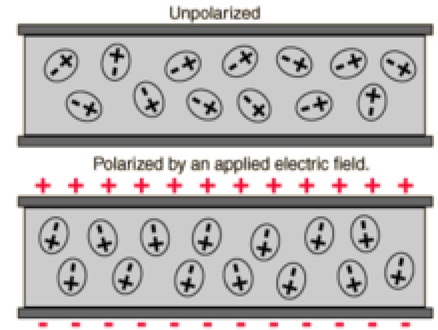
Solid state physics for NANO

UNIVERSITÄT SIEGEN
FESTKÖRPERPHYSIK

Lecture 10: Dielectric properties

Prof. Dr. U. Pietsch

Dielectric properties



Materie in electric field

$$D = \varepsilon_0 E + P$$

$$D = \varepsilon_0 E(1 + \chi_e)$$

$$D = \varepsilon_0 \varepsilon E$$

P – Polarisability

χ – dielectric susceptibility

ε - permitivity

$$\chi_e = \frac{\varepsilon_0 P}{E}$$

Within electric field, alignment of electrical dipoles

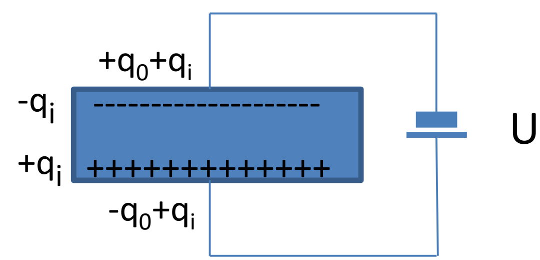
Dipole moment $\vec{p} = \alpha E_{loc}$

$$\vec{p}_i = \alpha_{ij} E_j^{loc}$$

α– polarisability, atomic property

$$E_0 = E_{ext} = \frac{U}{d} + \frac{P}{3\varepsilon_0} = E + \frac{P}{3\varepsilon_0}$$

Field of a sphere



James Clerk Maxwell

1872 - 1946

Polarisability is of atomic nature

- Orientation of permanant dipoles
- Ionic polarisation (changing spacing between ions of different charge)
- Electronic polarisation (relative displacement of electron cloud with respect to ionic core)

Local E_{loc} is $E_{loc} = E + \frac{P}{3\varepsilon_0}$

Polarisability = Dipole moment/volume

$$P = \sum_i N_i \alpha_i E_i^{loc} = \sum_i N_i \alpha_i (E + \frac{P}{3\varepsilon_0}) \qquad \varepsilon = \frac{\varepsilon_0 E + P}{\varepsilon_0 E} = 1 - \frac{P}{\varepsilon_0 E}$$

$$P = \frac{E \sum_i N_i \alpha_i}{1 - \frac{1}{3\varepsilon_0} \sum_i N_i \alpha_i} \qquad \chi = \frac{P}{\varepsilon_0 E} \qquad \chi = \frac{\sum N_i \alpha_i}{\varepsilon_0 (1 - \frac{1}{3\varepsilon_0} \sum N_i \alpha_i)} = \varepsilon - 1$$

