LECTURE #19

QUANTUM THEORY OF THE HARMONIC CRYSTAL

THUS FAR OUR ANALYSIS OF PHONONS HAS EXPLOITED CONCEPTS AND TECHNIQUES FROM CLASSICAL PHYSICS. HOWEVER, PHONONS ARE QUANTUM ENTITIES THAT WILL EXPLOIT THE QUANTUM STATISTICAL MECHANICS OF BOSONS.

SINCE PHONONS AND PHOTONS HAVE SIMILAR (BUT NOT IDENTICAL) BEHAVIOR, WE WILL FIRST REVIEW THE QUANTUM THEORY OF PHOTONS.

PHOTONS: QUANTA OF THE ELECTROMAGNETIC FIELD

PROPERTIES:

(1) PHOTONS ARE IDENTICAL BOSONS WITH SPIN 1
(2) PHOTONS ARE MASSLESS $\Rightarrow$ RELATIVISTIC
(3) $E = h\nu = \hbar\omega$
(4) WAVE NUMBER: $k = \frac{2\pi}{\lambda} = \frac{\omega}{c} \Rightarrow \omega = ck$
(5) TWO SPIN STATES (POLARIZATIONS) : $m_s = \pm 1$
(6) # OF PHOTONS IS NOT A CONSERVED QUANTITY (AS TEMP $\uparrow$, # OF PHOTONS/VOLUME $\uparrow$)

RECALL: FROM QUANTUM STATISTICAL MECHANICS:

$$N_n = \frac{d_n}{e^{(\alpha + \beta E_n)} - 1}$$

MOST PROBABLE OCCUPATION # FOR IDENTICAL BOSONS

PROPERTY #6 $\Rightarrow$ $\sum_{n=1}^{\infty} N_n \neq N$

$\therefore$ THE LAGRANGE MULTIPLIER, α, DOES NOT APPLY

$\Downarrow$

$$\boxed{\alpha = 0}$$

AS ALWAYS, $\boxed{\beta = \frac{1}{K_B T}}$

PROPERTY #3 $\Rightarrow$ $\boxed{E_n = \hbar \omega}$

d_n IS THE # OF STATES WITH ENERGY $E_n = \hbar\omega$

FOR FREE PHOTONS IN A BOX OF VOLUME V,

SPIN

$$d_n = \frac{2\left(\frac{1}{8}\right) 4\pi k^2}{\pi^3/V} = \frac{V}{\pi^2} k^2 dk$$

BUT, PROPERTY #4 $\Rightarrow$ $k = \frac{\omega}{c}$, $dk = \frac{d\omega}{c}$

$$\therefore \boxed{d_n = \frac{V}{\pi^2 c^3} \omega^2 d\omega}$$

$$N_n = \frac{V\omega^2 d\omega}{\pi^2 c^3 \left(e^{\hbar\omega/K_B T} - 1\right)}$$

NOTE: THE ENERGY DENSITY IN FREQUENCY RANGE $d\omega$ IS:

$$\rho(\omega) d\omega = N_n \hbar\omega / V = \frac{\hbar \omega^3 d\omega}{\pi^2 c^3 \left(e^{\hbar\omega/K_B T} - 1\right)}$$

$$\therefore \boxed{\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3 \left(e^{\hbar\omega/K_B T} - 1\right)}}$$

PLANCK FORMULA FOR THE BLACKBODY SPECTRUM

<u>NOTE</u>: TO CALCULATE THE TOTAL ENERGY DENSITY, $\rho(\omega)$ IS INTEGRATED FROM $\omega = 0$ TO $\omega = \infty$ SINCE THE NUMBER OF ELECTROMAGNETIC MODES IN A CAVITY IS UNBOUNDED.

$\Rightarrow$ THIS INTEGRATION LEADS TO THE STEFAN-BOLTZMANN LAW OF RADIATION WHERE THE TOTAL ENERGY DENSITY IS PROPORTIONAL TO T^4.

