers. As a result a barrier potential must be developed to prevent agglomeration. Two widely methods to prevent the agglomeration of nanoparticles are electrostatic repulsion and steric exclusion.

Interactions between two particles

The total interaction between two particles which are electrostatic stabilized is the combination of the van der Waals attraction and the electrostatic repulsion. This can be expressed as

$$\Phi = \Phi_A + \Phi_R$$

The electrostatic stabilization of particles in a suspension is described by the DLVO theory, named after Derjaguin, Landau, Verwey and Overbeek. In this theory there are few important assumptions:

- i- infinite flat solid surface
- ii- uniform surface charge density
- iii- no redistribution of surface charge, i.e. the surface electric potential is constant
- iv- no change in the concentration profiles of charges, i.e. the potential remains unchanged
- v- solvent exerts influence via dielectric constant, i.e. no chemical reaction between the particles and the solvent.

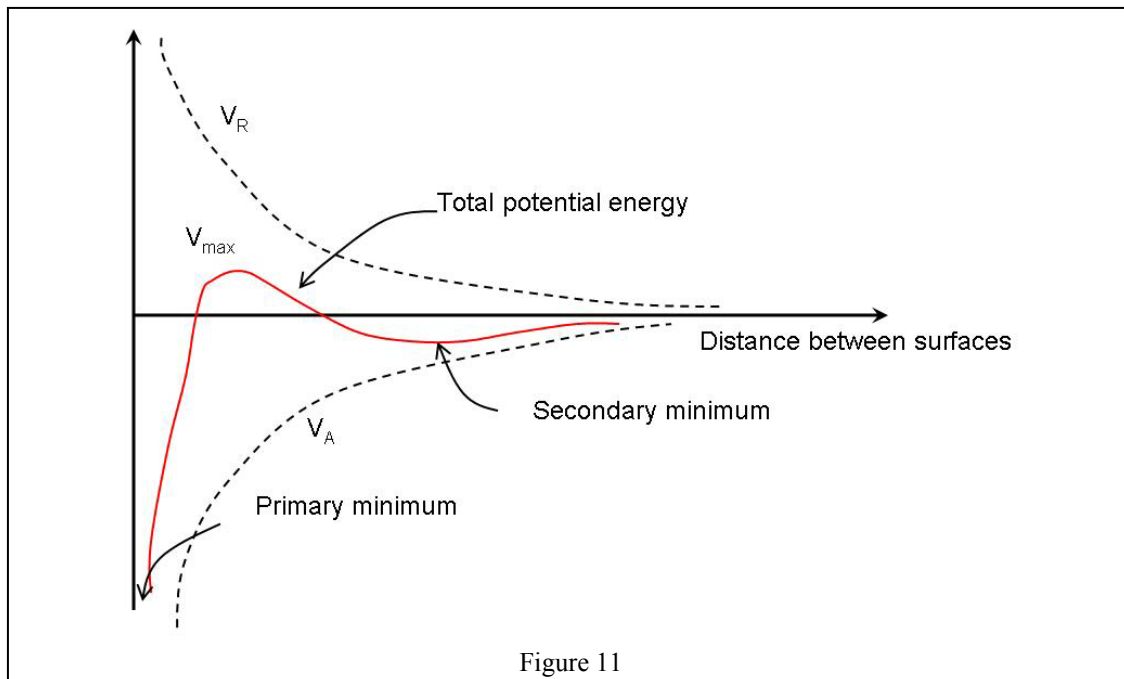


Figure 11 shows the van der Waals attraction potential (V_A) and the electric repulsion potential (V_R) as a function of the distance from the surface to the spherical particle. At distances far from the surface, both the van der Waals and the electric potentials are zero. Close to the surface there is a deep minimum (attraction) due to van der Waals potential. Also there is a local maximum located a little farther away from the surface where the electric potential dominates (compensates) the van der Waals attraction. This maximum is also known as the “repulsive barrier”. If the barrier is greater than ≈ 10 kT, the collision of two particles will not have sufficient energy to overcome this maximum and agglomeration will not occur. The electric potential depends on the concentration of counter ions (through the constant Debye-Hückel screening strength $1/\kappa$), so a way to adjust the maximum value of the repulsive barrier is by changing the concentration of ions in the solution.

