

**Department of Civil Engineering  
IIT Madras**



**Surface Properties**



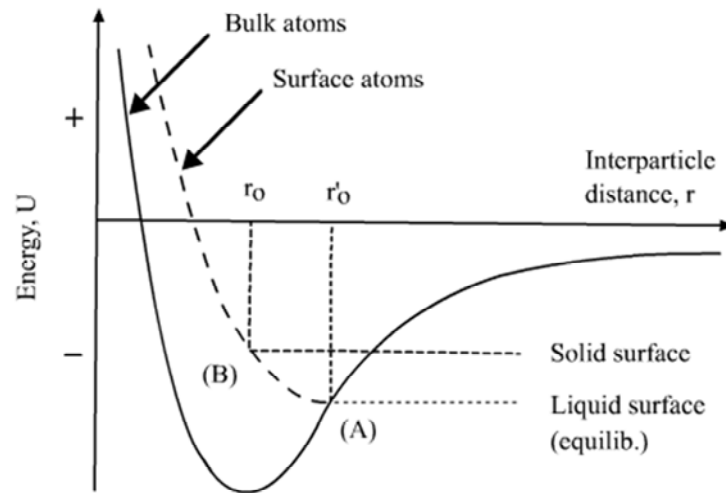
**Modern Construction Materials – Lecture 6  
Prof. Ravindra Gettu  
IIT Madras**

## **Surfaces**

- Surfaces are areas of abnormality (or defects) in relation to the structure that they bound.
- Atoms or ions on a surface are subjected to asymmetric bonding forces.
- Surfaces are the only part of the material accessible to chemical change.
- The ratio of surface area to the total mass depends on the size and shape of the particles making up the bulk material.

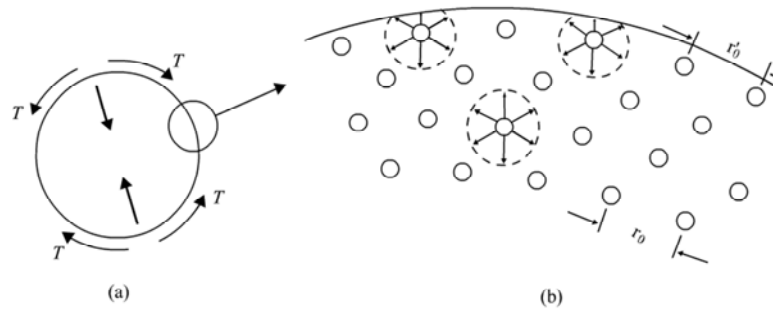
## Surface Energy

### Condon-Morse diagram for bulk and surface atoms



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## Surface Energy



- a) Equilibrium spherical shape of a fluid drop with circumferential surface stress (tension) and radial compressive stress
- b) Arrangement of atoms with increased spacing at the surface

Young et al.

## Surface Energy and Surface Tension

- The excess energy is known as *surface energy*.
- In liquids, the mobile structure permits the individual atoms to respond. The atoms act to reduce the surface area and thereby lower the energy. This results in *surface tension*.
- Surface tension acts along the plane of a surface (or interface), and has units of force per unit length [N/m]. (The surface tension of water is 0.073 N/m at 20°C and 0.066 N/m at 60°C.)
- Solid surfaces have higher energies because the equilibrium interatomic spacing is not achieved.

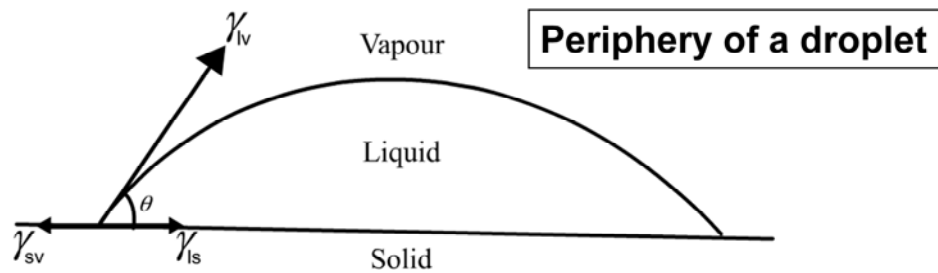
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## Wetting: Behaviour of liquids on solids

The behaviour depends on three surface tensions:

- liquid-solid  $\gamma_{ls}$
- liquid-vapour  $\gamma_{lv}$
- solid-vapour  $\gamma_{sv}$

