Modern Construction Materials
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Module No - 3
Lecture No - 6
Surface Properties

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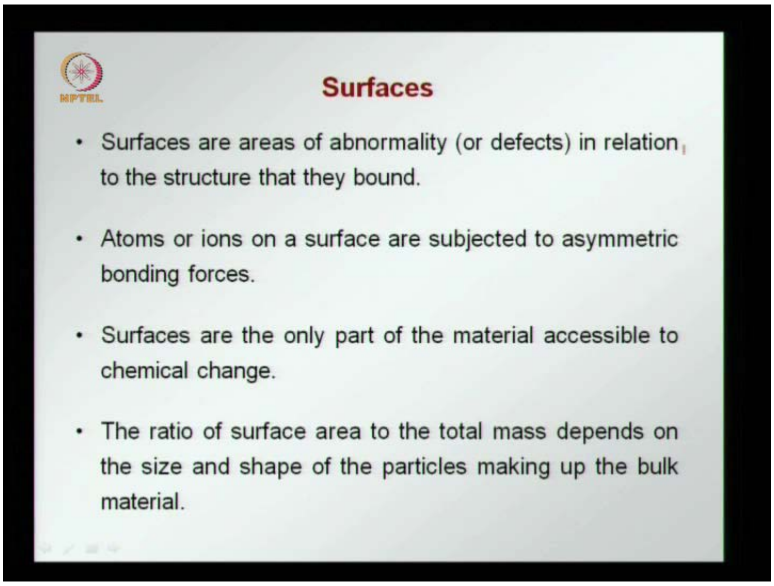

Surfaces

- 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.

Welcome to the sixth lecture of modern construction materials today. We are going to talk about surface properties. We have been looking at the structure of material starting from chemical bonding to the different phases that form within the material during solidification. Now, we look at some of the properties that are related to the surfaces of the materials surfaces or areas of abnormality in relation to the structure that they bound, if you remember when we talked about defects, we said that grain boundaries where surface defects.

Now, the surface of a body is also a similar defect in the sense that there is no continuity of the material beyond the surface and at the surface. What we find is the atoms or particles or ions are not bounded on all sides. So, they have asymmetric bonding forces only within from within the bulk of the material and not outside the material itself. So, that is why we say that the bonding forces are asymmetric.

Also what is important to understand or realize is that surfaces are the only part of the material accessible to chemical change, because you can have attack from outside chemicals. From outside can access the material can start entering the material through the surface, when we have materials that are made up of several particles.

The surface area depends on the size and shape of the particles that is the ratio of the surface area to the total mass depends on the size and shape of the particles. So, if we have smaller particles instead of larger one’s we will have a highest specific surface area. If we have angular particles flaky particles instead of rounder one’s again, you will have a higher specific surface area.

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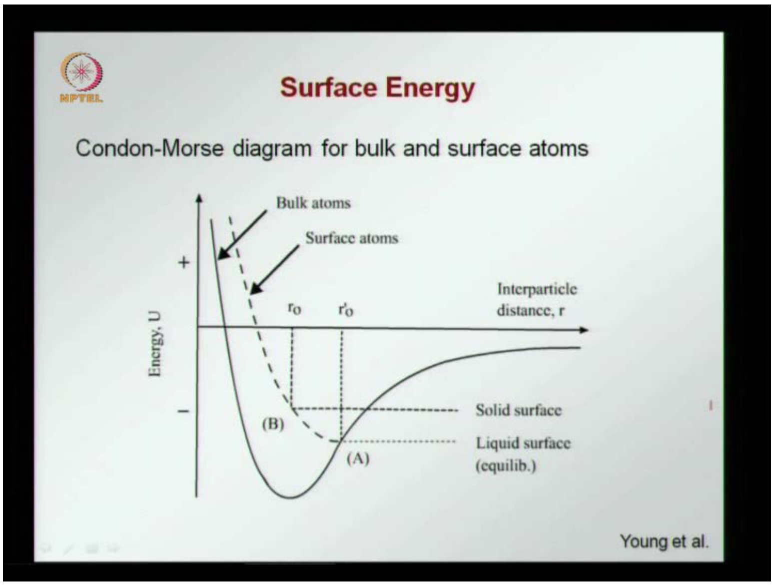

Surface Energy

Condon-Morse diagram for bulk and surface atoms

Young et al.

If we look at the Condon-Morse diagram, and see what modification we will have to make to understand. What happens in the surface you see here that dash line, which now corresponds to the surface atoms. The dark line corresponds to the Condon-Morse diagram that we have been looking at until. Now, where we have a curve giving us the result in between the attractive and the repulsive forces with this point. Being the point, where we have the least potential energy, which corresponds to a stable inter atomic or inter particle distance or subzero. Now, this is for an atom for a particle within the material.

When it is bounded on all sides by particles around, now on the surface you have an asymmetric bonding and therefore, the energy diagram is modified into this dashed line and instead of the energy level being at this point for the same inter particle distance. Now, we are here the energy level is much higher than the minimum energy level, because we have removed a some part of the material or some part of the material above this particular atom that we are discussing is missing.

So, this difference is called the surface energy this additional energy that we have above the minimum is called the surface energy. Now, we know that the material will try to decrease its energy to reaches stable value in a solid this spacing here is fixed, because the atoms or particles do not have much mobility. So, at this surface we realize that the surface energy will be higher by this among and they could be surface phenomenon.

Which will occur to decrease the energy to this point now in a liquid however, what will happen is that there is greater mobility.

Of the atoms the surface deforms to reach an equilibrium distance, which has a lower energy than this. So, in a liquid we reach equilibrium on the original Condon-Morse diagram or the bulk Condon-Morse diagram with the distance. Now, being are prime subzero instead of r 0 the inter particle distance is now larger this means that on the surface of a liquid. The distance between atoms and particles is larger than within the bulk of the material.

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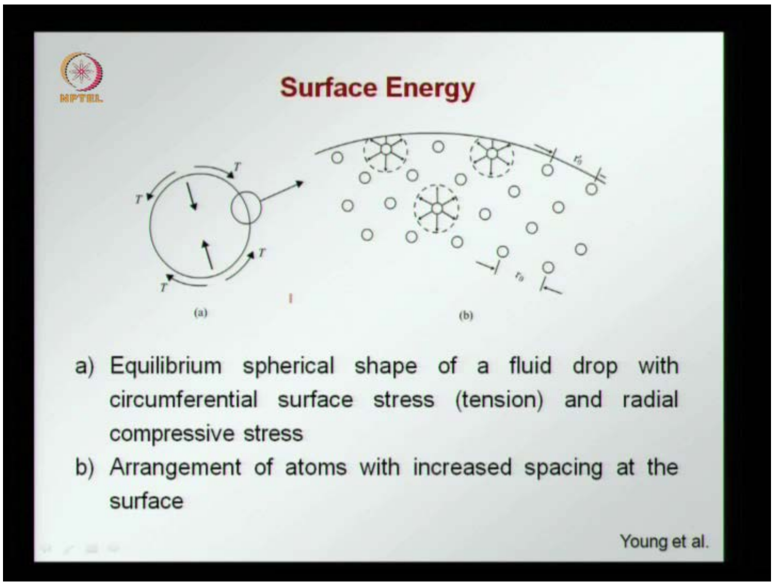

Surface Energy

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.

So, suppose we take a spherical droplet of any fluid. We will find that inside they will be compressive forces and on the surface we will have tensile forces, because they there has been a change of the inter particle distance on the surface. The inter particle distance now is larger. So, the surface is stretched there are tensile forces induced by this change in the particle distance on the surface. This tension on the surface induces compression within to balance out the stresses.

So, that is what we see here and on the surface. We have a higher inter particle distance r prime sub 0, which is more than r 0 which is inside the bulk and this arises, because of the asymmetry of the bonding forces that are around any particular particle or atom you see here that in the bulk there are atoms all around. So, the bonding forces are symmetric whereas, on the surface we do not have this part. So, there is a part missing of the material, and therefore the energy now is higher above the minimum and to accommodate this in a liquid the inter particles distance increases inducing surface tension.

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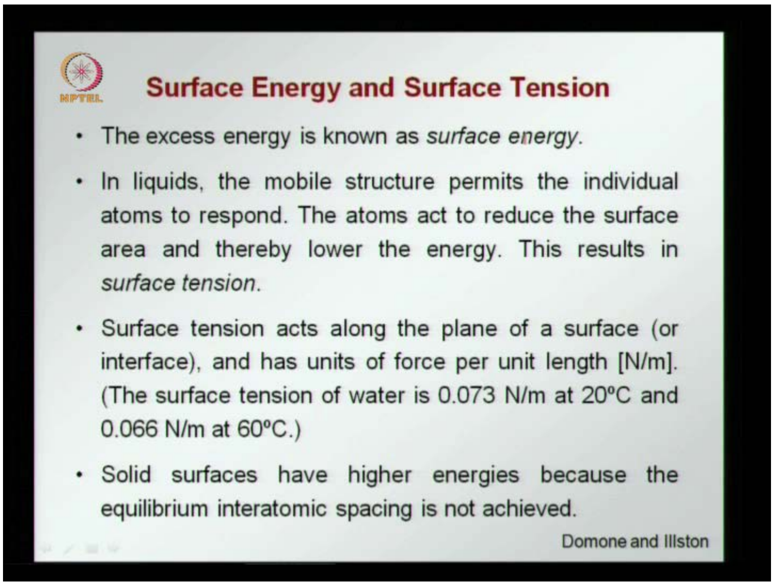

Surface Energy and Surface Tension

- 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.

Domone and Illston

So, as I said the extra energy the excess energy above the minimum potential energy that is there in the bulk of the material is call surface energy. In liquids the structure has mobility the atoms are more free to move then in a solid. So, the individual atoms respond to this higher energy the atoms act to reduce the surface area and therefore, lower the energy. This reduction in the surface area this stretching that is induced results in. What is called surface tension? Surface tension acts along the plane of the surface or any interface, and it has the units of force per unit length say netwon per meter.

For example we can look at the surface tension of water, which is 0.073 netwon per meter at 20 degree centigrade. Surface tension is temperature dependent and we see in water that at 60 degrees, we have a lower surface tension. So, surface tension can be generally decreases as the temperature increases. Now, in a solid we say that there is less mobility on the surface therefore, the energy at the surface is much higher than in an equivalent liquid, because the equilibrium inter atomic space is not achieved and we have a higher surface energy. This higher surface energy makes solid surface is prone to combine with chemicals from the atmosphere and attack by these chemicals, which leads to phenomena such as corrosion.

