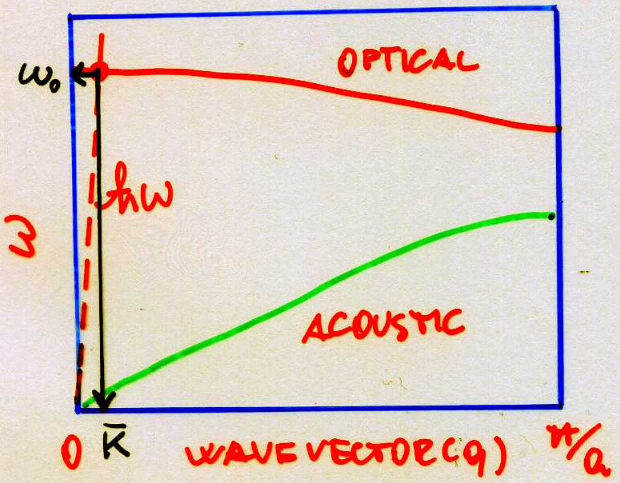
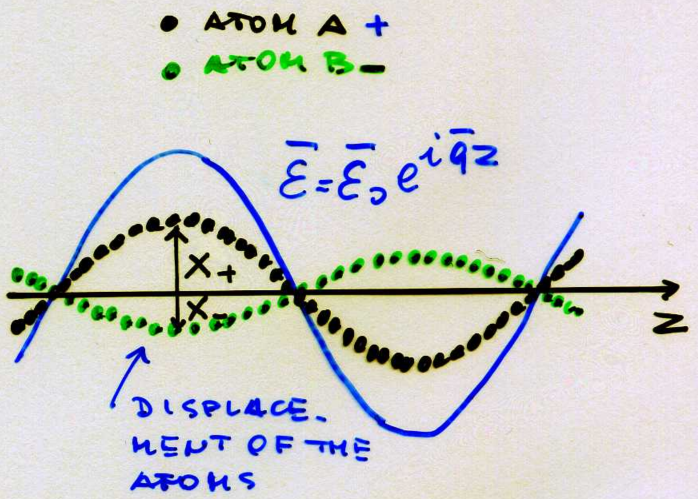
IN THIS CASE A POLAR BOND IS FORMED AND THE SOLID CAN BE DEPICTED AS A SEQUENCE OF DIPOLES. THIS IS THE RESON WHY MONO-ELEMENT MATERIALS, SUCH AS Si, THERE ARE NO IR-ACTIVE MODES.





AS DEPICTED ABOVE THE INTERACTION OF THE LIGTH WITH A TO PHONON MAY TAKE PLACE ONLY IF THE PHOTON AND THE PHONON HAVE THE SAME FREQUENCY AND WAVEVECTOR.

FOR TO MODES, WHEN THE SIZE OF THE UNIT CELL IS COMPARED TO THE SIZE OF THE PHONON λ, IT WILL BE CLEAR THAT SEVERAL UNIT CELLS WILL BE FOUND INSIDE A PHONON OSCILLATION, MOREOVER THE INTEACTION WITH THE LIGHT WILL TAKE PLACE FOR $q \simeq 0$. THIS CONDITIONS CAN BE USE TO SET THE FOLLOWING:

1 - THE DESCRIBE THE INTEACTION OF AN IR PHOTON WITH A SOLID WE CAN CONSIDER ONLY THE UNIT CELL

2 - SINCE $q \simeq 0$ THIS CAN BE DESCRIBE BY USING THE SAME PHYSICS USE FOR DESCRIBING THE INTERACTION BETWEEN AN IR PHONON AND A MOLECULE.