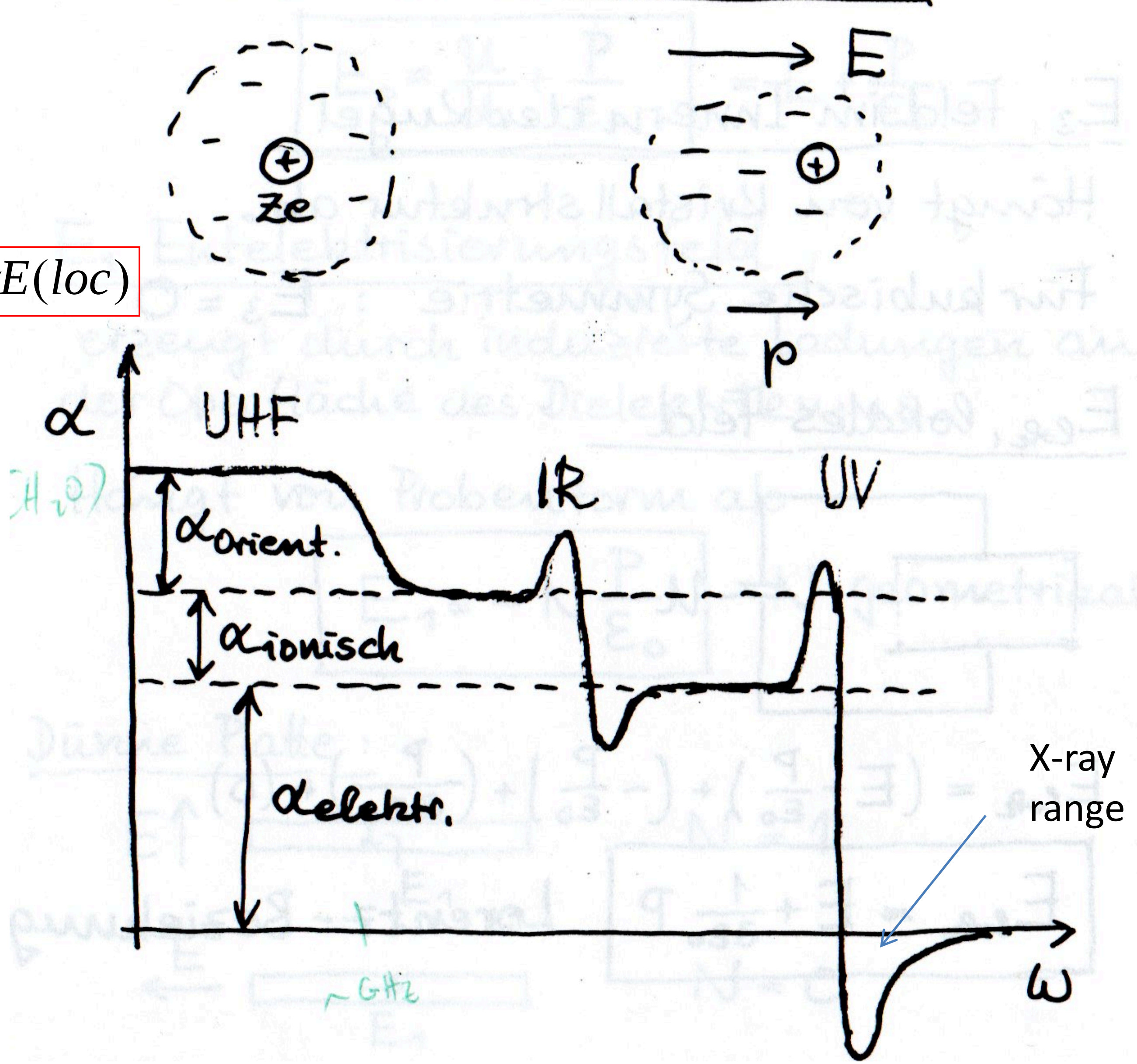
$$\boxed{\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{1}{3\varepsilon_0} \sum_i N_i \alpha_i}$$

