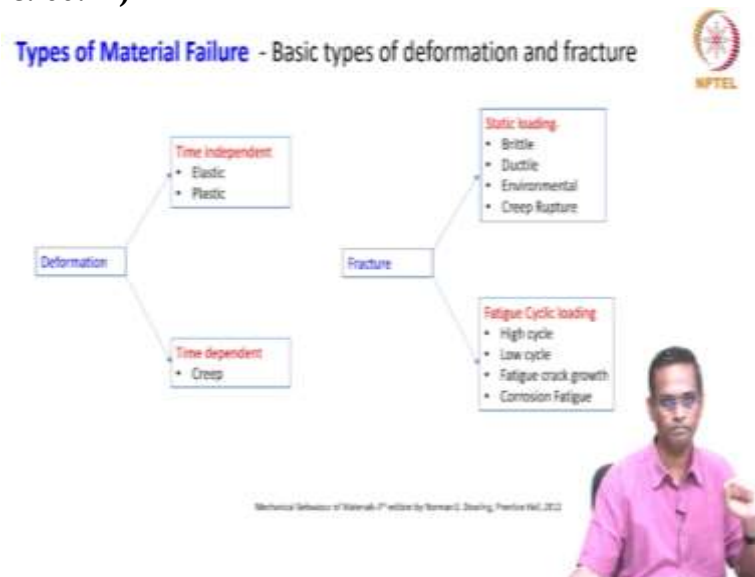


Mechanical Behaviour of Materials
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Lecture - 02
Chemical Bonding in Materials

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Hello, I am Professor Sankaran in the department of metallurgical and materials engineering, we go a little closer you concentrate more on technical aspects. Now types of material failure and basic types of deformation and fracture. So, in one line if you want to see these mechanical behaviour of material is all about studying the deformation and fracture of engineering materials.

So, we can now divide that into two, first is deformation. what type of deformation? One is time independent another is time dependent. So, time independent it can be elastic or it can be plastic and time dependent is creep. So, you know most of the material undergo elastic deformation and materials also undergo plastic deformation this is what we want to avoid in an engineering component or structures we want to avoid plastic deformation.

But we should know under what circumstances these you know failure occurs, that is the essential of the subject. So, these two deformations and whether it is elastic or plastic is a time independent it is not depending upon time. So, on the other hand, the deformation can be a time dependent. So, the one of the primary engineering property or failure is creep, it is a time dependent deformation. We will slowly look at it.

So, on the other hand, if you take the fracture you can look at it in two broad categories, whether fracture occurs under static loading or fracture occurs under cyclic loading so, there are two possibilities. So, under static loading, there are fractures or failure can be brittle in nature or ductile in nature or it could be environmental or creep rupture. So, some of these terms are becoming more technical now.

So, we should know what is brittle fracture? and what is the ductile fracture?. Brittle fracture is something what we have just seen in the spectacular failures photos like you know, the ship becoming two pieces, you know without any warning. Two pieces brittle fracture, ductile fracture, the pipe you are seeing the large deformation and then environmental is in a corrosion it could be oxidation corrosion, hot corrosion and so, on.

Creep rupture is like you know, time dependent as if you keep on you know, if the component are in structures are subjected to a deformation at a high temperature over a period of time then this type of failure coming to picture. Now, coming to cyclic loading. It is called fatigue, fatigue is cyclic loading, it can be high cycle, low cycle, fatigue crack growth, corrosion fatigue.

We will get into these details of each one of aspects. But high cycle generally it is a stress control fatigue normally for example, you know, the components which undergo stresses within you know elastic region, but for a very long time the distress controlled. So, low cycle means, the very word says that you know, the material will sustain only very low number of cycles.

That means you know that means the stresses are very high which will be the component is undergoing cyclic loading, much more plastic deformation or a strain control strain, lot of plastic strain is cycled, we will see all those in details. So, the high cycle means the components will sustain quite a bit of or quite a number of cycles very high cycles. So, that because the material itself is within the elastic region before yield point. So, we will see that when it comes to that point.

