

M. Fox: Ch. 10 (ignore 10.4-10.5)

- PHONON DISPERSION (AEM, ZIMAN, etc.)
- IR active modes (modes that carry a dipole)
- TWO-PHONON ABSORPTION
LYDDANE-SACHS-TELLER
- IR modes in metals & doped semiconductors
- Coupled modes; FANO RESONANCES & INTERF.-INDUCED TRANSPARENCY (EIT-LIKE)
- POLARITONS + LO (CARRIES A FIELD)
- PHONON LIFETIME (ANHARMONICITY)
MOLECULAR CRYSTALS
INTERNAL MODES

MOTION OF NUCLEI IN THE ADIABATIC APPROX.
IS DESCRIBED BY

$$H_{\text{IONS}} = \sum_i \frac{p_i^2}{2M_i} + \underbrace{V(\{r_i\})}_{\substack{\text{INCLUDES} \\ \text{DIRECT +} \\ \text{e}^- \text{-MEDIATED} \\ \text{INTERACTION}}}$$

TO LOWEST ORDER,
SYSTEM OF COUPLED OSCILLATORS

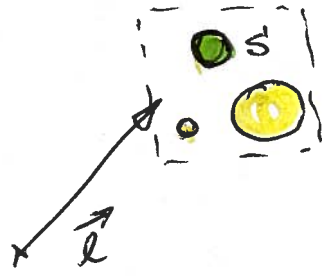
→ NORMAL MODES

Ω vs. \vec{q}
BLOCH
WAVEVECTOR

OF THESE MODES
IS KNOWN AS
PHONON DISPERSION

EXPAND V_T :

$V_T = \text{CONSTANT} + \text{FIRST-ORDER TERMS}$



$$+ \sum \frac{\partial^2 V_T}{\partial \vec{u}_{l,s} \partial \vec{u}_{l',s'}} \vec{u}_{l,s} \vec{u}_{l',s'} +$$

 labels the cell $\left\{ \begin{matrix} \vec{r}, s \\ \vec{r}', s' \end{matrix} \right.$ labels in a cell

 HIGHER-ORDER TERMS

 AN HARMONICITY

CLASSICAL EQS.:

$$M_s \ddot{\vec{u}}_{l,s} = - \sum_{l',s'} \frac{\partial^2 V_T}{\partial \vec{u}_{l,s} \partial \vec{u}_{l',s'}} \vec{u}_{l',s'} \Big|_{\text{equilibrium}}$$

DEFINE DYNAMIC MATRIX

$$G_{\vec{r},s, \vec{r}',s'} = \frac{\partial^2 V_T}{\partial \vec{u}_{\vec{r},s} \partial \vec{u}_{\vec{r}',s'}} \Big|_{\text{equilibrium}}$$



$$M_s \ddot{\vec{u}}_{l,s} = - \sum_{l',s'} G_{\vec{r},s, \vec{r}',s'} \vec{u}_{l',s'}$$

Force on \vec{r}, s due to displac. of s' th ion @ \vec{r}'

Solutions must satisfy Bloch Theorem

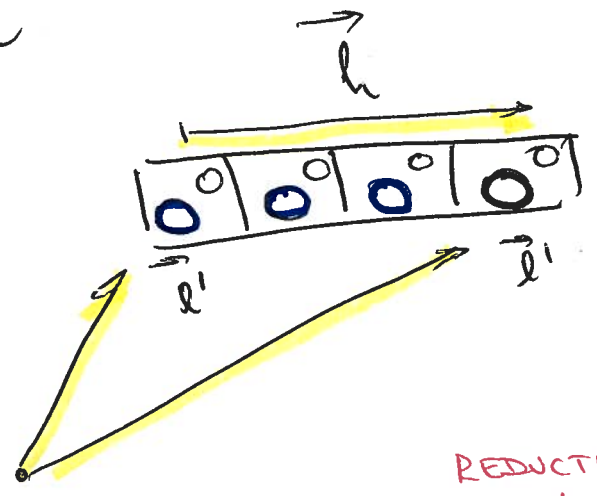
(3)

$$\vec{u}_{s, \vec{l}}(t) = e^{i \vec{q} \cdot \vec{l}} \underbrace{\vec{u}_{s0}}_{SO}(t)$$

arbitrary cell chosen as the (0,0,0) origin

→ $M_s e^{i \vec{q} \cdot \vec{l}} \vec{u}_{0,s} = - \sum_{\vec{l}', s'} G_{\vec{l}s, \vec{l}'s'} \vec{u}_{0,s'} e^{i \vec{q} \cdot \vec{l}'}$

WRITE $\vec{l}' = \vec{l} + \vec{h}$



REDUCTION TO A SINGLE CELL

→ $M_s \vec{u}_{0,s} = - \sum_{s'} G_{ss'}(\vec{q}) \vec{u}_{0,s'}$

WHERE

$$G_{s,s'}(\vec{q}) = \sum_{\vec{h}} \underbrace{G_{\vec{l}s, \vec{l}'s'}}_{G_{0s, \vec{h}s}} e^{i \vec{q} \cdot \vec{h}}$$

DEPENDS ONLY ON $\vec{l}' - \vec{l}$

ACCOUNTING FOR THE FACT THAT

(4)

\vec{u}_{ls} IS A VECTOR:

$$M_S u_i^{(s)} = -M_S \Omega^2 u_i^{(s)} = - \sum_{\substack{s', j \\ i, j}} G_{s, s'}(\vec{q}) u_j^{(s')}$$

$i, j = 1, 2, 3$

HOW DO WE SOLVE THIS?
 DETERMINANT

$$\left| M_S \Omega^2 \delta_{ij} \delta_{ss'} - G_{ss'}(\vec{q}) \right| = 0$$

IF THERE ARE n IONS/CELL $\rightarrow 3n \times 3n$
 FOR EACH VALUE OF \vec{q} (N ALLOWED VALUES)
 WE GET $3n$ SOLUTIONS, SOME OF WHICH CAN BE DEGENERATE

