Nanostructures and Nanomaterials: Characterization and Properties

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Lecture - 32
Surfaces and Interfaces

In this lecture, we will learn about surfaces and interfaces. Surfaces are the ones, which interact with directly with the environment, whereas interfaces are the ones, which interact with another media. So, it can be solid solid interface, solid liquid interface, solid vapour interface liquid liquid, liquid vapour interface or it can be totally vapour. It may not be interface, but it can be related to the interacting with the particular surface.

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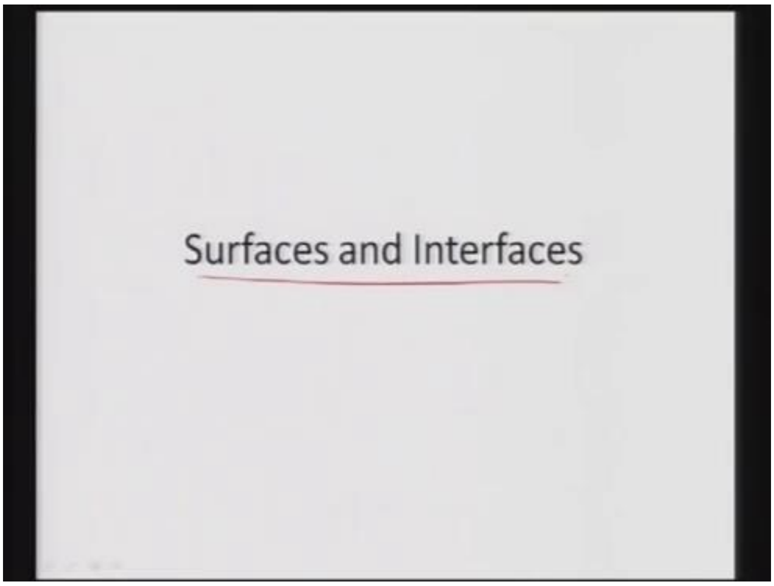

Surfaces and Interfaces

So, we can see that surfaces and interface they are highly critical and dictating the properties mainly for the engineering materials. So, that we can adopt them specifically for certain applications.

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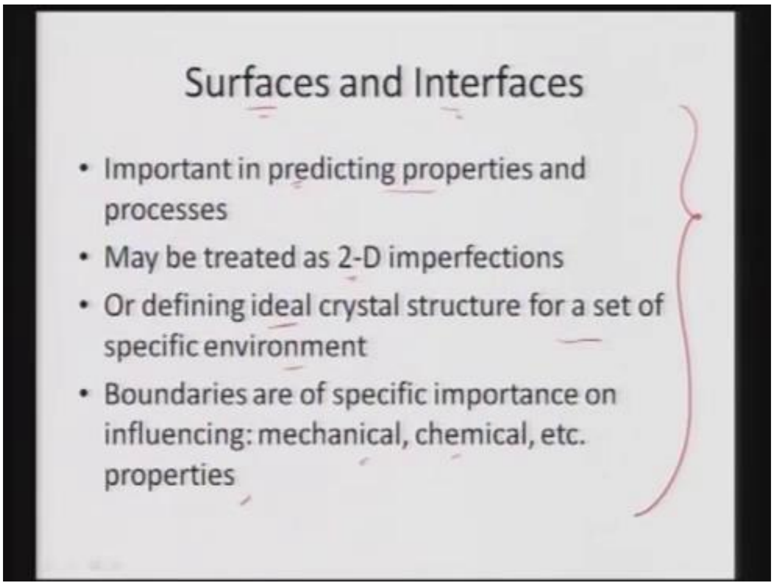

Surfaces and Interfaces

- Important in predicting properties and processes
- May be treated as 2-D imperfections
- Or defining ideal crystal structure for a set of specific environment
- Boundaries are of specific importance on influencing: mechanical, chemical, etc. properties

So, surfaces and interfaces between different grains and phases are highly important in predicting the properties and also controlling sudden processes. Surfaces can also be treated or interfaces can also be treated as 2 D imperfections or defects in the ideal structures of lattices. So, we can see that surfaces and interfaces they are highly important in predicting certain properties. These properties can be either mechanical, chemical, biological, electrical there can be so many properties.

So, boundaries are of very specific importance in enforcing these properties. Also this surface and interfaces can be helpful in defining ideal crystal structure for a set of specific environment. So, we can see that surface and interfaces, they play a very important role in dictating certain properties which are related to the electrical magnetic or even the even bulk chemical biological properties. So, these are highly critical.

So, only once we understand what are surfaces interfaces, then only we will be able to enumerate them for a certain application. Where these surfaces and interfaces they are highly critically specifically nanomaterials why, because the overall surface or the surface of the grain boundary region to the bulk volume. It is very high, that ratio between the grain boundary and the bulk of a particular grain in the nanomaterial is very, very high.

So, that is why we have very specific importance for surface and interfaces, because the overall volume of surface or interfaces very much comparable to that of bulk. So, what happens is, the interfere of grain boundary and the contribution from the surfaces or the grain boundaries or the grain. They are both equivalent or there is much more contribution of grain boundary in the nanomaterials.

Whereas, in bulk structures which are which are micro or macro or grains structures, in that case we have very large amount of grain bulk in comparison in that of grain boundary. So, in that case it is mainly dictated by the grain. So, in nanomaterials that is, because very essential that we consider surfaces and interfaces separately.

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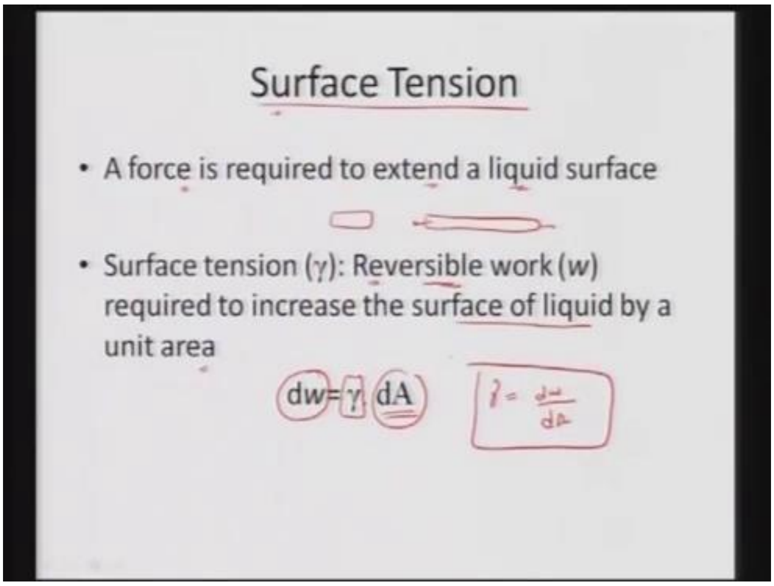

Surface Tension

- A force is required to extend a liquid surface
- Surface tension (γ): Reversible work (w) required to increase the surface of liquid by a unit area

$$dw = \gamma \, dA \qquad \boxed{\gamma = \frac{dw}{dA}}$$

We can go next. So, this surface and interfaces they are mainly given by 3 terms which are surface tension, surface traces and surface energy. So, we will come to them as we as we go along. So, let us see first surface tension. Surface tension is a force, which is required to extend the liquid surface. So, if you have a liquid surface, we require certain force to extend this liquid surface to something else or it is also being defined as reversible work required to increase a surface of a liquid by a unit area.

