Nanomaterials and their Properties
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Lecture - 21
Thermal Properties of Nanomaterials (III)

This lecture number 20 about the Thermal Properties of material. In fact, we started the topic and I finished the portion on change of melting temperature for nanoparticles. Now, as you know thermal properties has two components. One is the melting temperature that is reduction of melting temperature because of the nano size and the second one is the thermal transport how the heat get transported during different kinds of operations and the effect of size on that is the topic of discussion today.

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Well, in the last lecture, so, as I said we started this new topic on thermal properties of nanomaterials and discussed about the melting temperature of nanomaterials. And I showed you by different thermodynamical models how the melting temperature of nanomaterial will be depending will be varying depending on the size of the nanomaterials.

Today first we will do some recap of this thing and then we will go on to the new topic. So, as you know every lecture I ask this question to you; if you have any questions regarding this topic please keep it in your mind. And whenever we will discuss about these lectures you can always ask these questions.

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So, as the beginning of the lecture let me reiterate thermal property of nanomaterials will have two components. One the melting temperature of nanomaterials other one the thermal transport. And the first one which is the melting temperature of nanomaterials has been already covered.

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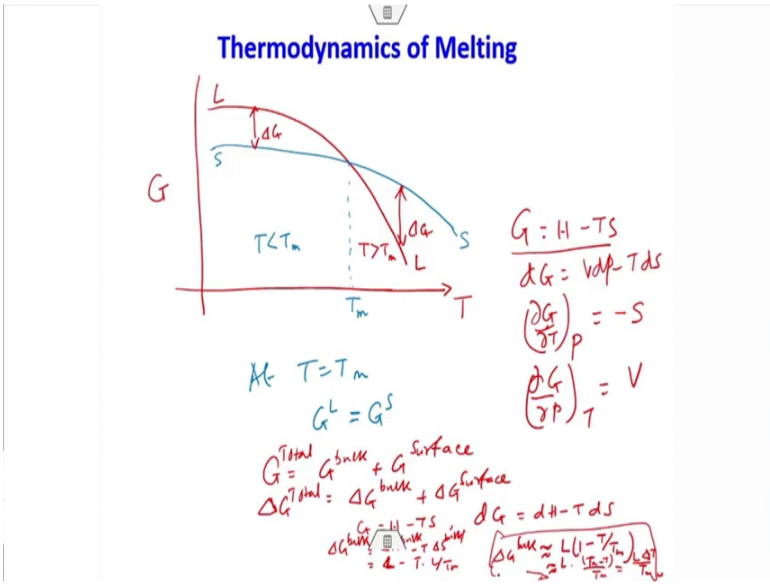

So, what you did in that? Well, what you did in that is very simple you know the basically first we need to know about thermodynamics of melting ok. What is that? Well, you know thermodynamics is basically talks about free energy versus temperature plots and as you know below the melting temperature solid phase is stable above the measure liquid phase more stable or stable actually.

So, because of these aspects free energy curves will have a crossover at the melting temperature and we can actually calculate the heat of fusion or the latitude of fusion as that by using free energy concepts that is what I did in the last lecture. And we have discussed many of these things very categorically how this can be obtained ok you can see here it is given.

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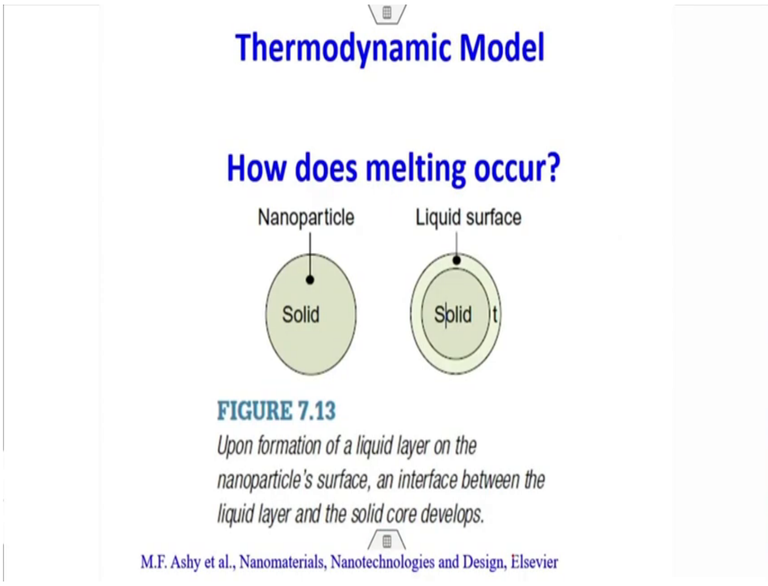

Well, most important thing for this discussion is how the melting starts. Normally, for a free nanoparticle melting will always start at the surface ok that is very clear at the surface melting will start. So, hence the liquid which will nucleate at the surface will slowly grow and move inside the solid spherical nanoparticles.

Well, you can use any kind of shape, but for the sake of simplicity and you know make the things clear we will use the spherical nanoparticles and showed how the liquid front which is forming at the surface of this nano particle can move inside and it can melt completely.

And this is how the melting normally happens in nanomaterials. It is very rare that liquid will nucleate inside the nanoparticles somewhat middle or any anywhere actually here or there is very very unlikely. Because to nuclear liquid you need to have certain kind of surface and that surface is provided by the outside surface of this material.

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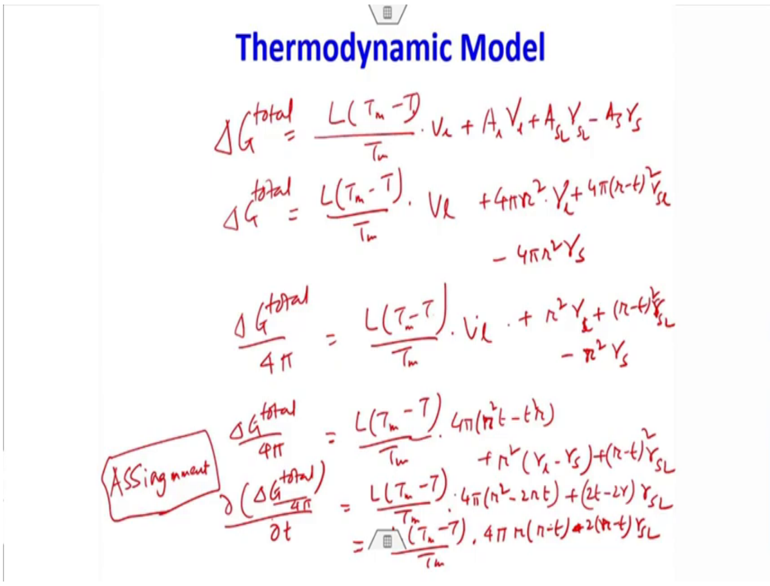

Upon knowing that what you did is simple free energy calculations free energy of melting for the bulk that is just given by $L\left(\frac{T_m - T}{T_m}\right) . V_l + A_l \gamma_l + A_{sl} \gamma_{sl} - A_s \gamma_s$.