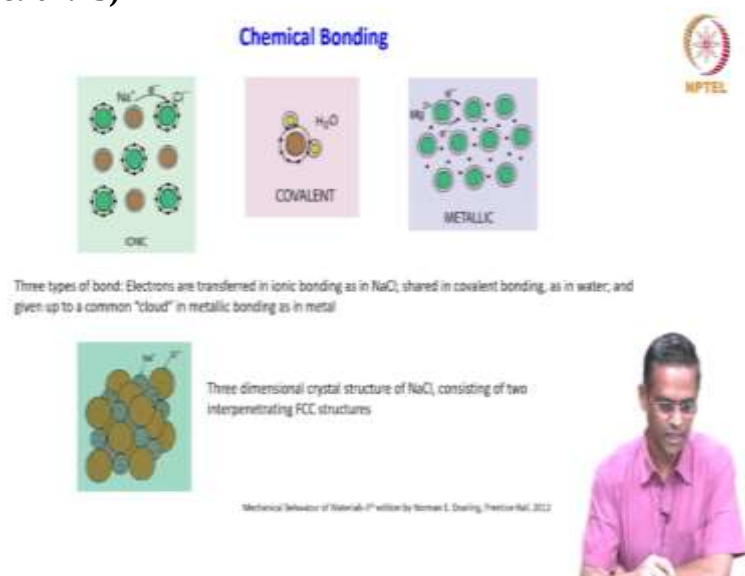
The fatigue crack growth. So, I just mentioned a couple of times before about these flaws and critical flaws and so, on. So, a flaw will grow if it is there in the component or any structures

or vehicles which are under use the flaw will grow but how much you know what is the speed of the growth? And at what condition it becomes critical or it attains a critical size?

These are all the important idea, very important. The fracture mechanics subject greatly deals with this and helps engineers to predict some of the life of these structures, very important. Similarly, the corrosion fatigue so, corrosion is also it can be static as well as cyclic. So, that is why it came under environmental heading in the static loading, but in cyclic loading as well the corrosion fatigue takes place.

So, this is also having primary, I mean it is also finding primary concern in most of the power plants kind of environment where you have materials undergo stresses are loading under severe environments. So, that is also very important.

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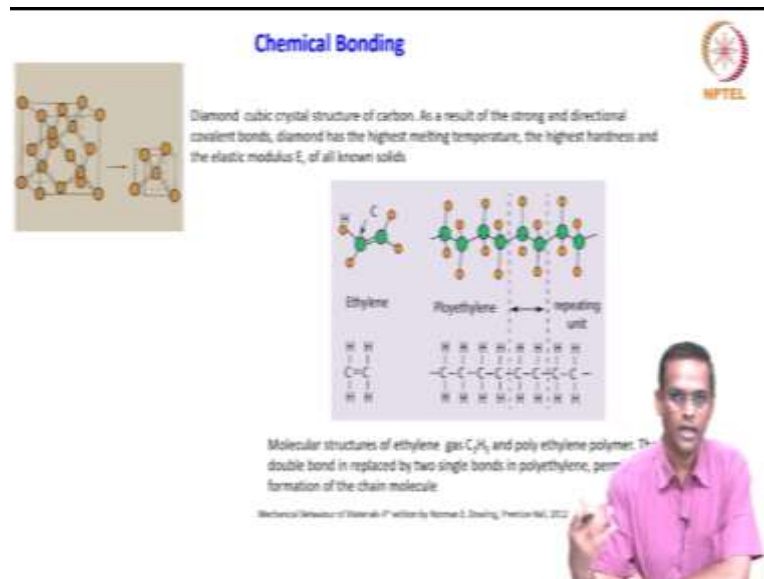
Before we get into the real syllabus or subjects as I mentioned, we will spend a lot of time on fundamentals. So, we will start with scratch chemical bonding, all of you are familiar with so, that it is always good to start with something which you are familiar. And then we connect why do you want to review this? What is the connection of chemical bonding with mechanical behaviour? That is exactly I want all of you to understand, there is a strong connection. So, let us now review what is the chemical bonding? See all of us know that there are primary chemical bonds and secondary chemical bonds what we are seeing here is ionic, sodium and chlorine ions which exhibits ionic bonding. The second one is the water molecule which exhibits the covalent bonding and it is a metallic it is a magnesium metal exhibiting a metallic bond.