OUT OF THE $3n$, 3 SOLUTIONS HAVE THE PROPERTY THAT

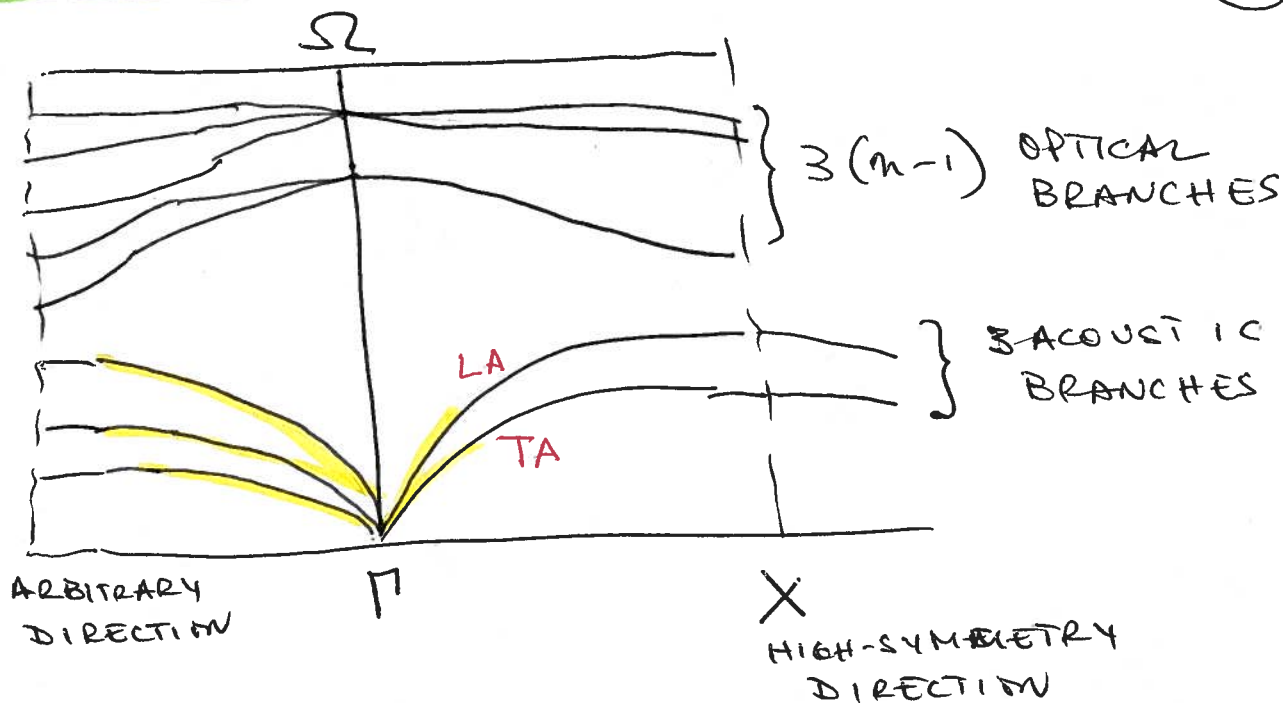
$$\Omega(\vec{q}) \rightarrow 0 \text{ as } \vec{q} \rightarrow 0$$

ACOUSTIC MODES

(energy can't change if we displace the solid as a whole)

PHONON DISPERSION

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THE ONLY MODES THAT COUPLE TO LIGHT ARE THOSE @ $q=0$ THAT CARRY AN ELECTRIC DIPOLE (MODES THAT TRANSFORM LIKE A VECTOR)

EVEN IF YOU DON'T KNOW GROUP THEORY, THIS IS EASY:

POINT GROUP OF CRYSTAL (32 GROUPS)



CHARACTER TABLE

- O_h (DIAMOND)
- T_d (INC-BLENDE)
- C_{4v}
- D_{3d}
- ...

IRREDUCIBLE REPS.

FOR

(x, y, z)



PHONON SYMMETRY

IN T_D , THE REP. IS " T_2 " (6)
 ZINC-BLEND 3-FOLD DEGENERATE

IN C_{6V} , THE REPS ARE " A_1 " & " E_1 "
 WURZITE 1-FOLD " z " 2-FOLD " x, y "

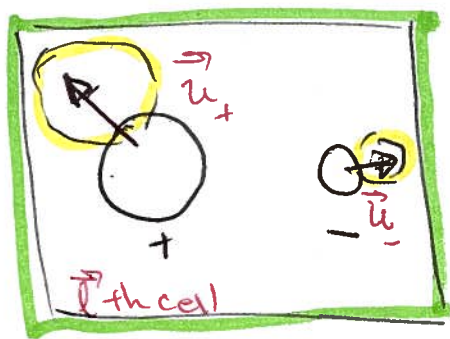
IF CRYSTAL HAS INVERSION SYMMETRY, ONLY ODD MODES CAN COUPLE TO LIGHT. THEN, LOOK FOR "UNGRADABLE" REPS.