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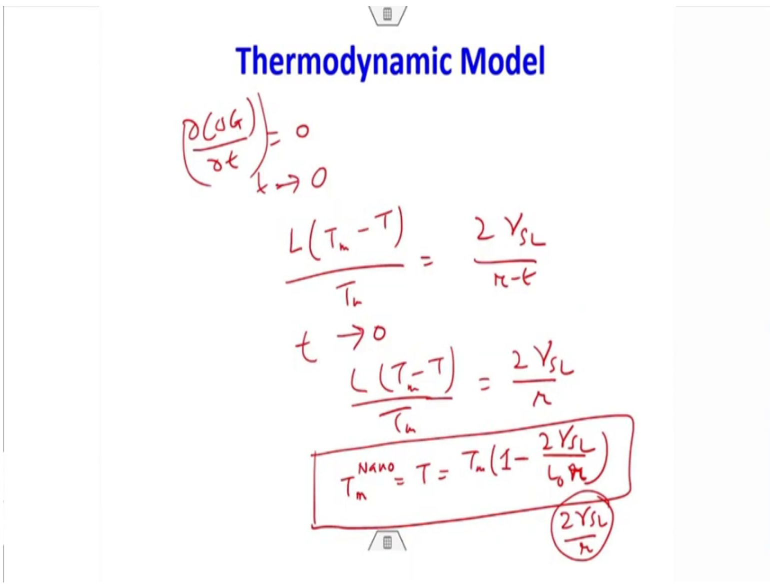

And then by doing the calculation you could you could show that you know where thickness goes to very small then we can arrive in the relationship between the change of melting temperature that is of the nanoparticle that is $T_m^{Nano} = T = T_m[1-\left(\frac{2\gamma_{sl}}{L_0 r}\right)]$.

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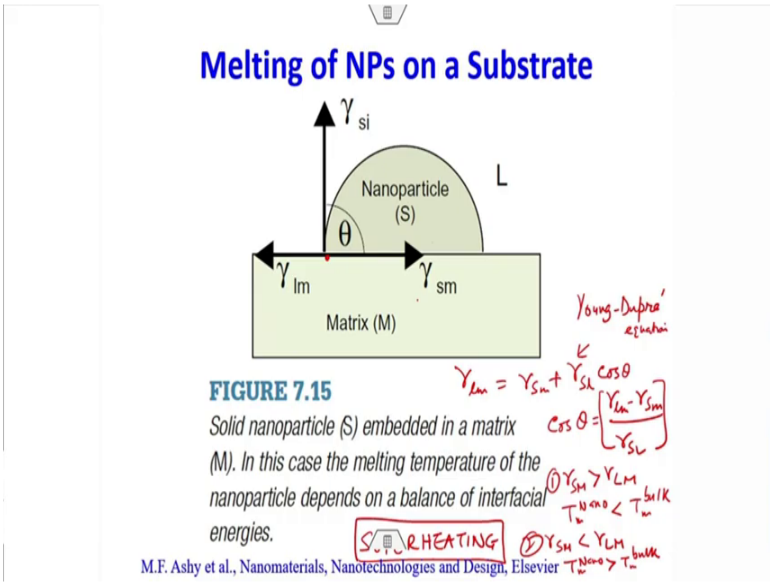

Well that is not the all is case. Some of the cases nanoparticles may not be free. They will be sitting on a substrate or they will be embedded in a matrix in that cases we need to use the concept of the Young equation to calculate the angle of weighting ok. And depending on that angle of weighting the (Refer Time: 04:57) basically that angle of weighting will depend on the balance of the surface energies or the interfacial energies between solid-liquid, solid matrix liquid matrix.

And you know this relationship cos theta is equal to gamma lm minus gamma sm by gamma sl. And then we can justify under what conditions temperature will go above the melting temperature or temperature will be below the melting temperature or otherwise you can have superheating or you can have depression of melting temperature ok.

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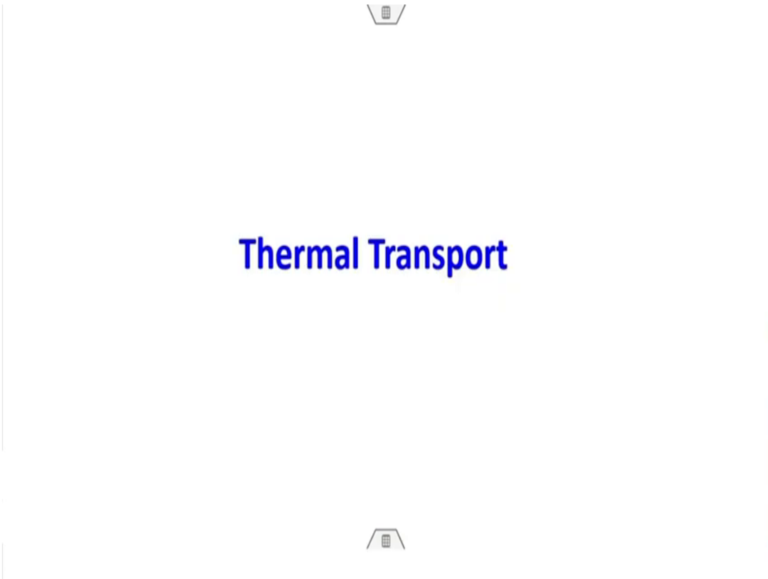

So, that is about the recap. Now, let us discuss about the thermal properties of the material. So, thermal properties of the materials are very important you have to understand they are very very important. Why? Because many of the thermodynamics as I said many of these semiconductor devices or microprocessors like in a computer or in a mobile phone or even in a normal machine where electronic devices are used ok. The goal is basically to transfer the heat away.

Remember many of these components which are used in a computer or in a laser or in any other device will be a nanometric scale that is the thin films which are depositing on these material on these you know components will be thickness having thickness less than 100 nanometers. So because of these aspects they are nano sized.

So, therefore, the heat generation in this materials will be quite large because they are doing operations. When you are operating computer or operating mobile phone you are doing all kinds of operation. Every operation needs generate heat and this heat needs to be dissipated, otherwise, temperature of the component will increase very rapidly and it will no longer function.

So, therefore, the goal of these kind of thing is to dissipate it or transport the heat away as quickly as possible. But there will be other application like thermal barriers ok. There are many many such applications like include turbine blades or even other cases of thermal barriers are required where you need to be you know reduce the thermal conduction

So heat transport, how is heat transport happens in a material? You have any idea? Well, heat transport can happen in two ways. Normally, we know heat transport happens by electronic conduction right. Electrons are the best conductors of heat and electricity right and they can transport these things simply by going to high energy level.