Clausius –Mosotti relation between ε and α (polarisability)

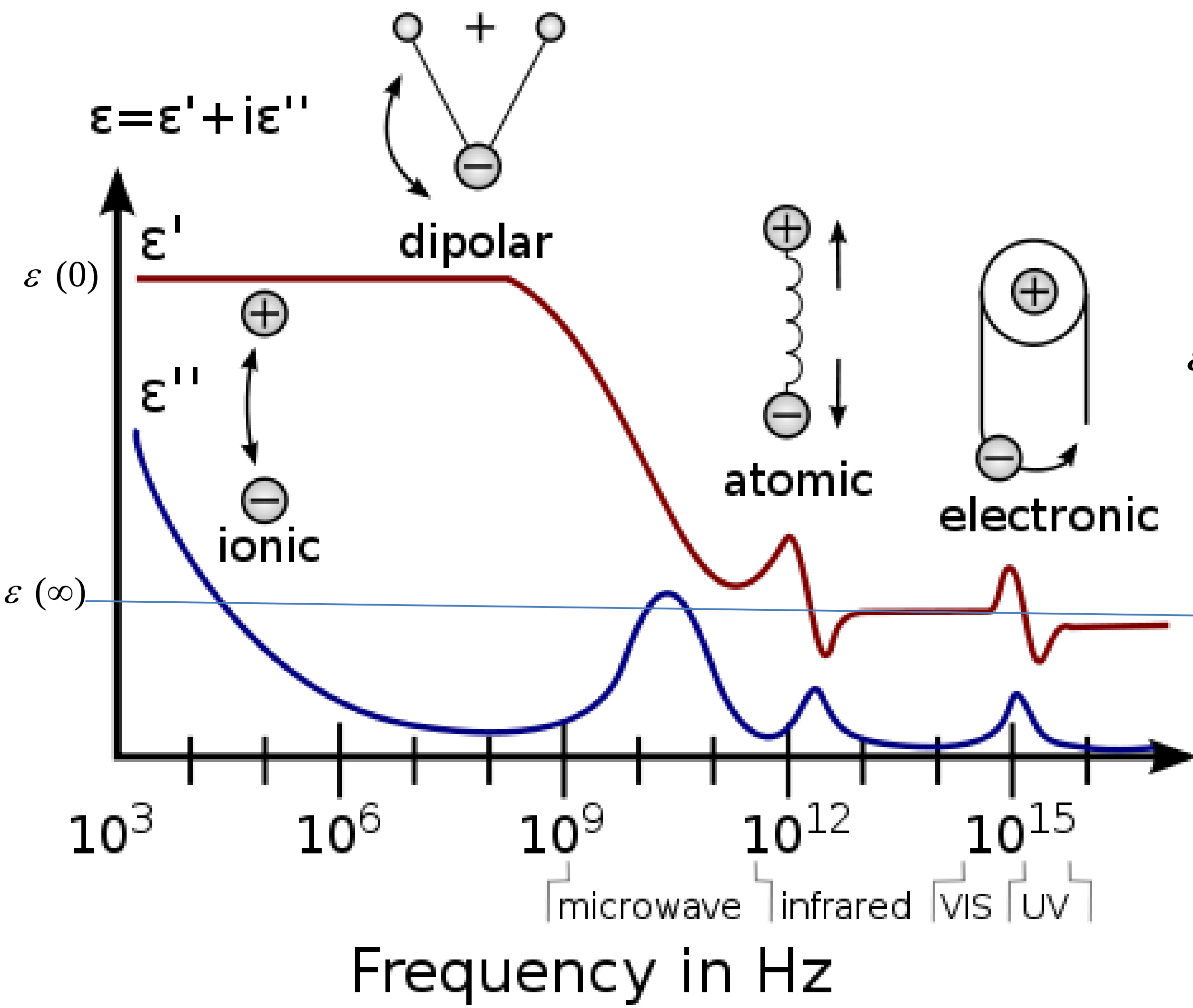
$$\boxed{E(loc) = E + \frac{1}{3\varepsilon_0} P}$$

