

Structure of Materials

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Why Composites are Important?

- Composites can be very strong and stiff, yet very light in weight, so ratios of strength-to-weight and stiffness-to-weight are several times greater than steel or aluminum
- Fatigue properties are generally better than for common engineering metals
- Toughness is often greater too
- Composites can be designed that do not corrode like steel
- It is possible to achieve combinations of properties not attainable with metals, ceramics, or polymers alone

Structure of Composites

Composites are materials made from two or more constituent materials with different physical and chemical properties, that when combined, produce a material with characteristics different from the individual components.

Examples:

- Cemented carbides (WC with Co binder)
- Plastic molding compounds containing fillers
- Rubber mixed with carbon black
- Wood (a natural composite as distinguished from a synthesized composite)

The individual components remain separate and distinct within the finished structure. The new material may be preferred for many reasons: common examples include materials that are stronger, lighter, or less expensive when compared to traditional materials



Example: concrete is a mixture of cement and aggregate, giving a robust, strong material.

Disadvantages and Limitations of Composite Materials

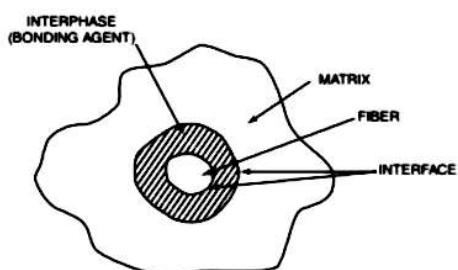
- Properties of many important composites are anisotropic - the properties differ depending on the direction in which they are measured – this may be an advantage or a disadvantage
- Many of the polymer-based composites are subject to attack by chemicals or solvents, just as the polymers themselves are susceptible to attack
- Composite materials are generally expensive
- Manufacturing methods for shaping composite materials are often slow and costly

Constituents of the Composite Materials

Main Constituents of Composite Material

The main constituents of composites are the matrix and the reinforcement materials. The **matrix** forms the volume of the composite material within which the **reinforcing agent** is embedded. The matrix fits together all parts of the composite, while the reinforcements usually serve to strengthen the composite.

For the composite to operate effectively, the phases must bond where they join at the interface:



Constituents of the Composite Materials

Functions of the matrix: The matrix material can be a polymer, metal, or other inorganic substance.

The Matrix Material:

- ❖ Provides the bulk form of the part or product made of the composite material;
- ❖ Holds the embedded phase in place, usually enclosing and often concealing it;
- ❖ When a load is applied, the matrix shares the load with the secondary phase, in some cases deforming so that the stress is essentially born by the reinforcing agent

Reinforcing Agents: A function must be embedded in the matrix to change the structure.

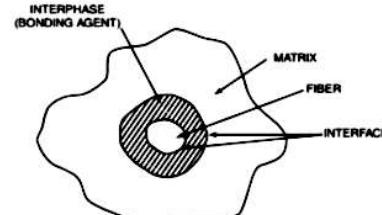
Shape of Reinforcements: Reinforcing agents are most commonly one of the following shapes:

- ❖ Fibers (a);
 - ❖ Particles (b);
 - ❖ Flakes (c)
- ❖ Textile materials, sheets of paper, folios.



Constituents of the Composite Materials

- ❖ The body constituent gives the composite its bulk form, and it is called the matrix.
- ❖ The other component is reinforcement, which determines the internal structure of the composite.
- ❖ The region between the body and structural constituents is called the interphase. It is quite common, but incorrect, to use the term interface to describe this region. An interface is a two-dimensional construction—an area having a common boundary between the constituents—whereas an interphase is a three-dimensional phase between the constituents and, as such, has its properties.
- ❖ It turns out that these interphase properties play a very important role in determining the ultimate properties of the bulk composite.



Constituents of the Composite Materials

Materials for Fibers: Fiber materials in fiber-reinforced composites:

- ❖ Glass – most widely used filament;
- ❖ Carbon – high elastic modulus;
- ❖ Boron – very high elastic modulus;
- ❖ Polymers – Kevlar;
- ❖ Ceramics – SiC and Al₂O₃
- ❖ Metals – steel.

The most important commercial use of fibers is in polymer composites.

Particles and Flakes: A second common shape of embedded phases are particles, ranging in size from microscopic to macroscopic.

Flakes are two-dimensional particles - small flat platelets.

The distribution of particles in the composite matrix is random, and therefore strength and other properties of the composite material are usually isotropic.

The strengthening mechanism depends on particle size.

Combination Effects in Composites

Combination Effects: by which a composite can offer improved properties over the individual components.

There are three ways:

Summation effect: when the contribution of each constituent is independent of the others.

Example 1: The density of a composite \Rightarrow is simply the weighted average of the densities of its constituents. The density of each component is independent of the other components.

Example 2: Elastic modulus is also a summation effect,

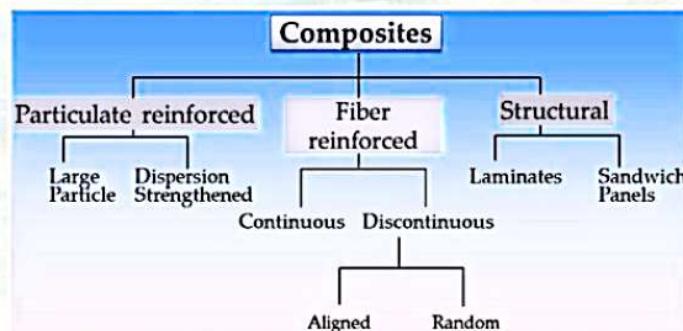
with the upper limit $E_c(u) = V_p E_p + V_m E_m$ and the lower limit $E_c(l) = \frac{E_m E_p}{V_m E_p + V_p E_m}$

where E_m and E_p are the elastic moduli of the matrix and particulate, respectively; and V_m and V_p are their respective volume fractions.

$E_c(u)$ and $E_c(l)$ is that summation properties can be added appropriately to give an estimate of the composite properties.

Classification of Composite Materials

- Traditional composites – composite materials that occur in nature or have been produced by civilizations for many years
 - Examples: wood, concrete, asphalt
- Synthetic composites - modern material systems normally associated with the manufacturing industries, in which the components are first produced separately and then combined in a controlled way to achieve the desired structure, properties, and part geometry



Combination Effects in Composites

Complementation effect: when each constituent contributes separate properties.

Example: laminar composites are sandwich-type composites composed of several layers of materials. Sometimes the outer layer is simply a protective coating, which contributes only a specific property to the overall composite.

Synergistic effect: An interaction effect arises between some constituent properties that are not independent of each other. In this case, the composite property may be higher than either of the components.

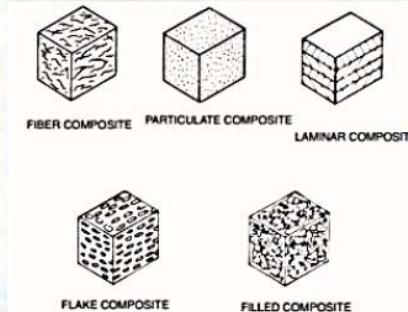
Example: The strength of some glass-fiber-reinforced plastic composites is greater than either the matrix or the reinforcement component by itself.

Classification of the Composite Materials

After the kind of the matrix composites can be divided into three groups:

- ❖ Metal Matrix Composites (MMCs) - mixtures of ceramics and metals, such as cemented carbides and other cermets;
- ❖ Ceramic Matrix Composites (CMCs) - Al_2O_3 and SiC embedded with fibers to improve properties, especially in high-temperature applications;
- ❖ Polymer Matrix Composites (PMCs) - thermosetting resins are widely used in PMCs. Examples: epoxy and polyester with fiber reinforcement, and phenolic with powders.

According to the type of reinforcing agents, the composites can be classified:



Classification of the Composite Materials

There are five general types of composites when categorized by bulk form.

- ❖ **Fiber composites** consist of fibers; with or without a matrix. By definition, a fiber is a particle longer than 100 µm with a length-to-diameter ratio (aspect ratio) greater than 10:1.
- ❖ **Flake composites** consist of flakes, with or without a matrix. A flake is a flat, plate-like material.
- ❖ **Particulate composites** can also have either a matrix or no matrix along with the particulate reinforcement. Particulates are roughly spherical in shape in comparison to fibers or flakes.
- ❖ **In a filled composite**, the reinforcement, which may be a three-dimensional fibrous or porous structure, is continuous and often considered the primary phase, with a second material added through such processes as chemical vapor infiltration (CVI).
- ❖ **Laminar composites** are composed of distinct layers. The layers may be of different materials or the same material with different orientations.

Fiber Materials Composites

- a) One-dimensional reinforcement occurs when the fibers are oriented along their primary axis. This offers maximum mechanical strength along the orientation axis, but results in anisotropic composites; that is, the mechanical and physical properties are not the same in all directions.
- b) Planar reinforcement occurs with two-dimensional orienting of the fibers, as often occurs with woven fabrics. The fabric, as is common in woven glass fibers, is produced in sheets, and it is laid down (much like a laminate) to produce a two-dimensional reinforcement structure.
- c) Three-dimensional reinforcement results from the random orientation of the fibers. This creates an isotropic composite, in which the properties are the same in all directions, but the reinforcing value is often decreased compared to the aligned fibers.

The second factor is fiber length which affects the composite that can be manufactured. Very long fibers can create difficulties with methods used to create discontinuously reinforced FMCs and can result in nonuniform mechanical properties.

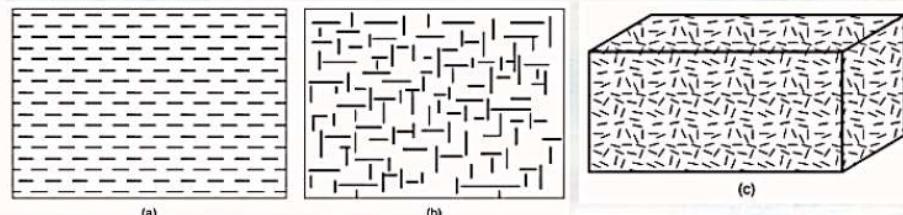
Fiber Materials Composites

Continuous-fiber-reinforced composites

- ❖ made from fiber rovings (bundles of twisted filaments) that have been woven into two-dimensional sheets
- ❖ The sheet can be cut and formed to a desired shape that is then incorporated into a composite matrix, typically a thermosetting resin such as epoxy.
- ❖ the properties of the resulting composite are highly dependent not only on the type of fiber and matrix used but also on the processing techniques with which they are formed.

Discontinuous-fiber-reinforced composites

Four main factors contribute to the performance level of a fiber in discontinuously reinforced FMCs. The first factor is fiber orientation.



Types of fiber reinforcement orientation (a) one-dimensional, (b) two-dimensional, and (c) three-dimensional.

Fiber Materials Composites

The third factor is related to fiber geometry, namely, the fiber shape. Usually, a fiber is a particulate with a length greater than 100 µm and an aspect ratio greater than 10:1. Composite's aspect ratio can vary widely as many reinforcement filaments have aspect ratios much larger than 10:1. The fiber cross-section may not be exactly circular after reinforcement. It could have hexagonal, ellipsoidal, cylindrical, annular (hollow fiber), and dumbbell-shaped fiber cross-sections are quite common. "Dumbbell"-shaped fibers are preferable as these shapes help distribute these stresses.

The fourth factor affecting the reinforcement performance is its composition. Chemistry affects properties, and strength is usually the most important property of a reinforcing fiber. It is worth noting that the design consideration for reinforcement materials (or the matrix, for that matter) is not the absolute value of a particular design criterion. This fact is extremely important for many applications, such as automotive and aerospace composites, for which weight savings are paramount

Interfaces of Composites

The Composite Interphase is the region between the matrix and the reinforcement that affects the mechanical properties of the composite. It can transfer loads from the matrix to the reinforcement which has an impact on the strength of the composite.

Several factors that affect the composition and spatial extent of the interphase.

- ✓ Wettability by which the liquid matrix wets the reinforcing constituent before solidification.

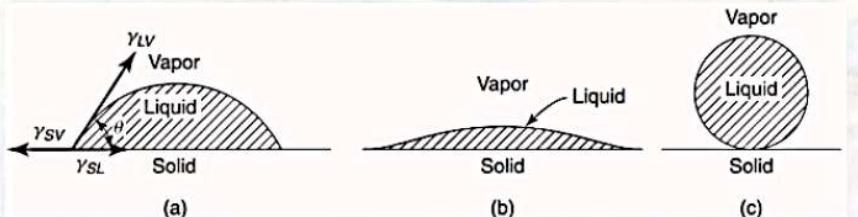


Figure: Interaction of a liquid droplet with a solid substrate: (a) Partially wetting ($0^\circ < \theta < 180^\circ$), (b) completely wetting ($\theta \approx 0^\circ$), and (c) completely nonwetting ($\theta = 180^\circ$). Interfacial energies between the solid–liquid, solid–vapor, and vapor–liquid are represented by γ_{SL} , γ_{SV} , and γ_{LV} , respectively

Functionally Graded Materials (FGMs)

Functionally graded materials (FGMs) were conceived and developed in 1980. It was recognized as a new material and the material requirements would be extreme for the particular application.

- The ceramic surface will be used to provide high-temperature gases at thousands of degrees.
- metallic materials would be required to provide sufficient thermal conductivity and mechanical strength to cool the surface.

FGMs are common on coatings. Plasma vapor deposition (PVD), chemical vapor deposition (CVD), thermal spray processing, and plasma spray processing are but a few of the techniques used to form FGMs.

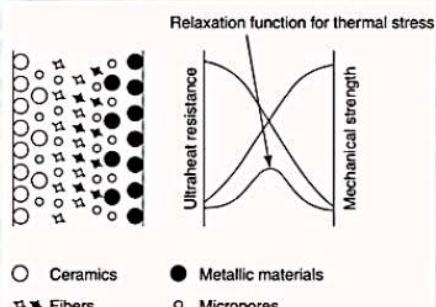


Figure: Conceptual diagram of functionally graded materials (FGMs).

Interfaces of Composites

➤ **Interfacial contact angle** which measures the ability of a liquid to wet a solid. low contact angles are representative of "good" wetting (i.e., favorable liquid–solid interactions), whereas high contact angles (greater than about 90°) are indicative of "poor" wetting and unfavorable liquid–solid interactions. A favorable liquid–solid interaction is desirable to obtain good matrix–fiber interactions.

➤ **Wetting agents** that improve the wettability of the composite in case of the disparate chemistries of constituents.

➤ **Inherent reactivity between the components:** The reinforcement and matrix can react with one another, either due to direct chemical reaction or through longer-term diffusion of components from one phase to another.

Optimization of the interphase properties in advanced composites is currently the focus of much research.

Biological Materials

Biological Materials Science is a new and rapidly growing branch of Materials Science and Engineering. It has three distinct but interrelated components:

- Biological Materials: natural materials
- Biomaterials: synthetic materials in biomedical applications
- Biomimetics: bioinspired materials and design

Biological Material means any plants, seeds, microorganisms, cells, parts of cells, DNA, RNA, cDNA, proteins, peptides, enzymes, and any combination of the foregoing, and/or other organic matter and/or biologically active compounds.

Proteins → hard biologics—Bone
soft biologics — muscle and skin.

Proteins are composed of 20 amino acids (technically, 19 amino acids and one imino acid). The amino acid is in its dissociated state, such that the terminal hydrogen on the carboxyl group moves to the amino group, thereby creating a carboxylate group (COO^-) and an ammonium group (NH_3^+) known as a **zwitterion**. The molecule remains neutral overall, and there may be several stable zwitterion forms, depending on the amino acid.

Thermodynamics of system

Thermodynamics of Condensed phases

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The sign convention for W depends on condensed, closed, and open systems, the work term mostly arises from pressure-volume (PV) work. In a closed system, the macroscopic kinetic and potential energies, E_k , and E_p , respectively, are not of importance, so that the functional form of the First Law is $U = Q$.

In differential form for infinitesimal changes of state, $dU = dQ$

Enthalpy, H is defined as the internal energy plus the pressure-volume product, PV. The definition of enthalpy for infinitesimal changes in state is

$$dH = dU + d(PV)$$

For condensed systems, the $d(PV)$ term is negligible which leads to $dH = dQ$

And in integrated form is $H = Q$

Entropy is a measure of randomness or disorder in a system. The Second Law of Thermodynamics states that the entropy change of all processes must be positive. The differential change in entropy for a closed system from one state to another is, by definition, directly proportional to the change in reversible heat, and inversely proportional to the absolute temperature, T,

$$dS = \frac{dq}{T}$$

At constant-temperature processes, $\Delta S = \frac{q}{T}$.

The relationship between the entropy and enthalpy for constant pressure and temperature processes: $\Delta S = \Delta H/T$

And the Third Law of Thermodynamics, which states that the entropy of a perfect crystal is zero at zero absolute temperature

The internal energy, U of a system is the sum of the microscopic kinetic and potential energies of the particles. Kinetic energy is the energy due to the motion of the particles, including translation, rotation, and vibration. The potential energy is the energy due to composition. The quantity U represents the change of internal energy for the system from some initial state to some final state.

The total energy of a system, E represents the change of total energy from an initial state to a final state. The total energy is comprised of the internal energy, U, the kinetic energy of the system, and the potential energy of the system.

The First Law of Thermodynamics can be written for a closed system (no transfer of matter between the system and surroundings) as:

$$U + E_k + E_p = \pm Q \pm W$$

where Q is the heat transferred between the surroundings and the system W is the work performed.

Case-1: exothermic processes in which heat is transferred from the system to the surroundings have a negative sign in front of Q;

Case-2: endothermic processes, in which heat is transferred from the surroundings to our system, have a positive sign.

The Gibbs free energy for a closed system is defined in terms of the enthalpy and entropy as, $G = H - TS$

At constant pressure and temperature, $dG = dH - TdS$.

$G < 0$ Process proceeds spontaneously - thermodynamically favored

$G > 0$ Process not spontaneous

$G = 0$ Process at equilibrium

The chemical potential, μ can be defined in terms of the partial derivative of any of the previous thermodynamic quantities with respect to the number of moles of species i , n_i , at constant n_j (where j indicates all species other than i) and thermodynamic quantities as indicated:

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i} \right)_{S,V,n_j} = \left(\frac{\partial G}{\partial n_i} \right)_{S,V,n_j}$$

The advantage of the chemical potential over the other thermodynamic quantities, U, H, and G, is an intensive quantity—that is, is independent of the number of moles or quantity of species present. Internal energy, enthalpy, free energy, and entropy are all extensive variables.

Mixture-Solution-Phases

- ❖ Almost all materials have more than one phase in them. Thus engineering materials attain their special properties. The macroscopic basic unit of a material is called a component. It refers to an independent chemical species. The components of a system may be elements, ions, or compounds.
- ❖ A phase can be defined as a homogeneous portion of a system that has uniform physical and chemical characteristics i.e. it is physically distinct from other phases, chemically homogeneous and mechanically separable portion of a system.
- ❖ A component can exist in many phases. E.g.: Water exists as ice, liquid water, and water vapor. Carbon exists as graphite and diamond.
- ❖ When two phases are present in a system, it is not necessary that there be a difference in both physical and chemical properties; a disparity in one or the other set of properties is sufficient.
- ❖ A solution (liquid or solid) is a phase with more than one component; a mixture is a material with more than one phase.
- ❖ Solute (a minor component of two in a solution) does not change the structural pattern of the solvent, and the composition of any solution can be varied.
- ❖ In mixtures, there are different phases, each with its atomic arrangement. It is possible to have a mixture of two different solutions!

Gibbs Phase rule

The Gibbs phase rule is derived from the notion that distinct phases are in equilibrium with each other under certain conditions, reducing the number of independent variables under such conditions. According to this rule if a closed confined heterogeneous thermodynamic system isn't affected by gravity, electric or magnetic pressure but is influenced by concentration, temperature, and pressure then the possible number of degrees of freedom (F) in the system can be described as—

$$F = C - \phi + 2$$

where, F = degree of freedom, ϕ = phase, and C = component

- This rule is useful in determining the pressure and temperature of a geothermal system.
- Such conditions mentioned in this rule are applicable to all phases of a system.
- The stability of the different phases in a system can be determined with the help of this rule.
- Gibbs assumed that the system's various components did not interact with one another.

Gibbs Phase rule

Variables mentioned in Gibb's phase rule have important significance in the derived equation—

1.Degrees of freedom (F): With the help of degrees of freedom a system can be described by the number of parameters involved in it. It is described as a thermodynamic system without influencing the other parameters in the system.

2.Component (C): Components in a system are the subtraction of chemical entities present in the system and the number of chemical reactions occurring between them. For example, considering water (H_2O) there are two hydrogen atoms and one oxygen atom. These two entities are not reacting with each other or with the water so the number of components in the system is three.

3.Phase (ϕ): One system can exist in different phases such as solid, liquid, and vapor. For example, water can exist in three different phases such as, for solid ice, liquid water, and gas vapor.

Derivation of Gibbs Phase rule

Consider a confined heterogeneous equilibrium system with ' ϕ ' phases and 'C' components. The degrees of freedom in the system are denoted as 'F'.

- ❖ The first variable pressure affects the system but is the same for all phases.
- ❖ Temperature is also the same for all the phases in the system.
- ❖ Although the concentration of each phase in the system has to be determined independently.

For simplifying the composition of each phase in the system the ($C-1$) number of component's concentration needs to be specified independently.

Now, for phase ' ϕ ' the concentration can be expressed as, $\phi(C-1)$
So, the total number of degrees of freedom in the system

$$F = \phi(C-1) + 2 \dots \dots \dots \text{(i)}$$

Now, on the other hand, if the chemical potential of all phases is the same in the system then it can be said that the system is in equilibrium.

Then, $\phi - 1$ is the number of equilibria for each ϕ phase of each component.

The number of equilibria for ϕ phases for C components is $C(\phi - 1)$.
 $\dots \dots \dots \text{(ii)}$

Equating both the equation (i) and equation (ii)—

$$F = [\phi(C-1) + 2] - [C(\phi - 1)]$$

$$F = [(C\phi - \phi + 2) - (C\phi - C)]$$

$$F = (C\phi - \phi + 2 - C\phi + C)$$

$$F = C - \phi + 2$$

This is the derived form of Gibb's phase rule

Derivation of Gibbs Phase rule

Consider a single component, A which has a specified composition that can exist in two phases α and β .

A phase is defined as a homogeneous portion of a system that has uniform physical and chemical characteristics. It need not be continuous. For example, a carbonated beverage consists of two phases: the continuous liquid phase and the gas phase, which is dispersed in the liquid phase as discrete bubbles.

Consider, that phase α and phase β are in equilibrium with one another which means that there is probably an exchange of atoms between the two phases; i.e., some of the solid phase α is melting to form β , and some of the liquid phase β is solidifying to form α . These processes are occurring at essentially equal rates such that the relative amounts of each phase are unchanged. This is known as a dynamic equilibrium.

In terms of intensive variables, equilibrium means that

$$T_\alpha = T_\beta, \quad P_\alpha = P_\beta, \quad \mu_\alpha = \mu_\beta$$

where T_α , P_α and μ_α are the temperature, pressure and chemical potential of the solid phase α ; T_β , P_β and μ_β temperature, pressure and chemical potential of the solid phase β .

Derivation of Gibbs Phase rule

There are a total of $(\phi - 1)$ equalities for temperature, pressure, and chemical potential of each of the components, C.

There are C equations, so the total number of equations is $(C + 2)$.

Thus, we have $(\phi - 1)(C + 2)$ total equalities, or restrictions for equilibrium.

The total number of intensive variables in the system is $\phi(C + 1)$.

Degrees of freedom = number of intensive variables – number of independent restrictions

$$F = [\phi(C + 1)] - [(\phi - 1)(C + 2)]$$

$$F = C\phi + \phi - C\phi + C - 2\phi + 2$$

$$F = C - \phi + 2$$

❖ In the case of a single component and two phases, C = 1 and $\phi = 2$, the phase rule is $F = 1 - 2 + 2 = 1$

This means that when phases α and β coexist at equilibrium, only one variable may be changed independently. If temperature is changed, pressure cannot be changed simultaneously without affecting the balance of equilibrium.

❖ If, $F = 2$, both temperature and pressure can be changed without affecting the balance of equilibrium (number of phases present).

❖ $F = 0$, none of the intensive variables can be changed without altering the equilibrium between phases.

Thus, we have six intensive quantities that establish equilibrium between the two phases. However, these six variables are not all independent. Changing any one of them can affect the others. This can be shown mathematically by assuming that the chemical potential is a function of temperature and pressure:

$$\mu_\alpha = \mu_\alpha(T_\alpha, P_\alpha)$$

$$\mu_\beta = \mu_\beta(T_\beta, P_\beta)$$

Therefore, for a one-component system containing two phases in equilibrium, we have three thermodynamic conditions of equilibrium and four unknown parameters, $T_\alpha, P_\alpha, T_\beta, P_\beta$.

Consider C-independent, non-reacting components and have an arbitrary number of phases, ϕ .

$$T_\alpha = T_\beta = T_\gamma = \dots = T_\phi$$

$$P_\alpha = P_\beta = P_\gamma = \dots = P_\phi$$

$$\mu_{1\alpha} = \mu_{1\beta} = \mu_{1\gamma} = \dots = \mu_{1\phi}$$

$$\mu_{2\alpha} = \mu_{2\beta} = \mu_{2\gamma} = \dots = \mu_{2\phi}$$

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$$\mu_{C\alpha} = \mu_{2\beta} = \mu_{3\gamma} = \dots = \mu_{2\phi}$$

Phase Diagram

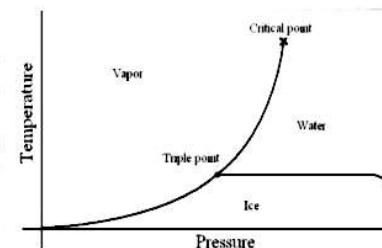
❖ A diagram that depicts the existence of different phases of a system under equilibrium is termed a **phase diagram**.

Phase diagram represents:

- It shows phases present at different compositions and temperatures under slow cooling (equilibrium) conditions.
- It indicates the equilibrium solid solubility of one element/compound in another.
- It suggests the temperature at which an alloy starts to solidify and the range of solidification.
- It signals the temperature at which different phases start to melt.
- The amount of each phase in a two-phase mixture can be obtained

❖ Phase diagrams are classified according to the number of components present in a particular system

If a system consists of just one component (e.g.: water), the equilibrium of phases is depicted by a **unary phase diagram**. The component may exist in different forms, thus variables here are – temperature and pressure.



Unary Phase Diagram

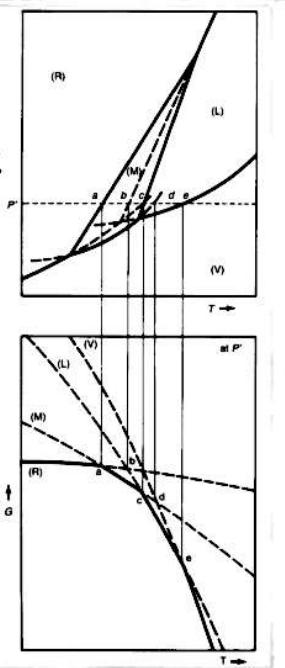
There are four phases for sulfur: two solid forms (a low-temperature orthorhombic form, R, and a high-temperature monoclinic form, M), liquid (L), and vapor (or gas, V).

At constant pressure, each phase has a different enthalpy and entropy associated with it.

The solid line in this figure represents the minimum free energy, regardless of which phase it represents, at a specified temperature.

The orthorhombic form, R, is the most stable at low temperatures.

As temperature increased, monoclinic (M) becomes more stable at point a, followed by the liquid, L, at point c, and finally the vapor phase (V) at point e.



Unary phase diagram (top) and Gibbs free energy plot (bottom) for elemental sulfur

Unary Phase Diagram

> P versus T plots at various pressures are produced by simply translating the information of G versus T plot where point a in the bottom figure now becomes a point on the solid-solid equilibrium line between the orthorhombic and monoclinic forms of sulfur.

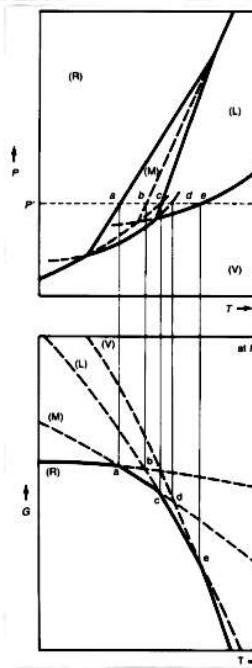
> Point b is distinctly in the monoclinic phase field, M.

> Point c is an equilibrium phase boundary between the monoclinic and liquid, L, forms of sulfur. This is the melting (or solidification) point of sulfur at pressure P.

> Point d is distinctly in the liquid region, and point e is on the liquid-vapor equilibrium line.

These plots of pressure versus temperature for a single-component system are called **unary phase diagrams**.

Many phases but only one component—no chemical transformations



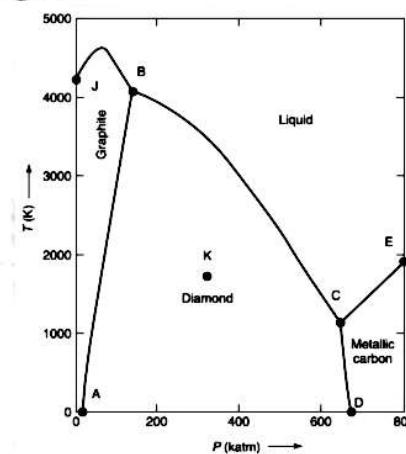
Unary phase diagram (top) and Gibbs free energy plot (bottom) for elemental sulfur

Unary Phase Diagram

Consider the TP phase diagram for the equilibrium between two solid forms of carbon: graphite and diamond. This equilibrium is shown graphically by the line A-B. $F = 1$ ($C = 1$ component, carbon; $\varphi = 2$, graphite and diamond). This means that temperature change requires a corresponding change in pressure to maintain this equilibrium.

Similarly, B-C (diamond–liquid), C-D (diamond–metallic carbon), C-E (metallic carbon–liquid), and J-B (graphite–liquid) represent lines of $F = 1$.

Point K is such a point. It is located in the diamond phase field, where both temperature and pressure can be changed independently without creating or destroying the phase.



$F = 2$ results in an area (phase field), and $F = 1$ results in a line (phase boundary). $F = 0$ should occur at a point. Point B = $\varphi = 3$; graphite, diamond, and liquid; C = 1, carbon.

Point C = no degrees of freedom at this point = the three phases in coexistence are solid, liquid, and vapor, this invariant point is known as the triple point

Thermodynamics of Condensed phases

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Phase Equilibria in Binary-Component Systems

Most metals of practical importance are mixtures of two or more metals. The "intimate mixtures" of metals are called alloys, and when the bond between the metals is partially ionic, they are termed intermetallic.

Under equilibrium conditions, the solubility of one element in another depends on the relative atomic radii, the electronegativity difference between the two elements, the similarity in crystal structures, and the valencies of the two elements. These factors contribute to the free energy of the metallic mixture and determine whether the species are soluble in one another, whether they form intermetallic compounds, or whether they separate into two distinct phases of different compositions.

The free energy of a mixture of two pure elements, A and B, is:

$$G = H - TS \dots\dots\dots(1)$$

But the enthalpy and entropy for the mixture are now taken as a combination of the enthalpies and entropies of components A and B, plus parameters that accounts for the interaction of the two species due to differences in crystal structure, electronegativity, valence, and atom radii, known as the enthalpy and entropy of mixing, H_{mix} and S_{mix} , respectively:

$$H = X_A H_A^0 + X_B H_B^0 + \Delta H_{mix} \dots\dots\dots(2)$$

$$S = X_A S_A^0 + X_B S_B^0 + \Delta S_{mix} \dots\dots\dots(3)$$

X_A and X_B are the mole fractions of component A and B, respectively, and are related by $(X_A + X_B) = 1$.

Therefore, it is found from equⁿ (6) that the entropy of mixing in a binary component solution depends only on the composition (relative number of moles of components) in the solution and not on the temperature.

Similarly, the enthalpy of mixing can be approximated by the internal energy of mixing for condensed phases, which in turn can be related to the mole fractions of the two components, and an interaction energy, α , which also has units of joules:

$$\Delta H_{mix} = \alpha X_A X_B \dots\dots\dots(7)$$

Case-1: $\alpha < 0$, exothermic mixing occurs ($\Delta H_{mix} < 0$) because an A-B bond is stronger (more negative) than either the A-A or B-B bonds and nearest neighbors are not favored in the system.

Case-2: $\alpha > 0$ Endothermic mixing ($\Delta H_{mix} > 0$) occurs when nearest neighbors are favored, and A-A and B-B bonds are stronger (more negative) than A-B bonds.

Case-3: For an ideal solution, the bond energies of A-A, B-B, and A-B bonds are identical, there is no preference for either atom as the nearest neighbor in the solution, and both the interaction energy and the heat of mixing are zero.

$$\alpha^{ideal} = \Delta H_{mix}^{ideal} = 0 \dots\dots\dots(8)$$

- ✓ A superscript circle has been used on the enthalpies and entropies of pure components A and B to indicate that these are standard state enthalpies and entropies of the pure components.
- ✓ The standard state of a component in a condensed system is its stable state at the particular temperature and pressure of interest. So, depending on the temperature and pressure of the system, the standard state could be either a liquid or a solid for either components A and B.

Substitution of Eqs. (2) and (3) into Eq. (1), The free energy of the mixture

$$G = X_A (H_A^0 - TS_A^0) + X_B (H_B^0 - TS_B^0) + \Delta H_{mix} - T\Delta S_{mix}$$

$$G = X_A G_A^0 + X_B G_B^0 + \Delta G_{mix} \dots\dots\dots(4)$$

Where,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \dots\dots\dots(5)$$

Eq. (4) contains an ill-defined parameter that has been introduced specifically to account for the mixing of the two species, namely, ΔG_{mix} .

The entropy of mixing process are assumed to be related to the increase in the number of spatial configurations, ΔS_{conf} , where, R is the gas constant.

$$\Delta S_{conf} = \Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B) \dots\dots\dots(6)$$

The free energy of mixing is found by substituting (6) and (7) into (5) to obtain

$$\Delta G_{mix} = \alpha X_A X_B + RT(X_A \ln X_A + X_B \ln X_B) \dots\dots\dots(9)$$

which is then substituted into (4) for G_{mix}

$$G^{reg} = X_A G_A^0 + X_B G_B^0 + \alpha X_A X_B + RT(X_A \ln X_A + X_B \ln X_B) \dots\dots\dots(10)$$

Solutions whose free energies follow Eq. (10) are said to be regular, to distinguish them from irregular solutions, wherein the entropy of mixing is governed by a relationship other than Eq. (6).

In case of Ideal solution ($\alpha = 0$), the free energy for a mixture reduces to

$$G^{ideal} = X_A G_A^0 + X_B G_B^0 + RT(X_A \ln X_A + X_B \ln X_B) \dots\dots\dots(11)$$

At this point, the mixtures can be either solid or liquid, depending on the temperature, and both solid and liquid mixtures may coexist at certain temperatures and compositions.

The conditions for equilibrium between two phases in coexistence are still the same as for the case of a single component.

See Example Problem 2.1

Binary Phase Diagram- Completely soluble case

Consider a system consisting of two pure elements A and B; the mixture may be either liquid or solid. The free energy of mixing versus composition can be plotted by considering the equilibrium phases of a binary component system. The change in free energy is counted when the two components are taken from separate, standard states into the mixture.

Figures a to e show the free energy of mixing curves as a function of concentration at decreasing temperatures ($T_5 > T_4 > T_3 > T_2 > T_1$).

(here plotted as X_B , where $X_B = 1.0$ at pure B and $X_B = 0$ at pure A)

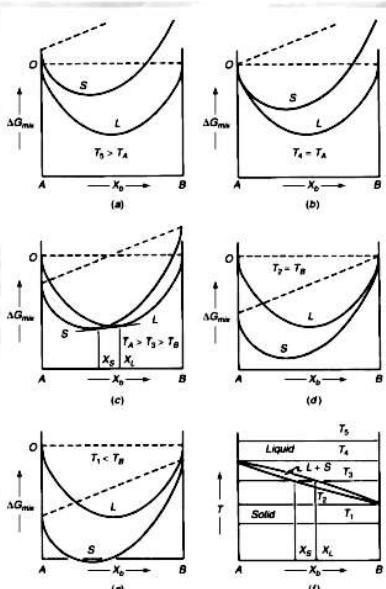
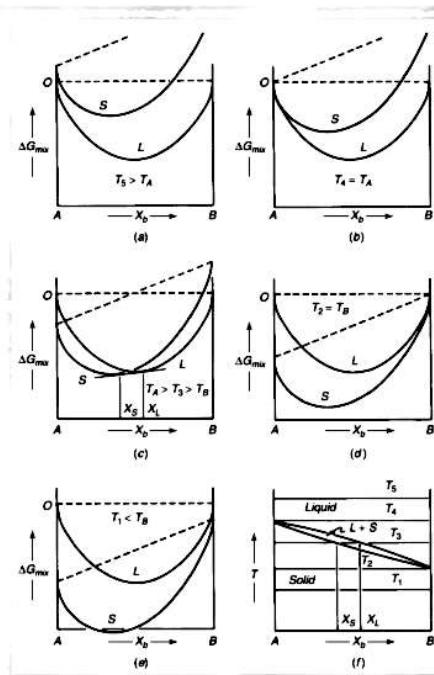


Fig: Free energy of mixing curves for solid and liquid phases at various temperatures (a-e) and resulting temperature-composition phase diagram for a completely soluble binary component system (f).

✓ In Fig. a, at a temperature T_5 , the liquid phase free energy of mixing is lower than the solid phase free energy of mixing at all compositions. This means that the liquid is more stable at this temperature for all compositions, and indeed this is the case in Fig. f. Any composition at temperature T_5 will be located in the single phase, liquid region of the phase diagram.

✓ A similar situation applies to temperature T_4 , shown in Fig. b. Any changes in the composition of the system at these temperatures e.g., adding more B to the mixture) will be reflected in a commensurate change in the composition of the liquid phase.

✓ At temperatures T_2 and T_1 , Fig. d and e, respectively, the solid solution is the most stable at all compositions. Since A and B mix completely at all compositions, any change in composition at these temperatures e.g., adding more A to the mixture) will result in a corresponding change in the solid alloy.



- Temperatures T_1 and T_2 are at or below the melting point (T_B) of the lowest melting point species, B.
- Temperatures T_4 and T_5 are at or above the melting point (T_A) of the higher melting species, A.
- Temperature T_3 is between the melting points of the individual components.

Figure f results from the application of the equilibrium criteria at all temperatures, from T_1 through T_5 .

Note: the binary-component phase diagram is a plot of temperature versus composition and not pressure versus temperature like the unary phase diagram. For the unary diagram, there is one component, so the composition is fixed. For the binary diagram, we have three intensive variables (temperature, pressure, and composition). Therefore, pressure is used to keep fixed at 1 atm to make a temperature-composition as an x-y diagram.

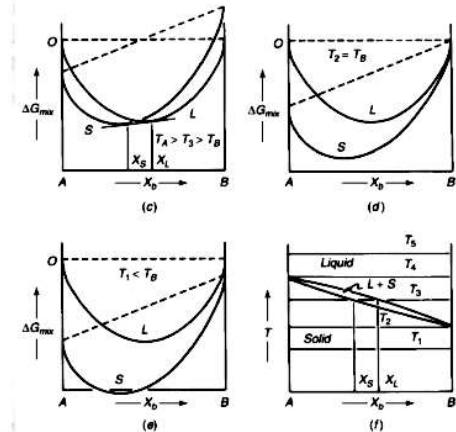
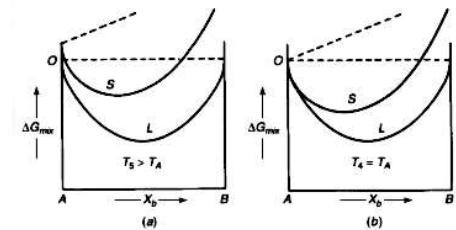
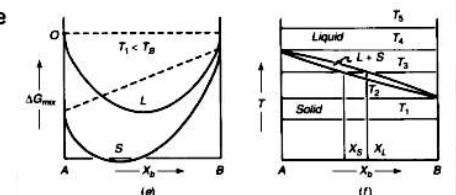
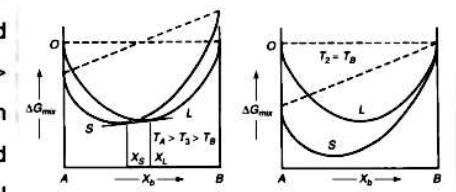
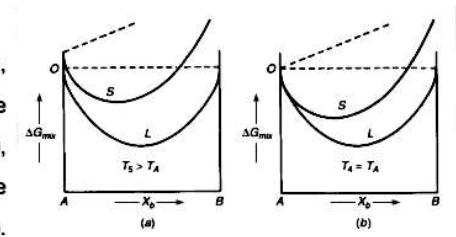


Figure c is a little more complex. Here, the solid phase has the lowest free energy at A-rich compositions ($X_B < X_S$), and the liquid phase has the lowest free energy at B-rich compositions ($X_B > X_L$).

In between the two minima of the solid and liquid free energy curves, $X_S > X_B > X_L$, both the liquid and solid phases can coexist. As pressure is already fixed and the temperature is varying, the chemical potentials of the two phases should be equal to be stable.

For the two phases under consideration,

$$\mu_S = \left(\frac{\partial \Delta G_{mix,S}}{\partial X_B} \right)_{T,P,n_L} = \mu_L = \left(\frac{\partial \Delta G_{mix,L}}{\partial X_B} \right)_{T,P,n_S}$$



Graphically, this condition can only occur when the two free energy of mixing curves share the same tangent as shown in Fig. c, which represents the derivative of the curve at that point. This situation exists at all temperatures between T_4 and T_2 . Therefore, there exists a two-phase region at all compositions between these two temperatures, as reflected in Fig. f.

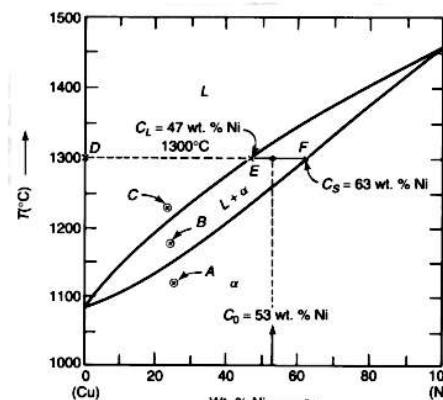
The minima of the two free energy mixing curves at any given temperature are located by taking the second derivative and setting it equal to zero:

$$\left(\frac{\partial^2 \Delta G_{\text{mix},S}}{\partial X_B^2}\right) = 0, \left(\frac{\partial^2 \Delta G_{\text{mix},L}}{\partial X_B^2}\right) = 0$$

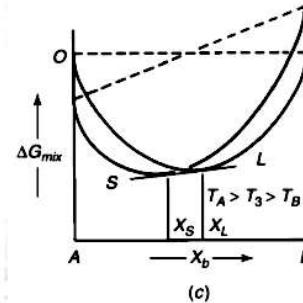
The locus of points generated by these conditions at various temperatures constructs the phase boundary lines between the solid and liquid phases as shown in Fig. f. There is a different solid and liquid composition, X_S and X_L , resulting from the tangent between the free energy of mixing curves, at all temperatures between T_2 and T_4 , as illustrated in Fig. c.

Example: Figure shows the binary phase diagram for the system Cu–Ni. Here, the composition is indicated in terms of the weight fraction of one of the components, in this case Ni, and not mole fraction. The conversion between the two is straightforward if the molecular weights are known, and the weight fraction is used only because it is more useful experimentally than mole fraction.

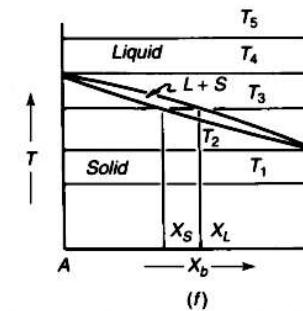
- ✓ In terms of the phase rule, here only one non-compositional intensive variable, T (pressure is fixed), so $N = 1$. Points A and C in Figure indicate that the liquid and solid regions ($\varphi = 1; C = 2$) correspond to $F = 2$, which means that both temperature and composition can be altered independently in these regions.
- ✓ Point B is in the liquid + solid two-phase region ($\varphi = 2; C = 2$), so that $F = 1$. Temperature and composition are not independent in this region; any temperature change necessarily results in a change in the composition of both the liquid and the solid phases. The liquidus and solidus phase boundaries are included in this two-phase region.



The Cu–Ni phase diagram, illustrating the use of the lever rule

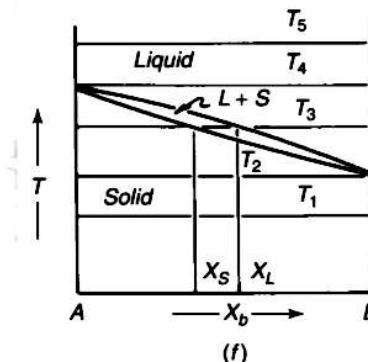


(c)



(f)

At Fig.f, there is a two-phase region in which both solid and liquid phases can coexist for the binary solution of components A and B, which mix perfectly at all compositions. The uppermost boundary between the liquid and liquid + solid phase regions in Fig. f is known as the **liquidus**, or the point at which a solid first begins to form when a melt of constant composition is cooled under equilibrium conditions. Similarly, the lower phase boundary between the solid and liquid + solid phase regions is known as the **solidus**, or the point at which solidification is complete upon further equilibrium cooling at a fixed composition

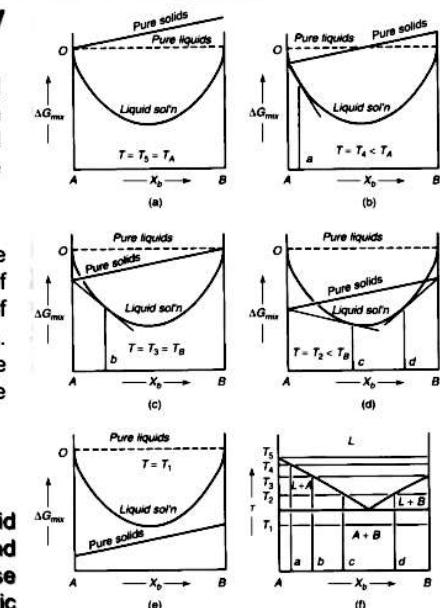


(f)

Binary Phase Diagram- slightly soluble case

Consider that the two elements, A and B, are only slightly soluble in each other, or when more than one solid alloy phase can be formed from the two components.