As you provide heat energy to system electrons will be energized they will go to the higher energy level and they can the dissipate at the heat, but you know that is only possible in cases where large number of electrons are available like in a metallic materials where free electrons are easily available.

But for what about semiconductors or insulators or maybe some non metallic materials where large pool of electrons are not freely available? Their heat transport will must be happening in a different way right. So, their heat transport happens by what is known as a lattice vibration or phonons ok.

So, in metals electron mechanism of heat transport is significantly efficient and phonon processes then the phonon processor due the fact that in metals there is a large number of free electrons are available. And electrons are not easily scattered ok electrons can easily move and take out the heat they are not scattered that is the advantage of metal.

But in case of non metals that is not the case, electrons will not be easily available and even if they available they will be scattered because of many many scatterer available in non metals ok. Obviously, scatterer will always available in metals, but they will be little bit less in numbers. So, in those cases it is only the lattice vibrations or the phonons that dictates the heat transport right.

So, before we go in to discuss about the effect of the electronic conduction and the lattice vibrations conduction or connection to lattice vibration. Let us first discuss about these aspects in a quite different way. So, I know that any of all of you know something about electronic conductions ok. The energy levels, band diagrams you are little bit aware of that ok, when you will bring it back when at the end of this lecture when we talk about quantum confinement of electronics levels.

So, basically what does it mean to say is that before we go into effect of this nano size on the conduction of heat by electron or the phonons let us first discuss about what these are that is very important.

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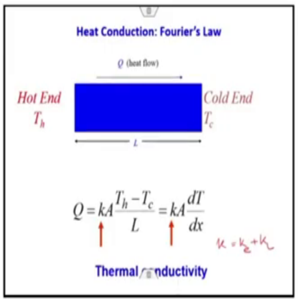

As you know heat conduction is governed by Fourier's law right all of you know that. So, if you have a small piece of the sample, length is L, ok and cross-sectional area is A, and you have a hot end cold end, the heat will be transported from hot end to cold end. The Q is the heat amount of heat transported per unit area per unit time perpendicular to the plane of the surface of this material that is what is known as a flux that will be equal to thermal conductivity multiplied by what?

Thermal conductivity multiplied by kA, A is this cross sectional area and the temperature gradient that you know. That means, Q $\propto \frac{\Delta T}{\Delta x}$ in one dimensional case that is what is shown here. This is the case. This is the proportion to $\frac{\partial T}{\partial x}$.

So, if that is the case, so, what is the important aspect here that controls the heat transport and which is an intrinsic property of the material is the thermal conductivity, right. So, thermal conductivity k of any material will have two components; thermal conductivity, electronic conduction and thermal conductivity due to lattice vibration correct.

So, now, design of materials in this aspect is basically to look into these two separately. But we know that they may be there they are will be related to each other, but basically most of us or the scientists in the world they always like to have the electronic contributions and the lattice contribution separately and see in which material where the electronic conductions or the lattice vibration electric conductions which one is higher which one have significant role. So, this is the basically the thing.

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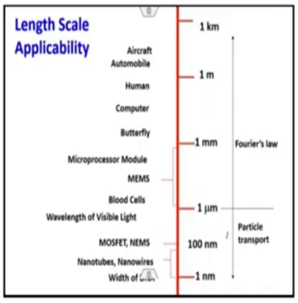

Now, if you know the length scale or applicability of these things, if you consider aircraft or a human ok. You can understand that they are pretty big, right. Even a computer is also pretty big, but if you look at a microprocessor model or a blood cell or may MOSFET ok or if you look at even nanotubes nanowires they are pretty small.

So, therefore, Fourier's law this obviously, will be applicable to all. But the transport in case of nanoscale material like in case of, NEMS, nanotubes or even microprocessor models will be governed by particle transports ok that means, it will be governed by either electrons or the phonons ok.

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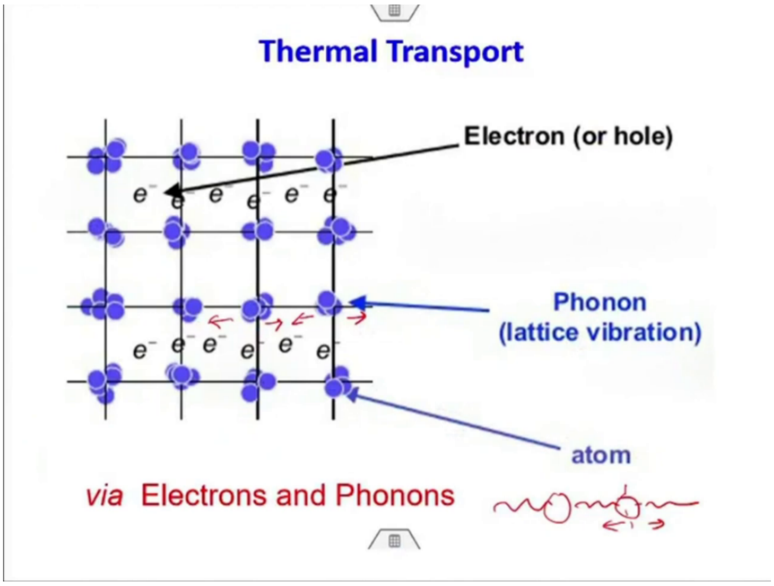

So far so good. So, let us we let us talk about what are these aspects because that is something which is we should know very well. This is a one dimensional or two dimensional lattice rather. As you see in the periodic lattice you have atoms at each cross each points actually here, here, here, here, everywhere and this is basically arranged in a nice periodic manner. So, that is a periodic potential exist in this material because the atoms will have positive protons and the neutrons and they are surrounded by electrons ok.

And now as I said in metals electrons are freely available because electrons are not bound to any particular atom they are most likely behave like electron cloud right. So, because electrons are freely available in metal if the moment you heat up or provide the heat to the system electrons will take out the heat they will get energized and that is how they can conduct as the heat or they can transfer the heat actually that is the important thing.

You can also have holes like in semiconductors which can also act as a transporting agent for the of the heat right that is possible. But other thing which is possible is that as you heat the material now listen to carefully me at heat the materials what would happen?

As you heat the materials, the atoms will also vibrate from the equilibrium positions. As the atom vibrates from the equilibrium positions, they can actually get pushed or pulled. As they pushed get pushed and pulled, they create a vibration in the material or vibration in the lattice ok correct.

So, if this atom particular say these atoms or this set of atoms are moving like this or this set of atoms are moving like this they are going to make a push when they come close or they are going to pull it to each other when they are going away. By doing that; that means, they will be acting like a simple harmonic oscillator and by doing that a wave will be created inside the material that can propagate and that wave can then carry the heat and that is what is known as it will phonon or lattice vibrations ok. Am I clear?

So, let me tell you again. So, as you hit the materials the atoms put sitting at each of these lattice positions they will also try to they will also vibrate right from the mean or equilibrium positions. As they vibrate the atoms can push or pull each other. As you see if they are coming close to each they will push and they are going away from each other they will pull right.