$\gamma_{sv} - (\gamma_{ls} + \gamma_{lv})$  is called the spreading force

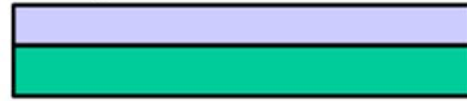


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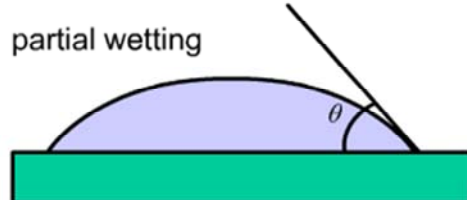
## Wetting: Behaviour of liquids on solids

- When  $\gamma_{sv} - (\gamma_{ls} + \gamma_{lv})$  is positive, then  $\theta = 0^\circ$ ; complete wetting of the solid occurs. The energy of the system is lowered when the solid-vapour interface is replaced by a solid-liquid and liquid-vapour interface.
- When  $\gamma_{sv} - (\gamma_{ls} + \gamma_{lv})$  is negative, then  $\theta > 0^\circ$ ; partial or no wetting occurs.

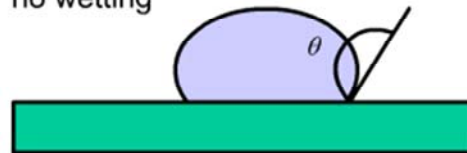
wetting



partial wetting

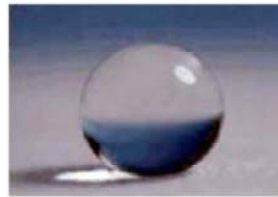
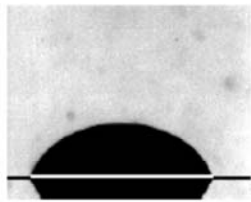
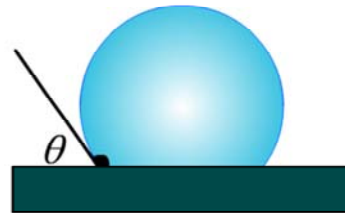
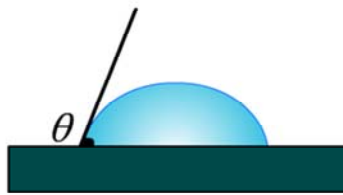


no wetting



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### Wetting: Behaviour of liquids on solids



Water-repellent surface



## Superhydrophobic Surfaces

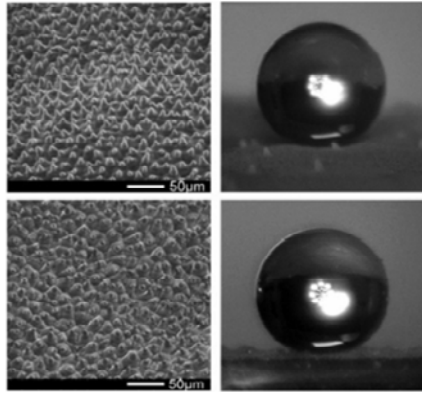
Lotus leaves are known for the superhydrophobicity; their textured surface with hierarchical micro- and nano-scale structures leads water droplets to roll off the leaf and carry away dust particles and debris.



## **Superhydrophobic Surfaces**

- Researchers in China and France have created superhydrophobic polymer structures by directly replicating the surface of a lotus leaf with poly(dimethylsiloxane) or PDMS.
- Such self-cleaning and water-resistant synthetic mimics of the lotus leaf could have applications as coatings and for reducing friction in microchannels.

## Superhydrophobic Surfaces



Both lotus leaf (top)  
and replicated polymer  
structure (bottom) have  
the same hydrophobic  
behaviour

### **Adhesion of Liquid to Solid**

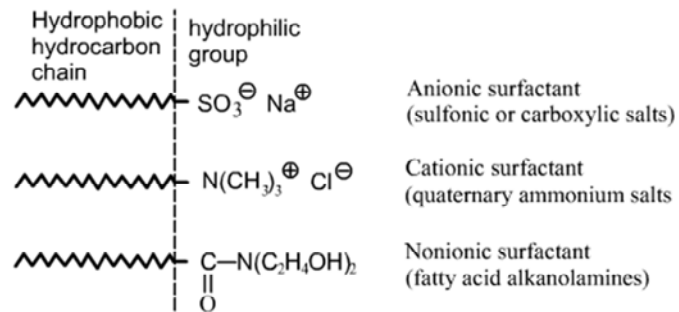
- The ability of adhesives (e.g., glue, solder) to spread and thoroughly wet surfaces is very important.
- The work needed to break away the adhesive (considered as a viscous liquid) from the solid is the work required to create a liquid-vapour and a solid-vapour interface from an equivalent area of liquid-solid interface.
- Surface tension is also the cause of the adhesion between two surfaces separated by a thin film of liquid.