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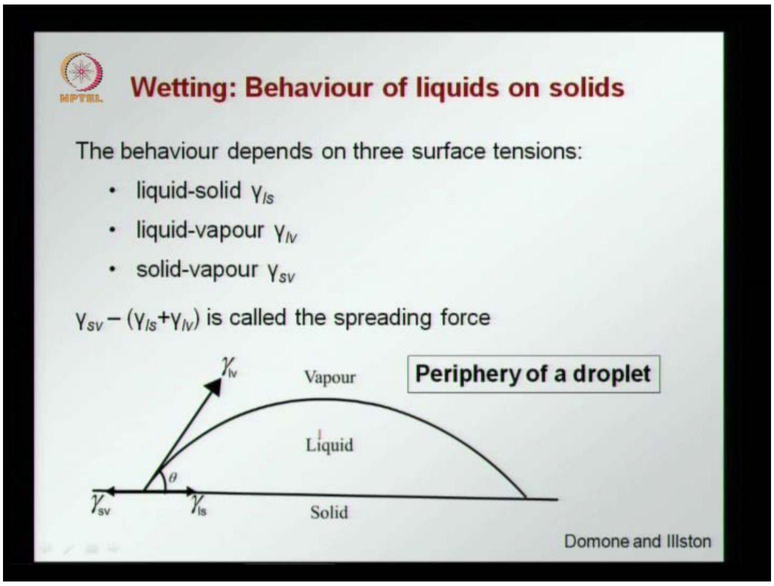

Wetting: Behaviour of liquids on solids

The behaviour depends on three surface tensions:

- liquid-solid γ_{ls}
- liquid-vapour γ_{lv}
- solid-vapour γ_{sv}

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

Periphery of a droplet

Domone and Illston

Now, in a liquid solid interface we have a phenomenon call wetting. This wetting behavior depends on three surface tensions this three surface tensions are related to three interfaces the liquid solid interface, if we see the diagram at the bottom.

We have a solid surface and on top of that. So, we have a droplet of liquid. So, we have a liquid solid interface and the surface tension here is given by gamma l s. Then we have an interface between the vapor and the liquid. So, there is a surface tension between the liquid and vapor given by gamma l v. Then we have a dry interface where we have the solid vapor interface represented by the surface tension gamma s v this quantity, which is the difference between gamma s v the solid vapor surface tension and the some of the liquid solid surface tension, and the liquids vapor in surface tension is called the spreading force. So, if this value given here is positive then the liquids spreads out, if it is very small negative then instead of spreading we have a droplet.

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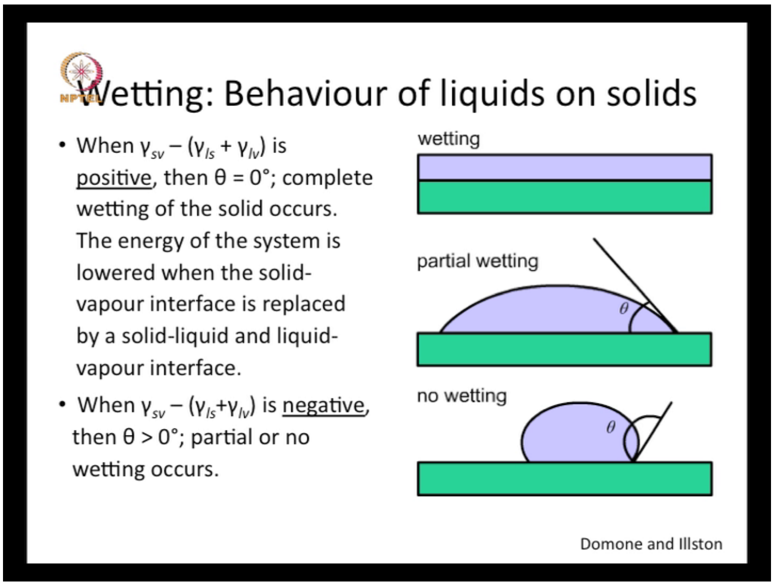

Wetting: Behaviour of liquids on solids

- When $\gamma_{sv} - (\gamma_{ls} + \gamma_{lv})$ is positive, then θ = 0°; 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 θ > 0°; partial or no wetting occurs.

Domone and Illston

So, here we have these different cases, when gamma s v minus this sum of gamma l s and gamma l v is positive; that means, the spreading force is high then we have theta, which is the angle of wetting equal to 0.

So, as surface is completely wet complete wetting of the solid surface occurs. Here the energy of the system is now load, when there is wetting that is the dry surface. The solid vapor interface is now replaced by a solid liquid plus l liquid vapor interface. This lowest the energy of the system on the other hand, we can have cases where gamma s v is less than the sum of gamma l s plus gamma l v that is this term becomes negative. In this case theta is greater than 0 partial are no wetting occurs partial wetting, were you have a droplet like in the middle figure or you can have no wetting, and the droplet being almost spherical.

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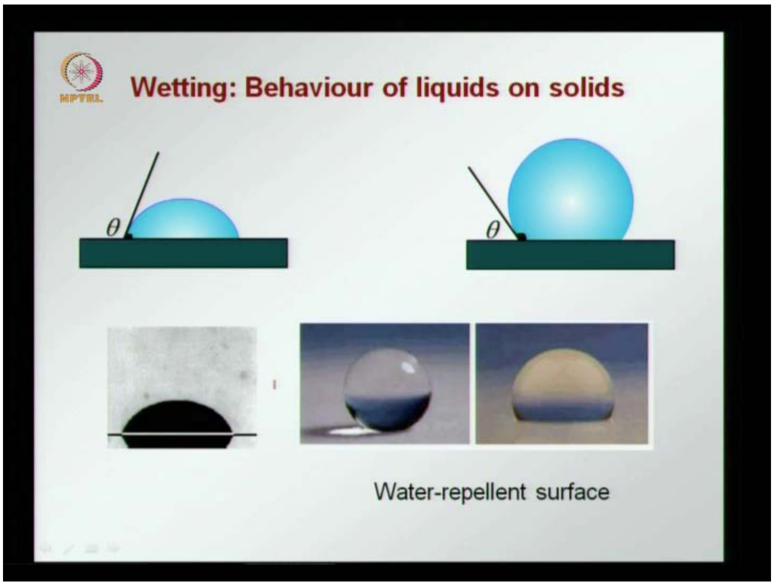

Wetting: Behaviour of liquids on solids

Water-repellent surface

So, in both cases what we understand is that the system tries to lower the energy, and depending on the values of the surface tensions you can have complete wetting partial wetting or no wetting at all.

Which is the case of hydro phobic situation completely wetting will be in hydrophilic situation. So, you see some examples here of partial wetting on the left theta is more than 0, and in this case you have a droplet form you can have a case, where theta more than 90 degrees leading to a water repellent surface or a hydrophobic surface. Where you find the droplet now tense to become more and more spherical, it can even become completely spherical in the case of a super hydrophobic surface, which is completely repelling the water.

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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.

And the water becomes a spherical droplet. An example of this type of super hydrophobic surface is that of lotus leaves, which are known for the super hydrophobicity the texture of the lotus leaves and many other aquatic plants is such that they have several levels of micro and nano scale structures. There is a hierarchy of micro and nano scale structures.

Which leaves to water droplets not wetting the leaf surface, but rolling of the leaf and, when they roll off they leave the surface dry and also carry away dust particles and, if you seen in some of these pictures. You will see that the droplets are almost spherical like. We saw in that diagram before.

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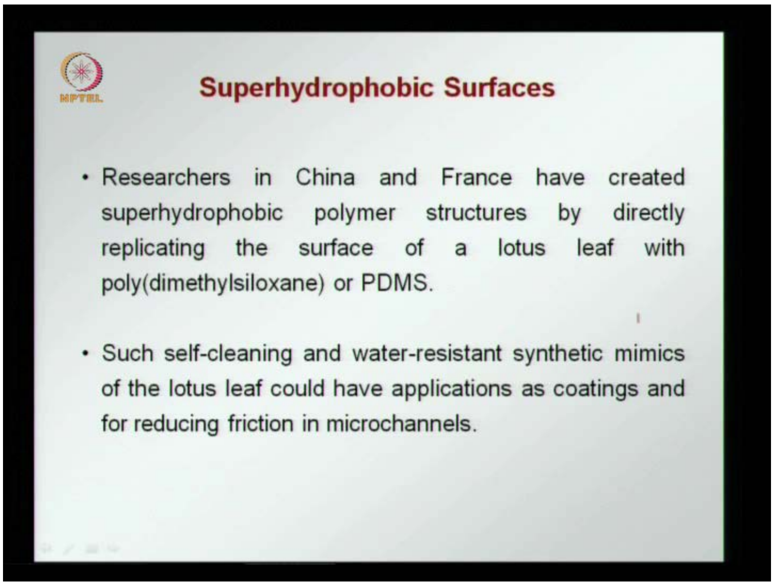

Superhydrophobic Surfaces

- 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.

Now, some researchers have try to mimic this super hydrophobic surface that we see in nature in lotus leafs and. So, on by using polymers researchers in china and france have replicated the surface of a lotus leaf with a polymer called poly dimethyisiloxane or p d m s, and created a synthetic mimic that can self clean and be water resistant. That is there is no wetting of the surface, and the water rolls of taking away dirt and dust and this could have applications in coatings and, where we want to reduce friction in micro surfaces.

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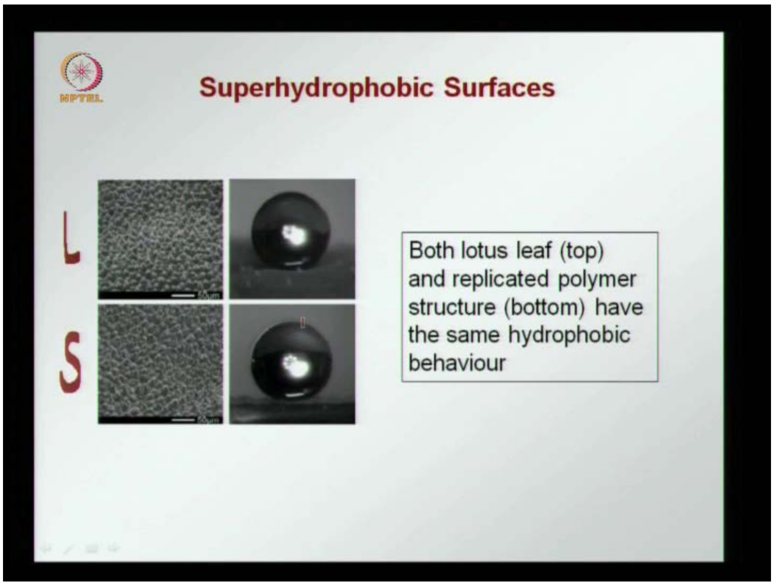

Superhydrophobic Surfaces

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

This is a picture showing at the top the lotus leaf, and you see the texture here. Its not that smooth texture, but in the micro scale we see the small rigid and small humps and this is at the bottom is the synthetic surface, which has the same hydrophobic behavior. Which you seen the figures here, where you see a water droplet that is almost spherical and same here. So, there is lot research going on to create super hydrophobic surfaces mimicking, what we see in nature in leaf such as that of the lotus plant.