THE DISPLACEMENT OF THE POSITIVE IONS (A+) AND THE NEGATIVE IONS (B−) IN THE SOLID ARE IN THE OPPOSITE DIRECTIONS

THE MOTION EQUATIONS ARE THE FOLLOWING (IN 1D):

$$m_+ \frac{d^2 x_+}{dt^2} = -K\left(x_+ - x_-\right) + q\,\bar{\mathcal{E}}(t)$$

$$m_- \frac{d^2 x_-}{dt^2} = -K\left(x_- - x_+\right) - q\,\bar{\mathcal{E}}(t)$$

WHERE m_+ AND m_- ARE THE MASSES OF THE TWO IONS, K IS THE "SPRING" CONSTANT OF THE MATERIAL AND X_+, X_- ARE THE DISPLACEMENT. BY DIVIDING THE TWO EQS. WE OBTAIN

$$\frac{d^2}{dt^2}\left(x_+ - x_-\right) = -\frac{K}{\mu}\left(x_+ - x_-\right) + \frac{q}{\mu}\,\bar{\mathcal{E}}(t)$$

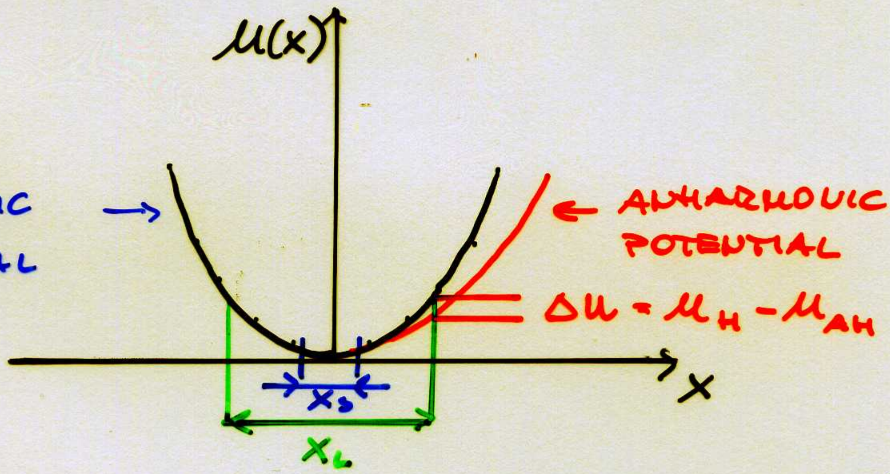
BEING μ THE REDUCED MASS. SETTING $x = X_+ - X_-$ FOR THE RELATIVE DISPLACEMENT OF THE ATOM IN THE UNIT CELL, WE OBTAIN

$$\frac{d^2 x}{dt^2} + \Omega_{TO}^2\, x = \frac{q}{\mu}\,\bar{\mathcal{E}}(t)$$

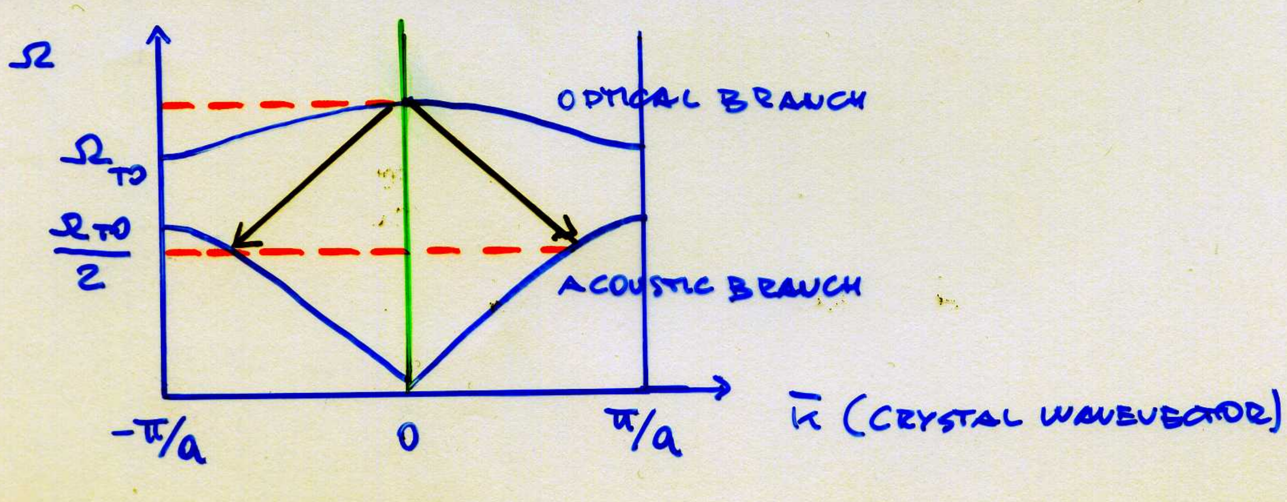
WHERE $\Omega_{TO}^2 = K/\mu$. Ω_{TO} IS THE FREQUENCY OF THE MODE AT $\bar{k}=0$ (AT THE Γ POINT OF THE B.Z.) IN THE ABSENCE OF THE EXTERNAL FIELD (NATURAL MODE). THIS IS THE EQ. OF MOTION OF A FORCED AND UNDAMPED OSCILLATOR. HOWEVER, WE KNOW FROM THE EXPERIMENTS THAT PHONONS DO HAVE A LIFETIME; THIS IMPLIES THAT THEY LOOSE THEIR ENERGY. THE ORIGIN OF THESE LOSSES HAS TO BE FOUND IN THE ANHARMONIC COMPONENTS OF THE IONS OSCILLATIONS INSIDE THE CRYSTAL POTENTIAL. THIS TYPE OF ANHARMONIC MOTION IS RESPONSIBLE FOR THE FAST DECAY OF THE PHONON (1–10 ps) (OPTICAL PHONON). HOWEVER, IN THIS PROCESS MOMENTUM AND ENERGY MUST BE CONSERVED. A TYPICAL DECAY FOR AN OPTICAL PHONON IS THROUGH THE GENERATION OF ACOUSTIC PHONONS. THIS PROCESS CAN BE DESCRIBED EITHER BY