So, what the situation is? Whether pushing or pulling it is lead to creation of a vibration in the material right. And because of this vibration in the material the wave will be generated inside the material and that is wave is known as a lattice wave alright, fine. So, that is the basically things which is known as a phonon.

Now, this can help in two ways in the material, one the heat transport other one is the sound movement of sound inside the material. That is something which is very well known in the in the system or let me just tell you in a very clearly manner what is a phonon is, ok.

You know the question is people always ask how heat spreads in the material; obviously, one is electronic other one is the lattice vibrations. They are nothing but the low frequency vibrations ok, for the sound and high frequency vibration for the heat ok. So, phonons can be considered as a particle of heat actually in material.

So, the crystals atoms are as I showed atoms are nicely arranged in a uniform repeating way, when heated the atoms will oscillate in the crystal behaving like a spring right. Just like a spring. I will come back to it very soon atoms are oscillating and they will behave like a spring. So, if this atom is moving like this or this the springs will get pulled and pushed right you do not know that right.

So, any kind of crystalline structures the bonding can be thought of like a springs actually. We know that. I am not going back to it all of you have learned about it. So, they are actually like a springs by which this bonding has happened. So as you move the atoms from its mean equilibrium position because of the application of heat the spring will be pulled or pushed.

And because of these ok when the pushed and pulling happen it can set up a traveling wave to the crystal. And so, that is like a sitting on one edge of a humpling you can also set up a vibration in the in the in the length of the surface right that that is exactly same as like that.

So, you can see when you are playing a piano ok. If you see if you press the keys ok, you can see on the other side where the piano is open how the wave moves. It is exactly like that. So, by heating you are pushing these atoms or you are basically pressing the atoms and they are actually setting up a wave which you can travel through this material.

This is one way of thinking. The other way thinking is like this. These phonons are nothing but units of vibrational energy that can arise from oscillating atoms within the crystal that I have already told you. So, as a solid consisting of specific repeating 3D, you know basically arrangement atoms. So, atom as behave as the connecting by springs ok that the bonded in a crystalline lattice.

Now, thermal energy makes this lattice vibrate. This can generate mechanical waves actually which can be actually heat or sound. So, packet of waves can travel through this crystal with a different energy and momentum and quantum mechanics these waves can be considered as a particles.

So, phonons and photons they can be correlated. Photons are actually quant of energy, phonons are actually quant of heat. They are similar, but quantum vibrational micronical energy is what is phonon is. Now, we know that photons do not interact with phonons can interact in a material.

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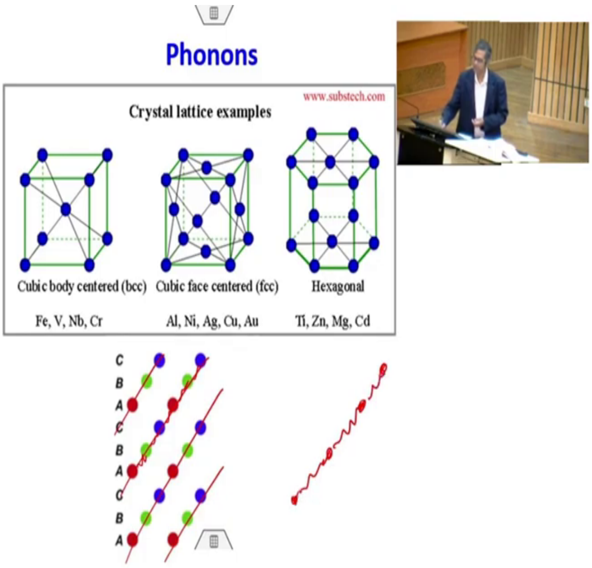

So, hope this you have understand. Now, that to make it very clear, the crystalline structure is basically 3D right. Like in the case of bcc or fcc or hexagonal structure in a metal, the atoms are arranged in a nice manner. So, if you put it on the plane ok that is how the FCC structure will like ABC ABC ABC stacking as it will look like.

So, now they arrange like an along a line you can assume that. So, they are connected by springs right or let me just show it separately they are connected by springs ok. These are the atoms. So, they are connected by spring. I am telling you again and again. So, that you understand, do not forget.

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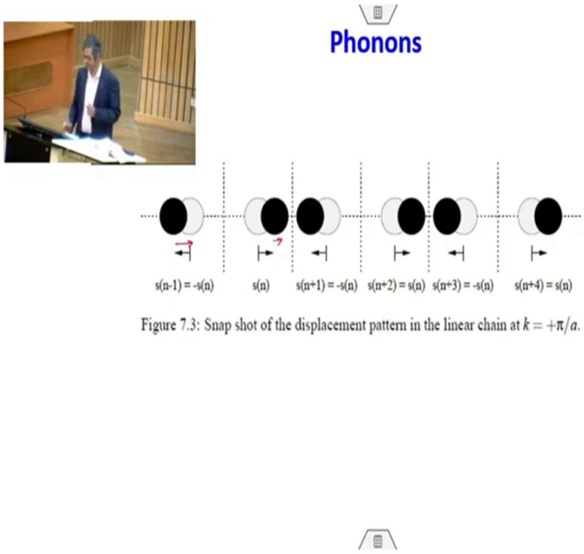

So, now, if you if you heat at the temperature these atom this atom ok, let me just go there. What is that? Yeah. So, this atom so, if you if you move if you apply heat this atom can move like this. So, this similarly for this atom also will move like this. Because of this a lattice wave will be traveling through the material and that is what is known as a phonon correct.

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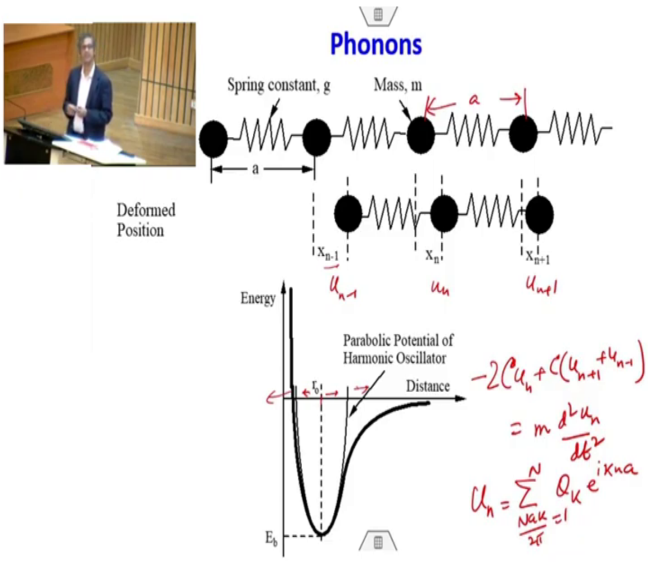

So, that is exactly is what is shown here. Now, in terms of energetics concept in terms of energetic concept means in terms of potential energy concept this can be explained also in the following manner. How, we can explain that? Well, as you know we know that if I have two atoms sitting by side by side there is their energetic balance depends on attractive force and repulsive force between them.