AT THE END OF THIS PROCESS, WE END UP WITH A SMALL SET OF OPTICAL MODES THAT ARE "IR ACTIVE"

Lecture #9

MICROSCOPIC MODEL

CONSIDER CRYSTAL WITH TWO IONS / CE
 ASSUME STRUCTURE IS CUBIC & MATERIAL IS AN INSULATOR



SZIGETI EFF. CHARGE

$$\vec{S}_D = Z^* e (\vec{u}_+ - \vec{u}_-)$$

electric dipole moment normal mode coordinate
 3-fold degenerate

INSTEAD OF $\vec{u}_+ - \vec{u}_- \equiv \vec{Q}$, IT'S CONVENIENT TO USE THE VARIABLE

$$\vec{W} = \left[\frac{M_+ M_-}{M_+ + M_-} \right]^{1/2} \frac{1}{\sqrt{V_c}} (\vec{u}_+ - \vec{u}_-)$$

reduced mass V_c , volume of cell

THE ION HAMILTONIAN IS VOLUME OF CRYSTAL

(7)

$$H_{ion} = \frac{V}{2} \left[\vec{P}_W^2 + \overset{\rightarrow}{\Omega}_0^2 |\vec{W}|^2 \right]$$

energy density

COUPLING OF EM FIELD TO NORMAL MODE IS

$$H_{EM-LATTICE} = - \frac{\vec{P}_D}{V_C} \cdot \int_{CRYSTAL} \vec{E} dV$$

LOCAL ELECTRIC FIELD; see later

$$= - \frac{ze^*}{\sqrt{V_C M R}} \vec{W} \cdot \int_{CRYSTAL} \vec{E} dV$$

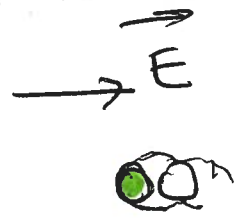
SAME FOR EACH CELL

FINALLY, WE HAVE THE TERM

$$H_{ELECTRON-EM} = \frac{1}{4\pi} \int \vec{D} \cdot \vec{E} dV = \int \frac{|\vec{E}|^2 dV}{4\pi} + \int \vec{P}_{electronic} \cdot \vec{E} dV$$

WHAT IS $\vec{P}_{electronic}$?

\vec{P}_D INDUCED BY DISPLACEMENT OF ELECTRONIC CLOUD ASSOCIATED W/EACH ION



DIPOLE MOMENT = $(\alpha + \alpha) \vec{E}$

POLARIZABILITY

THEN, WE GET

$$\frac{d^2 \vec{w}}{dt^2} = -\Omega_0^2 \vec{w} + \frac{z^* e}{(M_R \nu_c)^{1/2}} \vec{E} \quad \vec{E} = b_{11} \vec{w} + b_{12} \vec{E}$$

SHORT RANGE
LONG RANGE FORCES DUE TO GA

$$\vec{P} = \frac{z^* e}{(M_R \nu_c)^{1/2}} \vec{w} + \frac{(\alpha_e^+ + \alpha_e^-)}{\nu_c} \vec{E}$$

POLARIZ.
IONIC
ELECTRONIC

FOR TIME-DEPENDENCE $\sim e^{-i\Omega t}$

$$\left\{ \begin{aligned} -(\Omega^2 - \Omega_0^2) \vec{w} &= \frac{z^* e}{(M_R \nu_c)^{1/2}} \vec{E} \\ \vec{P} &= \left[\frac{(\alpha^+ + \alpha^-)}{\nu_c} - \frac{z^{*2} e^2 / M_R \nu_c}{\Omega^2 - \Omega_0^2} \right] \vec{E} \end{aligned} \right.$$

WHAT IS THE RELATIONSHIP BETWEEN

$$\vec{P} \perp \vec{E} ?$$

FOR STANDARD, TRANSVERSE WAVES

$$\vec{P} = \chi_T \vec{E} = \frac{(\epsilon_T - 1)}{4\pi} \vec{E}$$

AND WE GET

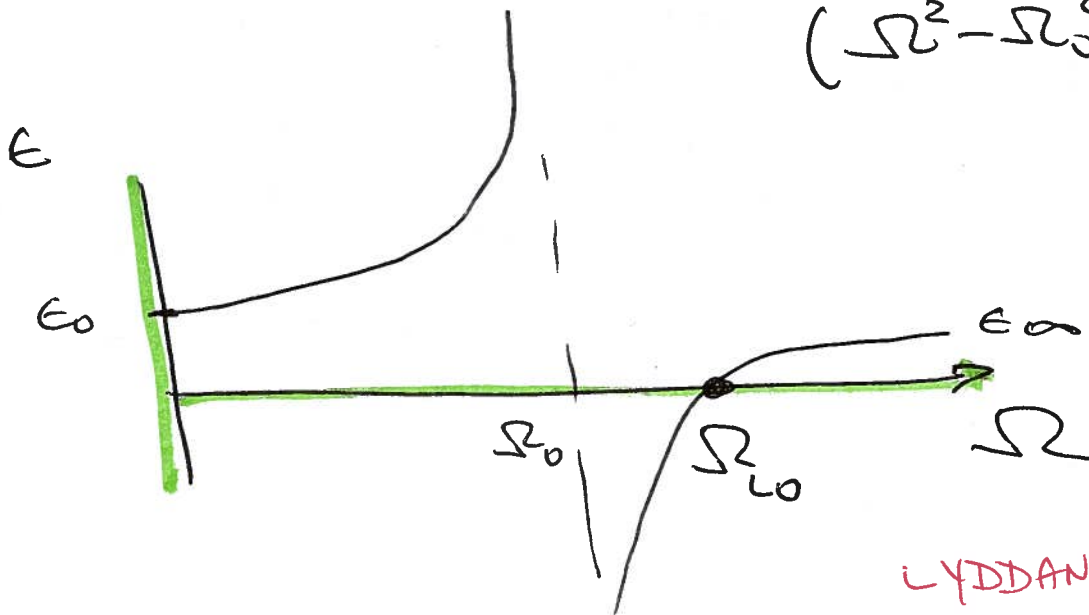
9

$$\epsilon(\Omega) = 1 + \frac{4\pi(\alpha^+ + \alpha^-)}{\nu_c} - \frac{4\pi z^* e^2 / M_p \nu_c}{(\Omega^2 - \Omega_0^2)}$$