Polarizability is function of frequence

$$p = \alpha E(loc)$$



Frequency dependence of dielectric function



Kramers – Kronig relation

$$\varepsilon'(\omega) = \varepsilon_0 + \frac{2}{\pi}\int_0^{\infty} \frac{\omega'\varepsilon''(\omega')}{\omega'^2 - \omega^2}\, d\omega'$$

$$\varepsilon''(\omega) = -\frac{2\omega}{\pi}\int_0^{\infty} \frac{\varepsilon'(\omega') - \varepsilon_0}{\omega'^2 - \omega^2}\, d\omega'$$

$$\varepsilon(0) = \varepsilon_0 + \frac{2}{\pi}\int_0^{\infty} \frac{\varepsilon''(\omega')}{\omega}\, d\omega'$$

Dielectric function

$$\sqrt{\varepsilon} = n + iK$$

Measurable: refractive index (n), extinction coefficient (K)

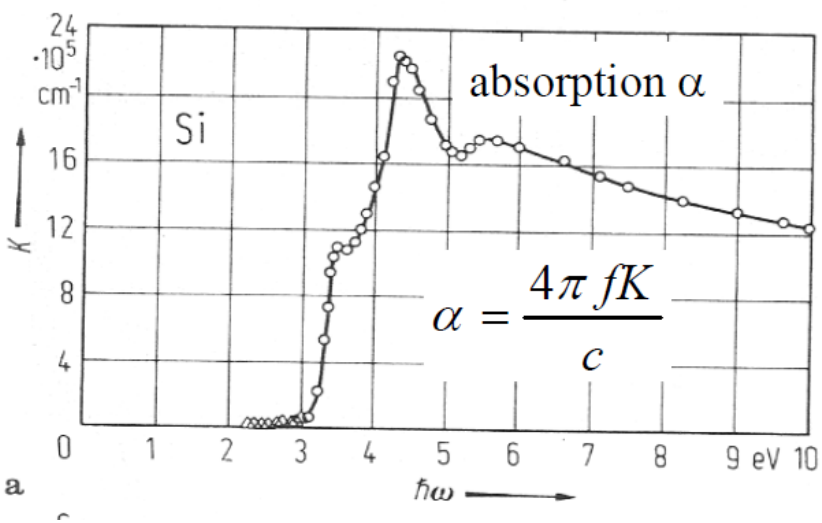
$$\varepsilon = n^2 - K^2 + i2nK$$

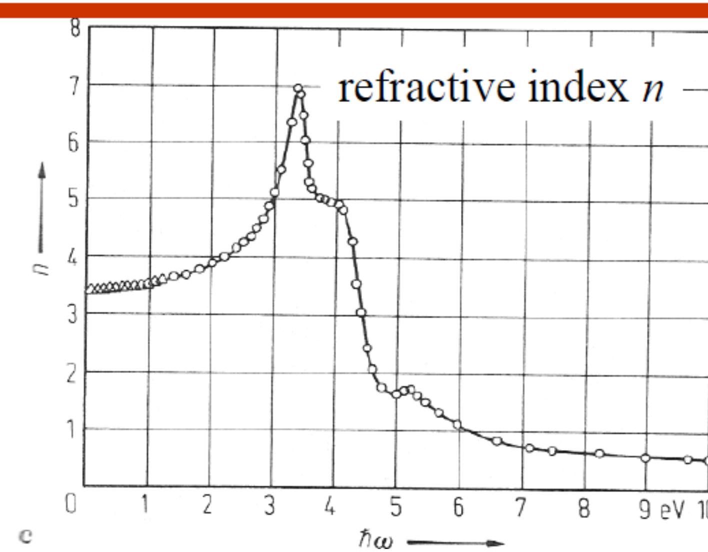
Intensity $I(x) = I(0)\exp(-\alpha x)$ J m^{-2} s^{-1}

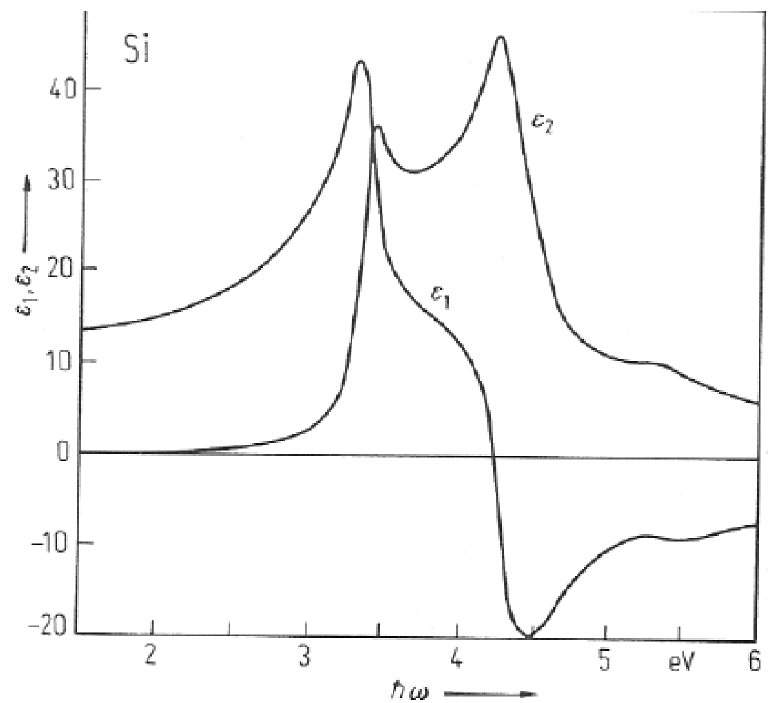
absorption coefficient → $\alpha = \dfrac{4\pi f K}{c}$ (frequency f, extinction coefficient K)

http://www.reading.ac.uk/infrared/library/substrateopticaltheory/
ir-substrateopticaltheory-absorptionandextinctioncoefficienttheory.asp