So, we will slowly describe this bonding, what is ionic bond? Ionic bond is you know electrons are transferred in ionic bonding as in NaCl that means you have this you know sodium ion and chlorine ion. So, electrons are transferred from sodium to chlorine. So it is completely transferred, then they stay as ions, that is why it is called ionic bonding.

So, when it comes to water, the bond between the hydrogen and the chlorine, is the electrons are shared in the covalent bonding as in water. But the water has got some more typical interesting properties. What you see here is this bond is covalent bond but water is also very, all of you would have studied this also will exhibit a dipole moment. So, you have this hydrogen atom and this portion of oxygen sorry this portion of oxygen will have negatively charged because of this excess electron here and this side it is positive and this side is negative. So, it will be a dipole moment or permanent dipole moment. So, water is also called a polar solvent so, all of you know. So, now, here we are showing the hydrogen I mean here we are taking water as an example, but any molecule which exhibit this kind of a dipole also will form a bond that is secondary bond anyway we will discuss that next one. So, the covalent bond is electrons are shared between them and what is metallic bond?

Metallic bond is given up to common cloud so, it is a very general description. So, what it means is your ions are there positive ions or the metal ions are there they are embedded in the sea of electrons. So, that is called described here as a cloud. So, this and all you all know it but, our idea here is each one of this bond we will connect to its strength and mechanical behaviour, that is the idea. So, here is the 3 dimensional crystal structure of sodium chloride consisting of 2 interpenetrating FCC structures, ionic solid.

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So, what you are seeing here is another very popular crystal structure or material I would say diamond, which has got a diamond cubic crystal structure of carbon it is a allotrope of carbon. All of you know this as a result of a strong and a directional covalent bond. So, this is one interesting aspect of covalent bonding which is relevant to any mechanical behaviour. Covalent bonds are directional in nature and they are very strong.

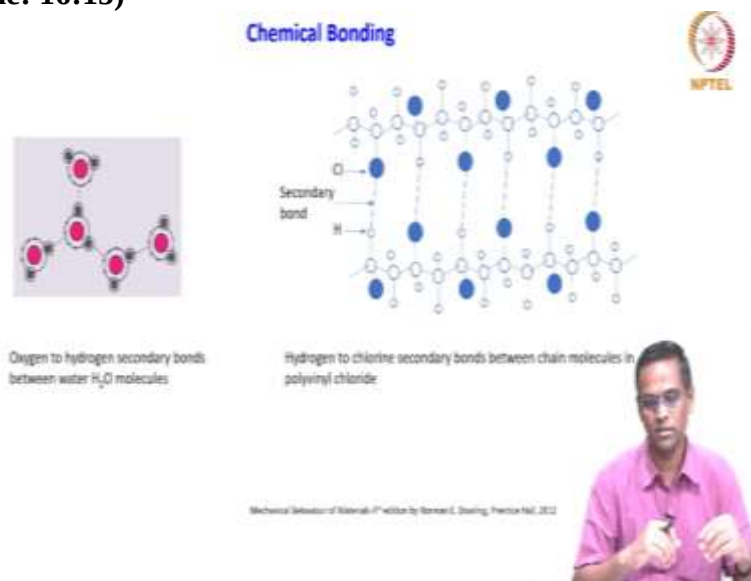
And that is why diamond has the highest melting point or melting temperature and it is also having highest hardness and elastic modulus of all known solids. So, it gives some idea, if you have a covalent bond in all directions, not necessarily only one, for example, even in water, you had you know covalent bond between hydrogen and oxygen, but that is not uniform everywhere, it is just one bond. So, that type of bond is also called hydrogen bonding we will come to that. We will talk about do not confuse with that. So, water is got a very, you know, you can talk about dipole bonds, you can talk about hydrogen bond we can talk about covalent bond. So, water is very interesting solvent or interesting liquid, but here we are talking about if you have a covalent bond, uniform covalent bond with its neighbour.

Suppose, for example, if you take the single unit here, the each carbon has got, you know, the tetragonal unit, so, they are all you know, covalent bond. So, that is why they are very strong and material which exhibits this kind of directional covalent bond uniform with its neighbours which generally exhibit high melting point high hardness and high elastic modulus that is very important.

