PHYS 460 - LECTURE 7

IN RECENT LECTURES, WE HAVE BEEN ADDRESSING THE ISSUE OF PERIODIC ATOMIC LATTICES AND HOW BEST DESCRIBE. WE TALKED ABOUT RECIPROCAL SPACE AND BRILLOUIN ZONES AND THE NUMBER AND TYPES OF WAVES SUPPORTED INSIDE A PERIODIC STRUCTURE. WE ARE GOING TO USE THESE CONCEPTS IN DESCRIBING ELECTRON MOTION, BUT FIRST I WOULD LIKE TO DISCUSS A DIFFERENT SET OF MOTIONS, WHICH INVOKE MANY OF THE SAME IDEAS: PHONONS

THE NEXT COUPLE OF LECTURES THEN WILL DEAL WITH THE ANSWER TO A VERY SAMPLE QUESTION: WHAT HAPPENS IF WE RELAX THE CONSTRAINT THAT NULEI SIT ON RIGID LATTICES? HOW DO WE DESCRIBE DEVIATIONS OF ATOMS FROM EQUILIBRIUM POSITIONS?

THE ANSWER, OF COURSE, IS THAT ATOMS JIGGLE ABOUT THEIR EQUILIBRIUM POSITIONS, AND SINCE THEY ARE INTERACTING, THIS MOTION INVOLVES (IT TURNS OUT) SOME CORRELATIONS BETWEEN ATOMS. THESE CORRELATED VIBRATIONAL MODES ARE WHAT WE CALL "PHONONS", AND THEY ARE OF FUNDAMENTAL IMPORTANCE.

THE IMPORTANCE OF PHONONS IS CLEAR FROM THEIR IMMEDIATE IMPACT ON MEASURABLE QUANTITIES. IN FACT, THOUGH I CHOSE TO START DISCUSSING DRUDE THEORY AND METALS, SIMON INSTEAD POINTED ~~TO~~ FIRST TO

A CLASS OF THEORIES DEVELOPED AROUND THE SAME TIME. TO EXPLAIN WHAT WAS KNOWN (FOR ALMOST 80 YEARS) ABOUT THE HEAT CAPACITY OF SOLIDS: $C_V = \frac{\partial \langle E \rangle}{\partial T}\Big|_V$

EXPERIMENTAL FACT ① $C_V = \gamma T + A T^3$ AT LOW TEMPS

$\gamma \neq 0$ FOR METALS

$A \neq 0$ FOR <u>EVERYTHING</u>

② $C_V \rightarrow 3 k_B$ per atom as $T \rightarrow \infty$

(OR $C_V \rightarrow 3R$ per mole)

LAW OF DULONG-PETIT

SIMON GIVES THE FOLLOWING TIMELINE (WHICH I WILL REPEAT AS THE MENTIONED THEORIES ARE STILL DISCUSSED TODAY!)

1819 – STATEMENT LAW OF DULONG-PETIT

1896 – DEVELOPMENT OF BOLTZMAN THEORY OF ATOMIC MOTION

1907 – EINSTEIN THEORY OF ATOMIC MOTION (AND DERIVATION OF BOSE STATISTICS)

1912 – DEBYE THEORY OF ATOMIC MOTION (AND DEFINITION QUANTIZATION OF LATICE MOTION)

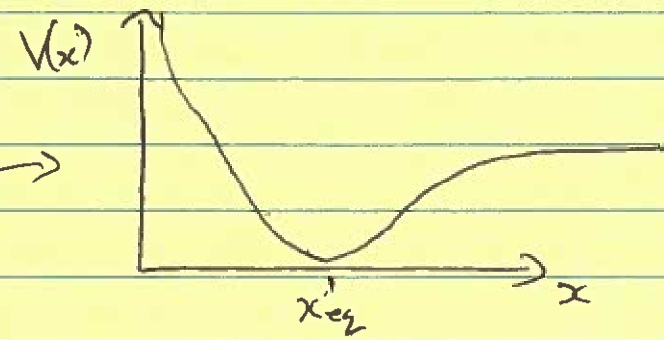
~~A~~ THE LATTER TWO THEORIES PRECEDED THE ADVENT OF QUANTUM MECHANICS, BUT ULTIMATELY

CAN BE CAPTURED BY THE SAME ANALYSIS. BOTH THEORIES (AND MOST MODERN THEORIES) ARE BUILT ON THE IDEA THAT WE CAN MODEL ATOMIC INTERACTIONS AS A SERIES OF SPRINGS

WHY DOES THIS WORK? (AND IT DOES!)