$\epsilon(\Omega \gg \Omega_0) \equiv \epsilon_\infty$

$$1 + \frac{4\pi(\alpha^+ + \alpha^-)}{\nu_c} + \frac{4\pi z^* e^2 / M_p \nu_c}{\Omega_0^2} = \epsilon(\Omega=0) \equiv \epsilon_0$$

→
$$\epsilon(\Omega) = \epsilon_\infty - \frac{(\epsilon_0 - \epsilon_\infty) \Omega_0^2}{(\Omega^2 - \Omega_0^2)}$$

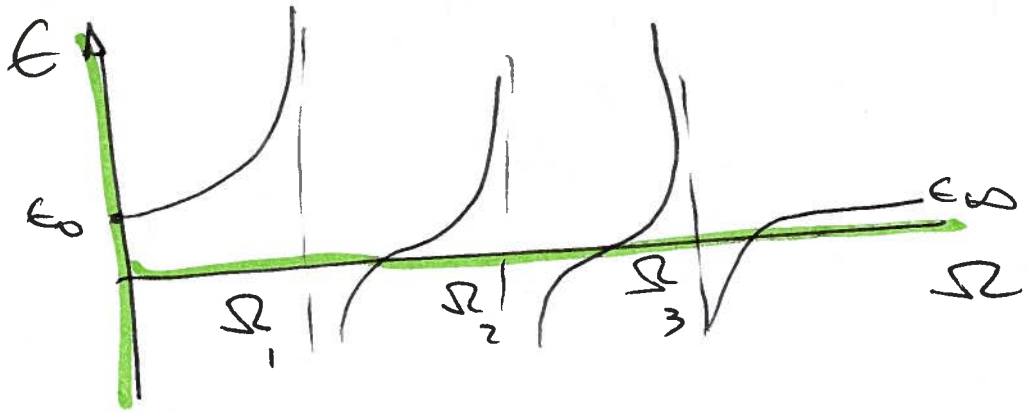


LYDDANE-SACHS-TELLER

$$\epsilon_\infty (\Omega_{L0}^2 - \Omega_0^2) = (\epsilon_0 - \epsilon_\infty) \Omega_0^2 \rightarrow \frac{\Omega_{L0}}{\Omega_0} = \sqrt{\frac{\epsilon_0}{\epsilon_\infty}}$$

MORE THAN ONE MODE ?

(10)



$$\frac{E_0}{E_\infty} = \prod_{j=1}^N \frac{\Omega_{LO, j}^2}{\Omega_{TO, j}^2}$$
 GENERALIZED LST

CHAVES & PORTO, SSC. 13, 865 (1973)
 SIEMERS & RACÉ, PRB 41, 3455

NOTE ON LOCAL FIELDS

$$\vec{E}_{LOCAL} = \vec{E} + \frac{4\pi}{3} \vec{P}$$
 KITTEL, INTROSS. 5th., P 406

$$b_{12} = \frac{ze}{\sqrt{M_e \nu_c}} \left[1 - \frac{4\pi}{3} \frac{(\alpha^+ + \alpha^-)}{\nu_c} \right]^{-1}$$

$$b_{22} = \frac{(\alpha^+ + \alpha^-)}{\nu_c} \left[1 - \frac{4\pi}{3} \frac{(\alpha^+ + \alpha^-)}{\nu_c} \right]^{-1}$$

LOCAL FIELD CORRECTION.

AFTER SOME ALGEBRA

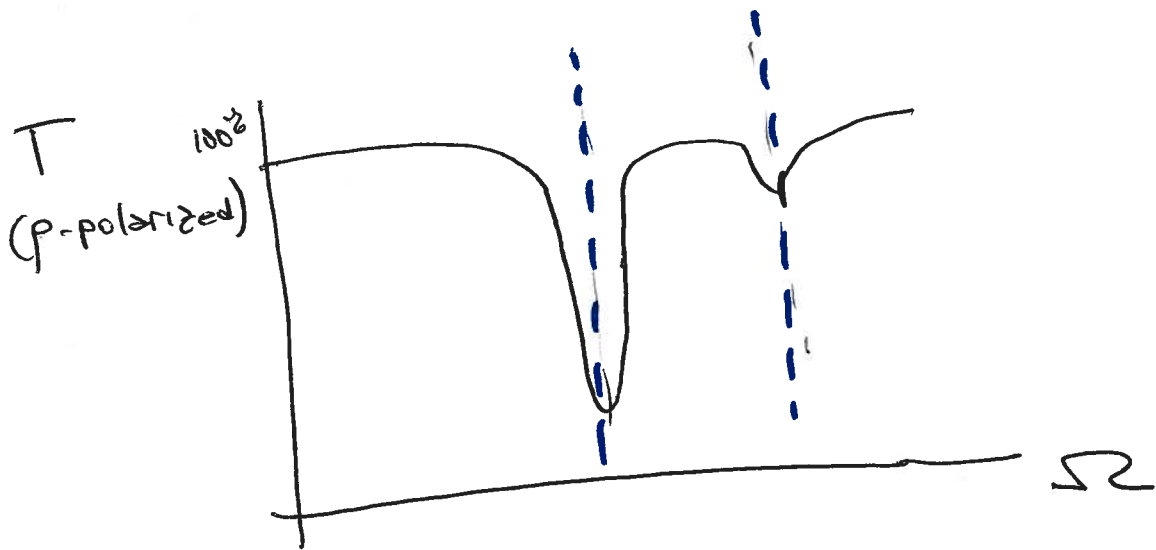
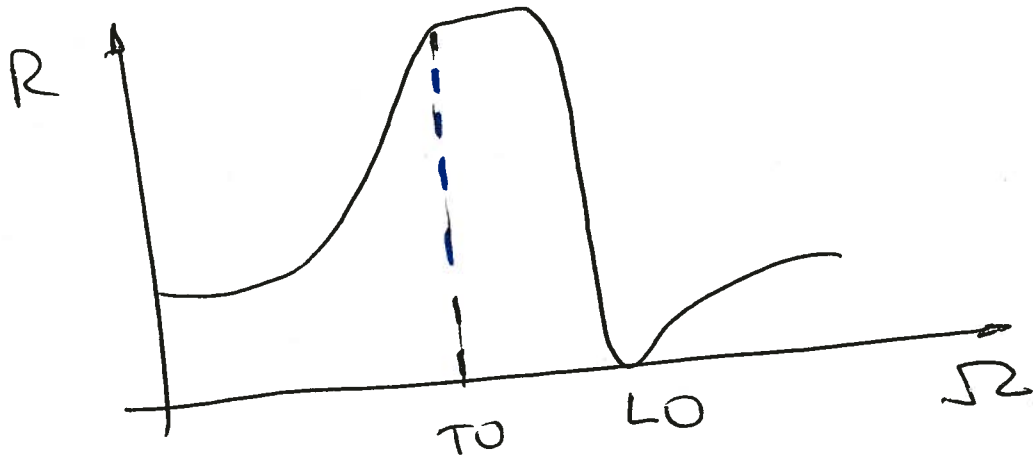
$$\frac{4\pi (Z^* e)^2}{M_R \omega_c} \equiv \omega_{TO}^2 \frac{(\epsilon_0 - \epsilon_\infty)}{(\epsilon_\infty + 2)^2}$$

