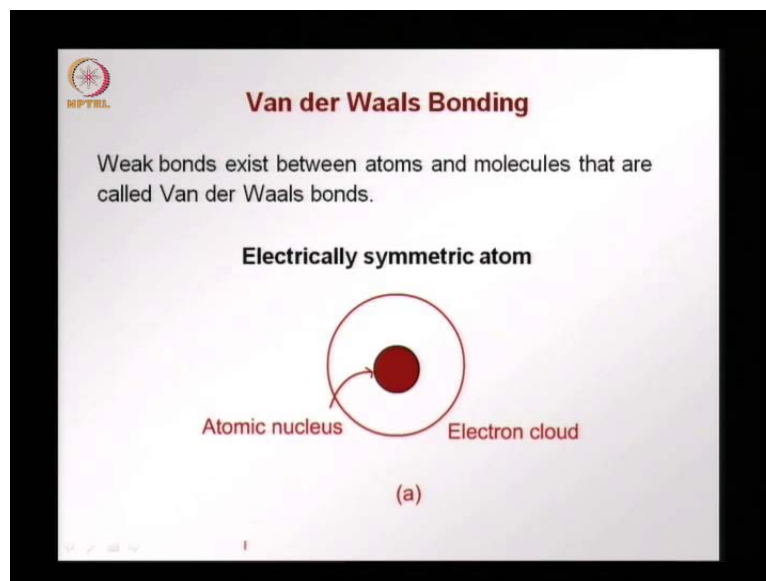


Modern Construction Materials
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Module - 2
Lecture - 2
Part 2 of 2
Review of Atomic Bonding– II

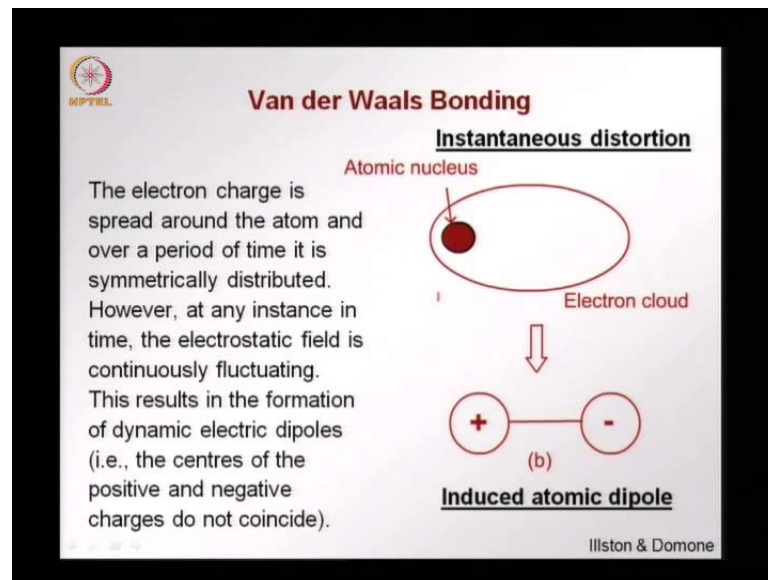
We will continue with review of atomic bonding. We have looks so far at strong bonds; we have discuss the ionic bond, the covalent bond, and the metallic bond. Now we will look at the weaker bonds, the Van der Waals bonds, and the hydrogen bonds and then we will go on to see how the type of bond affects the behavior of the element of the material.

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Now in Van der Waals bonds, we have a weak bond between atoms and molecules. We have to look at the electrical configuration of the atom to understand how the Van der Waals bond forms. Over a period of time, we find that the atom is electrically symmetric that is the centered of the positive charge and the centre of the negative charge coincide, the positive charge coming from the protons and the electron cloud giving the negative charge.

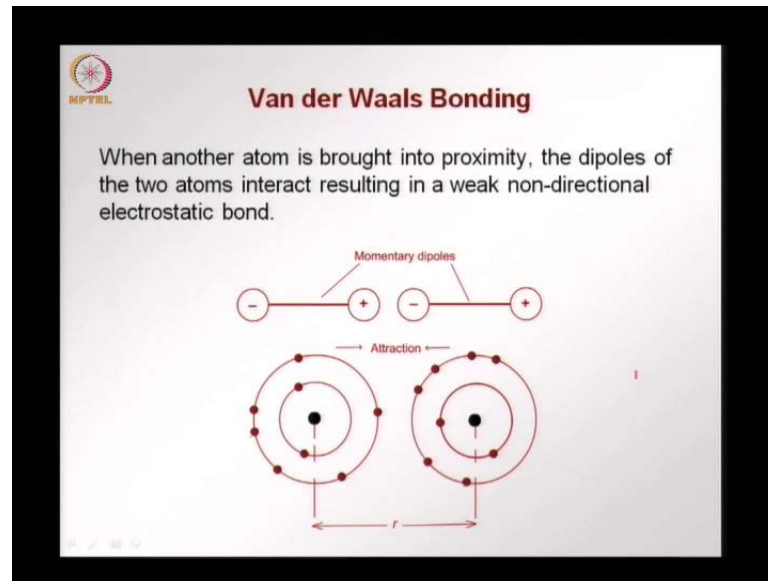
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At any instant in time, what we find these that there is distortion in this electrical configuration. We could imagine that at a particular instant, there are more electrons, there is a more of a negative charge on one side of the atom, and the positive charge is on the other side. So, the centre of the positive charge and the centre of the negative charge do not coincide at any particular instant of time, and this induces what we called an atomic dipole. Where the positive charge centre and the negative charge centre are separated by a certain distance, giving raise to this dipole. So, this we can imagine is occurring at any particular instant of time, this is changing continuously, and therefore, it is dynamic.

So, as I have said the electron charge spread around the atom is symmetrically distributed over a period of time. However, at any particular instant, at any instant in time, this electrostatic field is continuously moving fluctuating, and this gives raise to these dynamic electric dipoles; dipole meaning that the centers of the positive and negative charge do not coincide. So, we can see that now instead of the atom being always electrically neutral; at particular instant of time, we have a charge non-symmetric with a one end being more positive and the other end being more negative.

