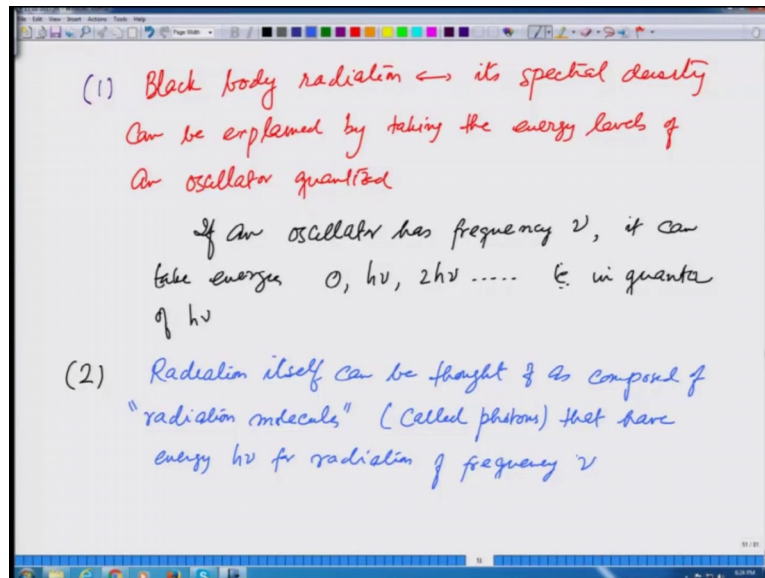


Introduction to Quantum Mechanics
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Lecture - 09
Quantum hypothesis and specific heat of solids

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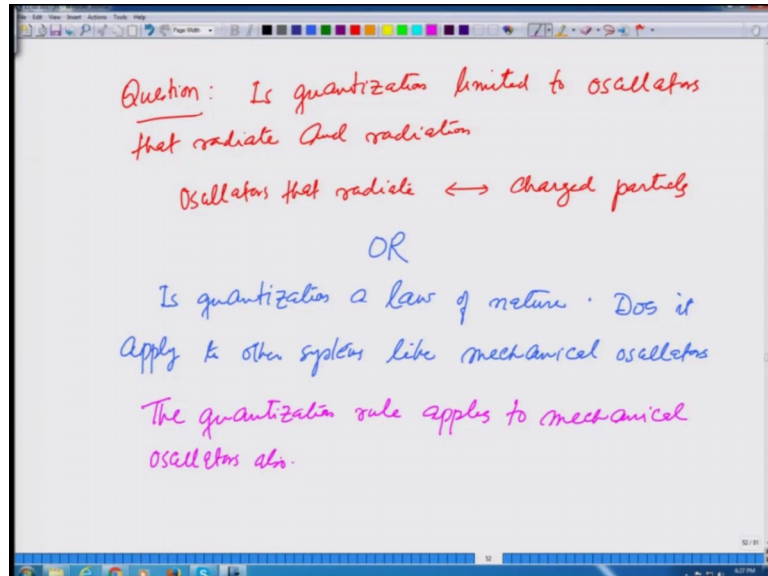


So, what we have done in the lecture so far is that established through experiments and that is very important to understand experiments that number one: black body radiation and that means its spectral density can be explained by taking the energy levels of an oscillator quantized. And what does that mean? That means, if an oscillator has frequency ν , it can take energies $0, h\nu, 2h\nu$ and so on n that is n quanta of $h\nu$ and through this, we obtained a spectral density curve that fit at the experiments perfectly and it also went to in the 2 limits ν over T being very large and very small, it went to the respective Wien's and Rayleigh Jean's formula.

Number 2; not only this, what we also saw is that radiation itself can be thought of as composed of let us call radiation molecules and I am using that term, the literately to show you because it came from the considerations of entropy change of radiation when it expanded, keeping the energy same and the volume increase from v_1 to v_2 and it was the same as an ideal gas. So, radiation molecule and then called photons that have energy $h\nu$ for radiation of frequency ν .

So, on one hand, I have oscillators that radiate that have energy $h\nu$ and so on the other radiation itself has energy $h\nu$.