So, when you to do a certain work a certain work has to be done to increase a surface area of a liquid. So, we have to increase the surface of this particular liquid by a unit area. So, we can see that with this term is dictated by surface tension. Surface tension is the reversible work required to increase the surface of a liquid by a unit area. So, gamma is equal to d w by d A.

Surface tension is mainly responsible for the solodization of a liquid particle. So, we realize that the surface tension is equivalent to surface energy for liquids. Whereas, it is not. So, in the case of solids. Surface tension is the one, which makes the deformation of a surface, because of this additional force, which is existent which does work on the liquid.

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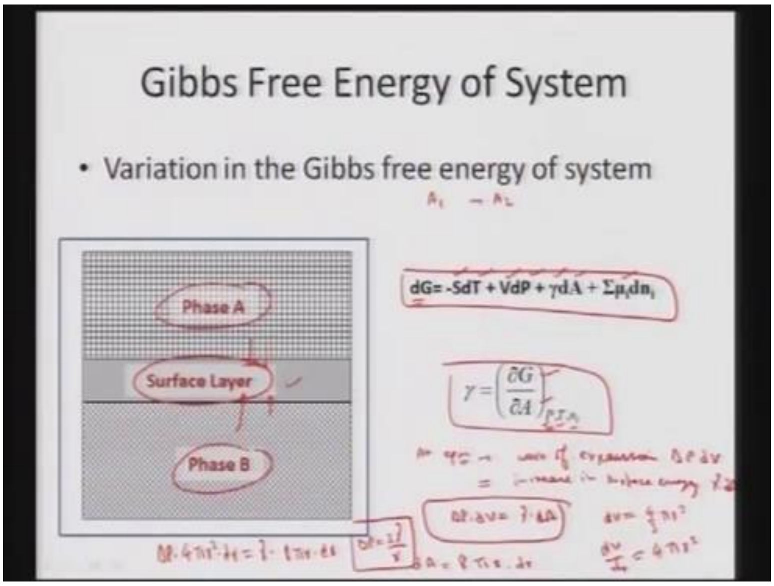

Gibbs Free Energy of System

- Variation in the Gibbs free energy of system

$A_1 \rightarrow A_2$

$dG = -SdT + VdP + \gamma dA + \Sigma \mu_i dn_i$

$\gamma = \left(\frac{\partial G}{\partial A}\right)_{P,T,n_i}$

At eq $\rightarrow$ work of expansion $\Delta P\, dV$
= increase in surface energy $\gamma\, dA$

$\Delta P \cdot dV = \gamma \cdot dA$

$dV = \frac{4}{3}\pi r^3$

$\frac{dV}{dr} = 4\pi r^2$

$dA = 8\pi r \cdot dr$

$\Delta P \cdot 4\pi r^2 \cdot dr = \gamma \cdot 8\pi r \cdot dr$

$\Delta P = \frac{2\gamma}{r}$

So, we can see that the Gibbs free energy of a system can be defined as basically a variation in the Gibbs free energy of a system, is in changing from one kilometer straight to others. So, if you have say a 1 to going to a 2. So, we can see that the overall free energy Gibbs free energy of a system is being given by this particular equation, which is dependent on the entropy, the temperature, volume, the pressure, the surface tension the volume the area and also the chemical potential.

So, we see can realize that, once we keep all other entities constant, the pressure temperature and the number of molts of an entity. We can see that, we can get surface tension as a function of free energy Gibbs free energy with respect to changing the area. So, at equilibrium what will happen work of expansion, that is given by p d v will equal the increase in the surface energy. This gamma multiplied by d A.

So, we can realize that delta p d v will equal gamma into d A. So, is essentially what is happening we have phase a, we have phase b and there is always some surface layer, that it takes overall generation of the enhancement in the free energy. How these two interact, will give out the overall surface layer, which will dictate the overall free energy of the new system. This can again be expanded that delta p into d v in gamma is equal to gamma into d A.

So, we can realize that d v, d v can be given as 4 pi r square the overall volume of a global one entity 4 by 3 pi r cube. So, we can see that d v by d r will equal 4 pi r square. Similarly, the d can be given as nothing but 4 pi r square. So, d A will be 8 pi r multiplied by d r here also you have. So, what we can see that delta p into d v. So, what we can see is that delta p into d v is 4 pi r square d r which equals gamma multiplied by 8 pi r into d r or we can see that delta p is equal to 2 gamma by r. This is the case for a spherical entity. So, in case when we do not have a spherical entity we can always say delta p is equal to gamma multiplied by 1 by r 1 plus 1 by r 2 where r 1 and r 2 are different curvatures.

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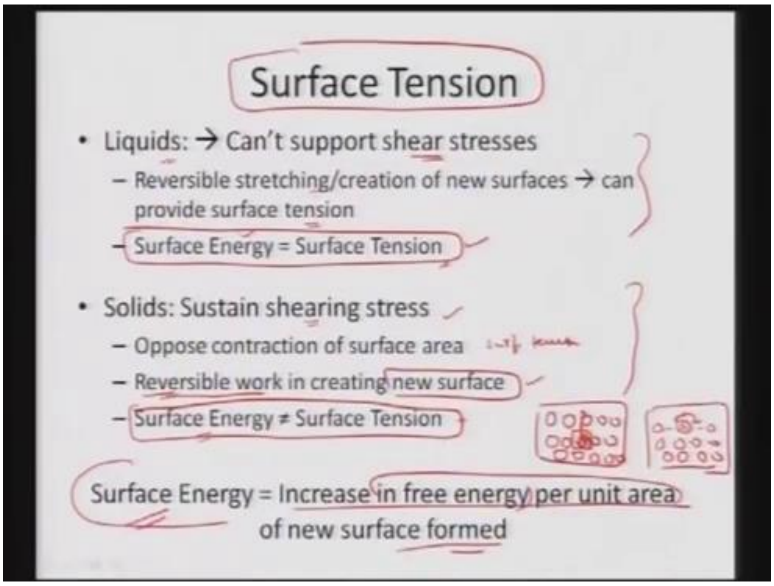

Surface Tension

- Liquids: → Can't support shear stresses
  - Reversible stretching/creation of new surfaces → can provide surface tension
  - Surface Energy = Surface Tension
- Solids: Sustain shearing stress
  - Oppose contraction of surface area
  - Reversible work in creating new surface
  - Surface Energy ≠ Surface Tension

Surface Energy = Increase in free energy per unit area of new surface formed

So, basically what surface tension can be defined as that liquids they cannot surface shear stresses. So, what is happening is reversible stretching or creation of new surfaces can provide surface tension. So, surface tension is being generated, because of the stretching of the reversible stretching of the new surfaces. So, for liquids we can see the surface energy is equal to surface tension, because there is no change in the surface no change in the surface tension, because of the change in the, because of application of stresses.