ALSO ENTERS IN FRÖHLICH INTERACTION

(1)

Z^* IS A MEASURE OF IONICITY

	NaCl	MgO	ZnS	GeAs
Z^*	0.74	1.76	0.96	0.51



PHYSICAL MEANING OF Ω_{LO} :

(12)

$$\vec{\nabla} \cdot \vec{D} = 0 \quad \rightarrow \quad \epsilon \vec{k} \cdot \vec{D} = 0$$

LONGITUDINAL SOLUTIONS ARE OK IF $\epsilon = 0$

$$(\vec{E} = -4\pi\vec{P})$$

$\vec{\nabla} \cdot \vec{E} = 0$
Coulomb-like

LO MODES CARRY A LONGITUDINAL (COULOMB-LIKE) ELECTRIC FIELD

BUT TIME VARYING

THIS IS WHY THEY INTERACT STRONGLY WITH CARRIERS ... FRÖHLICH INTER.

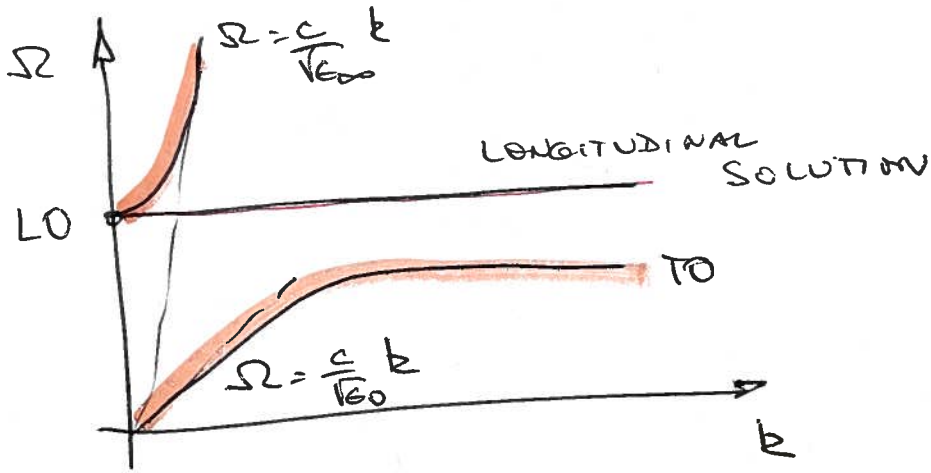
$$\frac{\vec{r}}{r^3} \equiv \frac{1}{(2\pi)^2} \int e^{i\vec{q} \cdot \vec{r}} \frac{\vec{q}}{q^2} d^3q$$

LONGITUDINAL

TRANSVERSE SOLUTIONS

$$\omega^2 = \frac{c^2 k^2}{\epsilon(\omega)} = \frac{c^2 k^2}{n^2(\omega)}$$

$$\epsilon = \epsilon_{\infty} \frac{(\omega^2 - \omega_{LO}^2)}{(\omega^2 - \omega_{TO}^2)}$$