Attractive force is basically attraction between electron cloud and the positive you know that is the proton or the nucleus of the material. And repulsive force is basically electron cloud overlap ok. So, the balance of these two forces will provide us the equilibrium positions of the atom and energy and that is what is given by r_0 and E_b right.

So, now as you heat it up this atoms are trying to oscillate from the mean positions of r_0 ok they will oscillate. That is obvious because if you finding energy, so, if there are atoms of property energy they will try to move. And then once they try to move, so, they will go away from the mean equilibrium positions ok. So, as they go away this push pull will easily happen.

So, that is what is shown here. This is the equilibrium position, this is deformed position. You can see the deform positions there is a motion of the atom at n-1 position compared to n and n+1 positions. So, one can actually set of equations based on this movement of the atoms actually easily which we will see much later ok which we will see even in next couple of slides also.

So, as you know this kind of concepts are easily available in many books. Most important books which you can follow is the Solid State Physics by Kittel and it is very nicely descripted there and let me show the book. This is the book Solid State Physics by Kittel you can see this is nicely Charles Kittels book nicely describes all the concepts very and easily.

So, phonons are very important in conducts matter because this play very important role in thermal conductivity and electrical conductivity. Not only that only that they also provide many other concepts ok. So, now, as you see I am showing you C positions of the atoms which is 1 at n-1, one is at n and one is n+1 and with the displacement of u_{n-1}, u_n, u_{n+1} ok because of thermal energy right.

So, n is the level of n^{th} atom ok of the total n and let us suppose distance between two atom is a, ok distance between two atom is a, if we assume that and mass is already given as m right.

So if you do that a simple you know mass simple balance calculations, simple balance calculation means simple displacement balance calculation.

You can write down this equation -2(u_n+C(u_{n+1}+ u_{n-1}), C is the elastic constant. Why here constant elastic constant? Because they are springs actually. So, whenever you are talking about the motion or the you know spring expanding or contacting you always consider spring constant a spring constant is what is known as elastic constant actually.

So, this is ok can be written like this ok. Why you are considering minus 2n? Because this central atom is basically pulled by both the two other side atoms like which is as n-1 position which is n+1 position. This must be equal to m$\frac{d^2x}{dt^2}$ ok m multiplied by acceleration. Why? You should know that this is nothing but Newton's laws of motion. The force is equal to mass into acceleration.

So, force is this, elastic constant C, this is elastic constant C multiplied C(u_{n+1}+ u_{n-1}), because this will be pulled and then this C is u_{n+1} u_{n+1} ok. So, now, you know we can solve this equation very easily. All of you have done that solution expected to be this will be oscillatory solutions and this is normally done by discrete Fourier transformations.

And so, therefore, u_n will be obtained like this ok,u_n= $\sum_{NaK/2\pi}^{N} Q_k e^{-ikNa}$ right. You must be thinking what is K. K is the Fourier space constant ok, normally it is inverse of the distance ok that is always like in case of in case of photons K= $\frac{2\pi}{\lambda}$ right. So, in this case also its K= $\frac{2\pi}{a}$, a is the inter atomic distance correct.

So, Q is known as a normal coordinates continuum field modes ok. And you know you can always if you if you make this equation and put it there this is a solution of the equations you can get two couple equations and one of them will give you thermal acoustic modes other one will provide you the thermal modes ok.

So, that is how actually one can solve these linear problems of chains very easily, but in reality they are not linear chains they may be linear chains, but they will not be in one dimension they will be in three dimensions. So, that one is to consider the three dimensional structure of the material and do this calculations which is very complex that is why normally we do not do it in the literature.

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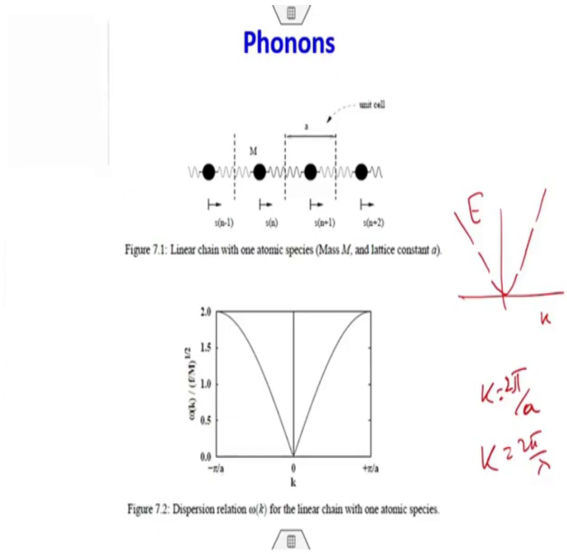

And you know this is the phonon dispersion curve, you can see between this omega K ok that is what is your dispersion versus the K space. You can see K= $\frac{2\pi}{a}$, right the K is basically always given as $\frac{2\pi}{a}$, a is the distance in case of photons we use K= $\frac{2\pi}{\lambda}$, λ is the wavelength right.

So, once you do such a kind of mathematical analysis in unit cell they exactly shown there this is how the phonons dispersant curve will like. What does it mean? It means that the energy levels which are permitted or the vibrations which are permitted is given by these two curves. All of you remember that in case of metals, the energy band looks like this. The in E-K curve also looks like this they looks like this right.

So there is a similarity between these two, but they are not similar always remember that. So, because there will be some you know gaps here and there will be some small gaps oops it goes like that. So, it can be like this which are not allowed energy band energy levels which are not allowed for the electrons ok that is for the bulk actually.

So, this is something which is very important and you should understand it ok. Now, one can do this treatment quantum mechanically also by doing Hamiltonian concepts which I am not doing it because you may not need it for your purpose.

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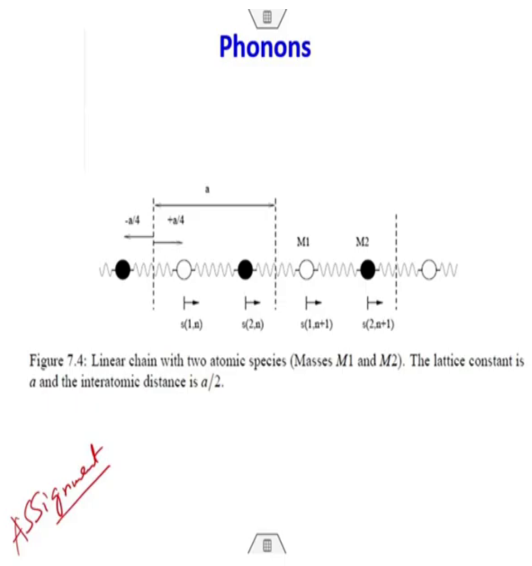

Fine one can actually think of this chain consisting of two sets of atom with different masses M_1, M_2 and do the similar equation. And like that you should do as a part of assignments also and solve this problem ok. This is very very important to do this kind of simple solution of the simple differential equations using certain condition boundary conditions and initial conditions ok.