A CLASSICAL MODEL AS WELL AS BY A QED MODEL (QUANTIZATION OF THE PHONON FIELD). HERE IT IS SUFFICIENT TO ADOPT THE CLASSICAL PICTURE. AN ANHARMONIC POTENTIAL CAN BE DESCRIBE ANALYTICALLY AS

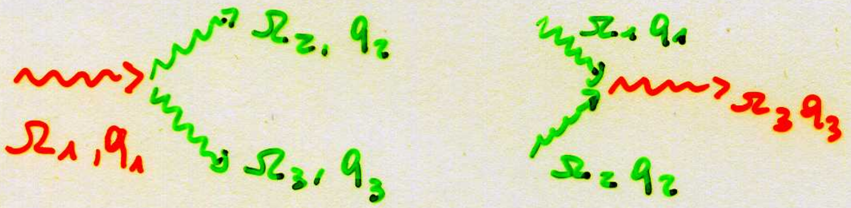
$\mathcal{U}(x) = C_1 + C_2 x^2 + C_3 x^3 + \dots$ SETTING $C_1 = 0$ THIS POTENTIAL CAN BE USED TO DESCRIBE THE INTERATOMIC INTERACTIONS. THIS POTENTIAL CAN BE ALSO RATIONALIZED BY CONSIDERING THE FOLLOWING PICTURE



IT IS CLEAR FROM THIS PICTURE THAT FOR SMALL X (x_s) THE ANHARMONIC COMPONENT IS NEGLIGIBLE, WHEREAS FOR LARGE DISPLACEMENTS (x_L) THE ANHARMONIC COMPONENT MUST BE ACCOUNTED FOR. FOR THE HARMONIC POTENTIAL THE RESTORING FORCE $-d\mathcal{U}/dx$ IS PROPORTIONAL TO THE DISPLACEMENT ($\bar{F} = -k\bar{x}$). THE TERMS AT HIGHER POWER (x^3, x^4 etc.) REPRESENT THE ANHARMONIC CONTRIBUTION AND THEY ARE THE RESPONSIBLE FOR THE PHONON-PHONON SCATTERING.



