Introduction to Soft Matter
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Lecture No 12
Interatomic Bonds

So, welcome everybody, welcome back to one more lecture on introduction to Soft Matter. So, last time we were discussing bonds, and atomic, the scale of the atom itself. And once we have that atoms then they actually bond together to form larger objects which we call molecules. And with, when it comes to atomic bonds, we have, we discussed that there are three primary type of bonds.

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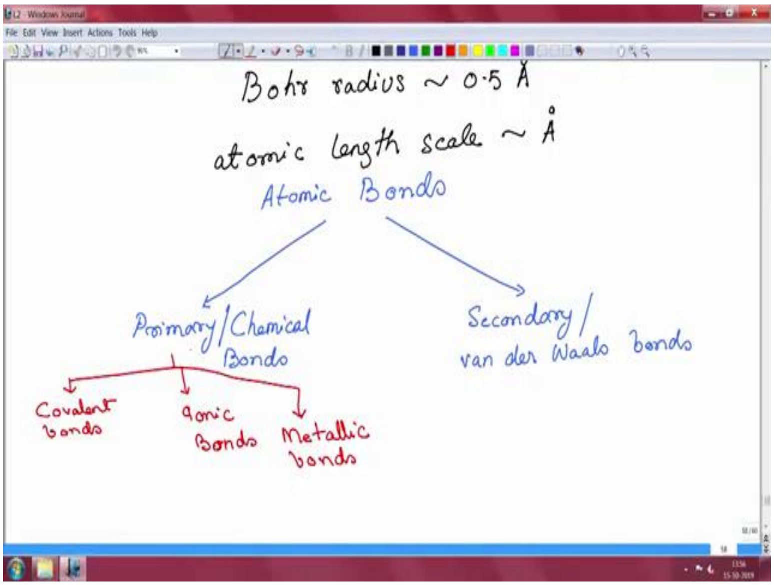

One would be the Covalent bond and then the Ionic bonds and the Metallic bonds.

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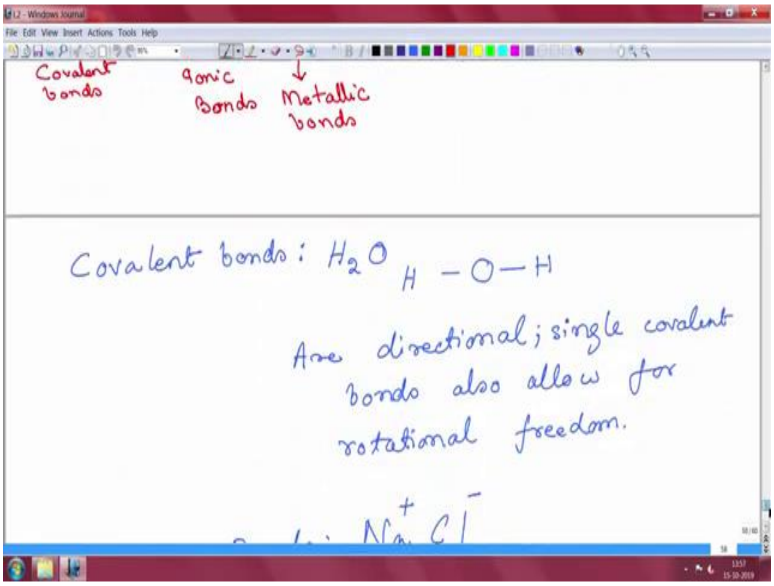

Covalent bonds

Ionic Bonds

Metallic bonds

Covalent bonds : H_2O $H - O - H$

Are directional; single covalent bonds also allow for rotational freedom.

$Na^+ Cl^-$

For the covalent bond, we discussed that they are the highly directional. They also allow for rotational freedom specifically, especially when they are single bonds, double bonds have less, have a stronger restriction on the rotation etc. For Ionic bonds you have an example for example salt and they are held together by electrostatic forces.

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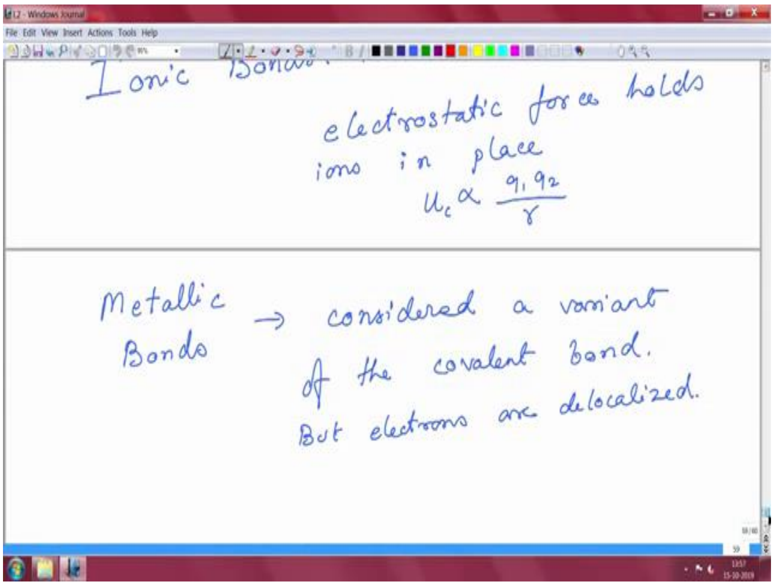

Ionic Bonds:

electrostatic forces holds ions in place

$U_c \propto \frac{q_1 q_2}{r}$

Metallic Bonds → considered a variant of the covalent bond. But electrons are delocalized.