In a so, therefore, in a linear chain this is exactly I showed you this is how what will happen displacement pattern in a linear change when you are talking about atomic vibrations. Atoms will move like that way from a mean positions to the to the you know both the sides actually left or right and that will lead to pull and push what I discussed in the last lecture.

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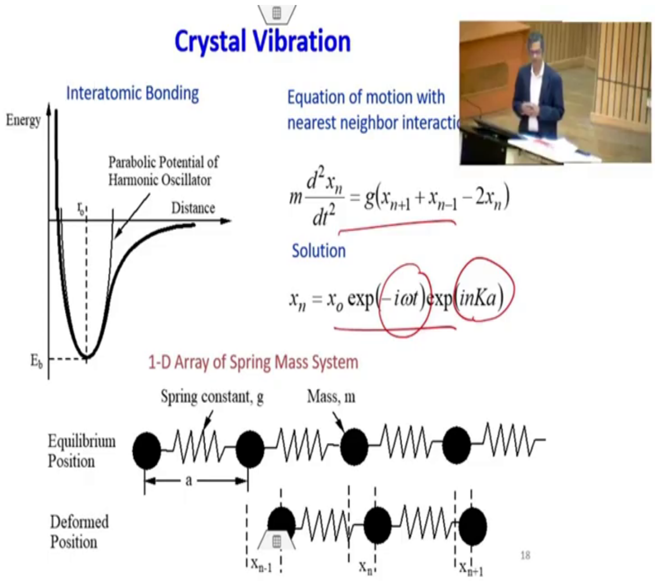

Well, so, that this is the equations I told you and this is the solution of the equations which has two parts exponential parts you see here and this is the time dependent part ok. So, there are two parts of the solutions and as usual and the two parts of solution will give you the whole solution of the whole problem.

This is not difficult. And now in what I am asking you to do is that you have a two different mass of the setting not same mass then how to derive the equation and how to solve the equation that is what is the assignment for you.

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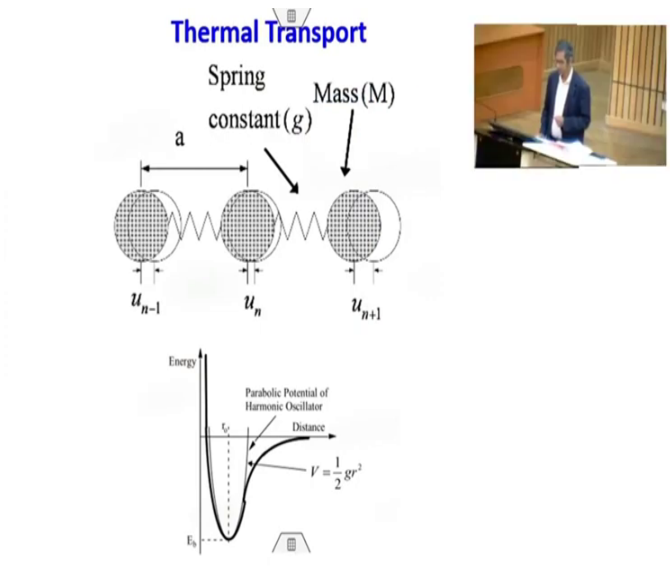

Well so, in a nutshell this is what is phonon and this is these waves will lead to heat transport from material from one part to other part. Now, what happens in nanoscale? Let us discuss ok.

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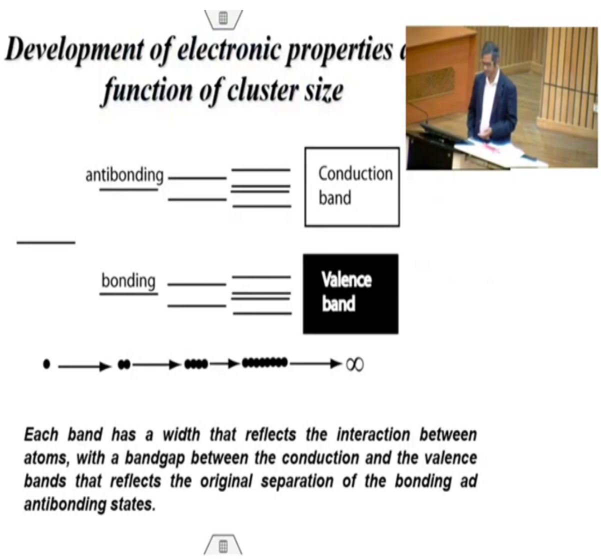

As you know the let us first talk about electrons then we will go to phonons. You know in any materials electrons will occupy bonding and antibonding orbitals, let us start from there correct. And so, therefore, you can have electrons can be quantized the energy levels and that will be forming bands and this band structure is well known in the materials. So, they can be they can be staying in the valence band the conduction bands. The energy gap between the valance band conduction band is known as the energy barrier or the band gap right.

So, in a metal there is overlap between the valence band the conduction band that means, there is no band gap exist in the metal. So, therefore, electrons can easily move from the valence band to the conduction band. That is why we say that in a metal electrons are not bound to a specific atom they are free and we always call them as a electron free electron gas because they behave like a gas, so, then moving from one place to other place.

If you if you put a gas here and if you allow them, it will diffuse from one place to this place to some other one corner of this room, ok. Same thing in a metal electrons are freely moving. So, therefore, there is no band gap, but in a semiconductor or an insulator there is a definite band gap. Electrons cannot simply freely move.

So, in a semiconductor band gap its small so that if you provide some energy thermal energy or maybe some two piece some elements then you can actually move the electrons from valence band to electron bands. Insulators you cannot do that because the gap is so large, electrons can no longer travel from valence band to the conduction band.

And this is what is the common notion of the electronic structure in a material that we all know correct. Everybody knows in this world that this is this band structure exists in a crystalline material correct. So, each band has a width that reflects the interaction between the atoms and the band gap between the conduction and valence bands which reflects the original separation the bonding antibonding states. This is something which you should remember.

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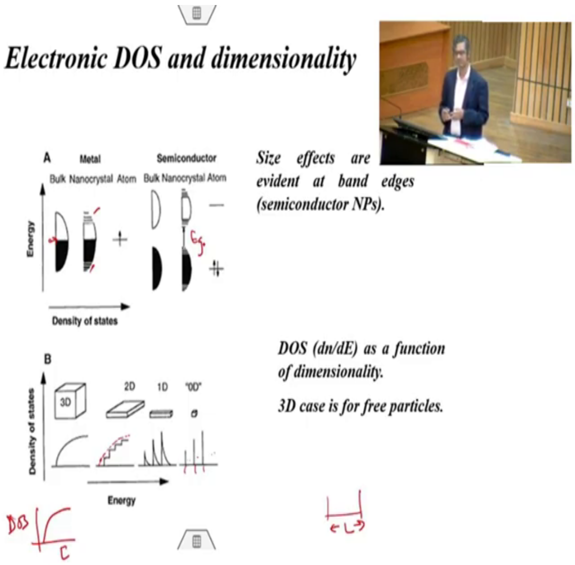

So, now what happens in a when you have nanoparticles, right? So, let us compare bulk versus nanoparticles in composite density of states. In a bulk like here in metal because in metal you have free electrons, in a bulk you can see the conduction bands and the valence bands they are overlapping. And this is the free energy level to which the to the highest energy level to its electrons occupied energy bands with the electrons occupied.