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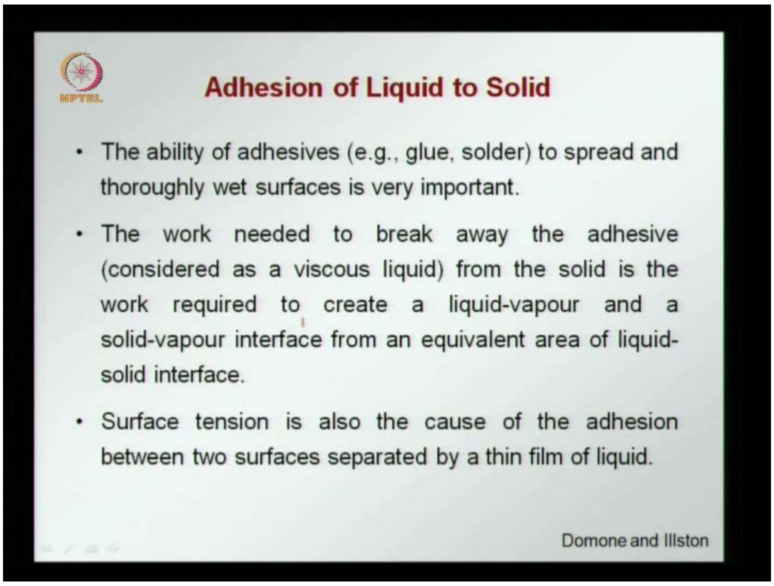

Adhesion of Liquid to Solid

- 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.

Domone and Illston

Now, we talked about hydrophobic surfaces. We can have cases where we want complete hydrophilisity that is we want complete wetting that is in the case of adhesives, when we use a glue or a solder. We want this material to spread and thoroughly wet the solid surface. They should be complete wetting with a drop of glue or a drop of solder, we want a good wetting of the solid surface. So, that there is good bonding we do not want droplet forming, but we want uniform wetting and we can also imagine. That how the adhesive works is by creating a liquid solid interface, and in order to break that we need to expand a lot of energy.

If we think of the adhesive as a viscous liquid to break that bond between the adhesive and the solid. We have to create a liquid vapor and a solid vapor interface instead of just a liquid solid interface on the equivalent area. So, this requires some energy and that is why we need to expend a force to break what has been adored or in adhesive made joint. Surface tension is also the cause of adhesion between two surfaces separated by a thin film of liquid. When you have two plates or two solid surfaces separated by a very thin film of liquid.

We find that surface tension bonds the two surfaces together, and it requires a lot of energy to separate them. A good example that you might have come across is, when you have two cups or two glasses one inside the other and it. So, happens that the surface between them or the interface is wet, and it is always difficult to separate the two glasses, because of this surface tension of the water or any other liquid bonding the two together.

We also know from this explanation that, when we have to use an adhesive such as a synoacriliate one of this quick glues. We have to produce a thin surface of adhesive. The adhesive layer should not be very thick, the thinner the layer of adhesive better is the bond, because than the surface forces are larger.

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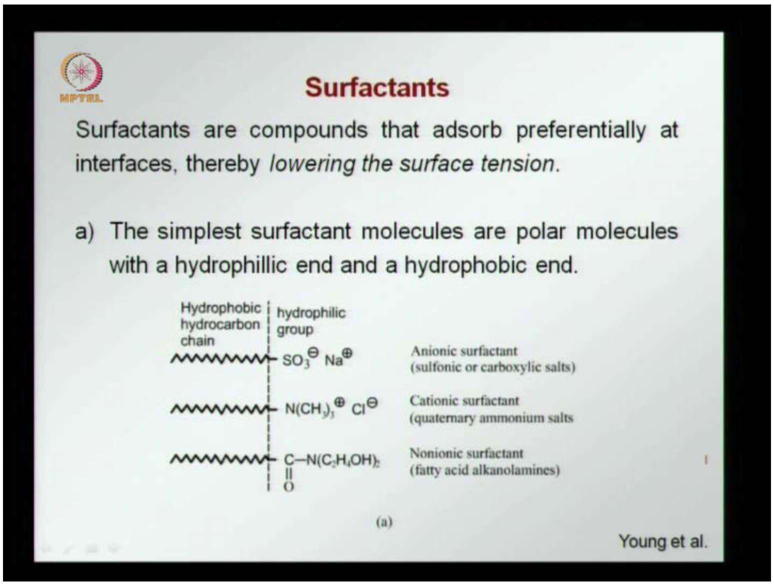

Surfactants

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

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

Young et al.

Now there are materials, which modify the surface tension surfactants are compounds that absorb preferentially at the interfaces. That is they have a tendency to be absorbed on the interfaces, and they lower the surface tension. Some simple surfactant molecules are given in this diagram taking from young et al and these are polar molecules with a hydrophilic end, and a hydrophobic end, the hydrophilic ends sticks out into water and changes.

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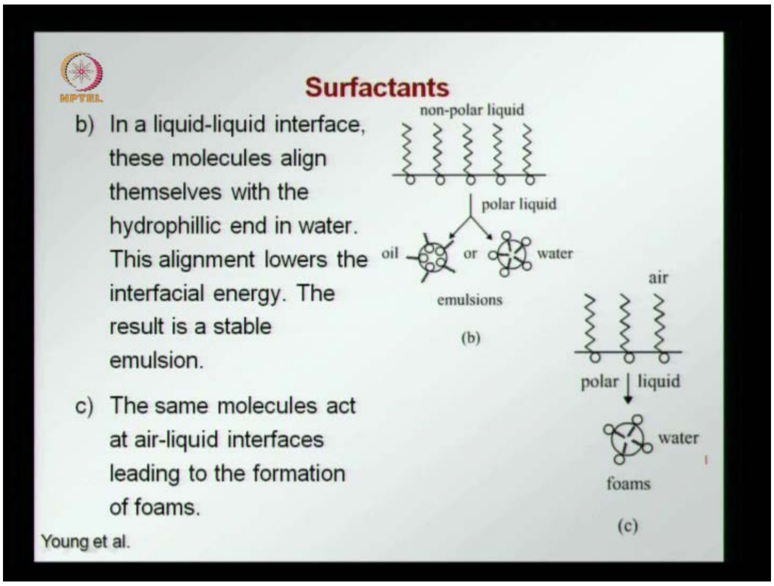

Surfactants

b) In a liquid-liquid interface, these molecules align themselves with the hydrophillic 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.

Young et al.

How the surface now behaves, if we consider a liquid-liquid interface the surfactant molecules align themselves with the hydrophilic end in water, and this sort of alignment lowers the interfacial energy and it results in an emulsion like. We have here, if we have two liquids are non polar liquid and a polar liquid. They will not readily mix and they will separate when they are mix together, but when we have an emulsion we need the two liquid to form a uniform mix and in that face the surfactant comes in handy and you can create an emulsion.

In civil engineering, we use a lot of emulsions one that comes to mind very easily is that of paints lot of paints that are used or emulsion. Now, surfactants are also use to create foams, and this case what happens is the surfactant molecules act on the liquid air interface. We have the liquid here, and this surfactants now attach themselves to the surface and create the possibility of having foams. So, that the air inside the water remains in a stable manner.

So, we have a foam and foams again are used a lot in civil engineering for insulation. We use polyurethane foams, we even have foamed concrete where there are air bubbles, which are stabilize within the cement matrix to reduce the density or to improve the thermal properties.

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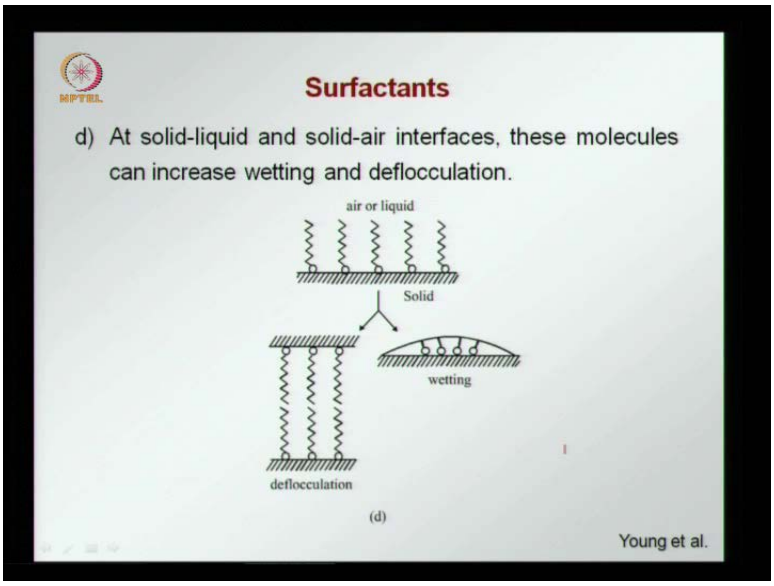

Surfactants

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

Young et al.

At solid liquid and solid air interfaces the molecules of surfactants can increase wetting and deflocculation. In some cases we can have the surfactant creating better wetting make the surface more hydrophilic that is instead of droplets forming. You have water or any other liquid spreading over the surface to improve the wetting and example of this is, what we have in self cleaning glasses. In self cleaning glasses the surface is modify such that water coming from rain forms a uniform film on the surface. That is there is complete wetting and as this water runs down the glass. It carries away dirt and dust, and living thus glass clean.

That is an example where we want wetting to occur and we want to hydrophilic surface. Now, in lot of cases we want the surface to be hydrophobic, or we want deflocculation that is we want separation. We do not want the adjacent surfaces to bond not stick to each other and example that again comes to mind is, what happens in the case of a plasticizer or a super plasticizer. When we added to concrete the polymers bond to the surface of the cement particles and ensure that the cement particles do not flock together or stick together do not agglomerate.

This ensures that more water is available for the mobility of the cement paste and you have higher workability in the concrete. You can also have a case, where you want a hydrophobic surface. For example, when we use a cement motor or any other material for water proof. We do not want water to enter into the cement motor and we would rather have hydrophobic surface therefore, we can use a surfactant to make the surface reject water and ensure that water does not wet the surface.

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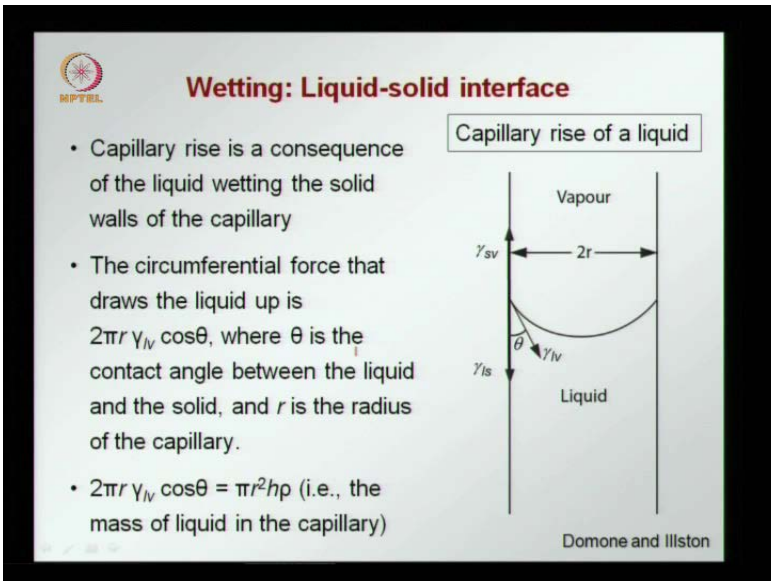

Wetting: Liquid-solid interface

- 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 θ 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

Domone and Illston

Another consequence of surface tension is capillary rise, when we have the liquid wetting the solid walls of a capillary a thin tube of pipe the force that is generated in the capillary rise is given here. We have now the three surface tensions that we saw before this is the solid vapor surface tension liquid solid surface tension and the liquid vapor surface extension.