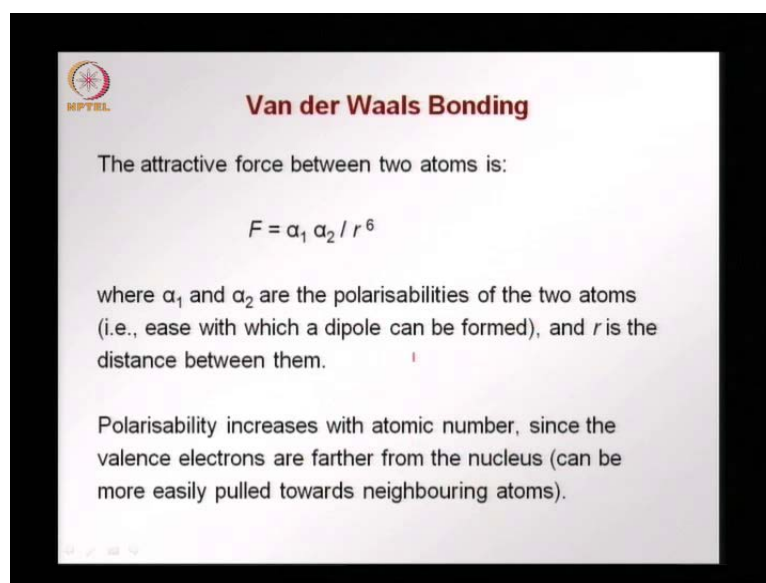
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When you have atoms interacting with each other, one atom coming close to another atom, we could have that dipoles interacting with attractive forces occurring between the atoms. When the negative charged end of one of the atom is attracted by the positive charge end of the other atom. So, as we said here when two atoms are brought into proximity; that means, when they come to close to each other that dipoles of the two atoms interact resulting in a weak non-directional electrostatic bond. This is a weak bond and this again depends on the distance r between two atoms that are interacting.

So, these were the dipoles that we saw being generated due to the instantaneous distortion of the electrostatic field. This gave raise to one end being more positive, the other end being negative. For example, here you see that they could be more electrons on this side, shifting the centre of the electrical charges to the left, the right side becomes more positively charged. In this case, you have the opposite happening, you have more of the electrons in the other side at a particular instance, and we have then the positive charge side being attracted to the negative charge side of this atom.

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Van der Waals Bonding

The attractive force between two atoms is:

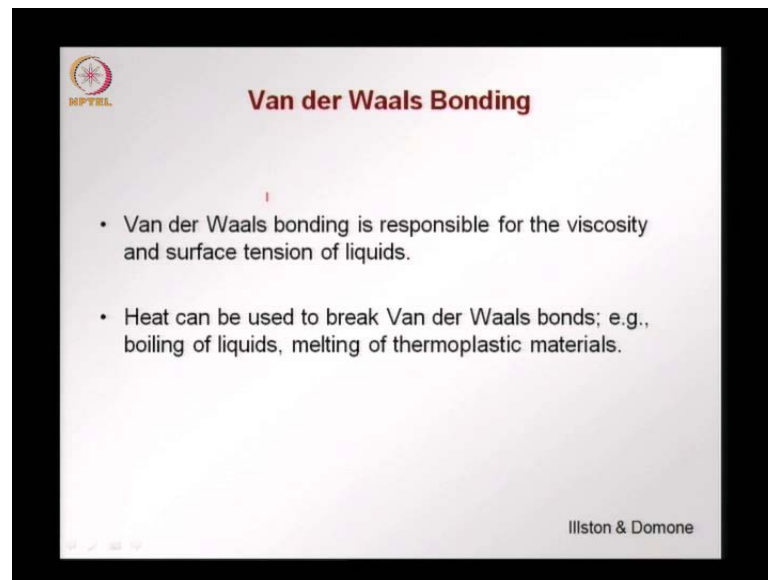
$$F = \alpha_1 \alpha_2 / r^6$$

where α_1 and α_2 are the polarisabilities of the two atoms (i.e., ease with which a dipole can be formed), and r is the distance between them.

Polarisability increases with atomic number, since the valence electrons are farther from the nucleus (can be more easily pulled towards neighbouring atoms).

The attractive forces between the two atoms due to Van der Waals bonds is given by this; as the product of alpha 1 and alpha 1 which are called the polarisabilities of the two atoms divided by r which is the distance between the two atoms raise to the power of 6. So, it is alpha 1 times alpha 2 divided by r to the power of 6. And what we find is that as the distance between the atoms increases, the attractive force decreases by a power of 6 that is why it is called very weak bond. Because even a small increase in the distance between the atoms, decreases the attractive force between the atom very significant. The polarisability that is the alpha values increases with atomic number, that is as the atomic number increases the valence electrons of farther away from the nucleus, you can imagine that atom is bigger. The valence electrons are farther away from the nucleus and so when they are moving around there is more distortion of the electrostatic field and they can be pulled more easily towards neighboring atoms also. So, this polarisability alpha increases with atomic number higher, the atomic number more would be the polarisability and therefore more would be the attractive forces between the two.

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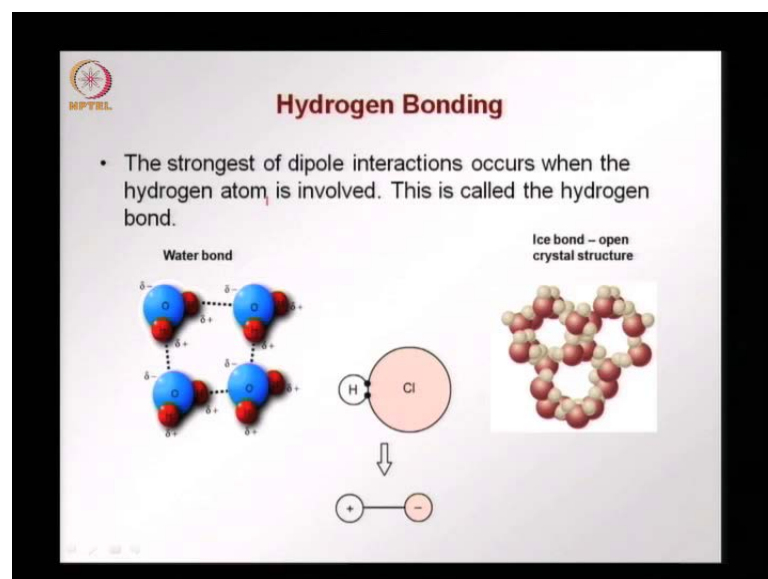
Van der Waals Bonding

- Van der Waals bonding is responsible for the viscosity and surface tension of liquids.
- Heat can be used to break Van der Waals bonds; e.g., boiling of liquids, melting of thermoplastic materials.

Illston & Domone

Van der Waals bonds since given though it is a weak bond is responsible for a lot of phenomena including viscosity and surface tension that we look at later. The heat is something which can break Van der Waals bonds easily which explains the boiling of liquids, how liquids become gases, the melting of the thermoplastic materials with a bonds, separating very easily due to the due to the heat energy. So, all this phenomenon can be explained look at Van der Waals bonds.

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Hydrogen Bonding

- The strongest of dipole interactions occurs when the hydrogen atom is involved. This is called the hydrogen bond.