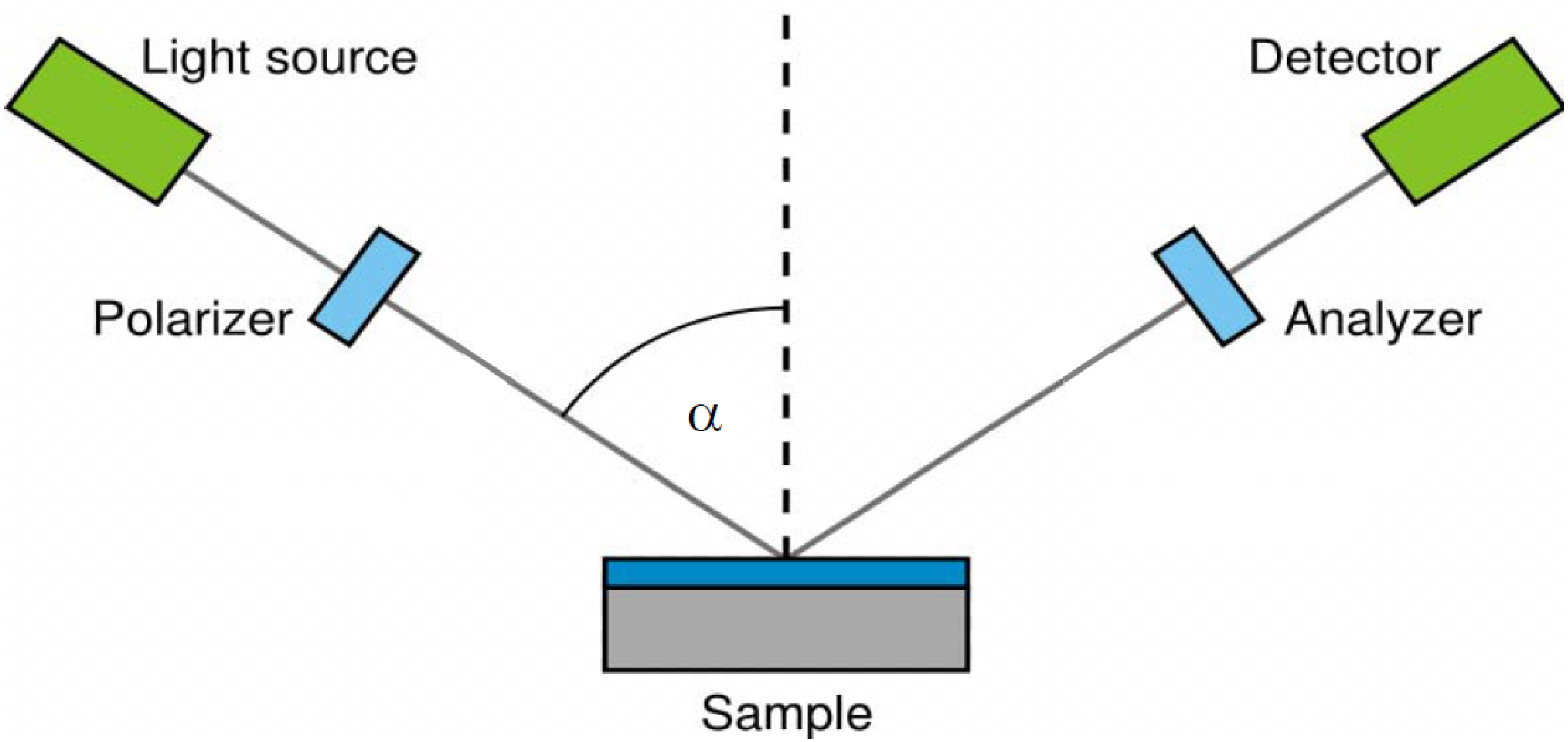
Dielectric function of silicon $\sqrt{\varepsilon(\omega)} = n(\omega) + iK(\omega)$