Then coming to these polymeric materials, which is what we are showing here, is ethylene and polymers are all molecular structures. They are all molecular structures this is a molecular structure of ethylene gas C_2H_4 polyethylene polymer the double bond is repeated

by two single bonds in polyethylene permitting formation of chain molecules. You see, so far we have just looked at atoms, whether you know talk about metallic bond? Whether you talk about ionic bond, covalent bond? We were just talking the bond between atoms, but now, here we are switching over to molecular structures so, there is a difference. So, molecular structures have chains, so, mostly of chain molecules, polymers are all made up of chain molecules. So, within this chain, you have this carbon hydrogen this covalent bond and how these chain molecules are getting together or held together that is again an interesting point of view, you have to think about it.

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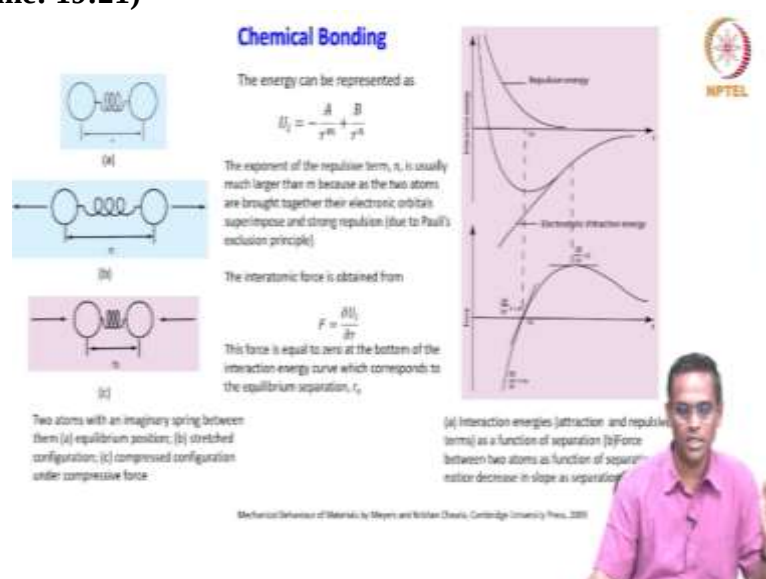


So, that is where we are going to discuss about this secondary bonds. So, the first one, what you are seeing here is again, oxygen to hydrogen, secondary bonds between water molecules, so, each one is water. So, you see that hydrogen, this is an oxygen so, there is a bond these are all called hydrogen bonding like I mentioned, you can also have you know, water also exhibits dipole. And here we are now, not talking about that there are any molecule which exhibits a dipole will also show permanent dipole bonds and in water we are now talking about hydrogen bonds here. So, secondary bonds primarily you know known as Vander Waals forces because of the electrostatic interactions. And they are weak forces or weak bonds, that is why it is called secondary bonds and you also have hydrogen bonds and dipole bonds.

So, most we are now here referring to hydrogen bonding. Similarly, if you look at this hydrogen to chlorine, secondary bonds between the chain molecules in polyvinyl chloride. So, this is one unit this whole unit and this is another unit they are all just held by this secondary bond. So, this is hydrogen and chlorine this is that are, held between these two. So,

this particular schematic shows that, you know all the polymeric materials are having primarily chain molecules and they are held together by Vander Waals forces or secondary bonds. So, that is how you should keep in mind, but the bonding between each of this carbon atom and hydrogen, they are all covalent bonds. So, we will come when we discuss you know, the external force on each one of them, then we will understand why this bonding is important. So, for example, the question here is suppose if I am just taking a polymeric material, and then I am trying to apply external load, which bond will respond first, or which bond will resist to keep the material intact or which are the forces will act against the external forces? That is, the question so, these are the aspects we will look at it as we move along.

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So, here is a model, consider two atoms, they are all held by some imaginary springs. The distance between these two items is r_0 that means that two items are held together in equilibrium position, or stable position. And then, the next image shows that these two atoms are pulled apart in a tension, so, the r_0 become r_1 and the image (c), shows the two atoms are getting compressed the distance becomes r_2 , please remember all this deformation are within elastic limits we are talking about elastic deformation.