Water bond

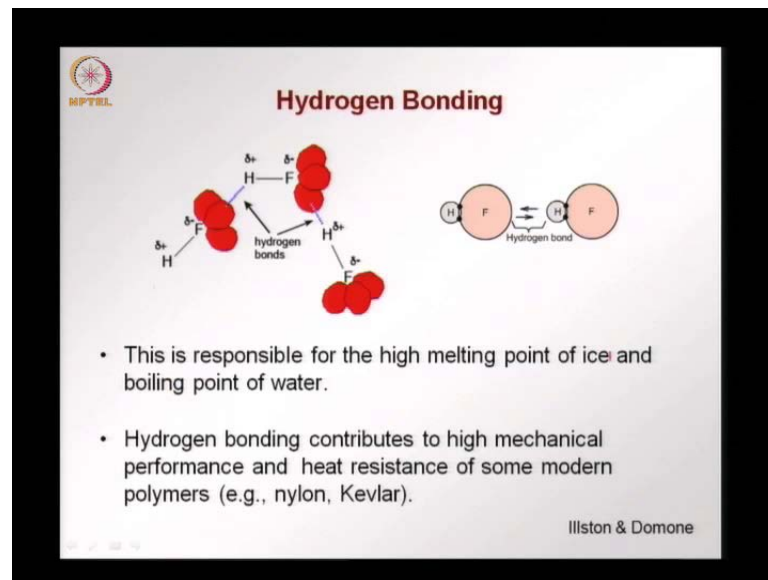
Ice bond – open crystal structure

H **Cl**

+ **-**


A specific type of Van der Waals bond that is stronger is the hydrogen bond, where we have a very strong dipole interaction when the hydrogen atom is involved. And this we can imagine because of the size of this small hydrogen atom, there is a big distance between the positive and the negative charge of this molecules coming about, because the hydrogen atoms is much smaller than all the other atoms. So, you have a dipole that is very easily form between the hydrogen an any other element. So, for example, here chlorine, where you have the positively charge end of the dipole coincide with the hydrogen atoms, and this due to the specific nature in which hydrogen bonds is directional, and this gives raise to specific structure. For example, in the bonding of the ice crystal, you see certain type of configuration with a lot of space in between.

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The hydrogen bond, since it is stronger than the other Van der Waals bonds is also responsible for giving the high melting point to ice, and high boiling point to water. The hydrogen bond also contributes to good mechanical performance, high mechanical performance and high heat resistance of some polymers with have hydrogen in that. For example, nylon and Kevlar which have higher mechanical properties, superior mechanical performance than other similar materials bonded just with Van der Waals forces.

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Atomic Bonding: Summary of bond types

Bond Type	Bond Energies (kJ . mol ⁻¹)	Typical Materials	Typical Elements	Remarks
Ionic	500-1200 ^a	Ceramic Oxides Gypsum Rock salt Calcite	Compounds of Gp I, Gp II	All exist as crystalline solids.
Covalent	150-750 ^{a,b}	Diamond Glasses Silicon carbide	Gp IV, Gp V, Gp VI	States of matter at room temperature depend on intermolecular attraction.
Metallic	50-850 ^a	Metals	Elements of Gp I-III, Transition metals. Heavy elements of Gp IV and V.	May be liquid or solid depending on binding energies.

Now let us look at the different bonds that we have considered. We looked at three strong bonds, the ionic bond, the covalent bond and the metallic bond. This column gives the bond energies, higher the bond energy, the stronger is the bond. And we see here the ionic bond as much higher value than the others - 500 to 1200 kilo joules per mole. And the covalent bond as a range that is the lower, and the metallic bond lowest. Typical materials that have these bonds; in the ionic bond we have a lot of salts which exist as crystalline solids. Covalent bonds we looked at examples of silica and diamond, there are other materials such as polymers, which have covalent bonds. Metals elements in groups I, II, III transition metals; heavy elements of group IV and V and so on also have metallic bonds.

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Atomic Bonding: Summary of bond types

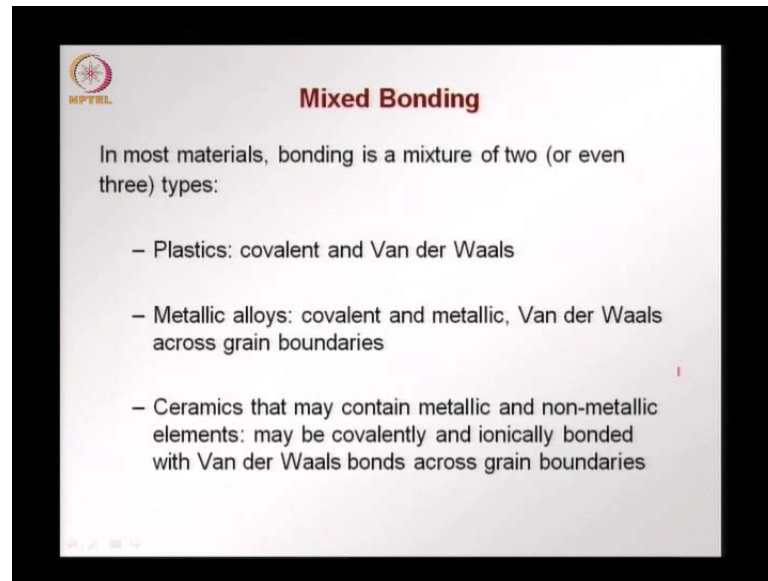
Bond Type	Bond Energies (kJ . mol ⁻¹)	Typical Materials	Typical Elements	Remarks
Hydrogen	10-30 ^c	Water	F, O, N	Can be considered weak ionic or strong van der Waals. Strongly influences material behaviour.
van der Waals	0.05-5	Thermoplastic polymers	Compounds of all elements	Primarily intermolecular bonds. Dominate the behavior and microstructure of construction materials, such as concrete and asphalt.

^a Lattice energies of crystal.
^b Isolated multiple covalent bonds (as formed in N₂, for example can be as strong as 950 kJ . mol⁻¹.
^c Single hydrogen bond is about 2 kJ . mol⁻¹.

Young et al.

The two weak bonds are the secondary bonds that we looked at where the hydrogen bond and the Van der Waals bonds and between the two hydrogen bond is stronger. As about 10 to 30 kilo joule per mole, and we have the Van der Waals bond which is slightly weaker. Water is a typical example of a material having hydrogen bond, and Van der Waals bonds are therein all materials wherever we have atoms and molecules coming together. So, these are primarily what we called intermolecular bonds, and they dominate the behavior even though they are weak bonds, they dominate the behavior and microstructure of many constructions materials including concrete and asphalt, where the microstructure is held together by these Van der Waals forces.

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The slide features a logo in the top left corner with the text 'MPTEL' below it. The title 'Mixed Bonding' is centered at the top in a bold, dark red font. The main text is in a standard black font, starting with an introductory sentence followed by a bulleted list of three material categories and their bonding characteristics.