So, there is a specific band right, electrons cannot remain there, but as you make in nano crystalline states. They there will be no specific bands. Electrons will stay even in different discrete energy levels. That is what is shown here and there. We can see discrete energy levels electrons can stay actually right. Am I clear?

So, the 3D the density of states will look like a continuous band ok. This is the density of stage versus energy plot. So, you can clearly see for 3D materials this will behave like this. As your energy level increases the energy level increases the density of state is increasing. Am I clear?

So, that is because you have large number of electrons and they free to move any direction that is why. But, the moment you reduce the size on of the systems and make it nano crystalline energy bands will undergo discretization. Like here it is a 2D material that is a thin film on a substrate you can clearly see instead of a continuous band which is existing in the last case like this ok, you have a discrete energy levels like that.

Why does it happen? That is mainly because of the size ok. What is the effect of size? It is very simple. Electrons have specific wavelengths right. So, when the wavelength of the electrons will be matching with the size of the of these thin films ok or (Refer Time: 33:34) of the matter then there will be interference coming from the size effect right; that is what is known as the effect of dimensionality.

Now, if you do a 1D again there will be more further discretion will happen and 0D it will be like a discrete levels. So, this discretion of this continuous spectrum is what is known as the quantum confinement you are saying. So, there are two words are quantum and confinement. So, what I mean to say is that electron energies are confined to these levels in between they cannot stay. They cannot occupy these energy levels they are not allowed actually and that is coming because of the low dimensionality of the system.

So in a zero dimensional material, where x, y, z directions are nanometric scales electron energy is bounded. So, electrons can only take up specific energy levels. It cannot move into other energy levels like these which are vacant positions and this is known as a quantum confinement. It is just like electrons in a well.

So, if you put electrons in a well of length L what will happen to the energy bands? That is exactly the same thing happens in 3D correct or in 1D or even 2D. In a semiconductor between a bulk and nano crystals again same thing can happen, but only there is a band gap right E g correct. Discretion can happen both in the valance band as well in the conduction band. It can happen in both cases. Insulator this does not matter, it does not make any sense that is why you do not discuss much.

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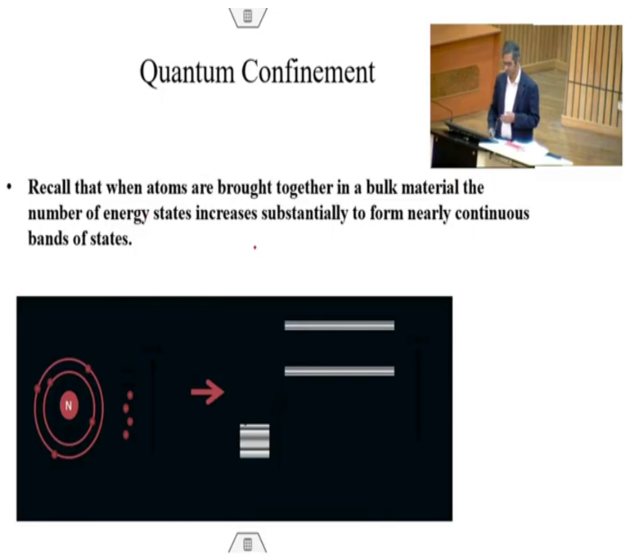

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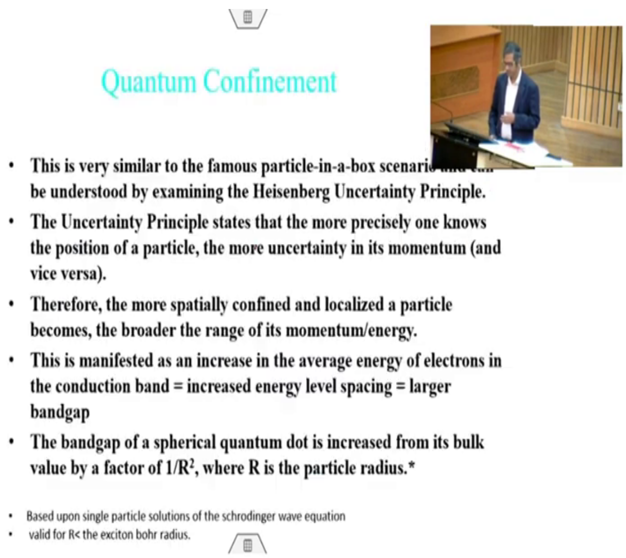

So, quantum confinement is very simple problem. It is familiar to a famous particle in a box situation. And can be understood by simply examining the Heisenberg uncertainty principle. What does it tells? It said that more precisely you know the position of particle more uncertainty you have in momentum right.

Therefore, more partially confined spatially confined localized a particle becomes border will be range of its moment of energy. So, that moment yours the directions or the size of these in a spatial dimension x, y, z are confined their small r fixed ok. The border will be range of this momentum energy ok that is what is the situation. And this is manifest as an increase in the average energy of the electrons in the conduction band equal to increase of energy level spacing and the larger the band gap. So band gap as spherical quantum dot is increased from its bulk or value $1/R^2$. What R is the size or radius of the particle, ok.

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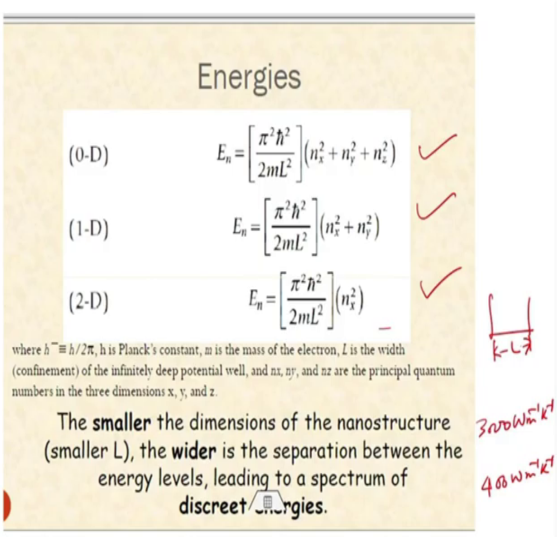

So, now as you know, if you I already discussed your particle in the box situation. What are the particle in the box situations? If you put a particle in a box suppose in case of 0D in case of 2D let us start with that and the 2D is here ok and L is the width of the box. Well, width of the box here L in 2D. In 2D your one of the dimensions is nanometric other two dimensions are non-nanometric domain.