Here, the phase boundaries are constructed from the free energy of mixing curves as a function of composition at various temperatures. The primary difference here is that the solid free energy curve is a straight line instead of a curve with a minimum.

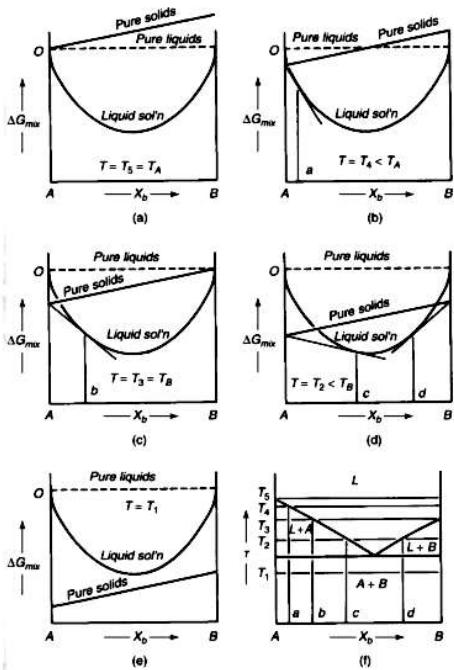


Free energy of mixing for solid and liquid phases at various temperatures (a-e) and resulting temperature–composition phase diagram for a slightly soluble eutectic binary component system

At intermediate temperatures, tangents can be drawn between the free energy curves of the pure solids (which occur at the pure component free energies) and the liquid solution, sometimes involving both pure components. An interesting phenomenon occurs when the free energy of the pure solids segment is tangent to the liquid solution (located exactly at the minimum of the liquid solution free energy curve).

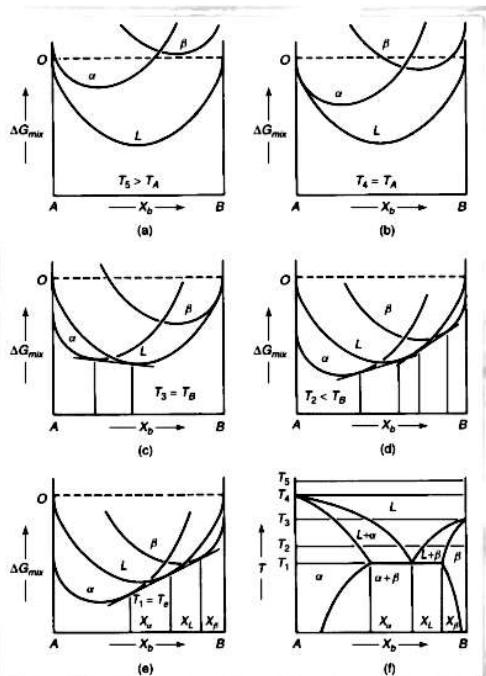
Eutectic Point: where the liquid, solid A, and solid B coexist at this temperature-composition combination. According to the phase rule, there should be zero degrees of freedom ($\varphi = 3, C = 2, N = 1$).

When A and B are insoluble in the solid phase, a phase diagram such as that shown in Fig. f can result.



Binary Phase Diagram- mostly insoluble case

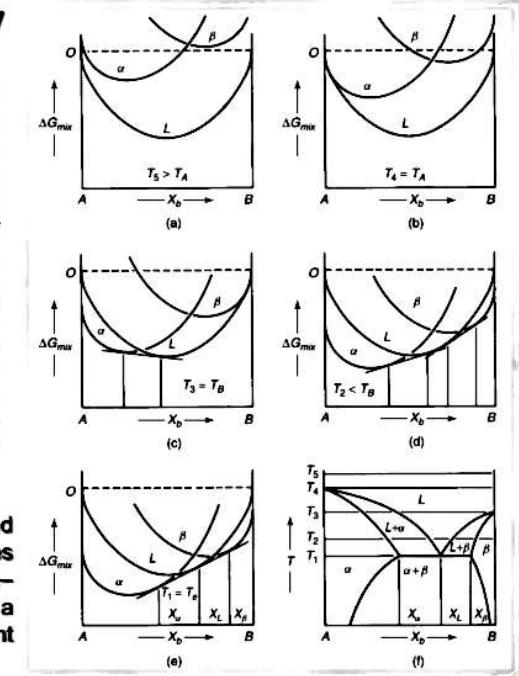
Here, A and B are always soluble in each other to some extent. Thus, the composition of the solid α phase will vary, as will that of the β phase. This can be thought of as each major component having the ability to dissolve small amounts of the impurity phase, either as interstitial or substitutional impurities. This phase diagram also has a eutectic point, found at the intersection of the X_L composition line and the T_1 isotherm.



Binary Phase Diagram- mostly insoluble case

Consider that two different solid solutions of A and B can form, here labeled α and β , as shown in Fig. f. Again, the phase diagram is constructed from the free energy of mixing as a function of concentration curves. In this case, it is always possible to draw a tangent between the free energy curves of the α and β phases at low temperatures, and in some cases, one tangent will be sufficient to touch all three curves for the α , β and liquid phases, as shown in Fig. d and e.

Free energy of mixing for solid and liquid phases at various temperatures (a-e) and resulting temperature-composition phase diagram for a mostly insoluble binary component system (f).



Summary of Phase Relationships in a Phase Diagram

- ❖ One-phase regions may touch each other only at single points, never along boundary lines.
- ❖ Adjacent one-phase regions are separated from each other by two-phase regions involving the same two phases.
- ❖ Three two-phase regions must originate upon every three-phase isotherm; that is, six boundary lines must radiate from each three-phase reaction horizontally.
- ❖ Two three-phase isotherms may be connected by a two-phase region provided that two phases are common to both of the three-phase equilibria.

Lever Rule

The lever rule establishes the relationship between the composition of the two phases and the relative amount of each phase in a phase diagram.

The phase rule tells us that there is only one degree of freedom in a two-phase region of a binary component phase diagram—for example, the solid + liquid region of the Cu-Ni phase. If the temperature is changed in this region, the compositions of the two phases must also change. This means that the relative amounts of the two phases must be adjusted. If there is an equal amount (in terms of weight) of the solid and liquid phases, regardless of their compositions, removing some of component B from the liquid and moving it to the solid reduces the weight of the liquid phase and increases the weight of the solid phase. Lets develop the **Lever rule** by way of example.

Consider the initial alloy composition $C_0 = 53$ wt% Ni, 47 wt% Cu indicated by the vertical arrow and dashed line in Fig. At 1300°C. This composition will exist as both liquid and solid (called the α phase). According to the two-phase region in the diagram. Let W_α and W_L be the fractional amounts by weight of solid and liquid, such that:

$$W_\alpha + W_\beta = 1 \dots\dots\dots(1)$$

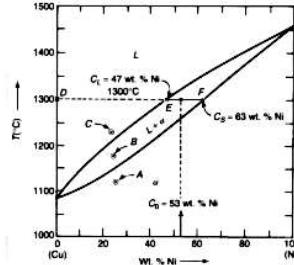


Fig-1:The Cu–Ni phase diagram

Important points of Lever Rule

- First, it can only be used in the form of weight percentages. Mole percentages must first be converted to weight percentages when concentrations are expressed in terms of weight percentages.
 - Second, the weight fractions of liquid and solid in terms of compositions can be used by simply measuring the distances of the corresponding line segments directly off the diagram. For example, the line EF in Fig-1 represents the quantity $C_S - C_L$. If it is measured using a ruler in, then $C_0 - C_L$ could be measured similarly, and W_a determined from a ratio of these two measurements. This method is much more accurate than extrapolating lines from the phase boundaries down to the abscissa (which can introduce error) and then interpolating the composition from markings that may, in some cases, only give markers every 20 wt% or so.
 - Finally, with the lever rule, the ratio of line segments is a little bit counterintuitive or contradictory. That is, the line segment in the numerator for the weight fraction of solids [Eq. (4)] is that opposite the solid-liquid + solid phase boundary, and the line segment in the numerator for the liquid fraction [Eq. (3)] is opposite the liquid-solid + liquid phase boundary. A little practice will eliminate this confusion.

Also, the mass of each component distributed between the two phases must equal their masses in the original composition:

From the solution of Eqs. (1) and (2), the weight fraction of liquid in terms of the compositions.

$$W_{\beta} = \frac{c_s - c_0}{f_s - f_0} \dots \quad (3)$$

and the weight fraction of solid in terms of composition

$$W_a = \frac{C_0 - C_L}{C_0 - C_U} \dots \dots \dots (4)$$

Equations (3) and (4) are the lever rule and can be used to determine the relative amounts of each phase in any two-phase region of a binary component phase diagram.

For the example under consideration, the amount of liquid present turns out to be

$$W_{\beta} = \frac{63 - 53}{63 - 47} = 0.625$$

Therefore, 62.5% by weight of the alloy is present as liquid, and 37.5% is solid in Cu-Ni alloy.

The compositions of the two phases are determined by extending the horizontal line, or tie line, to the phase boundaries (line EF in Fig-1), then reading the compositions of these phases off the abscissa. The liquid phase has a composition of 47 wt% Ni/53 wt% Cu (**point E**), and the solid phase is 63 wt% Ni/37% Cu (**point F**).

Three Phase Transformations in Binary Systems

If the phase transformations occur over minute temperature at the eutectic point these transformations are known as three-phase transformations, because they involve three distinct phases that coexist at the transformation temperature. Here, the Greek letters α , β , γ , and so on, designate solid phases, and L designates the liquid phase. Subscripts differentiate between immiscible phases of different compositions. For example, L_I and L_{II} are immiscible liquids, and α_I and α_{II} are allotropic solid phases (different crystal structures).

The Cu-Zn system displays several intermediate solid solutions that arise due to limited solubility between the two elements. For example, at low wt% Zn, which incidentally is the composition of alloys known as brass, the relatively pure copper α phase can accommodate small amounts of Zn as an impurity in the crystal structure. This is known as a **terminal solid phase**, and the solubility limit where intermediate solid solutions (such as $\alpha + \beta$) begin to occur is called the **solvus line**. Some of the three-phase transformations that are found in this diagram include a **peritectic** ($\delta + L \rightarrow \varepsilon$) and a **eutectoid** ($\delta \rightarrow \gamma + \varepsilon$). Remember that these three-phase transformations are defined for equilibrium cooling processes, not heating or nonequilibrium conditions.

Different reaction types such as Monotectic, Monotectoid, Eutectic, Eutectoid, Syntectic, Peritectic, and Peritectoid in common three-phase transformations.

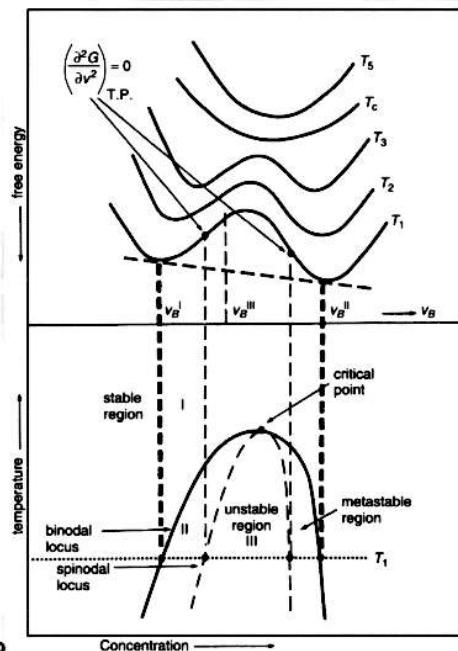
Thermodynamics of Condensed phases

Dr. Kazi Hanium Maria
Course teacher
PH-407

Phase diagram: The free energy is plotted as a function of composition in the top part of the curve, and the resulting temperature-composition plot is shown at the bottom of the diagram.

- At high temperatures, T_5 , the polymer and solvent are miscible, and a single phase is formed (Region I).
- As T decreases, the solution begins to separate into two phases. Phase separation, or immiscibility, begins at the critical temperature, T_c .

Figure: Polymer-solvent phase diagram showing binodal, spinodal, and miscibility gap



Now substitute the enthalpy of mixing (Eq. 3) and the entropy of mixing (Eq. 4) into Eq. (1), the free energy of mixing for a polymer solution:

$$\Delta G_{mix} = k_B T [x N_A v_B + N_A \ln v_A + N_B \ln v_B] \dots \dots \dots (5)$$

From this expression, a phase diagram for a polymer solution can be developed.

Consider a binary component system consisting of a liquid, A, a poor solvent for a polymer, B. Here two possible cases arise:

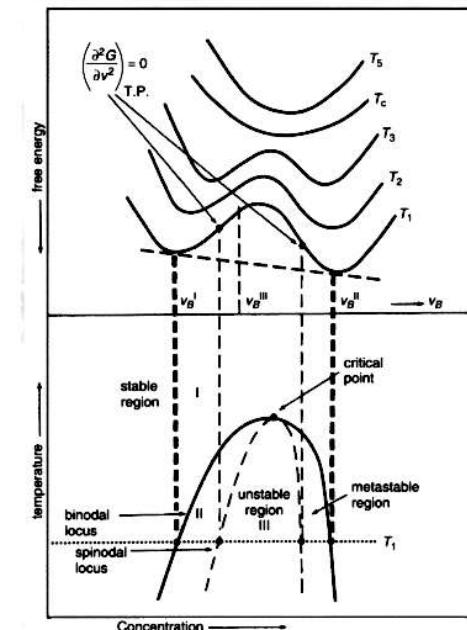
1. The complete miscibility occurs when the Gibbs free energy mixing is less than the Gibbs free energies of the components.
2. The solution maintains its homogeneity only as long as ΔG_{mix} remains less than the Gibbs free energy of any two possible coexisting phases.

- The free energy curve begins to have maxima, minima, and inflection points, and the condition of phase stability is given by the chemical potentials.
- The chemical potentials of the two phases (here labeled L_1 and L_2) are equal and no longer met.

$$\begin{aligned} \mu_{L1} &= \left(\frac{\partial \Delta G_{mix}}{\partial v_B} \right)_{T, P, n_{L2}} \\ &= \mu_{L2} = \left(\frac{\partial \Delta G_{mix}}{\partial v_B} \right)_{T, P, n_{L1}} \dots \dots \dots (a) \end{aligned}$$

The locus of points swept out by the stability condition shown in Eq. (6) at various temperatures is called the binodal, or cloud point curve.

Figure: Polymer-solvent phase diagram showing binodal, spinodal, and miscibility gap

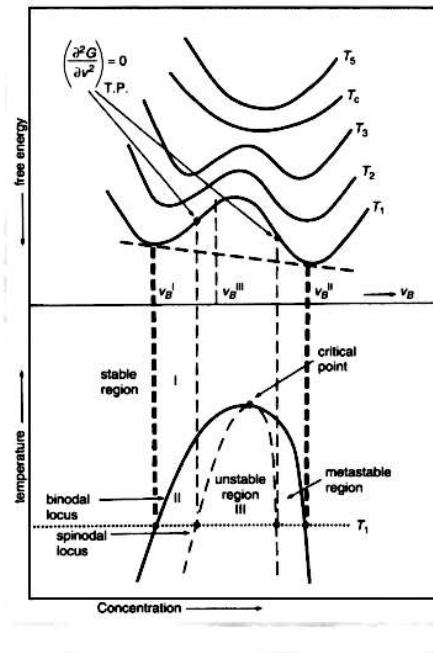


Binodal: generated by drawing the tangents to the minima of the free energy curves to map out the phase boundaries in solid-liquid equilibria.

Spinodal: generated by a similar mapping of the inflection points, mathematically described by the second derivative of the free energy versus composition curve:

$$\left(\frac{\partial^2 \Delta G_{mix}}{\partial v_B^2} \right) = 0 \dots \dots \dots \dots \quad (b)$$

The region between the binodal and spinodal curves (Region II) represents the region of two-phase metastability.



Cohesive Energy density

The selection of solvents for a polymer, or to assess the extent of polymer–liquid interactions is very important. A semi-empirical approach has been developed by Hildebrand based on the principle of “like dissolves like.” The treatment involves relating the enthalpy of mixing to a solubility parameter, δ and the cohesive energy density, δ_c .

$$\Delta H_{\text{mix}} \equiv (\delta_A - \delta_B)^2 v_A v_B, \dots \quad (1)$$

The cohesive energy density is the energy of vaporization per unit volume. The value of the solubility-parameter approach is that δ can be estimated for both polymer and solvent.

- As a first approximation and in the absence of strong interactions such as hydrogen bonding, solubility can be expected if $\delta_A - \delta_B$ is less than 3.5 ~ 4.0.
 - Values of δ for polymers of known structure can be estimated using the molar-attraction constants, E .

$$\delta_B = \frac{\rho \Sigma E}{M}$$

where ρ is the polymer density, and M_0 is the repeat unit molecular weight.

Below the spinodal (Region III), the solution is unstable, phase separation occurs, and two liquid solutions are formed whose relative amounts are given by the lever rule. Note that as temperature increases, the solvating power of the solvent increases, and a single polymer-solvent phase becomes stable.

Using the stability criteria of (Eq.a) and (Eq.b), the critical interaction parameter χ_c at the onset of phase separation:

where $v_{A,c}$ = volume fraction of the solvent at the critical point.

- Polymer in a poor solvent, results in an **upper critical solution temperature (UCST)**, which occurs due to (a) decreased attractive forces between like molecules at higher temperatures and (b) increased solubility.
 - a decrease in solubility can occur, and the corresponding critical temperature is located at the minimum of the miscibility curve, resulting in a **lower critical solution temperature (LCST)**.

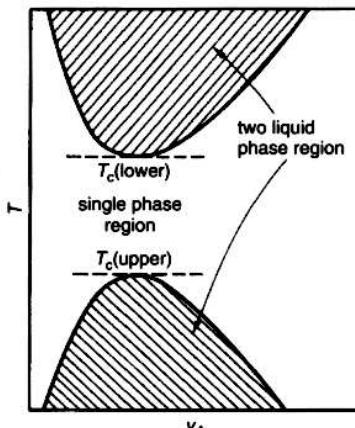


Figure: Schematic diagram of two-phase regions resulting in UCST (bottom) and LCST (top).

Flory-Huggins Approach

Polymer Blends: A polymer blend is created when two miscible polymers are mixed. In the case of composites, two polymers will blend to create a new material with improved performance.

However, in practice, it is difficult with polymer-polymer solutions, as most common polymers do not mix well with one another to form homogeneous, one-phase solutions.

Flory-Huggins Approach: Consider a polymer-polymer mixture where the heat of mixing for polymer pairs (labeled 1 and 2) are endothermic and can be approximated using the solubility parameter. The interaction parameter for a polymer-polymer mixture can be approximated:

$$\chi_{12} = \frac{V_0(\delta_1 - \delta_2)^2}{RT}$$

V_0 = reference volume, typically assuming a value of $100\text{ cm}^3/\text{mol}$

The critical value of χ_{12} at the onset of phase separation:

$$\chi_{12,c} = \frac{1}{2} \left(\frac{1}{x_1^{1/2}} + \frac{1}{x_2^{1/2}} \right)^2$$

where x_i is the degree of polymerization for each polymer, related to its actual degree of polymerization, x_n and the reference volume by:

$$x_i = x_n \left(\frac{V_R}{V_0} \right)$$

V_R = the molar volume of the repeat unit

Notes:

- If the enthalpy of polymer mixing is negative, this will encourage mixing.
- The miscible polymer blends can be formed when there exist specific intermolecular interactions, such as hydrogen bonds, dipole-dipole interactions, ion-dipole interactions, or charge transfer complex formation.
- Therefore, certain groups or repeat units should be identified to create the intermolecular attractions when incorporated in polymer chains.

The three processes are defined as these surfaces interact and form:

- ❖ Cohesion → No surface → 2A (or 2B) surfaces
- ❖ Adhesion → 1 AB surface → 1 A+1 B surface
- ❖ Spreading (B on A) → 1 A surface → 1 AB + 1 B surface

Cohesion: The separation process shown in Figure-a consists of the formation of two new interfaces, each of a unit cross-sectional area, at a location where no interface has previously existed. The free energy change associated with the separation process comes directly from the surface energy where two surfaces of unit surface area are formed. At constant T, P, the work required to form the two surfaces, is called the work of cohesion, W_{AA} . The free energy change for incompressible fluids:

$$\Delta G = 2\gamma_A = W_{AA} \dots\dots\dots (1)$$

Here γ_A is the surface energy of component A.

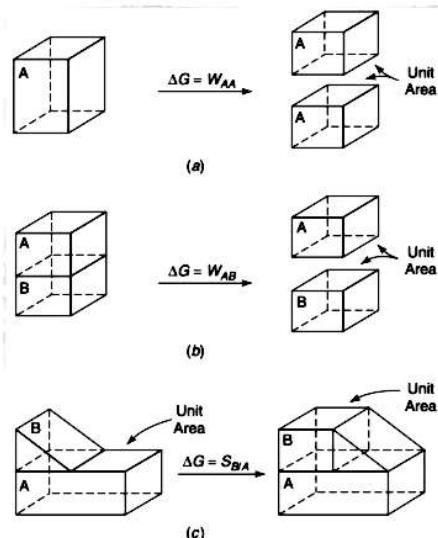


Figure: Schematic illustrations of the processes for which G equals (a) the work of cohesion, (b) the work of adhesion, and (c) the work of spreading.

Thermodynamics of Composites: Interphase

Let us consider two hypothetical phases in a composite, A and B, without specifying their physical state. There could be three cases:

- A and B could be a polymer melt and a glass fiber reinforcement during melt infiltration processing,
- A metal powder and ceramic powder could be consolidated at elevated temperature and pressure,
- Two immiscible polymer melts which are co-extruded and solidified into a two-phase, three-dimensional object.

In any of the three cases, the surface forms between the two phases are designated AB, and their surfaces are exposed to their own vapor, air, or inert gas labeled either A or B.

Interphase Formation:

- ✓ The physical properties of a composite are dictated to a large degree by the interphase between the matrix and reinforcement phases.
- ✓ The interphase gives the idea of the proportion relative to the other constituents. Such as, the surface-to-volume ratio of the reinforcement increases as its characteristic dimension decreases.
- ✓ The interphase can be formed by three possible processes: adhesion, cohesion, and spreading.

Adhesion: Figure b shows the formation of two free surfaces, A and B. The energy associated with their formation is the energy that was associated with the interface AB, γ_{AB} . The free energy change in this process is called adhesion.

$$\Delta G = \gamma_A + \gamma_B - \gamma_{AB} = W_{AB} \dots\dots\dots (2)$$

Here, W_{AB} = the work of adhesion
The work of adhesion measures the degree of attraction between the two phases.

Here, A is a solid (S) and B is a liquid (L),

γ_A = the solid surface energy, γ_S

γ_B = the liquid surface tension, γ_L

Using Young's equation, a relationship between the liquid-solid contact angle, θ , liquid surface tension, and the work of adhesion:

$$W_{SL} = \gamma_L (1 + \cos\theta) \dots\dots\dots (3)$$

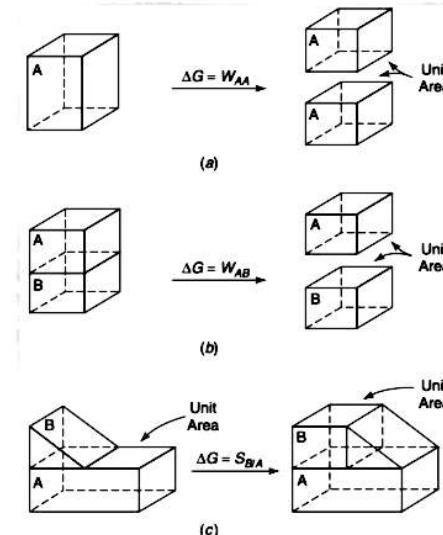


Figure: Schematic illustrations of the processes for which G equals (a) the work of cohesion, (b) the work of adhesion, and (c) the work of spreading.

Spreading: Figure c shows the spreading of B on A. Then the free energy change:

$$\Delta G = \gamma_{AB} + \gamma_B - \gamma_A \dots \dots \dots (4)$$

The negative value means that the process occurs spontaneously.

The spreading coefficient, $S_{B/A}$, is the negative of the free energy of spreading, which means that a thermodynamically favorable spreading process (negative free energy) leads to a positive value of the spreading coefficient.

By combining Eqs. (1), (2), and (4), the spreading coefficient can be related to the work of adhesion and work of cohesion:

$$S_{B/A} = W_{AB} - W_{BB}$$

Case-1: $W_{AB} > W_{BB}$, the A-B interaction is sufficiently strong to promote the wetting of A by B.

Case-2: $W_{BB} > W_{AB}$, no wetting occurs.

As the work required to overcome the attraction between two B molecules is not compensated for by the attraction between A and B. Hence, a negative spreading coefficient means that B will not spread over A.

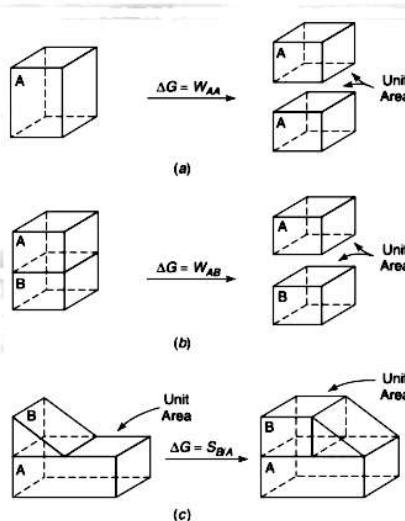


Figure: Schematic illustrations of the processes for which G equals (a) the work of cohesion, (b) the work of adhesion, and (c) the work of spreading.

With appropriate assumptions and simplifications, the following free energy expression can be obtained:

$$\Delta G_{mix} = n_d \left[C + \ln \varphi_d + \sigma - \left(\frac{b}{v_d} \right) (\rho - 1) \ln(1 - \varphi_d) + \chi v_d \varphi_d \right] + n_p \ln \varphi_p \dots \dots \dots (2)$$

n_d = number of disks in a unit volume

n_p = number of polymer molecules in a unit volume

v_d = the volume of an individual disk ($\pi D^2 L / 4$),

φ_d = Volume fraction of disks in the composite

$(1 - \varphi_d)$ = Volume fraction of polymer φ_p

σ = conformational free energy (ΔG_{conf})

ρ = the angle between two disks and b is $\pi^2 D^3 / 16$.

The chemical potentials of any two phases are equivalent at equilibrium. The chemical potentials are obtained directly from Eq. (2) by differentiation.

Composite Phase Diagrams

when two of the composite components are well mixed, the components are easily identified on the macroscopic scale. These macroscopic heterogeneities make it difficult to apply classical thermodynamics, which is based on interactions at the molecular level.

Clay particles are modeled as rigid disks dispersed in the polymer. The volume fraction of disks characterizes the composition of the mixture of disks. The disk length L , disk diameter D , polymer-disk interaction parameter χ , and disk orientation play important roles in the free energy expression. The free energy of mixing for the polymer-disk mixture has the following terms:

$$\Delta G_{mix} = \Delta G_{conf} + \Delta G_{ster} + \Delta G_{int} + \Delta G_{transl} \dots \dots \dots (1)$$

ΔG_{conf} = Free energy change associated with conformational losses due to alignment of the disks

ΔG_{ster} = Free energy change associated with steric interactions between disks

ΔG_{int} = Free energy change associated with nonspecific attractive forces between disks

ΔG_{transl} = Free energy change associated with translational entropy of the disks, respectively.

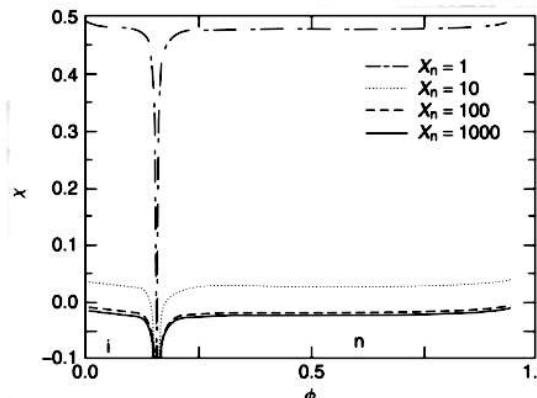


Figure: Phase diagram for clay disks and polymers of different degrees of polymerization, x_n

The phase diagram is presented as a plot of the interaction parameter versus the volume fraction of the disks. Consider, the diameter of the disks is 30 arbitrary units, and their length is 1. The regions of disk-polymer miscibility lie below the boundaries. Within the regions of miscibility, i indicates an isotropic phase, and n indicates a nematic liquid crystalline phase.

Kinetic Processes in Materials

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LAW OF MASS ACTION

Consider a reaction in which reactants A and B go to products C and D. The total free energy of the reaction is sum of individual free energy contributions. Such as:



where a , b , c , and d are the stoichiometric coefficients of species A , B , C , and D .

The Law of Mass Action states that the velocity of the reaction at a given temperature is proportional to the product of the active masses of the reacting substances.

The forward reaction rate, r_1 is a function of the concentrations of A and B raised to their corresponding exponents:

The reverse reaction rate, r_2 , is related to the number of products, C and D:

k_1 and k_2 are proportionality constants, or rate constants, for the forward and reverse reactions, respectively, and have units of inverse time (s^{-1}) and an appropriate inverse concentration.

KINETIC PROCESSES

- Thermodynamics defines whether a process is favorable or not; kinetics defines how quickly that process will take place.
 - Three categories of kinetic processes are of concern: the rate at which materials are formed, the rate at which they are transformed, and the rate at which they decompose.
 - In general, formation and decomposition are chemical processes, involving the reaction of two or more chemical species. On the other hand, transformations are usually physical processes, such as the melting of ice, and do not involve chemical reactions. In all cases, the rate at which the process is occurring is the important thing.
 - The thermodynamic free energy, G ; and the activation energy, E_a are two important concepts that are modified to determine the rate of processes in the formation, transformation, and decomposition of different materials

The forward and reverse reaction rates are equal at equilibrium, for which $\Delta G = 0$.

$$r_1 = r_2 \Rightarrow k_1[A][B] = k_2[C][D] \Rightarrow \frac{k_1}{k_2} = \frac{[A]^a[B]^b}{[C]^c[D]^d} = K \dots \dots \dots \quad (4)$$

K is the equilibrium constant for the reaction at constant temperature.

$\Delta G < 0$, the reaction proceeds spontaneously.

The free energy of a system is simply the sum of the free energy contributions of each of the components, such as their chemical potentials, μ_i , and the stoichiometric coefficients.

$$\Delta G = \sum n_i \mu_i \quad (5)$$

The standard Gibbs free energy, $\Delta G^0 = \sum v_i \mu_i^0$ (6)

The chemical potentials, μ_i and the standard chemical potentials, μ_i^0 , are related to each other by the activity of each species, a_i .

$$\mu_i \equiv \mu_i^0 + RT/\ln a_i \quad (7)$$

Here R is the gas constant and T is the absolute temperature.

The activity of a species is an indication of how far away from standard state of that species is.

If we subtract Eq. (6) from Eq. (5) and substitute Eq. (7) into the result, the relationship between the activity of the reactants and products have been obtained. The free energy for a reacting system:

At equilibrium, $\Delta G = 0$, and the activities of the products and reactants a_i , are related to their respective concentrations:

$$\Delta G^{\circ} = -RT \ln \left\{ \frac{[A]^a [B]^b}{[C]^c [D]^d} \right\} \quad (9)$$

Using Eq. (4), $\Delta G^0 = -RT \ln K$ (10)

Rearranging Eq. (10) gives: $K = \exp\left(\frac{-\Delta G^\circ}{RT}\right)$(11)

Equation (11) gives the effect of temperature on the equilibrium constant. Note that a plot of $\ln K$ versus $1/T$ should give a straight line of slope $-\Delta G^\circ/R$.

ACTIVATION ENERGY

The rate constant can be written by Arrhenius's expression:

E_a = activation energy, k_0 = preexponential factor

All molecules in a reaction must overcome an activation energy before they react and form products.

The Boltzmann distribution indicates that the fraction of molecules must have required energy $\exp\left(-\frac{E_a}{kT}\right)$ to react and proceed the reaction as shown in Eq. (1).

The quantity E_a is called the activation energy and represents the energy barrier for the reaction under consideration.

Figure shows that the reactants have to overcome an activation energy barrier of height E_a to achieve the activated complex state and proceed to products.

The heat of reaction.

ΔH = negative (exothermic reaction) or positive (endothermic reaction), in which case the products C and D have a higher final energy than the reactants.

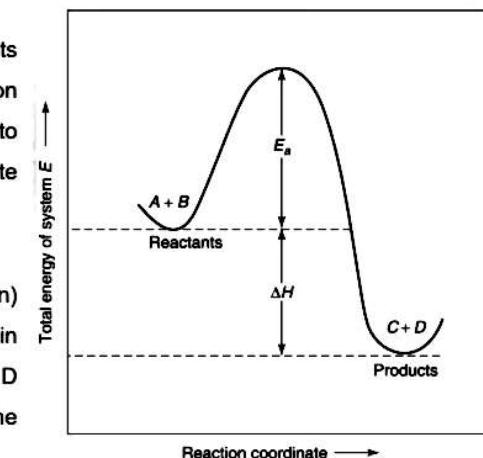


Figure: Activation energy barrier for a chemical reaction.

Thermodynamics of Condensed phases

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Ternary Systems

A Ternary system or three-component system has three independent components A, B, and C. It can be illustrated in a three-dimensional diagram where the concentration ratio in percentage is indicated by the triangle coordinates on an equilateral triangle. The corner points of this concentration triangle completely correspond to the pure components A, B, and C. The temperature axes are perpendicular to the triangle level thus creating three-dimensional condition planes.

Ternary systems are more frequently encountered in practice than binary systems. For example, air is often approximated as composed of nitrogen, oxygen, and argon, while dry natural gas can be rather crudely approximated as composed of methane, nitrogen, and carbon dioxide.

There are pseudo 3-component systems, which consist of multicomponent systems (more than 3 components) that can be described by lumping all components into 3 groups, or pseudo-components. In this case, each group is treated as a single component. For example, in CO_2 injection into an oil reservoir, CO_2 , C_1 , and C_2 are often lumped into a single light pseudo-component, while C_3 to C_6 form the intermediate pseudo-component, and the others (C_{6+}) are lumped together into a single heavy pseudo-component.

Intuitively, having more than two components requires a pictorial representation. A rectangular coordinate plot, having only two axes, will no longer suffice.

Gibbs first proposed the use of a triangular coordinate system.

Note: the relationship among the concentrations of the components is more complex than that of binary systems.

Ternary Phase Diagrams

- Here, A, B, and C the pure components are located at the vertices of the equilateral triangle.
- The base of the triangle opposite the corresponding vertex refers to 0% of that component so that the edge of the triangle connecting vertices B and C is 0 wt% A.
- lines parallel to BC, which are spaced a uniform distance apart and become shorter in length as they approach the vertex A, are lines of constant wt% A.
- Similarly, lines parallel to AC and AB represent lines of constant composition for components B and C, respectively.
- The triangular grid generated by these lines of constant composition helps to determine the overall composition of a point in the diagram.
- Point X in Figure is located at 30% A, 50% B, and 20% C. Obviously, the overall weight percentages of the components must add up to 100%.

Not all compositions fall neatly on the intersection of three grid lines, of course, but when the grid is present, it is relatively easy to interpolate between gridlines.

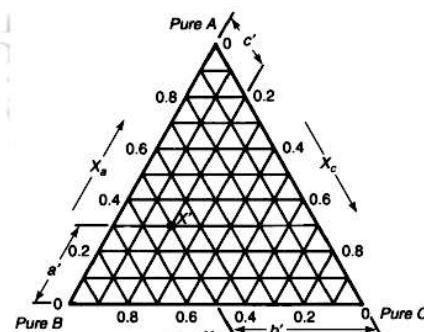


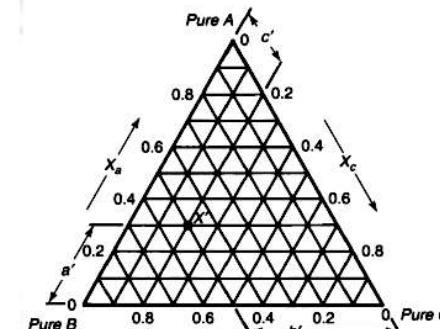
Figure: Illustration of how to express compositions on a three-component diagram.

Ternary Phase Diagrams

In a ternary system with components A-B-C, the sum of the mole fractions is unity, $(X_A + X_B + X_C) = 1$. When three components are mixed, making a ternary system, there are now four independently manipulable variables, viz. T , P , and two-mole fractions (the third being given by difference). Typically, pressure is fixed at 1 atm, so that three independent variables are needed to fix the system: temperature and two compositions. The third composition is, of course, fixed by the first two. Hence, there are two independent composition variables. A representation of composition, symmetrical concerning all three components, may be obtained with the equilateral composition triangle as shown in Fig.

Compositions at the corners of the triangle correspond to the pure components. Compositions along the edges of the triangle correspond to the three binary subsystems. Lines parallel to each edge constitute lines of constant composition for one of the components.

Figure: Illustration of how to express compositions on a three-component diagram.



Ternary Phase Diagrams

The ternary phase diagram can be expressed as mole fraction or mass percent.

Center of gravity rule which states that the sum of the perpendicular distances from any point within an equilateral triangle to the three sides is constant and equal to the altitude of the triangle.

Regarding Figure, this means that the quantity $(a + b + c)$ is a constant, regardless of where the point is located inside the triangle, and it represents the length from any edge to its opposite vertex. The relative amounts of the components are then given by the ratio of their respective line segments to the altitude like the lever rule in the Binary phase diagram.

$$\%A = \frac{100a}{(a+b+c)}$$

$$\%B = \frac{100b}{(a+b+c)}$$

$$\%C = \frac{100c}{(a+b+c)}$$

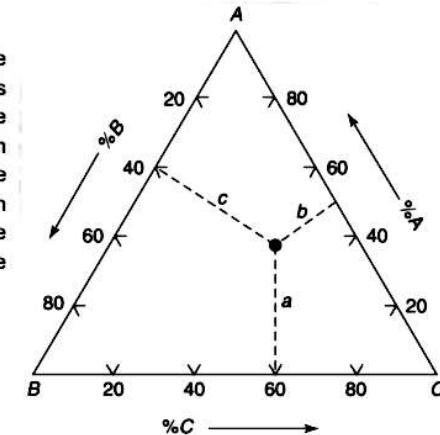


Figure: Illustration of center-of-gravity rule for determining compositions in ternary system.

Phase Equilibrium in Ternary Component systems

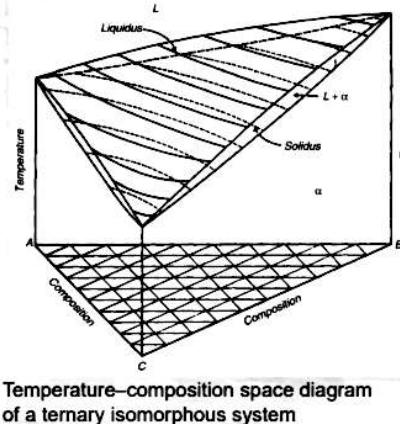
Isomorphous System: A system (ternary in this case) that has only one solid phase. All components are soluble in the other components. The ternary system is therefore made up of three binaries that exhibit total solid solubility.

The Liquidus Surface: A plot of the temperatures above which a homogeneous liquid forms for any given overall composition.

The Solidus Surface: A plot of the temperatures below which a homogeneous solid phase forms for any given overall composition.

Several important things to note from Figure.

- ❖ Pressure is assumed to be fixed.
- ❖ The phase rule still applies. The single-phase regions, α or liquid, have three degrees of freedom, $[F = C - \varphi + N = 3 - 1 + 1 = 3]$ so that the composition of all three components can be varied continuously in these regions.
- ❖ There is only one two-phase region, $L + \alpha$. Therefore, there are $[F = 3 - 2 + 1 = 2]$ two degrees of freedom.
- ❖ The upper surface of the two-phase region is the liquidus (solid line), and the lower surface of the region is the solidus (dashed line).



Phase Equilibrium in Ternary Component systems

At temperatures above the melting point of the highest-melting compound, the resulting diagram consists completely of a single-phase liquid region.

- ✓ Figure a shows a section below the liquidus where the temperature is lower than the melting temperature. Here, part of the diagram contains liquid, part contains solid, and part contains the liquid + solid two-phase region. The liquidus and solidus lines can now be identified, and what was once a two-phase region ($L + \alpha$) with three degrees of freedom is now a two-phase region with two degrees of freedom, just as in a binary-component diagram.
- ✓ Since the temperature has now been fixed, one degree of freedom has been lost.
- ✓ The two degrees of freedom in this region are both compositions, with the third compositional variable being fixed when the other two are determined.
- ✓ Unlike true binary-component phase diagrams, the tie lines connecting the two conjugate phases (in this case liquid and α) that coexist at temperature T_1 cannot be drawn as completely horizontal or vertical lines but must be determined experimentally. These tie lines are represented as dashed lines in the two-phase region.
- ✓ A similar type of diagram results from an isothermal section taken at T_2 , as in Figure b, which is slightly lower than T_1 . Finally, at T_3 , the isotherm is completely within the single-phase solid region as shown in Figure c.

Phase Equilibrium in Ternary Component systems

- Let's visualize that each vertical face of the diagram represents a complete binary component phase diagram.
- The C-B face in Figure occurs only at $A = 0$ for all temperatures, and the resulting diagram is similar to the binary component phase diagram for isomorphous substances. Similarly, the faces represented by A-B ($C = 0$) and A-C ($B = 0$) are independent binary phase diagrams. Thus, a ternary phase diagram contains all of the phases and three independent binary component phase diagrams as well.

- To simplify the representation, the complete temperature-composition ternary component phase diagram can be "sectioned" in two important ways. First, we can take horizontal "slices" of the diagram. Such sections are parallel to the base of the diagram and are, as such, necessarily at a fixed temperature, or isotherm.

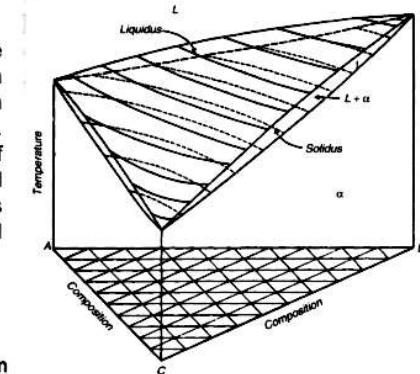


Figure: Temperature-composition space diagram of a ternary isomorphous system

Phase Equilibrium in Ternary Component systems

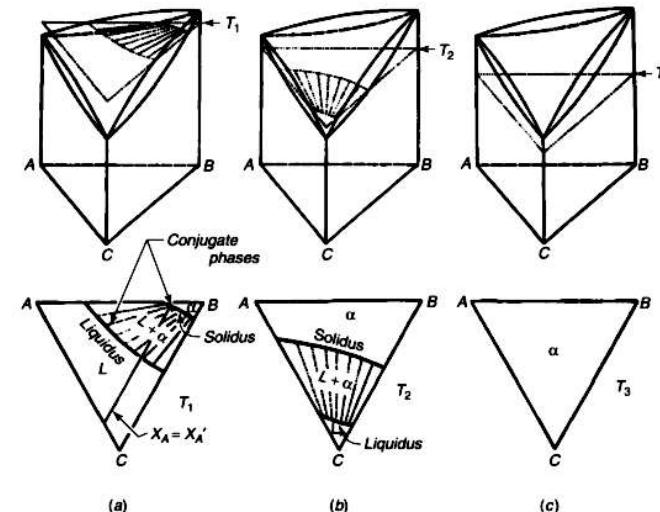
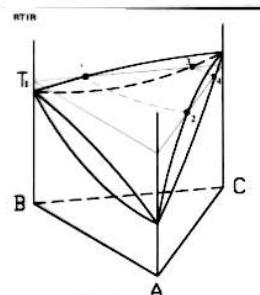
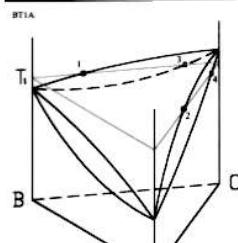


Figure: Isotherms through the ternary isomorphous phase diagram.

Ternary Isomorphous systems

Isothermal Section: A "horizontal" section of a ternary phase diagram obtained by cutting through the space diagram at a specified temperature.

Figures BT1A, BT1B, and BT1C show that at T_1 temperature, a horizontal line has been drawn which intersects the liquidus and solidus surfaces at points 1, 3, 4, and 2.



Connect points 1 and 2 with curvature reflecting the liquidus surface and points 3 and 4 with curvature reflecting the solidus surface.