IF WE CONSIDER THE FIRST BZ A PHOTON IS ABSORBED BY THE LATTICE BY RAMAN SCATTERING AND CREATE A PHONON AT $\bar{k}=0$. THIS OPTICAL PHONON HAS A $\bar{q}\simeq 0$. A PROPER TREATMENT OF THE RAMAN SCATTERING WILL REQUIRE NON-LINEAR OPTICS AND GROUP THEORY FORMALISMS. THESE TWO ARGUMENTS OVERTAKE THE SCOPE OF THIS LECTURES AND THEY WILL BE BRIEFLY REPORTED IN AN APPENDIX. AFTER THE EXCITATION OF THE OPTICAL PHONON AT A FREQUENCY Ω_{TO} AND $q\simeq 0$, THIS PHONON CAN DECAY IN TWO ACOUSTIC PHONONS AT FREQUENCY $\Omega_{TO}/2$ AND OPPOSITE MOMENTUM $\bar{q}$ AND $-\bar{q}$. THIS FOR WARRANTEE THE ENERGY AND MOMENTUM CONSERVATION. THIS THREE PHOTON PROCESS HAS VERY SHORT LIFETIMES THAT CAN BE DEDUCED FROM THE FWHM OF THE RAMAN SPECTRL LINES OR THEY CAN BE DIRECTLY OBSERVED BY SPECTROSCOPY IN THE TIME DOMAIN. A VISUALY EASIER WAY (BUT FORMALLY AND INTELLECTUALY MORE CORRECT AND PROFOUND) CAN BE GAINED USING THE Q.E.D. AND THE FEYNMAD DIAGRAMS



THIS DECAY PROCESSES CAN BE REPPRESENTED IN THE MOTION EQUATION BY A DEMPING TERM RATE γ AND THE MOTION EQUATIONS CAN BE REWRITEN AS

$$\frac{dx^2}{dt^2}+\gamma\frac{dx}{dt}+\Omega_{TO}^2 x=\frac{q}{\mu}\bar{E}(t)$$

THIS EQ. REPRESENTS THE RESPONSE OF A DAMPED T.O. PHONON MODE TO A RESONANT LIGHTWAVE. THIS EQ. IS FORMALY SIMILAR TO THE EQ. OF THE LORENTZ OSCILLATOR WHERE ω_0 IS

REPLACED BY μ, ω_0 BY Ω_{TO} AND $-e$ BY q. THE SOLUTION OF THIS EQ. HAS A SOLUTION GIVEN BY

$$x(t) = x_0 \,\mathbb{R}\left(\exp(-i\omega t - \phi')\right)$$

WHEN CONSIDERING $\bar{\mathcal{E}}(t) = \mathcal{E}_0 \cos(\omega t + \phi) = \mathcal{E}_0 \mathbb{R}\left[\exp(-i\omega t - \phi)\right]$

WHERE

$$x_0 = \frac{-q\mathcal{E}_0/\mu}{\Omega_{TO}^2 - \omega^2 - i\gamma\omega}$$

$$\bar{P}_{RES.} = Np = Nq\bar{x} = \frac{Nq^2}{\mu}\frac{1}{(\Omega_{TO}^2 - \omega^2 - i\gamma\omega)}\bar{\mathcal{E}}$$

N = NUMBER OF UNIT CELLS PER UNIT VOLUME

THIS EQ. CAN BE USED TO OBTAIN THE COMPLEX RELATIVE DIELECTRIC CONSTANT $\mathcal{E}_r$. THE ELECTRIC DISPLACEMENT $\bar{D}$ IS RELATED TO THE ELECTRIC FIELD $\bar{\mathcal{E}}$ AND POLARIZATION $\bar{P}$ THROUGH

$$\bar{D} = \varepsilon_0 \bar{\mathcal{E}} + \bar{P}$$

BEING INTERESTED IN THE OPTICAL RESPONSE AT A FREQUENCY CLOSE TO Ω_{TO} WE SPLIT THE POLARIZATION INTO A NON-RESONANT BACKGROUND TERM AND THE RESONANT TERM ARISING FROM THE DRIVEN RESPONSE OF THE OSCILLATOR

$$\bar{D} = \varepsilon_0\bar{\mathcal{E}} + \bar{P}_{BG} + \bar{P}_{RES} = \varepsilon_0\bar{\mathcal{E}} + \varepsilon_0\chi\bar{\mathcal{E}} + P_{RES}$$

IF THE MATERIAL IS ISOTROPIC $\bar{D} = \varepsilon_0\varepsilon_r\bar{\mathcal{E}}$ AND

$$\tilde{\varepsilon}_r(\omega) = 1 + \chi + \frac{Nq^2}{\varepsilon_0\mu}\frac{1}{(\Omega_{TO}^2 - \omega^2 - i\gamma\omega)}$$

WHERE $\tilde{\varepsilon}_r(\omega)$ IS THE COMPLEX DIELECTRIC FUNCTION AND χ IS THE NON-RESONANT SUSCEPTIBILITY OF THE MEDIUM.