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## Surfactants

Surfactants are compounds that adsorb preferentially at interfaces, thereby *lowering the surface tension*.

- a) The simplest surfactant molecules are polar molecules with a hydrophilic end and a hydrophobic end.

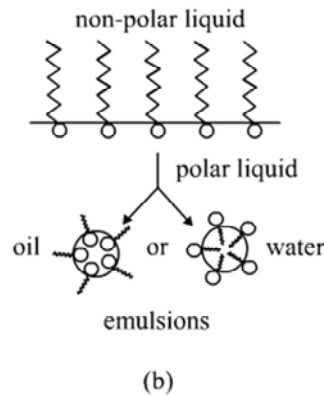


(a)

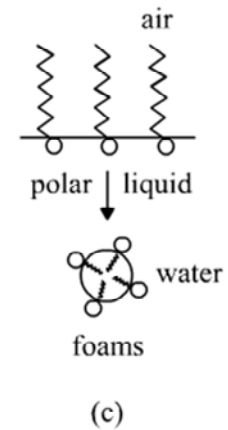
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## Surfactants

- b) In a liquid-liquid interface, these molecules align themselves with the hydrophilic end in water. This alignment lowers the interfacial energy. The result is a stable emulsion.



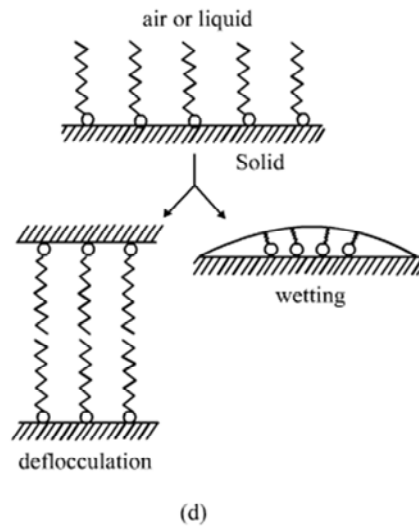
- c) The same molecules act at air-liquid interfaces leading to the formation of foams.



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## Surfactants

- d) At solid-liquid and solid-air interfaces, these molecules can increase wetting and deflocculation.

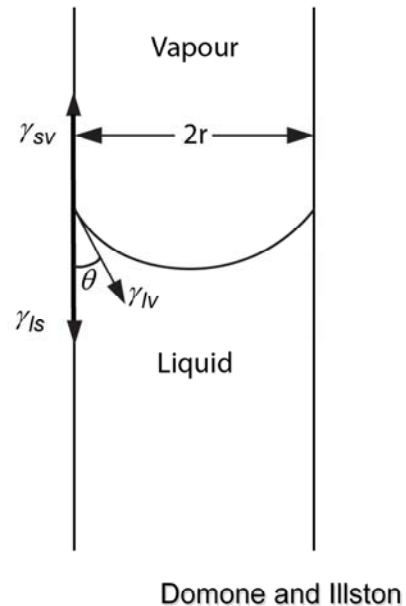


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## Wetting: Liquid-solid interface

- Capillary rise is a consequence of the liquid wetting the solid walls of the capillary
- The circumferential force that draws the liquid up is  $2\pi r \gamma_{lv} \cos\theta$ , where  $\theta$  is the contact angle between the liquid and the solid, and  $r$  is the radius of the capillary.
- $2\pi r \gamma_{lv} \cos\theta = \pi r^2 h \rho$  (i.e., the mass of liquid in the capillary)