So, in that case we will realize that, this liquids or liquids the surface energy is equal to surface tension, but what is happening in solids is that solids can sustain very high shearing stresses. So, what is happening is they are also opposing the contraction in the surface area. So, when surface tension is acting on the surface it will tend to restrict or change the deform the surfaces.

That will be opposed in case of solids and also what is happening depending on the orientation of a pedular crystal, the surface energy will also be very different. So, in case of solids it can sustain by shearing stresses and they oppose contraction of surface area which arise, because of surface tension. So, we can define that surface tension in solids is equal to reversible work in creating new surface.

So, as we can see that, in this case what is happening surface energy is equal to surface tension plus some extra term in terms of changing the surface tension with respect to the strain which is being generated. So, we can see that in case of solids the surface energy is not equal to surface tension. So that is the dissimilarity between liquids and solids, because in liquids we can see that surface energy is equal to surface tension, because what is happening is as soon as we are allow stretching, the surface full the relaxation is much more rapid, whereas in solids the relaxation is not that rapid. So, that is why it can oppose that contraction in the surface area. That in turn is resulting some opposition of contraction on surface area in solids. We can define the surface tension in solids is the reversible work in creating a new surface. Also the addition of the surface stresses which act on which act on it.

So, how we can define surface energy is, it is increase in free energy per unit area when a new surface is being formed. So, surface energy is always an additional term which is kind of incorporating. Why it is happening is, because let us consider that we have a particular material. So, we take a particular material with certain atoms which are arranged in certain fashion. Let us say if you consider one atom out here and we want to bring it to the surface.

So, what is happening now this atom has to break the bonding with the other atoms which are nearby and then in turn it can come to the surface, but with that it has broken the bonds which should have been on the top as well. So, in turn it has gotten some energy it is, because of breaking them outside. In this case that has to break the bonds and then come to surface. So, that increase in the free energy per unit area, when a new surface is being formed is called as surface energy.

So, that is that is the typical nature of surface energy whereas surface tension, we can see that surface energy is equal to surface tension, in liquids. Because liquids can easily sustain it can they can easily relax as soon as the work is done on them, whereas in solids they can oppose the contraction of surface area when surface tension is acting on it. So, surface energy is not equal to surface tension, there is some additional work which is also being incorporated. How that really occurs we will see in the next few slides.

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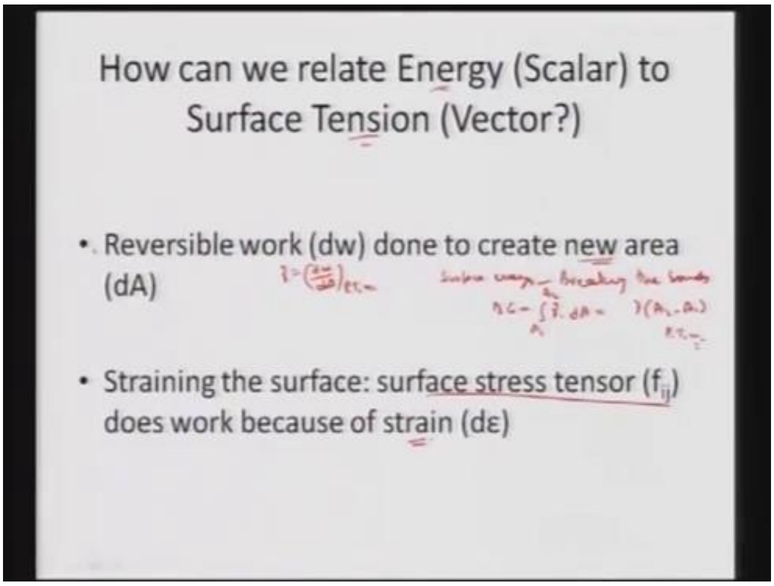

How can we relate Energy (Scalar) to Surface Tension (Vector?)

- Reversible work (dw) done to create new area (dA)

$\gamma = \left(\frac{dw}{dA}\right)_{P,T,n}$

Surface energy — Breaking the bonds

$\Delta G = \int_{A_1}^{A_2} \gamma \cdot dA = \gamma(A_2 - A_1)$

P,T,n

- Straining the surface: surface stress tensor (f_{ij}) does work because of strain ($d\varepsilon$)

So, we can see that the energy is a scalar quantity, whereas surface tension is a vector quantity. So, how we can really relate them. So, we can see that surface tension is equal to reversible wok to create new area that is d w by d A. So, gamma is equal to when other quantities are pressure temperature and the number of molts or chemical potential is kept constant. Whereas, what is happening in the second case is that, if you consider that surface energy we need to break the bonds.

So, for surface energy we are breaking the bonds and we are getting some enhancement in the free energy per unit radii of the new surface which is being formed. So, we can see that delta G can be equal to a 1 and a 2 are the two equilibrium, positions two equilibrium states. So, we have d A as equal to gamma into minus a 1 basically by keeping everything the pressure temperature and the n 1 as constant.

Now, second concept can be that gamma is a surface tension is a function of orientation of it as well. From solids we have plain of 1 1 1 which is being stretched or plain of 1 1 0 which is being stretched or plain 1 0 0 which is being stretched. The overall energy or the surface tension required for stretching the surface will be very different. So, we require a surface stress tensor that has to do work, because of the strain, which is to be induced on a particular surface orientation.

So, that that basically have some help helps us in controlling the energy to the surface tension which is the vector quantity. So, we requested an energy to deform a certain orientation of crystal or assisting the surface tension which does work on a particular surface.