THE DIELECTRIC FUNCTION $\tilde{\varepsilon}_r(\omega)$ CAN BE RE-WRITTEN BY INTRODUCING THE STATIC AND THE HIGH FREQUENCY CONSTANTS $\tilde{\varepsilon}_{ST}$ AND $\tilde{\varepsilon}_{\infty}$. IN THE LIMIT OF LOW AND HIGH FREQUENCY WE OBTAIN

$$\tilde{\varepsilon}_{ST} \equiv \tilde{\varepsilon}_r(0) = 1 + \chi + \frac{Nq^2}{\varepsilon_0\mu\Omega_{TO}^2}$$

$\tilde{\varepsilon}_\infty \equiv \tilde{\varepsilon}_r(\infty) = 1 + \chi$ THUS WE CAN WRITE

$$\tilde{\varepsilon}_r(\omega) = \tilde{\varepsilon}_\infty + (\tilde{\varepsilon}_{ST} - \tilde{\varepsilon}_\infty) \frac{\Omega_{TO}^2}{(\Omega_{TO}^2 - \omega^2 - i\gamma\omega)}$$

AN IMPORTANT CONSEQUENCE OF THIS EQUATION IS REPRESENTED BY THE CASE OF $\gamma \to 0$. IN THIS CASE WE CAN FIND A FREQUENCY ω' SUCH THAT $\varepsilon_r(\omega') = 0$. THEREFORE, WE CAN WRITE

$$\varepsilon_r(\omega') = 0 = \varepsilon_\infty + (\varepsilon_{ST} - \varepsilon_\infty) \frac{\Omega_{TO}^2}{(\Omega_{TO}^2 - \omega'^2)}$$

THIS CAN BE SOLVED FOR ω'

$$\omega' = \left(\frac{\varepsilon_{St}}{\varepsilon_\infty}\right)^{1/2} \Omega_{TO}$$

$\varepsilon_r = 0$ MEANS THAT IN A MEDIUM WITH NO FREE CHARGES, THE TOTAL CHARGE DENSITY WILL BE ZERO. HENCE THE GAUSS' LAW GIVES

$$\nabla \cdot \bar{D} = \nabla \cdot (\varepsilon_r \varepsilon_0 \bar{E}) = 0$$

FOR A MEDIUM WITH $\varepsilon_r \neq 0$. CONSIDERING $\bar{E}(\bar{r},t) = \bar{E}_0 e^{i(\bar{k}\cdot\bar{r} - \omega t)}$ AND SUBSTITUTING IN THE PREVIOUS EQ. WE OBTAIN $\bar{k} \cdot \bar{E} = 0$ THIS IMPLIES $\bar{k}$ AND $\bar{E}$ $\perp$. HOWEVER IF $\varepsilon_r = 0$ $\nabla \cdot \bar{D} = 0$ CAN BE SATISFIED ALSO FOR $\bar{k} \cdot \bar{E} \neq 0$. THIS RESULTS IMPLIES LONGITUDINAL WAVES. THEREFORE THE DIELECTRIC CAN SUPPORT LONGITUDINAL ELECTRIC FIELD AT FREQUENCIES WHERE $\varepsilon_r = 0$. IN THE SAME WAY THAT A T.O. MODE GENERATES A TRANSVERSAL ELECTRIC FIELD WAVE, THE L.O. MODES GENERATE A LONGITUDINAL ELECTRIC FIELD WAVE. THUS THE WAVE AT $\omega = \omega'$ CORRESPOND TO L.O. PHONON WAVES, AND WE IDENTIFY ω' WITH THE FREQUENCY OF THE L.O. MODE AT $q = 0$, NAMELY Ω_{LO}. THEREFORE WE CAN WRITE

THEREFORE, WE CAN WRITE

$$\frac{\Omega_{LO}^2}{\Omega_{TO}^2} = \frac{\varepsilon_{s0}}{\varepsilon_\infty}$$

THIS RELATION IS KNOWN AS LYDDANE-SACHS-TELLER (LST) RELATIONSHIP. ITS VALIDITY CAN BE CHECKED BY COMPARING THE VALUES OF Ω_{LO}/Ω_{TO} FROM RAMAN OR NEUTRON SCATTERING