And then finally, we also discussed that we have the Metallic bonds which are considered a variant of the covalent bond, but here the electrons are delocalized in a lattice.

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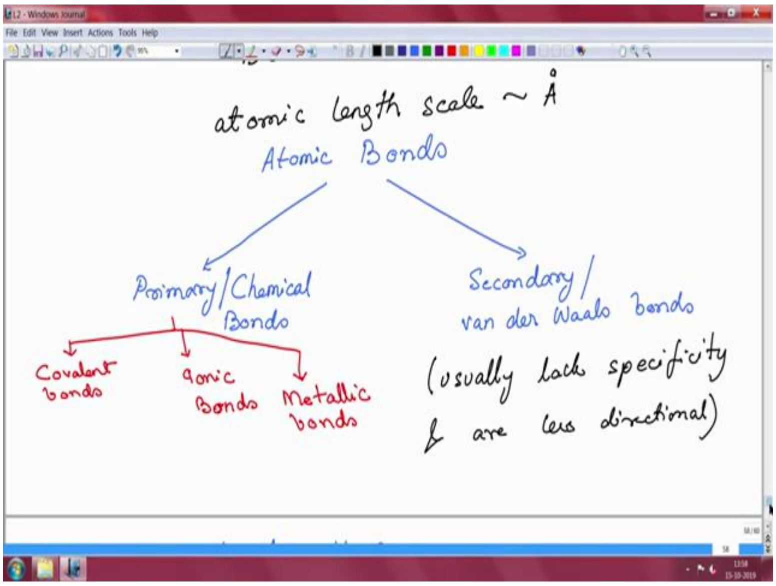

atomic length scale ~ Å

Atomic Bonds

Primary/Chemical Bonds

Secondary/ van der Waals bonds

Covalent bonds

Ionic Bonds

Metallic bonds

(usually lack specificity & are less directional)

So, the part that we did not discuss was the aspect of the secondary bonds okay. So, these are the Van der Waals bonds. So, in comparison to, to the primary bonds, they are usually they lack specificity, okay. So, they usually lack, specificity and obviously are going to be less directional and are less directional. So, but what are these bonds?

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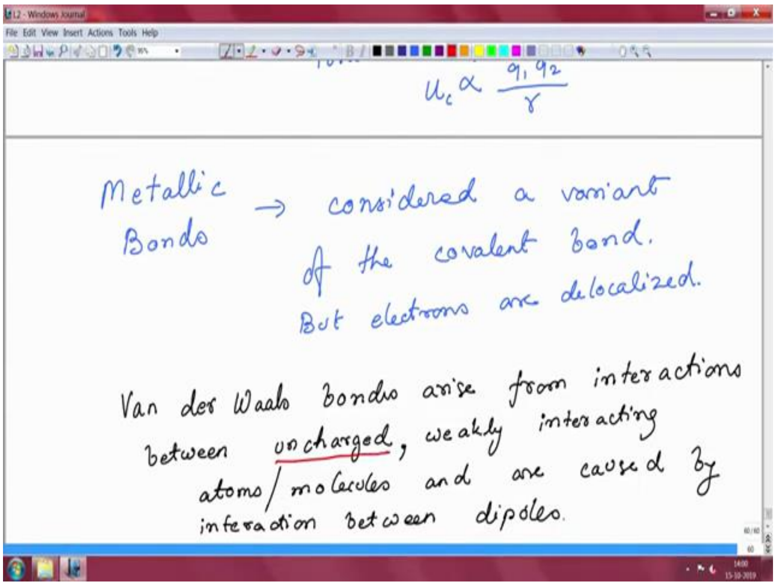

$U_c \propto \frac{q_1 q_2}{r}$

Metallic Bonds → considered a variant of the covalent bond. But electrons are delocalized.

Van der Waals bonds arise from interactions between uncharged, weakly interacting atoms/molecules and are caused by interaction between dipoles.

So, what are Van der Waals bonds? Now, Van der Waals bonds arise from interaction. So, bonds they arise, arise from interactions between uncharged. So, overall, the two entities should not have charges, uncharged weakly interacting molecules or atoms and they use and they are caused by attractive forces or interaction forces between dipoles, okay they are caused by interaction between dipoles. So, that is why we specifically said uncharged because they actually arise due to dipolar interaction.

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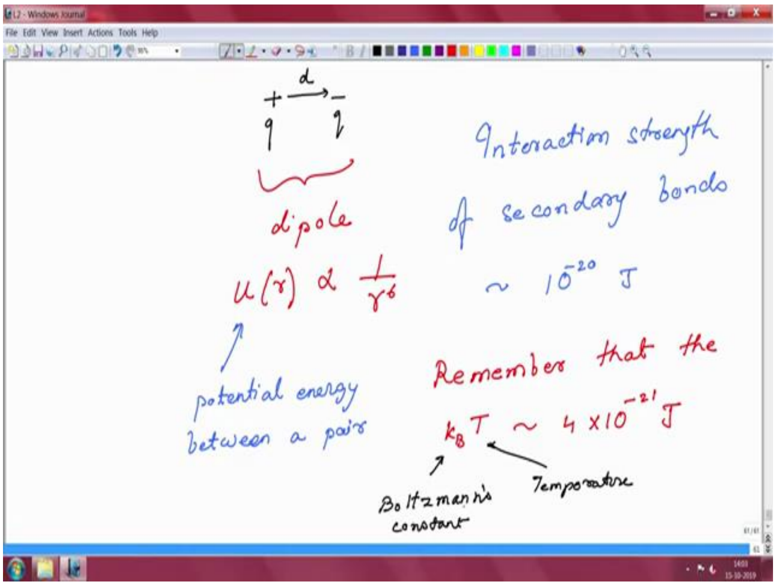