Now, here what causes the force due to capillary rise is the gamma l v. The liquid vapor interface surface tension and this creates now a circumferential force around this capillary. That pulls up this liquid and this force is given by 2 pi r, which is the circumference of the capillary multiplied by gamma l v times cos theta, the theta is this angle that you see here. This is balanced by the weight of this liquid given by pi r square, which is the cross sectional area h is the height, and rho is the density.

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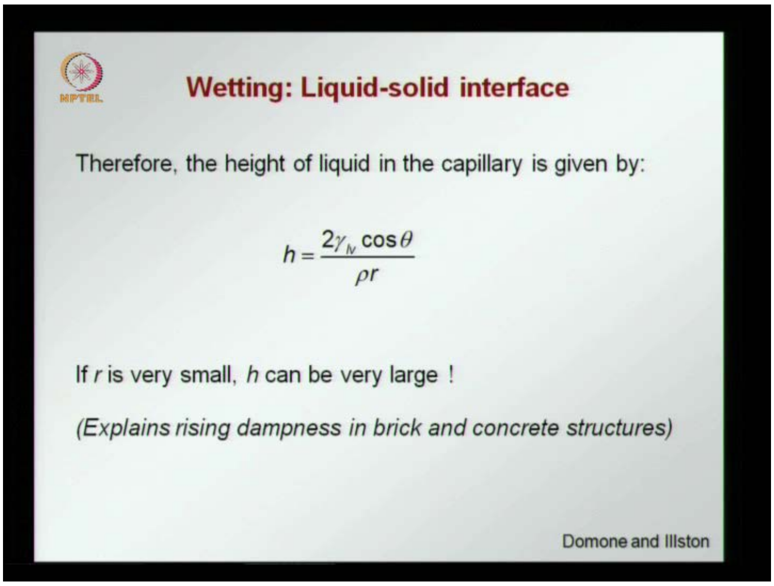

Wetting: Liquid-solid interface

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)

Domone and Illston

So, this is the mass of the liquid that is balancing the circumferential force that the surface tension has create consequently. We have this equation h is the height of the rise of liquid in the capillary equal to 2 gamma l v cos theta by rho r and. What we see from this equation is that, when r is very small, h can be very large.

This is very important for us, because this explains why we have rising dampness in brick and concrete structures. One might often wonder, why we see damp ness rising from the floor working against gravity, and the explanation is surface tension and, when we have fine force in materials like we do in brick and concrete structures the surface tension pulls up the water.

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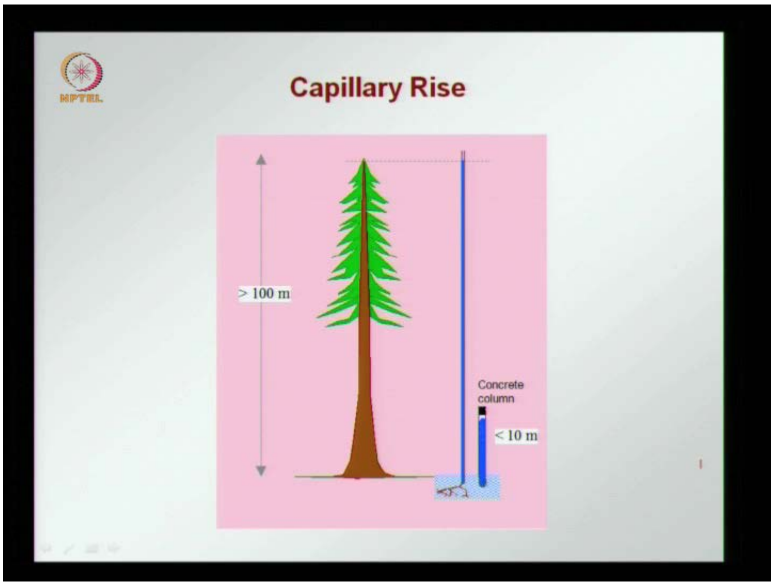

Capillary Rise

And we see dampness rising in walls and columns. We also have a very good example of capillary rise in trees. The fine capillaries that wake up the fibers in the tree pull up the sap and water that feed the tree and make it.

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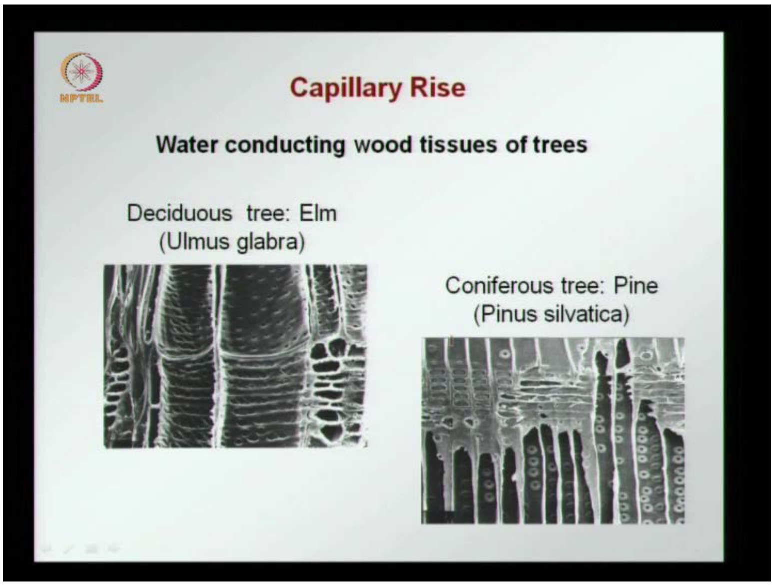

Capillary Rise

Water conducting wood tissues of trees

Deciduous tree: Elm
(Ulmus glabra)

Coniferous tree: Pine
(Pinus silvatica)

So, wide in concrete the damp ness rises much less, because the capillaries are not as fine is that we see in nature in trees and flowers. So, this are some pictures of good tissues, which act as this fine capillaries and pull up the water. This is in an elm tree and now, we see here the capillaries or the cubes in the pine tree. So, sap and water move up through this capillary cubes.

That are there in wood and later on, we will see that this is the reason why we have the micro structure that is there in wood. This makes wood an isentropic or orthotropic, because all the fibers are aligned along that longitudinal direction or the direction of the growth of the tree, and this leads to a certain orthotrophy of the properties in timber, and you do not have an isotropic material.

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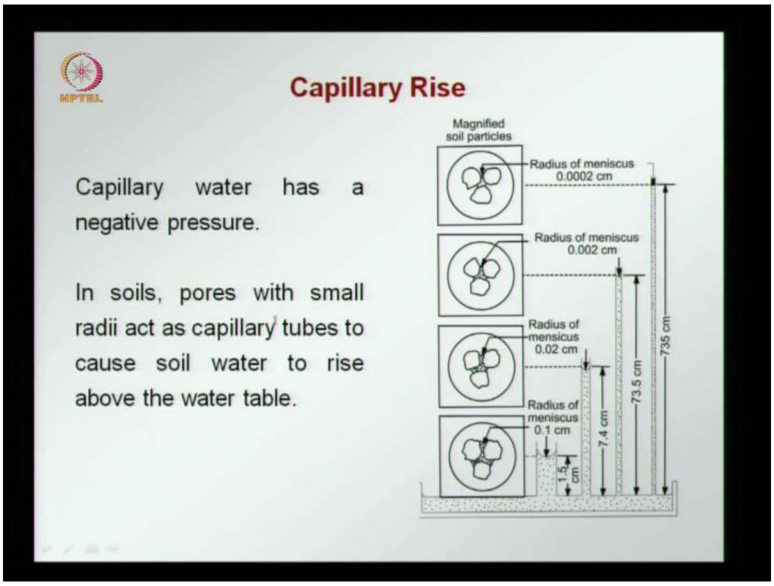

Capillary Rise

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.

Capillary rise is also important in soil, as we saw capillary rise gives rise to a negative pressure that is there is a section developed. We see here in this diagram that, when we have a capillary rise. There is a pulling up of water, which we saw earlier in the case of a capillary tube and, when the pores in the soil or finer. That is the particles are finer or close a pack we have smaller capillaries. This gives rise to higher capillary forces and the rises much high.

For example, where if we have force of the size of 0.0002 centimeters, we find that we can have about 730 centimeters of rise of water in the soil, where as if it is only is a 0.02 centimeters, we will have about 7 centimeters of soils.

So, this is important to understand that in soils with pores having small radii. You have capillary tubes forming, which cause the soil water to rise above the water table. The water table could be below a surface, but due to capillary rise the water is pulled up and this is important, when we look at materials that we use for filling see a plinth or the space below a floor.

If we use very fine material you will have smaller pores and therefore, the rise of water could be higher. So, this has to be the cut off by a course grained material at the top or some other way of cutting off the capillary rise. Otherwise, a fine grain soil or fine grain filling material will give rise to higher capillary rise.

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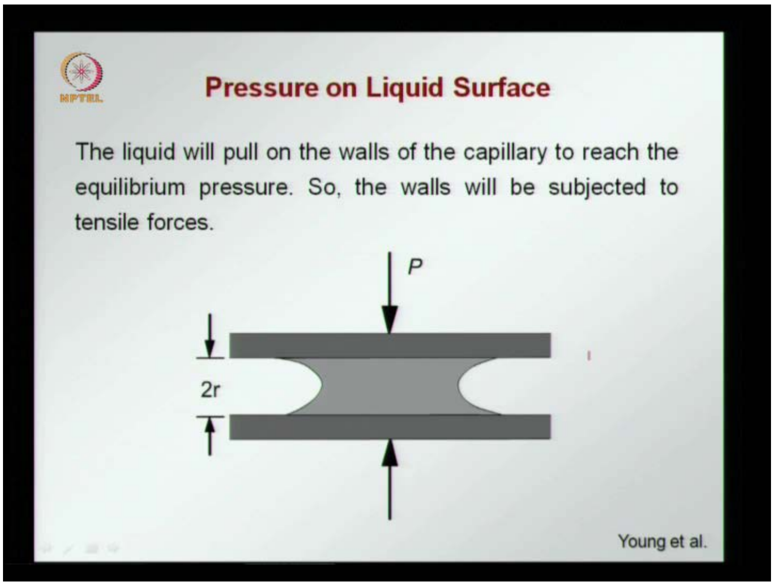

Pressure on Liquid Surface

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

Young et al.

Surface tension also can explain, why we have forces that are generated between the walls of the capillary. We see that at the meniscus, we have a force that is pulling on the sides of the capillary. This is equivalent to having a pressure that is built up to balance the surface tension, and the walls are now subjected to tensile forces.

In case we do not let walls move. We will have tensile forces pulling on this walls. If the wall is free to move, then it will deform to accommodate is tensile forces.