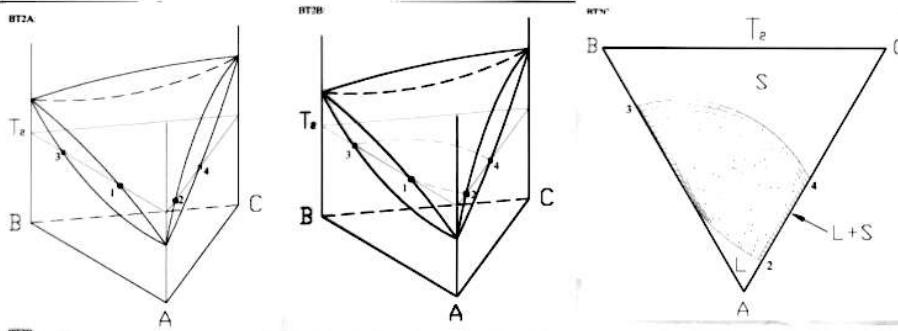
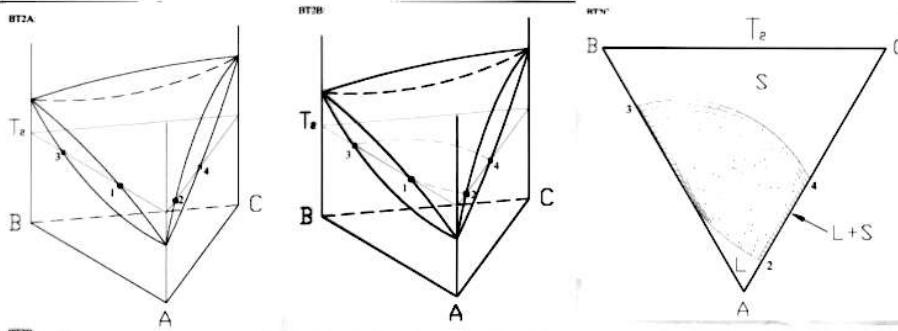
Ternary Isomorphous systems

Isothermal Section - continued Temperature = T_2 , below melting points of A and B, but above the melting point of C

Area A-1-2: homogeneous liquid phase

Area B-C-4-3: homogeneous solid phase

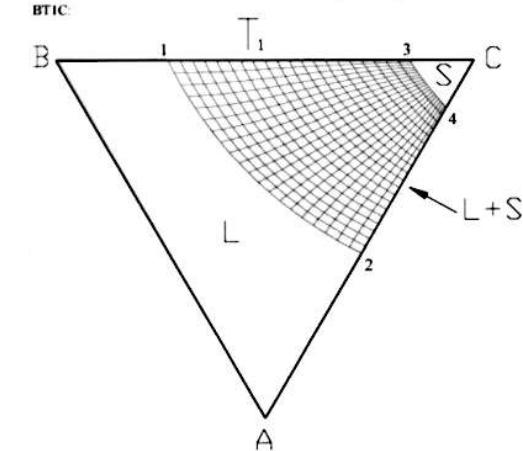
Area 1-2-3-4: two-phase region - liquid + soli



Ternary Isomorphous systems

- ✓ The line connecting points 1 and 2 represents the intersection of the isotherm with the liquidus surface.

- ✓ The line connecting points 3 and 4 represents the intersection of the isotherm with the solidus surface.



Area A-B-1-2: homogeneous liquid phase

Area C-3-4: homogeneous solid phase

1-2-3-4: two phase region - liquid + solid

Phase Equilibrium in Ternary Component systems

- ✓ The second type of "slice" through the temperature composition is a vertical section, known as an **isopleth**. Isopleths are sections of constant relative composition.
- ✓ The line X-B is drawn on the base of the diagram Figure a, and extended upwards along the temperature axis to generate the diagram, known as a pseudo-binary phase diagram, since it looks similar to a binary-component phase diagram, but is different.
- ✓ The liquidus and solidus lines do not converge at X on the pseudo-binary phase diagram. This section has been selected such that A and C are always in the ratio of 1:1 at any point on the diagram. The absolute amount of B can change, from 0% at X to 100% at B, thus changing the absolute amounts of A and C, but A and C always stay in the same proportion relative to one another.
- ✓ Vertical sections need not bisect a vertex. For example, a constant composition of one component or a constant relative composition of two components. Figure b shows a section taken at a constant composition for A, as indicated by the line Y-Z, extended upward along the temperature axis. The resulting pseudo-binary diagram is for a fixed composition of A, where the relative amounts of C and B are allowed to vary between pure C at Y and pure B at Z.

Phase Equilibrium in Ternary Component systems

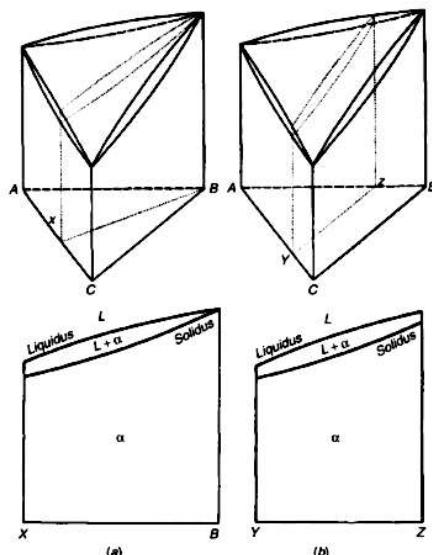


Figure: Examples of isopleths and pseudo-binary phase diagrams

The reversible work required to form the new surface, dW_s , is proportional to the surface area, dA ,

$$dW_s = \gamma dA \quad \dots \dots \dots (1)$$

γ is the proportionality constant that is called the surface energy.

❖ the surface energy is called surface tension when the bulk phase is a liquid,

$$\gamma = \frac{dW_s}{dA} \quad \dots \dots \dots (2)$$

i.e., surface energy is work per unit area and SI units are J/m².

We know that the reversible, non-pressure-volume work, dW_s , is equivalent to the free energy change, dG ,

So that Eq. (2.60) becomes, with proper use of partial differentials,

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{T,P,N_i} \quad \dots \dots \dots (3)$$

This relationship identifies the surface energy as the increment of the Gibbs free energy per unit change in area at constant temperature, pressure, and number of moles where the path-dependent variable dW_s in Eq. (2) has been replaced by a state variable, the Gibbs free energy.

Interfacial Thermodynamics: Surface Energy

A surface is an inhomogeneous boundary region between two adjacent phases.

Figure shows that atoms on the surface of a phase are necessarily different than those in the bulk. In particular, they have fewer nearest neighbors than the bulk, and they may be exposed to constituents from an adjacent phase.

- This means that less energy is required to remove an atom from a surface than to remove it from the bulk.
- Therefore, the potential energy of surface atoms is higher than bulk atoms. In turn, work is required to move atoms from the bulk to the surface.
- In this way, a new surface is created, and the surface area of the phase increases.

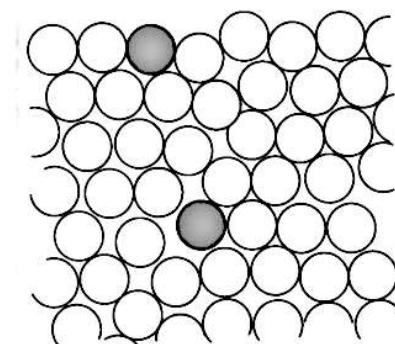


Figure: Schematic representation of surface and bulk atoms in a condensed phase.

The energy interpretation of γ has been identified with a specific thermodynamic function. As a result, many of the relationships that apply to G also apply to γ :

$$\gamma = H_s - TS_s \quad \dots \dots \dots (4)$$

where the subscript "s" on the enthalpy and entropy indicate that these are surface properties.

The surface atoms are fundamentally different from bulk atoms so they have different enthalpies and entropies associated with them. Differentiation of Eq. (4) for temperature at constant pressure gives:

$$\left(\frac{\partial \gamma}{\partial T} \right)_P = -S_s \quad \dots \dots \dots (5)$$

Substitution of Eq. (5) in (4) gives

$$\gamma = H_s + T \left(\frac{\partial \gamma}{\partial T} \right)_P \quad \dots \dots \dots (6)$$

Equation (6) is useful from an experimental standpoint because the measurements of surface energies at various temperatures can provide a measurement of the surface enthalpy. The surface enthalpy, H_s can also be determined because it is equivalent to the heat of sublimation or vaporization.

Notes:

- The surface energy is a direct result of intermolecular forces, its value will depend on the type of bond and the structural arrangement of the atoms.
- Normally, densely packed planes would have lower surface energies.
- Liquid hydrocarbons have weak van der Waals forces.

LaPlace Equation

Consider a generic curved surface such as that found in a sphere or cylinder as shown in Fig. The curved surface has two principal radii of curvature, R_1 and R_2 .

The front of this surface is indicated by the line xx_1 , and the back is represented by the line yy_1 . Let us now move the surface out by a differential element, dz . The front of the new surface is now given by $x'x'_1$, and the back is indicated by $y'y'_1$.

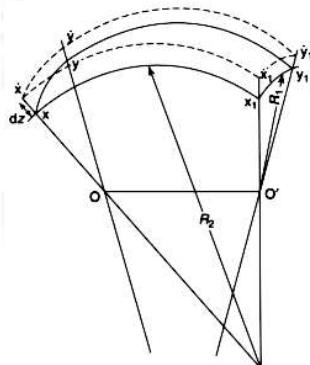


Fig: An element of a curved surface with principal radii R_1 and R_2 .

Adding Eqs. (2) and (3) together to arrive at the work against surface tension, equating them with the pressure-volume work in Eq. (1) and simplifying leads to the Laplace equation: $\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$(4)

The Laplace equation in this form is general and applies equally well to geometrical bodies whose radii of curvature are constant over the entire surface to more intricate shapes for which the R_s are a function of surface position.

Special cases: For spherical surfaces, $R_1 = R_2 = R$ = radius of the sphere,

and Eq. (4) becomes: $\Delta P = \frac{2\gamma}{R}$

For a cylindrical surface, R_1 (or R_2) is infinity, so the remaining radius, R , is the radius of the cylinder and Eq. (4) becomes, $\Delta P = \frac{\gamma}{R}$

Finally, for a planar surface, both radii of curvature become infinity, and Eq. (4) becomes, $\Delta P = 0$

The pressure difference may also be numerically zero in the instance where the two principal radii of curvature lie on opposite sides of the surface, such as in the case of a saddle.

LaPlace Equation

The work required to displace the surface this amount is supplied by a pressure difference, P . The pressure acts on an area given by $(xx_1)(xy_1)$ moving through the differential element dz , such that the total pressure-volume work associated with extending the surface through dz is

$$W = \Delta P(xx_1)(x_1y_1).....(1)$$

The pressure-volume work must be counterbalanced by surface tension forces. The work required to move against surface tension forces is best calculated by breaking it into two parts, W_1 and W_2 .

W_1 is the work required to move side xx_1 away from yy_1 , a distance $\left(\frac{x_1y_1}{R_1}\right)dz$ during the expansion:

$$W_1 = \frac{\gamma(xx_1)(x_1y_1)dz}{R_1}.....(2)$$

Similarly, the work required to move side xy away from x_1y_1 through a distance

$$\left(\frac{xx_1}{R_2}\right)dz \text{ is } W_2. \quad W_2 = \frac{\gamma(x_1y_1)(xx_1)dz}{R_2}.....(3)$$

Young Equation

Consider a liquid droplet in equilibrium with its vapor and a flat, solid surface at a constant temperature, as shown in Figure. The liquid-solid, liquid-vapor, and solid-vapor interfacial surface energies are defined as γ_{LS} , γ_{LV} , and γ_{SV} respectively. Technically, the liquid-vapor and solid-vapor interfacial energies should be for the liquid and solid in equilibrium with their respective vapors, which are probably not the same. Usually, the vapor is a nonreactive gas. Hence, γ_{LV} and γ_{SV} are the surface tension and solid surface energy are labeled as γ_L , and γ_S , respectively,

Contact angle: At equilibrium, an angle θ , is formed at the three-phase solid-liquid-gas junction which is called the contact angle. The values of contact angle can vary from zero to 180° .

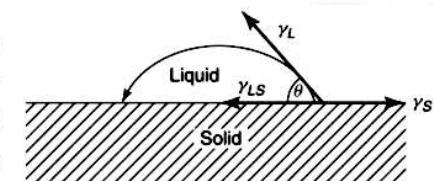


Figure: Schematic diagram of a liquid droplet on a solid surface.

Young Equation

Case-1: When $\theta = 0$, the liquid completely spreads off the solid surface, forming a thin monolayer. Such a condition is termed **wetting** means the liquid wet the solid.

Case-2: The other extreme is called nonwetting, and it occurs when the entire liquid droplet sits as a sphere on the solid. All values of contact angle between these two extremes are theoretically possible.

Here, the contact angle is considered an equilibrium condition. There are also dynamic, receding, and advancing contact angles associated with droplets as they spread and move on substrates.

Sintering and Densification

Sintering is a process in which a particulate material is consolidated during heat treatment. Curved surfaces and surface energies play a large role in the description of an important phenomenon in ceramic processing called **sintering**. Consolidation implies that within the material, particles have joined together into an aggregate that has strength.

Densification: After sintering, the density can be increased through the accompanying reduction in interparticle voids. However, some highly porous insulation products can be less dense after they have been sintered.

The total free energy of the particulate system, ΔG is composed of free energy changes in volume (ΔG_v), boundaries (ΔG_b), and surfaces (ΔG_s) which reduces by the driving force for sintering.

$$\Delta G = \Delta G_V + \Delta G_B + \Delta G_S \dots \dots \dots (1)$$

In conventional sintering, the dominant term in the free energy reduction is that due to surface area reduction. We know that the surface energy is the increment of the Gibbs free energy per unit change in area at constant temperature, pressure, and total number of

$$\text{moles: } \gamma = \left(\frac{\partial G}{\partial A} \right)$$

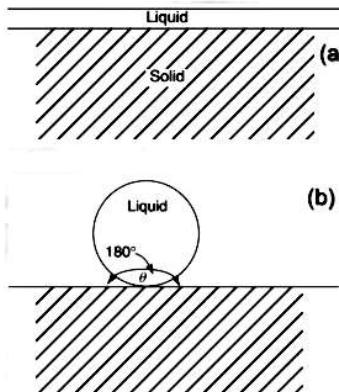


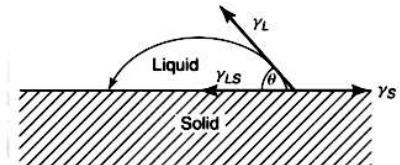
Figure Schematic illustration of (a) wetting and (b) nonwetting of a liquid on a solid.

Young Equation

The figure shows that the three interfacial surface energies make the force balance. The liquid-solid interfacial energy plus the component of the liquid-vapor interfacial energy that lies in the same direction must exactly balance the solid-vapor interfacial energy at equilibrium:

$$Y_L \cos\theta + \gamma_{SL} = \gamma$$

This equation is called Young's equation; it is named after Thomas Young, who first proposed it in 1805.



- ✓ The derivation presented here in terms of force balances is simplistic, but there are more rigorous thermodynamic arguments to support its development.
 - ✓ The contact angle, liquid surface tension, and solid surface energy can be experimentally determined.
 - ✓ The interfacial energy for the liquid–solid system, γ_{SL} can be calculated using Young's equation. As γ_{SL} , γ_L , and γ_S are known as a function of temperature, the contact angle is also dependent on the specified temperature.

Sintering and Densification

The free energy change due to surface area is,

Where, A_s is the surface area of the particles.

Three stages of solid-state sintering

Initial sintering involves the rearrangement of the powder particles and the formation of a strong bond or neck at the contact points between particles. The relative density of the powder may increase from 0.5 to 0.6 due mostly to an increase in particle packing.

Intermediate sintering occurs as the necks grow, the number of pores decreases substantially, and shrinkage of the particle assembly occurs. Grain boundaries form and some grains grow while others shrink. This stage continues while the pore channels are connected, called open porosity, but is considered over when the pores are isolated or in closed porosity. The majority of shrinkage occurs during intermediate sintering, and the relative density at the end of this stage is about 0.9.

Sintering and Densification

Final-stage sintering occurs as the pores become closed and are slowly eliminated by diffusion of vacancies from the pores along the grain boundaries. Little densification occurs in this stage, although grain sizes continue to grow.

During the initial stage, pore rounding causes a decrease in ΔG_S in proportion to the reduction of the surface area, as dictated by Eq. (2), but the formation of a grain boundary causes an increase in ΔG_b .

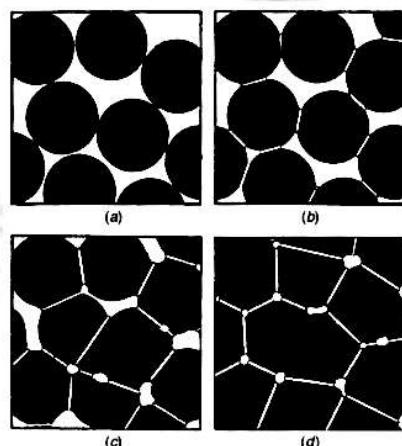


Figure: Development of ceramic microstructure during sintering: (a) Loose powder particles; (b) initial stage; (c) intermediate stage; and (d) final stage.

Solution Thermodynamics and Phase separation

Notes:

- ✓ Most polymers are synthesized in solution.
 - ✓ The solvent could be water, carbon tetrachloride, benzene, or any number of aqueous or organic solvents.
 - ✓ Many polymers are also processed in solution. They can be cast as solutions, and the solvent can be allowed to evaporate to leave only the polymer.
 - ✓ It is critically important to understand how a polymer molecule interacts with the solvent. Again, intermolecular forces will play an important role.

The free energy of mixing for a binary component system is

$$\Delta G_{\text{mix}} \equiv \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad \dots \dots \dots \quad (1)$$

For regular solutions, this relation becomes

$$\Delta G_{\text{mix}} \equiv \alpha X_A X_B + RT(X_A \ln X_A + X_B \ln X_B) \dots \dots \dots \quad (2)$$

The first term in Eq. (2) is the enthalpy of mixing, and the second term is the entropy of mixing.

Sintering and Densification

Dihedral angle, φ : the angle of intersection of the pore at the pore-grain boundary juncture which is related to the relative interfacial energies of the grain boundary, γ_{gb} and the solid surface, γ_s .

φ range from about 105° to 113° in ceramics, implying that γ_{gb}/γ_s is 1.1 to 1.2, whereas in metals this ratio ranges from 0.25 to 0.5.

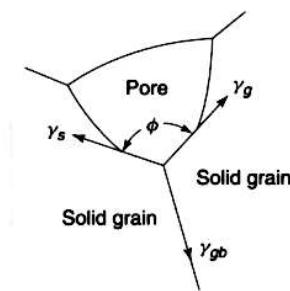


Figure: Schematic illustration of dihedral angle for solid-pore interaction

Solution Thermodynamics and Phase separation

For solutions of a polymer in a solvent, the entropy of mixing is given by

$$\Delta S_{mix} = -R(X_A \ln v_A + X_B \ln v_B) = -k_B(N_A \ln v_A + N_B \ln v_B) \dots\dots\dots(3)$$

k_B is Boltzmann's constant.

R/N_A is the gas constant per molecule

N_0 is Avogadro's number = $N_A + N_B$ (for one mole of solution)

v_A and v_B are the volume fractions of solvent and polymer.

Previously we know that, $\Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B)$

Now, in Eq. (3) the volume fractions of the components, v_A and v_B , are used for the entropy change for polymers, rather than the mole fraction used for most small molecules.

This change arises from the differences in size between the large polymer molecules and the small solvent molecules which would normally mean mole fractions close to unity for the solvent, especially when dilute solutions are being studied.

The enthalpy of mixing for a regular polymer-solvent solution:

$$\Delta H_{mix} = k_B T \chi N_A v_B = RT \chi v_A v_B \dots \dots \dots \quad (4)$$

N_A is the number of solvent molecules

v_A and v_B are the volume fraction of solvent and polymer molecules

Previously, for condensed phase, $\Delta H_{mix} = \alpha X_A X_B$

The mole fractions have been replaced with volume fractions for a regular polymer-solvent solution.

The interaction energy, α comprises of the gas constant R and temperature T.

χ = Flory-Huggins interaction parameter

- ✓ The interaction parameter is the interaction energy per solvent molecule per $k_B T$
- ✓ is inversely proportional to temperature.
- ✓ It is zero for ideal mixtures (zero enthalpy of mixing), positive for endothermic mixing, and negative for exothermic mixing. The interaction parameter is an important feature of polymer solution theory. It is an indication of how well the polymer interacts with the solvent. "Poor" solvents have values of χ close to 0.5, "good" solvents have lower, or negative, values. The typical range for most synthetic polymer solutions is $0.3 < \chi < 0.6$.
- ✓ χ is also predicted to have linear temperature dependence which suggest that the solvating power of the liquid should increase with the increase of temperature.

INTRODUCTION

Condensed Matter Physics

- ✓ "Condensed matter" refers to matter that is not in the gas phase but is condensed as liquid or solid. (condensed → denser!)
- ✓ Liquids and gases are separated by a meniscus; they differ only in density not structure (*i.e.* arrangement of molecules in space).
- ✓ Matter condenses when attractive intermolecular bond energies are comparable to or greater than thermal (*i.e.* kinetic) energy.

Soft Condensed Matter Physics

- Refers to condensed matter that exhibits characteristics of both solids and liquids
- The phrase "soft matter" was used by Pierre de Gennes as the title of his 1991 Nobel Prize acceptance speech.
- It exhibits Viscoelastic behaviour = viscous + elastic. Soft matter can flow like liquids (measurable viscosity) and can bear stress (elastic deformation)
- Examples: rubbers, gels, pastes, creams, paints, soaps, liquid crystals, proteins, cells

Soft Matter Physics

Dr. Kazi Hanium Maria

Course teacher

PH-407

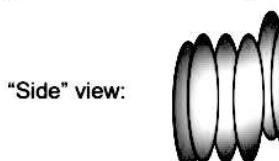
TYPES OF SOFT MATTER

- ❖ A **polymer** is a large molecule, typically with 50 or more repeat units.
- ❖ A colloid is a sub-mm particle of one phase dispersed in another.

Types of colloids: A liquid in a liquid = emulsion

liquid/solid in a gas = aerosol
solid in a liquid = sol
gas in a liquid = foam

- ❖ A liquid crystal is made up of molecules that exhibit a level of order that is intermediate between liquids (randomly arranged and oriented) and crystals (three-dimensional array).



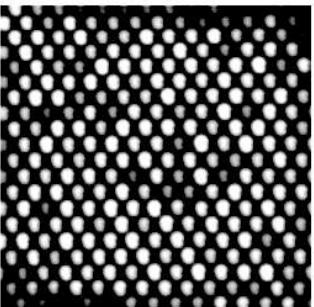
"Side" view:



"Top" view:

- ❖ A surfactant contains both a hydrophobic and a hydrophilic component; reduces interfacial tension; is used to make emulsions and to achieve "self-assembly".

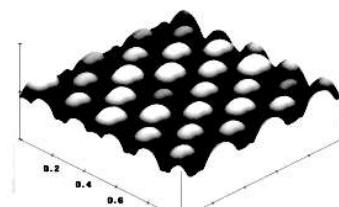
CHARACTERISTICS OF SOFT MATTER



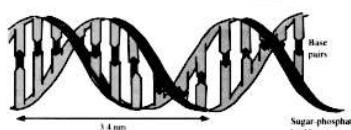
Acrylic Latex Paint
Monodisperse Particle Size

- Atomic spacing: ~ 0.1 nm
- "Pitch" of a DNA molecule: 3.4 nm
- Diameter of a surfactant micelle: ~6-7 nm
- Radius of a polymer molecule: ~10 nm
- Diam. of a colloidal particle (e.g. in paint): ~200 nm
- Bacteria cell: ~2 mm
- Diameter of a human hair: ~80 nm

Top view
3 mm x 3 mm scan



Vertical scale = 200nm



CHARACTERISTICS OF SOFT MATTER

- (3) Tendency to self-assemble into hierarchical structures (i.e. ordered on large-size scales)

Copolymer molecules spontaneously form a pattern in a thin film. (If one phase is etched away, the film can be used for lithography.)

- Surfactants can assemble into spherical micelles, cylindrical micelles, bi-layers (membranes), or saddle surfaces in bicontinuous structures.
- Surfactants can create a bicontinuous surface to separate an oil phase and a water phase.
- The hydrophilic end of the molecule orients itself towards the aqueous phase.
- The oil and water are completely separated but both are CONTINUOUS across the system.

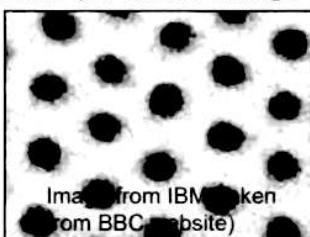
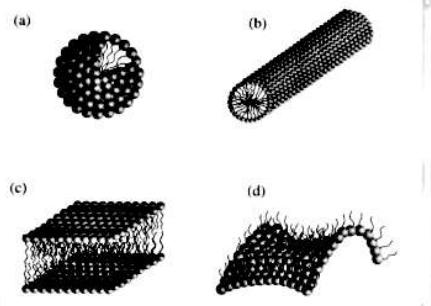


Image from IBM taken from BBC website



CHARACTERISTICS OF SOFT MATTER

- (1) Length scales between atomic and macroscopic

Intermediate Length Scales

- Mathematical descriptions of soft matter can ignore the atomic level.
- "Mean field" approaches define an average energy or force imposed by the neighbouring molecules.
- Physicists usually ignore the detailed chemical makeup of molecules; can treat molecules as "strings", rods, or discs.

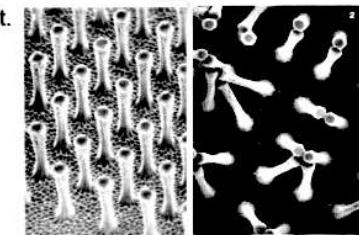
- (2) The importance of thermal fluctuations and Brownian motion

- Soft condensed matter is not static but in constant motion at the level of molecules and particles.
- Brownian motion is the result of a slight imbalance of momentum being transferred between liquid molecules and a colloidal particle.
- Thermal (kinetic) energy for a single monoatomic molecule is $3/2 kT$ (3 d.o.f.)
 $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$, so $kT = 4 \times 10^{-21} \text{ J}$ per molecule at room temperature (300 K).
- kT is a useful "gauge" of bond energy.

CHARACTERISTICS OF SOFT MATTER

- (4) Short-range forces and interfaces are important.

The structure of a gecko's foot has been mimicked to create an adhesive. However, the attractive adhesive forces can cause the synthetic "hairs" to stick together.

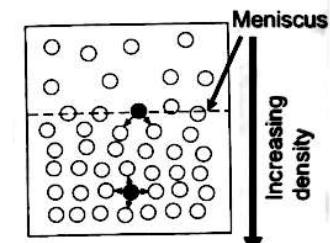


ORIGIN OF SURFACE TENSION (I.E. INTERFACIAL ENERGY)

- An interfacial energy g is associated with any interface between two phases (J m^{-2}) (also called a surface tension: Nm^{-1})

- Increasing the interfacial area requires the separation of neighboring molecules.
- In reducing the interfacial area, more molecules are brought into close contact.

- Force associated with neighboring molecules = surface tension.
- Surfaces become increasingly more important as particles become smaller.

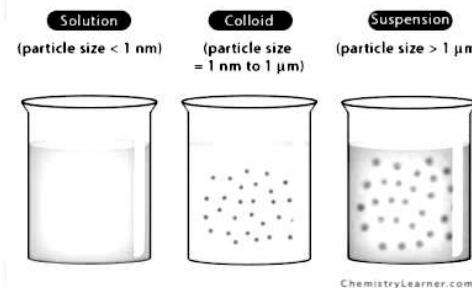


COLLOIDAL SYSTEM

A colloid is a phase-separated mixture in which one substance of microscopically dispersed particles (A) is suspended throughout another substance (B). Sometimes the dispersed substance alone is called the colloid; the term colloidal suspension refers unambiguously to the overall mixture.

Unlike a solution, whose solute and solvent constitute only one phase, a colloid has a dispersed phase (the suspended particles, A) and a continuous phase (the medium of suspension, B).

A system comprising dispersed objects in a continuous medium should be called a **colloidal system** when the size of the objects is such that no rapid phase separation occurs, either through sedimentation or creaming (when the density of the particles is less than that of the suspension liquid).



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TYPES OF COLLOIDS

Based on the nature of the interaction between the dispersion medium and the dispersed phase, colloids can be classified into lyophilic and lyophobic.

Lyophilic: If the dispersed phase has an affinity for the dispersion medium, the colloid is called a lyophilic colloid. The words *lyo* and *philic* mean 'liquid' and 'loving' respectively. Thus, even if the dispersed phase is separated from the dispersion medium, it can readily be reconstituted by simply mixing them. Moreover, they are difficult to coagulate due to their stable nature. They are also known as **intrinsic colloids**. Examples are starch, rubber, protein, etc.

Lyophobic: If the dispersed phase has little or no affinity for the dispersion medium, the colloid is called a lyophobic colloid. The words *lyo* and *phobic* mean 'liquid' and 'fearing' respectively. Hence, they are liquid-hating. They are difficult to prepare because the dispersed phase does not readily form a colloid with the dispersion medium; they require some special methods. They are unstable and require stabilizing agents for their preservation. They are also known as **extrinsic colloids**. Examples are sols of metals like silver and gold, sols of metallic hydroxides, etc.

TYPES OF COLLOIDS

Colloids can be classified according to different properties of the dispersed phase and medium. Firstly, based on the types of particles of the dispersed phase, colloids can be classified as:

Multimolecular colloids: When the dissolution of smaller molecules of substance or many atoms takes place, they combine to form a species whose size is in the range of colloidal size. The species formed is known as the multimolecular colloid. For example, the Sulphur solution contains particles that have thousands of S₈.

Macromolecular colloids: In this type of colloid, the macromolecules form a solution with a suitable solvent. The size of the particles of this macromolecular solution lies in the range of colloidal particle size. Thus, this solution is also known as the macromolecular colloids. The colloids formed here are similar to that of the actual solution in many respects and are very stable. Example: Starch, proteins, enzymes, and cellulose are the naturally occurring macromolecular colloids whereas polyethylene, synthetic rubber, etc. are the synthetic macromolecules.

Associated colloids: Some substances act as strong electrolytes when they are in low concentrations, but they react as colloidal solids when they are in high concentrations. In higher concentrations, particles aggregate showing colloidal behavior. These aggregated particles are known as the micelles. They are also known as the associated colloids. The formation of the micelles occurs above a particular temperature called the Kraft temperature (T_k) and a specific concentration called the critical micelle concentration. These colloids can be reverted by diluting it. Examples of some associated colloids are soaps and synthetic detergents.

DIFFERENCES BETWEEN LYOPHILIC & LYOPHOBIC COLLOIDS

Lyophilic colloids	Lyophobic colloids
1. Prepared by direct mixing with dispersion medium	1. Not prepared by direct mixing with the medium
2. Little or no charge on particles	2. Particles carry positive or negative charge
3. Particles generally solvated	3. No salvation of particles
4. Viscosity higher than dispersion medium; set to a gel	4. Viscosity almost the same as of medium; do not set to a gel
5. Precipitated by high concentration of electrolytes	5. Precipitated by low concentration of electrolytes
6. Reversible	6. Irreversible
7. Do not exhibit Tyndall effect	7. Exhibit Tyndall effect
8. Particles migrate to anode or cathode or not at all	8. Particles migrate to either anode or cathode.

COMPARISON OF COLLOIDAL SOLS

Lyophilic	Associated	Lyophobic
Dispersed phase (large organic mole. With colloidal size)	Dispersed phase (micelles of organic molec. Or ion –size below the colloidal range)	Dispersed phase (Inorganic particles as gold)
Molec. of dispersed phase are solvated Formed spontaneously	Hydrophilic and lyophilic portion are solvated , Formed at conc. above CMC	Not formed spontaneously
The viscosity ↑ with ↑ the dispersed phase conc.	The viscosity ↑ with ↑ the micelles conc.	Not greatly increase
Stable dispersion in presence of electrolytes	CMC↓ with electrolytes	Unstable dispersion in presence of electrolytes

CLASSIFICATIONS OF COLLOIDS

- A dispersion of gas bubbles in a liquid is referred to as foam (e.g., whipped cream); in wet foam, the volume fraction of the continuous phase is considerable whereas in dry foam it is very small.
- A dispersion of gas bubbles in a solid is called a solid foam (e.g., polyurethane foam).
- A dispersion of liquid droplets and small solid particles in a gas is an aerosol (e.g., mist) and a solid aerosol (e.g., smoke).
- A dispersion of liquid droplets in another immiscible liquid is an emulsion (e.g., mayonnaise).
- A dispersion of solid particles in a liquid is a sol (e.g., blood).
- A dispersion of liquid particles in a solid matrix is a gel (e.g., butter and cheese) and solid particles in a solid matrix make a solid sol (e.g., colored glass, porcelain).

CLASSIFICATIONS OF COLLOIDS

Disperse phase	Dispersion medium	Name	Examples
Liquid	Gas	Liquid aerosol	Fog, liquid sprays
Solid	Gas	Solid aerosol	Smoke
Gas	Liquid	Foam	Foams and froths
Liquid	Liquid	Emulsion	Milk, mayonnaise
Solid	Liquid	Sol, colloidal dispersion or suspension, paste (high solid content)	Silver iodide in photographic film, paints, toothpaste
Gas	Solid	Solid foam	Polyurethane foam, expanded polystyrene
Liquid	Solid	Solid emulsion	Tarmac, ice cream
Solid	Solid	Solid suspension	Opal, pearl, pigmented plastic

ADVANTAGES OF COLLOIDAL PREPARATION

- 1) Higher degree of catalytic activity: Due to increased surface area in colloidal preparation, the activity of a catalyst is generally accelerated.
- 2) Color: Colloidal preparations generally possess attractive color.
- 3) Taste: Colloidal preparation may also be used to pronounce the taste of a pharmaceutical preparation.
- 4) Better solubility, absorption and bioavailability
- 5) Compatibility with biological system: Ionic silver salt may itself produce toxicity-argyria and less bioavailability due to the formation of silver chloride which is insoluble and rapidly excreted from body. But it does not occur when colloidal preparations are used.
- 6) Stability: Colloidal preparation are stable than suspension and emulsion.

DISADVANTAGES OF COLLOIDAL PREPARATION

- ❖ As colloids are small in particle size so it is easily absorbed and gives extensive bioavailability which may support toxicity.
 - ❖ Preparation of lyophobic colloid is difficult
 - ❖ Stabilization of colloids is often difficult as it may be destabilized by a lot of factors (radiation, heat, drying etc.)
 - ❖ There is a great restriction on the particle size of the particles.

Now the equation of motion (position x and velocity v) in the presence of the two independent degrees of freedom is:

$$\frac{\xi}{2} \frac{dx^2}{dt} = xF_r - m \frac{d}{dt}(xv) - mv^2 \dots \dots \dots (5)$$

According to the equipartition theorem, the right-hand side is equal to $k_B T$. Upon integrating both sides over t we have:

where we have defined the diffusion coefficient D . The importance of this result is that it relates D to the microscopic viscous force ξ_v by the Stokes-Einstein relation:

Thus one can measure the Boltzmann constant k_B by observing the Brownian motion of colloids.

FORCES BETWEEN COLLOIDAL PARTICLES

Brownian Motion: Consider the equation of motion of a spherical particle experiencing viscous damping described by the Stokes formula, $F = 6\pi\eta Rv = \xi v$ and a random force F_r due to collisions with the continuous phase:

As the x , y , and z directions are uncoupled and equivalent, only one of them need to be considered:

where the F_r is the component of the random force along the x -axis. Now multiply both sides by x , rearrange, and replace $x \frac{d^2x}{dt^2}$ by $\frac{d}{dt} \left(x \frac{dx}{dt} \right) - \left(\frac{dx}{dt} \right)^2$

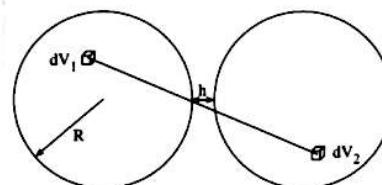
$$\text{Thus } \xi x \frac{dx}{dt} = x F_r - m \frac{d}{dt} \left(x \frac{dx}{dt} \right) - m \left(\frac{dx}{dt} \right)^2 \dots \dots \dots (3)$$

The left-hand side can be written as: $\xi x \frac{dx}{dt} = \frac{\xi}{2} \frac{dx^2}{dt}$ (4)

VAN DER WAALS FORCES

Attractive van der Waals forces between colloidal particles can be considered to result from dispersion interactions between the molecules on each particle. To calculate the effective interaction, it is assumed that the total potential is given by the sum of potentials between pairs of molecules. In this approximation, interactions between pairs of molecules are assumed to be unaffected by the presence of other molecules; i.e. many-body interactions are neglected.

The resulting pairwise summation can be performed analytically by integrating the pair potential for molecules in a microscopic volume dV_1 on particle 1 and in volume dV_2 on particle 2, over the volumes of the particles. The resulting potential depends on the shapes of the colloidal particles and their separation.



Illustrating the method for calculating interparticle forces between colloids. The forces between the volume elements dV of two particles are integrated

Case-1: In the case of two flat infinite surfaces separated in vacuo by a distance h , the potential per unit area is: $V = -\frac{A_H}{12\pi h^2} \dots\dots\dots(1)$

A_H is the Hamaker constant, which determines the effective strength of the van der Waals interaction between colloid particles. It is noteworthy that the attractive potential between colloid particles falls off much less steeply than the dispersion interaction between individual molecules. Thus, long-range forces between colloidal particles are important for their stability.

Case-2: For two spherical particles of radius R , where the interparticle separation is small ($h \ll R$), the Derjaguin approximation can be used to find out the potential between two curved surfaces. It is found that Eq. (1) is modified to

$$V = -\frac{A_H R}{12h} \dots\dots\dots(2)$$

Eqs. (1) and (2) are used to apply for colloidal particles in a vacuum. If there is a liquid medium between the particles, the van der Waals potential is substantially reduced. The Hamaker constant in these equations is then replaced by an effective value.

Case-3: Consider the interaction between two colloidal particles 1 and 2 in a medium 3. If the particles are far apart, then each interacts effectively with medium 3 independently and the total Hamaker constant is the sum of two-particle–medium terms. However, if particle 2 is brought close to particle 1, then particle 2 displaces a particle of type 3. Then particle 1 interacts with a similar body (particle 2), the only difference being that molecules of particle 2 have been replaced by those of medium 3. Thus the potential energy change associated with bringing particle 2 close to particle 1 in the presence of medium 3 is less than it would be in vacuo. The effective Hamaker constant is thus a sum of particle–particle plus medium–medium contributions.

Note: The Hamaker approach of pairwise addition of London dispersion forces is approximate because multi-body intermolecular interactions are neglected. In addition, it is implicitly assumed in the London equation that induced dipole–induced dipole interactions are not retarded by the finite time taken for one dipole to reorient in response to instantaneous fluctuations in the other. Because of these approximations, an alternative approach was introduced by Lifshitz. This method assumes that the interacting particles and the dispersion medium are all continuous; i.e. it is not a molecular theory.

CHARGE STABILIZATION

The surface of a colloidal particle can develop a charge through several mechanisms. Ion adsorption or desorption or adsorption/desorption of ionic surfactants leads to the developing of an electrical double layer in many colloidal dispersions. The concentration and nature of the electrolyte have a significant impact on the stability of charged colloid dispersions.

Schutze-Hardy's rule describes that the stability of charged colloids is related to the balance between the electrostatic (repulsive) forces between double layers, the (predominantly attractive) van der Waals forces, and the sol's nature. The valence of the counterion predominantly prevents the coagulation of a colloidal dispersion.

Derjaguin-Landau-Verwey-Overbeek (DLVO) theory is a quantitative model to describe the effect of the nature of the counterion, the valence of the co-ion, the concentration of the sol and the nature of the sol on the stability of the colloids.

Soft Matter Physics

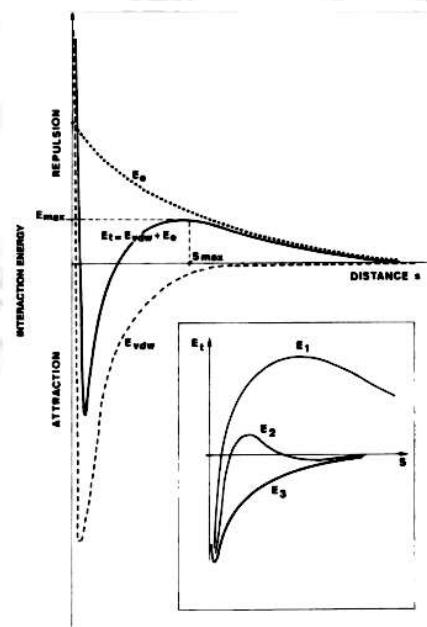
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Derjaguin–Landau–Verwey–Overbeek theory allows for both the forces between electrical double layers (repulsive for similarly charged particles) and long-range van der Waals forces that are usually attractive.

Hence, the total potential energy in this theory is the sum: $V = V_R + V_A$

V_R is the repulsive potential energy due to the overlap of electrical double layers on colloid particles and V_A is the attractive van der Waals energy.

Variation of energy (E) with distance for two spheres separated by distance (s). The total energy E_t is represented by the continuous curve

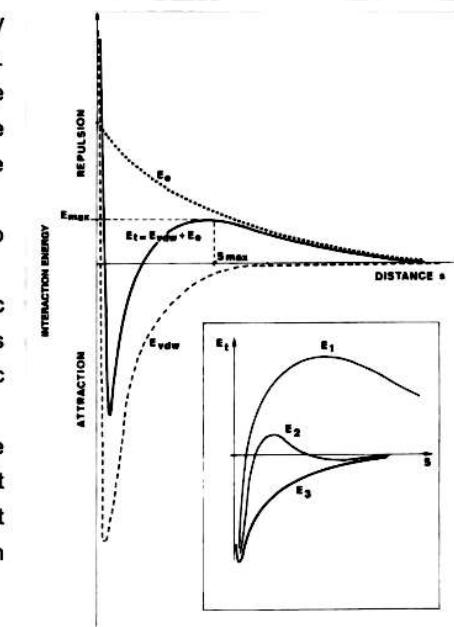


- Thermodynamic equilibrium occurs at the minimum value of E_t , when the particles are in contact (aggregation distance).
- If two particles are separated by a distance $s > s_{max}$, a net repulsive force arises in this region which did not allow the particles come close. (E_t increases as s decreases).
- The barrier at E_{max} must be crossed to reach the attractive region. Particles' thermal or kinetic energy must be greater than E_{max} . Otherwise, the system is in metastable state.
- To reduce the surface charges, the ionic strength should be raised by chemical intervention. Then repulsive term E_e is lowered and the curve $E_t = f(s)$ (shown in Fig. (inset)), is changed from the type marked E_1 to the type marked E_3 . The metastable state vanishes and The particles aggregate spontaneously to make coagulation or flocculation.
- In some cases, a curve of E_2 occurs with a second energy minimum. As the latter is extremely shallow, the resulting aggregation of particles is generally redispersible by merely shaking the sol.

Figure shows the variation of the energy (E) with separation (s) for two spheres. The zero energy is defined when the separation of the two spheres is infinite and is negative when the interparticle force dE/ds is attractive.

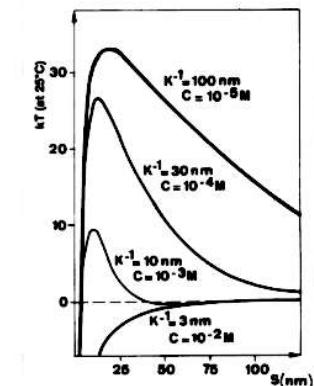
The total energy E_t is the sum of two terms:

- A repulsive term E_e of electrostatic origin decreases exponentially and is strongly dependent on the ionic strength of the medium.
- A strongly attractive but short-range term E_{vdw} exhibits energy well, at distances of a few nanometres, it becomes strongly repulsive (the Born energy).



The main features of the normal behavior of colloidal suspensions are:

- ✓ The existence of a metastable state in the solution, with no significant aggregation.
- ✓ The deep potential well explains why, when the particles are in contact (e.g., agglomerated powders, lumps, soiled surfaces) it can be difficult to redisperse the system (and difficult to keep the water clear when washing the dishes!).
- ✓ The van der Waals force is a key parameter in understanding the electrostatic forces but is practically insensitive to the ionic strength of the suspension liquid.
- ✓ Figure shows the curve of energy E against separation s for two particles of radius 100 nm and surface potential 26 mV with Hamaker's constant equal to 10^{-19} J. It would be difficult to produce stable aqueous suspensions of high ionic strength. Conversely, it may be sufficient to add salt to cause flocculation. This is exactly what happens when the sediments carried down by rivers encounter the salt waters of the sea ($I \approx 0.5 \text{ M}/\text{l}$). The resulting deposits silt up estuaries and favor the formation of deltas.



AMPHIPHILES

- ❖ **Amphiphile** molecules consist of a polar hydrophilic part, typically a head, and an apolar hydrophobic part, typically an alkyl chain.
- ❖ When dispersed in water, their dual nature causes the amphiphiles to self-organize such that the polar parts face water (thereby reducing the surface tension of water) whereas the apolar parts orient away from water.
- ❖ The terms amphiphile and surfactant are often used interchangeably. A molecule is said to be amphiphilic if it contains two parts with very different affinities; and it is called a surfactant when it tends to adsorb onto free surfaces or interfaces (liquid/liquid or liquid/solid), thereby modifying the surface energy.

When dispersed in water, amphiphiles self-assemble in various ways depending on the shape of the molecules. The key geometrical parameter is the ratio $v/l_c a_0$

v = the volume of the molecules,
 l_c = the length of the apolar chain,
 a_0 = the area per headgroup.

MORPHOLOGIES OF AMPHIPHILE SELF-ASSEMBLIES IN WATER

Lipid	Critical packing parameter $v/a_0 l_c$	Critical packing shape	Structures formed
Single-chained lipids (surfactants) with large head-group areas: SDS in low salt	<1/3	Cone	spherical micelles
Single-chained lipids with small head-group areas: SDS and CTAB in high salt, non-ionic lipids	1/3-1/2	Truncated cone	cylindrical micelles
Double-chained lipids with large head-group areas, fluid chains: phosphatidyl choline (lecithin), phosphatidyl serine, phosphatidyl glycerol, phosphatidyl inositol, phosphatidic acid, sphingomyelin, DGDG ^a , dihexadecyl phosphate, diacyl dimethyl ammonium salts	1/2-1	truncated cone	flexible bilayers, vesicles

If the amphiphile has a single short tail and the area of the head is large, then the amphiphile looks like an ice-cream cone.

If $\frac{v}{l_c a_0} \leq \frac{1}{3}$, amphiphiles will pack into spherical micelles.

In truncated-cone amphiphiles $\frac{1}{3} \leq \frac{v}{l_c a_0} \leq \frac{1}{2}$ and they form cylindrical micelles.

For $\frac{1}{2} \leq \frac{v}{l_c a_0} \leq 1$, the amphiphiles self-organize in bilayers and lamellar phases,

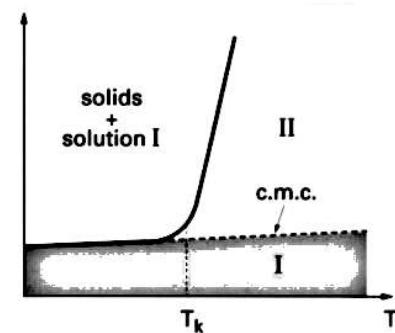
For $\frac{v}{l_c a_0} > 1$, they form inverted micelles, which can be either cylindrical or spherical.