The secondary minimum not always exists and is present only when the concentration of counter ions is high. If the secondary minimum is established, particles are likely to be associated with each other, which is known as “flocculation”.

Figure 12 schematically shows what happens when two particles interact. This interaction depends on the distance between the particles. When the two particles are far apart, or the distance between the surfaces is larger than the combined thickness of two electric double layers, there would be no interaction between the two particles.

As the distance reduces the repulsion increases and reaches a maximum when the distance between the two particles surfaces equals to the distance between the repulsive barrier and the surface. This repulsion can be understood in two ways. One is that the repulsion is a consequence of the overlap of the electric potentials of the two particles. The particles are not charged themselves, but the repulsion comes from the interaction of the two double layers.

The other way to understand this repulsion is considering the “osmotic flow”. When two particles approach each other, the concentration of ions in the region where the double layers overlap increases significantly. As a result of this increased ion concentration in the region between the two particles, the original equilibrium concentration of counter ions and surface charge determining ions is destroyed. To restore the equilibrium more solvent flows into the region where the double layers overlap and produces a flow that effectively repels the two particles. This osmotic force disappears when the distance between the two particles becomes equal to or larger than the sum of the thickness of the two double layers.

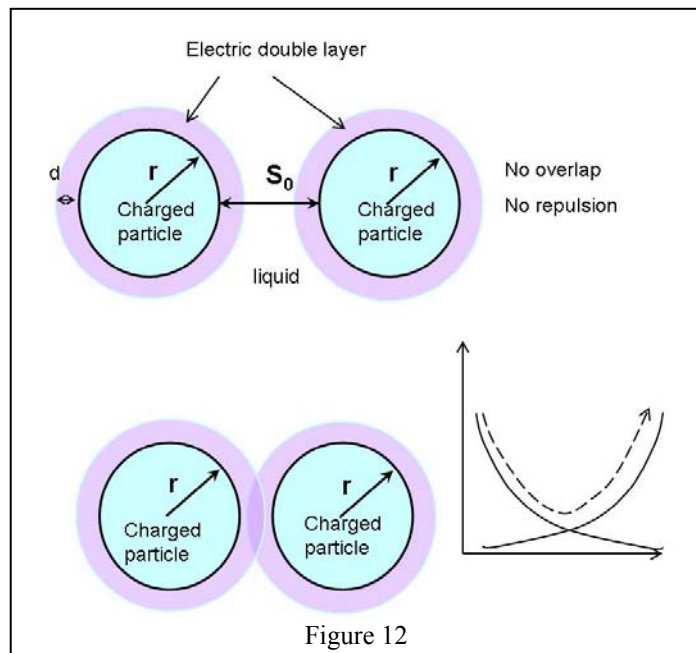


Figure 12

Steric stabilization

It is also called polymeric stabilization. It has some advantages as compared with the electrostatic stabilization:

- i- It is a thermodynamic stabilization method, so the particles are always redispersible
- ii- A very high concentration can be accommodated and the dispersion medium can be completely depleted.
- iii- It is not electrolyte sensitive
- iv- It is suited to multiple phase systems