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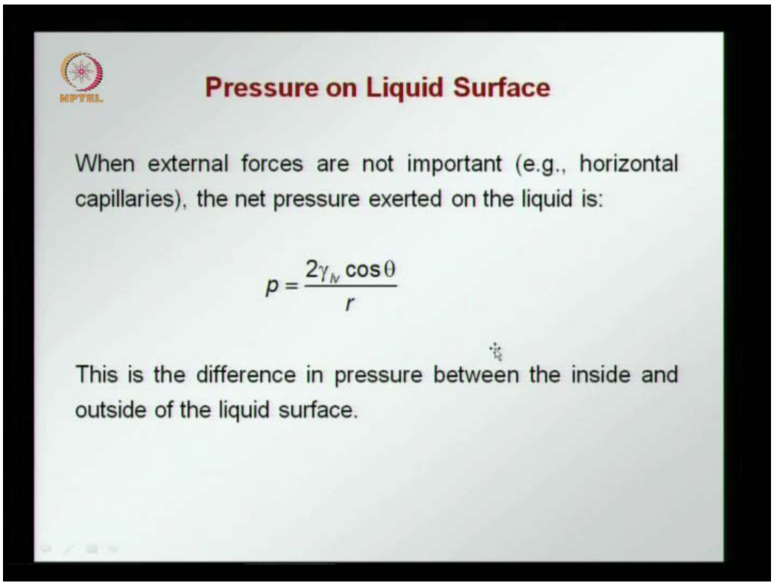

Pressure on Liquid Surface

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.

The force that is generated at the pressure the net pressure on the liquid. When we do not have any other external force applied the is equal to p, which is 2 times gamma l v, which is the surface tension between the liquid and vapor or the liquid vapor interface. Surface tension times cos theta divided by r, when r is very small. That is the distance between the plates or the capillary walls is very small.

You have a very high pressure being built up and this also explains, what I told you before about how an adhesive layer thick ness should be as thin as possible. So, that we have high force joining the two surfaces that, we want to use the adhesive to bond p now is in difference in pressure betweens the inside and the outside of the liquid surfaces.

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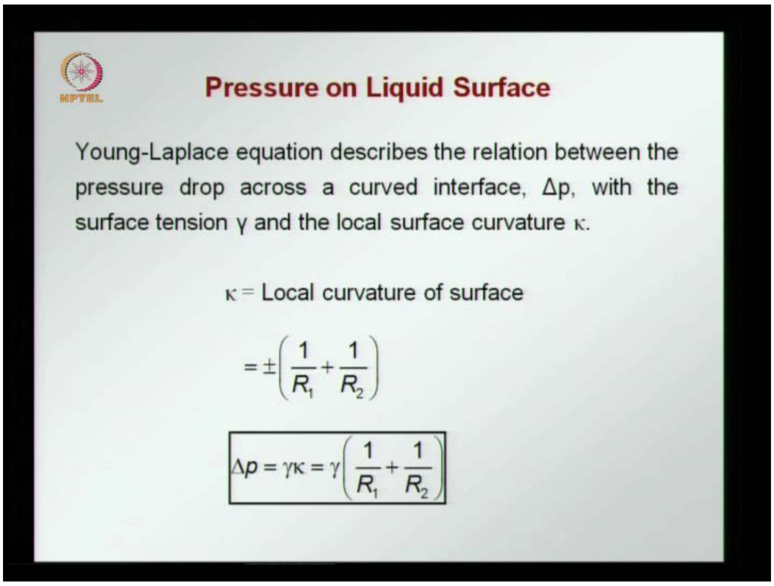

Pressure on Liquid Surface

Young-Laplace equation describes the relation between the pressure drop across a curved interface, Δp, with the surface tension γ and the local surface curvature κ.

$$\kappa = \text{Local curvature of surface}$$

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

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

The Young- Laplace equation gives us the relation between the pressure drop across a curved interface. Now, delta p in a liquid which has surface tension gamma and the surface curvature is kappa surface. Curvature kappa is given by the some of the inverses of the two radii of curvature R 1 and R 2. And now, the pressure drop is given by gamma times kappa or gamma times the some of the inverses of the two radian.

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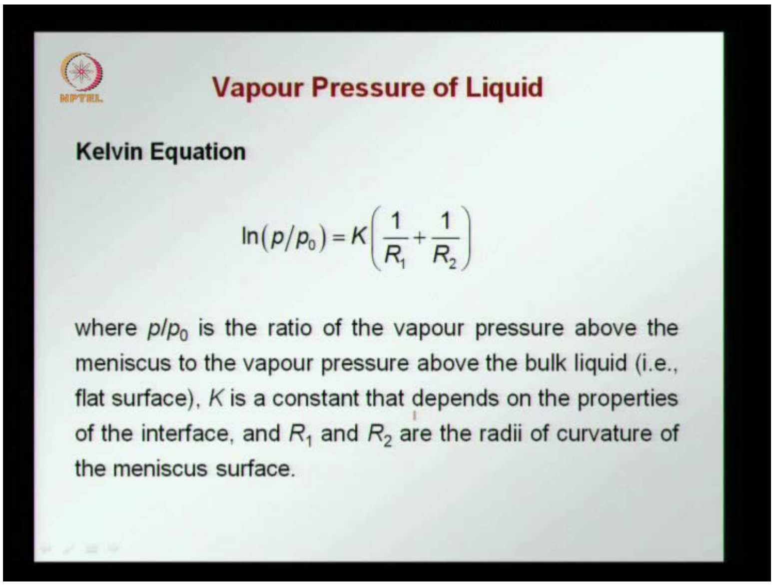

Vapour Pressure of Liquid

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.

The kelvin equation gives us the relation between the ratio of vapor pressure above the meniscus to the vapor pressure above the bulk liquid. That is where the surfaces is flat as shown here. The natural log of p divided by p 0, this term is now the ratio of the vapor pressure above the meniscus. The curved surface and the flat surface of the bulk liquid is equal to k, which is a constant depending on the properties of the interface, and the some of the inverses of the radii of curvature. This equation gives us some explanations of interesting phenomena that we absorb in materials.

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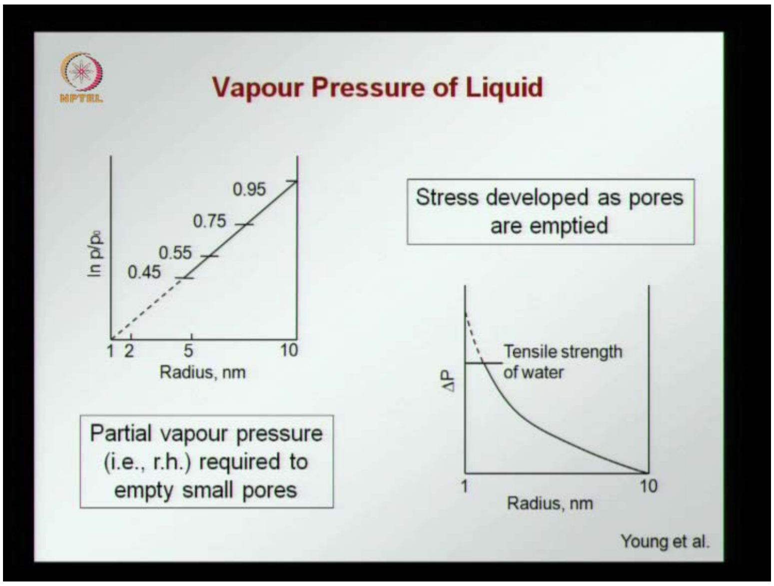

Vapour Pressure of Liquid

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

Stress developed as pores are emptied

Young et al.

For example on the left hand side we see a graph of the natural log of p divide p 0, which is the ratio of vapor pressures. As a function of the radii of the pores in poles, that are close to 10 nanometers in radius or larger evaporation of water. In the pores will start as soon as the relative humidity is less than 100 percent. However, what we find is when the pores are smaller.

We require a much larger lowering of the relative humidity for the pores to start dry. For example, when you have a pore of 5 nanometers in radius, the relative humidity has to be as low as 50 percent for that pore to start drying. So, this means that in many materials even though the environment is relatively dry the pore is not completely dry, or the material does not completely dry. On the right hand side, we see a diagram of this stress develop the pore pressure develop verses the radius and, what we find is that as the pore radius becomes smaller and smaller.

There is a large of force that is trying to pull on the water surface, pull the walls of the pores together until the tensile strength of the water it reached, and actually the water surface breaks, because the tensile strength is been reached and this type of force that is trying to pull on the water surface leads to contraction or shrinkage in materials then drying occurs. So, as the pore is being empty stress develops on the meniscus tending to pull the walls of the pores together, and this is what we observed as shrinkage in a material that is drying.

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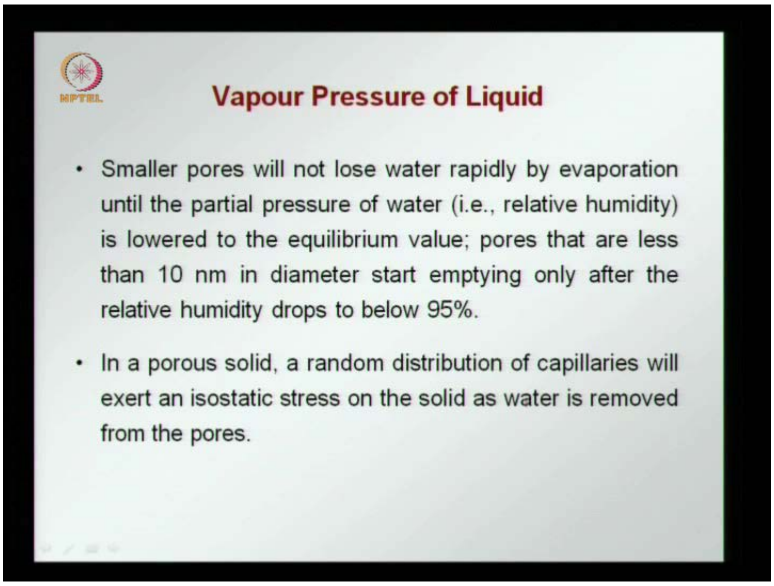

Vapour Pressure of Liquid

- 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.

So, what we saw is that smaller pores do not lose water rapidly by evaporation, until the partial pressure of water that is the relative humidity is lowered. Significantly, that is lowered to the equilibrium value pores that are less than 10 nanometers in diameter start emptying only after the relative humidity drops to below 90 or 95 percent.

So, materials which have very tiny pores will not dry until the relative humidity drops there is significant. And also we saw that there is a stress generated as the material dries. So, as water is being removed from pores say in a brick or a concrete or even wood. We have stress that is built up in the distribution of capillaries, which exists in these materials which are porous and this creates contraction or shrinkage of the materials.

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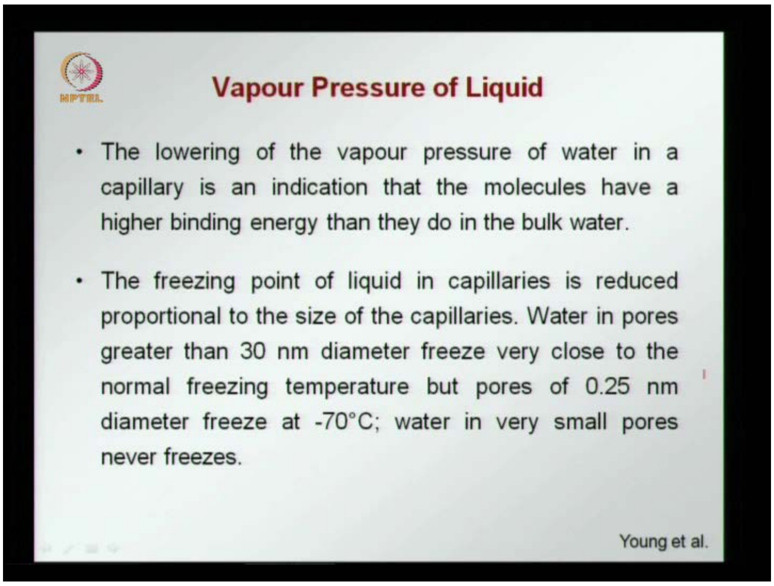

Vapour Pressure of Liquid

- 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°C; water in very small pores never freezes.