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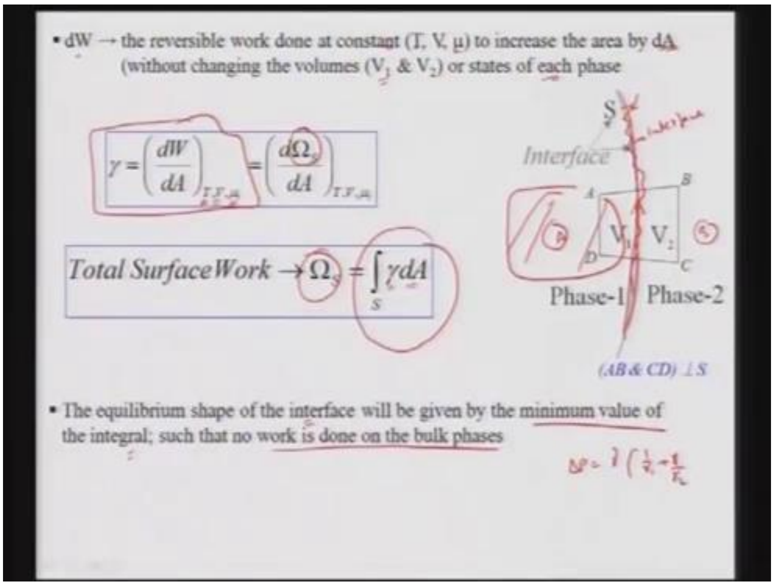

- dW → the reversible work done at constant (T, V, μ) to increase the area by dA (without changing the volumes (V_1 & V_2) or states of each phase

$$\gamma = \left(\frac{dW}{dA}\right)_{T,V,\mu} = \left(\frac{d\Omega_s}{dA}\right)_{T,V,\mu}$$

$$\text{Total Surface Work} \rightarrow \Omega_s = \int_S \gamma dA$$

- The equilibrium shape of the interface will be given by the minimum value of the integral; such that no work is done on the bulk phases

Seeing that d w is the reversible work that is being done while keeping the temperature volume, the chemical potential constant to increase the area per unit area d A without changing any volume or state of each phase. So, gamma we saw that gamma is equal to d w by d A while keeping temperature volume and the chemical potential as the constant. The total surface work is can be given by gamma or the omega s, that is the function again of the gamma into d A.

So, what we can see if we have phase one or phase a to phase b. The inter layer between them is called an interface, that considers as the 2 D effect. So, equilibrium shape of this interface will be given by the minimum value of the integral. So, we have the integral out here. So, equilibrium shape can be given by the minimum value of this particular integral. So, that no work is done on the bulk phases. So, bulk phases will not do any work, the work is done by mainly by the interface. So, that will dictate the overall curvature of this particular interface. As we saw earlier that depends on the pressure difference which can again be given by gamma 1 by r 1 plus 1 by r 2.

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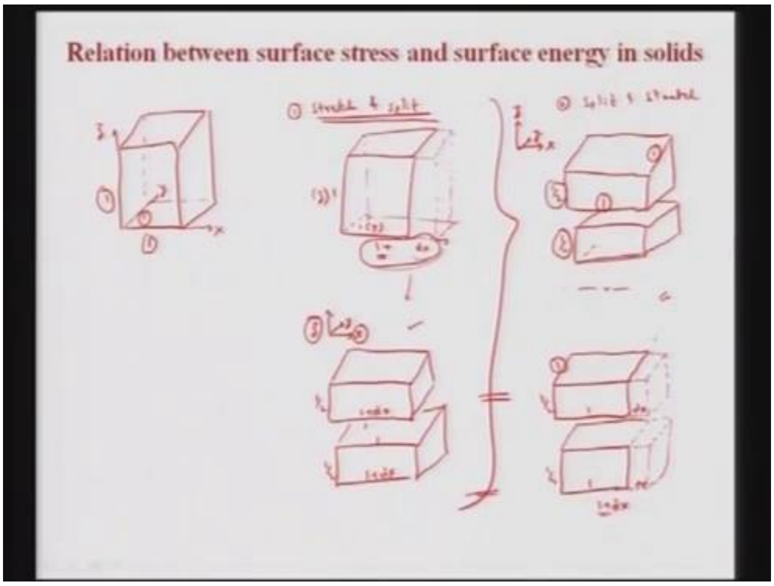

Relation between surface stress and surface energy in solids

So, if you have to induce a relationship, which is between the surface stresses and the surface energy in solids. So, what we can do we can try do kind of do a small experiment virtual experiment, to see the difference between what is happening when the how the surface stresses and surface energy are basically being related in the current work.

So, let us take a crystal. So, let us take a crystal assuming all the lengths breadths and heights are unity. So, we can see that we have a unit crystal. So, we can take as x z and along y. So, what we do what we can do here is we can stretch. So, first step is we can stretch and split whereas in second case, what we can do we can split and then stretch. So, once we are stretching it.

So, let us say we stretch it along the x direction while keeping y and z as constant and then do the splitting. So, what we have done. So, what we have done, instead of x, now we have delta x. So, now what we have done we have now increased it. So, along x we have made it, 1 plus d x. In this case it is z, it is again 1 and then we have again 1 on the y. So, we have y as 1 z as 1, but in x we have 1 plus d x.

Now, we have some additional surface along the x direction and then we what do what do you then then we split it. So, that I can get a crystal. So, in this case what I am getting. So, I have 1 plus d x and then 1 plus d x this is length is 1. Now, in this case I have z as half. So, this is the first case. So, we took a crystal of 1 1 1 each of unit length along x along y and along z. So, we have unit length along x y and z. What we are doing in the first case is, we are stretching and splitting. it means we are stretching along the x direction. So, instead of 1 unit distance I am extending it to 1 plus d x.

Then I am splitting it along the x direction. So, it has been split along z. So, we can see along z it has been split, it has been stretched along x and it has been split along z direction. In second case what we can, we can split it first along z direction. So, in this case we achieve the splitting first. So, in this case we have 1, we have half, again this is 1.

So, along x I have 1 as z along y also I have travel along 1 unit length, but along z I have not split it. So, I can get half of 2 2 cells which have height of half and the second step is to stretch it them along the x direction. So, I can get the similar crystal as I got in the first case. So, in this case what I am getting. Now I am getting this crystal, the top crystal the top half crystal. Now, I am extending it I am extending it to half. So, I can extend it to d x. So I had 1 and then d x and a same crystal I will try to get d x out here.

So, I have now half 1 and then 1 plus d x along the x side. So, what do we have with this similar final conditions, but in first case what is happening, we are first stretching it and then splitting it, but in second case what we are doing, we are first splitting it, then stretching it. So, in this case I can get to see the work which is done by the extra surfaces. So, in first case we are stretching and then splitting. So, once we are stretching it have some additional surface available. Then we can see, what is the work, which is done by the additional surface.