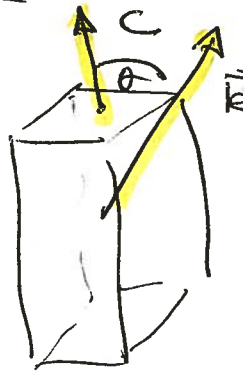
COUPLED MODES



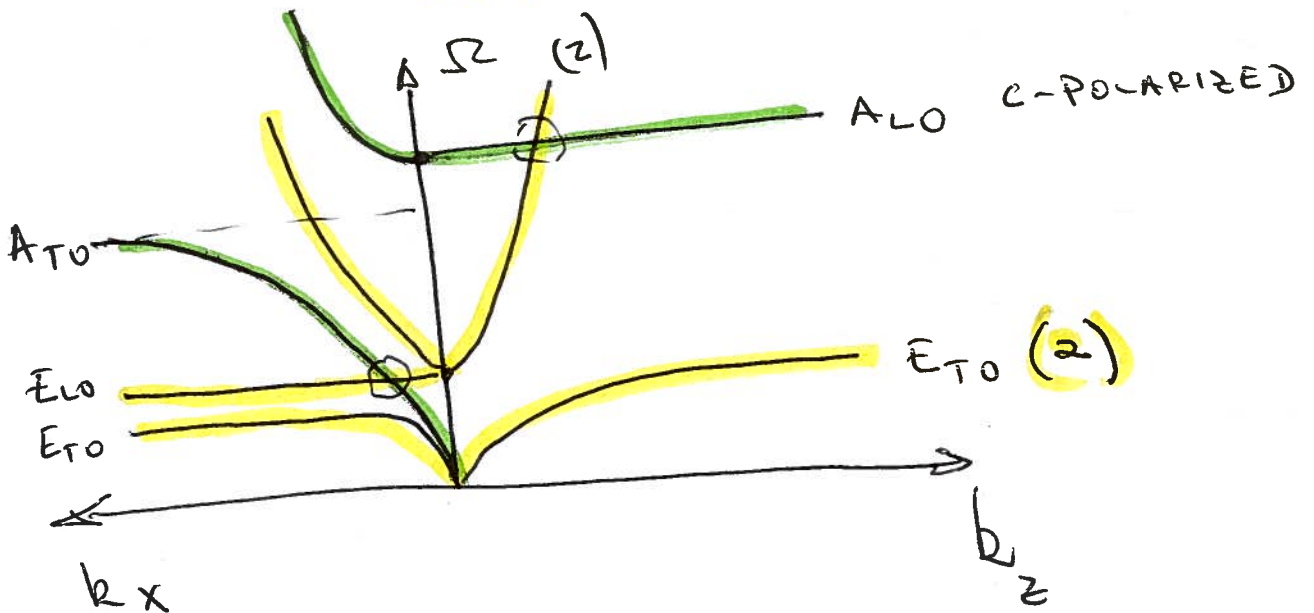
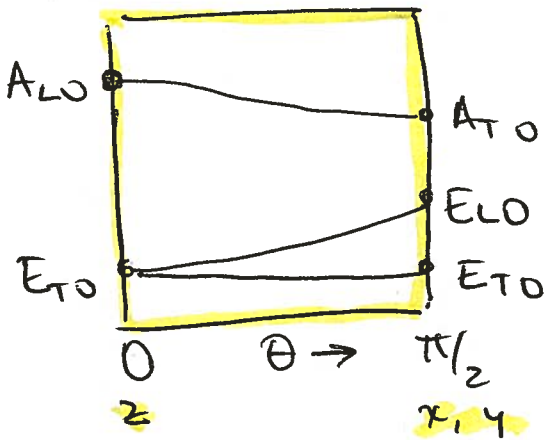
POLARITONS

● EMPHASIZE SPLITTING & LACK OF SPONTANEOUS DECAY

● ROLE OF ANISOTROPY



TETRAAGONAL CRYSTAL



TWO-PHONON ABSORPTION

\vec{P} = FIRST-ORDER TERMS

LABELS PHONON BRANCH

$$+ \sum_{\substack{bb' \\ \vec{q}}} C(\vec{q}) u_{\vec{q}}^b u_{-\vec{q}}^{b'}$$

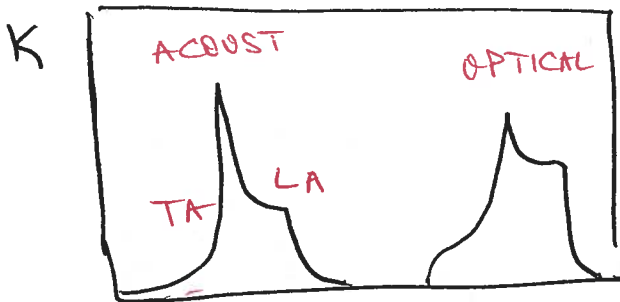
CONSTANTS

NOISE

WEAKER SELECTION RULES

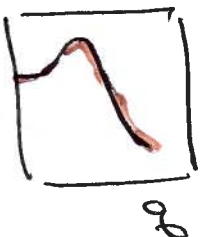
SINCE EVERY CELL MUST UNDERGO SAME DISPLACEMENTS, LIGHT COUPLES TO PAIR OF MODES, SO THAT $\vec{q}_1 + \vec{q}_2 = 0$

SPECTRUM DOMINATED USUALLY BY OVERTONES $\rightarrow \propto$ DENSITY OF STATES



WEIGHTING FACTORS

DISCUSS NON-ANALYTICAL VAN HOVE SINGULARITIES — DIAMOND



WHY IS H₂O BLUE?

4-5 PHONON ABSORPTION

O-H BOND

IR MODES IN METALS AND (15)

→ DOPED SEMICONDUCTOR

PHONONS ALONE :

$$\epsilon_{PH} = \epsilon_{\infty} \frac{\omega^2 - \omega_{LO}^2}{\omega^2 - \omega_{TO}^2}$$

CARRIERS ALONE

$$\epsilon_c = 1 - \frac{\omega_p^2}{\omega^2} \quad \omega_p^2 = \frac{4\pi n e^2}{m^* \epsilon_0}$$

ϵ_0 OR ϵ_{∞}

$$\epsilon_{TOTAL} \equiv \epsilon_{PH} + \epsilon_c - 1$$

$$= \epsilon_{\infty} \left[\frac{\omega^2 - \omega_{LO}^2}{\omega^2 - \omega_{TO}^2} \right] - \frac{\omega_p^2}{\omega^2}$$

