Solid State Physics
Lecture 15
Equilibrium Lattice Constant and Cohesive Energy

Hello, we have discussed the van der Waals attractive interaction and the repulsive interaction for rising due to Pauli Exclusion Principle. Now, we will discuss the Equilibrium Lattice Constant. (Refer Slide Time: 00:39)

If we neglect the kinetic energy of the inert gas atoms, the cohesive energy of the inert, of the gas crystal is given by summing over the Lennard Jones potential that we have found earlier. If there are capital N number of atoms in the crystal then the total potential energy from the expression for Lennard Jones potential can be found as U_{tot} is the total potential $= \frac{1}{2}N\ 4\epsilon[\Sigma'_j(\frac{\sigma}{p_{ij}R})^{12} - \Sigma'_j(\frac{\sigma}{p_{ij}R})^6]$. So, what do we mean by sum prime? Sum prime means that $i \neq j$; j is running over all its possible values, but it cannot include i; i is excluded. But why are we talking about that? Are we summing over i at all? Yes, we are doing that, we are also summing over i and if you can see that if we sum over also i that will give us a factor of the total number of atoms. So, this N comes because we have also summed over i. Sum prime in both cases; exclude the situation that $i = j$ that is excluded. Let me write that clearly, $i = j$ this situation is excluded by putting this prime here. Why half? Because we have double counted each interaction; we have counted the interaction twice, so we have to put a factor of half, so that each interaction is counted only once. Now, let us consider an example. If we consider fcc structure, that is the structure for most of the inert gas crystals. So, this is the most relevant example, we can calculate $\Sigma'_j p_{ij}{}^{-12}$. So, what is p_{ij} here? $p_{ij}R$, R is the nearest neighbour distance; so this gives us the distance between two atoms. So, p_{ij} is rather a scaling factor. That, so $p_{ij}{}^{-12}$; if we Σ'_j, we will get 12.13188 for fcc structure. And if we perform the other $\Sigma'_j(\frac{\sigma}{p_{ij}R})^6$, that is going to give us 14.45392. So, in fcc we have 12 nearest neighbours and the these two series is they rapidly converge. Now, the nearest neighbours contribute the maximum of the interaction energy in the inert gas crystal, which is obvious. If we consider hcp structure, then what happens to this sum? $p_{ij}{}^{-12}$, this sum goes to 12.13229 and this one $p_{ij}{}^{-6}$, that goes to 14.45489. So, you can see that the numbers are not much different; up to the second decimal place it is exactly the same, there is no difference whatsoever. And only helium has hcp structure among the inert gas crystals, everything else have fcc structure; but we can express these values as the same value, there is no problem. (Refer Slide Time: 07:02)

If we do that, then we if we consider U total as the total energy of the crystal; the equilibrium value of the distance nearest neighbour distance if we write that as R_0, then we shall have $\frac{dU_{tot}}{dR}|_{R=R_0}$, this will be 0; because the potential has a minimum here. And if we calculate in cgs unit this from the Lennard Jones potential, from the sum the that we have found this quantity,U_{tot}; differentiating that we will find $-2N\epsilon[12 \cdot (12.13)\frac{\sigma^{12}}{R^{13}} - 6 \cdot (14.45)\frac{\sigma^6}{R^7}]$. Which after solving for R_0, so, here at $R = R_0$, these quantities will be R_0. And if we now solve for R_0; we will find $\frac{R_0}{\sigma} = 1.09$. So, after determining this, can we find the cohesive energy? So, what is cohesive energy? The cohesive energy of the inert gas crystals at absolute zero and at zero pressure when there is no external pressure is obtained by putting the value of R_0 in the expression of U_{tot} that we have calculated earlier. So, that means $U_{tot}(R_0)$ this quantity gives us the cohesive energy, which is $-(2.15)(4N\epsilon)$. And this is the expression this is same for all inert gases, rather inert crystals; but there is a quantum mechanical correction on top of this. So, let us discuss the origin of the quantum mechanical correction and this quantum mechanical correction is more pronounced for lighter atoms like helium than heavier atoms. (Refer Slide Time: 11:08)

So, we can understand the origin of the quantum mechanical correction by considering a simple model. If we consider an atom confined by fixed boundaries and if the particle has the quantum wavelength λ, which is the Broglie wavelength; then the particle will have a kinetic energy, that is

$\frac{p^2}{2M}$ for atoms, that is given as= $\frac{(\frac{h}{\lambda})^2}{2M}$. What is p? According to the Broglie hypothesis, we know that $p = \frac{h}{\lambda}$ the Broglie wavelength. From this model the quantum zero point correction to the energy is inversely proportional to the mass. So, if we have heavier mass, there would be less correction and if we have lighter mass, we will have more quantum correction in the system.