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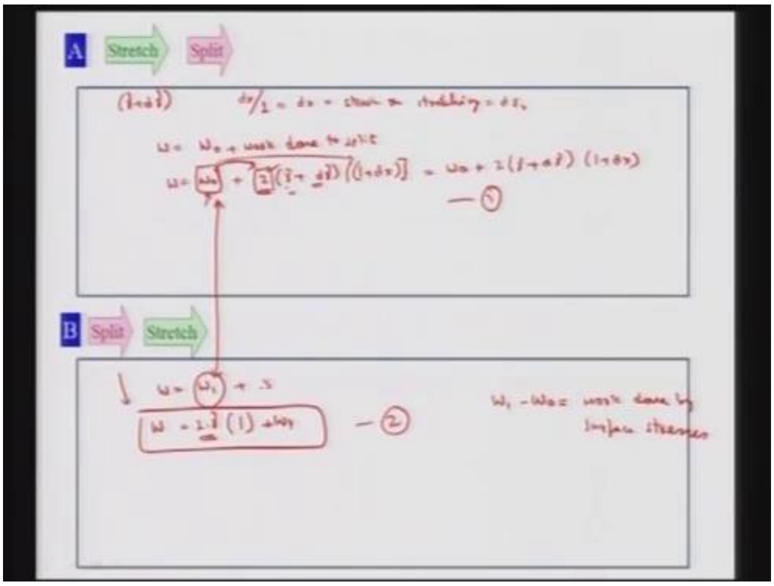

Whereas second case I am first splitting it and then it is being stretched. So, we can see the corresponding part of this this can be. So, when I am stretching it and splitting it. So, in stretching what I was getting I was getting an overall new surface energy, which was gamma plus d gamma, because I have now new surface. Also the work done on stretching was now considering to be w knot. So, w naught is the work done on stretching, what is the strain which is being developed on stretching is, it is the extra work which is d x divided by total length initial length, it is equal to d x. So, d x is the strain which is being developed on the stretching.

So, strain of stretching is given by d epsilon along x direction. So, we can see the overall work done, the total work is given by work done to stretch that is w naught plus work done to split. Now, we can see that the total work is given by work done to stretch plus work done by split was 2 gamma plus d gamma, because we are creating 2 new surfaces it is not 1, but 2 crystals 2 crystals which are generated, because of stretching and then splitting. So, once we split we are seeing 2 surfaces.

So, once the stretching worked into stretching is w naught that for splitting we are creating 2 new surfaces which are gamma plus d gamma. This is the new surface, because of the stretching. Now, it has being multiplied by the strain, which has been developed. That is 1 plus d x multiplied by the term. So, what we can see this is equal to w naught plus 2 gamma plus d gamma. This gamma plus d gamma multiplied by 1 plus d

x. The second case what is happening, the total work done is equal to work done to split and work done to stretch.

So, work done to split, work done to stretch is a w 1, because in this case I have only 1 1 1 along all the 3 direction and that is being stretched. So, the work done in stretching is different than what was the work done in the layer case, which has stretching in this case the stretching was then first. So, that resulted a change in the surface energy and the overall length which was to which it was extended.

Then second case when I am splitting it, I am getting a total surface energy of 2 gamma multiplied by 1. So, I can see that the total work done is given by 2 gamma plus w 1. So, I have equation 1 and equation 2 and they have to be equal, because the final condition is the same for both of them. So, we can see the work done on stretching the split halves is different from the work done in unsplit halves, because of some surface stresses.

So, the overall change or difference between them is arising, because of the work done which is being done by the surface stresses. So, we can see w 1 minus w naught is equal to work done by the surface stresses, because in this case I had only the surface of 1 1 1. That was being stretched in first case what is happening first we stretched and then we split it.

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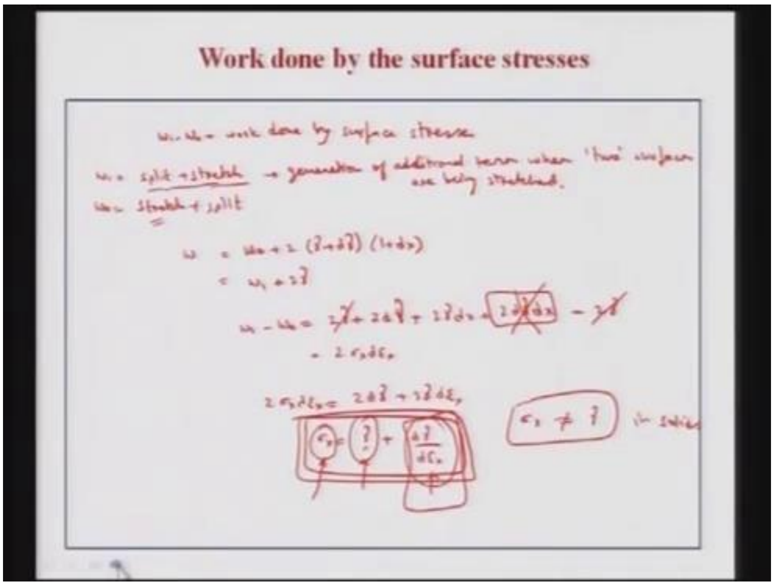

Work done by the surface stresses

$w_1 - w_0$ = work done by surface stresses

w_1 = split + stretch → generation of additional term when 'two' surfaces are being stretched.

w_0 = stretch + split

$w = w_0 + 2(\gamma + d\gamma)(1 + dx)$

$= w_1 + 2\gamma$

$w_1 - w_0 = \cancel{2\gamma} + 2d\gamma + 2\gamma dx + \boxed{\cancel{2d\gamma dx}} - \cancel{2\gamma}$

$= 2\sigma_x d\varepsilon_x$

$2\sigma_x d\varepsilon_x = 2d\gamma + 2\gamma d\varepsilon_x$

$\boxed{\sigma_x = \gamma + \frac{d\gamma}{d\varepsilon_x}}$

$\boxed{\sigma_x \neq \gamma}$ in solids

So, we can see that once we subtract the splitting minus splitting and stretching minus stretching. Then splitting we are allowing some work done, which is to be done by the surface stresses. So, we can see that, because w 1. So, in this case we are seeing the generation of additional surface when two surfaces are being stretched. So, we can see that w 1 minus w naught which is equal to w naught plus 2 times gamma plus g gamma 1 plus d x. So, now w 1 minus w naught will equal 2 gamma which is 2 d gamma.

This term also equals the work done which is done by the surface stresses. This also equals 2 times sigma x d epsilon x. We can see that is equal to 2 d gamma. This term is very small. So, we can ignore this term, now we can see then that that we can see that d epsilon can be taken away.

So, we can see that sigma x is equal to gamma plus. So, we can see that the work which is being done by the surface stresses equal the surface tension plus the change in surface tension, because of the stretching which is been due to the strain which is being generated in the material. So, that part we can see that surface stresses and surface tension they are not equal. So, we can see that surface stresses, it does not equal the surface tension in case of solids.

So, in this case we can clearly see that the work which is being done by a surface stress is very-very different when we split and stretch. So, in this case what we are doing we are now allowing any additional surface to act on a material and that is resulting the enhancement in the surface overall energy which is being generated. In comparison to the stretching and splitting and that part we can see that additional work is being done by the surface stresses.