So, you are able to pull it in tension, you are able to compress the two atoms together. So, what happens when you have these kinds of two atoms which are held in equilibrium position you try to pull it and try to compress it, what happens? So, you can clearly see that there is something happens to interatomic forces or interatomic energy which is plotted against function as a function of r .

So, if you look at the top image and let us describe this is a plot between interaction energy versus separation, r . The top curve is repulsive energy and the bottom is electrostatic attractive energy. So, the net forces in between is a potential well or the potential well sorry, potential well curve, that is how it is just been popularly known. So, when it is repulsive when it is attractive?

So, when as the separation goes up, then the attractive forces are increasing when the atoms are coming closer and closer and then the repulsion energy goes up. So, it can be and you can also calculate the force that is what is shown in the bottom figure the force versus separation. The interesting point notice, if you look at this the force is zero at r_0 there is no force net force is zero at r_0 .

When the two atoms are in the equilibrium position there is no force, then the as the separation between two atoms becoming larger than the slope changes and it reaches a maximum, so, derivative is 0. So, the decrease in slope as separation increases the slope becomes almost decreases and becomes 0. So, the energy can be represented by the formula

$$U_i = -\frac{A}{r^m} + \frac{B}{r^n}$$

so, the first one is attraction and second one is repulsion. The exponent of the repulsive term n in this term is usually much larger than m , because as the 2 atoms are brought together they are electronic orbitals super impose and strong repulsion as you go in this direction this curve due to Pauli's exclusion principle. So, this all we know, but we are now trying to connect all of them. So, the inter atomic force is obtained by

$$F = \frac{\partial U_i}{\partial r}$$

As shown in this figure, the force is zero at the bottom of the interaction energy curve. So, here if you look at this curve, it is a bottom we are referring to that is the force is 0 at the bottom and which also corresponds to r_0 here. So, this we are just introducing this curve here, but we will spend more time on this curve it is called the Condon Morse curve. So, we will also connect this property to the elastic modulus. And we will also connect this to you know, atomistic you know. I would say atomistic relation with its elastic properties you know what is the atomic basis for the elastic properties of materials? So, we will spend more time on this curve so, this is just an introduction.

(Refer Slide Time: 25:41)

Chemical Bonding

Bond energy, Bond type and Bond length

- When the distance of separation is r_0 , the attractive and the repulsive forces exactly balance each other and the net force is zero. This distance corresponds to stable equilibrium with a minimum in potential energy W . The magnitude of the minimum energy W_0 is called the **bond energy** (kJ mol^{-1})
- According to the strength, chemical bonds can be grouped into primary and secondary bonds. Primary bonds have bond energies in the range $100 - 1000 \text{ kJ mol}^{-1}$
- Covalent, metallic and ionic bonds are all **primary bonds**. Among these, covalent and ionic bonds are generally stronger than metallic bonds. **Secondary bonds** have energies in the range $1-50 \text{ kJ mol}^{-1}$ one or two orders of magnitude smaller than those of primary bonds. Van der Waals bond and Hydrogen bond
- It is useful to classify materials according to the bond type that is **dominant** in a given material. It helps in predicting the approximate properties and behaviour of a material under given set of conditions.



NPTEL

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So, if you look at chemical bonding much more closely so same curve here, this is F_r a subscript r is supposed to be subscript, a is supposed to be subscript attraction force repulsive force. So, this is the equilibrium distance r_0 and this is a resultant force and this bottom one is a potential energy the previous one what we have just looked at before is force versus separation inter atomic energy versus separation.

There are so, many ways to look at the physical event so many ways. So, here force is the same force versus separation is there but it is potential energy W versus separation. So, we will try to look at bond energy bond type and bond length. When do you say bond length what kind of each bond has got a characteristic bond length each molecule is characterised with bond length. So, when the distance of separation is r_0 , the attractive and repulsive forces exactly balance each other and the net force is zero, this is what we have seen the distance corresponds to the stable equilibrium with a minimum in potential energy the magnitude of the minimum energy W_0 is called bond energy. So, we are bringing this potential energy versus separation curve to bring the idea of bond energy. So, what is that energy?