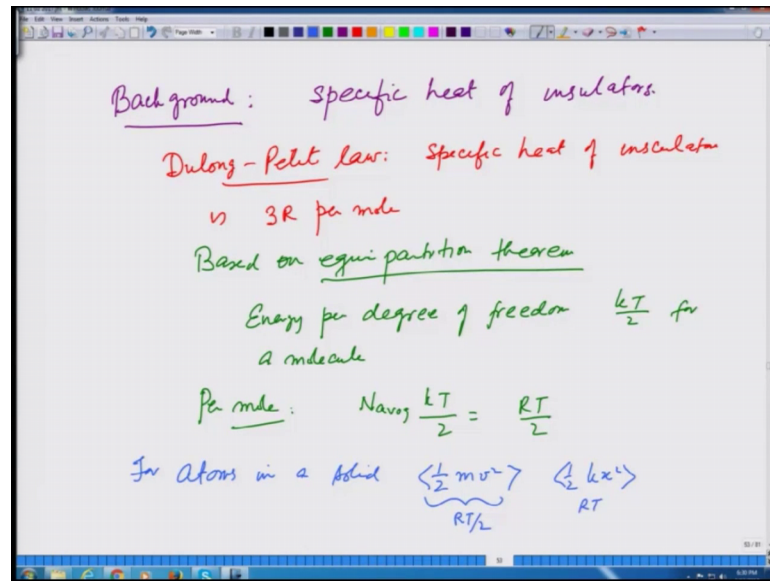
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Now the question that arises and let me write that question is quantization; that means, energy coming in units of $h\nu$ and so on limited to oscillators that radiate and radiation explain. Now, let me explain that oscillators that radiate are charged particles and as they accelerate and go back and forth, they start giving out radiation of the same frequency and radiation of course, as light or whatever. So, is it limited to this or is it more general or so, let us see that question or is quantization a law of nature and; that means, does it apply to other systems like mechanical oscillators and we will see atoms and all that.

And it turns out that this is more general and it becomes a law of nature. So, all this built up slowly. Now, in this lecture, what we are going to discuss is that the quantization rule applies to mechanical oscillators, also one thing you must keep in mind through all this is that test of any theory or hypothesis is its confirmation by experiments that is what science says whatever I can propose should be very far fixable by experiments or must explain an experiment and experiments based on the experiments or experiments to do that check that theory.

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So, a background, I am going to give you a specific heat of insulators and what was known in this was something called that Dulong Petit law that said that specific heat of insulators is $3R$ per mole and this was based on equipartition theorem; recall what equipartition theorem is; equipartition theorem says that energy per degree of freedom is $kT/2$ for a molecule. So, per mole energy is going to be n Avogadro times $kT/2$ which is nothing but $RT/2$ what Dulong and Petit law observed is that for atoms in a solid energy is $1/2 m v^2$ average kinetic energy and $1/2 k x^2$ average potential energy both are quadratic and both average $RT/2$ $RT/2$ for each degree of freedom.

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3d solid (3 dimensional)

Each atom has energy

$$KE = \left\langle \frac{3}{2} m v^2 \right\rangle_{av} = \frac{3RT}{2} / \text{mole}$$
$$PE = \left\langle \frac{3}{2} k x^2 \right\rangle_{av} = \frac{3RT}{2} / \text{mole}$$
$$\text{Total Energy} = 3RT$$
$$\text{Specific heat} = \frac{d(3RT)}{dT} = 3R \approx 24 \text{ J/mole}$$

C

T →

This could not be explained by classical equipartition theorem

T

Now, this is in one dimensional case in 3 d, what we are going to have? So, if this is 3 d solid by 3 d, I mean 3 dimensional, each atom has 3 degrees of freedom. So, each atom has energies kinetic energy is 3 by 2 m v square which average value by this. This bracket I mean average is 3 R T by 2 per mole and potential energy is 3 by 2 k x square; average is going to be 3 R T by 2 per mole. So, the total energy is going to be 3 R T.

And therefore, specific heat; that means, specific heat per mole is going to be 3 R T d by d T equals 3 R which is roughly 24 joules per mole, R is roughly a joules. Now this is fine, this is what was observed that if you plot specific heat versus T, it was roughly 24 joules. However, as T went down, as T was reduced, what one observed was that the specific heat went down and become 0 like this for T tending to 0 and this could not be explained, this could not be explained by classical equipartition theorem could quantum theory come to rescue and that is precisely what happens.

Now, we have already seen earlier while discussing the development of quantum theory that equipartition was theorem did not hold in case of black body radiation, if it did Rayleigh Jean's formula would have been, alright. So, one should not expect that it would hold in other systems if this is the general theory. So, let us see now, how quantum mechanics ideas quantum mechanical ideas at that time explained the specific heat going to 0 as T goes to 0.

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Average energy / oscillator = $\frac{h\nu}{e^{h\nu/kT} - 1}$

An oscillator can have energies $0, h\nu, 2h\nu, \dots$

Probability of having energy $n h\nu$ = $\frac{e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}}$

$$E_{av} = \frac{\sum_{n=0}^{\infty} n h\nu e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

For N particles $E(T) = (3N) \left(\frac{h\nu}{e^{h\nu/kT} - 1} \right)$

$$E(T) = \frac{3N h\nu}{e^{h\nu/kT} - 1}$$

Now we have already calculated that average energy per oscillator is equal to $h\nu$ equals divided by $e^{h\nu/kT} - 1$. This is what we had calculated, just to recap; how did we do that; we said that an oscillator can have energies $0, h\nu, 2h\nu$ and so on and probability of having energy $n h\nu$ is nothing but $e^{-nh\nu/kT}$ divided by summation over n equals 0 to infinity $e^{-nh\nu/kT}$. And we multiply it by the probability with the energy and we got the average energy average; $E_{average}$ at temperature T was equal to $h\nu e^{-nh\nu/kT}$ summed over n equal 0 to infinity divided by summation n equals 0 to infinity $e^{-nh\nu/kT}$ and this gave me $h\nu$ over $e^{h\nu/kT} - 1$.