Capillary rise of a liquid





### **Wetting: Liquid-solid interface**

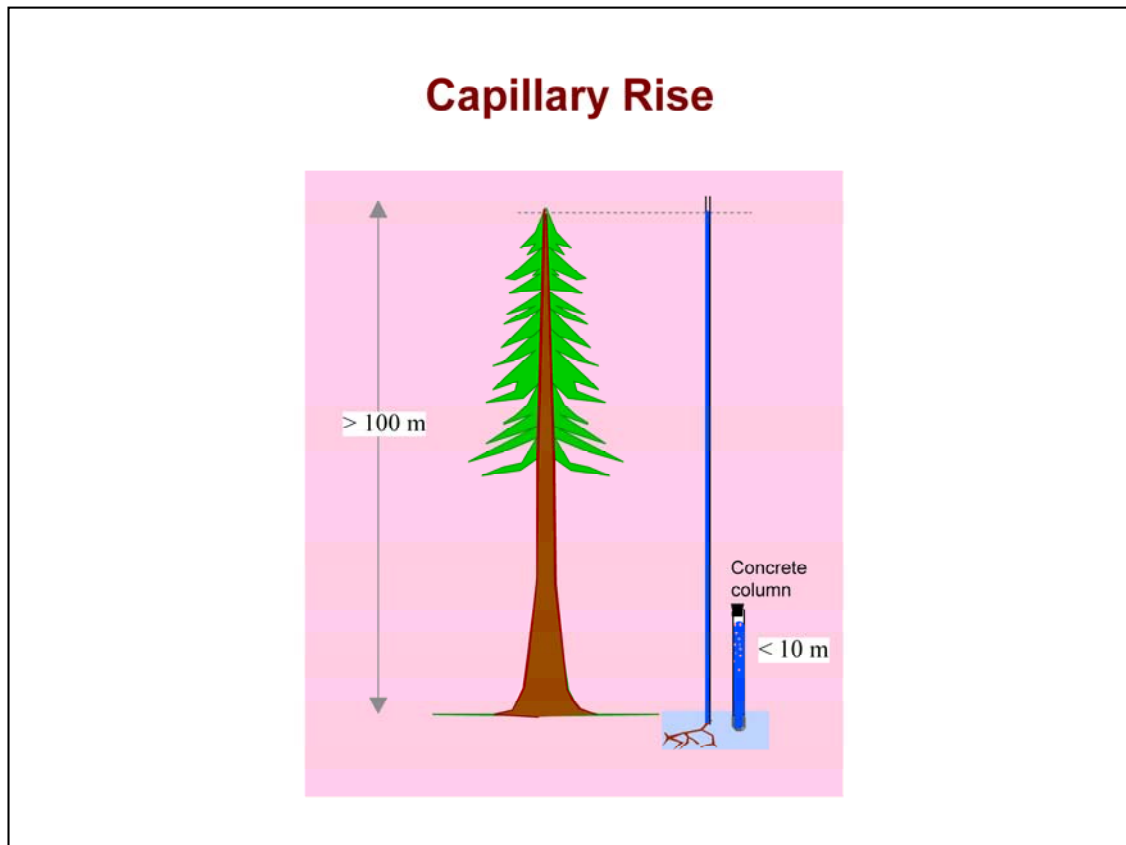
Therefore, the height of liquid in the capillary is given by:

$$h = \frac{2\gamma_{lv} \cos \theta}{\rho r}$$

If  $r$  is very small,  $h$  can be very large !

*(Explains rising dampness in brick and concrete structures)*

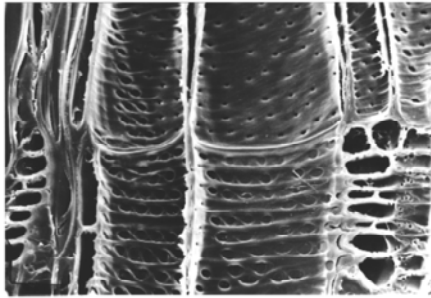
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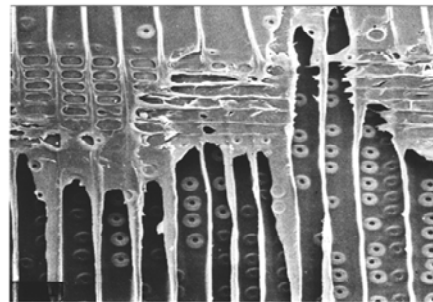
## Capillary Rise

### Water conducting wood tissues of trees

Deciduous tree: Elm  
(*Ulmus glabra*)