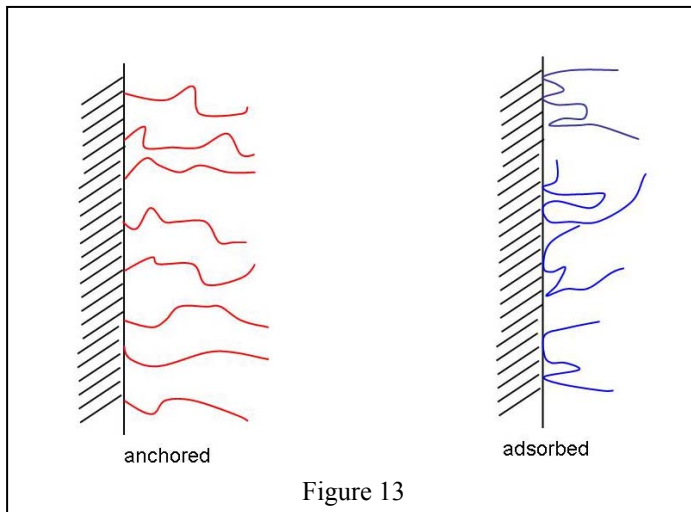
Solvent and polymer

Solvents can be grouped into aqueous solvents and organic solvents. They can also be classified into protic solvents (exchange protons) and aprotic solvents that do not exchange protons. The following table gives some examples

Solvent	Formula	Dielectric constant	Type
Acetone	C ₃ H ₆ O	20.7	aprotic
Acetic Acid	C ₂ H ₄ O ₂	6.2	protic
Ammonia	NH ₃	16.9	protic
Benzene	C ₆ H ₆	2.3	aprotic
Chloroform	CHCl ₃	4.8	aprotic
Dimethylsulfoxide	(CH ₃) ₂ SO	45	aprotic
Dioxanne	C ₄ H ₈ O ₂	2.2	aprotic
water	H ₂ O	78.5	protic
methanol	CH ₃ OH	32.6	protic
ethanol	C ₂ H ₅ OH	24.3	protic
formamide	CH ₃ ON	110.0	protic
dimethylformamide	C ₃ H ₇ NO	36.7	aprotic
nitrobenzene	C ₆ H ₅ NO ₂	34.8	aprotic
tetrahydrofuran	C ₄ H ₈ O	7.3	aprotic
carbon tetrachloride	CCl ₄	2.2	aprotic
diethyl ether	C ₄ H ₁₀ O	4.3	aprotic
Pyridine	C ₅ H ₅ N	14.2	aprotic

Only polymers that can be dissolved into solvents are suited for steric stabilization. When a polymer dissolves into a solvent, the polymer interacts with the solvent. Such interaction varies with the system and the temperature. When the polymer dissolved in a solvent tends to expand to minimize its Gibbs free energy it is called a “good” solvent. On the other hand, if the polymer tends to coil up or collapse, it is called a “poor” solvent. The characteristic of good or poor solvent depends on the temperature. If the temperature increases, the polymer tends to expand and the solvent is good. The temperature at which a solvent transfer from a poor solvent to a good solvent is called the “theta” temperature or the Flory-Huggins temperature.

Depending on the interaction between the polymer and the solid surface, a polymer can be grouped into:



- 1- Anchored polymer which irreversibly binds to the solid surface by one end only
- 2- Adsorbing polymer which binds weakly at random points along the polymer backbone
- 3- Non-adsorbing polymer which does not attach to the surface and does not contribute to polymer stabilization