WE KNOW THAT ATOM POTENTIAL LOOKS SOMETHING LIKE THIS.

eg COVALENT BOND POTENTIAL →



HOWEVER, FOR ANY CONTINUOUS FUNCTION NEAR $x = x_{eq}$, WE CAN ALWAYS TAYLOR EXPAND

$$V(x) = V(x_{eq}) + \left.\frac{dV}{dx}\right|_{x=x_{eq}} (x - x_{eq}) + \frac{1}{2!} \left.\frac{d^2V}{dx^2}\right|_{x=x_{eq}} (x - x_{eq})^2 + \ldots$$

$$= V(x_{eq}) + \frac{K}{2}(x - x_{eq})^2 + \ldots$$

WHERE WE DEFINED $K \equiv \left.\frac{d^2V}{dx^2}\right|_{x=x_{eq}}$

AND USED THE FACT THAT $\left.\frac{dV}{dx}\right|_{x=x_{eq}} = 0$

THUS, FOR SMALL ENOUGH MOTIONS, RESTORING FORCES LOOK LIKE $F = -\frac{dV}{dx} = -K(x - x_{eq})$

→ HOOKES LAW!

ALL PHYSICS IS SPRING PHYSICS

OK, SO SINCE THE EXACT FORM OF $V(x)$ DOESN'T MATTER, LET'S JUST START BY MAKING SOME GENERAL PREDICTIONS FOR A BUNCH (N) OSCILLATORS.

ACKNOWLEDGING THAT THESE ATOMS HAVE A QUANTUM NATURE, LET'S JUST START BY NOTING (RECALLING) THAT THE SOLUTION TO ANY HARMONIC POTENTIAL IS A SERIES OF MODES WITH ENERGIES

$$E_n = \hbar\omega(\vec{k})\left(n+\tfrac{1}{2}\right)$$

WHERE $n \in \mathbb{N}$ AND $\omega(\vec{k})$ IS SOME CHARACTERISTIC FREQUENCY THAT COULD HAVE SOME DEPENDENCE ON $\vec{k}$

THESE "QUANTA OF VIBRATION" ARE WHAT WE CALL "PHONONS" IN DIRECT ANALOGY TO PHOTONS (QUANTA OF EM WAVES). JUST LIKE PHOTONS, WE TEND TO TREAT THEM AS PARTICLES OF ENERGY. WHEN THE SYSTEM IS IN STATE $n=3$, FOR EXAMPLE, WE TALK ABOUT THE SYSTEM HAVING 3 PHONONS. SINCE THESE PHONONS CAN EXIST IN THE SAME STATE, $\vec{k}$, THEY ARE <u>BOSONS</u>

$\Rightarrow$ AT FINITE TEMP: $\underbrace{n_B}_{\#\text{ bosons}}\left(\frac{\hbar\omega}{k_BT}\right) = \underbrace{\frac{1}{e^{\frac{\hbar\omega}{k_BT}}-1}}_{\text{"BOSE" filling factor}}$

THUS, EVEN THIS MINIMAL AMOUNT OF INFORMATION, WE CAN CALCULATE THE TOTAL AMOUNT OF VIBRATIONAL ENERGY IN THE SYSTEM

$$\mathcal{U}_{TOTAL} = \underbrace{\sum_{\vec{k}}}_{\text{ALL STATES}} \underbrace{\hbar\omega(\vec{k})}_{\text{ENERGY OF STATE } \vec{k}} \left(\underbrace{n_B\left(\frac{\hbar\omega}{k_B T}\right)}_{\text{BOSE FACTOR}} + \frac{1}{2} \right)$$

FOR DENSE SYSTEMS, THIS SUM CAN BE SWAPPED FOR AN INTEGRAL

$$\mathcal{U}_{TOTAL} = \int d\vec{k}\, g(\vec{k})\, \hbar\omega(\vec{k}) \left(n_B + \tfrac{1}{2}\right)$$