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The fact that we see this lowering of the vapor pressure in a capillary indicates that the molecules. Now, have a higher binding energy on the surface, then they do in the bulk water. So, in the curved surface in the meniscus the binding energy is higher that is, why we have to create a more adverse situation for the drying to occur. Similar phenomena also effects freezing.

We find that the freezing point of liquid say water in capillaries is reduce proportional to the size of the capillaries smaller the size of the capillary, or the pore lower has to be the temperature before the water freezes, water in pores greater than 30 nanometer and diameter freeze close to the normal freezing temperature of 0 degrees celsius.

But when we have very tiny pores of 0.25 nanometer water will freeze in those pores only. When the temperature drops to minus 70 degrees that is water in very small pores never freezes. And this is important when we look at freeze star damage in concrete and other materials.

There we have the movement of water as the temperature is dropping not all the water freezes. Suddenly at the same temperature, but water in larger pores freezes first and then the smaller pores and so on. So, this freezing water moves and creates a lot of stresses in the capillaries, which eventually lead to cracking and damage.

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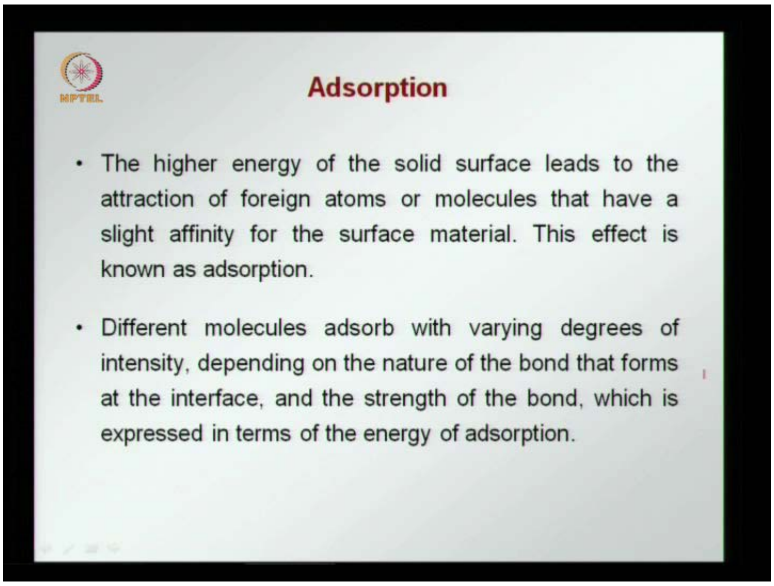

Adsorption

- 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.

There are other surface phenomena that were also important one is adsorption. We saw that the solid surface has a higher energy, because of the asymmetric bonding that is there for the atoms and particles on the surface. So, this higher energy leads to the attraction of foreign atoms, other materials that are outside the solid surface in as atoms or molecules, and if these has some affinity they have some attraction for the surface, then this higher energy attracts them and adsorbs them. This effect known as adsorption is now related to this higher surface energy that we see in solids.

Different molecules will adsorb with varying degrees of intensity. So, depending on the nature of the bond that forms and the type of molecule. We can have more adsorption, or less the strength of the bond also effects the degree of intensity, and all this can be express in terms of and energy of a adsorption just like. We saw lattice energy in bulk material.

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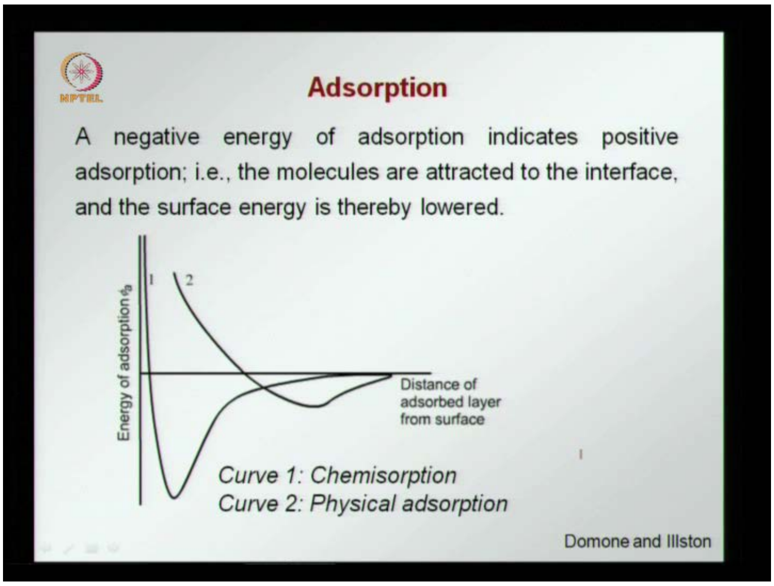

Adsorption

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

Curve 1: Chemisorption
Curve 2: Physical adsorption

Domone and Illston

So, in this graph we see the energy of adsorption as a function of the distance of the adsorbed layer from the surface in the x axis, the negative energy in the case a positive adsorption lower is this well similar to, what we saw in the Conden-Morse diagram more is the adsorption on the surface. Now, you see in this graph that there are two plots the curve label as one is for chemise option.

Where we also have a chemical bond forming on the surface between the adsorb material, and the host material. Physical adsorption has less of this attractive energy, the well or this drop as is not as much as here, this is called physical adsorption. You just have physical phenomenon and weak forces like van der waals forces, and hydrogen bonds keeping the adsorb molecule on the surface.

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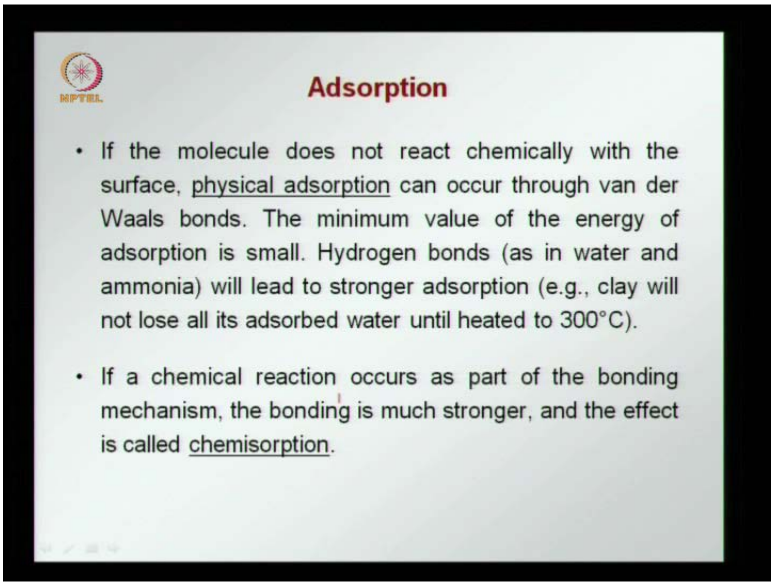

Adsorption

- 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.

So, when the molecule does not react chemically with the surface. We have physical adsorption occurring through van der waals bonds, and the minimum value of the energy of the adsorption is small, we saw in the previous graph. That the drop in energy was not as much as in chemical adsorption or chemisorption.

If we have hydrogen bonds as in the case of water and ammonia. We will have stronger adsorption we saw in the second lecture that hydrogen bonds whereas, specific type of van der waals bonds and due to stronger dipoles. We have stronger bonds then in the case of the van der waals bonds and this therefore, leads to stronger adsorption.

And an example of this is in clay, that clay will not lose all its adsorbed water, until it is heat in to 300 degrees celsius. So, lot of energy in terms of heat is required to break the adsorption energy, or to release the water that is help by adsorption by the clay surfaces. If there is a chemical reaction then the bonding is stronger and the effect is now call chemisorption.

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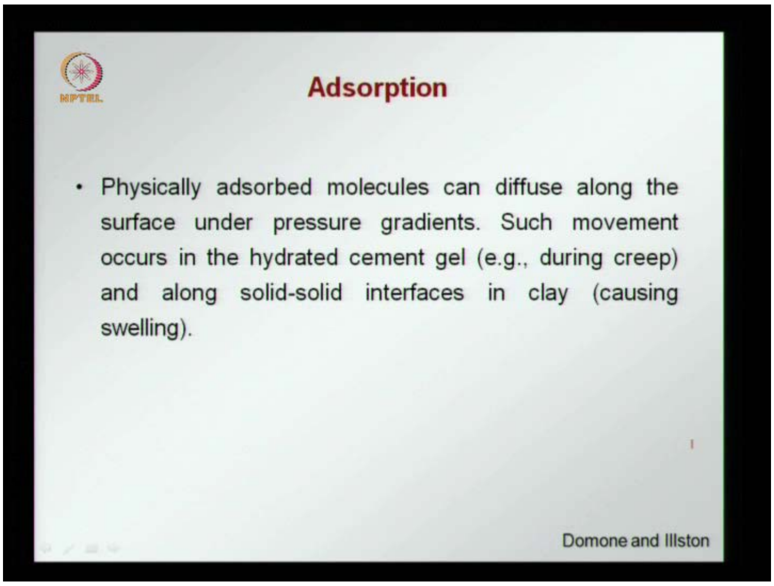

Adsorption

- 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).

Domone and Illston

We also know that physically adsorb molecules can diffuse along the surface under pressure gradients. That is if you have water adsorb on a surface and. If pressure is applied that dry is the water. These adsorb molecules instead of being released into the atmosphere will travel across the surface such movement occurs during creep in hydrated cement gel plus the calcium silicate hydrate gel water moves during creep and also in clays. We have water moving along the interfaces between the clay platelets this was discussed in a previous lecture, and this causes swelling. We have water moving into the interface between the clay platelets giving rise to swelling in some types of clay.

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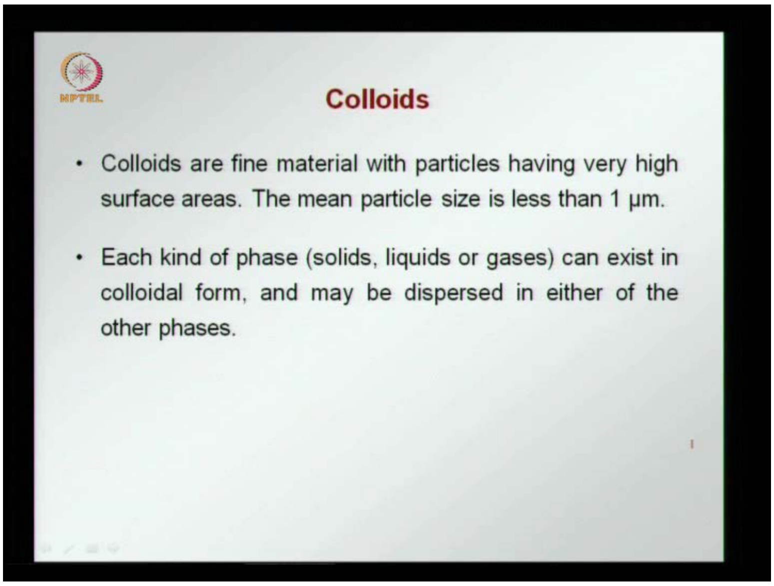

Colloids

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

Finally a phenomenon that affects the behavior of many materials also based on surface property is that related to colloids. Colloids are fine materials, which have very high surface areas and we are talking here about particles, which size is less than a micron. We can have different types of colloids depending on the phases involve solids liquids and gases can all exists in colloidal form, and can be dispersed in either of the other phases.