This is how the shape of the phospholipids, which is controlled by their chemical structure, generates the curvature of phospholipid self-assemblies.

AMPHIPHILES IN SOLUTIONS

Consider the solubility of an amphiphile in water (e.g., from the remaining solid residue) to observe the variation of temperature and pressure.

➤ At room temperature and pressure, there is a variation in molecular structure as solubility is also strongly dependent on temperature for a given chemically pure molecule. We observe a sudden increase in solubility at the Kraft temperature, T_K .



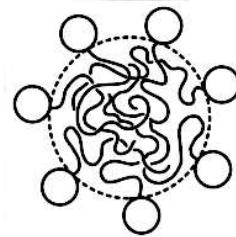
➤ Various physical characterizations can be used to separate the solution into two regions (I) and (II). (I) contains only monomers, whereas (II), located above the critical micellar concentration (c.m.c.), contains monomers and micelles.

Variation in solubility S of a surfactant in water with temperature. The shaded region (I) contains only monomers in solution, whereas region (II), located above the critical micellar concentration (c.m.c.), contains monomers and micelles

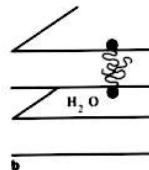
MICELLAR SHAPES AND PHASE BEHAVIOR

- Amphiphilic molecules spontaneously self-assemble to form small aggregates called **micelles**.

Schematic representation showing the internal structure of a spherical micelle. Hydrophobic chains are in a condensed liquid state in the core of the micelle. Each one is linked at one end to a polar head on the other side of the interface. Typical diameter of a ball is between 30 and 50 Å.



Hexagonal Phase



Lamellar Phase

a

b

Schematic representation showing the structure of two mesomorphic structures occurring in concentrated amphiphilic solutions. (a) Hexagonal phase. Amphiphilic molecules assemble into long cylinders organised periodically in space. (b) Lamellar phase. Amphiphilic molecules make up infinite bilayers, stacked periodically

MICELLAR SHAPES AND PHASE BEHAVIOR

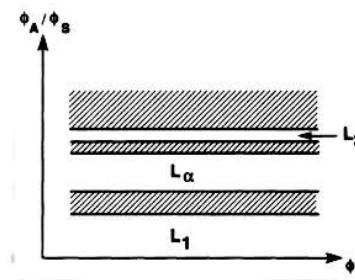
Three single-phase regions on the diagram, are separated by multiphase regions.

- Micellar Phase:** The phase marked L_1 is the least rich in alcohol. It is isotropic and transparent, and it is very fluid for low values of ϕ_A/ϕ_s . In this case, viscosity rises rapidly when this parameter is increased.
- Lamellar Phase:** has the intermediate values of ϕ_A/ϕ_s , an optically birefringent phase occurs, denoted L_α on the diagram.
- Sponge Phase** has high values of the ratio ϕ_A/ϕ_s , a stable and generally very narrow phase occurs, which is optically isotropic and transparent, and very fluid. This phase, denoted L_3 on the diagram.

Note: It is quite remarkable that the boundaries of the various phases on the diagram are approximately horizontal. This means that changes of phase in such systems are largely determined by the chemical composition ϕ_A/ϕ_s of the objects, not by the concentration ϕ .

MICELLAR SHAPES AND PHASE BEHAVIOR

Consider a dilute solution of a mixture of an ionic surfactant and a co-surfactant in salt water. Figure shows the typical phase behavior for fixed temperature and salinity. The horizontal axis represents the total volume fraction ϕ of amphiphile molecules and the vertical axis gives the ratio ϕ_A/ϕ_s of cosurfactant concentration ϕ_A to surfactant concentration ϕ_s . Almost all the amphiphile molecules aggregate together into micelles. ϕ therefore represents the volume fraction of these objects, whilst ϕ_A/ϕ_s represents their chemical composition for the two chemical species which make them up.



Schematic phase diagram for surfactant/cosurfactant/salt water systems at constant temperature and salinity

MICELLAR SHAPES AND PHASE BEHAVIOR

- | Aggregate Morphology | Phase |
|-------------------------------|---------------------------|
| globular micelles | micellar phase L_1 |
| cylindrical wormlike micelles | lamellar phase L_α |
| bilayers | sponge phase L_3 |
- Changes in shape do not correspond in a one-one manner with phase changes.
- The transformation from sphere to cylinder in the micellar phase does not induce a phase change.
- Conversely, the change from lamellar phase L_α to sponge phase L_3 is not accompanied by morphological change. This shows that local morphology is not sufficient to determine phase behavior.
- Spherical micelles have constant size and their spatial distribution is like a point particle gas which confined within the volume defined by the quantity of aqueous solvent.
- By their one- or two-dimensional nature, the long cylinders and bilayers are more complex.
- They possess internal degrees of freedom affecting the structure and physical properties of the phases they make up.

Correspondence between phase behaviour (micellar, lamellar and sponge) and morphological sequence (spherical, cylindrical and bilayer)

MODELS FOR MICELLIZATION

Open association model: Several models have been developed to describe micellization in surfactants. In the open association model, there is a continuous distribution of micelles containing 1, 2, 3, ..., n molecules. However, the open association model does not lead to a critical micelle concentration and so is generally inapplicable to amphiphiles in solution.

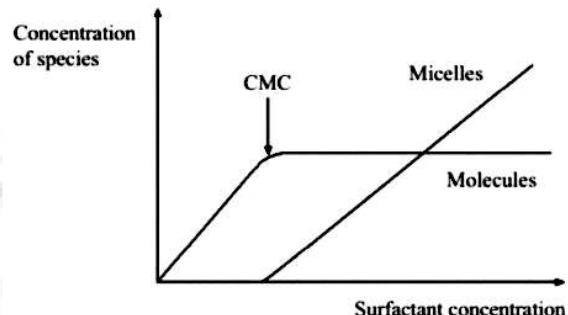
Closed association model: The closed association model can account for the observation of a critical micelle concentration. It is also known as the **mass action model**. It is assumed that there is a dynamic equilibrium between molecules and micelles containing p molecules. In practice, micelles are not monodisperse i.e. there is a range of values of association number. Usually, the dispersity in p amounts to about 20–30 % of its value, which is not large enough to change the behavior captured by models for monodisperse micelles.

The Gibbs energy change of micellization per mole of micelles is then at equilibrium,

C_p = the concentration (in mol dm⁻³) of micelles of association number p , and C_c is the concentration of unassociated surfactant molecules.

Here, the fact is used that for a fully ionized surfactant, the concentration of surfactant and counterions is equal and equal to the CMC at this concentration. The closed association model means that above the CMC, added molecules go into micelles.

The fraction of unassociated molecules and of micelles are plotted together in Fig.



Mole fraction of unassociated molecules and micelles as a function of total surfactant concentration

Then the Gibbs energy change of micellization per mole of micelles is

Per mole of surfactant molecules this becomes:

$$\Delta_{mic}G^\ominus = -\frac{RT}{n}\ln K = -\frac{RT}{n}\ln C_p + RT\ln C_s \dots \dots \dots (4)$$

Assuming p is large, the first term on the right-hand side can be neglected and at the CMC we have:

$$\Delta_{mic}G^\ominus = RT \ln C_{CM}$$

For an ionic surfactant, the equilibrium involves in addition the counterions (denoted C). Equilibrium (1) can be expressed as:

$$pS^x + (p-n)C_y \rightleftharpoons S_p^e$$

Here $\alpha = n/p$ is the degree of dissociation of the surfactant and x and y are the charges of surfactant and counterion respectively.

$$\Delta G^\ominus = -RT \ln K$$

in the case of large association numbers

$$\Delta_{mic}G^\ominus = RT(2 - \frac{n}{n})\ln C_{CMC}$$

Soft Matter Physics

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SURFACE CHARGES

Surface charges are the result of the repulsive interparticle forces between the presence of ionized species on the surface of the colloids.

These surface charges may have various origins:

- In the case of the clays, the compounds are made up of intercalated layers of aluminosilicates where negative charges rise by the isomorphic substitution of Si^{4+} ions by Al^{3+} or Mg^{2+} in the crystal lattice and are balanced by cations like Na^+ , K^+ or Ca^{2+} . However, bulky ions couldn't fit into the crystal lattice and hence, are liberated during dispersion in water.
- Usually, the ionizable groups exist only on the surface of the particle. In the case of silica crystal (SiO_2), each oxygen atom only bonds with silicon atoms whereas on the surface, there are $\equiv \text{Si} - \text{OH}$ groups that are amphoteric and may be ionized. Depending on the pH, SiO^- or SiOH_2^+ can be formed. Similarly, other ionizable functional groups (sulfates, phosphates, carboxylates, sulfonates, and so on) are chemically bonded to a dispersed material and present on the interfaces.
- In a colloidal suspension, the surface may be either positively or negatively charged depending on the adsorption of excess +/- ions during synthesis or subsequently.

Therefore, the presence of impurities in the colloidal suspensions influences the surface charge of the particles.

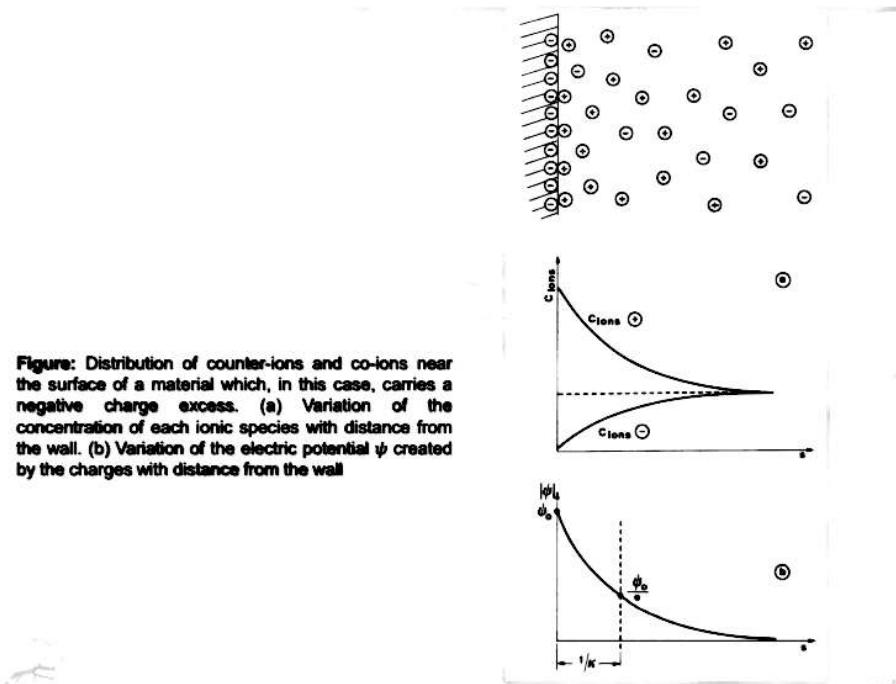


Figure: Distribution of counter-ions and co-ions near the surface of a material which, in this case, carries a negative charge excess. (a) Variation of the concentration of each ionic species with distance from the wall. (b) Variation of the electric potential ψ created by the charges with distance from the wall

The colloidal medium remains electrically neutral even with the presence of surface charges. Because:

- The positive and negative ions are not distributed homogeneously throughout the continuous medium.
- Ions of charge opposite to the surface charges (counter-ions) tend to concentrate near the surface, whereas those of the same charge (co-ions) are repelled.
- This happens regardless of the thermal motions that oppose such a preferential distribution.
- Far from the interface, the solution returns to its traditional constitution with identical concentrations of the two charge types.
- The ion distribution depends on the nature of the immersed solid and the nature of the ion concentration introduced into the liquid.

The electric potential ψ is related to the charge density at any point by a simple differential equation (the Poisson-Boltzmann equation).

$$\psi = \psi_0 e^{-ks}$$

where ψ_0 is the potential at the surface of the object and s is the distance from the surface (see Fig. b). The parameter κ is the inverse of a length, and $1/\kappa$ is known as the Debye length. It is inversely proportional to the square root of the ionic strength.

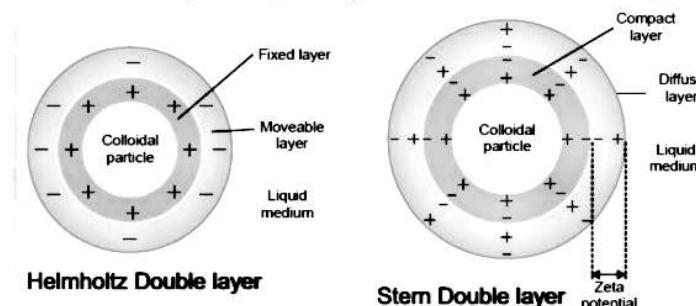
ELECTRIC DOUBLE-LAYER FORCES

The surface of a colloidal particle acquires a positive charge by selective adsorption of a layer of positive ions around it. This layer attracts counterions from the medium which form a second layer of negative charges. The combination of the two layers of +ve and -ve charges around the sol particle was called the Helmholtz Double layer.

More recent considerations have shown that the double layer is made of :

- (a) a Compact layer of positive and negative charges which are fixed firmly on the particle surface.
- (b) a Diffuse layer of counterions (negative ions) diffused into the medium containing positive ions.

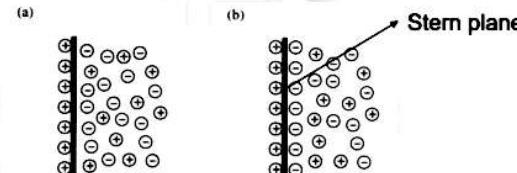
The combination of the compact and diffuse layer is referred to as the Stern Double layer.



ELECTRIC DOUBLE-LAYER FORCES

Double layer: The surface charge attracts counterions which tend to segregate into a layer adjacent to the layer of surface charges in the colloid particle. Thus an electric double layer is created.

In the **diffuse double-layer model**, the ionic atmosphere is supposed to consist of two regions. Close to the colloid particle, counterions tend to predominate due to strong electrostatic forces. Ions further away from the particle are assumed to be organized more diffusely, according to a balance of electrical forces and those resulting from random thermal motion. In this outer diffuse region (Fig. a), the concentration of counterions thus decreases gradually away from the surface.



Models for the electric double layer around a charged colloid particle:
(a) diffuse double layer model, (b) Stern model

In the **Stern model**, the interface between the inner region and outer diffuse region of the counterion atmosphere is a sharp plane (Stern plane) and the inner region consists of a single layer of counterions termed the Stern layer (Fig. b).

Using appropriate boundary conditions, equⁿ (4) can be solved.

In case of, $(ze\Phi_0/k_B T) \ll 1$,

- ✓ the surface potential is 0 (i.e. that at $x = 0$)
- ✓ much smaller than $k_B T$
- ✓ the electrolyte is weakly charged

And the potential simplifies to

$$\Phi = \Phi_0 \exp(-kx) \dots \dots \dots (5)$$

Φ decays exponentially with increasing distance.

$$k = \left(\frac{e^2 \sum_i c_i z_i^2}{\epsilon k_B T} \right)^{1/2}$$

$1/k$ is known as the Debye screening length and has dimension of length.

In the distribution of the charge around the particle, there is a difference in potential between the compact layer and the bulk of the solution across the diffuse layer. This is called by **Electrokinetic or Zeta potential**.

The diffuse double layer can be described by the Gouy-Chapman equation, which is a solution of the Poisson-Boltzmann equation for a planar diffuse double layer. The Poisson-Boltzmann equation describes:

- An electrical potential to the charge distribution
- Concentration of charged species

The concentrations of positive and negative ions given by:

$$c_+ = c_0 \exp\left(\frac{-ze\Phi}{k_B T}\right) \dots \dots \dots (1)$$

$$c_- = c_0 \exp\left(\frac{+ze\Phi}{k_B T}\right) \dots \dots \dots (2)$$

c_0 = the number density (molar concentration = c_0/N_A) of each ionic species of valence z .

Then, the excess charge density, $\rho = ze(c_+ - c_-)$ (3)

The potential as a function of distance, x from the charged plane can be obtained by inserting the excess charge density this into Poisson's equation:

$$\frac{d\Phi^2}{dx^2} = \frac{\rho}{\epsilon} \dots \dots \dots (4)$$

$\epsilon = \epsilon_r/\epsilon_0$ = the permittivity of the solution

ϵ_r = relative permittivity and ϵ_0 = permittivity of a vacuum

Kinetic Processes in Materials

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KINETIC PROCESSES

- Thermodynamics defines whether a process is favorable or not; kinetics defines how quickly that process will take place.
- Three categories of kinetic processes are of concern: the rate at which materials are formed, the rate at which they are transformed, and the rate at which they decompose.
- In general, formation and decomposition are chemical processes, involving the reaction of two or more chemical species. On the other hand, transformations are usually physical processes, such as the melting of ice, and do not involve chemical reactions. In all cases, the rate at which the process is occurring is the important thing.
- The thermodynamic free energy, G ; and the activation energy, E_a are two important concepts that are modified to determine the rate of processes in the formation, transformation, and decomposition of different materials

The forward and reverse reaction rates are equal at equilibrium, for which $\Delta G = 0$,

$$r_1 = r_2 \Rightarrow k_1[A][B] = k_2[C][D] \Rightarrow \frac{k_1}{k_2} = \frac{[A]^a[B]^b}{[C]^c[D]^d} = K \dots \dots \dots (4)$$

K is the equilibrium constant for the reaction at constant temperature.

$\Delta G < 0$, the reaction proceeds spontaneously

The free energy of a system is simply the sum of the free energy contributions of each of the components, such as their chemical potentials, μ_i , and the stoichiometric coefficients.

$$\Delta G = \sum v_i \mu_i \dots \dots \dots (5)$$

The standard Gibbs free energy, $\Delta G^0 = \sum v_i \mu_i^0 \dots \dots \dots (6)$

The chemical potentials, μ_i and the standard chemical potentials, μ_i^0 , are related to each other by the activity of each species, a_i .

$$\mu_i = \mu_i^0 + RT \ln a_i \dots \dots \dots (7)$$

Here, R is the gas constant and T is the absolute temperature.

The activity of a species is an indication of how far away from standard state of that species is.

If we subtract Eq. (6) from Eq. (5) and substitute Eq. (7) into the result, the relationship between the activity of the reactants and products have been obtained. The free energy for a reacting system:

$$\Delta G - \Delta G^0 = RT \sum v_i \ln a_i \dots \dots \dots (8)$$

LAW OF MASS ACTION

Consider a reaction in which reactants A and B go to products C and D. The total free energy of the reaction is sum of individual free energy contributions. Such as:



where a , b , c , and d are the stoichiometric coefficients of species A, B, C, and D.

The Law of Mass Action states that the velocity of the reaction at a given temperature is proportional to the product of the active masses of the reacting substances.

The forward reaction rate, r_1 is a function of the concentrations of A and B raised to their corresponding exponents:

$$r_1 = k_1[A]^a[B]^b \dots \dots \dots (2)$$

The reverse reaction rate, r_2 is related to the number of products, C and D:

$$r_2 = k_2[C]^c[D]^d \dots \dots \dots (3)$$

k_1 and k_2 are proportionality constants, or rate constants, for the forward and reverse reactions, respectively, and have units of inverse time (s^{-1}) and an appropriate inverse concentration,

At equilibrium, $\Delta G = 0$, and the activities of the products and reactants a_i , are related to their respective concentrations:

$$\Delta G^0 = -RT \ln \left\{ \frac{[A]^a[B]^b}{[C]^c[D]^d} \right\} \dots \dots \dots (9)$$

$$\text{Using Eq. (4), } \Delta G^0 = -RT \ln K \dots \dots \dots (10)$$

$$\text{Rearranging Eq. (10) gives: } K = \exp \left(\frac{-\Delta G^0}{RT} \right) \dots \dots \dots (11)$$

Equation (11) gives the effect of temperature on the equilibrium constant. Note that a plot of $\ln K$ versus $1/T$ should give a straight line of slope $-\Delta G^0/R$.

ACTIVATION ENERGY

The rate constant can be written by Arrhenius's expression:

$$k = k_0 \exp \left(-\frac{E_a}{RT} \right) \dots \dots \dots (1)$$

E_a = activation energy, k_0 = preexponential factor

All molecules in a reaction must overcome an activation energy before they react and form products.

The Boltzmann distribution indicates that the fraction of molecules must have required energy $\exp \left(-\frac{E_a}{RT} \right)$ to reacts and proceed the reaction as shown in Eq. (1).

The quantity E_a is called the activation energy and represents the energy barrier for the reaction under consideration.

Figure shows that the reactants have to overcome an activation energy barrier of height E_a to achieve the activated complex state and proceed to products.

The heat of reaction,

ΔH = negative (exothermic reaction) or positive (endothermic reaction), in which case the products C and D have a higher final energy than the reactants.

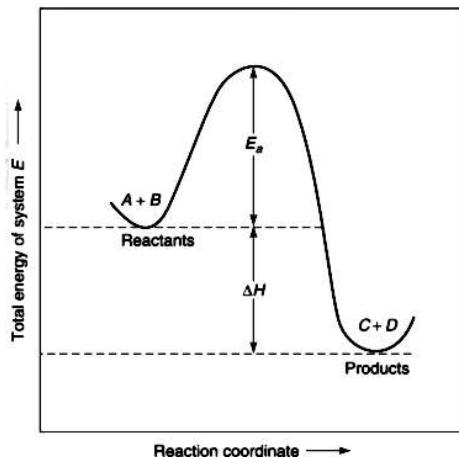


Figure: Activation energy barrier for a chemical reaction.

From these plots, the rate of dissolution and rate of formation can be determined for each temperature. The Arrhenius equation in both instances allows us to calculate the activation energy for both processes by plotting $\ln k_i$ versus $1/T$, with the slope of each line equal to $-E_a/R$.

The equivalent activation energies tell us that the rate of the chemical reaction between these two metals determines the overall rate of TiAl₃ formation.

KINETICS OF PHASE TRANSFORMATIONS IN METALS AND ALLOYS

Consider the isothermal transformation of a disordered (amorphous) solid to an ordered (crystalline) solid. There must be enough thermal energy to allow individual atoms to move around and reorient themselves. It is generally found that at constant temperature, the amount of amorphous material transformed to crystalline material, dx (on a volume basis) per unit time dt , is given by:

$$\frac{dx}{dt} = nk(1-x)t^{n-1} \dots \dots \dots (1)$$

Here the quantity $(1 - x)$ is the fraction of amorphous material remaining, n is the reaction order, t is time, and k is the reaction rate constant.

KINETICS OF METALS AND ALLOYS

Kinetics of Intermetallic Formation: Intermetallic are more like compounds than alloys (which are more like mixtures). Both are composed entirely of metallic elements.

Consider an intermetallic, TiAl₃. The dissolution of elemental titanium, Ti, in molten aluminum, Al, at various temperatures leads to the formation of intermetallic TiAl₃ layers.

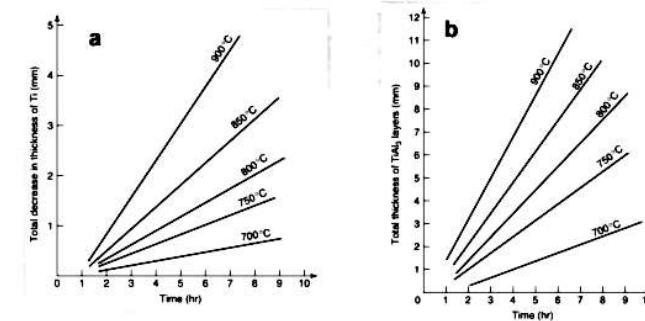


Figure a shows the experimental data for the decrease in thickness of the titanium as a function of time, and Figure b shows the increase in thickness of the titanium aluminide layer with time.

The solution to this equation for the amount of amorphous materials transformed, x , at time t , is known as the Johnson-Mehl-Avrami (JMA) equation:

$$x = 1 - \exp[-kt^n] \dots \dots \dots (2)$$

Taking the natural log of this equation twice yields a useful form of the JMA equation:

$$\ln[-\ln(1-x)] = \ln k + n \ln t \dots \dots \dots (3)$$

Thus, a plot of $\ln[-\ln(1-x)]$ versus $\ln t$ yields a straight line of slope n whose value indicates the reaction order. It has some physical interpretation, depending on whether the crystals are growing at the surface of a material or in the bulk (sometimes called volume crystallization).

Values of the Growth Dimension, n (Reaction Order), for Different Crystallization Processes

Mechanism	n
Bulk nucleation, 3-dimensional growth	4
Bulk nucleation, 2-dimensional growth	3
Bulk nucleation, 1-dimensional growth	2
Surface nucleation	1

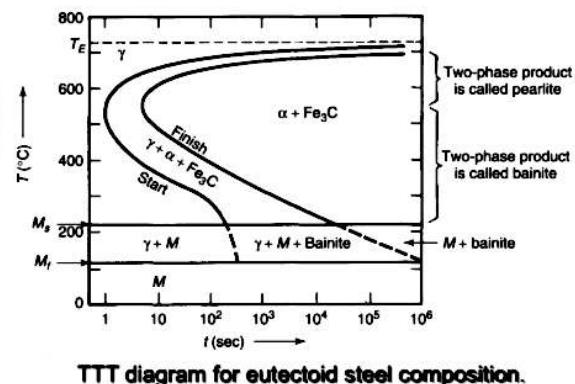
It is difficult to perform complete isothermal experiments even in a controlled laboratory environment. The kinetics of non-isothermal phase transformations are more complex. Some useful relationships have been developed that allow for the evaluation of kinetic parameters under non-isothermal conditions. One such equation takes into account the heating rate, $\dot{\theta}$:

$$\ln[-\ln(1-x)] = n \ln \dot{\theta} + \ln k + \text{constant} \dots \dots \dots (4)$$

An equation developed by Kissinger and modified by others can be used to determine the activation energy using the temperature at which the transformation rate is a maximum T_p for various heating rates:

$$\ln \left(\frac{\dot{\theta}}{T_p^2} \right) = \text{constant} \dots \dots \dots (5)$$

The temperature of the maximum transformation rate is easily determined using either of two similar techniques called differential scanning calorimetry (DSC) or differential thermal analysis (DTA).



The martensitic transformation plays an important role in a special class of alloys called shape memory alloys. These materials have the unique ability to "remember" their dimensions before deformation, and they return to their original shape upon undergoing the martensitic transition. This process is shown schematically in Figure for the one-way shape memory effect (SME).

MARTENSITIC TRANSFORMATIONS

- ✓ Displacive or martensitic transformations where phase transformations in the solid phase are so rapid that they approach the speed of sound. These congruent phase transformations (no change in composition) involve the displacement of atoms over short distances, rather than diffusion.
- ✓ The term "martensitic" comes from this type of transformation that is observed in the cooling of austenitic steel.
- ✓ Martensite is a supersaturated solution of carbon in ferrite with interstitial carbon atoms in the body-centered tetragonal structure that forms when face-centered cubic iron with carbon, called austenite, is rapidly cooled to about 260°C.
- ✓ The amount of austenite transformed to martensite is a function of the temperature only, varying from 0 to 100% between the temperatures M_s and M_f , as indicated in the accompanying time-temperature-transformation (TTT) curve.
- ✓ Martensitic transformations occur in a variety of nonferrous alloy systems, particularly for allotropes that transform at low temperatures. The reasons behind this are that
 - (a) The free energy difference between the high-temperature and low-temperature phases becomes more negative with decreasing temperature,
 - (b) The crystal structures of allotropes are relatively simple and similar to one another.

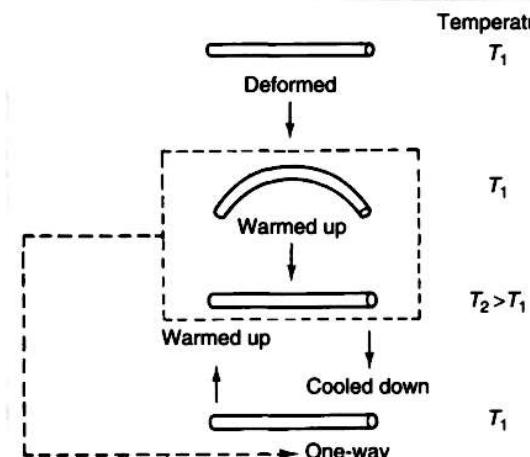
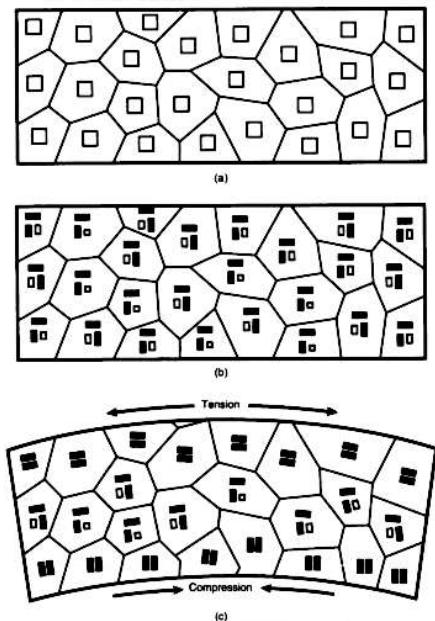


Illustration of the one-way shape memory effect

There is also a two-way shape memory effect. The shape memory effect is the result of a partial ordering of the structure as the BCC to CsCl structure transition takes place.

The martensitic phase is easily deformed, and a distorted multidomain martensite phase results. When the object is reheated, the austenitic phase (BCC in this case) reforms and returns to its original structure. The shape memory effect has been studied for applications ranging from drive shafts that stiffen in response to increased shaft vibration, to orthodontic wires and other potential biomedical uses.

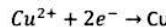


Shape-memory alloys transform from (a) a partially ordered, high-temperature austenitic phase to (b) a mixed austenite-martensite low-temperature state to (c) an ordered mixed-phase state under deformation

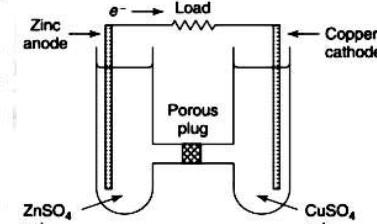
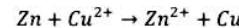
Electrochemical Reactions

Consider a simple galvanic cell, composed of two metal electrodes, zinc and copper, immersed in two different aqueous solutions of unit activity connected by an electrical circuit, and separated by a semipermeable membrane. The membrane allows the passage of ions, but not the bulk flow of the aqueous solutions from one side of the cell to the other. Electrons are liberated at the anode by the oxidation (increase in the oxidation number) of the zinc electrode: $Zn \rightarrow Zn^{2+} + 2e^-$ $e^- \longrightarrow$ Load

Electrons flow through the circuit connecting the two electrodes, and they are consumed at the cathode by the reduction (decrease in oxidation number) of copper ions in solution:



The overall reaction, then, is the sum of these two half-reactions:



Schematic diagram of an electrochemical cell

The remaining salt ions result from the reaction pass from right to left through the semipermeable membrane to balance the charges arising from the zinc ions forming at the anode. Current continues to pass through the circuit, and the zinc electrode slowly dissolves while the copper electrode slowly grows through the precipitation of copper. High-resistance voltmeter between the copper and zinc electrodes measures a potential difference of approximately 1.1 V.

KINETICS OF CORROSION IN METALS AND ALLOYS

Corrosion is the deterioration of a material by reaction with its environment.

A study showed that metallic corrosion costs the U.S. economy about \$300 billion each year and that 30% of this cost could be prevented by using modern corrosion control techniques.

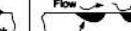
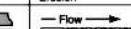
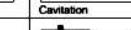
Types of Corrosion: Corrosion is classified into two general categories: macroscopic and microscopic.

- ✓ Macroscopic corrosion is basically "outside-in" corrosion and includes such phenomena as pitting and galvanic (two-metal) corrosion.
 - ✓ Microscopic corrosion is more of an "inside-out" process, where such environmental influences as mechanical stress can cause intergranular corrosion and eventually crack deep within the sample.

Another way to classify corrosion is according to the type of environment—wet versus dry corrosion.

However, the classification system is important.

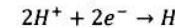
- (a) Recognizing that many different forms of corrosion exist
 - (b) understanding the fundamental kinetic processes behind these different types.

Macroscopic Corrosion	
	
Uniform	Pitting
	
Deposit	Attack Flow Erosion
	
Crevice	Attack Cavitation
	
Galvanic	Load → Movement Fretting
	
Coating	Water Line Attack
	
Filiform Corrosion	

Microscopic Corrosion	
	
Selective Corrosion	Exfoliation
	
Intergranular	End-Grain Attack
(Specific Environment)	(Environment)
	
Stress → → Stress Stress Corrosion Cracking	Cyclic Stress Corrosion Fatigue

Types of corrosion

The half-reactions for most metals have been calculated relative to a standard reference electrode, which is arbitrarily selected as the reduction of hydrogen:



- ✓ The hydrogen electromotive force (EMF) is defined as exactly zero, and all other half-cell EMFs are listed relative to the hydrogen electrode at 25°C.
 - ✓ By convention, the half-cell EMFs are listed as reduction reactions with electrons on the left side of the reaction.
 - ✓ All reactions must be reversible, and the corresponding oxidation potential is found by reversing the reaction and reversing the sign on the voltage.
 - ✓ It is important to note that the EMF potentials do not need to be multiplied by a factor when balancing half-reactions with different oxidation numbers
 - ✓ Most environmental conditions do not allow for the calculation of these potentials at 25°C.; in this case, temperature effects cannot be easily neglected.

Example: A car battery has less "cranking power" on a cold winter morning than it does on a warm summer day.

- ✓ Temperature effects can be taken into account by returning to the free energy, which already accounts for temperature fluctuations.

$$\Delta G - \Delta G^0 = RT \prod_i a_i^{v_i} \dots \quad (1)$$

EXCHANGE CURRENT DENSITY

In this case, the free energy is generated by electrochemical work instead of enthalpies and entropies:

$$\Delta G = -nEF \dots \dots \dots (2)$$

n = number of electrons taking part in the reaction,

F = constant called the Faraday constant (96,500 coulombs/mol)

E = the potential of the half-reaction in volts.

The corresponding standard state free energy:

$$\Delta G^0 = -nE^0 FG^0 \dots \dots \dots (3)$$

The well-known Nernst equation can be obtained by substituting of Eqs. (2) and (3) into Eq. (1) which tells us the electrical potential of a half-cell when the reactants are not at unit activity.

$$E - E^0 = \frac{RT}{nF} \ln(\prod_i a_i^{v_i}) \quad = \text{The Nernst equation}$$

- The electrochemical cell is a combination of two half-cells, with the oxidation reaction occurring at the anode and the reduction reaction occurring at the cathode resulting in a net flow of electrons from the anode to the cathode.
- Equilibrium conditions dictate that the rate of oxidation and reduction, r_{oxid} and r_{red} , be equal, where both rates can be obtained from Faraday's Law:

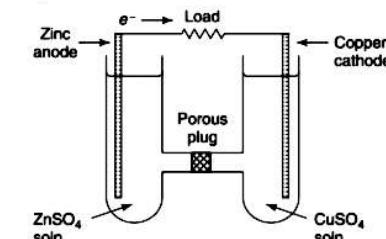
$$r_{oxid} = r_{red} = \frac{i_0}{nF}$$

Here,

F = Faraday constant

n = number of electrons taking part in the reaction,

i_0 = a new quantity called the exchange current density.



Schematic diagram of an electrochemical cell

Exchange current densities are influenced by temperature, surface roughness, and such factors as the ratio of oxidized and reduced species present in the system.

POLARIZATION

The net current flow produced in a cell results in a deviation of each half-cell potential from the equilibrium value which is termed polarization.

$$\eta = E - E^0 = \text{overpotential}$$

There are two primary types of polarization.

Activation polarization:

- is an activated process and possesses an activation barrier.
- There are two parts to the activation process, either one of which can determine the rate of the reaction at the electrode.
- The slowest step, or rate-determining step, can be either
 - (a) electron transfer at the electrode-solution interface or
 - (b) formation of atoms at the electrode surface.

The activation polarization component of the overpotential, η_a is related to the actual rate of oxidation or reduction, i , and the exchange current density:

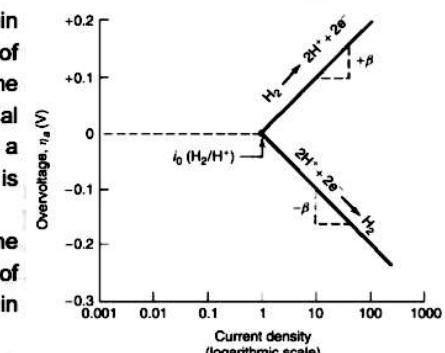
$$\eta_a = \pm \beta \log\left(\frac{i}{i_0}\right) = \text{Tafel equation.} \dots \dots \dots (1)$$

Here, $\beta = \frac{2.3RT}{anF}$ = constant

Here, α is the symmetry coefficient, which describes the shape of the rate-controlling energy barrier.

Tafel equation is represented graphically in the following Figure, the resulting plot of which is called an Evans diagram. The linear relationship between overpotential and current density is normally valid over a range of about ± 50 mV, but linearity is assumed for most Evans diagrams.

- The reaction rate, as represented by the current density, changes by one order of magnitude for each 100-mV change in overpotential.
- At $\eta_a = 0$, the rates of oxidation and reduction are equal, and the current density is given by the exchange current density, $i = i_0$.



Evans diagram showing effect of activation polarization on overpotential for a hydrogen electrode. R

Concentration polarization results from the depletion of ions at the electrode surface as the reaction proceeds.

- A concentration gradient builds up between the electrode surface and the bulk solution.
- The reaction rate is controlled by the rate of diffusion of ions from the bulk to the electrode surface. Hence, the limiting current under concentration polarization, i_L , is proportional to the diffusion coefficient for the reacting ion, D :

$$i_L = \frac{DnFC_0}{x}$$

C_0 = the concentration of reacting ions in the bulk solution,
 x = the thickness of the depleted region near the electrode, or the distance through which the ions must travel from the bulk to the electrode, termed the Nernst diffusion layer.

The overpotential for concentration polarization:

$$\eta_c = \frac{2.3RT}{nF} \log \left(1 - \frac{i}{i_L} \right) \dots\dots\dots (2)$$

CORROSION RATE

The current densities give us an estimate of the rate of the electrochemical reactions involved in corrosion, but they do not give us a direct measurement of the corrosion rate.

A simple, empirical expression can be used to quantify the rate of corrosion in terms of a quantity called the corrosion penetration rate (CPR):

$$CPR = \frac{KW}{\rho AT}$$

where W is the weight loss of the sample per unit time, t .

The variables ρ is the density of the material

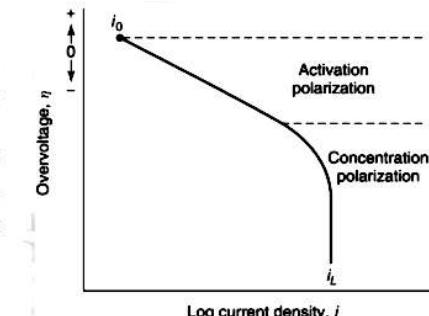
A is the exposed surface area of the sample.

The constant K varies with the system of units being used;

$K=534$ to give CPR in mils per year (mpy, where 1 mil = 0.001 inch),

$K = 87.6$ to give CPR in mm/y

Both activation and concentration polarization typically occur at the same electrode, although activation polarization is predominant at low reaction rates (small current densities) and concentration polarization controls at higher reaction rates.



Effect of activation and concentration polarization on overpotential.

The combined effect of activation and concentration polarization on the current density can be obtained by adding the contributions from each [Eqs. (1) and (2)], with appropriate signs for a reduction process only to obtain the Butler–Volmer equation:

$$\eta_{reduction} = -\beta \log \left(\frac{i}{i_0} \right) + \frac{2.3RT}{nF} \log \left(1 - \frac{i}{i_L} \right) \dots\dots\dots (3)$$

Eqs. (3) allows us to determine the kinetics of most corrosion reactions from only three parameters: β , i_0 , and i_L .

KINETIC PROCESS IN CERAMICS AND GLASSES

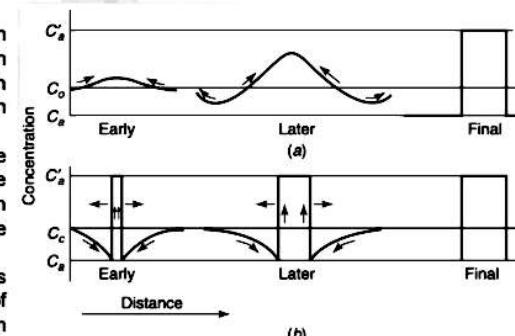
Crystallization depends on two primary phenomena called nucleation and growth.

- ❖ Nucleation is the initial formation of small particles of the product phase from the parent phase. The resulting nuclei are composed of a few molecules.
- ❖ The growth step involves the increase in the size of the nucleated particles.

In the case of martensitic transformations, displacement of a molecule takes place while spinodal decomposition and nucleation and growth processes involve diffusion.

The figure shows a comparison between a spinodal transformation and a nucleation and growth transformation based on composition and spatial extent.

- Spinodal transformations are large in spatial extent but involve relatively small concentration differences throughout the sample,
- The nucleation process involves the formation of small domains of composition very different from the parent phase, which then grow in spatial extent via concentration-gradient-driven diffusion.



Schematic comparison of dimensional changes that occur in (a) spinodal and (b) nucleation and growth transformation processes

NUCLEATION RATE

An overall nucleation rate: $N = v n_s n^*$ (1)

N = the number of critical nuclei that form per unit volume per unit time,
 n_s = the number of molecules in contact with the critical nucleus
 n^* = the number of critical size clusters per unit volume
 v = the collision frequency of single molecules with the nuclei

The number of critical nuclei, n^* can be related to the free energy barrier, ΔG^* through an Arrhenius-type expression:

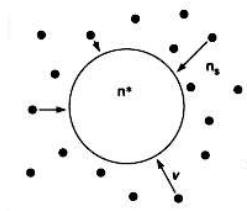
$$n^* = n_0 \exp(-\Delta G^0 / k_B T) \dots \dots \dots (2)$$

n_0 = n_0 the number of single molecules per unit volume,
 k_B = Boltzmann's constant
 T = the absolute temperature.

The collision frequency, v , can be expressed by an Arrhenius relation:

$$v = v_0 \exp(-\frac{\Delta G_m}{k_B T}) \dots \dots \dots (3)$$

v_0 = molecular jump frequency
 ΔG_m = activation energy for transport across the nucleus-matrix interface, which is related to short-range diffusion.



Schematic illustration of a nucleation site formation.

NUCLEATION RATE

Substitution of these two values into the first exponential in Eq. (5) gives us the temperature dependence of the nucleation rate for homogeneous nucleation:

$$N = v_0 n_s n_0 \exp\left[\frac{-16\pi\gamma^3 T^2}{3k_B T \Delta H_v^2 (T_m - T)^2}\right] \exp\left(-\frac{\Delta G_m}{k_B T}\right) \dots \dots \dots (6)$$

Which is more cumbersome than Eq. (4), it contains some directly measurable parameters such as the interfacial surface energy, γ , and the heat of fusion, ΔH_v . It also contains the temperature difference ($T_m - T$) which is the degree of undercooling (temperature is below the melting point).

The two exponentials in Eq. (6) compete against each other. As T decreases below the melting point:

- ($T_m - T$) becomes larger and always a positive value. The term inside the first exponential becomes smaller, but because it is negative, the entire exponential gets bigger and the nucleation rate increases due to this exponential—the driving force for nucleation becomes greater.
- The term in the second exponential becomes more negative, the exponential gets smaller and the nucleation rate decreases due to this exponential term—diffusion becomes more difficult as the temperature decreases and particles cannot migrate to the nucleation surface

NUCLEATION RATE

Putting these expressions back into Eq. (1) gives

$$N = v n_s n_0 \exp\left(-\frac{\Delta G^*}{k_B T}\right) \exp\left(-\frac{\Delta G_m}{k_B T}\right) \dots \dots \dots (4)$$

For heterogeneous nucleation, we simply use ΔG_s^* instead of ΔG^* :

$$N = v_0 n_s n_0 \exp\left(-\frac{\Delta G_s^*}{k_B T}\right) \exp\left(-\frac{\Delta G_m}{k_B T}\right) \dots \dots \dots (5)$$

Eqs. (4) and (5) describe the rate at which nuclei form as a function of temperature. n_s and n_0 have dimensions of number per unit volume, and v_0 has units of time^{-1} .

By making some simplifications and assumptions, Eqs. (4) and (5) can give idea about some measurable, physical properties of the system. The free energy for homogeneous nucleation is given by:

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$$

For liquid-solid transitions at temperatures close to T_m ,

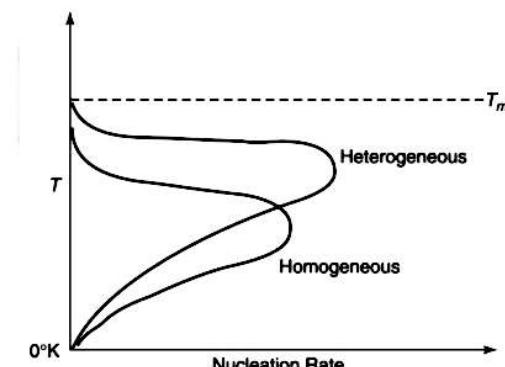
$$\Delta G_v = \frac{\Delta H_v(T_m - T)}{T_m}$$

ΔH_v = heat of transformation per unit volume.

NUCLEATION RATE

These generalizations are true for both homogeneous and heterogeneous nucleation. As a result, the two competing exponentials give rise to a maximum nucleation rate at some temperature below the melting point as illustrated in Figure.

- The heterogeneous nucleation has a higher absolute nucleation rate than homogeneous nucleation.
- The heterogeneous occurs at a higher temperature (lower degree of undercooling) than homogeneous nucleation.



Effects of temperature and undercooling on homogeneous and heterogeneous nucleation rates.