$u(r) \propto \frac{1}{r^6}$

Interaction strength of secondary bonds $\sim 10^{-20}$ J

Remember that the $k_B T \sim 4 \times 10^{-21}$ J

And if you remember from your perhaps undergraduate or high school level physics that a dipole is created when you have two charges which are separated from each other and by a certain distance d and this entity is called a dipole. So, molecules and atoms they have their own dipoles sometimes, sometimes the dipoles can be induced by each other. And sometimes the electron clouds themselves are fluctuating in nature. So, there are temporary dipoles in the system. So, those altogether give rise to the Van der Waals forces.

And here the interaction potential energy is usually so the interaction potential energy, usually scale as 1 by r to the power 6, okay. So, I will just quickly write this what this is, this is interatomic potential, potential energy between a pair. And interaction strength, just write it on the side, interaction strength of secondary bonds is usually of the order of 10 to the power minus 20 joules.

Now, just remember that the KBT energy, so, when we are talking about molecules and atoms, the energy scale that we should consider is the KBT energy where KB, this is your Boltzmann constant and this is your absolute, this is your temperature in Kelvin scale. This energy is usually of the order of the order of 4 into 10 to the power minus 21 joules. So, we see that the Van der Waals forces adjust slightly more energetic than the KBT energy okay.

And even this small increase over the KBT energy is enough to cause Van der Waals forces to bring together many different entities together into, into a structure.

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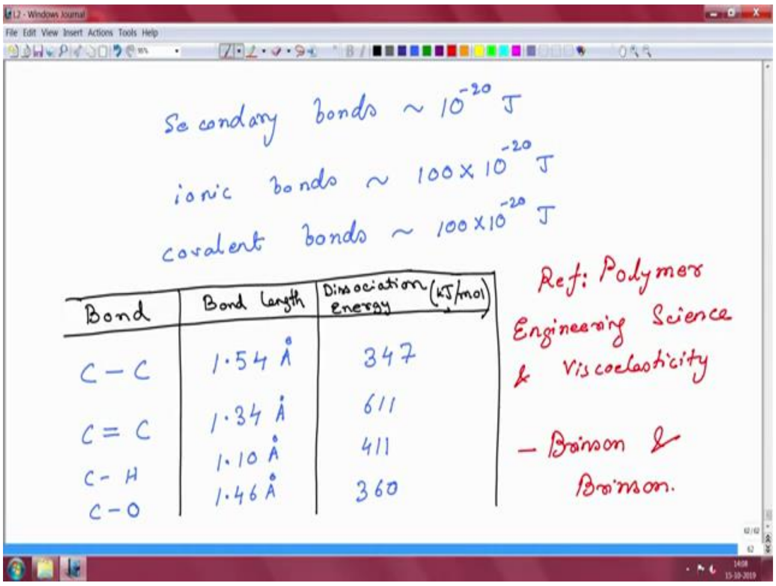

Secondary bonds ~ 10^{-20} J

ionic bonds ~ 100×10^{-20} J

covalent bonds ~ 100×10^{-20} J

Bond	Bond Length	Dissociation energy (kJ/mol)
C − C	1.54 Å	347
C = C	1.34 Å	611
C − H	1.10 Å	411
C − O	1.46 Å	360

Ref: Polymer Engineering Science & Viscoelasticity
— Brinson & Brinson.

Now, since we are discussing the various energies, so I will just maybe write down again, secondary bonds are of the order of 10 to the power minus 20 joules. Ionic bonds, on the other hand, have a much larger energy, and usually 100 times higher than the secondary bonds and the covalent bonds also have energies of the order of 100 minus 20 joules sometimes less, sometimes more so, but is of the order of it. So, we are not worried about the exact value here. So, this symbol means approximately or of the order of here.

And so, these are the various primary ways in which and the metallic bonds by the way, they are more or less of the order of the covalent bonds itself. So, the atoms are going to be held together by some of these forces. So, we should, so, the atom is itself when we discuss with the bore radius itself is of the order of 0.5 Angstroms. So, what is going to be let us say you put two atoms close by to each other, then they are held together by two, by a bond. So, what is the distance or the equilibrium distance between the two, okay? So, that would that is usually called a bond length.

So, when you have covalent bonds, and I am going to use a source to get these values. So, let us say the type of bond and this is the bond length and the dissociation energy and this is in kilojoules per mole. So, so for example, if you have the carbon carbon single bond, this bond length is usually around 1.54 Angstroms and the dissociation energy is 347 kilojoules per mole.

For a carbon carbon double bond, they are actually the, the distance between the two atoms decreases and now this is 1.34 Angstroms and here the value is 611 kilojoules per mole once again for a carbon hydrogen bond you have the bond length being 1.10 Angstroms and this value is 411 and for a carbon oxygen, carbon oxygen bond, single bond this is 1.46 Angstroms and this value is 360.