Ellipsometry

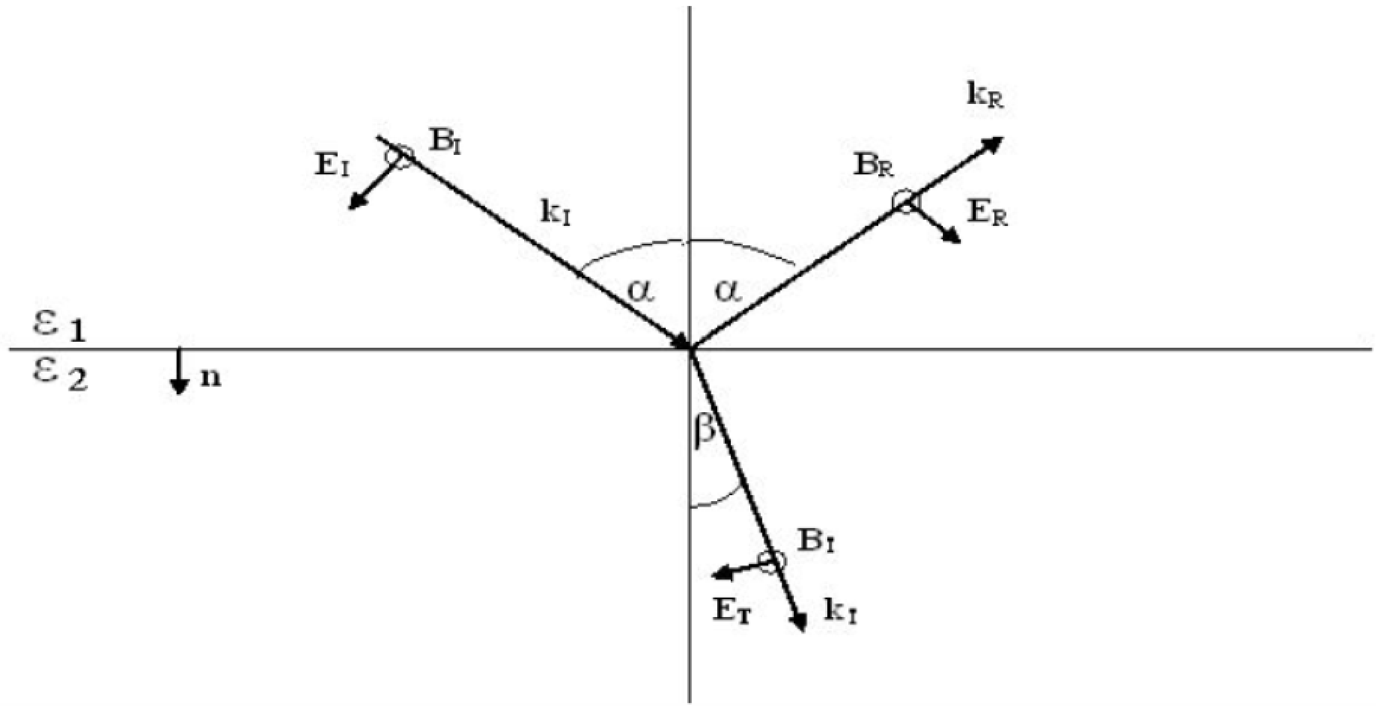


Ellipsometry measures the change of polarization upon reflection. The measured signal depends on the thickness and the dielectric constant.

http://en.wikipedia.org/wiki/Ellipsometry

$$\hat{n} \times \vec{E}_R = \hat{n} \times \left(\vec{E}_I + \vec{E}_T \right)$$ Parallel components of *E* are continuous

$$\hat{n} \cdot \varepsilon_2 \vec{E}_R = \hat{n} \cdot \varepsilon_1 \left(\vec{E}_I + \vec{E}_T \right)$$ Perpendicular components of *D* are continuous



reflectance coefficient $\longrightarrow$ $$r = \frac{E_{0R}}{E_{0I}} = \frac{(n_2 + iK_2)\cos\alpha - (n_1 + iK_1)\cos\beta}{(n_2 + iK_2)\cos\alpha + (n_1 + iK_1)\cos\beta}$$

http://lamp.tu-graz.ac.at/~hadley/ss2/studentpresentations/2010/ellipsometry_nau.pdf

Reflection coefficient

$$r = \frac{E_{0R}}{E_{0I}} = \frac{(n_2 + iK_2)\cos\alpha - (n_1 + iK_1)\cos\beta}{(n_2 + iK_2)\cos\alpha + (n_1 + iK_1)\cos\beta}$$

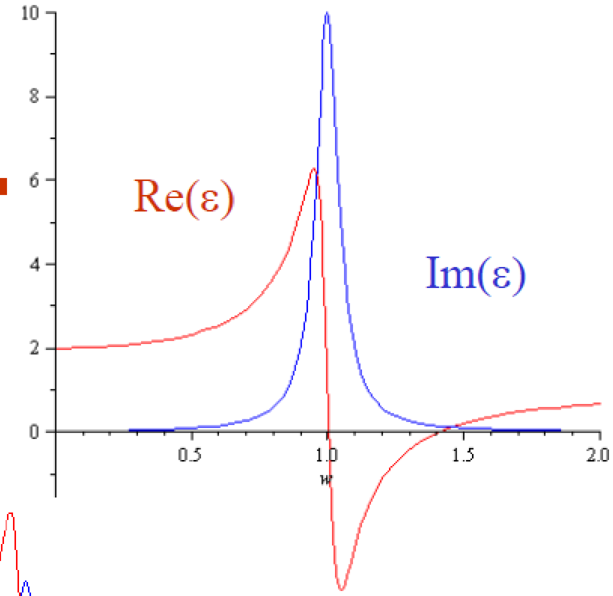
Kittel gives the result for reflection at normal incidence ($\cos\alpha = 1$, $\cos\beta = 1$) from vacuum ($n_1 = 1$, $K_1 = 0$).

$$r = \frac{n_2 + iK_2 - 1}{n_2 + iK_2 + 1}$$

It is difficult to measure the phase of the reflectance coefficient. The reflectance is the fraction of the intensity that is reflected. For normal incidence from vacuum:

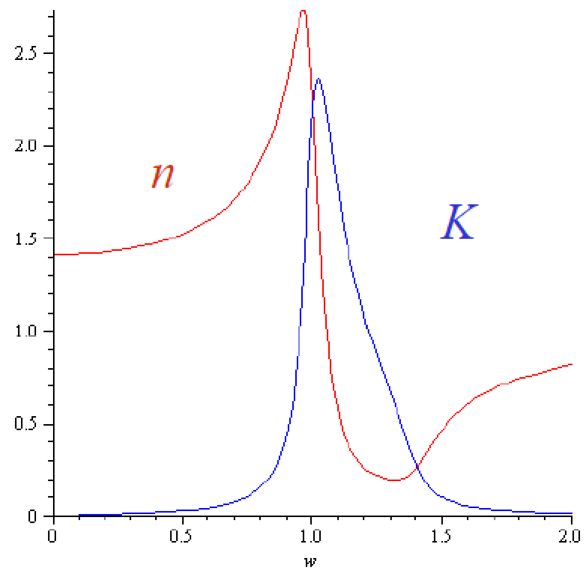
$$R = r^* r = \frac{(n_2 - 1)^2 + K_2^2}{(n_2 + 1)^2 + K_2^2}$$