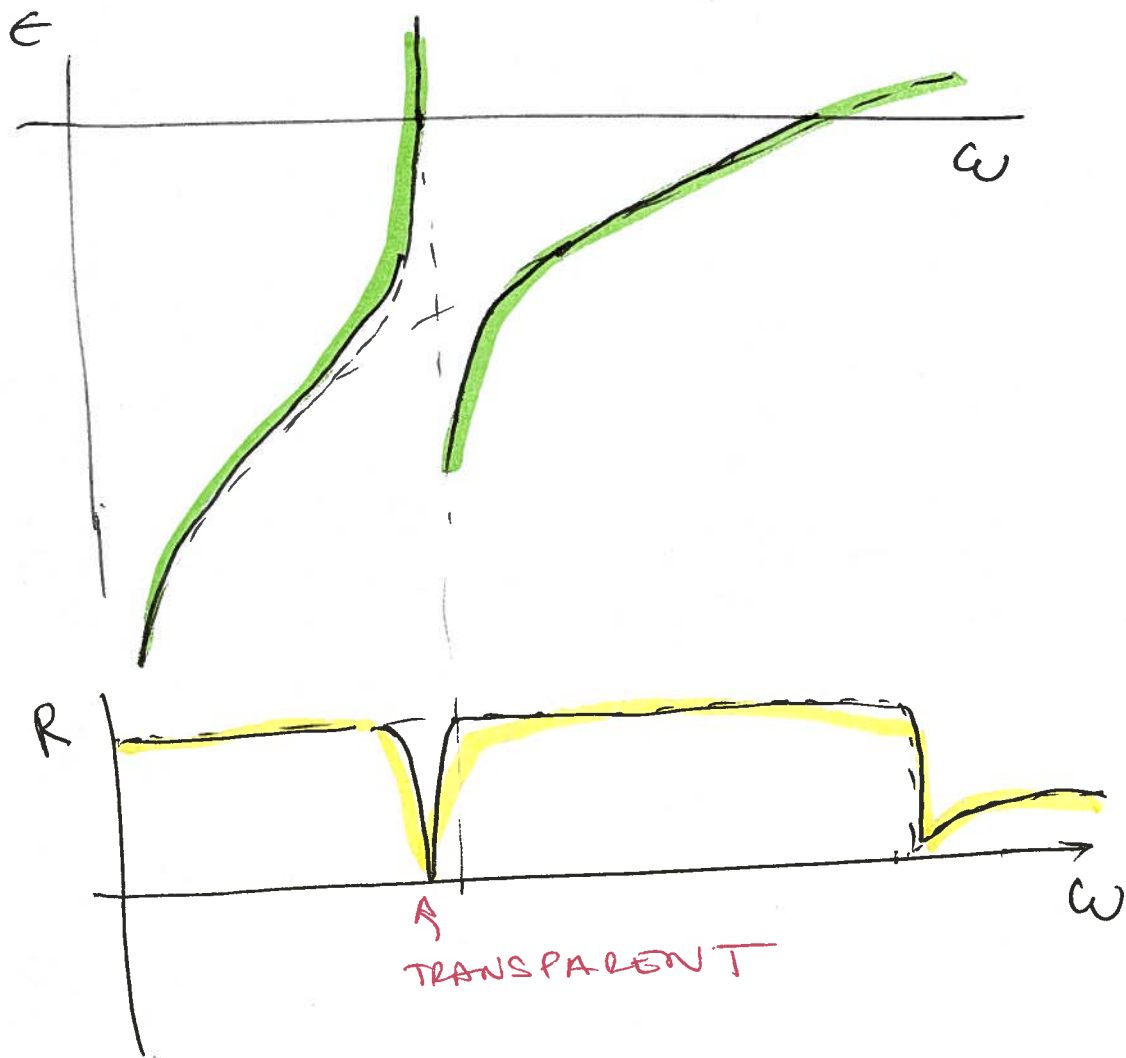
PROOF IS EQUIVALENT TO
SHOW THAT

$$\chi_{TOTAL} = \chi_{PH} + \chi_c$$

WHICH FOLLOWS FROM THE GENERAL EXPRESSION
IF PHONONS & CARRIERS

$\epsilon \in \omega_p \gg \omega_{LO}$

(15)



NEW MODES

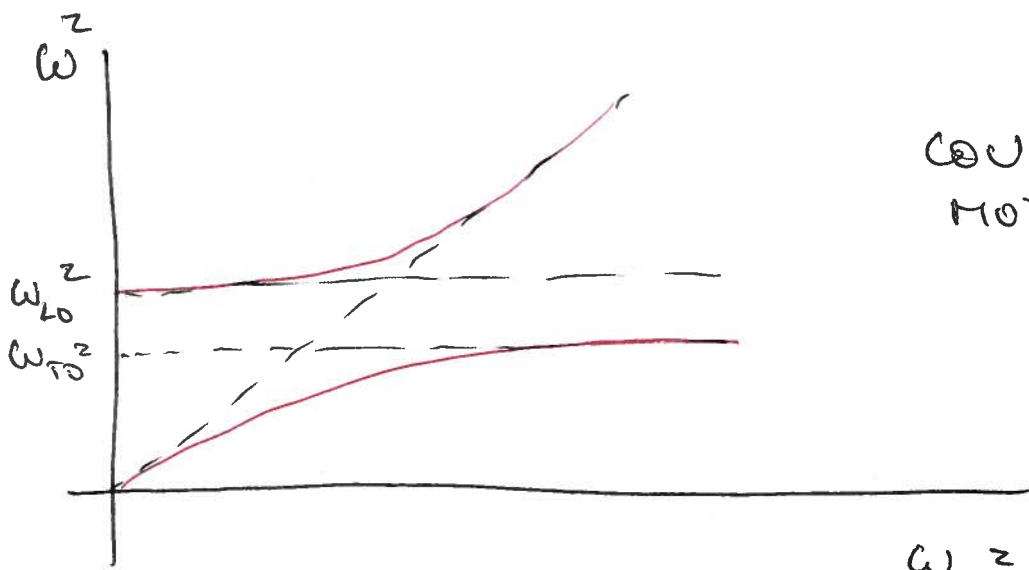
$\epsilon_{PHONON} = 0 \rightarrow \omega_{LO}$

$\epsilon_{CARRIER} = 0 \rightarrow \omega_p$

$\epsilon_{TOTAL} = 0$

LO - PLASMON COUPLED MODES

$$\epsilon_{\infty} \omega^2 (\omega^2 - \omega_{LO}^2) = \omega_p^2 (\omega^2 - \omega_{TO}^2)$$