So, you can you need to consider only one of the direction that x. So, their energy levels will be varying like this $\frac{\mu^2\hbar}{2mL^2}n_x^2$. Well, you may be thinking how this equation is derived. This equation is derived simply solving the Schrodinger you know equation and by putting something kinds of you know basic conditions or the boundary conditions actually, but I do not want to solve these things, it is available in the books actually, you find it that.

So, now, $\frac{\hbar}{2mL^2}$ or 2 m is basically momentum ok, you know that basically is coming from the momentum all of you should know that. And L^2 is the basically coming from the length of the box. So, therefore, its energy E_n which is the energy of the any of the band it depends on n x square alright only in x directions.

So, you can add up this for 1D and 2D. In 1D it will be $n_x^2 + n_x^2 + n_z^2$. So, what does it mean? In 1D energy levels are quantized only and confined in x directions, y and z they are free to move. There is no specific you know confinement energy levels in the y and z. Electrons can take any energy levels they want in the y and z directions for 2D materials. For 1D z directions are free x and y are not free. For 0D none is at none are free.

So, one of the dimensions of a nanostructure there is one of the L. What is the separation between the energy levels? That is very clear that is the effect of L. So, leading to spectrum and discrete energy levels. So, this case of energy levels which is shown you here this is coming because of that solution of this problem ok, solution of these quantization problems from the quantum mechanics and this whole thing is known as a quantum confinement or the aspect of quantum confinement.

So, now, as we discuss electrons can get quantized it is confined or they can undergo quantum confinements. Phonons can also because phonons also have wavelengths. So, if the wavelengths of the phonons will it becomes same as the dimension of the material then phonons can also be undergoing the similar kind of situation or confinement situations ok.

So, what will the effect of these aspects? The confinement of electrons and confinement of the phonons what will the effect of these ok both of these two? How, you know that is very important ok. So, how we are going to deal with it? So, let me just discuss a few cases today. One case may be and then we will come back to the next lecture. And this whole thing is nicely described in the book of you know by Ashby Michael Ashby and others.

So, in the bulk homogeneous solid materials wavelengths of the phonons and other electrons will be much much smaller than the length of the material length of the microstructure rather.

Let us talk about microstructure, but the length of the material may be different, but the grain structure microscope is what is very important.

So in a homogeneous bulk material the wavelength of phonons or the electrons will not make anything any difference at all because this length of the microstructures is much much bigger than the wavelengths of this material. But, in nanomaterial length scale of microstructure will be of the similar you know scale as the wavelength of the electrons or the phonons ok.

So, therefore, the quantum confinements is bound to occur or bound to take place. We will talk about phonons first. So, nano material quantum confinement comes in several ways right, you have 0D, 1D, 2D nano materials. 0D nano materials like nano particles, quantum confinements as I discussed can happen in all the three directions.

In one dimensional materials like nanowires or nanotubes confinement happens in two directions and 2D nano materials like a thin films or may be nano coatings quantum confinement can happen in one direction that is exactly as shown in this slide. So, in 0D it can happen three direction, in 1D it can happen two direction and 2D it can happen in one directions.

And this quantum confinement effect is the same for the electrons also. So, you know a good way or a very good way to understand this quantum confinement phase to consider the that presence of surfaces in 1D, 2D and 3D materials or 2D and 1D and 0D material not 3D and these surfaces can cause change in distribution of the phonon frequency their interactions.

So, as I should I tell you that unlike photons phonons can interact and they can change the velocity after the interaction. So, one group of phonons can come and then meet other groups phonon and then the resulting phonon can have a different completely different velocity a complete different frequency or wavelength actually. It is possible which is not possible in case of photons.

So, therefore, both the phonon wavelengths and the appearance of the phonon modes can get changed. And these process can lead to change in the velocity of the phonons and that end lead to oh that is that is nice a group velocity as you know and this is nothing but a group of ring ring of waves forming when you throw stone in the water.

If you throw a stone in the water a ring of waves forms. And if you have several stones falling on the water several ring of waves falls and then they come and interact and create a new wave. And when they create a new wave the group velocity of these waves will be completely different from the individual waves. So, this is something which is unique thing can happen in phonons and this is very important that this interaction of the phonons actually depends on the dimension of the material right.

Now, so, therefore, in zero dimensional structure, what happens? In zero dimensional structure what can happen? The one dimensional, so, a phonon bottleneck occurs in zero dimensional nano structure it will be correct. Phonons cannot move very easily into any other directions, that is what is called prolonged bottlenecks because all energy levels are quantized or they confined. So, because of the confinement in x, y, z directions phonons cannot move.

So, we can make a zero dimensional nanomaterials like quantum dots completely insulator outer metals. Can you imagine that? Metals can never be insulator, insulate in the sense of heat transport right, but you can make it. You can make it by confining the electronic band levels and the phonon energy levels in a zero dimension material that is the this is a real bottlenecks. So, that is why many of these quantum dots can be used for insulators.

See what happens in one dimensional nanomaterials? Which is very interesting. One dimensional nanometrials has two dimensions in nanometric domain and one other directions dimensions in micro meter domains ok. So, they can act as like a phonon waveguide similar to like optical waveguides optical ones for lights ok.

So, for example, if you take a carbon nanotubes. Several investigation shows carbon nanotube has a very high thermal conductivity along the length of the tube. That means, what? The phonons are actually moving very fast in another length of tube just like waveguide ok.

So and it have been found that this value of thermal conductivity can reach as high as 3000 watt per meter per Kelvin. Here pure copper which is a very good thermal conductivity. The conductivity value is only is 400 watt per meter kelvin. So, we are talking about orders of magnitude higher of thermal conductivity in carbon nanotubes in the direction of the tube.

And that is can mainly happen because of what? Because of basically this waveguide because the phonons cannot move freely along other two directions which are spatially confined, phonons move very fast in the z directions ok. So that is something which is very interesting.

Now, what will happen 2D materials we will discuss in a next lecture because the thin film all things will come into picture. So, this is something which you should remember. So, this what I discussed in the lecture let me just summarize. So, I talked about thermal transport. Thermal transport happens because of the electron and as well as the phonon in the materials. Electrons we know that they can easily you know absorb energy and take the energy away.

Phonons are something new. Phonons are lattice vibrations. They are created because of the motion of the atoms from the mean p positions leading to push and pull of the atoms and creating a traveling wave in the material and this waves can take out the energy from one part of the crystal to the other part of the crystal.

Interestingly nanomaterials both electrons energy levels as well as the phononic energy levels can be confined depending on the type of nanomaterials 0D, 1D or 2D and this is a significant effect on the thermal transport and I showed you the case of 0D and the 1D materials today.

Thank you.