GROWTH

The tiny nuclei grow into large crystals through the addition of molecules to the solid phase. There are two primary types of crystal growth:

- ✓ thermally activated (diffusion-controlled)
 - ✓ diffusionless (martensitic).

The development of the proper growth rate expression is highly dependent upon the type of phase transformation—that is, crystallization from the melt, vapor phase, or dilute solution. The growth rate expression is based upon an Arrhenius-type expression:

$$\mathbb{R} = A \left[1 - \exp\left(\frac{\Delta G}{k_B T}\right) \right] \dots \dots \dots (1)$$

R = the growth rate.

ΔG = the molar free energy difference between the product and parent phase

A = a preexponential factor that depends on the type of theory one wishes to employ. It can be directly related to the liquid phase viscosity, as in $A = \eta a_0$.

$$v = \frac{k_B T}{3\pi a^3 \eta}$$

= the frequency factor for transport across the interphase.

η = the viscosity of the liquid phase; a_0 = molecular diameter;

If A related to the diffusivity of atoms across the interphase, as in $A = KD$

$K = \text{constant}$

$D = D_{\text{exp}}(-\Delta H^0/k_B T)$ = the diffusivity of atoms jumping across interphase

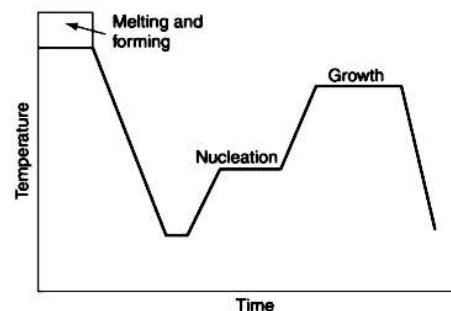
These two expressions are quite similar since D and n are interrelated.

PHASE TRANSFORMATION RATE

The breaking down of the liquid to solid phase transformation into two separate steps, nucleation, and growth, is not entirely artificial. An interesting application of the distinct nature of the nucleation and growth processes is found in the formation of glass ceramics.

The Figure shows that certain glass-forming inorganic materials can be heat-treated in very controlled ways to affect the structure of the crystals that form.

- A glass can be rapidly cooled below its melting point, and then heated to the maximum nucleation rate, which (recall) is below both the melting point and the maximum growth rate.
 - At this temperature and with sufficient time, many small nuclei will be formed.



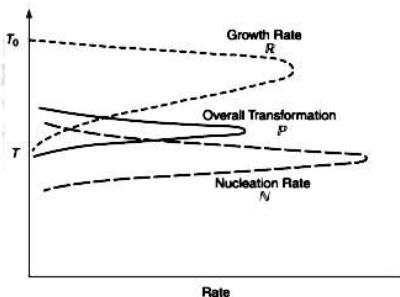
Schematic time-temperature cycle for the controlled crystallization of a glass-ceramic body

PHASE TRANSFORMATION RATE

The overall transformation rate is the product of the nucleation and growth expressions: $P = N \times R$

Where, $N = v_0 n_s n_0 \exp\left(-\frac{\Delta G_s^*}{k_B T}\right) \exp\left(-\frac{\Delta G_m}{k_B T}\right)$, $\mathbb{R} = A \left[1 - \exp\left(\frac{\Delta G}{k_B T}\right)\right]$

The overall transformation rate is shown qualitatively in Figure. The maximum nucleation rate occurs at a lower temperature than the maximum growth rate, and the maximum transformation rate may not be at either of these two rate maxima. There is some finite transformation rate, even at very low temperatures. That is why some glasses can crystallize over very long periods. As long as there is some molecular motion, there is a probability of crystallization taking place.



Schematic representation of transformation rates involved in crystallization by nucleation and growth kinetics

- Then the glass replete with many tiny nuclei is heated to the maximum growth rate temperature and held there while the crystals grow.
 - Though the crystals can only grow so large, they soon run into another growing crystal from a neighboring nucleation site.
 - In this way, the size of the crystals, or crystallites can be controlled in the glass and a glass ceramic is formed.

Properties of Glass-ceramics:

- ✓ they are crystalline materials but are transparent in many cases.
 - ✓ They possess unique physical properties, such as low thermal expansion, due to the large amount of interphase relative to the same material made of larger crystals.
 - ✓ In the extreme, crystallites on the order of 10^{-9} meters in diameter can be formed, resulting in so-called nanostructured ceramics.
 - ✓ These nanostructured ceramics materials also have unique physical properties, which may lead to improved ductility and thermal properties in ceramics.

KINETICS OF CERAMIC AND GLASS CORROSION BY LIQUIDS

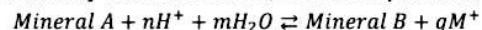
Heterogeneous dissolution:

Indirect dissolution, or incongruent dissolution occurs through the formation of a reaction product between the solid and the solvent. This reaction product is generally less soluble than the bulk ceramic solid, and it may form an attached surface layer on the solid. The interfacial layer formation, diffusion through the interfacial layer, or diffusion through the liquid determine the rate-limiting step of this corrosion.

Homogeneous dissolution:

Direct dissolution or congruent dissolution occurs when the solid, crystalline ceramic material dissolves directly into the liquid through dissociation or reaction. The concentrations of the ceramic species in solution and diffusion coefficients of the species, determine the rate of direct dissolution.

Minerals dissolve into aqueous solutions through the diffusion of leachable species into a stationary thin film of water, about 110 µm thick.



M^+ is the soluble species. The equilibrium constant for this equation:

$$K = \frac{[M^+]^q}{[H^+]^n [H_2O]^m}$$

Here the solids species (minerals) have unit activity. In dilute solutions and at low pressure (1 atm), the activity of water is also approximately unity. At higher pressures, the activity of water is approximately proportional to the pressure.

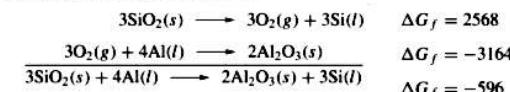
It is evident from the equilibrium constant relationship:

- the dissolution of ceramics is highly dependent upon the pH ($[H^+]$) of the aqueous medium.
- Generally, at low pH values (acidic environments) the equilibrium shifts to the right, and corrosion is promoted.
- At high pH values (basic environments) retard corrosion by shifting the equilibrium back to the left.
- Not all ceramic materials behave the same at a given pH.

Corrosion in liquid media is highly dependent on the chemical nature of the liquid, such as; molten metal, molten ceramic, or aqueous solution. Usually, two industrially important cases have been considered:

1. attack by molten metals
2. attack by aqueous media.

The attack of most metal oxide ceramics by molten metals involves a simple exchange of one metal ion for another. For example, silicon dioxide in contact with molten aluminum is susceptible to the following corrosion reaction:

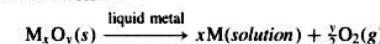


The free energy of reaction, ΔG of this exchange is the summation of the free energy of formation for the individual oxides.

Another way in which molten metal can attack an oxide is through compound formation, such as the formation of spinel which has a lower free energy of formation (-218 kJ/mol at 1000° C) compared to the simple oxidation-reduction reaction (-118 kJ/mol).



It is also possible that the molten metal can completely reduce the metal oxide ceramic, forming an alloy and gaseous oxygen:

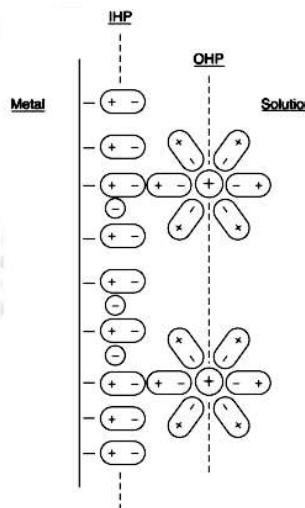


When the material begins to dissolve, ions form at the surface, water molecules orient themselves accordingly, and an electrical double layer is established. The first layer of charged ions and oriented water molecules is called the inner Helmholtz plane (IHP), and the second layer of oppositely charged particles is called the outer Helmholtz plane (OHP). The potential established between these two layers decreases from the surface into the solution. The extent to which this double layer is established and the magnitude of the charge on the surface is directly related to the pH of the surrounding solution. The pH value for which there is no net surface change is called the isolectric point (IEP).

$$IEP = 18.6 - 11.5z/d$$

z = oxidation state of the cation in the film

d = distance (in angstroms) of an adsorbed proton from the cation via the oxygen ion.



Formation of the electrical double layer of a surface in solution, showing the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP).

The hydrolysis of silicate glasses is also considered as the attack of polycrystalline ceramic materials by aqueous media. The effect of time and temperature on the acid corrosion (10% HCl) of silicate glasses has been developed to describe by the equation: $W = at^{b_1} \exp(-b_2/T)$

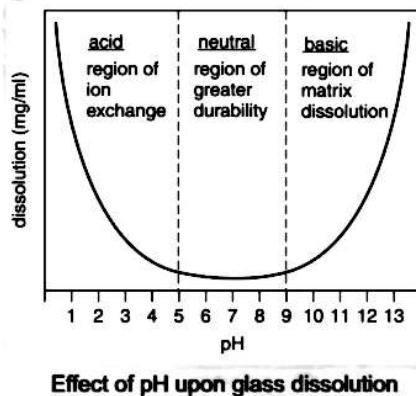
Here W = the weight loss, t = time, T = temperature,
 a , b_1 , and b_2 = are experimentally determined coefficients.

Glass dissolution rates are also a strong function of pH.

There are two competing mechanisms in glass dissolution:

- Ion exchange where the metal–oxygen bond is coordinated with hydrogen ions.
- Matrix dissolution where the metal–oxygen bond is coordinated to hydroxyl ions.

The corrosion of glasses affects their mechanical properties and determines their useful service lifetime on an industrial scale.



Case -1: when the total pressure of the system determines the rate-limiting step.

- ✓ At low pressure ($< 10^{-4}$ atm), gas transport is "line-of-sight" and the surface reaction might be rate-controlling.
- ✓ At intermediate pressure ($10^{-4} - 10^{-1}$ atm), bulk diffusion is usually rate-limiting.
- ✓ At high pressure ($> 10^{-1}$ atm), the layer formed at the surface controls the overall rate.

For gases, the concentration is related to the partial pressure of component A , P_A , which gives the functional dependence of corrosion rate on pressure.

Case-2: When the chemical reaction occurring at the surface is the rate-limiting step.

- ✓ The reaction rate can have any order, and the gas reacts with the ceramic substrate to produce products.
- ✓ Both oxide ceramics, and non-oxide ceramics (such as carbides, nitrides, or borides) undergo common decomposition reactions in the presence of oxygen.
- ✓ These ceramics are particularly susceptible to corrosion since they are often used at elevated temperatures in oxidizing and/or corrosive environments.

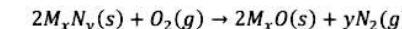
KINETICS OF CERAMIC AND GLASS CORROSION BY GASES

The attack of ceramics and glasses by gaseous reactants is much more prevalent than corrosion due to liquids. The corrosion rate can be limited by any number of steps in the dissolution process:

- Diffusion of the gas to the solid.
- Adsorption of the gas molecule onto the solid surface.
- Surface diffusion of the adsorbed gas.
- Decomposition of reactants at surface sites.
- Reaction at the surface.
- Removal of products from reaction sites.
- Surface diffusion of products.
- Desorption of gas molecules from the surface.
- Diffusion of products away from the solid.

Most of the possible rate-limiting steps involve the movement of atoms—diffusion, adsorption, desorption, and only one direct chemical reaction.

Example: metal nitrides can be oxidized to form oxides:



Here, the reaction rate, r is a function of the partial pressure of the gaseous species, P_i , since solids are taken to have unit activity:

$$r = kP_{N_2}^y/P_{O_2}$$

The chemical composition of the build surface changes over the course of the reaction. The diffusion of species back through this surface reaction layer or boundary layer becomes the rate-limiting step.

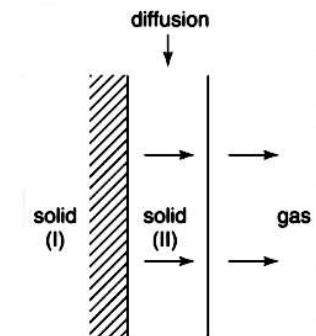
The kinetics are associated with the growth of this boundary layer. For thin reaction films ($< 5\text{ nm}$), the film thickness changes with time according to one of three general forms: logarithmic, inverse logarithmic, or asymptotic.

$$\begin{aligned} x &= k_1 \log t \\ \frac{1}{x} &= k_2 - k_3 \log t \\ x &= k_4 [1 - \exp(-k_5 t)] \end{aligned}$$

For thick films ($> 5\text{ nm}$), the film thickness follows either a parabolic or rectilinear relationship with time.

$$x^2 = k_6 t \text{ and } x = k_7$$

Here, k_i are the reaction rate constants.



Diffusion of reaction products through the boundary layer.

KINETICS OF POLYMERIZATION

Polymerization reactions are generally grouped into:

Stepwise (also known as condensation) reactions: Condensation reactions are characterized by the reaction of two functional groups that result in the loss of a small molecule. Thus, the repeat unit has a different molecular formula than the monomer from which it was formed. The small molecule formed during condensation is often water, though the specific formation of water is not a necessity for a condensation reaction.

Radical chain (sometimes called addition) reactions, depending upon the nature in which the monomers react with each other or with growing polymer chains to form higher-molecular-weight structures. Addition polymerizations are those in which no loss of a small molecule occurs. This type of polymerization reaction usually requires an active center, such as a free radical or an ion, to proceed.

The kinetics of this reaction are analyzed by monitoring the disappearance of one of the reactants, or the formation of the product. The rate expression for a catalyzed reaction to follow the disappearance of the adipic acid:

In the absence of an added strong acid, the reaction is self-catalyzed by a second molecule of the adipic acid, so the reaction is second order in acid:

In case of equal amounts of diamine and diacid, the duration of the reaction are same $[COOH] = [NH] = c$, and a second-order differential equation:

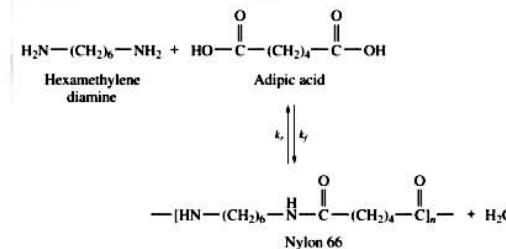
$$\frac{1}{c} = kt + \text{constant} \dots \dots \dots (4)$$

The fraction of functional groups reacted at any time is called the extent of reaction, $p = (c_0 - c)/c_0$.

c_0 is the initial concentration.

KINETICS OF STEPWISE POLYMERIZATION

Consider the reaction of hexamethylene diamine and adipic acid:



- There is the characteristic loss of a small molecule for stepwise reactions. In the above reaction, it is water, and the loss of water results in an amide ($HN - CO$) linkage; hence the resulting polymer is called a polyamide. This particular polyamide's trade name is **nylon**.
 - Nylon is named depending on the exact formula of the diamine and diacid used to form the polyamide.
 - **Nylon 66** contains six carbon units between the nitrogens in the diamine and six carbon units (including the carbons which contain the double-bonded oxygens) in the diacid.

In terms of the extent of reaction, the rate expression becomes:

$$c_0 kt = \frac{1}{1-n} + constant \dots \dots \dots (5)$$

The quantity $1/(1-p)$ is called the number-average degree of polymerization, \bar{x}_n , which represents the initial number of structural units present in the monomer relative to the total number of molecules. Both monomer and polymer chains, present at any time t :

Note that the degree of polymerization increases linearly with time.

CHARACTERISTICS OF STEPWISE AND ADDITION POLYMERIZATION REACTIONS

Stepwise Polymerization	Addition Polymerization
Any two molecular species present can react	Only growth reaction adds repeating units one at a time to the chain
Monomer disappears early in the reaction	Monomer concentration decreases steadily throughout the reaction
Polymer molecular weight rises steadily throughout the reaction	High polymer is formed immediately, polymer molecular weight changes little throughout the reaction

KINETICS OF ADDITION POLYMERIZATION

Addition polymerizations proceed with the addition of many monomer units to a single active center on the growing polymer chain. There are many types of addition polymerizations (such as anionic, cationic, and coordination polymerizations). Among many types of active centers, the most common active center is a radical, usually formed at a double bond in the monomer. As a result, addition polymerizations are sometimes called free radical polymerizations. Vinyl polymerization provides a good example of the kinetics of addition polymerizations.

If the fraction of radicals formed in the dissociation step leads to successful radical chains then the rate of initiation is given by the change in initiated monomer concentration with time:

$$\frac{d[M\bullet]}{dt} = 2fk_d[I] \dots \dots \dots (1)$$

Here, $[I]$ is the concentration of the initiator

$[M\bullet]$ is the radical concentration.

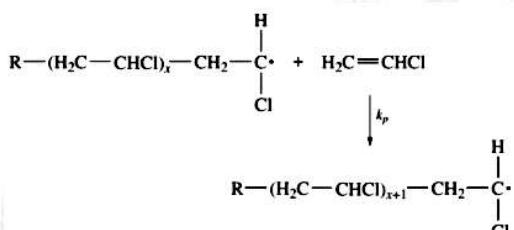
Propagation:

- After the initiation of the monomer radical, high polymer is formed through the addition of monomer units to the radical in the propagation phase of the polymerization.
- Each time a monomer unit is added, the radical transfers to the end of the chain to allow the polymerization to continue:

The rate expression for propagation is given by the rate of monomer disappearance:

$$-\frac{d[M]}{dt} = k_p[M][M\bullet] \dots \dots \dots (2)$$

where $[M]$ is the instantaneous monomer concentration.



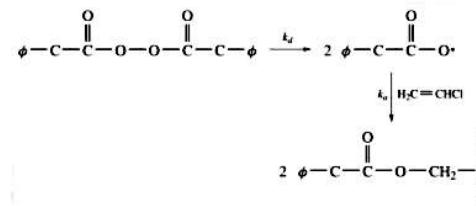
RADICAL POLYMERIZATION

- In the 1930s, Paul Flory showed that radical polymerizations generally consist of three distinct steps: initiation, propagation, and termination.
 - The free radical must first be initiated, then must propagate through the addition of monomers to the chain, and must eventually be terminated, either through consumption of the monomer or through the addition of an agent that kills the free radicals.
- Initiation of radicals:**
- ✓ There are many ways to initiate radicals, such as ultraviolet radiation, electrochemical initiation, or oxidation-reduction reactions.
 - ✓ The most common is the addition of an initiator that transfers its radicals to the monomer to begin the polymerization. Benzoyl peroxide, are common initiators that can transfer its radical to a monomer unit:

where ϕ is a phenol group.

Most of these initiators have efficiencies of between 60% and nearly 100%.

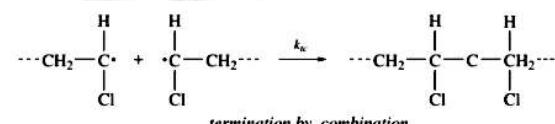
Recombination of the radical pairs is the most common cause of low efficiency.



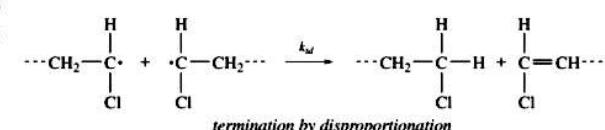
It is assumed that the rate constant for propagation, k_p , is the same for all propagation reactions in which a monomer is added to a growing radical chain, regardless of the molecular weight of the chain.

Termination:

The propagation reactions proceed at multiple radical sites until the monomer is exhausted, or until combination or disproportionation types of termination reactions occur:



Each of these termination reactions has a similar rate expression that is second order in radical concentration.



The overall termination rate can be expressed as the rate of disappearance of the radicals due to both types of termination:

$$-\frac{d[M\bullet]}{dt} = 2k_t[M\bullet]^2 \dots \dots \dots (3)$$

In the case of chain transfer reactions, the radical is transferred from a growing polymer chain to a small molecule such as the initiator or a solvent molecule. These so-called chain transfer agents are often deliberately added to the reaction mix to either control the rate of the reaction or create branched polymers. The rate of the reaction can also be controlled with inhibitors or retarders. These additives also serve to help control the molecular weight of the polymer chain.

$$\text{The rate of disappearance of monomers: } \frac{-d[M]}{dt} = \sum k_{tr,i}[A][M] \quad (4)$$

$k_{tr,i}$ = the rate constant

[M] transfers radical to agent instead of adding monomer to continue chain

A = May be an initiator, a solvent, a monomer, or a chain-transfer agent

In the steady-state condition, the rate of initiation is equivalent to the rate of radical termination, and the radical concentration, [M], remains essentially constant with time. Therefore, from $\frac{d[M]}{dt} = 2fk_d[I]$ and $\frac{-d[M]}{dt} = 2k_t[M]^2$

$$[M] = \left(\frac{fk_d[I]}{k_t} \right)^{1/2} \quad (5)$$

The simplified form of overall rate expression for addition polymerization is:

$$\frac{1}{x_n} = \frac{\gamma k_t[M]^2 + \sum_i k_{tr,i}[A][M]}{k_p[M][M]} = \frac{\gamma k_t[M]}{k_p[M]} + \sum_i \left(\frac{k_{tr,i}[A]}{k_p[M]} \right)$$

By using the value of [M], a general expression for the instantaneous degree of polymerization as a function of rate constants and concentrations is:

$$\frac{1}{x_n} = \frac{\gamma fk_d k_t^{1/2}[I]}{k_p[M]} + \sum_i \left(\frac{k_{tr,i}[A]}{k_p[M]} \right) \quad (8)$$

The first term $\frac{\gamma fk_d k_t^{1/2}[I]}{k_p[M]}$ is the inverse of the degree of polymerization that would occur in the absence of chain transfer, $(\bar{x}_n)_0$.

The second term $\sum_i \left(\frac{k_{tr,i}[A]}{k_p[M]} \right)$ represents the effect of different chain transfer agents on the molecular weight.

Using the value of [M], the overall rate expression for addition polymerization:

$$\frac{-[M]}{dt} = k_p \left(\frac{fk_d[I]}{k_t} \right)^{1/2} [M] \quad (6)$$

For condensation-type reactions, there is a number-average degree of polymerization, \bar{x}_n

$$\bar{x}_n = \frac{\text{rate of growth}}{\sum \text{rates of reactions leading to dead polymer}}$$

Using the rate of growth equation, sum of reaction rates leading to dead polymer come from termination and chain transfer reaction:

$$\bar{x}_n = \frac{k_p[M][M]}{\gamma k_t[M]^2 + \sum_i k_{tr,i}[A][M]} \quad (7)$$

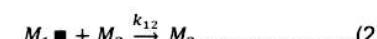
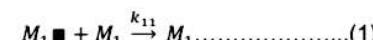
Here, $\gamma = 1$ for termination by coupling
 $= 2$ if termination is by disproportionation

Note that two dead polymer molecules are formed in the latter reaction but only one dead polymer molecule is formed in coupling.

KINETICS IN THE POLYMERIZATION OF COPOLYMERS

- A copolymer is a polymer composed of two or more different repeat units—the result of the simultaneous polymerization of two or more monomers.
- The most interesting copolymerization is of the free radical type. Because the reactivity of the radicals depends on the structure of the monomer to which they are attached. Such changes in reactivity between monomers are not generally found in condensation-type reactions.
- In chain polymerizations, the monomers can add to the growing chain in different ways at different rates.

Let us examine the simple system of two monomers M_1 and M_2 that are initiated to form radicals $M_1\bullet$ and $M_2\bullet$. There are four ways in which a monomer can add to a growing chain and four corresponding rate expressions:



The rate of disappearance of each monomer is:

$$\frac{-d[M_1]}{dt} = k_{11}[M_1][M_1] + k_{21}[M_2][M_1] \dots \dots \dots (5)$$

$$\frac{-d[M_2]}{dt} = k_{12}[M_1][M_2] + k_{22}[M_2][M_2] \dots \dots \dots (6)$$

The monomer reactivity ratio for monomer 1 and 2 are $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ respectively. The following relationship is known as the copolymer equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_1[M_1] + r_2[M_2])}. \quad (7)$$

Some special cases that are more easily described by introducing two types of ratios.

The first ratio is E_1 , the rate of change of monomer M_1 mole fraction.

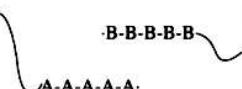
$$F_1 = \frac{d[M_1]/dt}{d[M_1]/dt + d[M_2]/dt} \dots \quad (8)$$

Similarly,

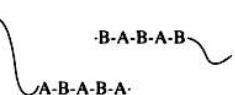
$$F_2 = \frac{d[M_2]/dt}{d[M_1]/dt + d[M_2]/dt} \dots \quad (9)$$

This form of the copolymer equation allows us to identify several simplifying cases:

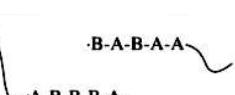
1. k_{12} and k_{21} are negligible; that is, a radical prefers to react with its monomer, and no copolymer is formed—only homopolymer.



2. k_{11} and k_{22} are negligible; that is, a radical prefers to react with the other monomer, $F_1 = F_2 = 0.5$, and a perfectly alternating copolymer is formed.



3. $k_{11} \approx k_{12}$ and $k_{22} \approx k_{21}$; $r_1 = r_2 = 1$; $F_1 = f_1$, and a perfectly random copolymer is formed.



4. if $r_1 r_2 = 1$, Equⁿ 12 becomes, $\frac{F_1}{1-F_1} = \frac{r_1 f_1}{1-f_1}$

The second useful ratio is the instantaneous concentration of a given monomer,

f_1 or f_2 :

It is important to distinguish between the concentration ratio, f_i , and the rate of change of concentration, F_i , since if monomers M_1 and M_2 are consumed at different rates, then $F_i \neq f_i$. Substitution of these ratios F_1 , F_2 , f_1 and f_2 into the copolymer equation gives

$$\frac{F_1}{F_2} = \frac{\binom{r_1 f_1}{f_2} + 1}{\binom{r_2 f_2}{f_1} + 1} \dots \dots \dots (11)$$

POLYMERIZATION PROCESSES

In the case of a polymer, Both kinetic principles and different methods of polymerization are important as heat generation and removal, can affect the polymerization kinetics. There are four common polymerization processes: bulk polymerization, solution polymerization, suspension polymerization, and emulsion polymerization.

Bulk Polymerization

- ✓ Monomer and polymer (with traces of initiator) are the only constituents in bulk polymerizations where the monomer must be soluble in the polymer to effectively proceed.
 - ✓ Bulk polymerization, also called mass or block polymerization, can occur in stirred-tank reactors or can be unstirred, in which instance it is called quiescent bulk polymerization.
 - ✓ The primary difficulty with bulk polymerizations is that the viscosity increases with the polymerization proceeds but thermal conductivity decreases. As a result heat removal becomes difficult.
 - ✓ Slow heat removal increases the temperature along with a corresponding increase in the reaction rate. This phenomenon is known as the autoacceleration or Trommsdorff effect and can lead to catastrophic results if not properly controlled.

- However, it is difficult to remove the traces of remaining monomer from the polymer due to decreased diffusion. Similarly, it is difficult to get the reactions to proceed to completion due to limited monomer mobility.
- A bulk polymerization reactor can be a tube into which the reactants are fed and from which the polymer mixture emerges at the end; it can be more of a traditional, continuous stirred-tank reactor (CSTR), or even a high-pressure autoclave-type reactor. A bulk polymerization process need not be continuous, but it should not be confused with a batch reaction.

Solution Polymerization:

- can proceed by adding a solvent to the monomer–polymer mixture whether heat removal can be improved dramatically over bulk reactions.
- The solvent must be removed after the polymerization is completed which leads to a primary disadvantage of solution polymerization.
- Another problem associated with radical chain polymerizations carried out in solution is associated with chain transfer to the solvent.
- Chain transfer can significantly affect the molecular weight of the final polymer and dominates over chain transfer to other types of molecules.

Suspension Polymerization:

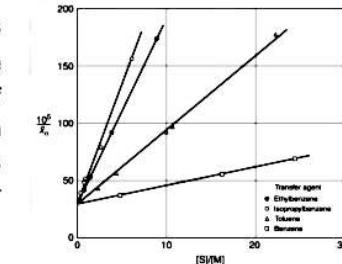
- ✓ Suspension polymerization has been employed when the monomer is insoluble in water solvent.
- ✓ The monomer and initiator form small droplets within the aqueous phase, and polymerization proceeds via bulk polymerization.
- ✓ Droplet sizes are typically between 10 and 1000 μm in diameter. Therefore, heat transfer to the suspending medium and subsequently to the reactor walls becomes efficient throughout the course of the reaction. The result of the polymerization within each of the droplets is a polymer “bead.”
- ✓ Though a few agglomerations of particles take place, the addition of a suspending agent (~ polyvinyl alcohol) minimizes coalescence, and the final polymer bead diameters are typically 100–1000 μm .
- ✓ The polymer beads are recovered by filtration, which is followed by a washing step. Suspension polymerization can be carried to nearly 90% completion at moderate pressures of 600 kPa and 80 °C with stirring at about 150 to 300 rpm.

- Therefore the degree of polymerization becomes:

$$\frac{1}{x_n} = \left(\frac{1}{x_n} \right)_0 + \frac{C_s[S]}{[M]}$$

where the first term describes the contributions of propagation to the molecular weight. $[S]$ and $[M]$ are concentrations of the solvent and monomer, respectively, and C_s is the ratio of rate constants $k_{tr,s}/k_p$.

- This equation shows that a plot of $\frac{1}{x_n}$ versus $[S]/[M]$ should yield a straight line, the intercept for which gives the degree of polymerization in the absence of chain transfer to solvent. This relationship has been borne out experimentally for polystyrene and several solvent systems.



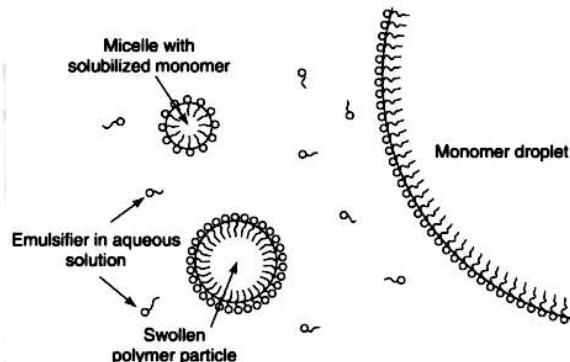
- The reactor equipment used for solution polymerizations is typically glass-lined stainless steel. Typical reaction conditions for this polymerization are 150–180 °C and 2.1–4.8 MPa.

Emulsion Polymerization:

- ✓ In emulsion polymerization, the monomer is insoluble in the solvent, water. Here, the initiator is water-soluble, the particles in which the propagation step occurs are smaller, typically 0.05–5 μm in diameter. The final beads are not usually filtered from the aqueous solution.
- ✓ The emulsifier, or surfactant, plays a very important role in emulsion polymerization. It is usually a long-chained hydrocarbon with a hydrophilic “head” and hydrophobic “tail.” This charge polarization causes the tails to surround the monomer molecules, with the heads pointing outward into the water phase, forming a spherical droplet called a micelle.
- ✓ As radicals initiate in the aqueous phase, they react with a few monomer molecules that are dissolved in the water. As the radicals slowly grow and become more hydrophobic, they become more stable inside of the micelles.
- ✓ Upon entering a micelle, the radicals cause rapid propagation and the micelle expands. It can be shown that the degree of polymerization in emulsion polymerization can be derived by neglecting chain transfer:

$$\frac{1}{x_n} = \frac{2fk_d[I]}{k_p[M^+][N^+]}$$

The superscript “+” on the monomer concentration indicates that this is the concentration of monomer in the micelle, not the solution. $[N^+]$ is the concentration of micelle-swollen polymer particles.



Schematic representation of micelle formation in emulsion polymerization

- ✓ The final product of emulsion polymerization is an emulsion —a stable, heterogeneous mixture of fine polymer beads in an aqueous solution, often called a latex emulsion.
- ✓ The rate at which heat can be removed limits the rate at which monomers can be added.
- ✓ Co-polymerizations can also be carried out in an emulsion reaction.

COMPARISON OF POLYMERIZATION PROCESSES

Type	Advantages	Disadvantages
Batch bulk	Minimum contamination Simple equipment	Poor heat control Broad MW distribution
Continuous bulk	Better heat control Narrower MW distribution	Requires stirring, separation, and recycle
Solution	Good heat control Direct use of solution possible	Not useful for dry polymer
Suspension	Excellent heat control Direct use of suspension possible	Solvent removal difficult Requires stirring Contamination by stabilizer possible Additional processing (washing, drying) required
Emulsion	Excellent heat control Narrow MW distribution High MW attainable Direct use of emulsion possible	Contamination by emulsifier likely Additional processing (washing, drying) required

Gas-Phase Polymerization:

- ✓ Not all polymerization reactions are carried out in the liquid phase. Gas-phase polymerization is needed to eliminate costly solvent and catalyst recovery equipment.
- ✓ A fluidized bed reactor is used whose pressure is about 2 MPa and the temperature is 85–100° C.
- ✓ Heat is removed as gas is circulated using external coolers.
- ✓ The growing particles remain in the reactor for 3–5 hours and emerge with an average diameter of about 500 µm.
- ✓ Small amounts of catalyst are used, so catalyst removal is often not necessary. Hydrogen is used as a chain transfer agent, and branching can be introduced by the addition of 1-butene.

KINETICS OF POLYMER DEGRADATION

Degradation of polymers occurs by the environment which involves the breaking of primary bonds, leading to reduced molecular weight and altered physical properties. There are six primary classes of polymer degradation: thermal, oxidative, radiative, chemical, mechanochemical, and biological.

Thermal Degradation: A polymer chain depolymerizes, or unzips. Like the formation reactions, there is initiation, chain transfer, and termination. Once a free radical has been initiated through some sort of random or chain-end scission process, the de-propagation step proceeds, and monomer fragments split off from the polymer chain in a stepwise manner. The monomer fragments are usually assumed to be volatile.

Oxidative Degradation: In this case, the degradation is highly dependent upon the type of polymer being considered and the presence of additives, inhibitors, and antioxidants. Usually, the diffusion of oxygen is rapid and is therefore not the rate-limiting kinetic step. Here, the process also begins with an initiation step by the formation of radicals which react with atmospheric oxygen. The oxidized radicals can then react with another polymer chain which is the propagation step. Then the rapid termination reactions proceed with low activation energies.

Radiative degradation in polymers can give rise to both low-molecular-weight species which are insoluble and infusible. Crosslinking leads to an increase in the molecular weight of the sample and is considered a degradative process since the resulting product has unfavorably altered physical properties.

There are generally two types of radiative degradation processes in polymers, grouped according to the amount of radiant energy involved and which result in different types of degradation.

- ✓ Photolysis occurs when ultraviolet light ($\lambda = 10^2 - 10^4 \text{ Å}$) imparts energy on the sample of the order $10^2 - 10^3 \text{ kJ/mol}$.
- ✓ Radiolysis occurs when higher radiant waves ($\lambda = 10^{-3} - 10^2 \text{ Å}$) impart the energy of the order $10^5 - 10^{10} \text{ kJ/mol}$ to the sample.

Chemical Degradation is the most important type of polymer degradation. It encompasses degradation due to both gaseous and liquid species on all polymer classes where slight changes in the chain chemistry can lead to enormous changes in chemical compatibility. The chemical degradation occurs in the presence of an appropriate polymer for a specific chemical environment.

Biological degradation in polymers is oftentimes advantageous. There is a class of polymers that have been developed to enhance their susceptibility to attack by biological agents to improve their biodegradability and reduce their long-term impact on the environment. Other important applications of biodegradable polymers are biomaterials, such as resorbable sutures, and controlled drug delivery devices.

There are generally two types of polymeric materials that are susceptible to biological agents such as water, enzymes, and microbes:

- (a) Natural materials like collagen, cellulose, and starch
- (b) synthetic polymers that can be optimized in terms of mechanical properties and rate of degradation for biological and biomedical applications

Mechanochemical Degradation occurs in polymers as the result of an applied mechanical force. This type of degradation is quite common in machining processes such as grinding, ball milling, and mastication. The degradation processes also follow the same fashion in that radicals are formed and cause subsequent reactions, such as oxidation and chain transfer, that can lead to either crosslinking or a reduction in molecular weight.

There are some unique aspects of mechanochemical degradation. Radical formation is nonrandom, and the location of chain scission depends on how the forces are applied to the polymer. Also, the molecular weight decreases rapidly from an initial degree of polymerization for polymers under mechanical shear, then levels off to a limiting degree of polymerization.

In addition to a reduction in molecular weight, mechanical forces generally lead to an increase in solubility, a narrowing of the molecular weight distribution, decreased tensile strength, decreased crystallinity, and increased plasticity. These effects are highly dependent upon the machining conditions (such as higher temperature, and decreased viscosity), the presence of radical scavengers, and the type of machining equipment.

KINETIC PROCESSES IN COMPOSITES

- ✓ Since industrial composites are made up of combinations of metals, polymers, and ceramics, the kinetic processes involved in the formation, transformation, and degradation of composites are the same as those of the individual components.
- ✓ Two gas-phase processes such as chemical vapor deposition (CVD) and chemical vapor infiltration (CVI) utilized for composite formation, that requires some individualized attention.

Chemical vapor deposition (CVD) involves the reaction of gaseous reactants to form solid products. There are two general types of CVD processes:

- (a) the thermal decomposition of a homogeneous gas to form a solid
- (b) the chemical reaction of two or more gaseous species to form a solid.

Both types of CVD reactions are used industrially to form a variety of important elements and compounds for semiconductor, superconductor, and ceramic coating applications.

In Chemical vapor infiltration (CVI), gaseous reactants are used to form solid products on a porous, uniform, and flat surface substrate. The porous substrate introduces an additional complexity to transport the reactants to the surface, which can play an important role in the reaction. The reactants can be introduced into the porous substrate by either a diffusive or convective process before the deposition step. As infiltration proceeds, the deposit (matrix) becomes thicker, eventually (in the ideal situation) filling the pores and producing a dense composite.

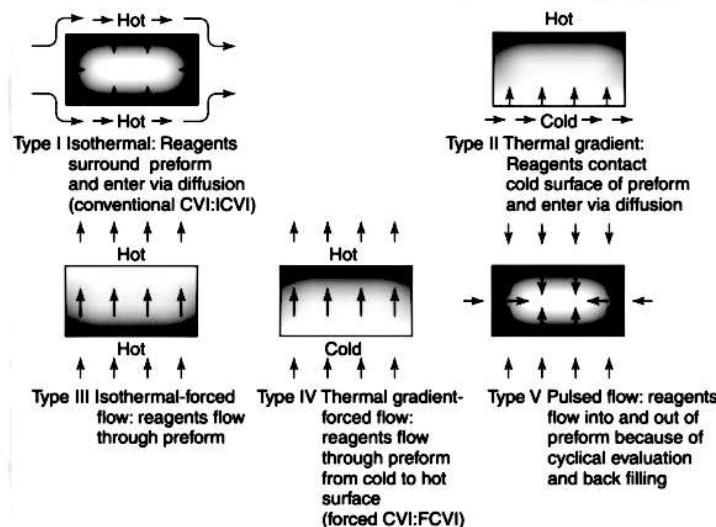
There are five general categories of CVI processes depending on the transport process (diffusion or convection) and imposed thermal gradient.

- ✓ Type I, known as isothermal CVI (ICVI) has no thermal gradients imposed, and reagents enter the substrate via diffusion. The disadvantage of this process is that the entire substrate is at the reaction temperature so that pores on the surface can close off before the inner pores are filled.
- ✓ Type II CVI has a thermal gradient where the reactants contact the substrate in a cold region and diffuse to the heated reaction zone.
- ✓ Type III and Type IV CVI are the forced convection analogs of Type I and Type II, respectively, where the reactants are now forced into the substrate by convection instead of being allowed to diffuse.
- ✓ Type V CVI is specialized where the reactants are forced into the substrate and gaseous products are also forcefully removed cyclically.

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KINETIC PROCESSES IN COMPOSITES



Classification of chemical vapor infiltration processes

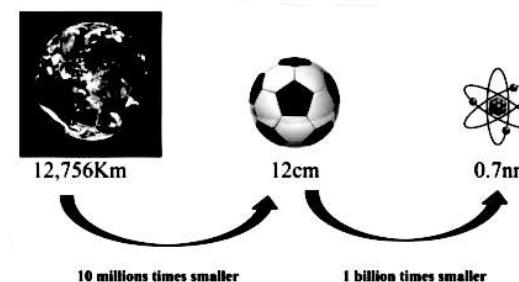
INTRODUCTION

What is a nanometer?

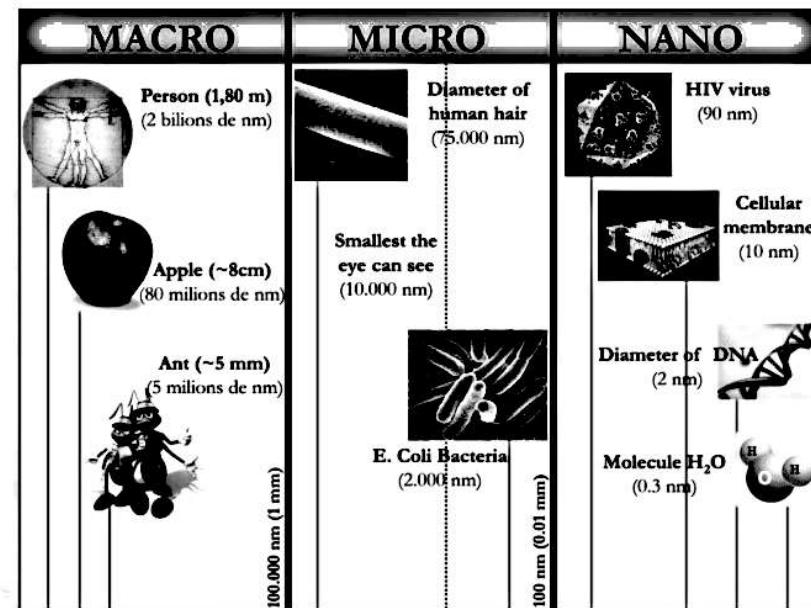
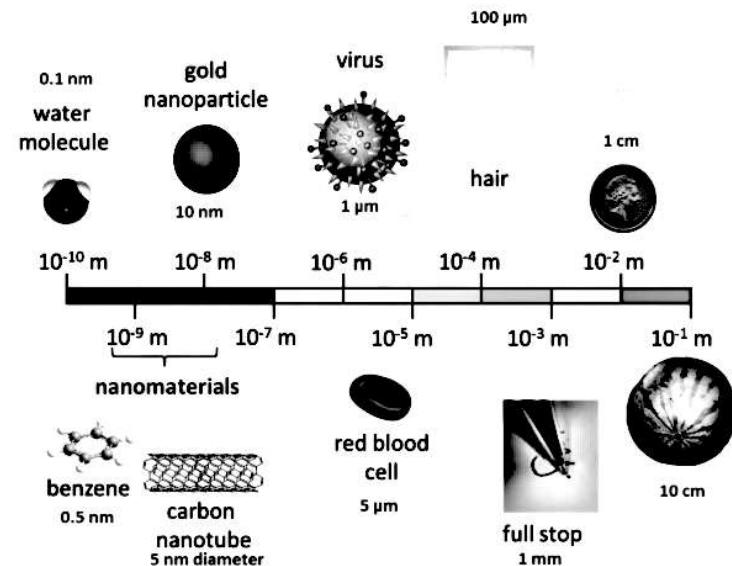
$1 \text{ nm} = 10^{-9} \text{ m} = 0.000000001 \text{ m}$ = one billionth of a meter
 = one-millionth of a millimeter (10^{-6} mm)
 = one-thousandths of a micrometer (10^{-3} mm)

- ~ roughly the width of 3 or 4 atoms
- ~ The average human hair is about 25000 nm wide

$1 \text{ nm} = 10 \text{ H}_2 \text{ or } 5 \text{ Si atoms aligned in a line}$

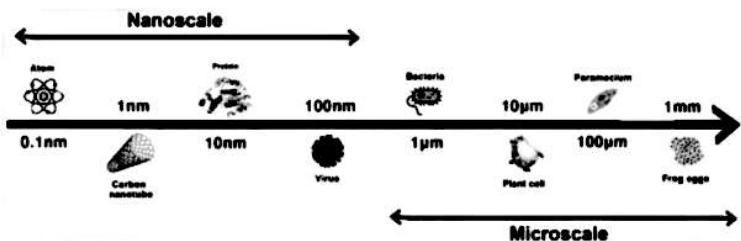


Technology is the making, usage and knowledge of tools, machines and techniques in order to solve a problem or perform a specific function.



NANOTECHNOLOGY

In Greek, "Nanotechnology" derives from the "nanos" which means dwarf and technology means systematic treatment of an art or craft. It is an advance to the future.



Nanotechnology is....
the control of matter on the atomic level
the ability to build using atoms as building blocks
the manufacture of novel materials with novel properties

WHY NANOTECHNOLOGY?

At the nanoscale, the physical, chemical, and biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matter.

Nanotechnology R&D is directed toward understanding and creating improved materials, devices, and systems that exploit these new properties.

What's the BIG deal about something so SMALL?

- Materials behave differently at this size scale.
- It's not just about miniaturization.
- At this scale—it's all about INTERFACES

HISTORY OF NANOTECHNOLOGY

~ 2000 Years Ago – Sulfide nano crystals used by Greeks and Romans to dye hair

~ 1000 Years Ago (Middle Ages) – Gold nano particles of different sizes used to produce different colors in stained glass windows

1959 – "There's plenty of room at the bottom" by R. FEYNMAN->

1974 – "Nanotechnology" - Taniguchi uses the term nanotechnology for the first time

1981 – IBM develops Scanning Tunneling Microscope

1985 – "Buckyball" - Scientists at Rice University and University of Sussex discover C₆₀

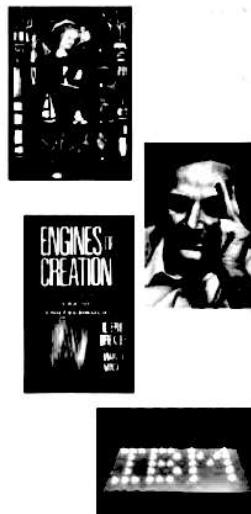
1986 – "Engines of Creation" - First book on nanotechnology by K. Eric Drexler. Atomic Force Microscope invented by Binnig, Quate and Gerber

1989 – IBM logo made with individual atoms

1991 – Carbon nanotube discovered by S. Iijima

1999 – "Nanomedicine" – 1st nanomedicine book by R. Freitas

2000 – "National Nanotechnology Initiative" launched



HISTORY OF NANOTECHNOLOGY

Richard Feynman's famous presentation "There's Plenty of Room at the Bottom" was in the 1959 at the American Physical Society.