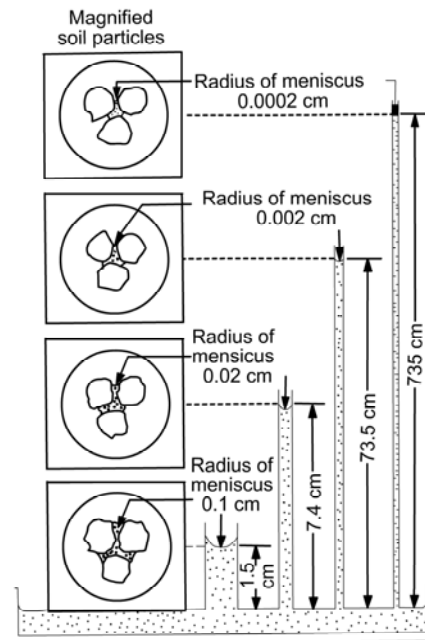
Coniferous tree: Pine  
(*Pinus silvatica*)



## Capillary Rise

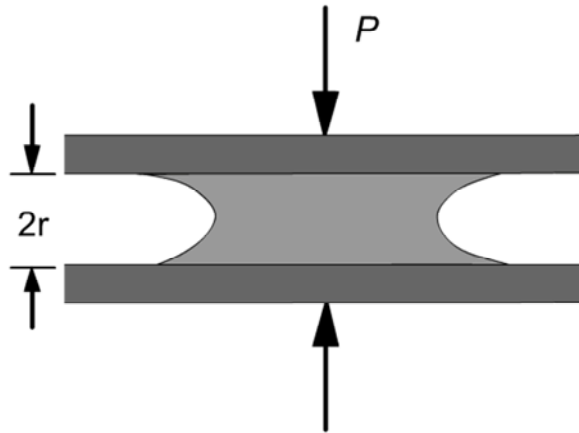
Capillary water has a negative pressure.

In soils, pores with small radii act as capillary tubes to cause soil water to rise above the water table.



### Pressure on Liquid Surface

The liquid will pull on the walls of the capillary to reach the equilibrium pressure. So, the walls will be subjected to tensile forces.



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### **Pressure on Liquid Surface**

When external forces are not important (e.g., horizontal capillaries), the net pressure exerted on the liquid is:

$$p = \frac{2\gamma_{lv} \cos \theta}{r}$$

This is the difference in pressure between the inside and outside of the liquid surface.

## Pressure on Liquid Surface

Young-Laplace equation describes the relation between the pressure drop across a curved interface,  $\Delta p$ , with the surface tension  $\gamma$  and the local surface curvature  $\kappa$ .

$\kappa$  = Local curvature of surface

$$= \pm \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

$$\Delta p = \gamma \kappa = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

## Vapour Pressure of Liquid

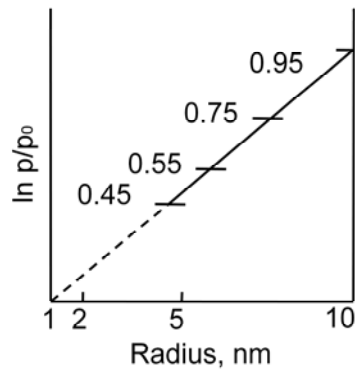
### Kelvin Equation

$$\ln(p/p_0) = K \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

where  $p/p_0$  is the ratio of the vapour pressure above the meniscus to the vapour pressure above the bulk liquid (i.e., flat surface),  $K$  is a constant that depends on the properties of the interface, and  $R_1$  and  $R_2$  are the radii of curvature of the meniscus surface.

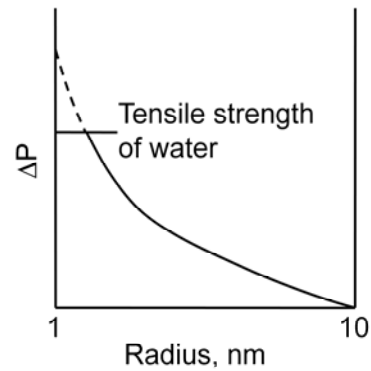


## Vapour Pressure of Liquid



Partial vapour pressure  
(i.e., r.h.) required to  
empty small pores

Stress developed as pores  
are emptied



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### **Vapour Pressure of Liquid**

- Smaller pores will not lose water rapidly by evaporation until the partial pressure of water (i.e., relative humidity) is lowered to the equilibrium value; pores that are less than 10 nm in diameter start emptying only after the relative humidity drops to below 95%.
- In a porous solid, a random distribution of capillaries will exert an isostatic stress on the solid as water is removed from the pores.

### **Vapour Pressure of Liquid**

- The lowering of the vapour pressure of water in a capillary is an indication that the molecules have a higher binding energy than they do in the bulk water.
- The freezing point of liquid in capillaries is reduced proportional to the size of the capillaries. Water in pores greater than 30 nm diameter freeze very close to the normal freezing temperature but pores of 0.25 nm diameter freeze at  $-70^{\circ}\text{C}$ ; water in very small pores never freezes.