That is the energy the minimum energy were the distance between the bottom of the potential well and the zero so, that is W_0 is a bond energy which is measured the unit is kJ mol^{-1} .

So, according to this strength, chemical bonds can be grouped into primary and secondary. See this we have already seen primary bond and secondary bond and how about their energies?

So, that is that question now, because we are going to talk about mechanical response. So, we start from this basic the primary bonds have bond energies in the range of 100 to 1000 kJ mol^{-1} . So, this is a primary bond. So, what are the primary bonds? They are ionic, covalent,

metallic so, they are in the range of $100\text{--}1000\text{ kJ mol}^{-1}$. And among these primary bonds, the covalent and ionic bonds are generally stronger than the metallic bonds so, very important.

So, keep that in mind covalent and ionic bonds are stronger than the metallic bond. Secondary bonds have the energies in the range of $1\text{--}50\text{ kJ mol}^{-1}$. It is much lower than the primary bond energies one or two orders of magnitude smaller than those of primary bonds. And the examples we have already seen Van der Waals bond and hydrogen bonds may come into this energy range.

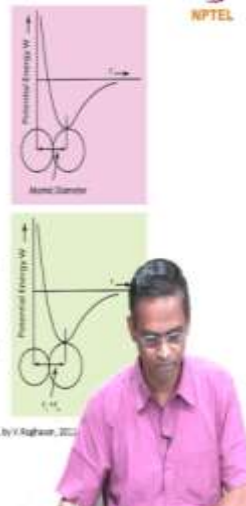
So, it is useful to classify materials according to the bond type, that is dominant in a given material, it helps in predicting the approximate properties and behaviour of a material under a given set of conditions. So, what does it mean, bond type and that is dominant in given material. So, you can have a bond which is more than one character that is what it means one can have you know, ionic bond and metallic bond, ionic and covalent.

So, which will dominate suppose if I have a material which has the characteristic of ionic and covalent or ionic and metallic so, which character is dominant, so, that is what means here. So, if you know that what is the type of dominant bond then it will again easier to predict the behaviour under set of conditions.

(Refer Slide Time: 30:58)

The relationship between atomic (or ionic) size and the bond length

- The length of a bond is defined as the **centre-to-centre distance of the bonding atoms**.
- Strong bonds pull the bonding atoms closer together and so have smaller bond lengths as compared to weak bonds.
- **Primary bonds** have lengths in the range of $1\text{--}2\text{ \AA}$ ($0.1\text{--}0.2\text{ nm}$). **Secondary bond** lengths are larger, in the range $2\text{--}5\text{ \AA}$ ($0.2\text{--}0.5\text{ nm}$).
- When bonding is between two neighbouring atoms of the same kind, the **atomic diameter is simply equal to the bond length**.
- Some ambiguity in this definition arises if the element in question exhibits different crystal forms.
- For example, the diameter of the iron atom is $2.48\text{ \AA}$ when it is surrounded by eight neighbours in the BCC crystal and $2.54\text{ \AA}$ when it has 12 types, as in the ionic bonding, the bond length is equal to the sum of their radii, $r_c + r_a$, as shown in the figure.



So, the relationship between atomic size and the bond length so, we looked at bond energy and bond length and bond type. So, now, we look at bond length and an atomic size how they are related. The length of the bond is defined as the centre to centre distance of the bonding atom. So, again we will refer to this potential well potential energy versus r . So, when the distance between the two atoms is r_0 the centre to centre distance is bond length.

So, that is when atom or an equilibrium position r_0 then the centre to centre distance is called bond length. So, strong bonds pull their bonding atoms closer together and so, have smaller bond lengths as compared to weaker one so, this is quite understandable. So, we have now seen the bond energies so, how strong they are. So, they will try to hold together more tightly than the weaker bonds like Van der Waals or hydrogen or dipole bonds.

So, for primary bonds they have the length in the range of 1-2 Å or (0.1 to 0.2 nm), secondary bond lengths they are much larger in the range of 2 to 5 Å or 0.2 to 2.5 nm. So, very important to give this so, this is a very interesting point when the bonding is between two neighbouring atoms of same kind, the atomic diameter is simply equal to the bond length.