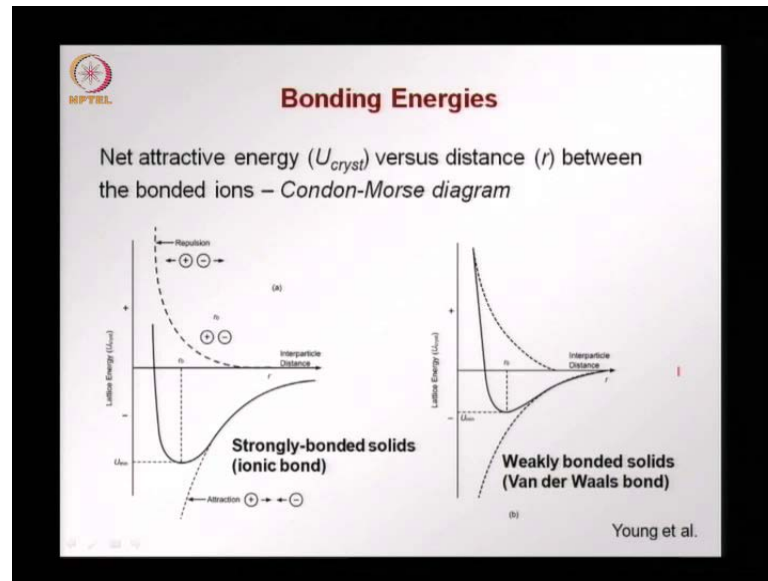
Mixed Bonding

In most materials, bonding is a mixture of two (or even three) types:

- Plastics: covalent and Van der Waals
- Metallic alloys: covalent and metallic, Van der Waals across grain boundaries
- Ceramics that may contain metallic and non-metallic elements: may be covalently and ionically bonded with Van der Waals bonds across grain boundaries

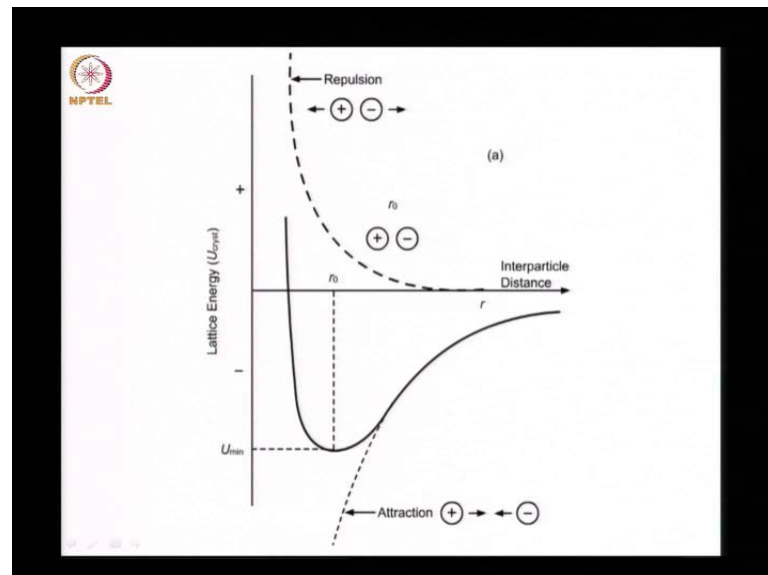
Now a material need not have just one type of bond in it. Most materials the bonding is a mixture of two or even three types of bonds. For example, in plastic, in polymers - we have covalent bonds within the chains and the chains are held together by Van der Waals bonds. In metallic alloys, we have both covalent and metallic bonds, and we have Van der Waals forces across the grain boundaries, across the different crystals forming the metal. In ceramics, we can have both metallic and non-metallic elements and these can be covalently and ionically bonded with again Van der Waals bonds across the grain boundaries. So, many of these bonds can coexist and do coexist in the material that we consider.

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Now let us look at how these bonds and the type of bond, and the relation between the potential energy and enter particle distance, how they do affect the properties or the behavior of the material. So, if you look at ionic bond as strongly bond it solid that you see in the left.

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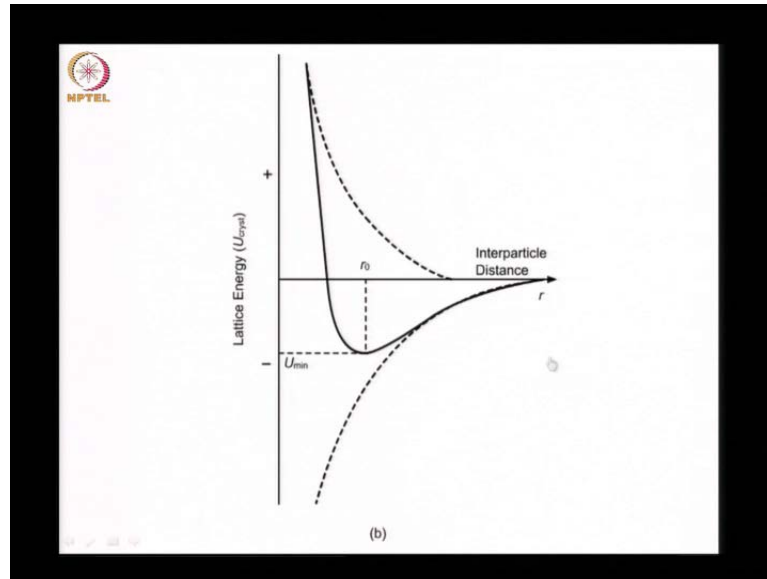
We have this diagram that we looked at initially, where we have on the y-axis the potential energy or the lattice energy in terms of a crystal; and on the x-axis, we have the inter-particle distance, inter-atomic distance or in the inter particle distance. And as we

said in the beginning of this lecture, when the atoms or particles come together, there is an attractive force, there is an energy that is attributed to the attractive force. This is pulling the atoms together, and these forces or these energy increases as the distance between the atoms decreases very far away there is a weak attractive force, and as we are coming together this attractive force increases.

Now there is also repulsive force, and this repulsive force becomes very high when the atoms are very close to each other. If you push the atoms together a lot, you have a very high repulsion occurring. And this over takes the attractive forces, when the distance become very small. What we see here in the dark line is the resultant between the attractive part and the repulsion part, and this dark line now gives the potential energy with respect to the inter atomic space, inter atomic distance are in a crystal the lattice energy and the inter particle distance. The inter particle distance mean r . And what we see now is a typical shape of this diagram, where you have as the inter particle distance decreases, the lattice energy decreases, reaches a minimum at a certain configuration defined by an inter particle distance r_0 .