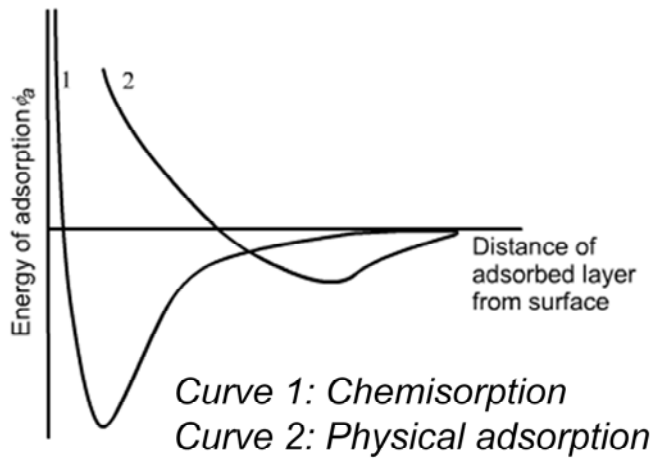
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## **Adsorption**

- The higher energy of the solid surface leads to the attraction of foreign atoms or molecules that have a slight affinity for the surface material. This effect is known as adsorption.
- Different molecules adsorb with varying degrees of intensity, depending on the nature of the bond that forms at the interface, and the strength of the bond, which is expressed in terms of the energy of adsorption.

## Adsorption

A negative energy of adsorption indicates positive adsorption; i.e., the molecules are attracted to the interface, and the surface energy is thereby lowered.



Domone and Illston

## Adsorption

- If the molecule does not react chemically with the surface, physical adsorption can occur through van der Waals bonds. The minimum value of the energy of adsorption is small. Hydrogen bonds (as in water and ammonia) will lead to stronger adsorption (e.g., clay will not lose all its adsorbed water until heated to 300°C).
- If a chemical reaction occurs as part of the bonding mechanism, the bonding is much stronger, and the effect is called chemisorption.

## **Adsorption**

- Physically adsorbed molecules can diffuse along the surface under pressure gradients. Such movement occurs in the hydrated cement gel (e.g., during creep) and along solid-solid interfaces in clay (causing swelling).

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## **Colloids**

- Colloids are fine material with particles having very high surface areas. The mean particle size is less than 1  $\mu\text{m}$ .
- Each kind of phase (solids, liquids or gases) can exist in colloidal form, and may be dispersed in either of the other phases.



## Colloids

### Classification of Colloids

Dispersed Phase	Surrounding phase	Type	Examples
Gas	Liquid	Foam	Soapy water, whipped cream
	Solid	Solid Foam	Air-entrained concrete
Liquid	Gas	Aerosol (Mist or Fog)	Atmospheric smogs Aerosol sprays
	Liquid	Emulsions	Emulsified bitumens
Solid	Gas	Smokes	Silica fume, fly ash
	Liquid	Solid	Cement paste Clay/water suspensions
	Solids	Dispersed solids	ThO in nickel

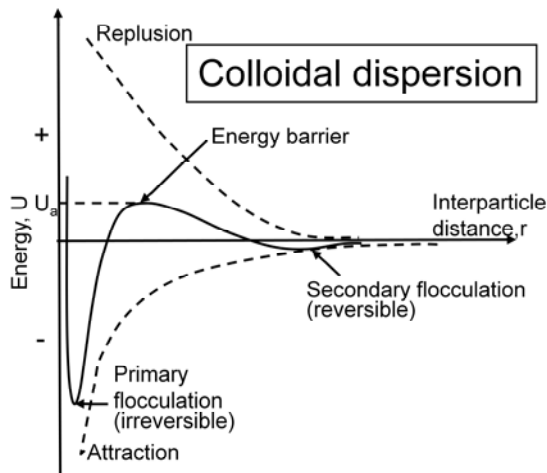
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### **Stability of Colloids**

- Colloids will agglomerate (or flocculate) if attractive forces predominate as two particles approach each other.
- Four major types of interactions:
  - Van der Waals attraction
  - Electrostatic attractions between charged particles of opposite signs (not common)
  - Electrostatic repulsion between double layers of charged particles
  - Repulsion between adsorbed layers