COUPLED
MODES

$$\omega_p^2 \propto \text{CARRIER DENSITY}$$

$$\omega^4 - \left(\frac{\omega_p^2}{\epsilon_\infty} + \omega_{LO}^2 \right) \omega^2 + \frac{\omega_p^2 \omega_{TO}^2}{\epsilon_\infty} = 0$$



AN HARMONICITY

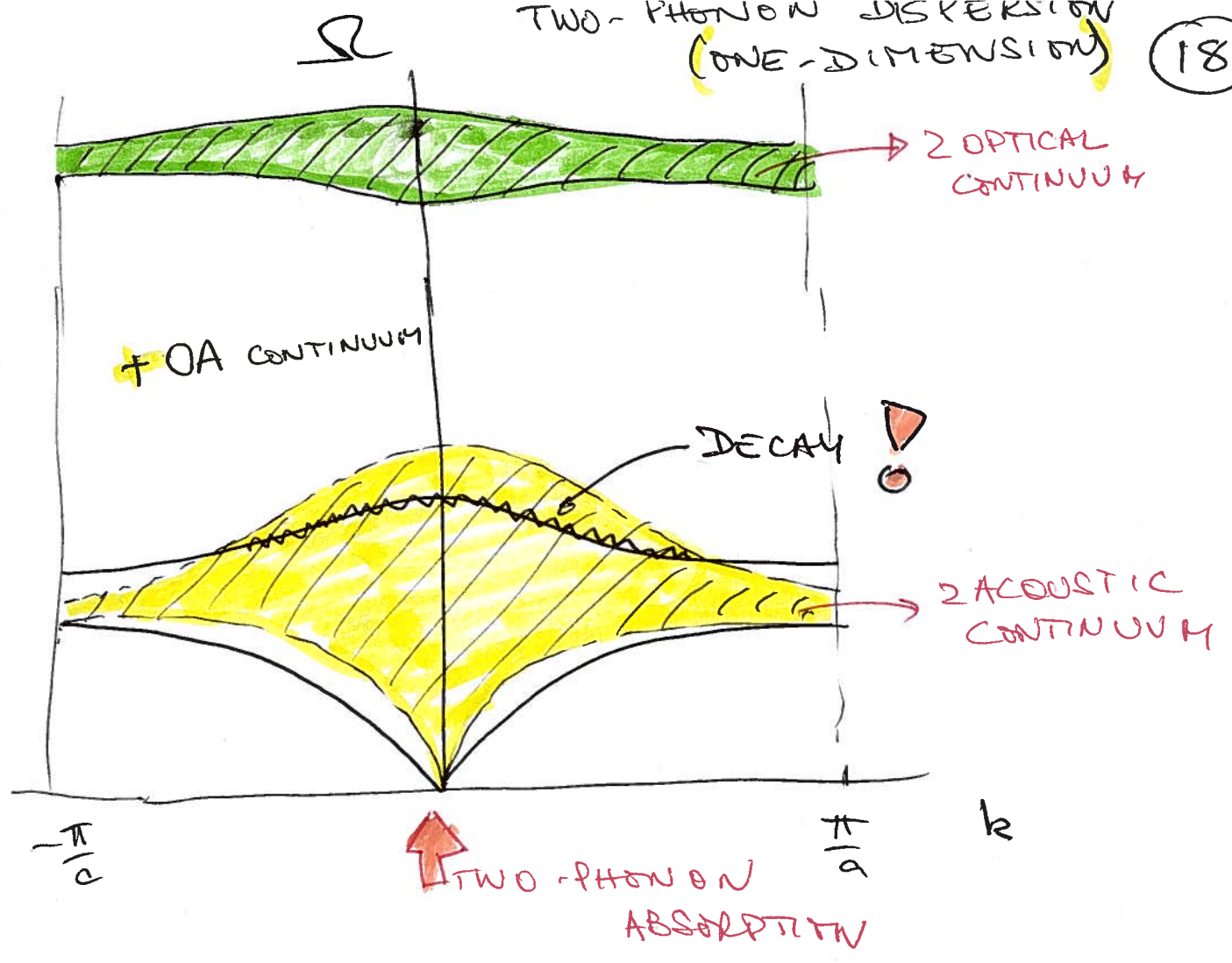
$$H_{ion} = \frac{1}{2} \left[P_k^b + \sum_{k_c}^2 Q_{k_c}^b \right] + \text{THIRD-ORDER} + \text{FOURTH-ORDER TERMS} + \dots$$

THIRD-ORDER $\sum_{k_1, k_2, k_3}^{b_1, b_2, b_3} Q_{k_1}^{b_1} Q_{k_2}^{b_2} Q_{k_3}^{b_3}$ $k_1 \pm k_2 \pm k_3 = 0$

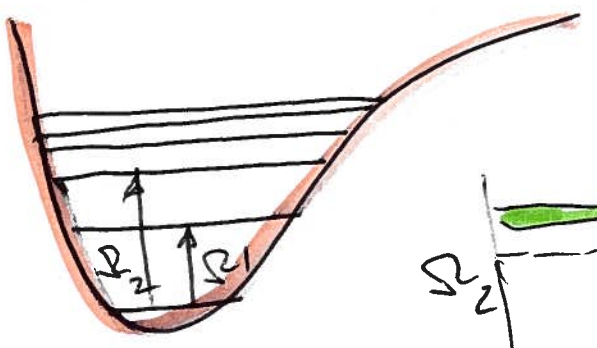


DECAY (IF $\Omega_1 = \Omega_2 + \Omega_3$)

TWO-PHONON DISPERSION (ONE-DIMENSIONAL)



COMPARE WITH MOLECULES



MOLECULAR SOLIDS