Now, these values I have seen in some sources that differ, the dissociation energy in particular this is slightly differ from these values. So, I will give you the reference from which I have sourced these. So, these are sourced from the book called “Polymer Engineering Science and Viscoelasticity by Brinson and Brinson”.

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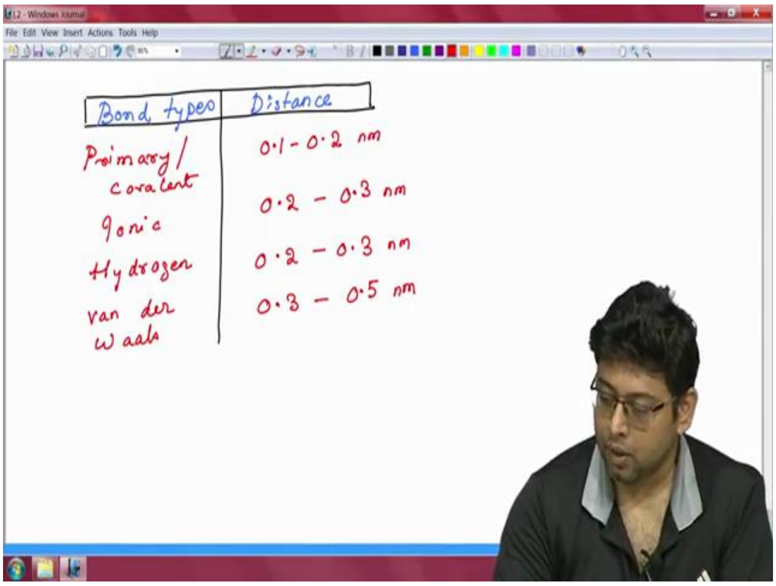

Bond types	Distance
Primary/ covalent	0.1 - 0.2 nm
Ionic	0.2 - 0.3 nm
Hydrogen	0.2 - 0.3 nm
van der Waals	0.3 - 0.5 nm

Now, since we are discussing these distances from the same source, I have put together the values for the Bond types. So, the Bond types and the distance this is approximate distance in these cases. So, for primary or covalent bonds, the distance between the typical distance between the atoms or the typical separation is somewhere between 0.1 to 0.2 nanometers. For Ionic bonds the distances can be slightly higher 0.2 to 0.3 nanometers.

For hydrogen bonds, the distances are larger or of the order of the Ionic bonds sometimes, and finally the Van der Waals bonds these are the rest of those Van der Waals bonds, the distances are usually in this disorder. So, we can see that for Van der Waals forces they act over slightly larger distances as compared to the covalent and that is the basic idea that we are trying to give here.

So, when atoms come together to form a substance they have to be held together by certain forces. Otherwise, the very basic nature would be to fly away from each other. And then the question is what is that mechanism that is holding them together and in a given circumstance, it has to be a combination one of these or a combination of one of these different bonds, which holds all the atoms together into a structure.

Now, why are we discussing all this? Remember in the very beginning where we discuss the definition of Soft Matter we said one of the definitions of Soft Matter was slightly intuitive and we said that a soft material is something that is in between a viscous fluid and that have a crystalline solid. So, we want to understand how these bonds etc. play a role when it comes to soft materials themselves.

So, since we discussed or we contrasted our soft materials with respect to crystalline solids and fluids, maybe we should keep on the discussion a little bit more and see how the contrast really plays out at this atomic level.

Okay, so in an atomic level, when we come to a crystalline solid, the very name crystalline solid tells you probably that the atoms are in some kind of a crystal lattice, and that is a case with metals. Now, they can be in a crystal lattice in many different ways.

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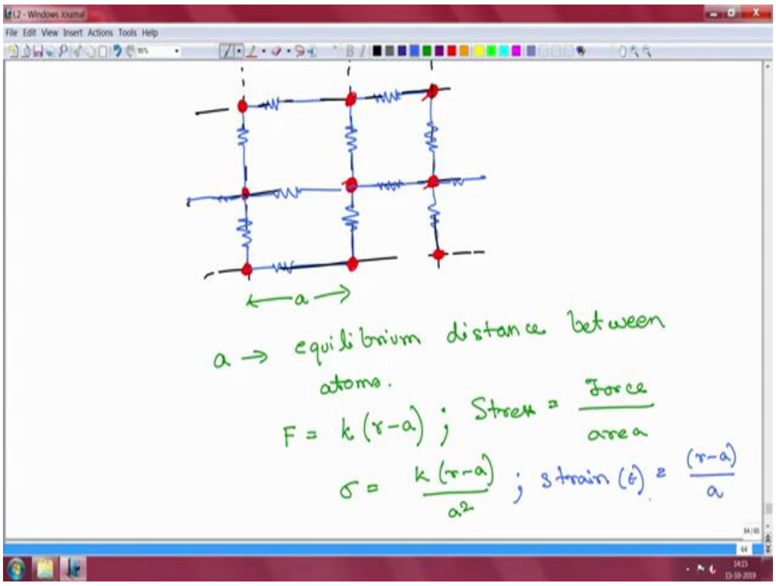

$a \rightarrow$ equilibrium distance between atoms.

$F = k(r-a)$; Stress $= \dfrac{\text{Force}}{\text{area}}$

$\sigma = \dfrac{k(r-a)}{a^2}$; strain $(\epsilon) = \dfrac{(r-a)}{a}$

But let us take a very simple, simple cubic lattice and say we have a, so if we draw a structure and let us say we are going to place some atoms at these places. So, these atoms are locked in a simple cubic lattice. Now, one can imagine that they are being held together very tightly and this behavior approximately resembles that of a spring. Okay, so I am not going to go ahead and complete it, but you get the idea.