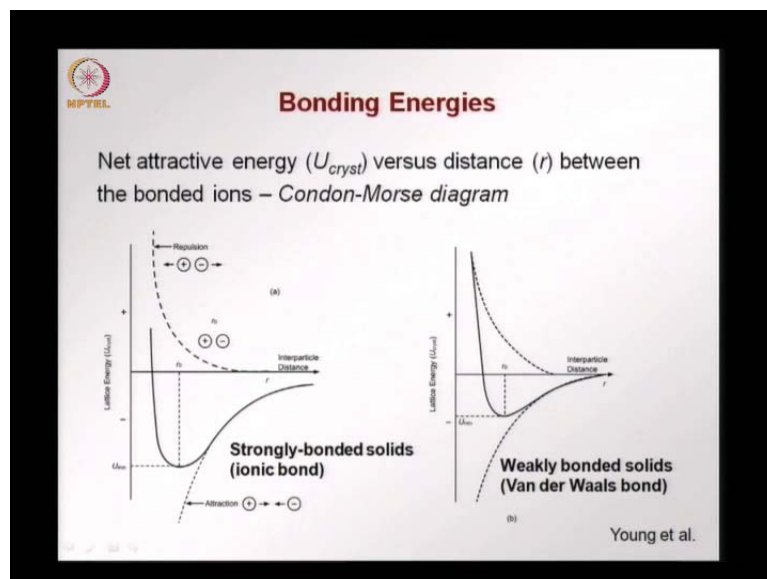
And then when the atoms or the particles are pushed closer to each other than this r_0 we find that now the repulsion becomes more and more, and if you go very close repulsion is much more than the attraction. So, for a strong bond, seen in ionic bond you will find that this part is lower that is the lowest energy that we see is more. So, this part which is called the well is deeper for a more strongly bonded material.

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We have also a similar diagram, but different values in the case of a weakly bond solid. We find that that diagram is similar, we have similar shape, but the value of this minimum lattice energy is less that is this well is less for shallower. What we find also that there is more asymmetry in the shape of this well in the case of a weak in the case of a strong bond we saw that it was deeper and came up like this.

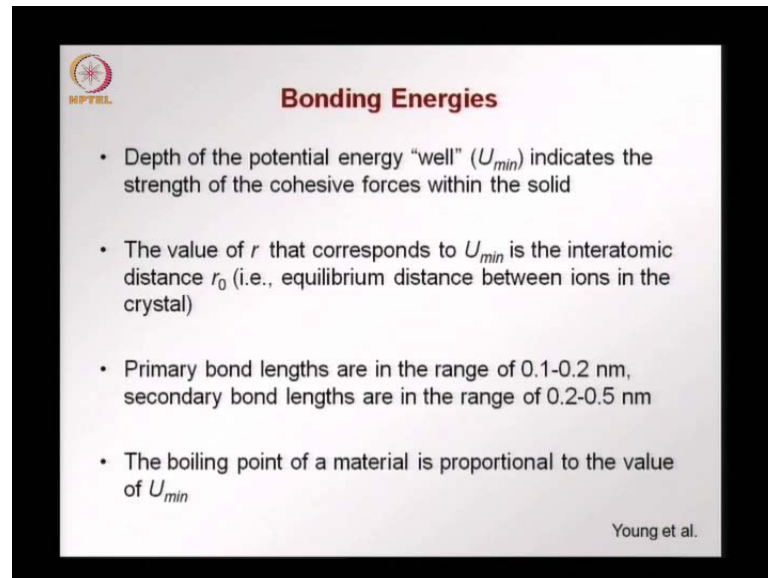
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In this case, we have a well, which is shallower and you have a more pronounced asymmetry around this part. Here you see that asymmetry is less than in a weak bond.

So, we see that there is a difference in how the energy particle distance occurs in a strong bond and a weak bond, and when we compare these two diagrams we start understanding other aspects that will deal with in a metal. This diagram is called the Condon-Morse diagram, and this gives us now the net attractive energy between different particles as a function of the distance between that.

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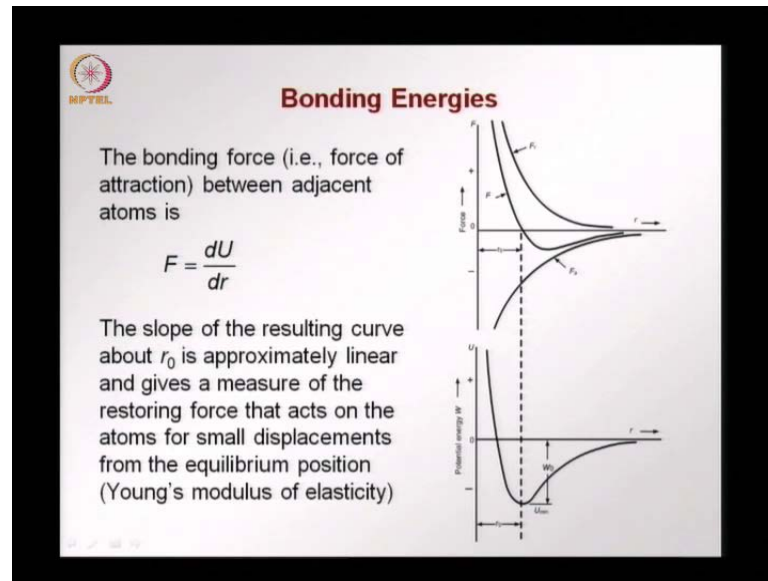


The slide is titled "Bonding Energies" and features a list of four bullet points. In the top left corner, there is a small logo with the text "NPTEL" below it. In the bottom right corner, the text "Young et al." is visible.

- Depth of the potential energy "well" (U_{min}) indicates the strength of the cohesive forces within the solid
- The value of r that corresponds to U_{min} is the interatomic distance r_0 (i.e., equilibrium distance between ions in the crystal)
- Primary bond lengths are in the range of 0.1-0.2 nm, secondary bond lengths are in the range of 0.2-0.5 nm
- The boiling point of a material is proportional to the value of U_{min}

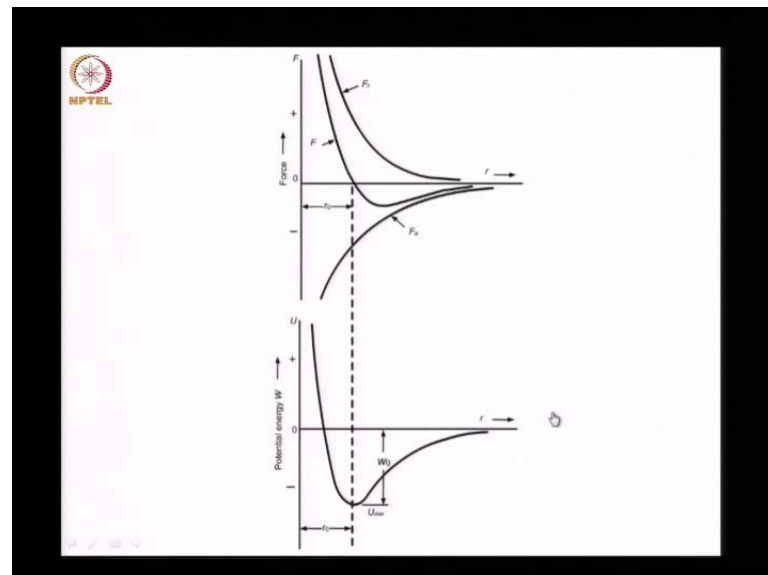
And as I said before that depth of the well indicates the strength of cohesive forces, the deeper the well are the higher or more is the minimum potential energy, we have a stronger bond. And the value of r which is the inter particle distance that corresponds to U_{min} is inter atomic distance r_0 where there is an equilibrium between the ions in the crystals, so that is the most stable state. These distances are not very large, they are sub nano metric, primary bond length that is the strong bond lengths are lower therein the order of 0.1 to 0.2 nano meters. The secondary bond lengths are slightly more 0.2 to 0.5 nanometers where still we are talking nano metric scale. These are very small distances that occur in the molecular level. Now in terms of the properties, we know that the boiling point of a material is proportional to the value of U_{min} that is as the well are the minimum energies more. The boiling point of a material is higher that is we need more energy to separate the bond when the bond is very strong.

