Solid State Physics
Lecture 13
Van der Waals attraction

Hello, so, far in this course we have discussed about the structure of Solid. The crystal structure the basis the lattice and how the combination of basis and lattice makes a complete crystal in infinite space. But, we did not consider what binds those atoms in the crystal together. So, here we will discuss about that, what is the binding force of the atoms that makes a crystal. (Refer Slide Time: 00:53)

You are familiar with ionic bonds, covalent bonds, but now let us discuss something interesting. So, if we consider inert gases, if we have very low temperature and high pressure, they can be formed into solids. How? They do not have any ionic force between the atoms. They do not have any covalent interaction as well, in case of inert gases the outermost shell is completely full. So, they are not supposed to interact with each other in any way and if they do not interact, how do they form a solid at all. So, they must interact. And, here we will discuss about different kind of interactions that binds the solid together. Nuclei as we know repel each other and there are electrons around it, that electron cloud also repels each other. Nuclei attract the electron cloud and the electron cloud also attracts the nuclei. And, this must be the main form of binding in crystal, there is very little contribution from magnetic forces. If at all they exist in a solid not every solid is magnetic, there are few solids that are magnetic and the magnetic interaction plays a very tiny role. The gravitational interaction between atoms have no role in crystal binding that can be purely neglected. Now, let us consider the case of the crystal of inert gases. The inert gases form the simplest crystals, the distribution of electron is similar to that of free atoms. So, they do not have any electron sharing or ionization or anything like that. The crystals are very weakly bound just because the interaction must not be strong in that kind of a situation. But, there is some kind of interaction. And, because of that weak binding it has very low melting temperature and all the inert gas crystals are transparent insulating solids. The atoms have very high ionization energies. And, the outermost electron shell are completely filled that must be the case and we can see that, the atoms are packed together in the closest possible way. He, He^4, these have hcp structure and everything else have fcc structure. You have calculated packing fractions and you now know that these are the closest possible binding. So, what holds these atoms the inert gas atoms together? Let us discuss about Van der Waals interaction. So, what is it? What kind of interaction it can be? If you consider two identical atoms of inert gas at the core of that atom there is a nucleus and surrounding is an electron cloud. If you consider the example of Helium there is only s-electrons. So, it is completely the electron distribution is completely spherically symmetric. And, if this arrangement is there, then you have learned from electrostatics that a spherically symmetric charge distribution, it is electric potential behaves as if the entire charge is located at the center of sphere. That means, you can as far as electrostatics is concerned. You can consider that the nucleus the positive charge is located at the center of the atom, the negative charge of that electron that is also located at the center of the atom. So, there is no charge. And, if there is no charge from an atom it cannot have any electric interaction, electrostatic interaction. Then what happens? Then, there can still be dipolar interaction if these two charge centers do not overlap if, they are allowed some fluctuations, some oscillation something like that. So, oscillating dipoles can give us some understanding of this. Let us consider that kind of a situation. As a model let us consider two identical linear harmonic oscillators and we will consider that, they are separated by a distance R, capital R. So, I am drawing one atom, one dipole here. This is the positive charge center and this is the negative charge center, another dipole here positive charge center, negative charge center. And, let us assume that these are connected by a spring so, that we can use the spring constant in our Hamiltonian. So, they are certainly not connected by spring, but we are just thinking that the force between the positive and negative charge centers, they interact with each other, like a spring kind of a potential. We consider the distance between the positive and negative charge centers here as x_1, here it is x_2, and the separation between them is given as capital R. So, how much is capital R? This much this is capital R so, this is our first oscillator and this is our second oscillator that we have considered. Now, each oscillator bears charges, that is $\pm e$, $+e$ here $-e$ here, with separation x_1 and x_2. The dipoles as oscillate along the x direction in one dimension we have considered for simplicity. Now, if we consider that p_1 and p_2 are the momentum. So, let me write it here p_1 is the momentum for this oscillator, p_2 is the momentum for this oscillator, and if C is the force constant corresponding to the spring and we consider identical atoms. So, it is the same force constant similar kind of spring, same force constant. We can write the Hamiltonian of the unperturbed system, that is there are two such oscillating dipoles and they are not interacting between each other. Without any interaction, if we try to write the Hamiltonian that we call the unperturbed Hamiltonian denoted as H_0 can be written as their mass is also identical. So, I am writing m for the mass $\frac{1}{2m}{p_1}^2 + \frac{1}{2m}{p_2}^2 + \frac{1}{2}C{x_1}^2 + \frac{1}{2}C{x_2}^2$, this is also the spring potential from the other dipole. Now, each coupled oscillator is assumed to have the frequency ω_0. What is ω_0? If, we shine light on these atoms individually the charge centers would oscillate about each other as a result of the light. So, there may be different frequencies, we are considering the strongest optical absorption line that is the resonance frequency for this atom. And, that resonance frequency is omega naught. If that is the case; that means, that is the characteristic of this spring. So, we can write that, the spring constant $C = m{\omega_0}^2$. This is the resonance condition for the strongest absorption line, optical absorption line for this atom. (Refer Slide Time: 10:46)