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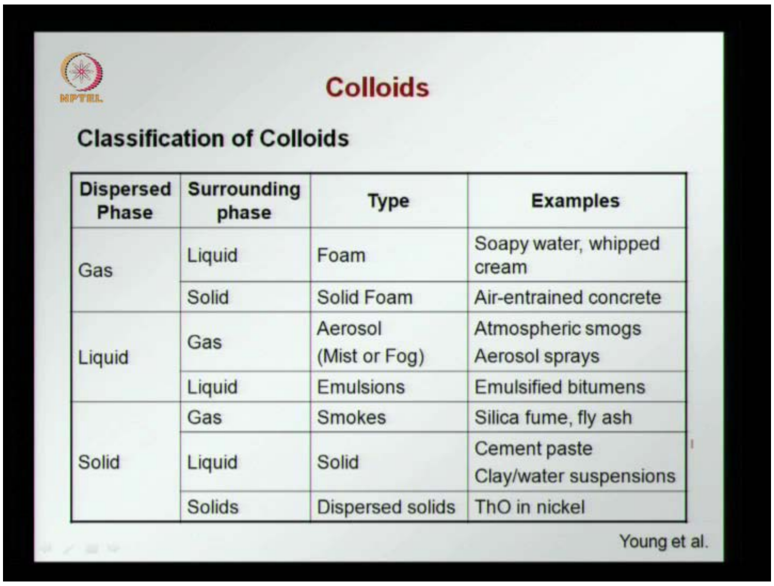

Colloids

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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We can see here in this table a classification of colloids, when we have gaseous phase dispersed in a liquid. We have four examples being whip cream soapy water foam that is used for insulation gas can also be dispersed in a solid giving a solid foam. An example is air-entrained concrete foamed concrete, then we can have liquid dispersed in gas giving an aerosol a spray liquid in liquid is an emulsion. We can have emulsified bitumens emulsified paints and solids can also be dispersed, when a solid is dispersed in a gas.

We have smoke and an example closer to civil engineering is in the case of silica fume or fly ash solid in liquid. We have examples of cement paste and clay water suspensions. This is the reason, why calcium silicate hydrate is called a gel, then we have a solid dispersion also possible example say of thorium oxide in nickel.

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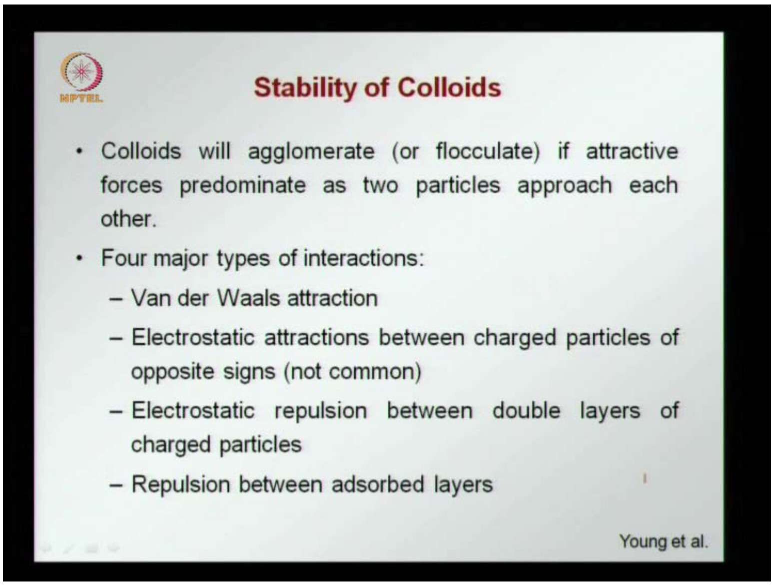

Stability of Colloids

- 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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Let us look at this stability of colloids, colloids agglomerate or flocculate when the attractive force is predominate this happens often. When two particles approach each other and, if there are attractive forces then they will tend to strict to each other and agglomerate or flocculate. There are several types of interactions possible first is van der waals forces that we have discussed earlier.

We can have electrostatic attraction between charge particles of opposite signs. This is not very common generally the particles will have the same sign or the same charge. This gives rise to electrostatic repulsion between bubble layers of charge particles, and then we can also have repulsion between adsorbed layers the charge is brought in by the adsorbed material can also lead to repulsion.

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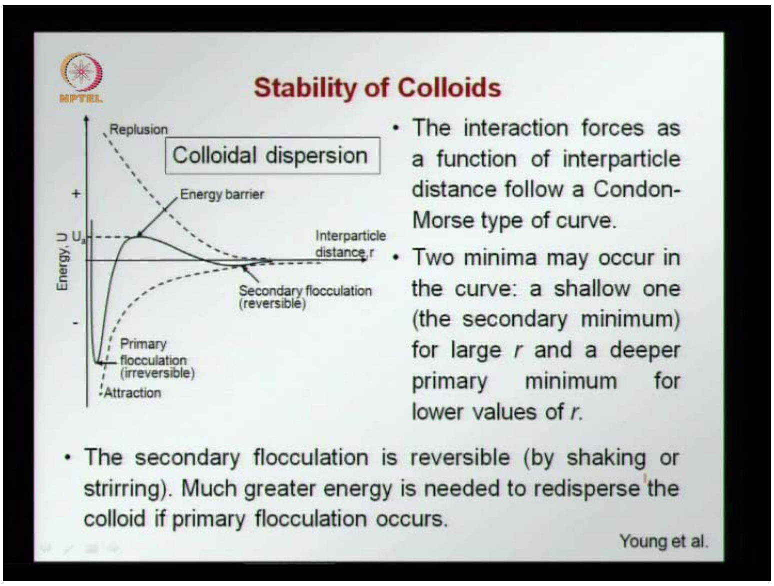

Stability of Colloids

- 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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We can again go back to Condon- Morse type curve to look at the interaction forces as a function of the inter particle distance. So, we have again energy on the y axis, and inter particle distance on the x axis, and we have here now repulsion by the force is that we discussed earlier. We can have repulsion due to same surface charges or because of adsorption, and then we can have some attractive forces, which are going to cause flocculation. So, van der waal's forces and other forces what we find is the energy diagram. Now, has a drop then hump and it comes back for a slide drop before becoming 0 this second drop is due to secondary flocculation, which is reversible.

The energy involved here is little. So, little bit of mechanical energy can dispersed the particles again. However, once this energy barrier this crossed and the material has flocculated, the colloids have flocculated causing primary flocculation this is almost irreversible the attractive energy is. So, high that the colloids are kept together has flocks or agglomerates.

So, what we see here is there are two minima in the curve a shallow one call the secondary flocculation and a deeper one, which is the primary flocculation secondary flocculation is reversible. That is by shaking this colloidal suspension or staring we can separate the flocks. However, much greater energy is required to re dispersed the colloids is primary flocculation occurs.

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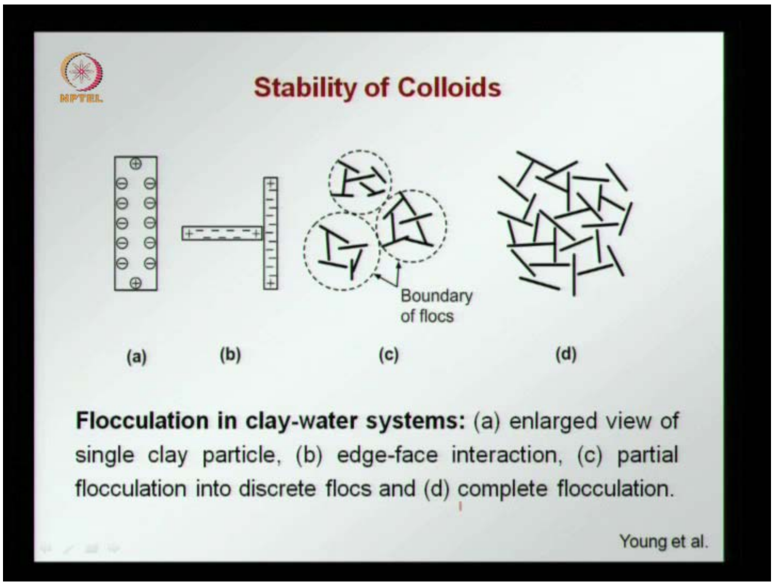

Stability of Colloids

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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So, this is irreversible the primary flocculation is irreversible or one example of flocculation in materials. That we deal with is see in clay water systems. On the left, we see a single clay plate and though this plate is now electrically neutral. We see some places, which we will have a certain charge another places, which will not have the same charge. And this gives rise to edge phase interactions there you have a positively charge end being attracted to a surface that is negatively charged. This gives rise to flocks is groups of particles have called flocks each will have a boundary, and they will be a separation between the flocks until there is complete flocculation has seen here.

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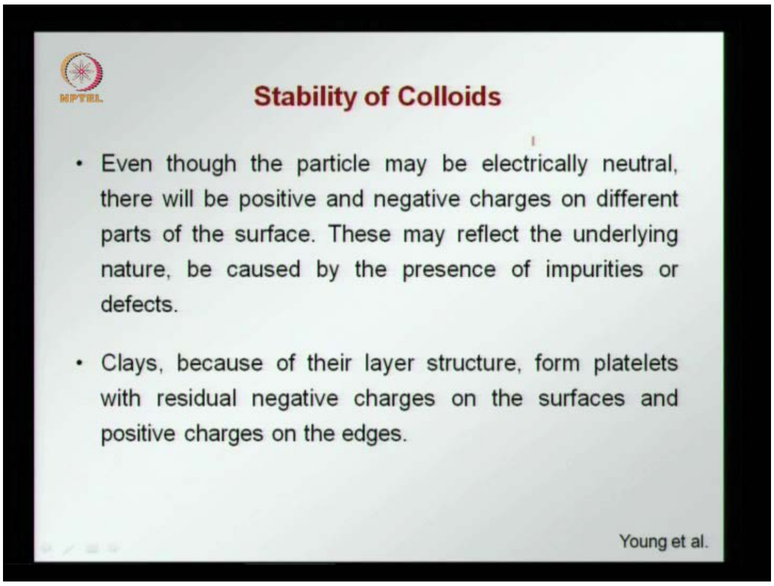

Stability of Colloids

- 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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So, as we said even though the particle see in this case. A clay particle may be electrically neutral they will be positive and negative charges on different parts of the surface. This may be due to the nature of the surface the impurities, and the defects that are present on different parts of the surface. Consequently, clays because of their layered structure form platelets with residual negative charges on the surface and positive charges on the edges, which gave rise to the flocks that we saw in the diagrams in the previous slide.