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We also can look at the force displacement behavior, understand the force displacement behavior when we look at the Condon-Morse diagram. When we differentiate that diagram between the energy and the inter-atomic distance, we find that we get the force diagram.

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Here on the lower part of the screen, you see the Condon-Morse diagram giving us the potential energy versus the distance or the separation between the atoms. Now when we differentiate energy, we get the force. So, we get the diagram at the top which is giving

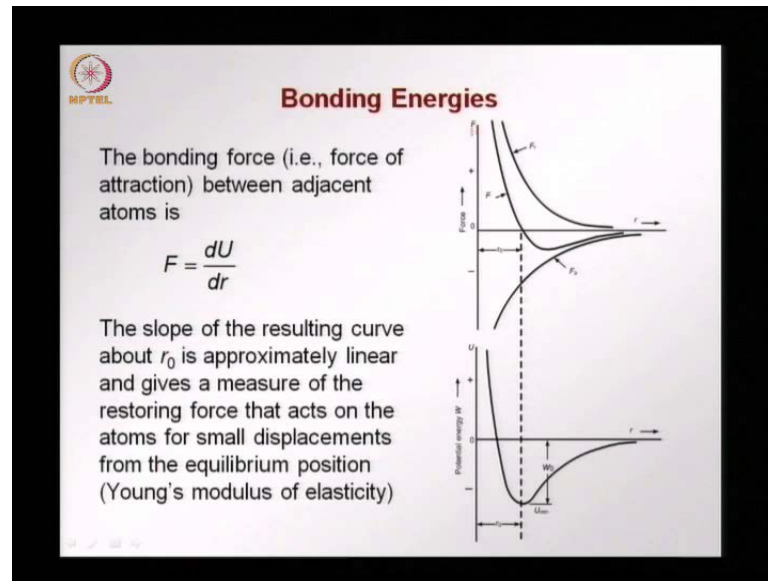
us the force between the two particles or the two atoms. Where here the curve labeled as F_a gives the attractive forces showing that as the inter particle separation decreases or the atoms comes closer together, there is a higher attractive force, this was what was giving us this bottom part of the potential energy. When the atoms are very close to each other or push the atoms together then we have the repulsive forces. The resultant of these two is given by this diagram.

So, here you find that at the point, where we had drop of the well, coincides with the zero force. We find that the diagram is symmetric about this point that is we have a similar behavior very close to the stable inter particle distance r_0 when we go either in compression or tension. So, if we are going to the left that means, we are compressing the solid at r_0 , the solid is at it stable state; when we are going to the right and increasing r beyond r_0 ; that means, we are pulling, separating or applying tension.

And if we remember that we can see some interesting this. When we pull on a solid or we try to separate the solid, we find that as the solid is stressed, they would be and linear part which would be the elastic part. Then there is a non-linear part, where you have nonlinearity then afterwards you need to reach a peak value which is giving us the tensile strength of the material. And then afterwards when we continue to stretch the bonds more when we continue to separate the bonds further, we find that the forces keeping the solid together decreases. And finally, becomes zero; that means, the material as completely broken or the bond is broken.

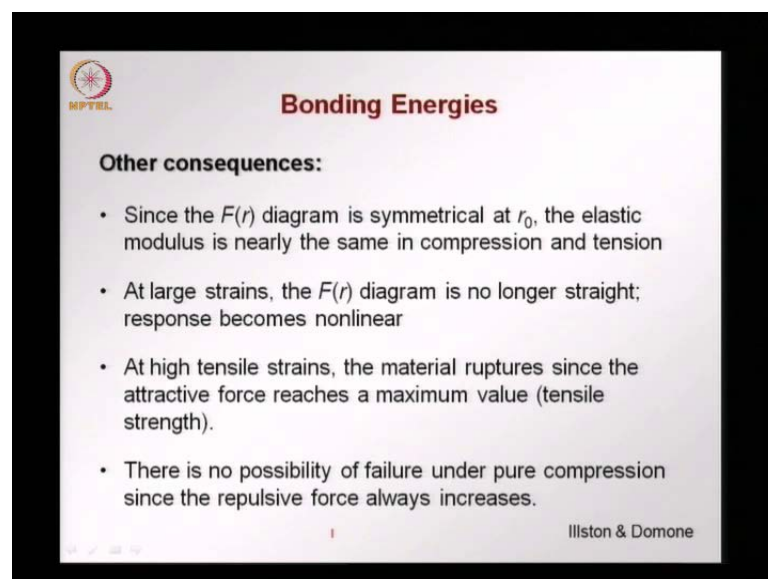
When we go to the other side, when we try to decrease the inter atomic spacing that is we are compressing or pushing the atoms together, we find that there is the repulsive part that is dominating, the repulsive part is dominating and we find also that the repulsive forces keep increasing as the push the material closer together. We also find from this diagram that failure can never occur in pure compression, because you are getting higher and higher repulsive forces. So, material will never break, when we have only compression acting on the material, because the repulsive forces become very very high.