OR

$$= \int d\omega\, g(\omega)\, \hbar\omega(\vec{k}) \left(n_B + \tfrac{1}{2}\right)$$

WHERE $g(\vec{k})$ AND $g(\omega)$ ARE DENSITY OF STATES FOR A GIVEN MODEL, ~~AND THE~~ ONCE ONE ~~[illegible]~~ HAS THE TOTAL ENERGY, IT IS A SIMPLE MATTER TO CALCULATE ~~SPECIFIC~~ HEAT CAPACITY

$$C_v = \left.\frac{\partial \mathcal{U}}{\partial T}\right|_V$$

WE ARE GOING TO CALCULATE THIS FOR A 1D CHAIN OF ATOMS, BUT LET'S PAUSE TO CONSIDER THE APPROXIMATIONS MADE BY THE HISTORICAL MODELS MENTIONED ABOVE

EINSTEIN MODEL

EINSTEIN TREATED ALL THE ATOMS IN THE SOLID AS INDEPENDENT OSCILLATORS, VIBRATING WITH THE SAME CHARACTERISTIC FREQUENCY, ω_E, (THE EINSTEIN FREQUENCY).

THUS THE ENERGY DENSITY OF STATES IS JUST A DELTA FUNCTION

$$g(\omega) = \delta(\omega - \omega_E)$$

$$\Rightarrow \quad U_{TOTAL} = \int_0^\infty \delta(\omega-\omega_E)\,\hbar\omega\left(n_B + \tfrac{1}{2}\right)$$

$$= \frac{\hbar\omega_E}{e^{\frac{\hbar\omega_E}{k_BT}} - 1} + \frac{\hbar\omega_E}{2}$$

$$C_V = \frac{\partial U}{\partial T} = \hbar\omega_E\left(\frac{+\hbar\omega_E}{k_BT^2}\right)\frac{e^{\frac{\hbar\omega_E}{k_BT}}}{\left(e^{\frac{\hbar\omega_E}{k_BT}} - 1\right)^2}$$

$$\approx k_B\left(\frac{\hbar\omega_E}{k_BT}\right)^2 \frac{\left(1 + \frac{\hbar\omega_E}{k_BT}\right)}{\left(1 + \frac{\hbar\omega_E}{k_BT} - 1\right)^2}$$

NOTE IN 3D HE WOULD POSTULATE OSCILLATORS IN x, y, z' GIVING AN ADDITIONAL FACTOR OF 3 $\longrightarrow$

$$\approx k_B \quad \text{as } T \to \infty$$

and

$$C_V \approx k_B\left(\frac{\hbar\omega_E}{k_BT}\right)^2 e^{-\frac{\hbar\omega_E}{k_BT}}$$

as $T \to 0$

THIS GIVES CORRECT LIMIT AT HIGH T, BUT FAILS AT LOW T $\longrightarrow$ STILL USED TODAY IN SPECIAL CASES

DEBYE MODEL

INSTEAD OF ASSUMING CONSTANT ω, DEBYE ALLOWED THE WAVES TO MOVE (i.e. THEY HAD SOME "DISPERSION", $\frac{d\omega}{dk} \neq 0$). HE CONSIDERED THE SIMPLEST SUCH MODEL, THE ONE OBEYED BY LIGHT AND SOUND WAVES IN ELASTIC MEDIA:

$$\omega(\vec{k}) = v\,|\vec{k}| \quad \text{FOR SPEED } v$$

$$\Rightarrow \mathcal{U}_{TOTAL} = 3\frac{L^3}{(2\pi)^3}\int d\vec{k}\;\hbar\omega(\vec{k})\left(n_B + \tfrac{1}{2}\right)$$

$$= 3\frac{(4\pi)L^3}{(2\pi)^3}\int_0^\infty k^2\,dk\;\hbar\omega(\vec{k})\left(n_B + \tfrac{1}{2}\right)$$

$$= 3\frac{(4\pi)L^3}{(2\pi)^3}\int_0^\infty \frac{\omega^2}{v^2}\,\frac{d\omega}{v}\;\hbar\omega\left(n_B + \tfrac{1}{2}\right)$$