And, now if we consider coulomb interaction so, what allows us to consider any coulomb interaction? If, we see that the charge positive charge center and negative charge center these are separated now in this kind of a situation then, there would be coulomb interaction. And, the coulomb interaction can the Hamiltonian the corresponding to coulomb interaction can be represented as $H_1 = \frac{e^2}{R} + \frac{e^2}{R+x_1-x_2} - \frac{e^2}{R+x_1} - \frac{e^2}{R-x_2}$. So, let us go back to the picture. The positive terms are repulsive term; that means, that is between the positive and positive charge center and the negative and negative charge center. The negative terms are attractive terms between the positive and negative charge center here and the negative and positive charge center here. Now, this Hamiltonian is written in CGS unit. In SI unit it will have some change some dressing would be different, but the physics will remain the same. And, we have already discussed that x_1, the absolute value of $|x_1|$ and absolute value of $|x_2|$, that is the difference between the distance between two charge centers, this is much less than capital R the inter atomic distance. This assumption is a very good assumption excellent assumption, this will be valid for every kind of solid. And, within this assumption we can write $H_1 \cong -\frac{2e^2x_1x_2}{}$. It will be a homework for you to show this, that within this assumption we can reduce H_1 to this approximate form. Now, once we have considered this approximate form, the total Hamiltonian with the approximate form of H_1, if we write $H_0 + H_1$ now and H_1 in this approximate form. We can diagonalize it and find the normal modes,where x_s is the symmetric mode that can be represented as $\frac{1}{\sqrt{2}}(x_1 + x_2)$. And, the anti-symmetric mode x_a, it can be given as $\frac{1}{\sqrt{2}}(x_1 - x_2)$. Showing this is a homework for you, you are supposed to consider you are supposed to add this form of H_1 with H_0 from the previous page, and diagonalize that Hamiltonian. If you diagonalize that Hamiltonian you can use Software's like Mathematica MATLAB or whatever you wish, or you can do it analytically also this is not a big Hamiltonian. You should get the symmetric normal mode, you should get this form and for the anti-symmetric normal mode you should get this form. Now, if we solve for x_1 and x_2 we can write down, x_1 in terms of x_s and x_a, $x_1 = \frac{1}{\sqrt{2}}(x_s + x_a)$. Similarly, $x_2 = \frac{1}{\sqrt{2}}(x_s - x_a)$. (Refer Slide Time: 15:57)

So, if we now write the symmetric and ant-symmetric momenta p_s and p_a; in terms of p_s and p_a we can write $p_1 = \frac{1}{\sqrt{2}}(p_s + p_a)$ and $p_2 = \frac{1}{\sqrt{2}}(p_s - p_a)$. The total Hamiltonian after these transformations can be represented using the normal mode coordinates and the normal mode momenta as $H = [\frac{1}{2m}{p_s}^2 + \frac{1}{2}(C - \frac{2e^2}{R^3}{x_s}^2] + [\frac{1}{2m}{p_a}^2 + \frac{1}{2}(C + \frac{2e^2}{R^3}{x_a}^2]$. This is the total Hamiltonian in terms of normal mode coordinates and normal mode momenta. Once, we have that the normal mode frequencies may be evaluated, the normal mode frequency in this case if we write that as ω can be written as $\sqrt{\frac{C\pm\frac{2e^2}{R^3}}{m}}$. And, this can be represented as $\omega_0[1 \pm \frac{1}{2}(\frac{2e^2}{CR^3}) - \frac{1}{8}(\frac{2e^2}{CR^3})^2 + ...]$ more higher order terms. So, what is omega naught here? ω_0 as we have represented earlier is $\sqrt{\frac{C}{m}}$ square root of this. And, we have obtained this expansion just by expanding the square root. Why did we do that? That will be clear soon, here in this square root we cannot perform few operations that for which we will need this. (Refer Slide Time: 19:51)

Now, let us consider the zero point energy for this coupled oscillating system. In case of classical oscillators we have no zero point energy, but here these are quantum oscillators. So, it cannot have absolute zero, energy it will have certain energy even at the lowest possibility. So, the lowest possible energy is non zero in this case. And, how do we obtain the zero point energy? The zero point energy for this system would be given as $\frac{1}{2}\hbar(\omega_s + \omega_a)$, this comes from the plus minus sign here and here. So, this gives us the zero point energy of this coupled oscillator system because, the interaction, because of this interaction that we have, the sum is less than the uncoupled value of zero point energy. If, we did not have any coupling between the two oscillators, if we consider no coupling, then we have the zero point energy for each oscillator given as $\frac{1}{2}\hbar\omega_0$ and multiply it with 2, because there are two oscillators, this will be the total zero point energy, here the zero point energy is less just because these two oscillators are interacting. Now, if we consider the difference between the zero point energies, that is ΔU that would be the cohesion, that would be the cohesive energy, that is given as $\frac{1}{2}\hbar(\Delta\omega_s + \Delta\omega_a)$. In order to find out $\Delta\omega_s$ and $\Delta\omega_a$, this expansion here this would be of enormous importance. Using this expansion, we can write down the delta expression for $\Delta U = -\hbar\omega_0\frac{1}{8}(\frac{2e^2}{CR^3})^2$ and; that means, we have $\frac{1}{R^6}$ kind of dependence and the rest are just a constant. So, it can be written as $-\frac{A}{R^6}$ where A is the positive constant. So, with a minus sign this is an attractive interaction you can clearly see and this is attractive just because, this zero point energy of the coupled oscillator is less than the zero point energy of the oscillator without considering any coupling. That is the reason that this difference this energy that we have found here is attractive. And, it goes as this attractive energy goes as $\sim R^{-6}$, this is the leading attractive term. Of course, if you take this expansion a bit further, you will get more attractive terms, but their contributions would be much less than this term. This kind of interaction is called the Van der Waals interaction. It also has other names like London interaction or simply the dipole dipole interaction, note something interesting. If we had classical mechanics in our mind we could not have derived any such interaction. Because, we derived this interaction by considering the difference between the zero point energies, in case of interacting and non-interacting system. In case of classical system there is no zero point energy and if there is no zero point energy there is no difference as well. So, this interaction energy that is the Van der Waals interaction energy that we have calculated now has purely quantum origin if there is no classical analog to this kind of interaction.