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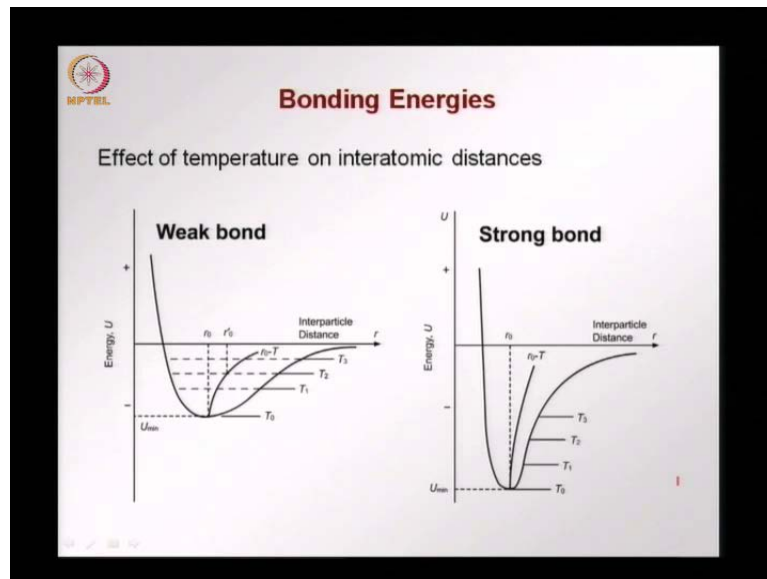
So, to summarize these diagram, the bonding force is can be given by the derivative of the energy by the distance or the separation between the atoms. The resulting curve - this curve about r_0 , we found that it is linear. This part gives the restoring force, that pulls the material back to its stable state. And this part being linear indicates why we have a elastic region, in most materials and also why we have young's modulus both in compression and tension which are equal.

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So, some of the consequences are that the $F(r)$ diagram that diagram of force with respect to the distance is symmetric at r_0 , about r_0 , and the elastic modulus is almost same in compression and tension. So, in most material, we assume that the young's modulus the same in compression and tension. And we can sort of explain this from the bond behavior in the particle level. At larger strain, we saw that the $F(r)$ diagram is no longer straight, it becomes non-linear; and also in most material that we use the always see a non-linear part in the mechanical behavior. As the tensile strain is higher, as we increase the distance between the particles, we pull on the material, the material reaches a point where it ruptures, it reaches a maximum value, which we can call the tensile strength. And beyond that the material does not have any forces holding it together and gives breaks upon. What we also saw is that under compression, the repulsive forces dominate and there is no possibility of failure under pure compression.

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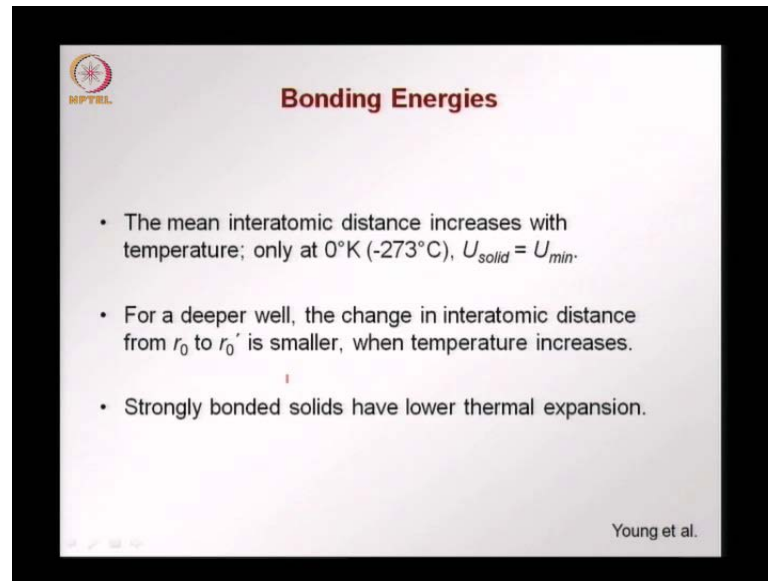
We can also draw some conclusions the effect of temperature on the behavior of the material by looking at Condon-Morse diagram. On the left, we have a weak bond and the right we have a strong bond. And if you look at this diagram, we see that above the minimum point for this graph. We find that there are many positions of r which will have the energy $-U$. At this point, there is a unique inter particle distance r_0 , where you minimum occurs of the minimum energy occurs, but at other values of energy we have different possible location, there is the same energy. So, this means that above this point which occurs only at absolute zero temperature; above this point at any other

temperature, there are many positions are many inter-particle separation which gives the same energy. So, this explains that there is an oscillation of movement of particles at any temperature above the absolute zero temperature, over a certain region.

So, T_1 the particles can be oscillating which separations over this distance; at T_2 , this distance is more, so they can be oscillation over a larger distance. At T_3 even larger distances you can have the inter particle separation moving above it. The average is this dark line, the average distances between the particles at each temperature is given by the dark line and what we find then is that these average distance for say a temperature T_2 will be r_0' , which is higher than r_0 . We find that the average distances at any temperature higher than T_0 will be always larger than r_0 , and this is the reason why we see expansion with temperature. What we are seen here is as the temperature is increasing, there is a larger oscillation and this average of these oscillation or the average of this separation always is higher than r_0 . The difference between r_0 and r_0' is the expansion the material undergoes at a certain temperature T_2 . And what we find that is in the weak bond as I mentioned earlier, there is a shallower well and you find that there is a bigger change in the inter particle separation then in a strong bond.

In a strong bond around this point there is not much asymmetric, around this point you see that the well is almost symmetric. And therefore, you draw the average between these distance, you find that initially it is very little and only a very high temperatures can cause a larger deviation of the inter particle distance from r_0 . So, for the same change in temperature, you have a smaller variation of the average inter-particle distance from r_0 . So, what we find is that in a strongly bonded material, the thermal expansion is less than in a weakly bonded material.

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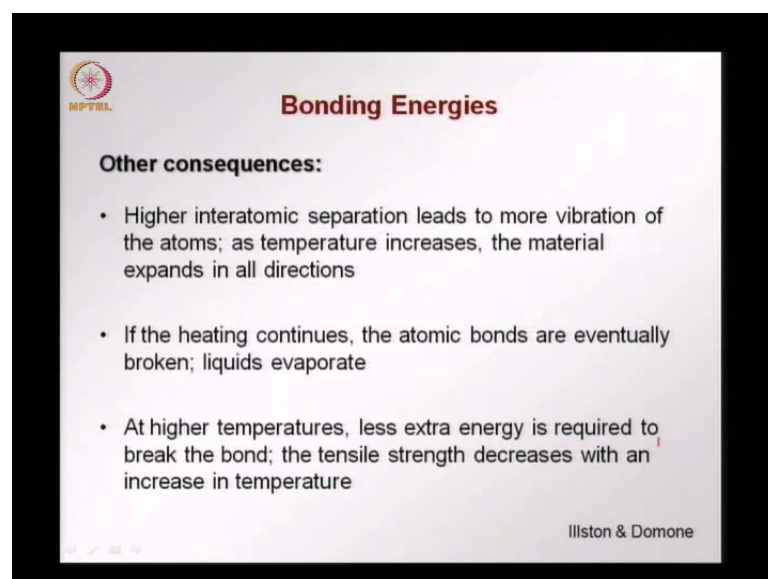
Bonding Energies

- The mean interatomic distance increases with temperature; only at 0°K (-273°C), $U_{solid} = U_{min}$.
- For a deeper well, the change in interatomic distance from r_0 to r_0' is smaller, when temperature increases.
- Strongly bonded solids have lower thermal expansion.