So, that is equal to 2 sigma x into d epsilon and that is being related to the difference in the work done, which is done, because of the stretch and split minus split and stress. So, that part we did see that and from that we can see that the surface stress equals the surface tension plus change in the surface tension, because of the strain. That actually results that surface stresses, they do not equal surface tension in case of solid, because there is some additional term, which arises which resists the deformation of the solid surfaces.

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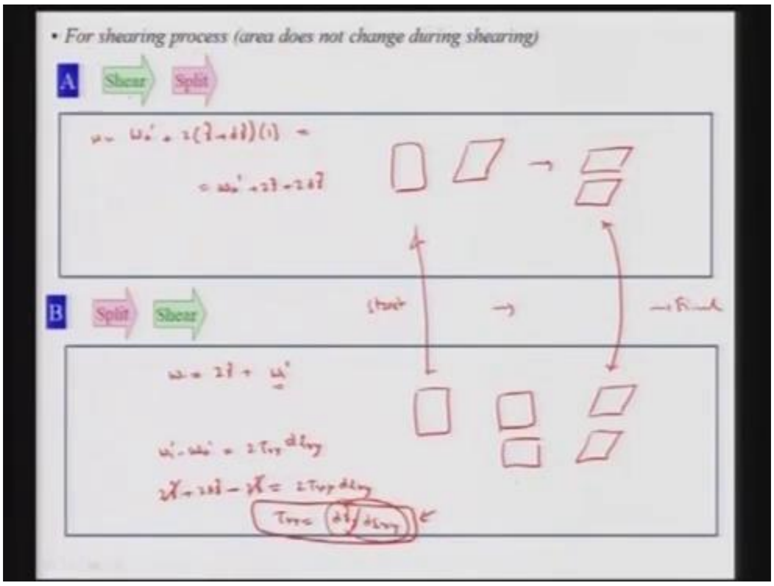

- For shearing process (area does not change during shearing)

A Shear → Split

$w = w_0' + 2(\gamma + d\gamma)(1) =$

$= w_0' + 2\gamma + 2d\gamma$

B Split → Shear

$w = 2\gamma + w_1'$

$w_1' - w_0' = 2\tau_{xy}\, d\varepsilon_{xy}$

$2\gamma + 2d\gamma - 2\gamma = 2\tau_{xy}\, d\varepsilon_{xy}$

$\boxed{\tau_{xy} = d\gamma / d\varepsilon_{xy}}$

Similar manner we can also see it for the shearing process that shearing and then splitting second case is splitting and then shearing. So, we can see the similar thing while incorporating the shear stresses. Similarly for shearing process we assuming that area does not change during the shearing. We can have shearing followed by splitting and then splitting followed by shearing. So, we can see that the total work done in shearing and then splitting. So, once we are shearing it, we can get an overall work done which is w naught plus half once is split it we have one enhancement in the change in the surface tension.

That is given by d gamma plus g gamma multiplied by 1. So, what do we get is w naught dash which is different from the work which was done by the surface stresses and this is now the shearing stresses. So, we have we see w naught dash plus 2 gamma plus 2 d gamma, but once we split and shear what do we see that we have to do work for splitting it first.

So, we can directly see that the total work done, in this case is equal to work done to split that is the 2 gamma plus work done to shear, that is w 1 dash. Again this is different from what we got obtained in the earlier case. So, in this case we have multilayer and then we split it first and then we shear it. When first case we are first shearing it and then we are cutting it down splitting it. So, we can see, we get this similar kind of shapes before and after, but overall thing is we start with the same entity. Then we finish it with the…

So, in this case also we can see the overall work which can be done the work, which is being done by the surface shear stresses. So, that is again w 1 minus w naught dash that is given by 2 tow x y d epsilon x y. So, what we can see here is we can see 2 gamma plus 2 d gamma minus 2 gamma which is equivalent to 2 tow x y d epsilon x y. So, we can see that tow x y is equal to d gamma by.

So, we can see the similar fashion that this term is not does not appear for the liquids. So, again for solids we can see the shearing stress is basically dependent on the changing the surface tension due to the shearing stress that is basically changing the overall surface energy of the system. So, we can see the surface energy is not equivalent to surface tension in case of solids. We can see that the shearing surface shearing stresses are also doing some work in case of solids. So, what is happening here.

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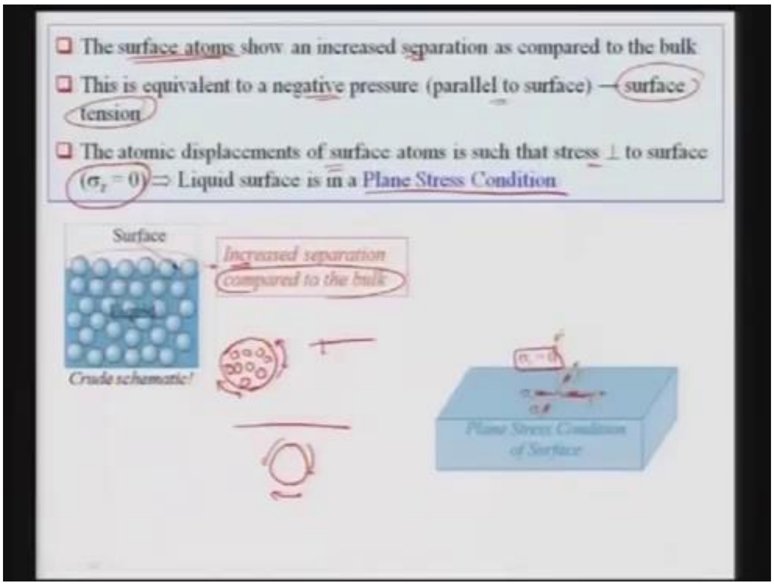

- The surface atoms show an increased separation as compared to the bulk
- This is equivalent to a negative pressure (parallel to surface) → surface tension
- The atomic displacements of surface atoms is such that stress ⊥ to surface ($\sigma_z = 0$) ⇒ Liquid surface is in a Plane Stress Condition

In this case we can see that the surface atoms they show an increased separation as compared to the bulk. So, in case of liquids we have some separation, but the surface will show some increased separation compared to that of bulk. That is some sort of a negative pressure, which is parallel to the surface. That is called surface tension, because that actually is what is doing it is. Now, constructing a liquid to form a contour shape that is why we have we can see that the rain droplets, they come out to be spheres. So, now it is trying to stretch this is the negative pressure it tries to stretch the along the surface try to compress them. So, in that in that stretch.

So, that is how you can see a surface tension we see a globular or the spherical nature of the liquids. The atomic displacement of the surface atoms such is that they are perpendicular to the surface. That means that sigma z is equal to zero or the liquid surface, the surface of the liquid is in a playing stress condition. There is no strain, which are acting beneath it or the stresses along the directions are zero.