So, let us say the distance between the atom is a, so the inter atomic distance here, we have a so, atoms are placed in a crystal lattice and the size of the lattice here is a. So, a is also the basically the equilibrium distance between the two, between the atoms. So, we will just write that so a is equilibrium distance between atoms. So, when you take, apply some force and you and you displace the atoms from this equilibrium distance to maybe a let us distance of r, there should be a restoring force on the atoms.

And that restoring force is, should be basically some spring constant times r minus a, where r is the displaced distance. So, and k is some kind of an effective spring constant here. So, now if we want to figure out how much is the stress or maybe I will just write it. So, to calculate stress, so, the stress is force times area I am just making some very simple calculations. So, force times area and here your area is given by a squared.

So, your stress term, it basically k r minus a like a square, but what is the corresponding strain? So, the strain here or epsilon let us say is some is r minus a by a. So, what is your so, so this is let us say this is some kind of tensile stress, and this is your tensile strength. So, what is your Young’s modulus in terms of?

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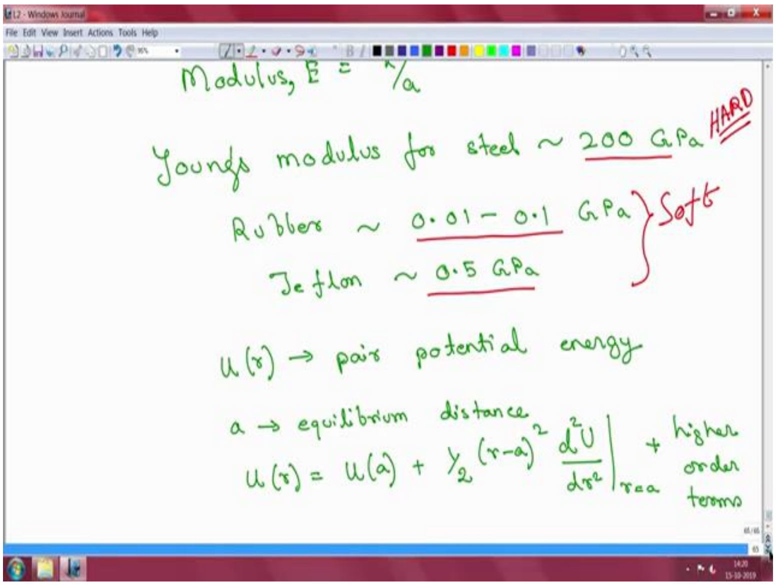

Modulus, $E = k/a$

Youngs modulus for steel ~ 200 GPa HARD

Rubber ~ 0.01 – 0.1 GPa

Teflon ~ 0.5 GPa

Soft

$U(r) \rightarrow$ pair potential energy

$a \rightarrow$ equilibrium distance

$$U(r) = U(a) + \frac{1}{2}(r-a)^2 \left.\frac{d^2U}{dr^2}\right|_{r=a} + \text{higher order terms}$$

So, the, so the modulus or let us say E is a stress versus the strain. So, if you do that here, you would end up with, so, sigma divided by Epsilon you would end up with k by a. So, this tells you that your, how your spring constant or this the springs that you have, this imaginary strings that you think are holding the atoms together.

If you wanted to assign an effect spring constant how you can do that, because modulus values are often known from experiments. So, if you know the interatomic separation you can also approximately calculate the spring constant.

Now, what is the young's modulus for steel? Sorry again and we are not interested in the exact values okay. So, young's modulus for steel is somewhere of the order of 2200 sorry 200 into 200 Giga Pascals, whereas for Rubber this value often comes out to be 0 somewhere around 0.1, 0.1, 0.01 to 0.1 Giga Pascals. For Teflon it can range in some 0.5 Giga Pascals okay.

So, the reason why I am, I am listing these is because I just want to highlight the difference in magnitude and the order of magnitude between these quantities. So, your steel is your traditional hard material. So, this is HARD, whereas these two are much softer than steel. So, a little bit loosely speaking I can say these are much softer materials. So, this also gives you an idea of when we said that Soft Matter is an intuitive name.

One way of looking at it is your traditional soft materials have moduli that are substantially lower than traditional hard materials and hard materials being something like metal ceramics. So, your Rubber and Teflon obviously, they qualify because their moduli are much much lower.

So, let us carry this on for a little bit longer this, this discussion. So, your atoms are actually separated and separated from each other and basically what is there is a potential energy associated with the an atomic pair.

So, let us call this pair potential energy as ur and your a is the equilibrium distance, as we discussed that before. So, when you take two atoms and you separate them from each other, slightly displace them from their equilibrium positions, then your u of r if I want to write it in terms of values of, at equilibrium, I could say that this is plus some higher order terms. So, the derivative does not exist, does not appear because a is the equilibrium distance. So, u has a minimum at r equal to a.