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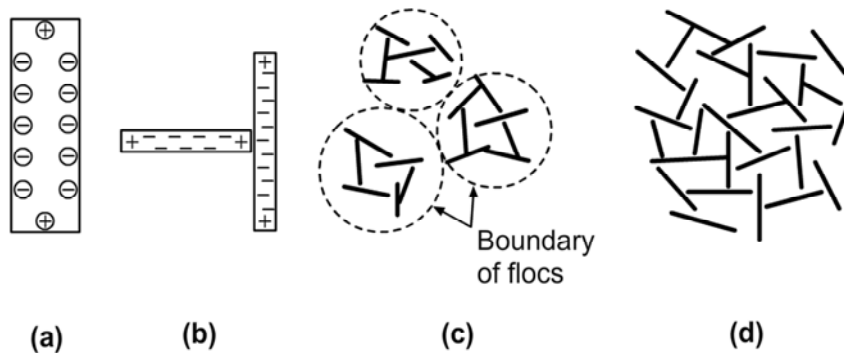
## Stability of Colloids



- The interaction forces as a function of interparticle distance follow a Condon-Morse type of curve.
- Two minima may occur in the curve: a shallow one (the secondary minimum) for large  $r$  and a deeper primary minimum for lower values of  $r$ .
- The secondary flocculation is reversible (by shaking or stirring). Much greater energy is needed to redisperse the colloid if primary flocculation occurs.

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### Stability of Colloids



**Flocculation in clay-water systems:** (a) enlarged view of single clay particle, (b) edge-face interaction, (c) partial flocculation into discrete flocs and (d) complete flocculation.

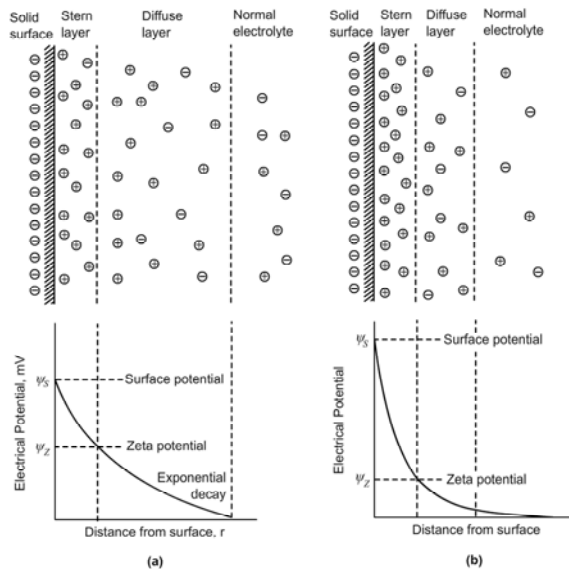
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### **Stability of Colloids**

- Even though the particle may be electrically neutral, there will be positive and negative charges on different parts of the surface. These may reflect the underlying nature, be caused by the presence of impurities or defects.
- Clays, because of their layer structure, form platelets with residual negative charges on the surfaces and positive charges on the edges.