BUT HOLD ON, THIS PREDICTS INFINITE VIBRATION ENERGY AT HIGH TEMPERATURES, WHICH ISN'T PHYSICAL. SO DEBYE INTRODUCES AN AD HOC CUTOFF FREQUENCY, AND SETS IT TO THE VALUE NEEDED TO ENSURE EXACTLY 3N SOUND WAVES ARE OCCUPIED AT HIGHEST T

$$3N = \int_0^{\omega_d \,\leftarrow\, \text{DEBYE FREQ}} 3\frac{(4\pi)L^3}{(2\pi)^3}\,\frac{\omega^2}{v^3}\,d\omega$$

$$\Rightarrow \boxed{\omega_d^3 = 6\pi^2 n v^3}$$

$$\Rightarrow \quad U_{TOTAL} = \frac{9N\hbar}{\omega_d^3} \int_0^{\omega_d} \frac{\omega^3 \, d\omega}{e^{\hbar\omega/k_BT} - 1} + \text{Const}$$

WHICH HAS NO ANALYTICAL SOLUTION,
WE CAN CHECK LIMITS THOUGH

AS $T \to \infty$

$$U_{TOTAL} \to \frac{9N\hbar}{\omega_d^3} \int_0^{\omega_d} \frac{\omega^3}{\frac{\hbar\omega}{k_BT}} \, d\omega$$

$$= \frac{9N \cancel{\hbar} k_BT}{\omega_d^3} \frac{\omega_d^3}{3}$$

$$= 3Nk_BT$$

AND AS $T \to 0$

$$U_{TOTAL} \to \frac{9N\hbar}{\omega_d^3} \int_0^{\infty} \omega^3 e^{-\frac{\hbar\omega}{k_BT}} \, d\omega$$

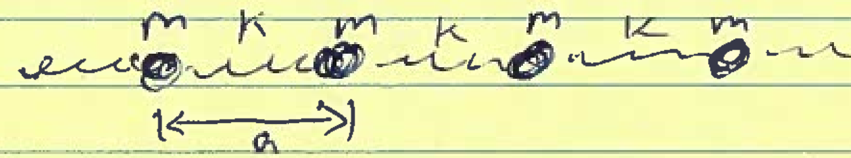
$$= \frac{9N\hbar}{\omega_d^3} \left(6 \left(\frac{k_BT}{\hbar} \right)^4 \right)$$

$$\Rightarrow \quad C_V \propto T^3$$

CHECK ✓ THIS BASIC EMPIRICAL AGREEMENT WITH NO FITTABLE PARAMETER (ω_d SET BY MEASURABLES) IS THE REASON THIS MODEL IS STILL USED

A MORE MICROSCOPIC DEFENSIBLE MODEL:
THE 1D MONATOMIC HARMONIC CHAIN

CONSIDER N ATOMS OF MASS, m, COUPLED WITH SPRINGS, WITH SPRING CONSTANT, K



LET a BE THE ATOM SEPARATION IN EQUILIBRIUM (i.e THE LATTICE CONSTANT)

THEN THE EQUILIBRIUM POSITION OF THE n^{th} ATOM WILL BE

$$x_n^{eq} = na$$

AND THE LENGTH OF THE CHAIN WILL BE

$$L = Na$$

THE SPRING ENERGY IN THE ith SPRING WILL BE

$$V(x_{i+1} - x_i) = \frac{K}{2}(x_{i+1} - x_i - a)^2$$

$$= \frac{K}{2}(\delta x_{i+1} - \delta x_i)^2$$

WHERE $\delta x_n = x_n - na$

$$\Rightarrow \quad V_{TOT} = \sum_i \frac{K}{2}(\delta x_{i+1} - \delta x_i)^2$$

$\Rightarrow$ FORCE ON n^{th} ATOM IS $F_n = -\frac{\partial V_{TOT}}{\partial x_n}$

$$m\,\delta\ddot{x}_n = K(\delta x_{n+1} - \delta x_n) + K(\delta x_{n-1} - \delta x_n)$$

$$= K(\delta x_{n+1} + \delta x_{n-1} - 2\delta x_n)$$

NOW SINCE WE ARE LOOKING FOR A "COLLECTIVE MODE" WITH A SHARED FREQUENCY, TRY

$$\delta x_n = A e^{i\omega t - ikna} \quad x\hat{e}_1$$

$$-m\omega^2 A e^{i\omega t - ikna} = K \cdot A e^{i\omega t}\left[e^{-ik(n+1)a} + e^{-ik(n-1)a} - 2e^{-ikna}\right]$$