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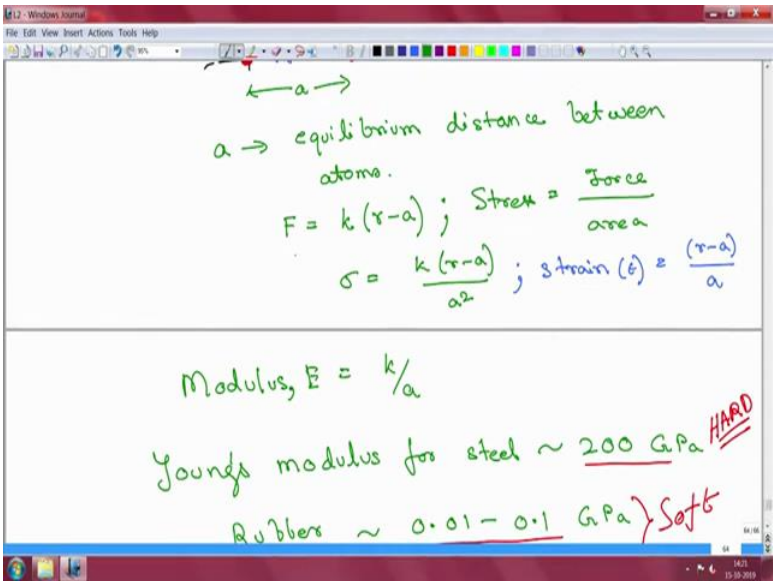

$\longleftarrow a \longrightarrow$

$a \rightarrow$ equilibrium distance between atoms.

$F = k(r-a)$; Stress $= \frac{\text{Force}}{\text{area}}$

$\sigma = \frac{k(r-a)}{a^2}$; strain $(\epsilon) = \frac{(r-a)}{a}$

Modulus, $E = k/a$

Youngs modulus for steel ~ 200 GPa HARD

Rubber ~ 0.01 – 0.1 GPa } Soft

So, now, if we had to compare our original formulation in which we had said that the force is equal to some this spring constant multiplied by r minus a, this gives the restorative force. So, this restorative force has to be related to the pair potential that we are discussing.

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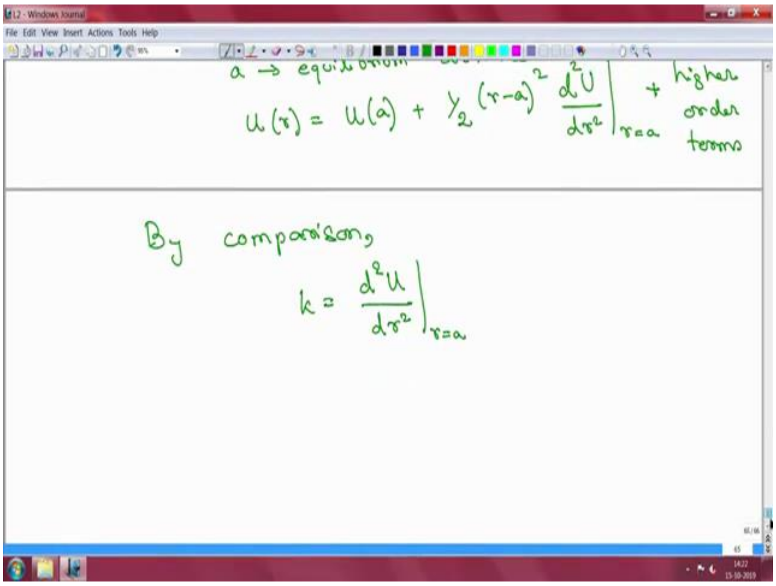

$a \rightarrow$ equilibrium

$U(r) = U(a) + \frac{1}{2}(r-a)^2 \left.\frac{d^2U}{dr^2}\right|_{r=a}$ + higher order terms

By comparison,

$$k = \left.\frac{d^2U}{dr^2}\right|_{r=a}$$

And if you compare the two, so by comparison you can say that k is equal to at r equal to a.

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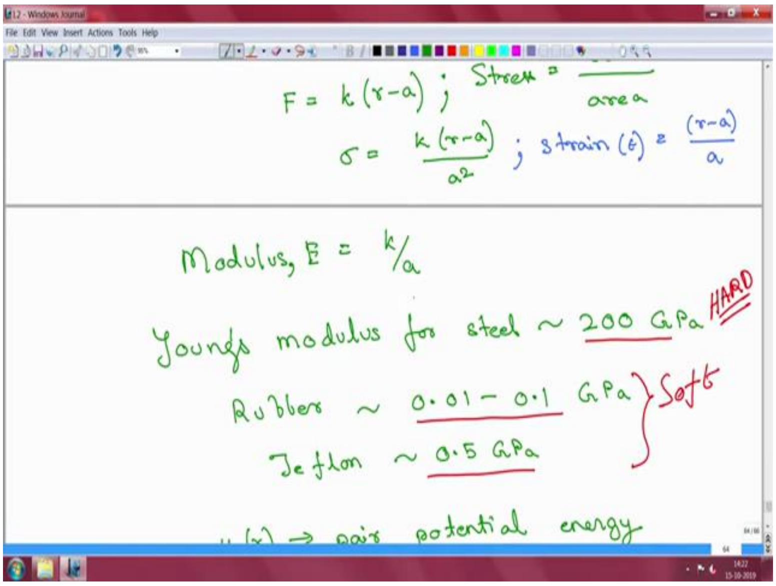

$F = k(r-a)$; Stress = $\frac{\quad}{\text{area}}$

$\sigma = \frac{k(r-a)}{a^2}$; strain (ϵ) = $\frac{(r-a)}{a}$

Modulus, $E = k/a$

Youngs modulus for steel ~ 200 GPa HARD

Rubber ~ 0.01 – 0.1 GPa

Teflon ~ 0.5 GPa

} Soft

$u(r) \rightarrow$ pair potential energy

So, now, what we want to do is, see where we are trying to go, we just got the Young’s modulus in terms of some spring constant. So, we are going to try and find out what we want to do is we want to find out this Young's modulus in terms of this pair potential energy.