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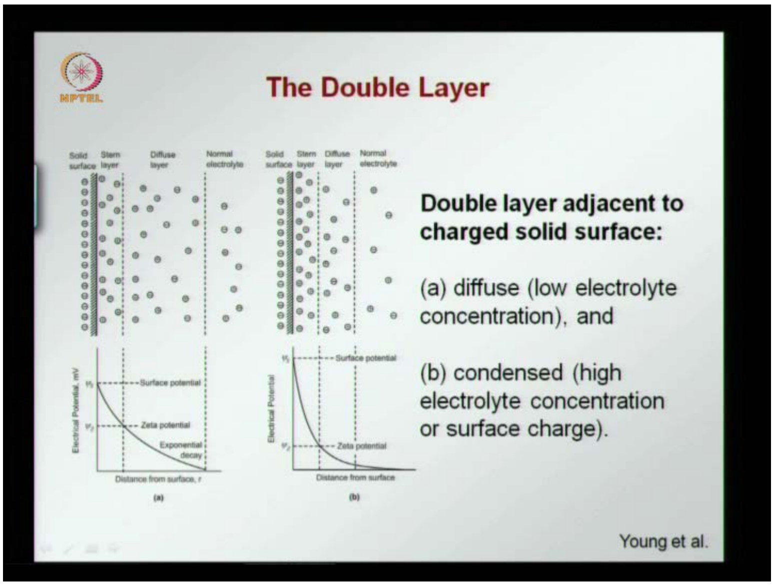

The Double Layer

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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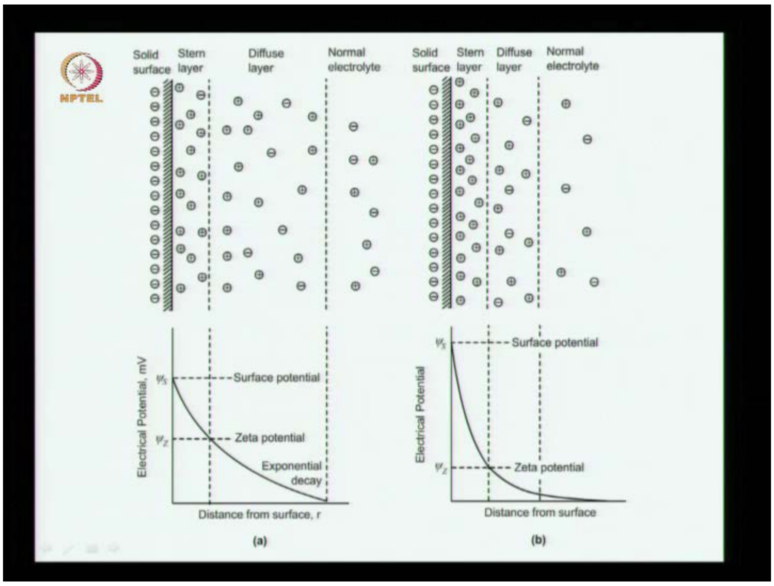

Now, one interesting phenomenon that occurs due to the surface charges is what we see in colloids or particles that are in an electrolytic solution. This is called the double layer phenomenon, and we have on the left a case where we have a solid surface. We have a solid surface with a negative charge we have an electrolyte here the solution in, which this solid particle is a suspended in or dispersed in and what the negative charges will do is attract some of the positive charges close to this surface this is called the stern layer.

And this stern layer will now move along with this solid surface as it moves within the solution or within the liquid away from the stern layer there is a diffuse layer, which has more positive charges closer to this stern layer. Because of these negative charges and this diffuses out to the normal electrolyte, which has a uniform distribution of negative and positive charges. So, if we look at the electrical potential has a function of the distance from this surface.

We find that the surface potential is very high, then it drops of and decaying to 0. Where we have the normal electrolyte that is at the end of the diffuse layer. The electrical potential at edge of the stern layer is called the zeta potential and this is important, because higher the zeta potential more will be the repulsion between surfaces that have a similar charge.

Now, not all materials in all not all combinations of materials will have a high surface potential and a high zeta potential. In this case, here we have a high surface potential which leads to a relatively thin diffuse layer leading to a low potential zeta potential. So, surface potential is high, but the decade is very rapid and the zeta potential is much low. So, we see here this double layer, which occurs adjacent to the charged solid particle.

We have a diffuse layer, which we saw here with a low electro light concentration in the case of a condensed double layer. We have a high electrolyte concentration or a high surface charge or surface potential.

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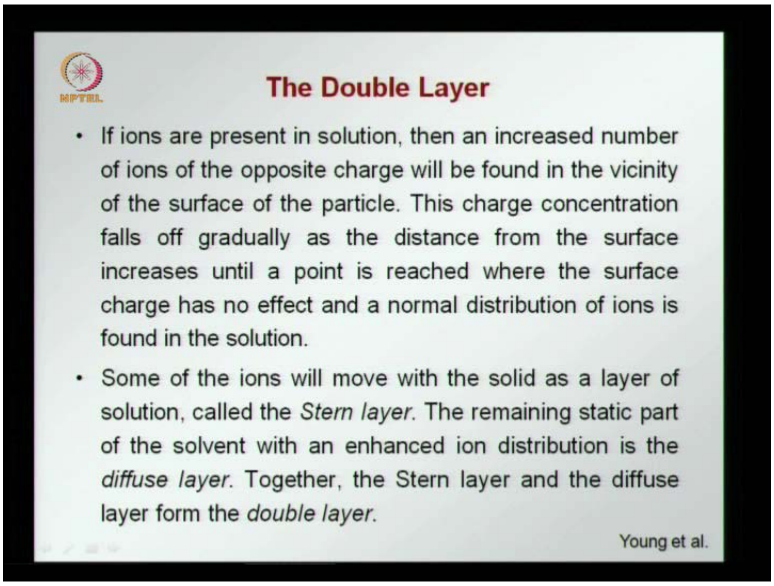

The Double Layer

- 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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Now, when ions are present in the solution then we saw that and increase number of ions of the opposite charge occur in the vicinity of the surface. We find an increased number of ions of the opposite charge occurring near the vicinity of the surface of the particle. The charge concentration decays as the distance from the surface increases, until we reach a normal distribution or uniform distribution of ions within the solution. Some of the ions move with the solid a layer that is closest to the surface moves along with the solid.

As the solid moves within the solution and this is called the stern layer, then there is a static part, which remains in the solvent. However, it has an enhanced ion distribution and this is called the diffuse layer, together the diffuse layer and the stern layer are called the double layer.

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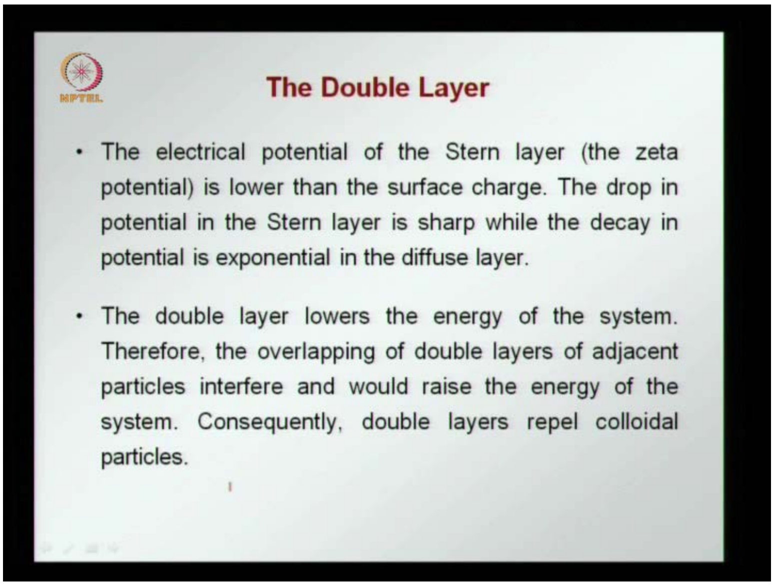

The Double Layer

- 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.

And we also saw that the electrical potential of the stern layer that is the zeta potential at the edge of the stern layer is lower than the surface charge. This drop in potential is sharp while the decay in potential is exponential in the diffuse layer. That is there is a sharp drop of electrical potential within the stern layer whereas, in the diffuse layer the decay is slower.

And this double layer now decreases the energy of the system therefore, when there is overlapping of the double layers of adjacent particles. We have two particles coming close to each other the overlapping raises the energy of the system and. Consequently, there is a repel in of the colloidal particles, that is the double layers formation repels the colloidal particles.

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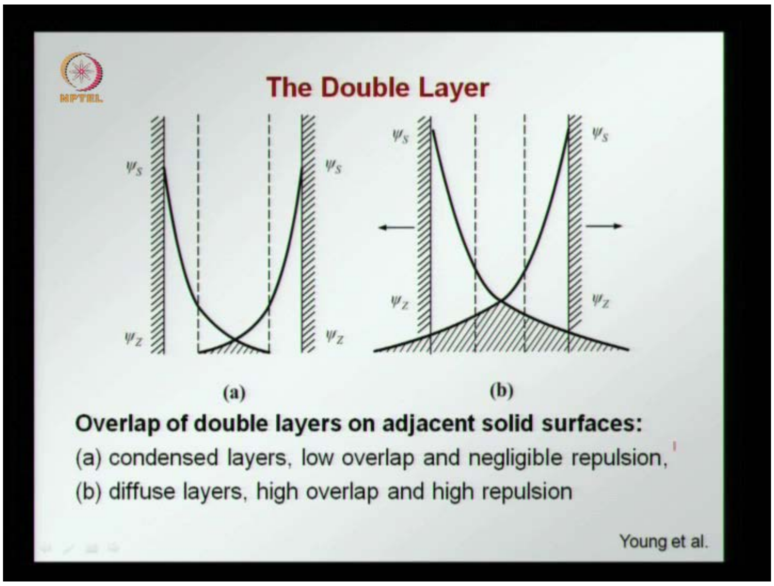

The Double Layer

(a) (b)

Overlap of double layers on adjacent solid surfaces:

(a) condensed layers, low overlap and negligible repulsion,

(b) diffuse layers, high overlap and high repulsion

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So, we see that here diagram particle in the case of a, we have a condensed layer much lower zeta potential and low overlap and the repulsion is less, but if we have a large diffuse layer. In the case of a large diffuse layer there is a high overlap and therefore, there is high repulsion and. This is the basis of the design of plasticizes and super plasticizes, which are meant to deflocculate cement particles. When the zeta potential of the system is higher there is better deflocuclation. The cement particles remain dispersed for a longer period of time and you have higher workability.

To summarize we looked at surface properties in this lecture. We started off by looking at how surface tension develops, why liquids have different spacing of the particles on the surface. And how this gives rise to tensile forces causing surface tension, and how surface tension can be used to explain capillary rise even rising dampness. We also looked at other phenomenon such as adsorption and colloidal behavior. We also saw how surfactants can modify materials to create emulsions foams and de-flocculation and earlier.

We had looked at the effect of wetting and how there is research going on to create surfaces that are hydrophilic to cause more wetting and hydrophobic surfaces to cause repulsion of water from the surface in the next lecture. We will be looking at mechanical properties. We will see mechanical behavior and from there on. We will be looking more and more at properties of materials moving away from just explanations of, how the microstructure forms, and how the microstructure behaves to more of engineering properties and the behavior in the engineering scale.

Thank you.