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## The Double Layer

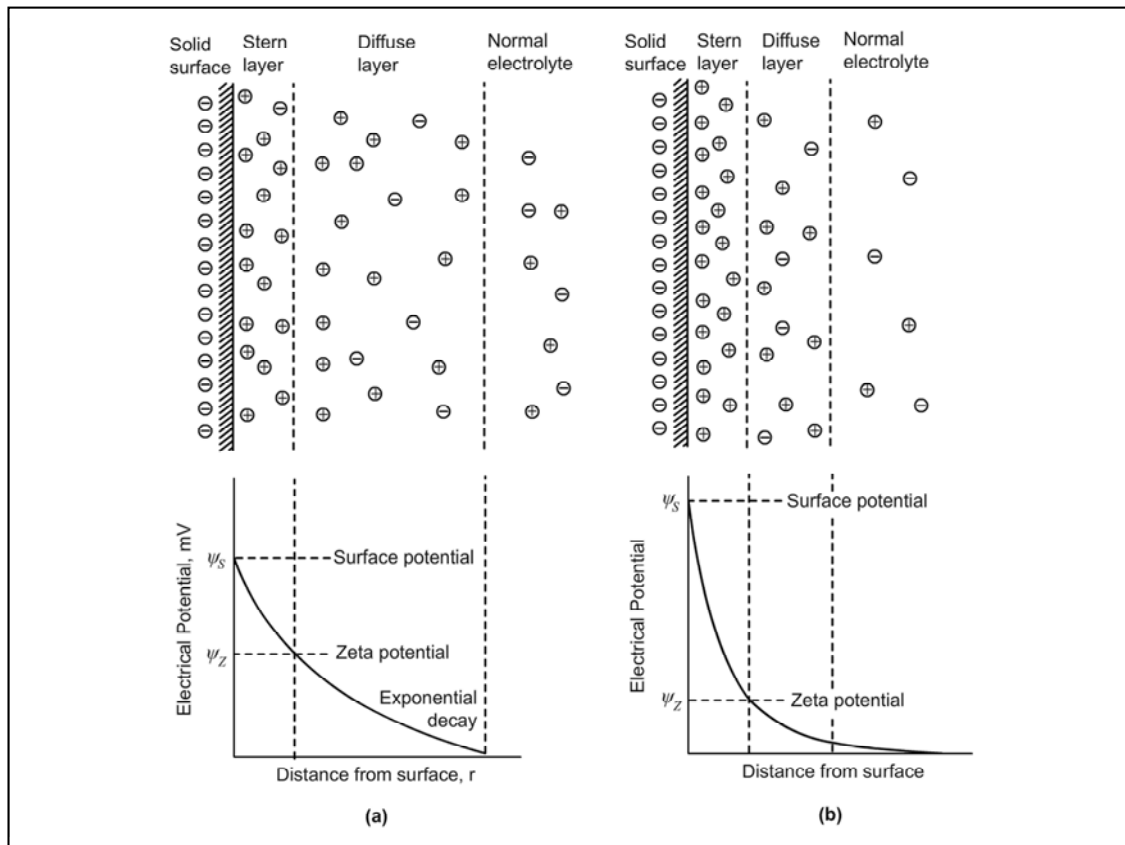


**Double layer adjacent to charged solid surface:**

(a) diffuse (low electrolyte concentration), and

(b) condensed (high electrolyte concentration or surface charge).

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### The Double Layer

- If ions are present in solution, then an increased number of ions of the opposite charge will be found in the vicinity of the surface of the particle. This charge concentration falls off gradually as the distance from the surface increases until a point is reached where the surface charge has no effect and a normal distribution of ions is found in the solution.
- Some of the ions will move with the solid as a layer of solution, called the *Stern layer*. The remaining static part of the solvent with an enhanced ion distribution is the *diffuse layer*. Together, the Stern layer and the diffuse layer form the *double layer*.

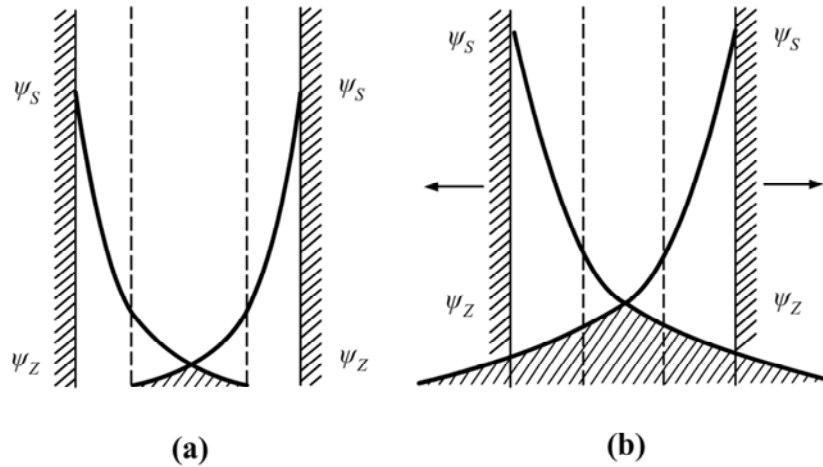
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### **The Double Layer**

- The electrical potential of the Stern layer (the zeta potential) is lower than the surface charge. The drop in potential in the Stern layer is sharp while the decay in potential is exponential in the diffuse layer.
- The double layer lowers the energy of the system. Therefore, the overlapping of double layers of adjacent particles interfere and would raise the energy of the system. Consequently, double layers repel colloidal particles.

### The Double Layer



**Overlap of double layers on adjacent solid surfaces:**

- (a) condensed layers, low overlap and negligible repulsion,
- (b) diffuse layers, high overlap and high repulsion

Young et al.

## References

- *The Science and Technology of Civil Engineering Materials*, J.F. Young, S. Mindess, R.J. Gray & A. Bentur, Prentice Hall, 1998