Young et al.

So, to summarize, the mean inter atomic distance increases with temperature only at 0 degrees Kelvin that is the absolute zero temperature, we have the potential energy of the solid equal to the minimum possible, where r_0 is the inter particle distance. At any other temperature, we find that the inter atomic distance changes keeps changing and the average r_0 is now higher for a weaker bond; for a stronger bond, the well is deeper we have a narrower well, and therefore, the change in the inter atomic distance is smaller as the temperature increases. So, from this, we can see why strongly bonded solids have lower thermal expansion than weakly bonded solids.

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Bonding Energies

Other consequences:

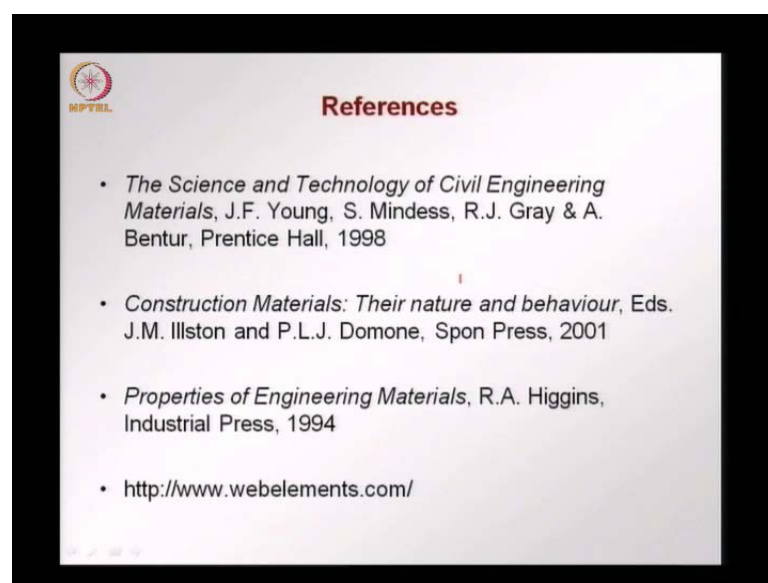
- Higher interatomic separation leads to more vibration of the atoms; as temperature increases, the material expands in all directions
- If the heating continues, the atomic bonds are eventually broken; liquids evaporate
- At higher temperatures, less extra energy is required to break the bond; the tensile strength decreases with an increase in temperature

Ilston & Domone

Other consequences as temperature increases, we saw that the inter atomic separation increases due to the vibration of the atoms, and this occurs in all direction that is why when we increase the temperature, and you see the expansion in the material it occurs in all directions, the material expands in all directions when the temperature increases. When the increase the temperature further, we increase the separation between the particles further. And they will be particles reaching a separation where the forces keeping the bond together are broken that is the attractive forces are so small, due to the large separation that is being created between the atoms that the atomic bond breaks and liquids evaporate. The bond is broken basically by the energy that is put in as heat leading to a increase in the separation between the particles and they are not held together any more and they are separated and the bond is broken.

Also, we see that to break a bond at higher temperatures will be easier, because already the bond is separated, the particles have a large distance between them, and therefore, to break that bond at a higher temperature, you need less energy. And this is reflected by the fact that the tensile strength of any material generally decreases with an increase in temperature. As you increase the temperature, it is easier to break a material; that means, the force required to a breaker material is smaller. So, these are some of the consequences that we can understand from looking at the Condon-Morse diagram comparing how the diagram looks a for weak bond and a strong bond.

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So, these are some of the references that give you more information about the bonds, the type of bonds and they are influencing the mechanical behavior. So, to summarize in this lecture, we have looked at how bonds are formed and the different types of chemical bonds, we looked at the strong bonds, the ionic bonds, the covalent bond and the metallic bond, and we looked at some of the properties. And in the second half of the lecture, we looked at the weaker bonds, the Van der Waals bonds, and the hydrogen bonds. And we saw how the Van der Waals and hydrogen bonds are formed because of the dipoles that occur due to the instantaneous distortion in the electrostatic field, where you have a separation between the centre of the positive charge and the centre of the negative charge.

So, this separation between the charges causes attraction between adjacent atoms, and you have the atoms being bonded by the weak bonds - the Van der Waals and the hydrogen bonds. And we also saw that the hydrogen bond is a directional bond, because the hydrogen atom is bonded in a certain configuration; the Van der Waals bond is a non-directional bond that creates bonds in all directions, not so the hydrogen bond. Then we went on to see, what is the Condon-Morse diagram which gives us the relation between the potential energy or the lattice energy and the separation between the particles.

And we saw how this diagram differs between a strong bond and a weak bond, and we also saw that this diagram has two very distinctive parts arising from the attractive forces, and another part which comes from the repulsive forces. The resultant is the figure showing us the energy versus the distance, this is non-symmetric. And when we have tensile forces, we find that the Condon-Morse diagram shows that initially the behavior is elastic. You have a linear behavior between the force and the interatomic distance, then there is non-linearity, there is a peak value which is associated with the tensile strength. And then when you keep separating the bond, the separation becomes so high that there are no further attractive forces to keep the material together and ultimately you have failure.

On the other hand, in compression, we find that when you push the atoms closer together when you have interatomic distances that are less than r_0 , which is the value corresponding to the minimum potential energy. You have very high repulsive forces and the forces that react due to the compressive forces that we applied, a very high and we will never have failure occurring in pure compression. We also saw how we can

understand thermal expansion from the Condon-Morse diagram, the well in the Condon-Morse diagram, where you reach minimum value in the potential energy is non-symmetric. And above the point of zero or absolute zero temperature - zero degree Kelvin, we find that there are many inter atomic distances which will have the same energy. And so, the particles can be in any position or vibrate over any position that gives you the same energy.

And if you take average distance, we find that this average distance now as we increase temperature is always more than r_0 , which is the stable inter atomic distance. And as temperature increases this r_0 prime or the average inter atomic separation increases, because of this we have expansion of the material in all directions as temperature increases. And also we saw while comparing the Condon-Morse diagrams of the weak bond and the strong bond that due to the shape of well-being narrower and deeper in a strong bond. We do not have much change in the inter atomic separation for a stronger bonded material when temperature increases well compared to the case of the shallow bond.

We also looked at typical bond energies for the case of the different bond, and we saw the ionic bond were strongest followed by the covalent bond, then the metallic bond then the hydrogen bond and the Van der Waals bonds. And we also looked at the examples where these different bonds occur, and what we also emphasize is that a material would have more than one particular type of bond. For example, in a polymer, we have covalent bonds within the chains and we have Van der Waals bonds between the chains that hold the polymer together.

In the next lecture, we will see how the structure of material developed linking this development of structure to the bonds, and that will take a little bit more to the formation of the structure, and we will see more of the properties being evidence when we discuss the structure of the metal.

Thank you.