Here he asked:

- Why can't we manipulate materials atom by atom?
- Why can't we control the synthesis of individual molecules?
- Why can't we write all of human knowledge on the head of a pin?
- Why can't we build machines to accomplish these things?



WHY "NANO" IS INTERESTING

- Particles are small
 - High surface-to-volume ratio
 - React differently
 - Act differently (new properties)
 - Interact with light differently
 - Are on the scale of small biological structures
- Quantum Mechanics meet Classical Mechanics
- Interesting "new" structures

CHALLENGES OF THIS SIZE SCALE

A critical issue for nanotechnology is that components, structures, and systems are in a size regime about whose fundamental behavior we have little understanding. They are:

- too small for direct measurements
- too large to be described by current rigorous first principle theoretical and computational methods
- exhibit too many fluctuations to be treated monolithically in time and space
- too few to be described by a statistical ensemble.

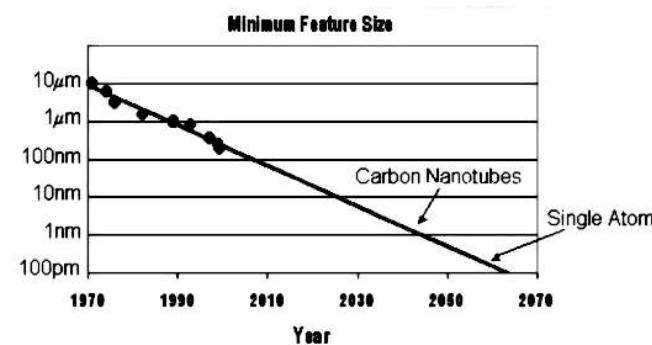
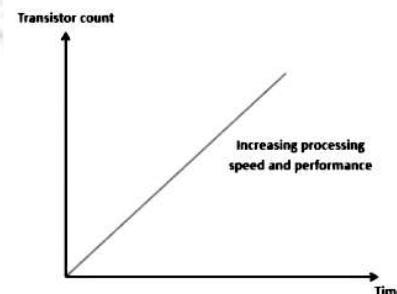
MOORE'S LAW

Gordon Moore predicted that the number of transistors on a typical circuit would double every 18-24 months, implying an exponential rise in computer power over time.

Moore's law was an observation made by Gordon Moore in 1965. Moore's empirical observations serve as its foundation. From observed statistics, he extrapolated the number of transistors on a microchip, doubling annually.

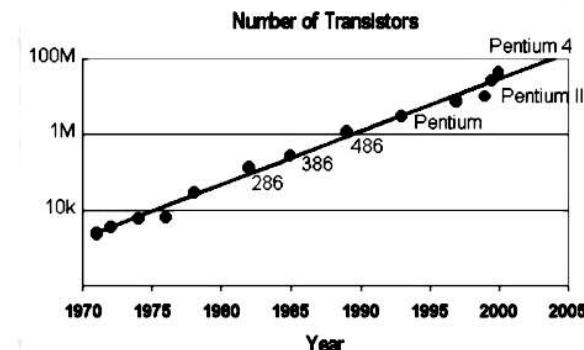
- The majority of this growth in chip density is due to four primary factors: die size, line dimension, technical brilliance, and technological innovation.

- Over the years, the law has seen a decline. The weakening results from the growing complexity involved in creating cutting-edge technologies.



- So far, the industry has kept up with the Moore Law prediction (shown as a black line). The problem, however, is that in the future the demands will be much greater.
- By 2010, we will need to define 50nm features. By 2040, wireline widths will be on the order of carbon nanotubes, and by 2060, features will be the size of individual atoms. It seems physically impossible to continue Moore's Law beyond this single-atom barrier, and other physical constraints will likely block the progress much sooner.
- Moreover, many analysts predict that it will not be physical barriers that cause Moore's prediction to collapse, but rather economic ones.

EXPLANATION OF MOORE'S LAW



The graph shows data points for the number of transistors in typical intel chips over the years (42 million in the Pentium 4 chip), and the straight line is the Moore's Law prediction. Clearly, Moore's Law has held for many years now. The question becomes: "How long can we continue?" The problem is that to increase the number of transistors per chip, the transistors must become smaller and smaller. This means that the manufacturing process must be able to define ever-smaller feature sizes year after year.

- Modern fabs cost billions to build and run, mostly due to the stringent clean-room conditions required (a single speck of dust can ruin your whole chip when your features are only 100nm across), and the cost of fabs increases geometrically, as does computer power.

Thus, we may soon reach a point where even the wealthiest banks in the world cannot finance the construction of the fabs.

- The purpose of presenting Moore's Law (and its limitations) is not to scare the reader (or investors) into believing that the computer industry will catastrophically collapse shortly but rather to point out that our current way of doing things cannot continue forever.
- It is not that computers cannot get more powerful than the preceding predictions (again, take a look at the human brain if you worry that a 1kg-sized computer cannot be more powerful than modern supercomputers), it is just that the industry will have to adapt to new technologies to create future-generation computers.
- In the short term, this means adopting new micro- and nano-fabrication techniques, to build conventional transistors ever smaller. In the long term, this means adopting entirely new fabrication techniques, which, for instance, circumvent current cleanroom requirements, or which exploit clever computer processing paradigms. In either case, more research in Nanotechnology is key.

NANOMATERIALS

The main reasons why nanomaterials show properties so different from those of the bulk are:

Surface Effects:

- Atoms at surfaces have fewer neighbors than atoms in the bulk. Because of this lower coordination number and unsatisfied bonds, surface atoms are less stabilized than bulk atoms.
- The smaller a particle, the larger the fraction of atoms at the surface and the higher the average binding energy per atom.
- The surface-to-volume ratio scales with the inverse size. Therefore numerous properties obey the same scaling law.
- Among them are the melting and other phase transition temperatures. Edge and corner atoms have an even lower coordination and bind foreign atoms and molecules more tightly.

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SURFACE EFFECTS

The fraction of atoms at the surface:

The surface of a sphere scales with the square of its radius "r", but its volume scales with r^3 . The total number of atoms N in this sphere scales linearly with volume. The fraction of atoms at the surface is called dispersion F , and it scales with the surface area divided by volume, ($F \propto 1/r$) and thus also with $N^{1/3}$. The same relation holds for long cylinders of radius r and for thin plates of thickness d .

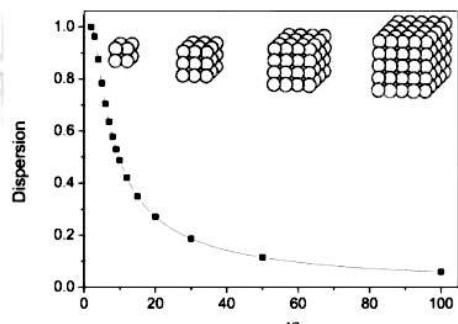
Consider a cube of n atoms along an edge and a total of $N = n^3$ atoms.

The number of atoms at the surface = $6n^2 - 12n + 8$

Here the number of atoms at the surface is $6n$ corrected for double counts at the 12 edges and for reinstalling the 8 corners. For large N the edge and corner corrections become negligible, leading to the $N^{1/3}$ scaling.

$$\text{The dispersion, } F = \frac{6n^2 - 12n + 8}{n^3} = \frac{6}{N^{1/3}} \left(1 - \frac{2}{N^{1/3}} + \frac{8}{6N^{2/3}} \right) \approx \frac{6}{N^{1/3}} \approx 6N^{-1/3}$$

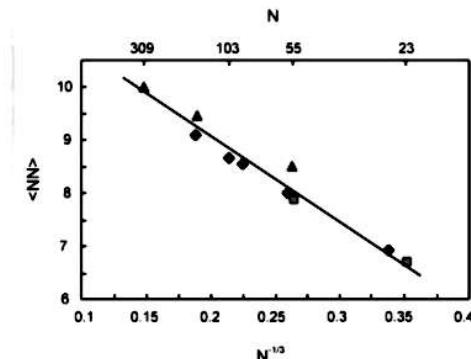
All properties which depend on the dispersion of a particle lead to a straight line when plotted against r^{-1} , d^{-1} or $N^{-1/3}$



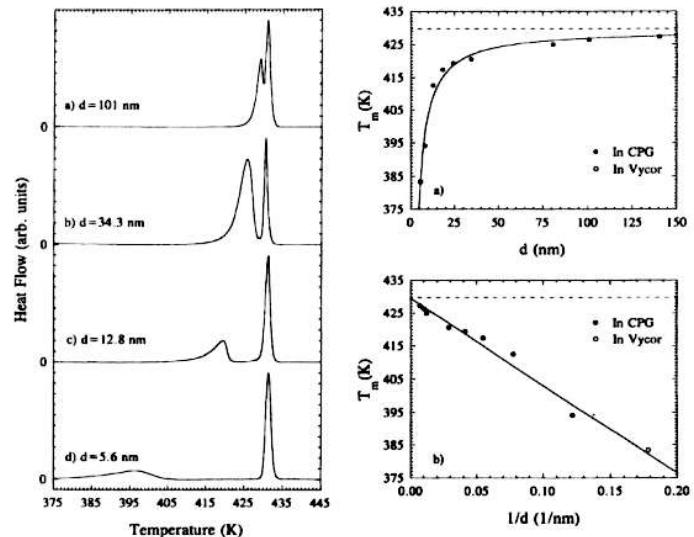
Evolution of the dispersion F as a function of n for cubic clusters

Atoms at the surface have fewer direct neighbors than atoms in the bulk. Therefore, particles with a large fraction of atoms at the surface have a low mean coordination number (which is the number of nearest neighbours). The dispersion and the mean coordination number $\langle NN \rangle$ obey the same scaling law and are equivalent measures of surface effects.

The linearity of a plot of $\langle NN \rangle$ against $N^{-1/3}$ is shown in Figure for small clusters of Mg atoms in various packing symmetries. In the limit of infinitely large clusters the line extrapolates to $\langle NN \rangle = 12$, the coordination number of close-packed spheres in the bulk.



Mean coordination number as a function of inverse radius, represented by $N^{-1/3}$, for magnesium clusters of different symmetries (triangles: icosahedra, squares: decahedra, diamonds: hexagonal close packing)

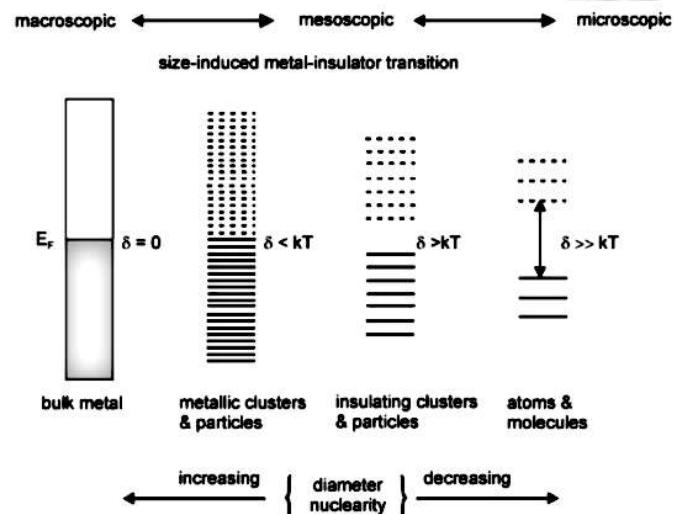


Left: Background-subtracted differential scanning calorimetry melting endotherms for indium confined in controlled pore glass (a-c) and in Vycor samples (d) with different pore diameters. Note that the melting feature of the pore-confined material moves to lower temperatures and broadens as the pores get narrower. Right: Melting temperature as a function of pore diameter and inverse diameter. The broken line represents the bulk melting point

QUANTUM SIZE EFFECTS

- In metals and semiconductors, the electronic wave functions of conduction electrons are delocalized over the entire particle.
- Electrons can therefore be described as 'particles in a box', and the densities of state and the energies of the particles depend crucially on the size of the box, which at first leads to a smooth size-dependence.
- However, when more atoms are added the shells are filled up, and discontinuities occur when a new shell at higher energy starts to be populated.
- Because of these discontinuities, there is no simple scaling. Instead, one finds behavior akin to that of atoms, with filled shells of extra stability.
- Therefore, such clusters are often called 'pseudo-atoms'.
- The HOMO-LUMO band gap of semiconductor particles and therefore their absorption and fluorescence wavelengths become size dependent.
- Ionization potentials and electron affinities are tuned between the atomic values and the work function of the bulk material by variation of the cluster size.
- These same properties relate to the availability of electrons for forming bonds or getting involved in redox reactions. Therefore, the catalytic activity and selectivity become functions of size".

QUANTUM SIZE EFFECTS



Evolution of the band gap and the density of states as the number of atoms in a system increases (from right to left). d is the so-called Kubo gap.

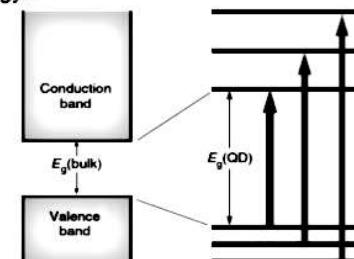
QUANTUM SIZE EFFECTS

The Quantum confinement results from electrons and holes being squeezed into a dimension that approaches a critical quantum measurement, called exciton Bohr radius.

$$\text{The Bohr radius of a particle is: } a_B = \frac{\hbar}{m^* e} a_0$$

ϵ = the dielectric constant of the material, m^* = the mass of the particle, m = the rest mass of the electron, a_0 = the Bohr radius of the hydrogen atom.

- When the particle size approaches Bohr exciton radius, the quantum confinement effect causes increasing of the excitonic transition energy and a blue shift in the absorption and luminescence band gap energy.
- Quantum confinement leads to a collapse of the continuous energy bands of bulk material into discrete, atomic-like energy levels.
- A quantum-confined structure is one in which the motion of the carriers (electron and hole) are confined in one or more directions by potential barriers.



A schematic of the discrete energy level of a semiconductor.

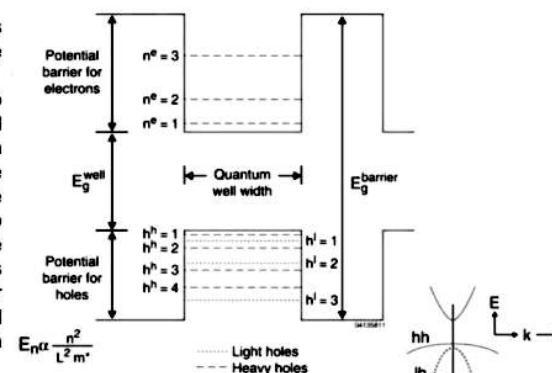
CLASSIFICATION OF QUANTUM CONFINED STRUCTURES

Structure	Quantum confinement	Number of free dimension
Bulk	0	3
Quantum well/superlattices	1	2
Quantum wire	2	1
Quantum dot/Nanocrystals	3	0

- **Zero dimensional or In QDs**, the charge carriers are confined in all three dimensions and the electrons exhibit a discrete atomic-like energy spectrum.
- **One-dimensional or Quantum wires** are formed when two dimensions of the system are confined.
- **Two-dimensional or in Quantum well**, charge carriers (electrons and holes) are confined to move in a plane and are free to move in two-dimensional.
- **Three-dimensional or in bulk material**, the free electrons can move in three directions.

QUANTUM WELL (QW)

- A quantum well is a particular kind of heterostructure in which one thin "well" layer is surrounded by two "barrier" layers. In that layer, both electrons and holes are confined, is so thin (typically about 100 Å or about 40 atomic layers) that the electron and hole are both act like waves. The allowed states in this structure correspond to standing waves in the direction perpendicular to the layers. Because only particular waves are standing waves, the system is quantized, hence the name "quantum well".
- A single quantum well is formed from one semiconductor sandwiched between two layers of a second semiconductor having a larger band gap. The center layer with the smaller band gap semiconductor forms the QW, while the two layers sandwiching the center layer create the potential barriers as shown in Figure.



One-dimensionally confined quantum well created by a thin small-band gap semiconductor layer sandwiched between two larger band gap semiconductor layers

Compared with bulk semiconductors, the quantum well has a higher density of electronic states near the edges of the conduction and valence bands. Therefore a higher concentration of carriers can contribute to the band edge emission. As more number of the dimension is confined, more discrete energy levels can be found, in other words, carrier movement is strongly confined in a given dimension.

- The quantum confinement effect corresponding to the size of the nanostructure can be estimated via a simple effective-mass approximation model. This method determines the confined energy levels of the nanostructures by solving the Schrodinger equation assuming the barriers have an infinite confining potential.
- The "effective mass" solutions of the Schrödinger equation for electrons confined in a quantum dot or NCs, quantum wire, and quantum well are:

$$\text{Quantum dots or Nanocrystals: } E_{n,m,l} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n^2}{L_z^2} + \frac{m^2}{L_y^2} + \frac{l^2}{L_x^2} \right), \psi = \phi(z)\phi(y)\phi(x)$$

$$\text{Quantum wire: } E_{n,m}(k_x) = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n^2}{L_z^2} + \frac{m^2}{L_y^2} \right) + \frac{\hbar^2 k_x^2}{2m}, \psi = \phi(z)\phi(y)\exp(ik_x x)$$

$$\text{Quantum well: } E_n(k_x, k_y) = \frac{\pi^2 \hbar^2 n^2}{2m L_z^2} + \frac{\hbar^2}{2m} (k_x^2 + k_y^2), \psi = \phi(z)\exp(ik_x x + ik_y y)$$

where $n, m, l = 1, 2, \dots$ the quantum confinement numbers, L_x , L_y and L_z are the confining dimensions, $\exp(ik_x x + ik_y y)$ is the wave function describing the electronic motion in x and y direction, similar to free electron wave functions.

➤ Two potential wells are formed in the QW structure; one well is for conduction-band electrons, the other for valence-band holes. The well depth for electrons is the difference (i.e. the offset) between the conduction-band edges of the well and barrier semiconductors, while the well depth for holes is the corresponding valence-band offset.

➤ Quantum wells are thin layered semiconductor structures in which we can observe and control many quantum mechanical effects. They derive most of their special properties from the quantum confinement of charge carriers (electrons and "holes") in thin layers (e.g. 40 atomic layers thick) of one semiconductor "well" material sandwiched between another semiconductor "barrier" layers.

➤ Multiple quantum well structures consist of a series of QWs (i.e. a series of alternating layers of wells and barriers). If the barrier thickness between adjacent wells is sufficient to prevent significant electronic coupling between the wells, then each well is electronically isolated; this type of structure is termed as multiple quantum well. Quantum wells are thin layered semiconductor structures in which we can observe and control many quantum mechanical effects. They derive most of their special

The basic properties of a quantum well can be determined by the simple "particle in a box" model. Schrödinger's equation in one dimension for the particle (e.g., electron or hole) is:

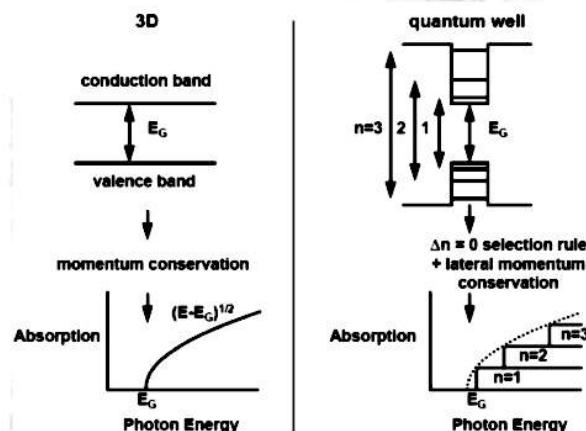
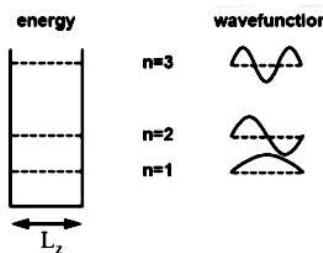
$$\frac{\hbar^2}{2m^*} \frac{d^2\phi_n}{dz^2} + V(z)\phi_n = E_n\phi_n$$

where $V(z)$ is the structural potential (i.e., the "quantum well" potential) seen by the particle along the direction of interest (z), m^* is the particle's (effective) mass, and E_n and ϕ_n are the Eigen energy and Eigen function associated with the n th solution to the equation. For simplicity, consider that the barriers on either side of the quantum well are infinitely high. Therefore, the wave function must be zero at the walls of the quantum well. The solution is:

$$E_n = \frac{\pi^2 \hbar^2 n^2}{2m^* L_z^2} \quad n = 1, 2, \dots$$

$$\phi_n = A \sin\left(\frac{n\pi z}{L_z}\right)$$

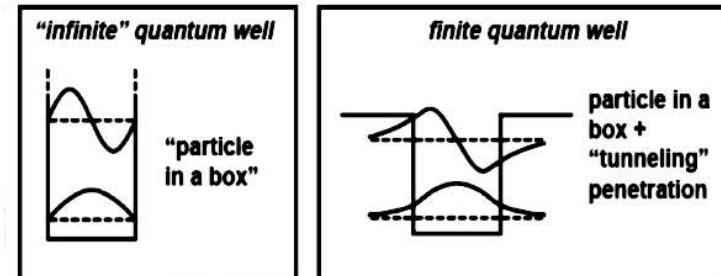
Infinite quantum well and associated wave functions



Optical absorption in bulk (i.e., 3D) semiconductors and in quantum wells

- There are no discrete energy states for electrons and holes in quantum wells.
- There are "sub-bands" starting at the energies calculated for the confined states.
- The electron in a given confined state can have kinetic energy for its in-plane motion in the quantum well and have energy greater than or equal to the simple confined-state energy for that sub-band.
- The density of states for motion in the plane of the quantum well layers is constant with energy, so the density of states for a given sub-band is a "step" that starts at the appropriate confinement energy.

The energy levels (or "confinement energies") are quadratically spaced, and the wave functions are sine waves. In this formula, the energy is referred to the energy of the bottom of the well. The first allowed energy (corresponding to $n=1$) is above the bottom of the well. Here, the energy level spacing becomes large for narrow wells (small L_z) and small effective mass m .



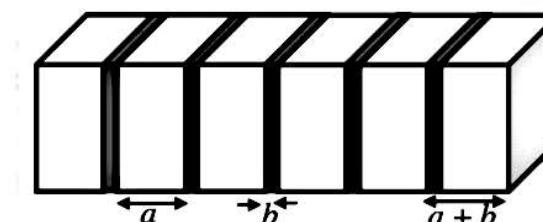
Comparison of "infinite" quantum well and "finite" quantum well behavior

- In contrast to bulk semiconductors, excitonic effects are clear in quantum wells at room temperature and significantly influence device performance.
- In a quantum well, the electrons and holes are still free to move in the directions parallel to the layers;

Quantum Well = QW = A single layer of material a (layer thickness L), sandwiched between 2 macroscopically large layers of material b. Usually, the bandgaps satisfy: $E_{gA} < E_{gB}$

Multiple Quantum Well = MQW = Alternating layers of materials a (thickness L) & b (thickness L'). In this case: $L' \gg L$. So, the e^- & e^+ in one a layer are independent of those in other a layers.

Superlattice = SL = Alternating layers of materials a & b with similar layer thicknesses.



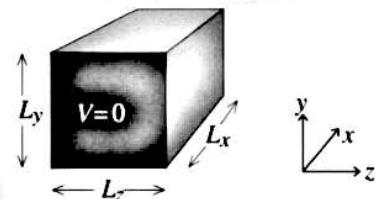
Superlattice layer structure.

QUANTUM DOTS (QDs)

- A quantum dot is a nanocrystal made of semiconductor materials that are small enough to exhibit quantum mechanical properties.
- For a semiconductor material, quantum dot structure is a small box with sides comparable to or smaller than the de-Broglie wavelength which is surrounded by a wider band-gap semiconductor material.
- This box behaves as a three-dimensional potential well for carriers (electron in the conduction band and the holes in the valence band).
- In quantum dot, carriers are narrowly confined in all three directions along each side of the box L_x , L_y and L_z along the x , y and z -axis respectively.
- Therefore, the energy is quantized along three directions. Thus the energy levels can no longer be referred to as subbands, are known as sublevel.

In case of infinitely deep quantum wells, of widths L_x , L_y and L_z , the confinement energy within this quantum box is:

Schematic illustration of a quantum box with side L_x , L_y and L_z



QUANTUM DOTS (QDs)

Quantum dots popularly known as artificial atoms, where the confinement potential replaces the potential of the nucleus. These man-made objects have lateral widths in the range of a few hundred to about 10 nm where the smallest ones are the self-assembled systems.

Wavelength in quantum dots can be controlled in nanocrystalline materials. The energy separation between the valance and conduction bands can be altered in nanocrystalline dots by changing the size of the nanoparticles.

Applications:

- Memory chips, quantum computation, quantum cryptography, quantum dot lasers.
- QDs are particularly significant for optical applications due to their theoretically high quantum field.
- In electronic applications, they have been proven to operate like the single electron transistor and show the Coulomb blockade effect.

Considering the case of an infinite potential separating the inside of the box from the outside, then the three-dimensional Schrodinger equation within the box is simply:

$$-\frac{\hbar^2}{2m^*} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) = E_{x,y,z} \psi(x, y, z)$$

The total energy $E_{x,y,z}$ can be written as a sum of the three terms E_x , E_y and E_z . The single three-dimensional equation can be decoupled into three one-dimensional equations:

$$\begin{aligned} -\frac{\hbar^2}{2m^*} \frac{\partial^2}{\partial x^2} \psi(x) &= E_x \psi(x) \\ -\frac{\hbar^2}{2m^*} \frac{\partial^2}{\partial y^2} \psi(y) &= E_y \psi(y) \\ -\frac{\hbar^2}{2m^*} \frac{\partial^2}{\partial z^2} \psi(z) &= E_z \psi(z) \end{aligned}$$

In case of infinitely deep quantum wells, of widths L_x , L_y and L_z , the confinement energy within this quantum box is:

$$E_{x,y,z} = \frac{\hbar^2 \pi^2}{2m^*} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

$$E = E_x + E_y + E_z$$

The energy spectrum is discrete and the density of state (DOS) is a series of δ - functions.

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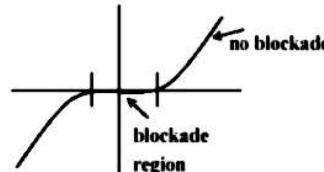
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COULOMB BLOCKADE EFFECT

- It is an effect of the charge quantization and a consequence of sequential (non-coherent) tunneling through a small system.
- The resistance to electron transport caused by electrostatic coulomb forces in certain electronic structures, including quantum dots and single electron transistors is called coulomb Blockade.
- The prohibition or suppression of tunneling is called the Coulomb Blockade. In simple words, the suppression of electron flow is called coulomb blockade.



Explanation: Coulomb forces are electrostatic. If we have two or more charges near one another, they exert coulomb forces upon each other. In the case of the same charge, the force is repulsive. In the case of a quantum dot, the charges are all negative electrons. The Coulomb force will be created by bringing them forcefully together. However, the isolated droplet of electrons does not willingly accept another but repels it. This is Coulomb blockade and it helps prevent constant tunneling to and from a quantum dot.

How much energy is necessary to block the tunneling electrons in the coulomb blockade?

- ⇒ Coulomb blockade needs more energy than a given electron can "spend" trying to tunnel in and out.
- ⇒ A free electron in a solid has a certain amount of energy depending on which band it is in.
- ⇒ Due to thermal vibrations of the atoms in the lattice, these free electrons will get extra energy to go to higher bands. The extra energy is equal to $K_B T$ [k_B = Boltzmann constant = 1.38×10^{-23} J/k]. With this extra energy, an excited electron might be able to tunnel through a small barrier.
- ⇒ The coulomb blockade can prevent unwanted tunneling, when the charging energy is much higher than the thermal energy of an electron.

Condition for coulomb blockade

The condition of the Coulomb blockade is therefore, $E_C >> K_B T$

This criterion can be more easily achievable if smaller the dot becomes.

The Coulomb blockade's effect can be measured. A quantum dot has a capacitance, ' C_{dot} ', a measure of how much electric charge it can store. $C_{dot} = G \epsilon d$

Where, ϵ ⇒ permittivity of the material surrounding the dot

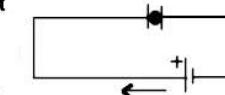
d ⇒ diameter of the dot

G ⇒ geometrical term [If the quantum dot is disk, $G = 4$,

if it is spherical particle, $G = 2\pi$].

Here, the capacitance is not like the one between a pair of parallel plates but an object isolated in space which can store charge on its own and hence have a Capacitance.

The energy needed to add negatively charged electron to the dot is known as the charging energy E_c . $E_c = \frac{e^2}{2C_{dot}}$, Where e = charge on the electron



$$\begin{aligned}\text{Energy required to tunnel} \\ E_c &= \frac{e^2}{2C} \\ &= \frac{e^2}{2} \frac{1}{4\pi \epsilon_0 \epsilon_r d}\end{aligned}$$

Therefore, E_c is inversely proportional to the dot's capacitance. In that case, a large capacitor can quite easily accomodate another electron without too much energy required. However, in the opposite case, with extremely small capacitors [quantum dots], the charging energy can be substantial [large]. As a result, small capacitors [quantum dots] are large enough to "block" tunneling electrons.

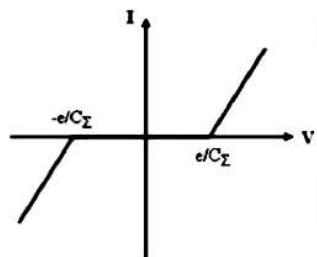
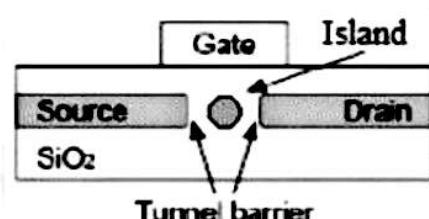
CONDITIONS FOR A COULOMB BLOCKADE

1) The Coulomb energy e^2/C needs to exceed the thermal energy $k_B T$. Otherwise, an extra electron can get onto the dot with thermal energy instead of being blocked by the Coulomb energy. A dot needs to be either small (< 10 nm at $300K$) or cold ($< 1K$ for a μm -sized dot).

2) The residence time $\Delta t = RC$ of an electron on the dot needs to be so long that the corresponding energy uncertainty $\Delta E = h/\Delta t = h/RC$ is less than the Coulomb energy e^2/C . That leads to a condition for the tunnel resistance between the dot and source/drain: $R > h/e^2 \approx 26 \text{ k}\Omega$

SINGLE ELECTRON TRANSISTOR

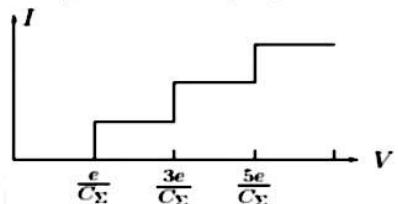
- The Single electron transistor is made of an island/quantum dot connected through two tunneling junctions to a drain and a source electrode. When there is no bias in any electrode, electrons in the system do not have enough energy to tunnel through the junctions i.e. the transistor is in off state.
- Unlike field effect transistors, single-electron transistors are based on an quantum phenomenon which is known as "tunnel effect".



I-V characteristics of Single electron transistor

CONCEPT OF SINGLE ELECTRON TUNNELING

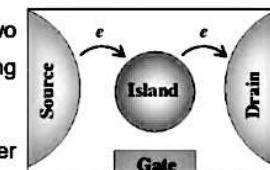
- The charging and discharging of tunnel junction and thermal fluctuations are closely related to each other.
- The transfer of electrons through the barriers between the quantum dots would result in charging of the neighboring quantum dots. Now this would increase the electrostatic energy which is given by, $E_c = \frac{e^2}{2C}$ Where C is the effective capacitance of the island. This electrostatic energy is also known as Coulomb energy or Coulomb blockade energy.
- Coulomb energy must be greater than the thermal fluctuations. Thus the required condition to observe the single electron phenomenon is as follows: $E_c = \frac{e^2}{2C} \gg K_B T$, where K_B is Boltzmann constant and T is the temperature in Kelvin. The sequence of entrance and leaving of an electron from one junction to another is generally known as "Correlated tunneling electrons".



I-V characteristics of the SET for asymmetric junction representing "Coulomb staircase state".

SINGLE ELECTRON TRANSISTOR

- Single electron transistor is the most fundamental three-terminal single electron device which is capable of offering low power consumption and high operating speed.
- A Single electron transistor consists of a small, low capacitance (C), conducting island (quantum dot) which is coupled to the source and drain leads by two tunnel junctions and capacitively coupled to one or more gate.
- Single electron device is based on an intrinsic quantum phenomenon known as the "tunnel effect". This single-electron tunneling technology presents the ability to control the transfer of individual electrons.
- These tunnel effects may be observed when two metallic electrodes are separated by an insulating barrier known as a tunnel junction.
- These three-terminal switching devices can transfer electrons from sources to drain one by one.



DENSITY OF STATE

The density of states is defined as the number of states per unit energy per unit volume of real space, which was expressed mathematically as: $g(E) = dN/dE$

$$\text{For bulk material, the total number of states, } N^{3D} = 2 \times \frac{4\pi K^3}{3} \times \frac{1}{(2\pi/L)^3} \times \frac{1}{L^3}$$

$$= 2 \times \frac{4\pi K^3}{3(2\pi)^3}$$

Here, $\frac{4\pi K^3}{3}$ = volume of the sphere of radius K
 $(2\pi/L)^3$ = volume occupied by one states
 L^3 = volume of the real space

The factor 2 has been introduced to allow for double occupancy of each state by the different carrier spin.

$$g(E) = dN/dE = dN/dK \frac{dK}{dE}$$

$$\frac{dN}{dK} = \frac{d}{dK} \left(2 \frac{4\pi K^3}{3(2\pi)^3} \right) = 2 \frac{4\pi K^2}{(2\pi)^3}$$

$$\text{Now, we know, } E = \frac{\hbar^2 K^2}{2m^*} \Rightarrow K = \left(\frac{2m^* E}{\hbar^2} \right)^{1/2}$$

$$\frac{dK}{dE} = \left(\frac{2m^*}{\hbar^2} \right)^{1/2} \frac{E^{-1/2}}{2}$$

The density of state in bulk: $g(E) = dN/dE = dN/dK dK/dE$

$$g^{3D}(E) = 2 \frac{4\pi K^2}{(2\pi)^3} \left(\frac{2m^*}{\hbar^2}\right)^{1/2} \frac{E^{-1/2}}{2} = \frac{1}{2\pi^2} K^2 \left(\frac{2m^*}{\hbar^2}\right)^{1/2} E^{-1/2} = \frac{1}{2\pi^2} \frac{2m^* E}{\hbar^2} \left(\frac{2m^*}{\hbar^2}\right)^{1/2} E^{-1/2}$$

$$= \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2}$$

Thus the density of states within a band and around a minimum where the energy can be represented as a parabolic function of momentum is continual and proportional to the square root of the energy

For quantum well, the total number of states, $N^{2D} = 2 \times \pi K^2 \times \frac{1}{(2\pi/L)^2} \times \frac{1}{L^2} = \frac{K^2}{2\pi}$

$$g^{2D}(E) = dN^{2D}/dE = dN^{2D}/dK dK/dE$$

$$dN^{2D}/dK = \frac{K}{\pi}$$

$$g^{2D}(E) = \frac{K}{\pi} \left(\frac{2m^*}{\hbar^2}\right)^{1/2} \frac{E^{-1/2}}{2} = \frac{1}{\pi} \left(\frac{2m^* E}{\hbar^2}\right)^{1/2} \left(\frac{2m^*}{\hbar^2}\right)^{1/2} \frac{E^{-1/2}}{2} = \frac{1}{\pi} \frac{m^*}{\hbar^2} = \frac{m^*}{\pi \hbar^2} E^0$$

This is the density of states for a single subband in a quantum well. If there are many (n) confined state within the Q well system, $g^{2D}(E) = \sum_{i=1}^n \frac{m^*}{\pi \hbar^2} \Theta(E - E_i)$

Θ = unit step function

The density of states for reduced dimensionality systems, rewritten in a standard form

Dimensionality	$\rho(E)$
3D	$\frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}}$
2D	$\frac{1}{2\pi} \left(\frac{2m^*}{\hbar^2}\right)^1 E^0$
1D	$\frac{1}{\pi} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{1}{2}} E^{-\frac{1}{2}}$

The situation for quantum dots is quite different. As the particles are confined in all directions, then there are no dispersion curves, and thus the density of states is just dependent upon the number of confined levels. One single isolated dot would therefore offer just two (spin-degenerate) states at the energy of each confined level, and a plot of the density of states versus energy would be a series of s-functions.

$$g^{0D}(E) = 2 \sum_i \delta(E - E_i)$$

For quantum wire, the total number of states, $N^{1D} = 2 \times 2K \times \frac{1}{2\pi/L} \times \frac{1}{L} = \frac{4K}{2\pi} = \frac{2K}{\pi}$

2 accounts for spin degeneracy.

$$g^{1D}(E) = dN^{1D}/dE = dN^{1D}/dK dK/dE$$

$$dN^{1D}/dK = \frac{2}{\pi}$$

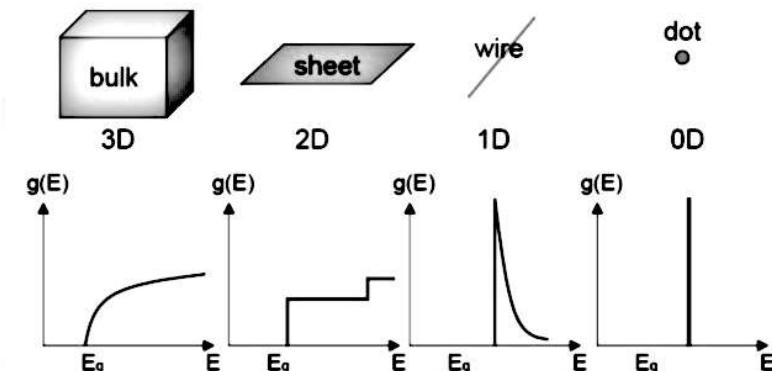
$$g^{1D}(E) = \frac{2}{\pi} \left(\frac{2m^*}{\hbar^2}\right)^{1/2} \frac{E^{-1/2}}{2} = \frac{1}{\pi} \left(\frac{2m^*}{\hbar^2}\right)^{1/2} E^{-1/2}$$

This is the density of states of a quantum wire. Quantum wires show maxima in the density of states at around the subband minima. If there are many (n) confined state within the Q wire system,

$$g^{1D}(E) = \sum_{i=1}^n \left(\frac{2m^*}{\hbar^2}\right)^{1/2} \frac{1}{\pi(E - E_i)^{1/2}} \Theta(E - E_i)$$

Therefore, comparing the density of states for bulk (3D), quantum wells (2D) and quantum wires (1D), it can be seen that successive reductions in degrees of freedom for the electron motion, lead to reductions in the functional form of $g(E)$ by the factors of $E^{1/2}$.

$g(E)$ = Density of states



The density of electron states of a semiconductor as a function of the dimension. The optical absorption spectrum is roughly proportional to the density of states.

BALLISTIC TRANSPORT

- If the length of a conduction path, L is reduced to become much less than the mean free path L_m , it would be expected that no collisions would take place, rendering the collision-based model useless.
- In case of $L \ll L_m$, electron transport occurs ballistically at very small length scales. Here we assume that electrons travel in the wire without scattering, i.e. the electrons do not collide with anything in the wire that changes their energy or momentum. This is **ballistic transport** where the electron behaves like a projectile traveling through the conductor.
- Interactions between electrons and the nuclei usually cause electron scattering. The probability of an electron collision is enhanced by defects and temperature (since the vibration of nuclei increases with temperature). Thus, the scattering rate can be decreased by lowering the temperature and working with very pure materials. But all materials have some scattering probability. So, the smaller the conductor, the greater the probability that charge transport will be ballistic. Thus, **ballistic transport** is a nanoscale phenomenon and can be engineered in nanodevices.



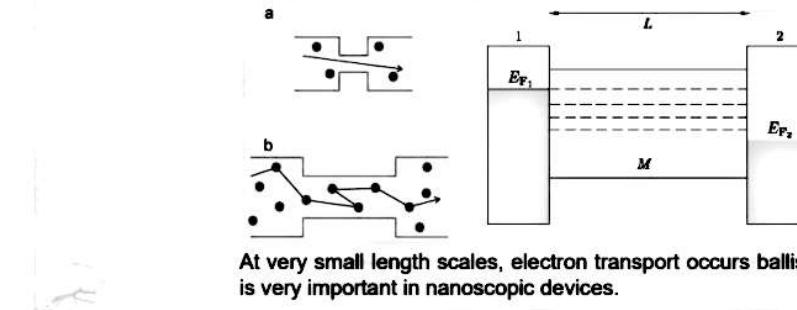
Here, consider an electron traveling through a regular lattice of nuclei. If the electron travels ballistically it has no interaction with the lattice. It travels with constant energy and momentum and will not necessarily be in equilibrium with the material. If the lattice scatters the electron, its energy and momentum will change. Scattering assists in the establishment of equilibrium within the material.

➤ For ballistic transport the electron has no interaction with the conductor. Thus, the electron is not necessarily in equilibrium with the conductor, i.e. the electron is not restricted to the lowest unoccupied energy states within the conductor.

➤ But scattering can bump electrons from high energy states to lower energies. There are two categories of scattering:

Elastic Scattering, where the scattering event may change the momentum of the electron but its energy remains constant;

Inelastic scattering, where the energy of the electron is not conserved. Equilibrium may be established by inelastic scattering.



At very small length scales, electron transport occurs ballistically. It is very important in nanoscopic devices.

Let, L is system length

L_m is mean free path

L_ϕ is the length over which an electron can travel before having an inelastic collision. It is also called phase-coherence length, where the length over which an electron wavefunction retains its coherence (i.e., its phase memory). It is usually on the order of 10 to 100 nm at low temperatures.

Elastic collisions do not interrupt phase coherence but inelastic collisions destroy phase coherence called dephasing events. Thermal effects play an important role in phase coherence. At higher temperatures, the lattice vibrates more as a result collisions occur. Due to thermal energy, at non-zero temperatures, an electron should be represented as wavepacket, $E \sim K_B T$. Increase of T leads increase of E , leading to thermal decoherence even in the absence of particle scattering. Decoherence of any kind is one of the reasons for systems to exhibit classical behavior and is one of the most problematic issues facing the development of quantum computers.

Generally, electron transport can be divided into two regimes:

1. $L \gg L_\varphi, L_m \Rightarrow$ classical transport, familiar for macroscopic case

→ Ohm's law applies, momentum and phase relaxation occur frequently as charges move through the system. Because of this, we cannot solve Schrodinger equation over the whole conductor length, L .

2. $L \ll L_m, L_\varphi \Rightarrow$ Ballistic transport

→ occurs over very small length scales and is coherent.

→ During ballistic transport, no momentum or phase relaxation. Thus, in a ballistic material, the electron wavefunction can be obtained from Schrodinger's equation

Synthesis of Nanomaterials

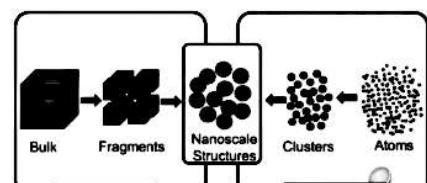
Two approaches for the Synthesis of Nanomaterials and the fabrication of nanostructure

Bottom-Up approach

- In the bottom-up approach, molecular components arrange themselves into more complex assemblies atom-by-atom, molecule-by-molecule, cluster by cluster from the bottom (e.g., growth of a crystal).
- Molecular components arrange themselves into some useful conformation using the concept of molecular self-assembly.

Top-down approach

- In this approach, nanoscale devices are created by using larger, externally controlled devices to direct their assembly.
- The top-down approach often uses the traditional workshop or microfabrication methods in which externally controlled tools are used to cut, mill and shape materials into the desired shape and order.
- Attrition and milling for making nanoparticles are typical top-down processes.



NANOMATERIAL SYNTHESIS

PROFESSOR DR. KAZI HANIUM MARIA

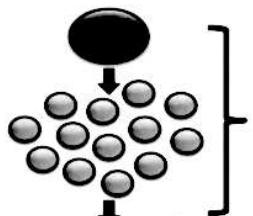
COURSE TEACHER

Top-down versus Bottom-up

Basis for Comparison	Top-Down Approach	Bottom-Up Approach
Basic	Successive cutting or grinding of bulk material to get nanoparticles	The buildup of material from bottom: atom or molecule to get nanoparticles
Starting materials	Solid-state	The starting material is either gaseous or liquid
Processing method	Physical method	Physical and chemical methods
Advantages	<ul style="list-style-type: none">• Large scale production:• Deposition over a large substrate is possible• Chemical purification is not required	<ul style="list-style-type: none">• Ultra-fine nanoparticles• Deposition parameters can be controlled• Cheaper method
Disadvantages	<ul style="list-style-type: none">• Broad size distribution• Varied particle shape• Control of deposition parameters is very difficult• Expensive technique	<ul style="list-style-type: none">• Large scale production is difficult• Chemical purification of nanoparticles is necessary

Synthesis of Nanomaterials

Bulk Material



MECHANICAL METHODS:

- ❖ Mechanical Milling
- ❖ Etching
- ❖ Laser Ablation
- ❖ Sputtering
- ❖ Electro-explosion

Nanoparticles

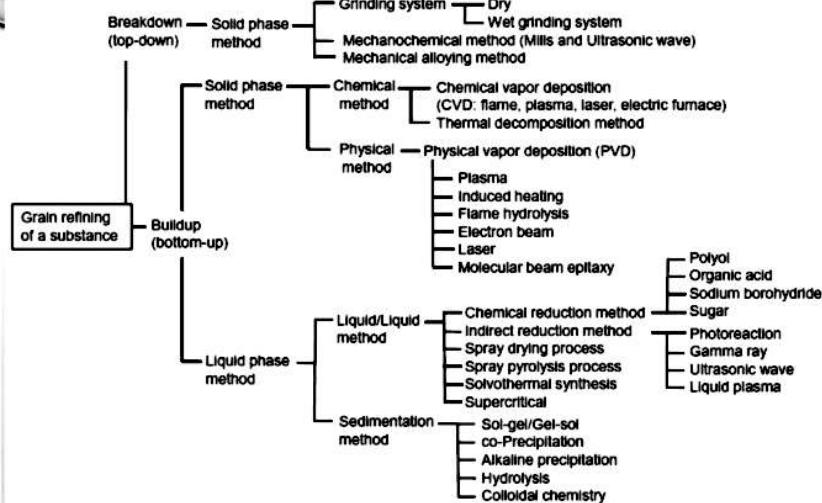
CHEMICAL METHODS:

- ❖ Supercritical Fluid Synthesis
- ❖ Spinning
- ❖ Sol-gel Process
- ❖ Laser Pyrolysis
- ❖ Chemical Vapour Deposition
- ❖ Molecular Condensation
- ❖ Chemical Reduction
- ❖ Green Synthesis

Nuclei and its growth

Molecular/Atomic Level

Synthesis of Nanomaterials



Hybrid Approach: An approach where both these techniques are employed is known as a hybrid approach. Lithography is an example in which the growth of thin film is a bottom-up method whereas etching is a top-down method.