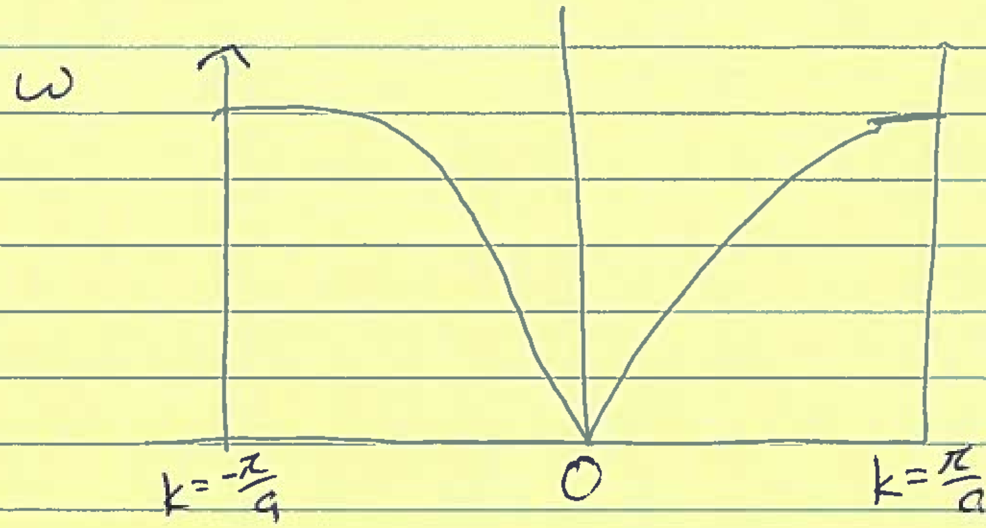
$$\Rightarrow \quad m\omega^2 = 2K\left[1 - \tfrac{1}{2}\left(e^{ika} + e^{-ika}\right)\right]$$

$$= 2K\left[1 - \cos(ka)\right]$$

$$= 2K \sin^2\left(\frac{ka}{2}\right)$$

$$\Rightarrow \quad \omega = 2\sqrt{\frac{K}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|$$

"DISPERSION RELATION"



THINGS TO NOTICES

1. PERIODIC IN k WITH PERIODICITY $k \rightarrow k + \frac{2\pi}{a}$. THIS IS SOMETHING WE HAVE SEEN BEFORE AND REFLECTS FACT THAT ALL PHYSICALLY DISTINCT STATES ARE SEEN IN 1ST BZ

$$Ae^{i\omega t - i(k+\frac{2\pi}{a})na} = Ae^{i\omega t - ikna} e^{-i2\pi n}$$
$$= Ae^{i\omega t - ikna}$$

2. FOR $ka \ll 1$

$$\omega = 2\sqrt{\frac{K}{m}}\ \frac{ka}{2}$$

$$\Rightarrow v_{sound} = a\sqrt{\frac{K}{m}}$$

3. FOR LARGER k, WE HAVE TO DEFINE TWO OTHER VELOCITIES

$$v_{group} = \frac{d\omega}{dk}$$ ← SPEED OF INFORMATION

AND $$v_{PHASE} = \frac{\omega}{k}$$

NOTICE $v_{group} = 0$ AT BZ BOUNDARY ALWAYS! THIS IS BECAUSE SOLUTIONS TO WAVE EQUATION THERE ARE STANDING WAVES.

④ NUMBER OF MODES.

I RUSHED THROUGH THIS BEFORE, BUT WE CAN USE POINT ① AND BOUNDARY CONDITION CONSTRAINTS TO COUNT ALL THE POSSIBLE HARMONIC MODES IN OUR SYSTEM.

PERIODIC B.C.'S SAY

$$e^{ik(N+1)a} = e^{ika}$$

$$\Rightarrow e^{ikNa} = 1$$

$$k = \frac{2\pi n}{Na} = \frac{2\pi n}{L} \qquad n \in \mathbb{Z}$$

THUS

$$\# \text{ modes} = \frac{2\pi/a}{\frac{2\pi}{Na}} = N = \# \text{ atoms}$$

MORE GENERALLY, IT IS # DEGREES OF FREEDOM