So, suppose if you do not have similar atoms you can have solid solutions or you can have ionic solid like sodium fluoride and so on where you do not have same type of atoms you have different types of items together, then what happens? Then you look at this similar potential energy versus separation curve for atoms of different kinds one is you know for example, ionic solid. So, this is an anion and this is a cation.

So,

$$r_c + r_a$$

This, is radius of cation and plus radius of anion so, this distance is that bond length. So, that is why there is some ambiguity in this definition arises, If the element in question exhibits different crystal forms. So, another question, it is not necessarily anion, cation issue, if it is same material exhibits a different crystal form for example, the diameter of iodine atom is 2.48 angstroms when it is surrounded by eight neighbours in the BCC crystal and 2.54 angstrom when it has twelve types as in the ionic bonding.

So, the bond length is equal to the sum of the radii $r_c + r_a$ as shown here. So, depending upon the crystal structure, suppose the same material is undergoing some transformation then also this question this ambiguity will come and in the case of ionic solids if the ions are different then also you have to look into the definitions with more careful, that is all we want to say here.

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Effect of temperature on the mean spacing between atoms forming a chemical bond



- The equilibrium distance of separation: shown applies to 0 K, where there is no thermal energy.
- At higher temperatures, under the influence of thermal energy, atoms vibrate about their mean positions, the amplitude of vibrations increasing with increasing temperature.
- As can be seen from the figure at temperature T_1 , the amplitude is a_1, b_1 and at T_2 ($T_2 > T_1$) the amplitude is a_2, b_2 .
- The corresponding mean spacings between the atoms are given by r_0' and r_0'' . As the repulsive force is short range in nature as compared to the attractive force, the potential energy curve is steeper on the left side of r_0 than on the right side. Therefore, $r_0' > r_0 > r_0''$ as shown in the figure.
- That is, the mean bond length increases on heating. In other words, the material exhibits **thermal expansion**.



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So, one last aspect I want to cover before I stop this lecture today, the effect of temperature on the mean spacing between atoms forming a chemical bond very important. So, what happens if the temperature is rising? Again we will use this potential energy versus separation curve. So, what are the descriptors the equilibrium distance of separation shown applies to 0 K, very important.

So, whatever we have just talked about this r_0 the distance between two atoms so, called equilibrium position is referred to 0 K, very important so, there is no thermal energy. So, at higher temperatures under the influence of thermal energy, atoms vibrate, very important atoms vibrate about their main positions. The amplitude of vibrations increases with increasing temperature.

So, this is what is shown here what you see here is r_0 is that 0 K and you take a temperature a T_1 then the r_0 is here " r_0' ". The atom will try to vibrate between two positions a_1 and b_1 at T_1 temperature and at T_2 the r_0 will become " r_0'' ", here and an atom will vibrate between these two positions a_2 and b_2 . So, this is what is shown here the amplitude is a_1, b_1 and at T_2 amplitude is a_2, b_2 .

Another important interesting observation is as the temperature goes up, you can see that you know the r_0 , which is here which is also increasing. So, the corresponding mean spacing between the atoms are all given by " r_0' " and " r_0'' " as the repulsive force is in short range in nature as compared to the attractive force. The potential energy curve is steeper on the left hand side very important point, you have to read this line again.

So, this is a net curve that is what we have seen from the previous description. So, the repulsive force is in short range as compared to the attractive force potential energy curves, so, the curve is steeper on the left hand side than the right hand side that is why you see that r_0 as the temperature increases the r_0 , you know keep on increasing very important observation.

So, it is kind of you know the curve is asymmetric nature of the curve and it gives a very important idea that is the mean bond length increases on heating. In other words, the material exhibits thermal expansion so, the most fundamental property of a material is thermal expansion. So, we are kind of you know arriving at 1 phenomenon which is you know have the atomic basis or chemical bond as a basis atomic basis thermal expansion.

The very fundamental property of any material now, we are showing that why it is expanding why thermal expansion happens or how this mean equilibrium distances keep on increasing with increase in the temperature? So I will stop here, we will continue in the next class.

Thank you.