<u>PHONONS</u>: QUANTA OF THE ENERGY OF AN ELASTIC WAVE

<u>PROPERTIES</u>:

(1) PHONONS ARE IDENTICAL BOSONS WITH SPIN 1
(2) PHONONS ARE NON-RELATIVISTIC
(3) $E = \hbar\omega$
(4) THE DISPERSION RELATION IS MORE COMPLEX THAN PHOTONS (e.g., OPTICAL AND ACOUSTICAL BRANCHES)
(5) THREE SPIN STATES (POLARIZATIONS): 2 TRANSVERSE AND 1 LONGITUDINAL
(6) # OF PHONONS IS NOT A CONSERVED QUANTITY (BUT THE # OF PHONONS IS BOUNDED SINCE THERE ARE A FINITE # OF OSCILLATORS PER VOLUME)

LIKE PHOTONS, THESE PROPERTIES IMPLY THAT $\alpha = 0$, $\beta = 1/k_BT$, AND $E_n = \hbar\omega$.

$$\therefore \quad N_n = \frac{d_n}{e^{\hbar\omega/k_BT} - 1}$$

d_n IS DICTATED BY THE DISPERSION RELATION WHICH QUALITATIVELY DIFFERS FOR THE OPTICAL AND ACOUSTICAL BRANCHES.

OPTICAL BRANCH → EINSTEIN MODEL

SINCE THE DISPERSION RELATION FOR THE OPTICAL BRANCH IS RELATIVELY FLAT, EINSTEIN ASSUMED THAT THE N ATOMS OF THE LATTICE ARE OSCILLATORS OF THE SAME FREQUENCY ω_0

3 POLARIZATIONS

$$\therefore \quad d_n = 3N\,\delta(\omega-\omega_0)\,d\omega$$

$$\therefore \quad N_n = \frac{3N\,\delta(\omega-\omega_0)\,d\omega}{e^{\hbar\omega/K_BT}-1}$$

$$\therefore \quad u = \int_0^\infty \frac{3N\hbar\omega\,\delta(\omega-\omega_0)\,d\omega}{V\left(e^{\hbar\omega/K_BT}-1\right)} = \frac{3n\hbar\omega_0}{e^{\hbar\omega_0/K_BT}-1}$$

$$c_v = \frac{\partial u}{\partial T} = -\frac{3n\hbar\omega_0}{\left(e^{\hbar\omega_0/K_BT}-1\right)^2}\,e^{\hbar\omega_0/K_BT}\left(-\frac{\hbar\omega_0}{K_BT^2}\right)$$

$$= 3nk_B\left(\frac{\hbar\omega_0}{K_BT}\right)^2 \frac{e^{\hbar\omega_0/K_BT}}{\left(e^{\hbar\omega_0/K_BT}-1\right)^2}$$

<u>DEFINE</u>: EINSTEIN TEMPERATURE: $\theta_E = \dfrac{\hbar\omega_0}{K_B}$

IF $T \gg \theta_E$, $\quad e^{\theta_E/T} \simeq 1 + \dfrac{\theta_E}{T} + \ldots$

$$\therefore \quad C_V \simeq 3nK_B\left(\frac{\theta_E}{T}\right)^2 \frac{1}{\left(1+\frac{\theta_E}{T}-1\right)^2} = 3nk_B\left(\frac{\theta_E}{T}\right)^2\left(\frac{T}{\theta_E}\right)^2 = 3nK_B$$

$\therefore$ FOR HIGH TEMPERATURES, $C_v \to 3nk_B$

(IN AGREEMENT WITH EXPERIMENTAL DATA)

HOWEVER, IN THE LOW TEMPERATURE LIMIT, C_v DROPS EXPONENTIALLY.

$\Rightarrow$ DIFFICULTY IN THERMALLY EXCITING OPTICAL PHONON MODES AT LOW TEMPERATURE

$\Rightarrow$ ACOUSTICAL MODES ARE NEEDED TO EXPLAIN $C_v \propto T^3$ AT INTERMEDIATE TEMPERATURES

ACOUSTICAL BRANCH → DEBYE MODEL

IN THE LIMIT OF SMALL K, WE SHOWED THAT THE DISPERSION RELATION FOR THE ACOUSTICAL BRANCH WAS LINEAR:

i.e., $\omega = vK$

$\therefore$ d_n IS THE SAME AS PHOTONS EXCEPT $c \to v$ AND SPIN DEGENERACY $2 \to 3$

$$\therefore \quad d_n = \frac{3V}{2\pi^2 v^3}\omega^2 d\omega \Rightarrow N_n = \frac{3V\omega^2 d\omega}{2\pi^2 v^3 (e^{\hbar\omega/k_BT} - 1)}$$