Synthesis of Nanomaterials

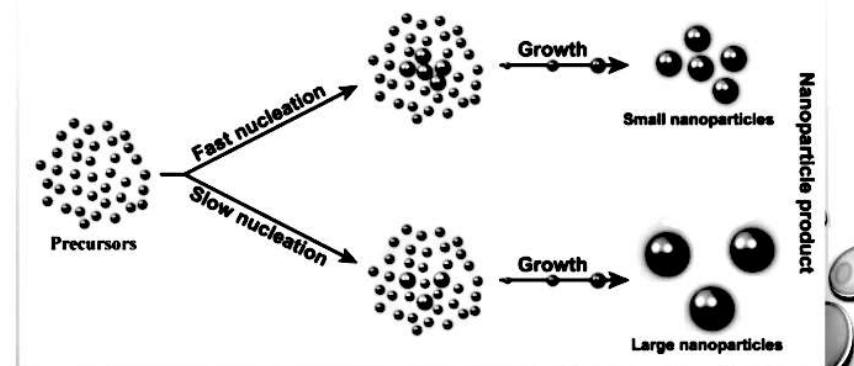
The synthesis of nanoparticles requires the use of a process that fulfills the following conditions:

- Control of particle size, size distributions, shape, crystal structure, and compositional distributions
- Improvement of the purity of nanoparticles
- Control of aggregation
- Stabilization of physical properties, structures, and reactants
- Higher reproducibility
- Higher mass production, scale-up, and lower costs.

Growth Kinetics: Nucleation and Growth Processes

Synthesis of nanoparticles is a combination of two-stage processes: nucleation and growth

- ❖ Most phase transformation begins with the formation of numerous small particles (clusters) of the new phase that increase in size until the transformation is complete.
- ❖ Nucleation is the process whereby nuclei (seeds) act as templates for crystal growth.

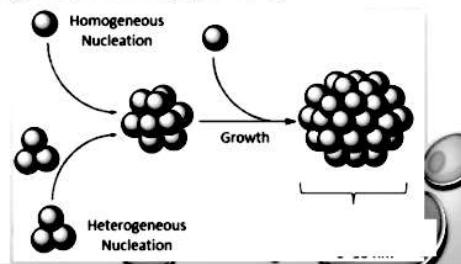


Nucleation

Nucleation is the first step in the formation of either a new thermodynamic phase or a new structure via self-assembly or self-organization. Nucleation is typically defined to be the process that determines how long we have to wait before the new phase or self-organized structure, appears. Nucleation is often found to be very sensitive to impurities in the system. There are two different categories of nucleation:

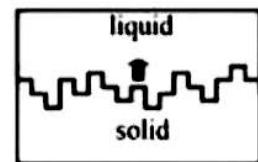
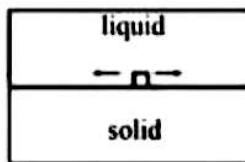
Heterogeneous nucleation: The nucleation of critical nuclei forming at defects such as surface imperfections, and grain boundaries is called heterogeneous nucleation. This type of nucleation is much easier since a stable "nucleation surface" is already present; requires slight supercooling (0.1-10°C).

Homogeneous nucleation: This happens spontaneously. Nucleation that randomly occurs away from a surface. Nuclei form uniformly throughout the parent phase; require considerable supercooling (typically 80-300 °C).



Growth Mechanisms

- > The next step after the nucleation is growth. Atomically rough (diffuse) interfaces migrate by continuous growth, whereas atomically flat interfaces migrate by ledge formation and lateral growth.
- > The rate of continuous growth (typical for metals) is typically controlled by heat transfer to the interfacial region for pure materials and by solute diffusion for alloys.

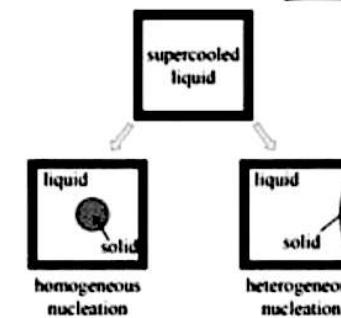


- > Growth in the case of atomically flat interfaces can proceed from existing interfacial steps (e.g. due to the screw dislocations or twin boundaries) or by surface nucleation and lateral growth of 2D materials.

Homogeneous: Solid nuclei spontaneously appear within the undercooled phase.

Heterogeneous: the new phase appears on the walls of the container, at the impurity particles, etc.

Let's consider the solidification of a liquid phase undercooled below the melting temperature as a simple example of a phase transformation.



Driving force

Solidification: If we cool a liquid below the liquids, the driving force for solidification increases. This driving force is often called undercooling or supercooling.

Phase change: For a pure substance with more than one allotrope, as it cools below the phase transformation temperature, the driving force for the phase change increases.

Supercooling: During the cooling of a liquid, solidification (nucleation) will begin only after the temperature has been lowered below the equilibrium solidification (or melting) temperature T_m . This phenomenon is termed supercooling or undercooling.

- > Small supercooling → Slow nucleation rate → few nuclei → large crystal
- > Large supercooling → Rapid nucleation rate → Many nuclei → Small crystal

The driving force to nucleate increases as ΔT increases.

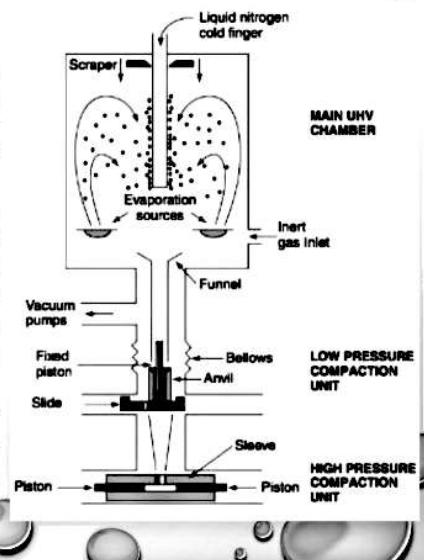
Physical Vapor Deposition (PVD)

> Involves generation and condensation of vapor phase species via thermal evaporation, sputtering, or laser ablation.

Inert-gas condensation:

This inert gas evaporation-condensation technique in which nanoparticles are formed via the evaporation of a metallic surface in an inert gas has been widely used in the synthesis of ultrafine metal particles.

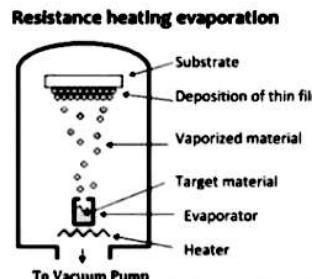
- ✓ In this process, a metal is evaporated inside an ultra-high vacuum (UHV) chamber filled with inert gas. The vaporized species collide with inert gas molecules, thus losing kinetic energy. As collisionless limits the mean free path, supersaturation can be achieved above the source of the vapor.
- ✓ At high supersaturation, the vapor rapidly from no of clusters that grow via coalescence and agglomeration. These clusters get condensed on liquid nitrogen-cooled surfaces to form nanoparticles.



Evaporation technique

Thermal evaporation methods include the simple case of emission at the heated source of the material which condenses on the cold substrate.

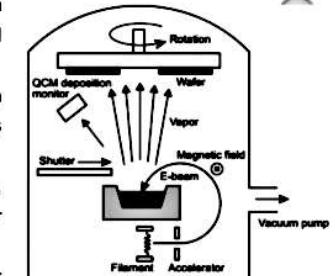
- ✓ The source can be a refractive wire or a crucible electrically heated and containing the material to be evaporated.
- ✓ The evaporation rate is determined by the vapor pressure of the source material at the evaporation temperature.
- ✓ The Joule heating of typical tungsten or molybdenum crucible allows for reaching 2800 K, which provides appreciable vapor pressures for most metals.
- ✓ A deposition chamber under a high vacuum ($<10^{-2}$ Pa) is necessary in order to avoid oxidation of the source.
- ✓ To prevent a harmful reaction between the source and the crucible, the heating can be done rapidly and the process is known as flash evaporation.
- ✓ The properties of the deposited films are usually different if thermally or flash evaporated. Inductive heating of the crucible is also possible.



Evaporation technique

❖ **Electron beam deposition (e-beam deposition)**, is a physical vapor deposition process similar to thermal evaporation.

- ❖ Source material is heated above its boiling/sublimation temperature and evaporated to form a film on the surfaces that the atom flux impinges in a low-pressure environment.
- ❖ This evaporation method has a core ability to cover steps, just like thermal evaporation, making this method ideal for lift-off processes.
- ❖ A noticeable advantage of e-beam evaporation over thermal evaporation is the possibility to add a larger amount of energy into the source material.
- ❖ This yields a higher-density film with increased adhesion to the substrate. Because the electron beam only heats the source material and not the entire crucible, a lower degree of contamination from the crucible will be present than in the case of thermal evaporation.
- ❖ By using a multiple crucible E-beam gun, several different materials can be deposited without breaking the vacuum.
- ❖ By applying a large voltage, electrons are drawn from the filament and focused as a beam on the source material by several bending magnets. The beam is swept across the surface of the source material to heat all the material.



Evaporation technique

Sputtering is a physical process in which atoms in a solid-state (target) are released and pass into the gas phase by bombardment with energetic ions (mainly noble gas ions). Sputtering is usually understood as sputter deposition, a high vacuum-based coating technique belonging to the group of PVD processes. Furthermore, sputtering in surface physics is used as a cleaning method for the preparation of high-purity surfaces and as a method for analyzing the chemical composition of surfaces.

The principle of Sputtering is to use the energy of a plasma (partially ionized gas) on the surface of a target (cathode), to pull the atoms of the material one by one and deposit them on the substrate. Therefore,

- ❖ a plasma is created by the ionization of a pure gas (usually Argon) by means of a potential difference (pulsed DC), or electromagnetic excitation (MF, RF); this plasma is composed of Ar^+ ions which are accelerated and confined around the target due to the presence of a magnetic field. Each ionized atom, by striking the target, transfers its energy and rips an atom, having enough energy to be projected to the substrate.
- ❖ The plasma is created at relatively high pressures (10^{-1} - 10^{-3} mbar), but it is necessary to start from a lower pressure before the introduction of Argon, to avoid contamination due to the residual gases.
- ❖ The diversity of sputtering target shapes (circular, rectangular, Delta, tubular...) and the materials used allows creating all types of thin layers, including alloys during a single run.

An additional benefit of e-beam evaporation is higher deposition rates than possible with either sputtering or resistive evaporation

Basics of the Sputtering Process

When bombarding a surface with ions, various effects may occur, depending on the ions used and their kinetic energy:

1. Material is removed from the bombarded target (cathode). This is the sputtering described here.
2. The ions are incorporated into the target material and enter there, possibly a chemical compound. This effect is then called (reactive) ion implantation.
3. The ions condense on the bombarded substrate, where they form a layer: ion beam deposition.

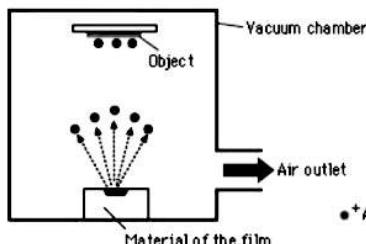


Chart A: Evaporation method

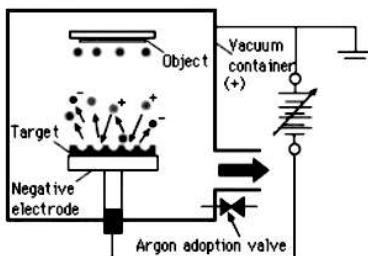


Chart B: Sputtering method

Plasma Processing methods

In general, plasma processing involves chemical and physical reactions between particles and solid surfaces in contact with the plasma. Some examples are plasma etching, thin film deposition, protective coating, surface hardening, ion implantation, etc. The plasma of inert gases is produced by DC (direct current) glow, arc discharges, or radio frequency discharge.

- ❖ A plasma is defined as a collection of positive and negative charges which act collectively.
- ❖ A major consequence of this collective behavior is the ability of the plasma to screen out local density perturbations and to create a sheath region between the plasma and contact surfaces. plasma processing is based on the concept of electrons and their movement in the electric field.

Plasma technology is a surface-sensitive method that allows selective modification in the nm range. By introducing energy into a gas, quasi-neutral plasma can be generated consisting of neutral particles, electrically charged particles, and highly reactive radicals. If a textile is to be functionalized is placed in a reaction chamber with any gas and the plasma is then ignited, the generated particles interact with the surface of the textile, In this way, the surface is specifically structured, chemically functionalized, or even coated with nm thin film depending on the type of gas.

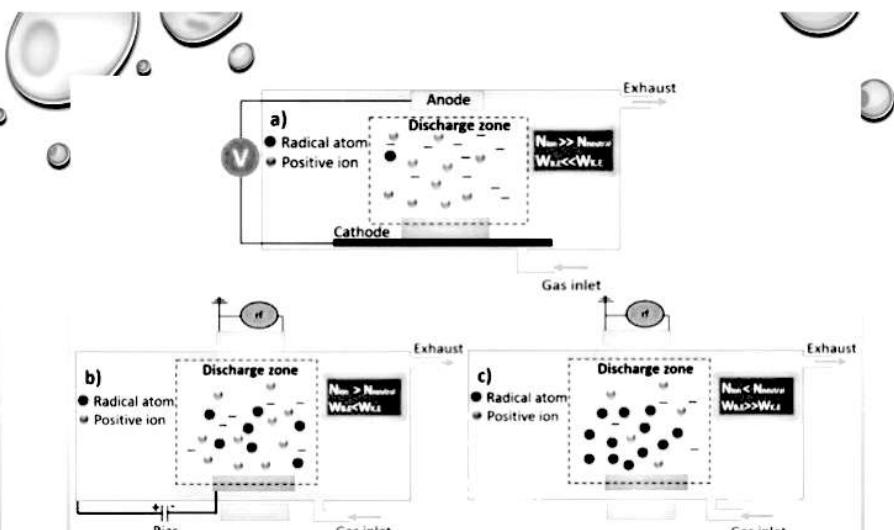
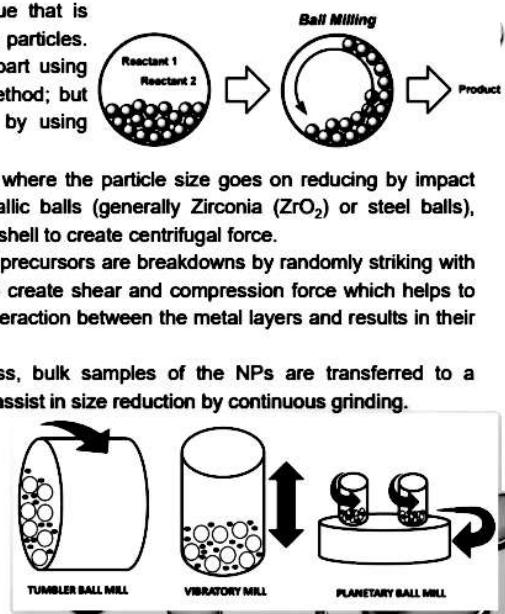


Figure: Schematic representation of various plasma processing systems for (a) sputtering; (b) reactive ion etching; and (c) highly dissociated weakly ionized plasma for chemical etching.

Ball Milling

Ball milling is a mechanical technique that is broadly used to grind powders into fine particles. The reactants are generally broken apart using solvent molecules in the traditional method; but in ball milling, reactants are broken by using mechanical forces.

- ✓ It is a shear-force dominant process where the particle size goes on reducing by impact and attrition mainly consists of metallic balls (generally Zirconia (ZrO_2) or steel balls), acting as grinding media and rotating shell to create centrifugal force.
- ✓ In this process, metal or metal oxide precursors are breakdowns by randomly striking with grinding media in the rotating shell to create shear and compression force which helps to overcome the weak Vander Waal's interaction between the metal layers and results in their splintering.
- ✓ To initiate the size reduction process, bulk samples of the NPs are transferred to a container containing heavy balls that assist in size reduction by continuous grinding.
- ✓ Reduction of particle size can be accomplished using numerous types of ball milling techniques such as high energy mills, planetary ball mills, attrition ball mills, low energy tumbling mills, and vibrating ball mills



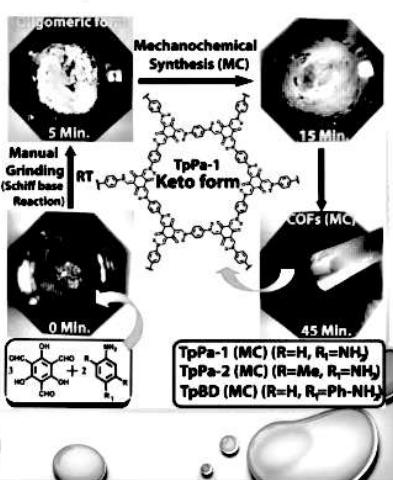
Mechanochemical Process

Mechanochemical synthesis is the combination of mechanical and chemical methods to get nanomaterials which is an entirely different process from the ball milling process. It is performed by solid-state displacement reaction during the ball milling process to obtain nanoparticles embedded in the by-product finally. Milling temperature, milling collision energy, volume, and particle size, milling time, the molar ratio of precursor, powder mixture to ball ratio are the main factors that influence the particle size and particle size distribution.

The advantages of this synthesis at relatively low temperatures:

1. To prevent the incorporation of oxygen into fluorides at pyro-hydrolysis and thus avoid several negative effects such as uncontrollable change of some physical characteristics;
2. To avoid severe limitations on the choice of fluorides as the components of complex fluoride materials for high-temperature synthesis reactions, such as different melting points of the components, their vapor pressures, and thermal decomposition.

The main drawbacks of this system are Contamination, long processing time, uncontrollable particle microstructure, and agglomeration.



What is Lithography?

Lithography (from Ancient Greek λίθος, lithos, meaning "stone", and γράφειν, graphein, meaning "to write") is a method of printing originally based on the immiscibility of oil and water. The printing is from a stone (lithographic limestone) or a metal plate with a smooth surface.

Lithography

Dr. Kazi Hanium Maria
Course teacher
PH407

Nanoscale lithography

There are two main methods producing Nano graphics:

◆ Modern chemical technology:

1. Atomic layer epitaxy;
2. Plasma enhanced chemical vapor deposition;
3. Metal organic chemical vapor deposition;
4. Molecular beam epitaxy

◆ Nanoscale Lithography

Nanolithography is the branch of nanotechnology concerned with the study and application of fabricating nanometer-scale structures, meaning patterns with at least one lateral dimension between 1 and 100 nm.

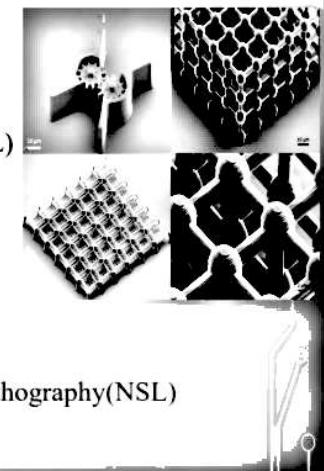
Importance of lithography

Lithography changes the fabrication and manufacturing of materials, devices, and systems via:

- ◆ higher degree of safety
- ◆ environmental competitiveness.
- ◆ improved stability and robustness
- ◆ higher degree of efficiency and capability, flexibility and integrity supportability and affordability, survivability and redundancy
- ◆ Predictable properties of nanocomposites and materials (e.g., lightweight and high strength, thermal stability, low volume, and size).

Classification of lithography

- ✓ Photolithography – an conventional and classical method
- ✓ Ion beam Lithography
- ✓ X-ray lithography
- ✓ Electron beam lithography (EBL)
- ✓ Soft lithography/Micro-contact printing (SL)
- ✓ Nano-imprint lithography (NIL)
- ✓ Scanning Probe lithography
 - Atomic Force Microscope lithography
 - Dip-pen nanolithography (DPN)
- ✓ Colloidal Lithography (CL)/ Nanosphere lithography(NSL)

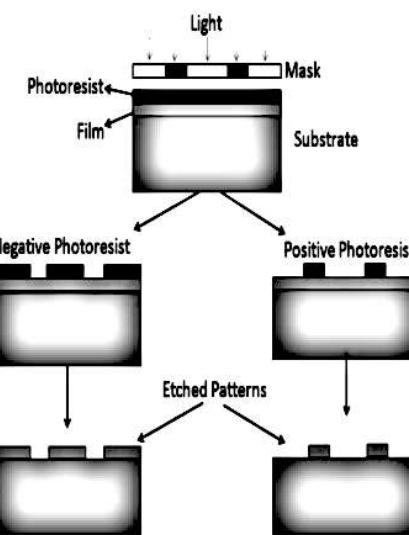


Photolithography

➤ Photolithography, also termed optical lithography or UV lithography, is a process used in microfabrication to pattern parts of a thin film or the bulk of a substrate. It uses light to transfer a geometric pattern from a photomask to a light-sensitive chemical "photoresist", or simply "resist," on the substrate. A series of chemical treatments then either engraves the exposure pattern into, or enables deposition of a new material in the desired pattern upon, the material underneath the photo resist.

- Projection Printing Technique
- Limited by diffraction limit

Schematic of Photolithography



Photolithography

- ✓ A photoresist is a light-sensitive material used in several industrial processes, such as photolithography and photoengraving, to form a patterned coating on a surface.
- ✓ A positive resist is a type of photoresist in which the portion of the photoresist that is exposed to light becomes soluble to the photoresist developer. The portion of the photoresist that is unexposed remains insoluble to the photoresist developer.
- ✓ A negative resist is a type of photoresist in which the portion of the photoresist that is exposed to light becomes insoluble to the photoresist developer. The unexposed portion of the photoresist is dissolved by the photoresist developer.

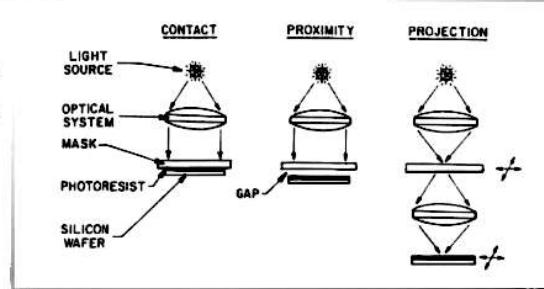
Photolithography

Photolithography steps:

1. Wafer cleaning
2. Barrier layer formation
3. Photoresist application
4. Prebaking
5. Mask Alignment and Exposure
 - Contact Printing
 - Proximity Printing
 - Projection printing
6. Development
7. Hand baking
8. Etching
9. Stripping

Applications

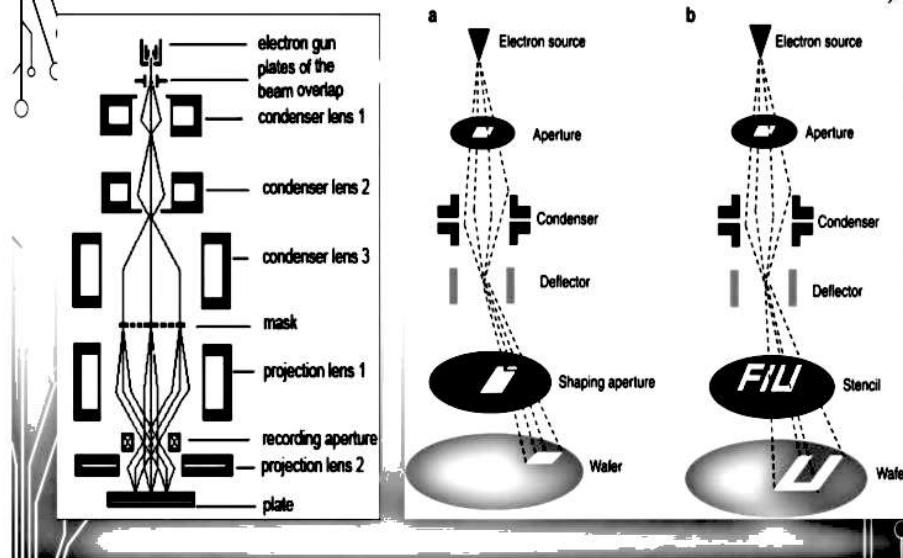
- IC designing process
- Printed electronic board
- Nameplate and printer plate



Electron-beam lithography

- Electron-beam lithography (often abbreviated as e-beam lithography) is the practice of scanning a focused beam of electrons to draw custom shapes on a surface covered with an electron-sensitive film called a resist ("exposing"). The electron beam changes the solubility of the resist, enabling selective removal of either the exposed or non-exposed regions of the resist by immersing it in a solvent ("developing").
- Allows accuracy down to as small as 10nm dimensions
- highly accurate and reliable pattern writing

Schematic of Electron-beam lithography



Electron-beam lithography

EBL components:

1. Electron source
2. Stigmators
3. Electron Lenses
4. Apertures
5. Blanking Plates

Proximity effect:

The smallest features produced by electron-beam lithography have generally been isolated features, as nested features exacerbate the proximity effect, whereby electrons from exposure of an adjacent region spill over into the exposure of the currently written feature, effectively enlarging its image, and reducing its contrast.

Electron-beam lithography

Advantages of E-beam Lithography

- Print complex pattern directly on wafers
- Eliminate diffraction problem
- Higher resolution up to 20 nm (Photolithography ~ 50 nm)
- Flexible technique

Disadvantages of E-beam Lithography

- Slower than optical lithography.(approximately 5 wafers/hour at less than 0.1 μ resolution)
- Expensive and complicated
- Forward scattering, backward scattering
- Secondary electrons

Applications:

- Very high resolution
- Fabrication of masks

X-ray lithography

- X-ray lithography, is a process used in electronic industry to selectively remove parts of a thin film. It uses X-rays to transfer a geometric pattern from a mask to a light-sensitive chemical photoresist, or simply "resist," on the substrate. A series of chemical treatments then engraves the produced pattern into the material underneath the photoresist.
- Allowing smaller feature sizes. Having short wavelengths (below 1 nm), X-rays overcome the diffraction limits of optical lithography.

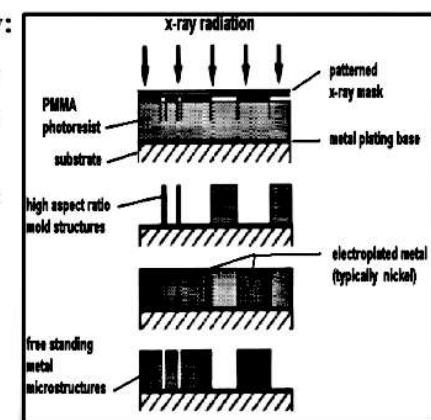
Schematic of X-ray lithography

Elements of X-ray Lithography:

1. A mask consisting of a pattern made with an X-ray absorbing material on a thin X-ray transparent membrane.
2. An X-ray source of sufficient brightness.
3. An X-ray sensitive resist material.

X-ray Lithography steps:

1. Irradiation
2. Development
3. Electroforming
4. Mould insert
5. Mould filling
6. Mould releases



Basic steps of the deep x-ray lithography process: The x-ray radiation comes from a synchrotron, is selectively passed or blocked by the patterned mask absorber, and penetrates the photoresist and deposits energy to expose the resist. The photoresist is then developed leaving cavities down to the metal plating base (provided sufficient energy was deposited to completely expose the resist). Metal is then electroplated onto the plating base and the cavities are filled. The remaining resist is removed leaving free-standing metal microstructures.

X-ray lithography

Advantages of X-ray Lithography

- Short wavelength from X-rays 0.4-4 nm
- No diffraction effect
- Simple to use
- No lens
- Faster than EBL
- Uniform refraction pattern
- Higher resolution for small feature size

Disadvantages of X-ray Lithography

- Thin lens
- Distortion in absorber
- Cannot be focused through lens
- Masks are expensive to produce

Modes of operation of AFL/SPL

Contact or static mode:

AFM tip makes soft contact with the sample. The tip is attached to the end of a cantilever with a low spring constant. The constant force causes the cantilever to bend to accommodate changes in topography.

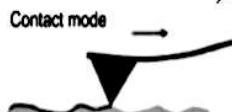
Non-Contact or dynamic mode:

The cantilever is vibrated near but not contact to the sample surface at a frequency (typically, 100-400 kHz) where its amplitude is typically a few

Intermittent or tapping mode:

The cantilever is driven to oscillate up and down. The amplitude of this oscillation is greater than 10 nm, typically 100 to 200 nm.

Contact mode



Noncontact mode



Tapping mode

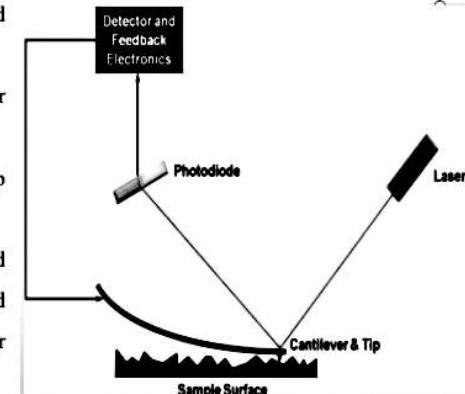


Three mode of operation of AFM
Lithography

Atomic force microscope lithography: scanning probe lithography (SPL)

AFM was invented in 1986. AFM can be used to study both insulating and conducting materials.

- ✓ AFM can be operated in liquid air or vacuum.
- ✓ In AFM, a tiny cantilever with a sharp tip is scanned across a surface.
- ✓ The interaction between the surface and the tip cause the cantilever to bend and the bending is monitored using a laser beam.
- ✓ In this way, height changes in nm can be measured and used to generate a 3D image of the surface.



Schematic of AFM Lithography

Atomic force microscope lithography

Advantage of AFM:

1. Topography of surface
2. Properties of Surface
3. Properties of single molecules
4. Force within molecules

Limitations of AFM:

1. Diffusion of ink from PDMS stamp to surface during patterning
2. Shrinking of stamp is one of the main problem in which stamp can shrink in size resulting difference in desired dimensions of the substrate patterning.

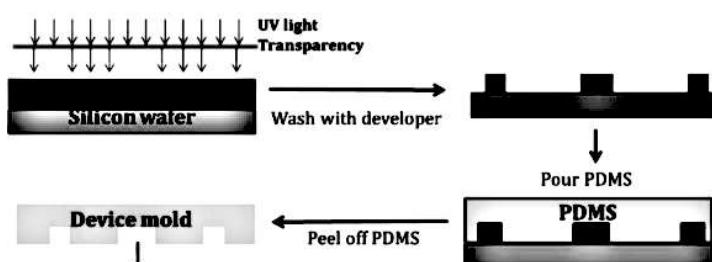
COMPARISON

	Source	Form	Disadvantages	Advantages
Photolithography	UV Light	Projection Printing	Limited by UV Wavelength	Cheap
Electron-beam lithography	Focused beam of electrons	Direct Writing	Expensive	Highly Accurate
X-Ray Lithography	X-Ray	Proximity Printing	Expensive/ Fragile Masks	Accurate/ Efficient Fast

Soft lithography/Micro-contact printing

- ✓ Soft lithography has been developed as an alternative to photolithography and a replication technology for both micro and nanofabrication.
- ✓ Soft lithography uses the design on a PDMS (poly di-methyl siloxane) stamp.
- ✓ PDMS is non-toxic, so can be used safely with biological materials, including living cells.
- ✓ A silicon master is replicated with PDMS. Master is fabricated by conventionally lithographic technique. The pro-polymer (viscous liquid) is poured over the master, cured at adjustable temperature for adjustable time. The polymer solidifies but remain flexible.
- ✓ The PDMS mould is peeled off from the master and a negative copy (stamp) is obtained. The stamp can then be used for printing a desired material from the stamp to a suitable surface.

Soft lithography/Micro-contact printing



Schematic of soft lithography (SL)

Applications of Soft lithography

1. Cell biology
2. Microelectronics
3. Surface Chemistry
4. Micromachining
5. Designing cell
6. Designing DNA and protein

Soft lithography/Micro-contact printing

Advantages of Soft lithography:

- Very simple and easy pattern procedures to create micro-scale features.
- This can be done in a traditional laboratory environment. No need clean room facility.
- Using single master, multiple stamps can be made.
- Reliability of individual stamps which can be used for many times.
- It is a cheaper method.

Limitation in Soft lithography :

- Diffusion of ink from PDMS stamp to surface during patterning
- Shrinking of stamp is one of main problem in which stamp can eventually shrink in size resulting difference in desired dimensions of the substrate patterning
- Contamination of substrate
- Stamp deformation

Nanoimprint lithography (NIL)

- NIL is a technique that combines the speed of optical lithography with the resolution of EBL.
- It is a simple process that uses a mould to emboss the resist with the required pattern. After embossing the resist, the compressed resist material is removed using anisotropic etching, exposing the substrate. It involves pressing and heating a thin film between a patterned template and a substrate.
- It is also flexible enough to be used at the chip level with several layers or at the wafer level when a single layer is required. It can give resolutions lower than 10nm with high throughput at low cost.
- One of the current barriers to production at these resolutions is the development of mould.

Nanoimprint lithography

Advantage of NIL:

- It can produce features at extremely small resolutions that cover a large area with a high throughput and relatively low cost.
- It can be adapted to transfer all components needed to create a thin film transistor on a plastic substrate.

Applications

- optical, photonic, electrical and biological devices such as photodetectors, silicon quantum-dot, quantum wire and ring transistors.
- Advances in mould manufacturing will have wide application of NIL in smaller devices.

Mould

Resist

Substrate

STEP 1. Press mould

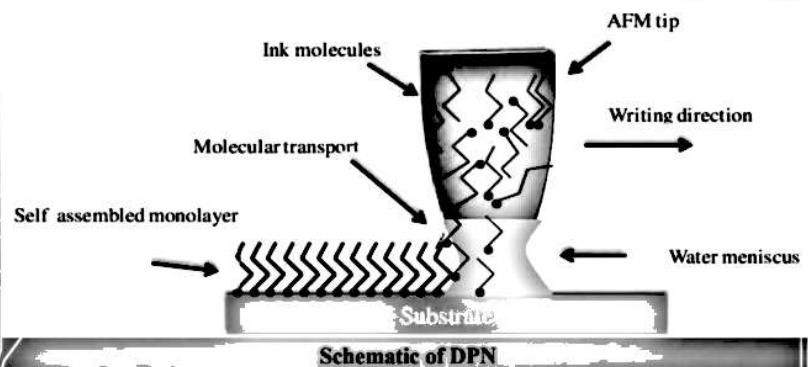
STEP 2. Remove mould

STEP 3. Pattern transfer

Schematic of NIL

Dip-pen lithography (DPN)

This process was first developed by Professor Chad Mirkin at Northwestern University Nanotechnology Institute for depositing thin organic films in patterns with feature sizes of around 10 nm (about 20 times better than the best optical lithography)



Dip-pen lithography (DPN)

- Dip Pen Nanolithography (DPN) is known as a soft-lithography technique that uses an AFM scanning probe tip to draw nanostructures.
- In this process, a probe tip is coated with liquid ink, which then flows onto the surface to make patterns wherever the tip makes contact.
- This kind of direct write technique provides high-resolution patterning capabilities for a number of molecular and biomolecular "inks" on a variety of substrates. Substrates are the base material that the images are printed on.
- In DPN technology, the ink on a sharp object is transported to a paper substrate via capillary forces. The capillary transport of molecules from the AFM tip to the solid substrate is used in DPN to directly "write" pattern consisting of a relatively small collection of molecules in nanometer dimensions.
- An AFM tip is used to write alkane thiols with 30-nm line width resolution on a gold thin film in a manner analogous to that of a dip pen. Molecules are delivered from the AFM tip to a solid substrate of interest via capillary transport, making DPN a potentially useful tool for creating and functionalizing nanoscale devices.

Dip-pen lithography (DPN)

Applications

DPN technique used to prepare sol gel templates that are used to prepare nanotubes and nanowires, and protein nanoarrays to detect the amount of proteins in biological samples such as blood.

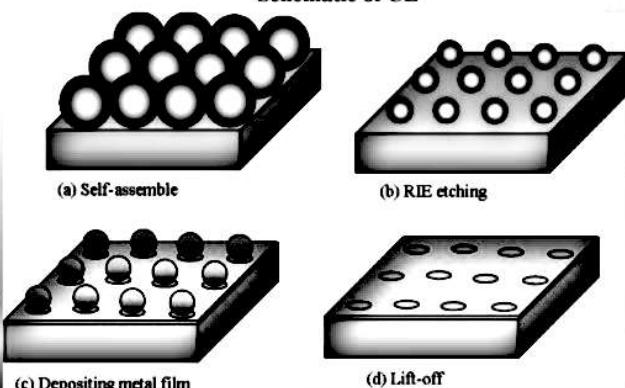
Several factors decide the resolution of DPN:

- The grain size of the substrate affects DPN resolution much as the texture of paper controls the resolution of conventional writing.
- The tip-substrate contact time and thus the scan speed influence DPN resolution.
- Chemisorption and self-assembly of the molecules can be used to limit the diffusion of the molecules after deposition.
- Relative humidity seems to affect the resolution of the lithographic process by controlling the rate of octadecanethiol (ODT) transport from the tip to the substrate.
The size of the water meniscus that bridges the tip and substrate depends on relative humidity.

Colloidal lithography (CL)

Colloidal lithography offers an extremely simple and accessible approach to defining primary patterns, varying from irregular or 'random' through to pseudo-regular. In combination with reactive ion or chemical etching, colloids can be employed as a mask to produce a master die with nanometric features, allowing the fabrication of polymer replicas.

Schematic of CL

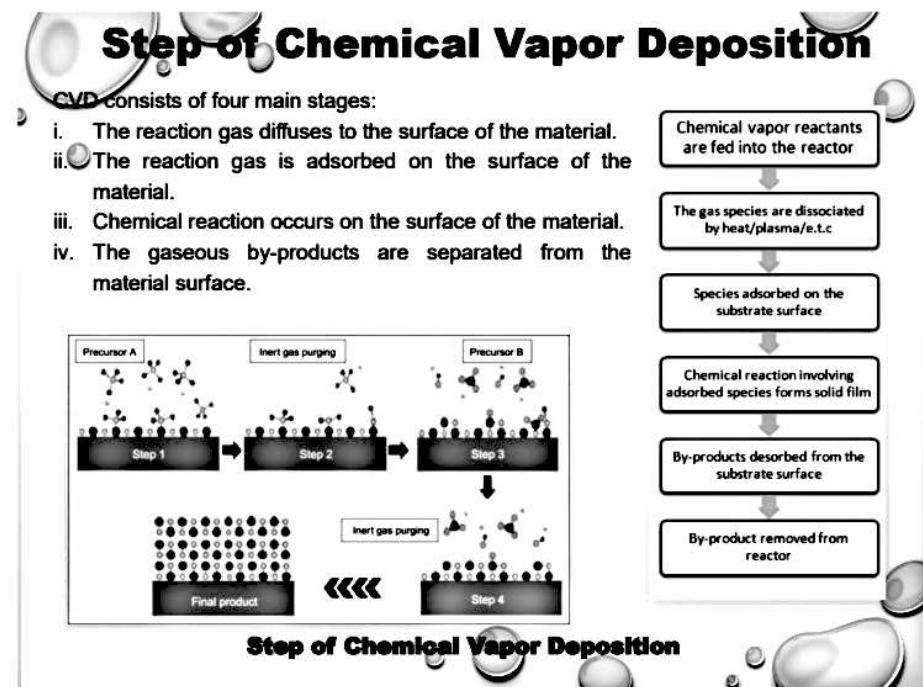
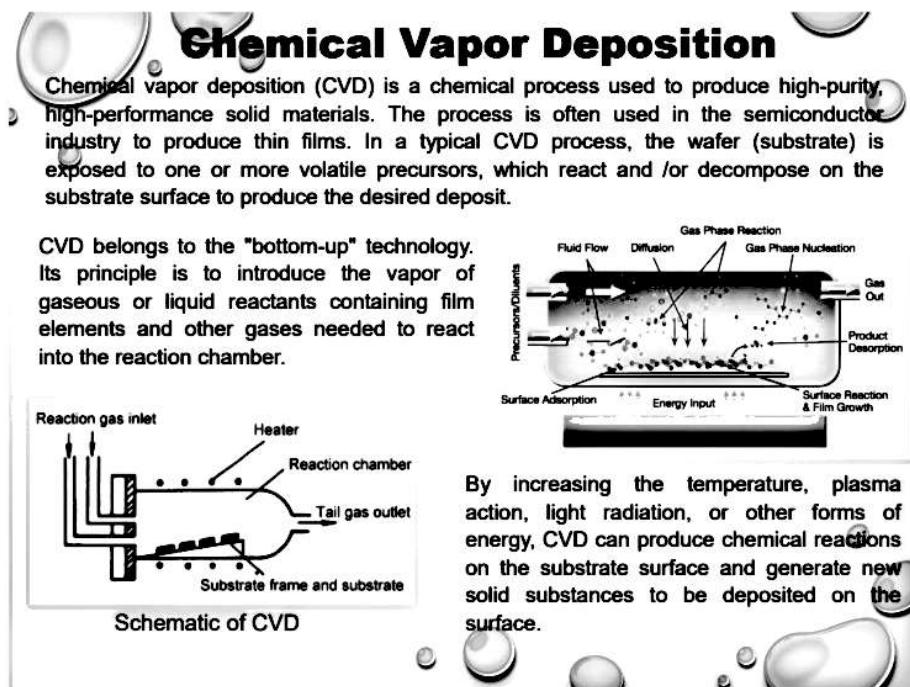
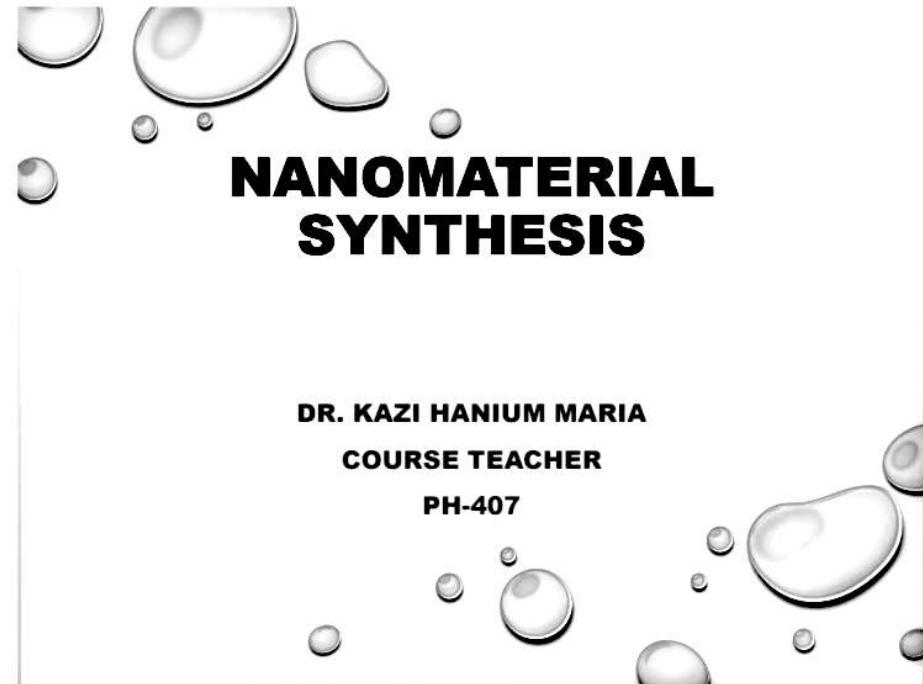
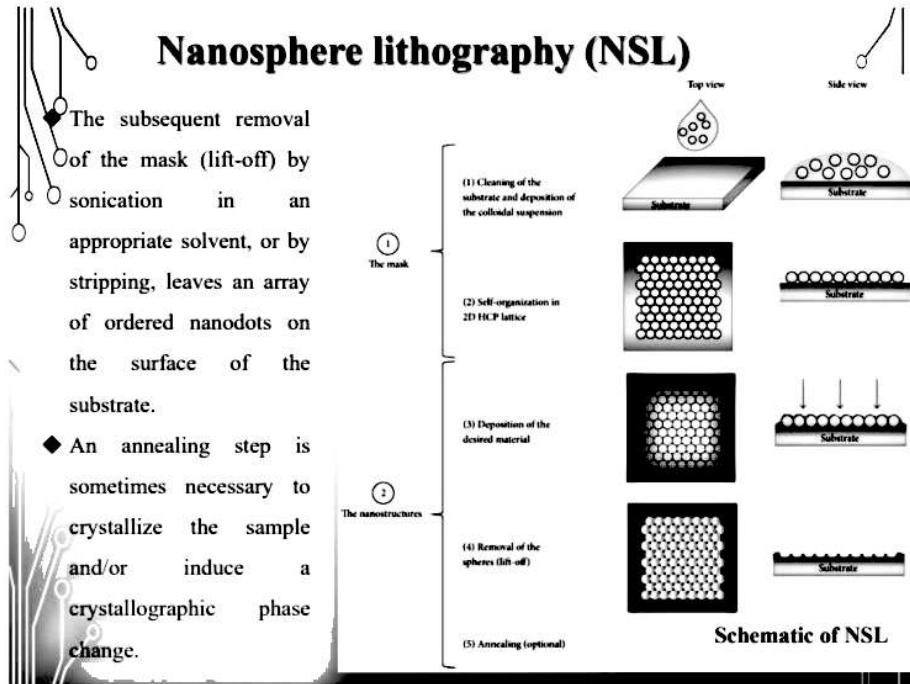


Colloidal lithography (CL)

- ◆ Colloidal lithography is a method to reproduce patterns in a variety of natural systems and is used more and more as an efficient fabrication tool in bio-, opto-, and nanotechnology.
- ◆ Nanoparticles in the colloid are made to form a mask on a given material surface, which can then be transferred by etching into nanostructures of various sizes, shapes, and patterns.
- ◆ Such nanostructures can be used in biology for detecting proteins and DNA, and for producing artificial crystals in photonics and gigahertz oscillators in spin-electronics.
- ◆ Scaling of colloidal patterning down to 10 nm and below, dimensions comparable or smaller than the main relaxation lengths in the relevant materials, including metals, is expected to enable a variety of new ballistic transport and photonic devices, such as spin-flip terahertz lasers

Nanosphere lithography (NSL)

- ◆ Nanosphere lithography (NSL) is a technique used for generating single layers of nanoscale features that are hexagonally close packed or in similar patterns. This method may produce regular and homogenous arrays of nanoparticles with different sizes and with precisely controlled spacing's. It is inexpensive and simple to implement.
- ◆ NSL consists of two main stages: mask preparation followed by nanostructure production. At the beginning, the flat substrate undergoes a chemical treatment to enhance its hydrophilic character, and then it is coated with a suspension containing monodisperse spherical colloids (e.g., polystyrene).
- ◆ Next, upon drying, self-organization of a monolayer or bilayer of hexagonal-close-packed (HCP) features takes place.
- ◆ The thus-formed mask is then used to selectively pattern the substrate via deposition of the material of interest through the interstices of the ordered beads.