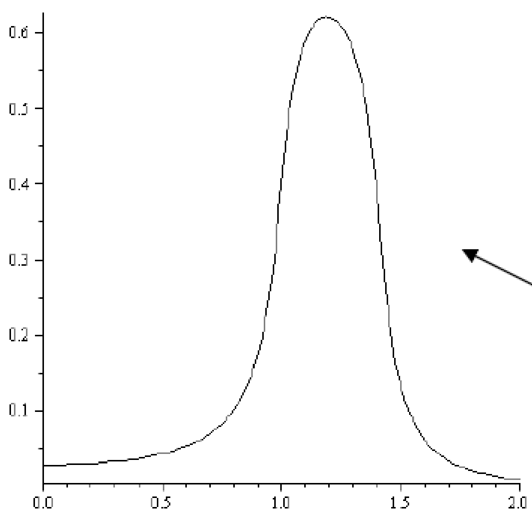
Reflectance, insulator



$$\varepsilon(\omega) = \varepsilon_\infty + \frac{(\varepsilon_{st} - \varepsilon_\infty)\,\omega_0^2\left(\omega_0^2 - \omega^2 + i\omega\gamma\right)}{\left(\omega_0^2 - \omega^2\right)^2 + \omega^2\gamma^2}$$

$$\sqrt{\varepsilon(\omega)} = n(\omega) + iK(\omega) \longrightarrow$$





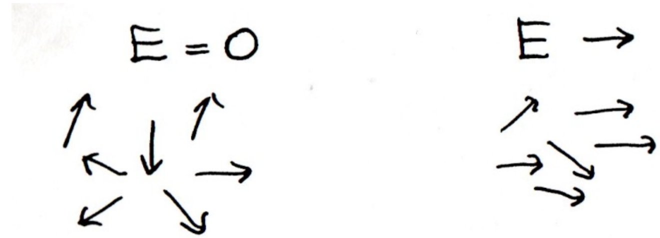
$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2}$$

Orientational polarisation: competition with thermal movement

Energy of dipole in field E $U = -\vec{p}\vec{E} = -pE\cos\theta$

Probability to rotate dipole by θ is $f = \exp(-U/kT) = \exp(\frac{pE\cos\theta}{kT})$

$$\langle p_E \rangle = \frac{\int p_E f(\theta) d\Omega}{\int f(\theta) d\Omega}$$



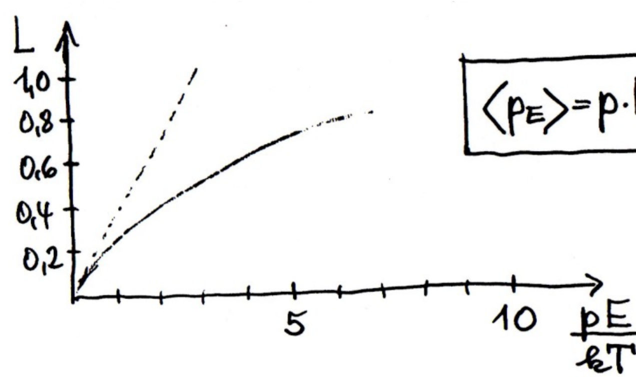
$p_E = p\cos\theta$ and $d\Omega = 2\pi\sin\theta\, d\theta$

$$\langle \cos\theta \rangle = \frac{\int 2\pi\sin\theta\cos\theta\exp(\frac{pE\cos\theta}{kT})d\theta}{\int 2\pi\sin\theta\exp(\frac{pE\cos\theta}{kT})d\theta} = \coth(\frac{pE}{kT}) =: L(u)$$

Langevin function $u = \frac{pE}{kT}$

Since pE << kT $\coth u = \frac{u}{3} + \frac{u^3}{45} + ...$

$$L(u) \approx \frac{u}{3} = \frac{pE}{3kT}$$



$$\langle p_E \rangle = p \cdot L\left(\frac{pE}{kT}\right)$$

For free electrons = electron plasma

From Maxwell equations

$$divE = \frac{\rho}{\varepsilon_0} = \frac{\rho_{ext} + \rho_{int}}{\varepsilon_0}$$

$$divD = div\varepsilon_0\varepsilon E = \rho_{ext}$$

In K-space

$$D(K) = \varepsilon(K)E(K)$$

$$\varepsilon(K) = \frac{\rho_{ext}(K)}{\rho(K)} = 1 - \frac{\rho_{ind}(K)}{\rho(K)}$$