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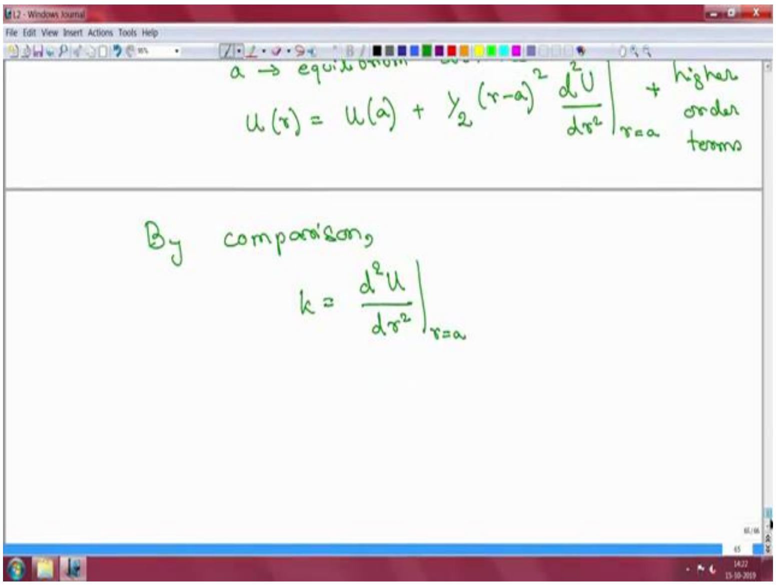

$a \rightarrow$ equilibrium

$u(r) = u(a) + \frac{1}{2}(r-a)^2 \left.\frac{d^2U}{dr^2}\right|_{r=a}$ + higher order terms

By comparison,

$k = \left.\frac{d^2u}{dr^2}\right|_{r=a}$

So, now, we know this relationship, but what is the functional form for u? You cannot calculate this derivative unless you know the functional form. So, let us make an assumption. So, let us say this ur is some kind of some u naught into f by r by a. So, this is I am non-dimensionalizing it. So, this is some dimensionless quantity, okay. And because you have at r equal to a, your u has a minimum value, some minimum value which is let us say minus u naught. So, this functional form is equal to minus 1.

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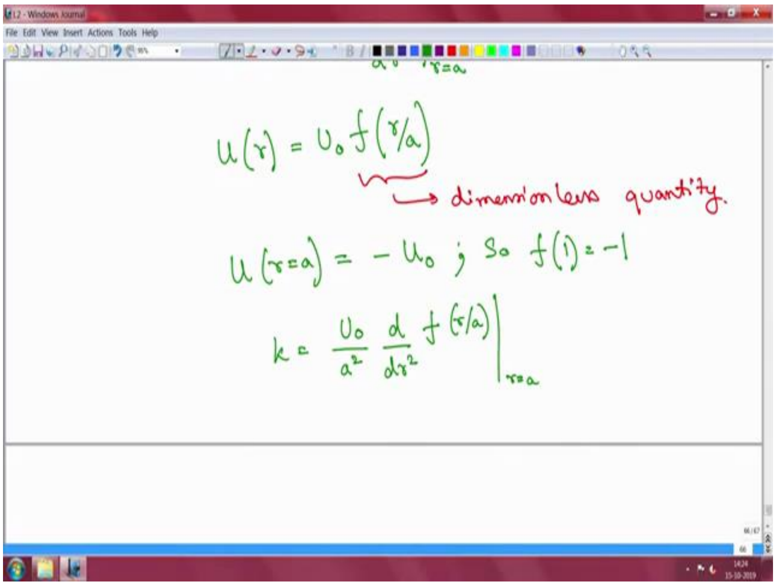

$$u(r) = U_0 f\left(\underbrace{r/a}\right) \longrightarrow \text{dimensionless quantity.}$$

$$u(r=a) = -U_0 \;;\; \text{So } f(1) = -1$$

$$k = \frac{U_0}{a^2}\frac{d}{dr^2} f(r/a)\Big|_{r=a}$$

So, so now if you take that particular form so u naught is representative of some kind of energy here right. So, we have, the u naught is the quantity where all the energy has gone in. So, if you evaluate now the derivative. So, this k now is basically is u naught if you evaluate k from that particular equation, what you will end up getting is k by a square by d r square f, evaluate this entire thing being evaluated at r equal to a. And we already know that (eps), the modulus is equal to k by a.