Figure 13 is a scheme of the two first cases

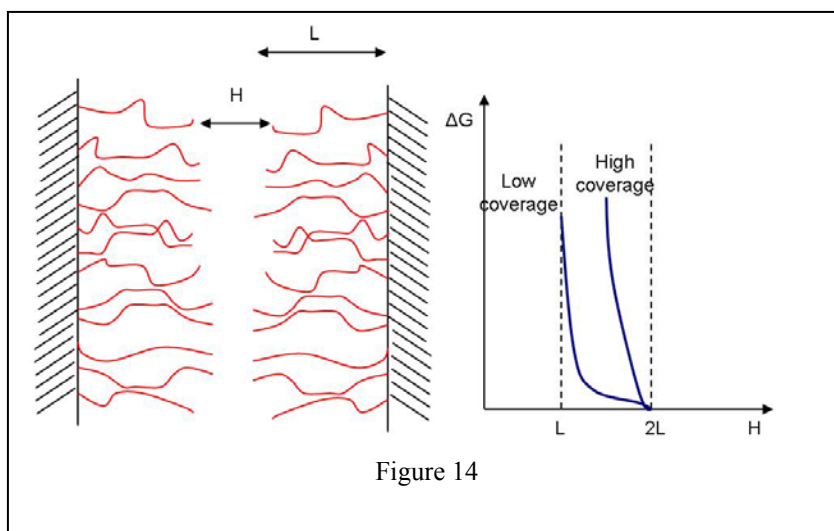
Interactions between polymer layers

Let us first consider what happens when two surfaces covered by anchored polymers approach each other. They will interact only when the separation H between the surfaces is smaller than $2L$ where L is the length of the polymer chain. When the distance is smaller than $2L$ but larger than L the interaction is between the polymer layers and the solvent. There is no interaction between the polymer layer of one particle and the surface of the other particle. If the polymer coverage of the surface is low (50% or so), when two particles approach, the polymer layers interpenetrate. This interpenetration reduces the mobility of the polymer chains and reduces the entropy ($\Delta S < 0$). Assuming that the change in the enthalpy due to the interpenetration is negligible ($\Delta H \approx 0$) then the change in the Gibbs function is

$$\Delta G = \Delta H - T \Delta S > 0$$

So the particles will repel each other to a distance equal or larger than $2L$.

When the surface coverage is large (100%) there would be no interpenetration. As a



result the two polymer layers will be compressed leading to the coil up of the layers in the two particles. Coil up of the polymer layer increases the Gibbs free energy and that provoke a repulsion between the particles.

Figure 14 shows schematically what happens with the

Gibbs free energy function in the two cases mentioned above.

The situation is rather different in a poor solvent with low polymer coverage in the surface of the solid. When the distance between the two particles is less than twice the thickness of the polymer layers but larger than the thickness of a single polymer layer ($L < H < 2L$), polymer adsorbed into the surface of one particle tends to penetrate into the polymer layer of the approach particle. This interpenetration promotes further coil up of the polymer chains and results in a further decrease of the Gibbs function and the two particles tend to associate each other. However with high coverage there will be no interpenetration and when the distance between the particles decreases produces a compressive force that increases the Gibbs function and the particles repel each other. Figure 15 shows schematically this case.

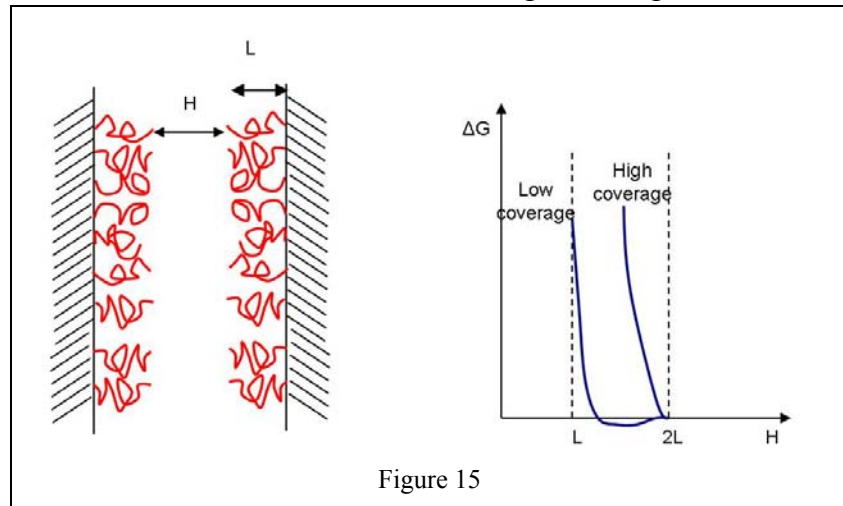


Figure 15