So, that is how we can see all the stresses are confined to x y plain and the stress along the z is zero. So, there is no zero stress along the. So, there is no. So, all the stretching is occurring along the x and y direction only. That makes a plain to become kinds of a globular in case of liquids when it is freely available. So, that has a very nice finding of this one that the surface atom surface atoms of the of the liquids that show an increased separation as compared to that of bulk and that is more or less like a negative pressure that is building on a surface. That pressure is makes it to be in a plain stress condition it or it means the stress along the z directions are zero.

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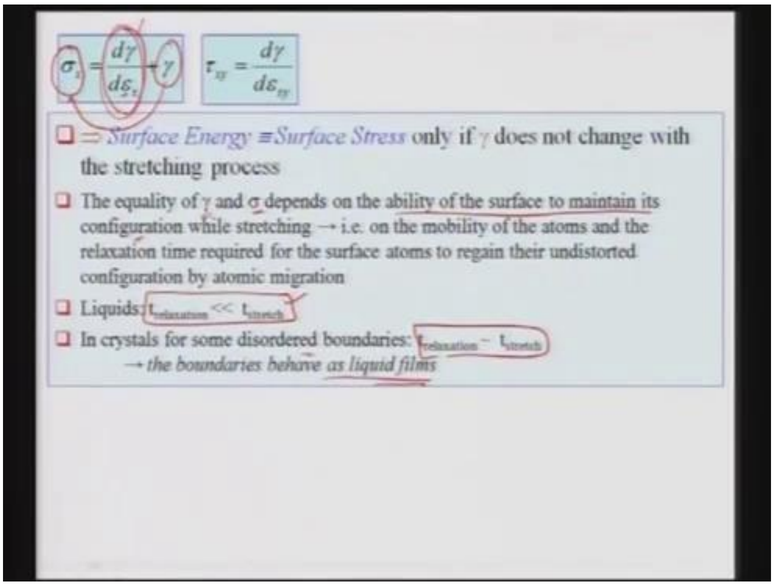

$\sigma_x = \frac{d\gamma}{d\varepsilon_x} + \gamma$ $\tau_{xy} = \frac{d\gamma}{d\varepsilon_{xy}}$

- ⇒ Surface Energy ≡ Surface Stress only if γ does not change with the stretching process
- The equality of γ and σ depends on the ability of the surface to maintain its configuration while stretching → i.e. on the mobility of the atoms and the relaxation time required for the surface atoms to regain their undistorted configuration by atomic migration
- Liquids: $t_{relaxation} << t_{stretch}$
- In crystals for some disordered boundaries: $t_{relaxation} \sim t_{stretch}$
  → *the boundaries behave as liquid films*

So, in summary we can see that the overall stresses which are acting, the surface stresses they are equivalent to surface tension plus an additional term. So, we can see surface energy will equal surface stress only for liquids, because this d sigma by d epsilon term is absent for liquids, but in case when we have this particular term, the surface stress is are basically being dictated in this case.

So, we can see we have additional term of changing the surface tension with respect to the strain that is being present on that. So, equality of gamma and sigma depend on the ability of surface to maintain it is configuration, while it is being stretched, because in liquid there is no strain in the third direction. So, what is happening the mobility of atoms is very, very fast in liquids that makes it equivalent, that sigma becomes equivalent to gamma, where in certain cases, like in grain boundaries or disordered grain boundaries we have t relaxation approximately equal to stretching. So, those cases it can behave as a liquid film, but in liquids as such the relaxation time is much smaller than the stretching time.

So, what is happening in that case is the, films are already in the equilibrium even when the stretching is being done So, in that case we can see that d sigma by d epsilon is basically not present. In that case we can see sigma x equal to gamma or surface energy is equal to surface stresses when gamma is not changing with the stretching process. So, that is the overall deal with the surface tension and surface energy or the surface stresses relation to the surface energy.

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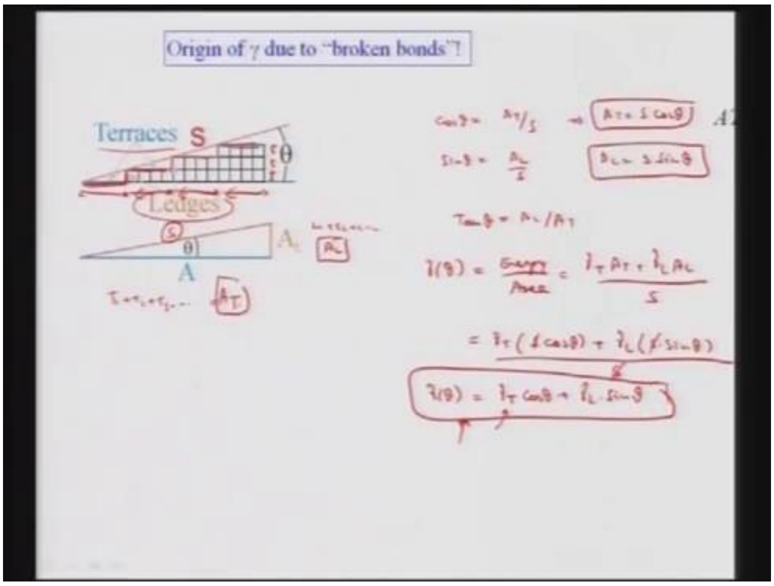

Origin of γ due to "broken bonds"?

$\cos\theta = A_T/S \rightarrow \boxed{A_T = S\cos\theta}$

$\sin\theta = \frac{A_L}{S} \quad \boxed{A_L = S\sin\theta}$

$\tan\theta = A_L/A_T$

$\gamma(\theta) = \frac{\text{Energy}}{\text{Area}} = \frac{\gamma_T A_T + \gamma_L A_L}{S}$

$= \frac{\gamma_T(\cancel{S}\cos\theta) + \gamma_L(\cancel{S}\sin\theta)}{\cancel{S}}$

$\boxed{\gamma(\theta) = \gamma_T\cos\theta + \gamma_L\sin\theta}$

So, we can see that the origin of gamma is attribute to the broken bounds. So, if you see the surface we can see that this roughness in the surface can be described by terraces or the ledges. So we have this terraces which are like a step structure and there is some vertical broken bonds which are the ledges in a system.

So, we can see the total length of the ledges is given by, the total length. So, this is A 1 plus A 2 plus A 3. So, we can see that the ledge or the terraces. So, terraces can be given t 1 plus t 2 plus t 3, because the total number. So, we can say to t and then we have total area of terraces and then area of ledges can be given by ledge L ledge 2 ledge 3. So, L 1 plus L 2 plus L 3 and so on.

So, we can see that total length of this is around A L and seeing the similarity we can see that cosine theta if we consider it like this. So, we can see that cosine theta is equal to b y h that is the base by hypotenuse. That means it is A t divided by total length that which is S sine theta is equal to perpendicular distance that is A L divided by S.