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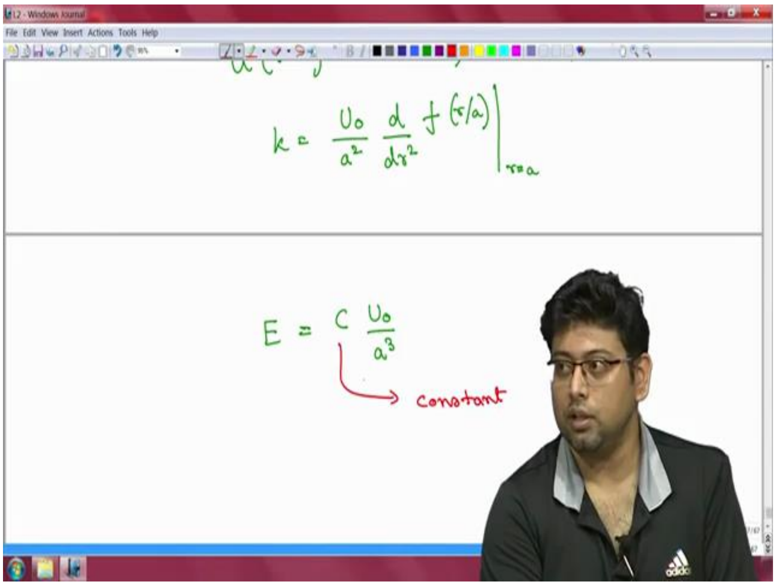

$$k = \frac{U_0}{a^2}\frac{d}{dr^2} f(r/a)\Big|_{r=a}$$

$$E = \underset{\downarrow\,\text{constant}}{C}\,\frac{U_0}{a^3}$$

So, if you put all of these together, what you end up with is you will find that E is some kind of a constant. So, this derivative let us say this is some constant and we bundle up all the constants into one then you will, you can very easily this is just one step algebra that I am skipping here. You can show that the modulus is some constant u naught by a cube, okay.

So, this is some constant. What this particular form shows us is that the modulus is basically a kind of energy density, right? That is u not by a cube. So, a cube represents is a volumetric term.

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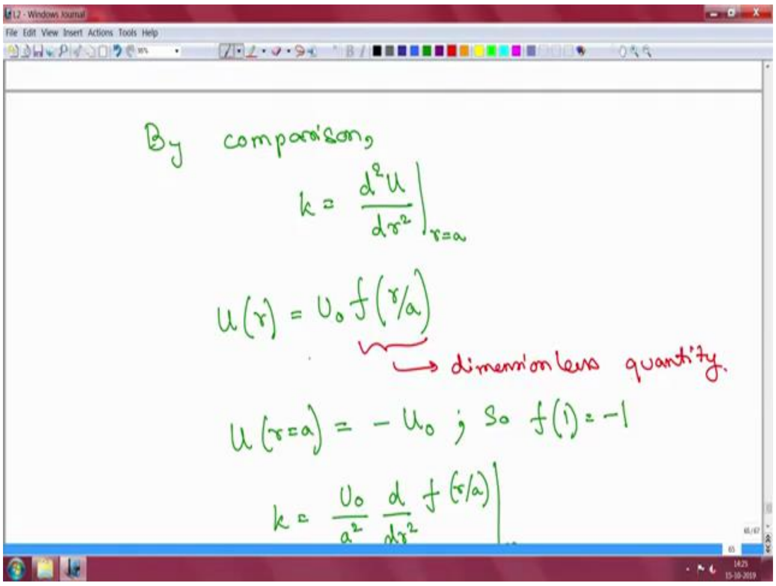

By comparison,

$$k = \left.\frac{d^2U}{dr^2}\right|_{r=a}$$

$$U(r) = U_0 \underbrace{f(r/a)}_{\text{dimensionless quantity.}}$$

$$U(r=a) = -U_0 \; ; \; \text{So } f(1) = -1$$

$$k = \frac{U_0}{a^2} \frac{d}{dr^2} f(r/a) \Big|$$

And u naught as we had already discussed before, it is a pair potential. And we had said that this is that f r by a, this is a dimensionless quantity. So, your u naught is the energy term, it has the dimensions of potential energy.

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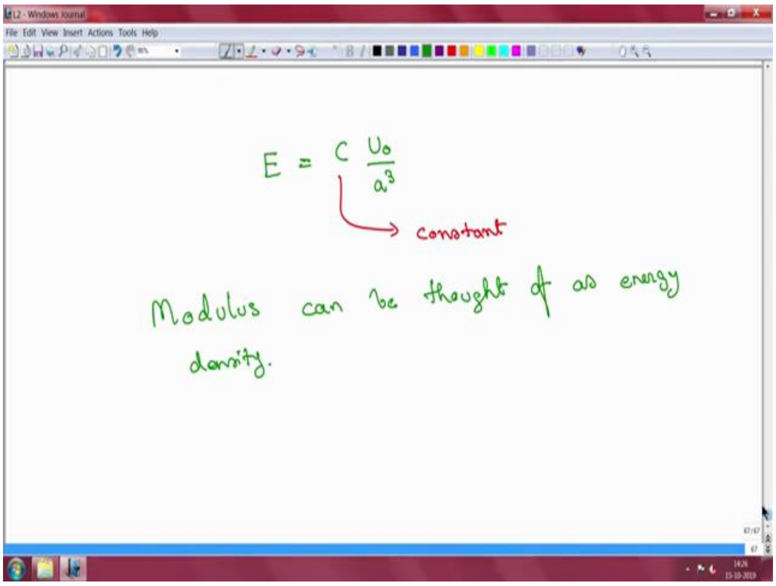

$$E = \underbrace{C}_{\text{constant}} \frac{U_0}{a^3}$$

Modulus can be thought of as energy density.

So the modulus some constant potential energy by some kind of a volume. So, basically, it is some kind of energy density. So, the modulus can be thought of as energy density, but what kind of energy? This is the energy that is getting stored. Because this atoms are being visualized as being held together by spring. So, the springs are storing energy and this is the energy density or the storage energy density that is there in the system.

So, today we will stop here and next last we will begin. We will start off from where we have left today. Okay, so we will stop here.