SINCE THERE ARE A FINITE NUMBER (3N) OF PHONON MODES, ω MUST BE BOUNDED.

$$\therefore \int_0^{\omega_D} \frac{3V}{2\pi^2 v^3}\omega^2 d\omega = \frac{V\omega_D^3}{2\pi^2 v^3} = 3N$$

$$\therefore \quad \boxed{\omega_D = v(6\pi^2 n)^{1/3}} \quad \text{DEBYE CUTOFF FREQUENCY}$$

$$\therefore u = \frac{1}{V}\int_0^{\omega_D} \frac{3V(\hbar\omega)\,\omega^2 d\omega}{2\pi^2 v^3 (e^{\hbar\omega/k_BT} - 1)}$$

$$\therefore c_V = \frac{\partial u}{\partial T} = \frac{3\hbar}{2\pi^2 v^3}\int_0^{\omega_D} -\frac{\omega^3 d\omega}{(e^{\hbar\omega/k_BT}-1)^2}\, e^{\hbar\omega/k_BT}\left(-\frac{\hbar\omega}{k_BT^2}\right)$$

$$= \frac{3\hbar^2}{2\pi^2 v^3 k_B T^2}\int_0^{\omega_D} \frac{\omega^4 e^{\hbar\omega/k_BT}}{(e^{\hbar\omega/k_BT}-1)^2}\, d\omega$$

LET $x = \frac{\hbar\omega}{k_BT} \Rightarrow \omega = \frac{k_BTx}{\hbar}$, $d\omega = \frac{k_BT}{\hbar}dx$

$x_D = \frac{\hbar\omega_D}{k_BT} = \frac{\theta_D}{T}$ (DEFINING $\theta_D = \frac{\hbar\omega_D}{k_B}$ = DEBYE TEMP.)

$$\therefore c_V = \frac{3\hbar^2}{2\pi^2 v^3 k_B T^2}\left(\frac{k_BT}{\hbar}\right)^5 \int_0^{x_D} \frac{x^4 e^x}{(e^x-1)^2}\, dx$$

$$= \frac{3k_B}{2\pi^2}\left(\frac{k_B}{\hbar v}\right)^3 T^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x-1)^2}\, dx$$

NOTE: $\theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar v}{k_B}(6\pi^2 n)^{1/3}$

$$\Rightarrow \left(\frac{k_B}{\hbar v}\right)^3 = \frac{6\pi^2 n}{\theta_D^3}$$

$$\therefore \boxed{c_V = 9k_B n\left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x-1)^2}\, dx}$$

NOTE: FOR $T \gg \theta_D$, $x_D \to 0 \Rightarrow e^x \approx 1 + x + \cdots$

$$\therefore c_V = 9k_B n\left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{x^4}{(1+x-1)^2}\, dx = 3k_B n\left(\frac{T}{\theta_D}\right)^3 x_d^3$$

$$= 3k_B n\left(\frac{T}{\theta_D}\right)^3\left(\frac{\theta_D}{T}\right)^3 = 3nk_B \quad \text{(AS EXPECTED)}$$

FOR $T \ll \theta_D$, $x_D \to \infty$

$$\therefore C_V = 9 k_B n \left(\frac{T}{\theta_D}\right)^3 \underbrace{\int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx}_{4\pi^4/15}$$

$$\therefore C_V = \frac{12\pi^4}{5} k_B n \left(\frac{T}{\theta_D}\right)^3$$

$\Rightarrow$ THE DEBYE MODEL LEADS TO $C_V \propto T^3$
(IN AGREEMENT WITH EXPERIMENTAL DATA)

OTHER NOTES ON PHONONS:

(1) PHONONS EFFECTIVELY ACT AS IF THEY HAVE A MOMENTUM $p = \hbar k$ (CRYSTAL MOMENTUM)

$\Rightarrow$ WHEN OTHER PARTICLES INTERACT WITH PHONONS, ENERGY AND MOMENTUM CONSERVATION WILL, OF COURSE, PLAY AN IMPORTANT ROLE.

(2) ANHARMONIC CRYSTAL INTERACTIONS (i.e., $V(x) = cx^2 - gx^3 - fx^4 - \cdots$) LEAD TO THEORIES OF:

(A) THERMAL EXPANSION
(B) CORRECTIONS TO ELASTIC CONSTANTS
(C) MULTI-PHONON INTERACTIONS