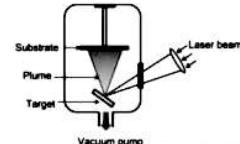


CVD	PVD	PECVD
ADVANTAGES <ul style="list-style-type: none"> Avoids the line-of-sight High deposition rate Production of thick coating layers Co-deposition of material at the same time 	ADVANTAGES <ul style="list-style-type: none"> Atomic level control of chemical composition Not requiring the usage of special precursors Safer than CVD due to the absence of toxic precursors or by-products 	ADVANTAGES <ul style="list-style-type: none"> Avoids the line-of-sight issue to certain extent High deposition rate Low temperatures Both organic and inorganic materials as precursors Unique chemical properties of the deposited films
DISADVANTAGES <ul style="list-style-type: none"> Requirement of high temperatures Possibility of toxicity of precursors Mostly inorganic materials have been used 	DISADVANTAGES <ul style="list-style-type: none"> Line-of-sight deposition Low deposition rate Production of thin coating layers Requirement of annealing time 	DISADVANTAGES <ul style="list-style-type: none"> Instability against humidity and aging Existence of compressive and residual stresses in the films Time consuming specially for super lattice structures Existence of toxic, explosive gases in the plasma stream High cost of equipment

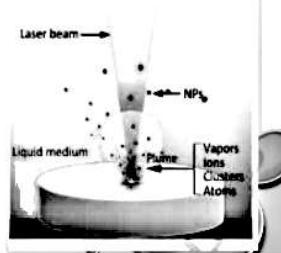
Laser Ablation

Pulsed laser ablation (PLA) is a process in which a pulsed laser beam is focused on a solid target material to remove material from the target surface. The term "ablation" means the removal of surface atoms by a multiphoton excitation process, i.e., thermal evaporation. This method consists of some basic steps to produce the nanoparticles of bulk materials in liquid. The steps in laser ablation include:

- ✓ Laser-matter interaction (irradiates the metal target in bulk liquid and starts the breakdown process),
- ✓ Plasma generation and plasma energy transfer to liquid,
- ✓ Cavitation, bubble formation, and bubble collapse when it reaches the maximum radius,
- ✓ Collapsing of the bubble and then particle release in solution.



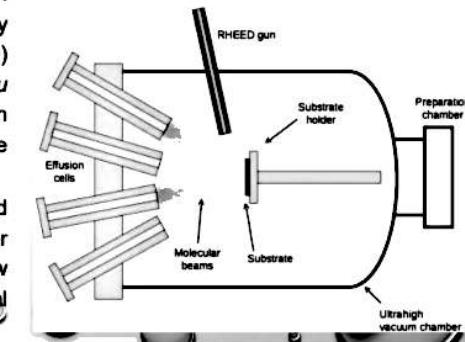
The structure of the plasma depends upon the target material, ambient medium (liquid or gas), ambient pressure, and laser used for ablation. This method has several advantages such as decreased agglomeration, and impurity problems, and this method is free from capping agents and chemical precursors and is environment friendly.



Molecular beam epitaxy

Molecular beam epitaxy (MBE) is an epitaxial process by which the growth of materials takes place under UHV conditions on a heated crystalline substrate by the interaction of adsorbed species supplied by atomic or molecular beams. The layers or deposits have:

- the same crystalline structure of the substrate or a structure with a similar symmetry
- A lattice parameter differing from that of the substrate by no more than ~10%. The beams generally have thermal energy and are produced by evaporation or sublimation of suitable materials contained in ultra-pure crucibles.
- The UHV environment ensures high purity and reflection of high energy electron diffraction (RHEED) capability, which allows *in situ* preparation of atomically clean substrates with specific surface reconstruction.
- The beam nature of deposition, and the kinetic mode of growth, together with RHEED oscillation, allow understanding and control of epitaxial growth.



Wet chemical Synthesis technique

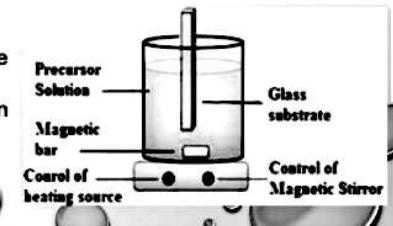
Wet chemical synthesis technique or liquid phase synthesis is a simple and cost-effective procedure to synthesize a wide range of nanomaterials without involving complicated equipment. This process routes to deal with chemical reactions in the solution phase using precursors at proper experimental conditions. Each wet-chemical synthesis method differs from the others, meaning that one cannot find a general rule for these kinds of synthesis approaches. These synthesis strategies have been used for the preparation of 2D nanomaterials which are unable to be prepared by top-down approaches.

Colloidal synthesis: Self-Assembled Monolayers: Colloidal methods are simple and well-established wet chemistry precipitation processes in which solutions of the different ions are mixed with controlled temperature and pressure to form insoluble precipitates.

Micro-emulsion method: reverse-Micelle structure and Langmuir-Blodgett films

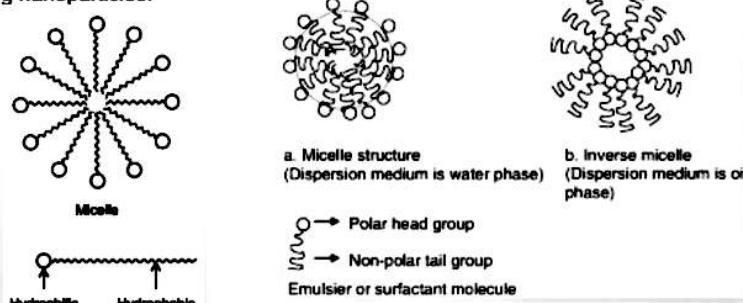
Sol-gel method: Dip coating method and spin coating methods

Spray pyrolysis method



Microemulsion method

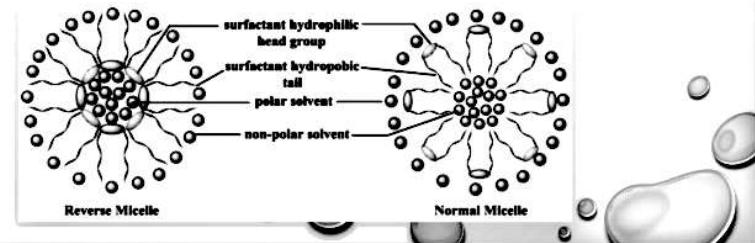
Microemulsions are isotropic, thermodynamically stable dispersion of oil, water, surfactant, and often cosurfactant. Microemulsion can be characterized as oil-in-water (O/W), water-in-oil (W/O), and bicontinuous systems. Water-in-oil microemulsions are composed of nm-sized water droplets that are dispersed in a continuous oil medium and stabilized by surfactant molecules. These droplets can serve as nanoreactors for producing nanoparticles.



micelle is a particle of superfine colloid with liquid dispersion medium comprising a core and stabilizing surface layer. Average size of micelles ranges from 1 nm to 100 nm.

Micelles are particles contained in lyophilic colloids (solutions of surfactants). In lyophilic sols, a micelle is an association of molecules (aggregates consisting of dozens and hundreds of amphiphilic molecules). A hydrophobic radical in each molecule is fixed to a polar (hydrophilic) group. When a micelle develops, several dozens or hundreds of molecules aggregate in such a manner that hydrophobic radicals form a core (inner element), while hydrophilic groups form the surface layer of a micelle. The concentration of surfactants in a solution that promotes development in the system of stable micelles balanced with non-associated molecules of surfactant is known as critical micelle concentration.

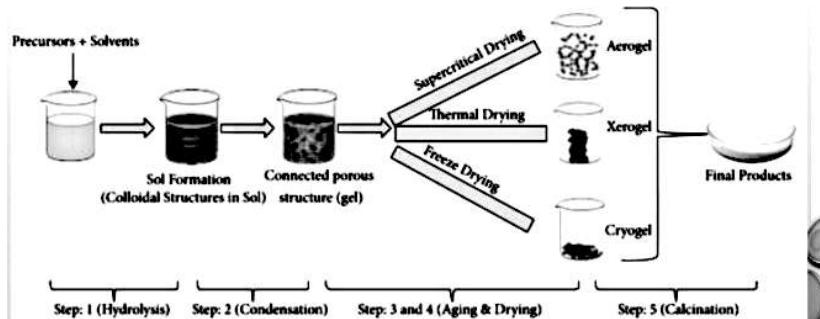
If the dispersion medium is represented by an organic liquid, molecules in a micelle may have a reverse orientation, when the core is made up of polar groups, and hydrophobic radicals are turned inwards called reverse micelle.



Sol-gel process

The sol-gel method is performed in the liquid phase and the reaction product of the synthesis could be either colloidal powders or films. The chemical and physical properties of the materials obtained by the sol-gel method are related to the experimental conditions applied. The sol-gel method involves two main reactions: hydrolysis of the precursor in the acidic or basic mediums and polycondensation of the hydrolyzed products.

Sol is a type of colloid in which a dispersed solid phase is mixed in a homogeneous liquid medium.



Step of Sol-gel process

As the name suggests, the Sol-gel method involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in the continuous liquid phase (gel).

The sol-gel process involves four steps:

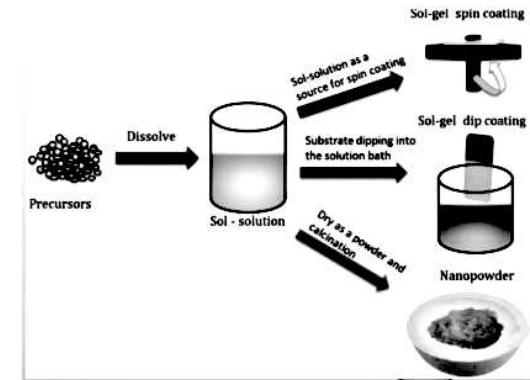
- ❖ First the hydrolysis reaction, in which the -OR group is replaced with an -OH group. The hydrolysis reaction can occur without a catalyst but is more rapid and complete when they are used. A catalyst can be a base (NaOH or NH₄OH) or an acid.
- ❖ In the 2nd step, the sol starts to condense and polymerize. This leads to the growth of particles which depending on various conditions such as pH, reach dimensions of a few nm.
- ❖ Next step is aging and drying as the condensation/ polymerization reaction is quite complex and involves many intermediate products, including cyclic structure. The particles then agglomerate. A network starts to form throughout the liquid medium, resulting in thickening, which forms a gel.
- ❖ Finally, anneal or calcine the sol at a different temperature to get powder or film surface.

Aerogel: where the liquid component of the gel has been replaced with a gas. The result is a solid with extremely low density and low thermal conductivity.

Xerogel: when the liquid phase of the gel is removed by evaporation. It may retain its original shape but often cracks due to extreme shrinkage that is experienced while being dried.

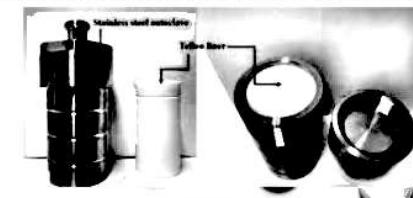
Sol-gel process

- May generate a fine coating to make sure of the adherence between the substrate and the top layer.
- Simple, inexpensive and effective method to yield excellent quality coverage
- Form high purity products
- Process time is longer
- Fine pores
- Organic solutions may be toxic

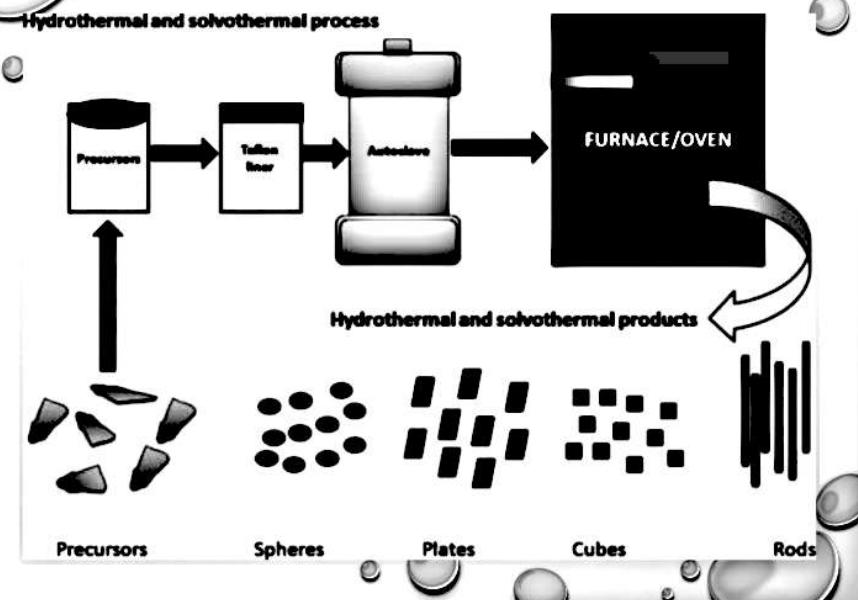


Solvothermal process

- Solvothermal synthesis involves the synthesis of nanomaterials using a solvent under elevated temperature (usually 100–1000°C) and pressure (1–10,000 atm).
- The process is typically carried out close to or above the boiling point of the reaction medium in a sealed vessel (e.g., in an autoclave).
- The reaction vessels have to be chemically inert. The reaction solution is heated above the boiling point of the solvent used in the sealed autoclave thereby building high pressure.
- Under such conditions, the solvent gets converted into a supercritical fluid where gas and liquid phases exist simultaneously.
- After the reaction is over, the autoclave is cooled to room temperature. Then, solvents and impurities are removed, to recover the desired product.
- If water is the solvent, the method is termed hydrothermal synthesis and is usually carried out below the supercritical temperature of water (374°C). The technique has been used to synthesize nanoparticles of different shapes like spheres, rods, tetrapod, etc. by tuning the reaction temperature, precursor concentration, and reaction time.



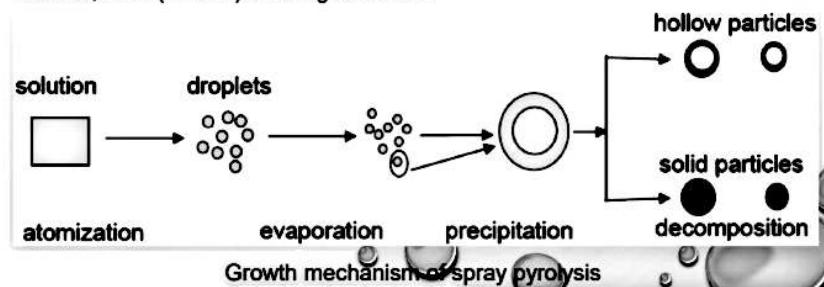
Schematic of Solvothermal process



Spray Pyrolysis

The spray pyrolysis method is based on forming an aerosol from various precursor solutions, which could be a solution of metallic salts or a colloidal solution. The generated solution droplets (aerosol) are then very rapidly heated in a furnace at a given temperature, thus passing through several stages:

- ❖ evaporation of the solvent from the surface of the droplets,
- ❖ drying the droplets containing the precipitated solute
- ❖ the annealing of the precipitate at high temperatures (thermolysis)
- ❖ formation of microporous particles of defined phase composition
- ❖ formation of solid particles
- ❖ sintering of solid particles as the particles obtained after thermolysis are very reactive, inner ("in situ") sintering is needed.



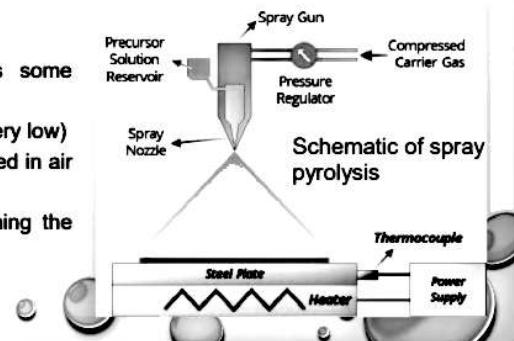
Spray Pyrolysis

Advantages of spray pyrolysis approach:

- It is a cost-effective method because of its simple equipment and experimental arrangement.
- It does not require the use of high-quality reagents and compositions.
- The morphology and size of particles can be efficiently controlled by varying the preparative conditions, nature of additives, flow rate, and concentration of reactants in the precursor solution.
- This is a continuous process by which it is possible to establish control over morphology and get fine powders with spherical particles and the desired diameter dictated by the size of the drops.

The spray pyrolysis technique has some disadvantages:

- It is not easy to scale up (yield is very low)
- oxidation of sulfides when processed in air atmosphere is possible
- there are difficulties with determining the growth temperature.



Important factors of Self-assembly

➤ The basic principle of nanochemistry lies in the self-assembly of a target structure from the spontaneous organization of building blocks.

There are five important factors that need to be taken into consideration for self-assembly:

- i. building block, scale, shape, and surface structure
- i. Attractive and repulsive interactions between the building blocks
- i. Association, dissociation, and adaptable motion of the building blocks in the assembly to attain the lowest energy structure
- i. Interaction of the building blocks with the solvents, interfaces, and templates
- i. the dynamics of the building blocks and mass transport.

Self-assembly

Self-assembly: is a bottom-up production technique. The 'assembly' connotes 'to put together or build' and the 'self' implies 'without outside help or on its own'. So the structures and patterns, large and small put themselves together from basic building blocks in a parallel manner.

- ❖ Self-assembly is the autonomous organization of components into patterns or structures without human intervention which are common throughout nature and technology.
- ❖ They involve components from the molecular (e.g., crystals) to planetary (e.g., weather systems) scale and many different types of interactions.
- ❖ It is a fundamental principle that creates structural organization from the disordered components in a system.

History of Self-assembly: The principles of self-assembly were conceptualized a long time ago (circa 400 BC). The ancient Greek philosopher Democritus expounded the idea that atoms and voids organized in different arrangements constitute all matter. He explained the growth of the universe from the minutest atomistic building blocks to the stars and galaxies. This is perhaps the oldest recorded version of matter undergoing self-assembly over all scales.

Building Blocks of Self-assembly

➤ Building blocks: The building blocks can be molecules or nano-scale clusters which are usually not monodisperse unless they are single atoms or molecules. The polydispersity present in the building blocks in terms of size and shape dictates the achievable degree of structural perfection of the assembly, and the defects in the assembled system.

➤ The making of building blocks with a particular surface structure, charge, and functionality is a challenging task. The surface properties control the interactions between the building blocks and their interactions with the environment as well which determines the geometry and the equilibrium separation between the building blocks in a self-assembled system.

➤ The aggregation and de-aggregation processes and the corrective movements of the self-assembled structure allow it to attain the most stable form. The driving forces for the molecular organization can be as varied as ionic, covalent, hydrogen bonding, or metal-ligand bonding interactions.

Templated Self-assembly

The self-assembly of molecules and materials can be directed by templates. The template can be constituted of molecules, molecular assemblies, or additive materials which serve to fill space, balance charge and direct the formation of a specific structure.

A template patterned at the nanoscale can direct the assembly process. The structure-directing templates which can make, organize and interconnect the building blocks can be porous hosts, lithographic patterns, and channels in polymer, alumina, and silicon membranes. Some of these templates are widely used to make nanowires, nanorods, and nanotubes. A well-known templating method is the use of surfactant micelles and liquid crystals. Many microporous and mesoporous inorganic solids have been prepared by this templating mechanism.

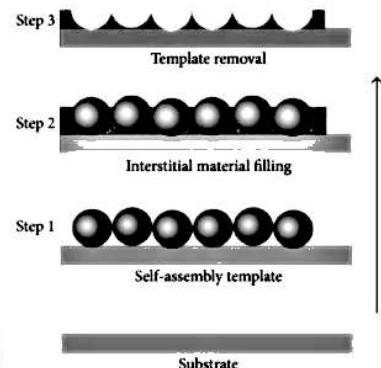
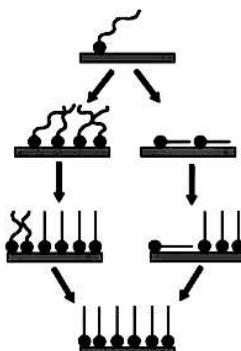


Figure: the natural self-assembly of templates and subsequently space filling the voids either by precipitation via chemical routes or by the electrochemical reduction of materials

Formation Self-assembled monolayer

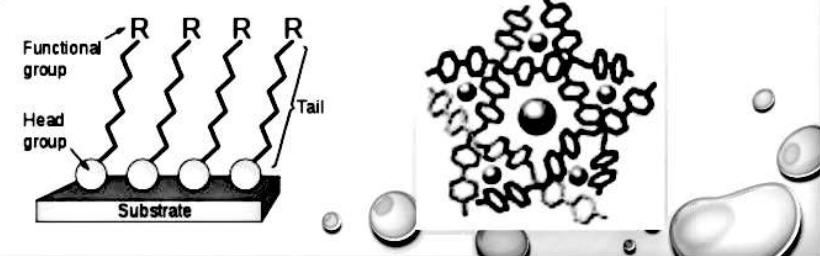
- ❖ SAMs are created by the chemisorption of "head groups" onto a substrate from either the vapor or liquid phase followed by a slow organization of "tail groups".
- ❖ Initially, at small molecular density on the surface, adsorbate molecules form either a disordered mass of molecules or form an ordered two-dimensional "lying down phase", and at higher molecular coverage, over a period of minutes to hours, begin to form three-dimensional crystalline or semicrystalline structures on the substrate surface.
- ❖ The "head groups" assemble together on the substrate, while the tail groups assemble far from the substrate.
- ❖ Areas of close-packed molecules nucleate and grow until the surface of the substrate is covered in a single monolayer.
- ❖ Adsorbate molecules adsorb readily because they lower the surface free energy of the substrate and are stable due to the strong chemisorption of the "head groups".
- ❖ These bonds create monolayers that are more stable than the physisorbed bonds of Langmuir-Blodgett films.
- ❖ The monolayer packs tightly due to van der Waals interactions, thereby reducing its own free energy.



Self-assembled monolayer (SAM)

Self-assembled monolayers (SAM): are produced when a substance spontaneously forms a layer one molecule thick on a surface. Additional layers can be added, leading to laminates where each layer is just a molecule in depth.

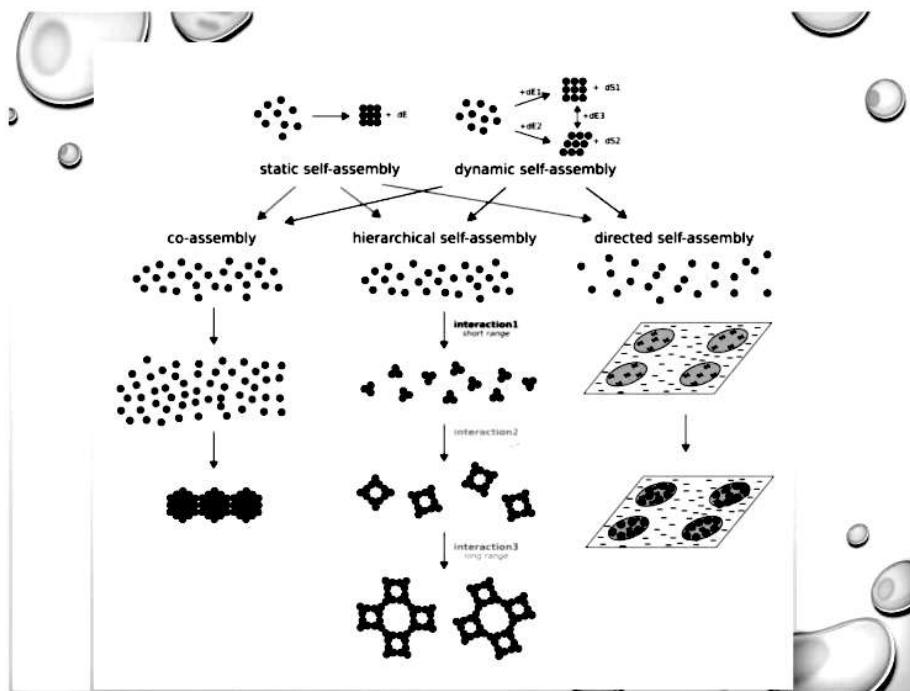
Self-assembled monolayers (SAM) of organic molecules are molecular assemblies formed spontaneously on surfaces by adsorption and are organized into more or less large ordered domains. Sometimes, molecules that form the monolayer do not interact strongly with the substrate. Therefore, the molecules possess a head group that has a strong affinity to the substrate and anchors the molecule to it which is depicted in Figure 1. Common head groups include thiols, silanes, phosphonates, etc.



Pinning down Self-assembly

The term self-assembly implies spontaneity, a structure builds itself from modular construction units, and an ordered pattern forms from a disordered state. The self that drives the assembly is the interaction among the building blocks rather than the generally stronger bonding force within them. The two main categories of self-assembly are called static and dynamic. The processes of static and dynamic self-assembly can be further roughly subdivided into co-assembly, directed self-assembly, and hierarchical self-assembly.

- **Static Self-assembly:** In the absence of external influences, building block static self-assembly is driven by energy minimization to form static equilibrium structures.
- **Dynamic self-assembly:** In the presence of outside influences, a dynamically self-assembling system may prevail that can adjust to its surrounding environment, by residing on an energetic minimum which is caused by the influx of energy in the system – once the energy stops flowing into the system, the minimum disappears and the system disassembles. Any living organism is a perfect example of dynamic self-assembly. It reduces entropy by absorbing energy from the environment. This gradient in entropy between the organism and the environment can be maintained only as long as energy is driven from the environment into the organism in the form of food and heat. Once that flux ceases, the organism disassembles



Difference between Static & Dynamic SA

- Dynamic self-assembly is more 'subtle' but potentially far more powerful than the static variety.
- Dynamic order arises from opposing interactions between autonomously moving components that exist out of equilibrium and which can be altered by dissipating energy into the system. The system returns to equilibrium when the influx of energy stops. The kinetics of this disassembly process is strongly dependent on the specific system involved and has to be taken into consideration for fabrication purposes.
- The static self-assembly generates structures that are at equilibrium and are thus permanent unless the environment is changed leading to a different equilibrium state.
- Dynamic self-assembling systems, both living and non-living, involve collections of interacting building blocks that can adapt or react to a chemical or physical stimulus in their surroundings.
- In dynamic self-assembly, groups of interacting building blocks can arrange into structures and patterns away from thermodynamic equilibrium and these patterns can be reconfigured by responding to external stimuli thereby making them adapt to their environment.
- Dynamic self-assembly can be achieved in practice by changing an energy flux delivered to a system of building blocks interacting through opposing attractive and repulsive forces.

Pinning down Self-assembly

Co-assembly represents cases in which the simultaneous self-assembly of different building blocks within the same system leads to a synergic architecture that could not have been produced by the isolated self-assembly of either building block.
Example: Formation of periodic mesoporous silicas by surfactant micelle templating of silicate building blocks. While the kinetics of the individual assembly processes involved is still subject to debate, the overall process is synergic.

Hierarchical self-assembly is the organization of a single building block over multiple length scales. The original building blocks organize into a 'first order' assembly, which becomes the building block for a larger 'second order' assembly. This process can lead to several orders of assembly. Biological systems are famous for employing this technique to create large functional structures out of molecular building blocks.
Example: Opal film casting of lyotropic liquid crystal templated periodic mesoporous silica, boasting four length scales in one construct, from
(i) the microscopic silica tetrahedral building units to
(ii) the mesoscopically ordered porosity to
(iii) the macroscopic air voids of the inverse opal replica
(iv) the overall form of the inverse periodic mesoporous silica opal film.

Directed assembly is a case where the self-assembly is directed by external forces that had been placed by design. This is the typical case for bottom-up-meets-top-down approaches where a lithographic pattern can be used to direct the self-assembly of colloids from solution on a substrate.



GOLD & SILVER NANOPARTICLE

Dr. Kazi Hanium Maria
Course teacher
PH-407

GOLD NANOPARTICLE

- ◆ Gold (Au) is unique compared to other metals because of its resistance to tarnishing.
- ◆ In 1857, Faraday First synthesized colloidal gold by reducing gold chloride using phosphorous.
- ◆ At first, Chinese civilization in 2500 BC, use Au for medical purposes. After that several ancient cultures have utilized Au-based materials for medicinal purposes for the treatment of a variety of diseases such as small pox, skin ulcers, measles and syphilis.
- ◆ In today's era of nanotechnology, gold nanoparticles (AuNPs) have been used for the treatment of diseases like arthritis.

GOLD NANOPARTICLE

- ◆ Bulk Gold (Au) is Yellow solid and inert in nature while gold nanoparticles are wine red solution and are reported to be anti-oxidant.
- ◆ Inter particle interactions and assembly of gold nanoparticles network play key role in the determination of properties of these particles.
- ◆ AuNPs exhibits various size ranging from 1 nm to 8 μm and also exhibit different shapes, such as, spherical, sub-octahedral, octahedral, decahedral, multiple twined, irregular shape, tetrahedral, nanotriangles, nanoprisms, hexagonal platelets and nanorods.
- ◆ Among all these shapes, triangular shaped nanoparticles show attractive optical properties.

ADVANTAGES OF GOLD NANOPARTICLE

- ◆ Au has higher absorption coefficient than Iodine (I) due to its higher atomic number and electron density. Therefore, it enhances CT contrast more than Iodine, so they have been used in X-ray CT (computed tomography) imaging as molecular probes.
- ◆ AuNPs are non-cytotoxic.
- ◆ AuNPs have large surface area due to which their surfaces are readily available for modification with targeting molecules or specific biomarkers and applicable in biomedical purposes.

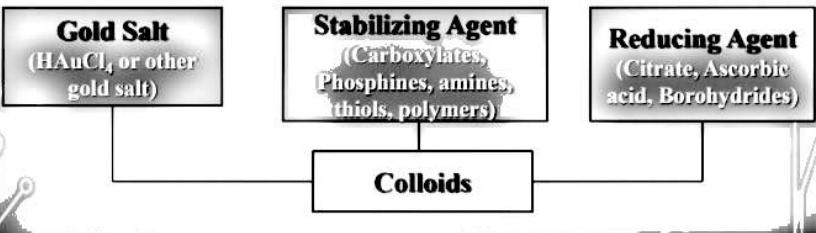
ROLE OF GOLD NANOPARTICLE IN BIOSCIENCE

- ◆ AuNPs are compatible and easily conjugate with biomolecules to tune the optical properties due to their size, shape and surface area.
- ◆ AuNPs are excellent therapeutic agents because they can easily travel into the target cells and can bear high drug load. They can cross the cell membrane and nucleus to interact with DNA because of their small size (18 nm) but cytotoxicity was not observed.
- ◆ It has simple and straightforward fabrication process.
- ◆ It is less hazardous and non-interference with other labeled biomaterials (antibody).
- ◆ AuNPs exhibits better fluorescence and chemi-luminescence. The NPs are designed to convert light into heat blasting away the surrounding cancerous tissue.

SYNTHESIS OF GOLD NANOPARTICLE

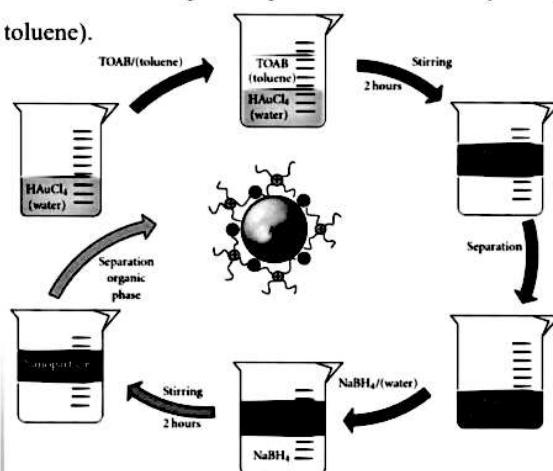
Top down methods: Photolithography and electron beam lithography requires the removal of matter from the bulk material to get desired nanostructure. In this way, there is extensive waste of material.

Bottom up method: includes nanosphere lithography, chemical, photochemical, electrochemical, templating, sonochemical and thermal reduction technique. This method involves assembly of atoms produce by reduction of ions into desired nanostructure. But this methods produces poor monodispersity.



BRUST METHOD

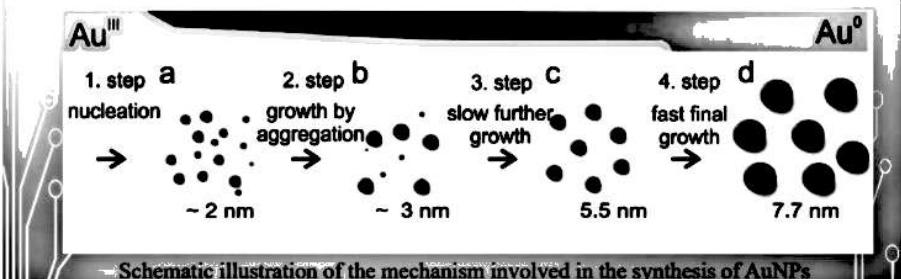
- This method used to produce AuNPs in organic liquids that are normally not miscible with water (like toluene).
- It involves the reaction of a chloroauric acid solution with tetraoctylammonium bromide (TOAB) solution in toluene and sodium borohydride as an anti-coagulant and a reducing agent.



Schematic illustration of the mechanism involved in the synthesis of AuNPs

TURKEVICH METHOD

- The principle of this method involves reduction of gold ions (Au^{3+}) to gold atoms (Au^0) in the presence of reducing agents like citrate, amino acids, ascorbic acid or UV light.
- Small amounts of hot chloroauric acid is reacted with small amounts of sodium citrate solution. The colloidal gold will form because the citrate ions acts as both a reducing agent and a capping agent.
- Thereby monodisperse gold nanospheres are produced. The size of the nanospheres can be controlled by varying the citrate/gold ratio.
- The major limitation of this method are the low yield and the restriction of using water as the solvent.



Schematic illustration of the mechanism involved in the synthesis of AuNPs

MARTIN METHOD

- Naked gold NPs are produce in water by reducing HAuCl_4 with NaBH_4 , even without any other stabilizer like citrate, AuNPs are stably dispersed.
- The key is to stabilize HAuCl_4 and NaBH_4 in the aqueous stock solutions with HCl for > 3 months and NaOH > 3 hours.

SEEDED GROWTH METHOD

- Here at first seed particles produced by reducing gold salt with a strong reducing agent like sodium borohydride.
- The seed particles are then added to a solution of metal salt in presence of a weak reducing agent (ascorbic acid) and structure detecting agent to prevent further nucleation and accelerate the anisotropic growth of AuNPs.

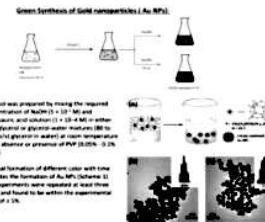
BIOSYNTHESIS OF GOLD NANOPARTICLE

To avoid the toxic element to producing AuNPs, biosynthesis of AuNPs using component like carbohydrate, lipid, nuclei acid or protein produced in nature.

Using plant constituents: The procedure involves mixing the gold salt with extracts of plant for definite amount of time under varied reaction conditions like pH, incubation time and temperature to obtain specific shapes and sizes of AuNPs.

Using microorganisms: Bacteria and yeast has been used for making AuNPs both intracellular and extracellular.

Using biomolecules: Biomolecules include amino acids, nuclei acids, carbohydrates and lipids. These molecules posses hydroxyl and carboxyl group which can reduce Au^{3+} ions to Au^0 neutral atoms. Au^0 are then capped to form stabilized AuNPs. This method can overcome the problem of biosafety.



MECHANISM OF GOLD NANOPARTICLE

- AuNPs have been engineered such that their plasmon resonance is tuned to near infrared (NIR) wavelengths, which allows them to absorb and convert this energy to heat leading to hyper thermic temperature of surrounding media.
- As a result, AuNPs have received increased attention for localized administration of hyperthermia for cancer cell ablation and this approach is currently in early clinical trials.

APPLICATIONS OF GOLD NANOPARTICLE

- For delivery of protein, peptides and nucleic acid
- Medical imaging, selective photothermal cancer therapy
- Diseases can be diagnosed through the detection of a biomolecules characteristic to a specific diseases type and stage.
- Detection of tumor is the functionalization of the NPs with an antibody specific to the tumor antigens and then detect the NPs by some spectroscopic technique.

SILVER NANOPARTICLE

AgNPs are ultra fine particles of silver. They are ten to a hundred nm large, and differ from the bulk silver as they have different colors such as yellow. They have unique physical, chemical, optical, high electrical conductivity, thermal and biological properties. Therefore, they have been used for several applications:

- Antibacterial agents in industrial, household and health care products.
 - In consumer, cosmetics, pharmaceutical and food industry.
 - Medical device coatings, optical sensors
 - In diagnostic, orthopedics, drug delivery, as anticancer agents.
 - Textiles, wound dressings, biomedical devices.
- The biological activity of AgNPs depends on factors:
- Surface chemistry, size and shape, size distribution.
 - Particle morphology, composition, coating/capping
 - Agglomeration, dissolution rate, particle reactivity in solution.
 - Efficiency of ion releases, cell type.
 - The type of reducing agents used for the synthesis of AgNPs.

HISTORY OF SILVER NANOPARTICLE

- ✓ The use of silver in wound management can be traced back to the 18th century, during which AgNO₃ was used in the treatment of ulcers.
- ✓ The antimicrobial activity of the silver ions was first identified in the 19th century.
- ✓ Colloidal silver was accepted by the US food and drug administration (FDA) as being effective for wound management in the 1920.
- ✓ However, after the introduction of penicillin in the 1940, antibiotics became the standard treatment for bacterial infections and the use of silver diminished.
- ✓ Silver began to be used again for the management of burn patients in the 1960, this time in the form of 0.5% AgNO₃ solution.
- ✓ AgNO₃ was combined with a sulphonamide antibiotic in 1968 to produce silver sulfadiazine cream, which created a broader spectrum silver-based antibacterial that continued to be prescribed mostly for the management of burns.
- ✓ More recently, clinicians have turned to wound dressings that incorporate varying levels of silver, because the emergence and increase of antibiotic-resistant bacteria have resulted in clinical limitations in the prescription of antibiotics.

APPLICATIONS OF SILVER NANOPARTICLE

- ✓ Bone cement
- ✓ Implantable devices
- ✓ Toothpastes
- ✓ Additive in polymerizable dental materials
- ✓ Surgical gowns
- ✓ Face masks
- ✓ Wound dressing and burn treatments
- ✓ Coating plastic catheters
- ✓ Disinfecting medical devices
- ✓ Food storage packaging
- ✓ Water treatment
- ✓ Textile coatings, socks and athletics clothing
- ✓ Packaging, cosmetics
- ✓ Washing machine
- ✓ Detergents, soaps and shampoos
- ✓ Air and water filters

SILVER NANOPARTICLE

Mechanics of antibacterial effect

- ✓ The bactericidal action of NPs increases as the particle size decreases.
- ✓ AgNPs with diameters smaller than 10 nm can directly interact with bacterium.
- ✓ AgNPs increases the permeability of membrane.
- ✓ It binds to thiol groups (-SH) in the respiratory enzymes and deactivate the enzymes.
- ✓ It interact with respiratory enzymes and generate reactive oxygen species-oxidative stress-apoptosis.
- ✓ It can interact with DNA and inhibits its replication.
- ✓ AgNPs undergo slow oxidation and form Ag⁺

TOXICITY OF SILVER NANOPARTICLE

- ✓ Argyria is the most frequent adverse outcome from exposure to AgNPs.
- ✓ For instance, prolonged ingestion of colloidal silver can change the color of skin and cause blue-grey appearance of the face (the symptoms of argyria).
- ✓ Some researchers have claimed that AgNPs possess low or zero toxicity to human cells. However, other studies show that AgNPs are toxic to mammalian cells derived from skin, liver, lung and brain.
- ✓ Generally, the toxicity of AgNPs depends on their size, shape, chemical composition and surface modification. Uncoated AgNPs are more toxic than coated one.

TOXICITY OF SILVER NANOPARTICLE

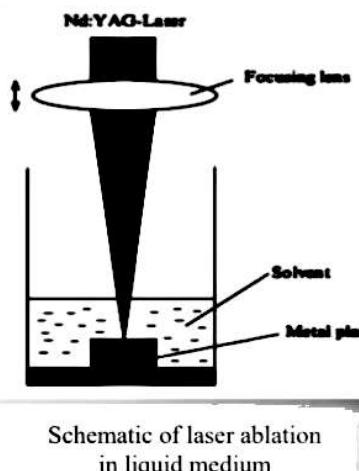


Argyria effect

SYNTHESIS OF SILVER NANOPARTICLE

The produced AgNPs depend on:

1. Wavelength of the laser.
2. The duration of the laser pulse (femto-, pico-, nanoseconds regime)
3. The ablation time duration,
4. The liquid medium
5. The presence of surfactants



Schematic of laser ablation in liquid medium

Advantage of Physical approach

1. Absence of solvent contamination in the prepared thin films.
2. Uniformity of NPs distribution.

SYNTHESIS OF SILVER NANOPARTICLE

Physical approach

1. Evaporation-condensation: vaporize the material into gas and then cool the gas. This method uses a tube furnace or a small ceramic heater. Using ceramic heater have more advantage than furnace. Because the evaporated vapor can cool faster than tube furnace. This physical method can be used for formation of small NPs in higher concentration.
2. Laser ablation: it occurs in solution. It can vaporize materials that cannot readily be evaporated. In this process, chemical reducing agents are found to be absent. Pure and uncontaminated metal colloids can be prepared by this technique.

SYNTHESIS OF SILVER NANOPARTICLE

Chemical approach

- ✓ Reduction of tri-sodium citrate
- ✓ Reduction of sodium borohydride
- ✓ UV irradiation,
- ✓ Gamma irradiation
- ✓ Laser irradiation,
- ✓ Microwave irradiation
- ✓ Sonochemical reduction,
- ✓ sonoelectrochemical methods
- ✓ Electrochemical method
- ✓ Tollens method

MECHANISM OF CHEMICAL APPROACH

- Different reducing agents such as sodium citrate, ascorbate, sodium borohydride (NaBH_4), elemental hydrogen, polyol process, Tollens reagent are used for reduction of Ag^+ ions.
- The reducing agents reduce silver ions (Ag^+) and leads to the formation of metallic silver (Ag^0), which is followed by agglomeration into clusters. These clusters eventually lead to formation of metallic colloidal silver particles.
- It is important to use protective agents to stabilize dispersive nanoparticles during the course of metal nanoparticles preparation, and protect the nanoparticles, avoiding their agglomeration.

SYNTHESIS OF SILVER NANOPARTICLE

Biological approach

The bio-reduction of metal ions by combinations of biomolecules found in the extracts of certain organisms (e.g. enzymes/proteins, amino acids, polysaccharides and vitamins) is environmentally benign. Compared to chemical methods, biological methods allow for more ease in the control of shape, size and distribution of the produced NPs by optimization of the synthesis methods, including the amount of reducing and stabilizing factors.

Synthesis of AgNPs by bacteria: culture supernatants of bacteria and lactobacillus strains can be used for synthesis of AgNPs.

MECHANISM OF CHEMICAL APPROACH

- The presence of surfactants comprising functionalities (e.g. thiols, amines, acids and alcohols) for interactions with particle surfaces can stabilize particle growth and protect particles from sedimentation and/or agglomeration.
- Stabilizers of NPs include surfactants and polymers with different functional groups, such as $-\text{COOH}$ and $-\text{NH}_2$.
- Polymeric compounds such as polyvinyl alcohol (PVA) and polyvinyl pyrrolidene (PVP) have been reported to be effective protective agents to stabilize NPs.

BIOLOGICAL APPROACH

Synthesis of AgNPs by fungi: The stability of AgNPs is due to capping by proteins. Proteins, enzymes, organic acids are responsible for the formation of AgNPs.

Fungus are: *Fusarium oxysporum*, *Aspergillus fumigatus*, *Aspergillus flavus*

Synthesis of AgNPs by Plants: such as green tea extract, black tea leaf extract, flavonoids, polyphenols are used to synthesis, as reducing and stabilizing agent in an aqueous solution in ambient conditions. Plants extracts are able to reduce silver ions faster than fungi or bacteria. NPs produced by plants are more stable.

Advantages of bio-approach: green synthesis and eco-friendly, low cost, can be used for large scale synthesis, no need to use high pressure, energy, temperature and toxic chemical, not require any special culture preparation and isolation techniques.