So, we can see that the time theta can be given as e y b that is A L divided by A t. So, the total the total gamma theta or the origin of gamma is arising, because of the total energy divided by area surface tension is given by area is equal to area. That is equal to now gamma t A t plus gamma L A L divided by the total length. So, in similarity we can see that gamma A t is A t can be given as S cosine theta. So, what we can see here is gamma t S cosine theta plus gamma L A L, is given as S sine theta.

We can see to out here that A t is equal to S cosine theta and A L is equal to S sine theta. So in this term we can see divided by S. So, we can cancel out S from here and now we can see that gamma theta the total gamma which is given by gamma of the terraces multiplied by cosine theta plus gamma L multiplied by sine theta. Now, we can see the overall origin of gamma is arising, because of the broken bonds.

As we can see the broken bonds are given by the total length along this side, this side. The whole contribution which is arising from this broken bonds is now being captures by this surface tension or surface energy for this particular case. So, in this case we can see that the overall surface energy is dependent on the surface energy of the terraces and the links or the ledges, which are basically being present in the material, because of broken bonds. So, as soon as we are starting to break the bonds we can see the change in the surface energy.

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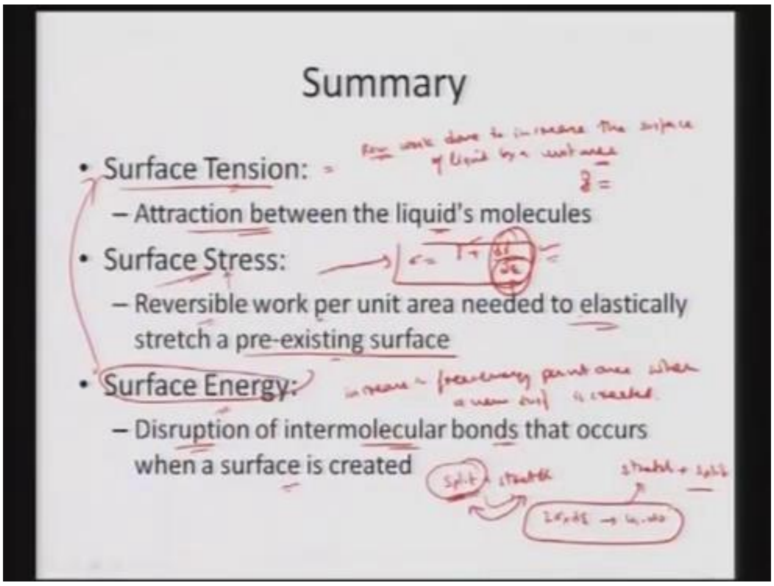

Summary

- Surface Tension:
  - Attraction between the liquid's molecules
- Surface Stress:
  - Reversible work per unit area needed to elastically stretch a pre-existing surface
- Surface Energy:
  - Disruption of intermolecular bonds that occurs when a surface is created

So, in summary we can basically say that the surface tension which is given by reversible work, which is done to increase the surface of liquid by a unit area. That creates the attraction between the liquids molecules. So, surface tension is being given as the reversible work, which is done to increase the surface of liquid by unit area. So, we need to do some work of that of reversible work area, which is done by the surface to increase the surface of a liquid by a unit.

Whereas surface stresses are the reversible work per unit area, you need to elastically stretch a pre-existing surface. Surface stresses are doing some work to elastically stretch already existing surface and surface energy is given by increase in surface energy, when we are increase in when we are we are creating a new surface.

So, increase in the increase in free energy per unit area when a new surface is being created. So, that causes a disruption of inter molecular bonds when a surface is being created. So, in summary we can see that the surface tension it is nothing but a reversible work to increase the surface of a liquid by a unit area. So, once you are increasing the surface by unit area, then we see some additional work of some work which is required to be done by that for increasing the surface area.

That is nothing but the surface tension. When surface tension starts depending on the straining of the material then it becomes essential to denote that by surface stresses. So, we can see the surface tension is equal to surface energy for liquids, but in solids what is happening. The stretching is basically being dependent on the overall surface tension is dependent on the orientation of that. That results the difference in the strain which arises in the different orientation.

So, once we take a plain of 1 0 0, 1 1 1, 1 1 0. So, depending on the orientation on the atoms out there the stretching will be very different and the surface energy of those will be very different. So, what is happening is we define them we define the solids where a term called surface stresses and that surface stress equals surface tension plus change in the surface tension due to with respect to change in the straining of the material.

So, we can say that surface stress equal to gamma plus d gamma by d epsilon and that is nothing but the surface stress. Surface tension is basically equivalent to surface energy, when we talk about liquids, but because in liquids d gamma by d epsilon term is totally absent. So, that we can see that the reversible work per unit area is you need to elastically stretch it to the existing surface.

So, we are taking the pre-existing surface and we are trying to elastically stretch it that gives rise to the surface stresses. Whereas surface energy, surface tension they are equivalent for liquids, whereas in case of solids it is a creating of new surface is being dictated by also change in the surface tension with respect to the strain that is being generated out there.

So, in this case we can see that surface energy or surface stresses are nothing but surface tension plus change in the surface tension with respect to the strain change in the strain that results the overall surface stresses. So, that is the difference between surface tension surface stresses and the surface energy. As we also see that we can evolve the surface stresses via splitting and then stretching and then first stretching and then splitting.

So, once we are splitting it, now we are creating two surfaces and then we are stretching it. So, that is that means that we now we are letting surface stresses to act on it, because once we split we now have one additional surface or two additional surfaces which are which have been generated. Whereas in stretching and splitting we take only the deformed surface and then we are splitting it.

So, we can see that we can allow surfaces to do additional work in reaching the final entity. So, from that we can always evolve what sort of stresses are being generated and how they can evolve in terms of adding a new term that is called d gamma by d epsilon to achieve the final thing.

So, then that is now being collided to the work which is being done. So, we can relate 2 sigma x d epsilon with respect to the w 1 minus w naught. That rebel results the overall dependence of surface stresses with respect to surface tension. With this we can see the complication that are arising. So, in simplicity surface tension is the reversible work which is done to increase the surface of a liquid by a unit area.

So, surface tension is that is directly related to the liquids. Surface stresses are the reversible work, which are needed to elastically deform or stretch a pre-existing surface. Whereas surface energy is the increase in the free energy per unit area, when a new surface is being created. So, that basically distinguish the three categories of surface tension surface stresses and surface energy.

Surface energy is a very generic term and that needs to be used for both surface tension as well as surface stresses. Whereas surface stresses is only limited to liquids surface stresses more for the solids. So, that is how we can see that how these three terms are very essential. Depending on them we can again tailor them for certain processing requirements or also determining the biological or electrical or mechanical properties based on these features. So, with this I end my lecture.

Thank you.