And therefore for N particles, I am going to have $3N$ that is $3N$ degrees of freedom and each degree of freedom has energy $e^{h\nu/kT} - 1$. This is going to be the energy of the system $E(T)$. So, for a solid that has N atoms, each degree of freedom has frequency ν the total energy $E(T)$ is given by $3N h\nu$ over $e^{h\nu/kT} - 1$.

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$$E(T) = \frac{3N h \nu}{e^{h\nu/kT} - 1}$$

$$C = \frac{dE}{dT} = 3N h \nu \frac{d}{dT} \left(\frac{1}{e^{h\nu/kT} - 1} \right)$$

$$= \frac{3N h \nu \times (e^{h\nu/kT}) \times \frac{h\nu}{kT^2}}{(e^{h\nu/kT} - 1)^2}$$

$$= \frac{3N h^2 \nu^2}{kT^2} \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

As $T \rightarrow 0$, $e^{h\nu/kT} \rightarrow \infty$

$$C = \frac{3 h^2 \nu^2}{kT^2} e^{-h\nu/kT} \rightarrow 0$$

So, we found applying quantum ideas energy for N particles is going to be $3 N h \nu$ over e raise to $h \nu$ over $k T$ minus 1 and therefore, specific heat; I am not going to the certainties of whether it is constant volume or constant pressure for solids, it does not really matter if their compressibility is very small.

So, C_p and C_b do not really differ by much is going to be dE by dT which is going to be $3 N h \nu$ d by dT of 1 over e raise to $h \nu$ over $k T$ minus 1 which is nothing but $3 N h \nu$ divided by e raise to $h \nu$ over $k T$ minus 1 square times e raise to $h \nu$ over $k T$ times $h \nu$ over $k T$ square. So, this is equal to $3 N h$ square ν square over $k T$ square e raise $h \nu$ over $k T$ over e raise to $h \nu$ over $k T$ minus 1 whole square and if you plot it as a function of temperature as T goes down, this fellow goes to 0 exponentially. To see this, let T go to 0, then e raise to $h \nu$ over $k T$ goes to a very large number. And therefore, I can write C as $3 h$ square ν square over $k T$ square e raise to minus $h \nu$ over $k T$ and that goes to 0.

So, that explained that specific heat should go to 0 as T goes to 0, if you follow quantum ideas and that again established the trust in quantum theory. Let us see if it needs to Dulong Petit law also.

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The image shows a handwritten derivation of the Einstein model for specific heat C . The derivation starts with the formula $C = \frac{3h^2\nu^2}{kT^2} \cdot \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$. It then states that as $T \rightarrow \infty$, $e^{h\nu/kT} \approx 1 + \frac{h\nu}{kT}$. Substituting this approximation into the formula, it shows the cancellation of terms, leading to $C = 3kN$ or $3k$ per atom, which is identified as $3R$. The final note states: "Model of calculating C is known as 'Einstein Model'".

$$C = \frac{3h^2\nu^2}{kT^2} \cdot \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

As $T \rightarrow \infty$, $e^{h\nu/kT} \approx 1 + \frac{h\nu}{kT}$

$$C = \frac{3h^2\nu^2}{kT^2} \times 1 \times \left(\frac{1}{1 + \frac{h\nu}{kT} - 1} \right)^2$$
$$= \frac{3h^2\nu^2}{kT^2} \times 1 \times \frac{k^2T^2}{h^2\nu^2}$$
$$= 3kN \quad 3k/\text{atom}$$
$$= 3R$$

Model of calculating C is known as "Einstein Model"

So, what we have calculated is C equals $3h^2\nu^2$ over kT^2 times $e^{h\nu/kT}$ divided by $(e^{h\nu/kT} - 1)^2$. Now as T goes to a large value, I can write $e^{h\nu/kT}$ roughly equal to $1 + \frac{h\nu}{kT}$. And therefore, C is $3h^2\nu^2$ over kT^2 times 1 times 1 over $1 + \frac{h\nu}{kT} - 1$ whole square and that becomes $3h^2\nu^2$ over kT^2 times 1 times k^2T^2 over $h^2\nu^2$. And if we cancel terms $h^2\nu^2$ rows 1 of the k s goes with 1 of the k s here and T^2 is also cancels and you get the result which is $3k$ times N or $3k$ per atom which is indeed $3R$.

So, not only when I apply quantum ideas to mechanical oscillators, I explain that C goes to 0 as T goes to 0 , it also goes to the correct limit in high temperature. By the way, this model of calculating C is known as Einstein model. So, I conclude this, this section by emphasizing that Einstein applied the ideas of an oscillator having quantized values of energies to explain the vanishing of specific heat of solids as temperature goes to 0 and that gave a little more trust in quantum theory.

In the coming 2 lectures this week, I am going to now discuss how quantum ideas were also applied to other systems to explain say hydrogen spectrum and the energy level of an oscillator in general, and this sort of started building up quantum theory.