Using external potential ϕ_{ext} and atomic potential ϕ

$$-\nabla\varphi_{ext} = D \qquad \nabla^2\varphi_{ext} = \frac{\rho_{ext}}{\varepsilon_0}$$

and

$$-\nabla\varphi = E \qquad \nabla^2\varphi = \frac{\rho}{\varepsilon_0}$$

→

$$\frac{\varphi_{ext}(K)}{\varphi(K)} = \frac{\rho_{ext}}{\rho} = \varepsilon(K)$$

From equation of motion of electron $m\frac{d^2x}{dt^2} = -eE$ → $\omega^2 mx = -eE$ $\qquad x = \frac{eE}{m\omega^2}$

Dipole moment $-ex = \frac{-e^2E}{m\omega^2}$ Polarisation of electron gas $P = -nex = -\frac{ne^2}{m\omega^2}E$

Dielectric function

$$\varepsilon(\omega) = \frac{D(\omega)}{\varepsilon_0 E(\omega)} = 1 + \frac{P(\omega)}{\varepsilon_0 E(\omega)}$$

dielectric function of electron gas

$$\varepsilon(\omega) = 1 - \frac{ne^2}{\varepsilon_0 m\omega^2}$$

Dielectric function of electron gas

$$\varepsilon(\omega) = 1 - \frac{ne^2}{\varepsilon_0 m \omega^2}$$

Defining plasma frequency

$$\omega_p^2 \equiv \frac{ne^2}{\varepsilon_0 m} \qquad \varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

If positive ion core background of DK is $\varepsilon(\infty)$

$$\varepsilon(\omega) = \varepsilon(\infty)(1 - \frac{\overline{\omega}_p^2}{\omega^2})$$

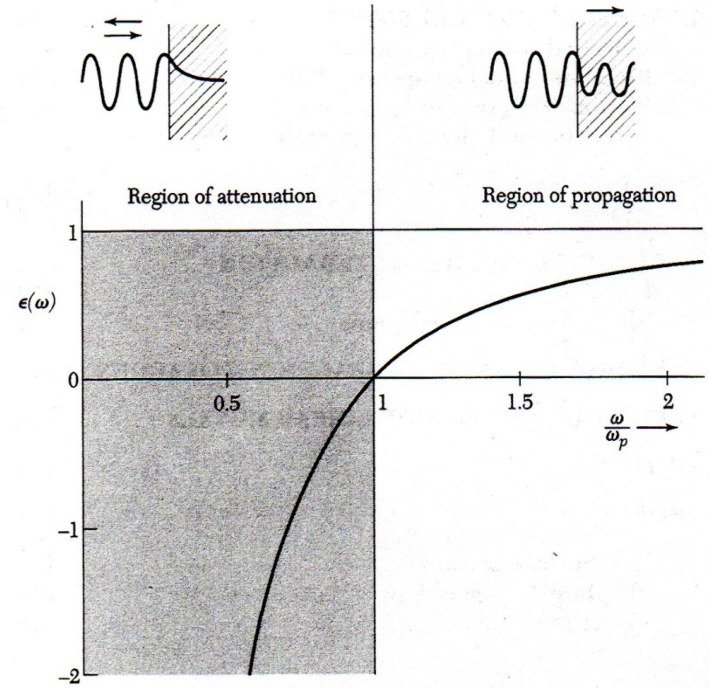
ε=0 at ω=ω_p

Because of wave equ. $\mu_0 \frac{\partial^2 D}{\partial t^2} = \nabla^2 E$

Wave function:

E= A exp(-iωt)exp(i**Kr**) and D=ε(ω,K)E

→ solution $\varepsilon(\omega, \vec{K})\varepsilon_0\mu_0\omega^2 = K^2$



- ε is real and >0, ω is real, K is real, electromagnetic wave propageates with phase velocity c/ε^ ½
- ε is real and <0, ω is real, K is inaginary, wave is damped with length 1/|K|
- ε is complex, ω is real, K is complex, wave damped in space,
- ε = $\varepsilon(\infty)$, finite response without applied force, ε(ω,K) defines frequency of free oscillation of medium
- ε =0, longitudinal pol. waves are possible

Transverse Optical modes of plasma oscillation

$$\varepsilon(\omega)\mu_0\varepsilon_0\omega^2 = \varepsilon(\infty)(\omega^2 - \overline{\omega}_p^2) = K^2$$

For $\omega < \overline{\omega}_p$ one has $K^2<0$

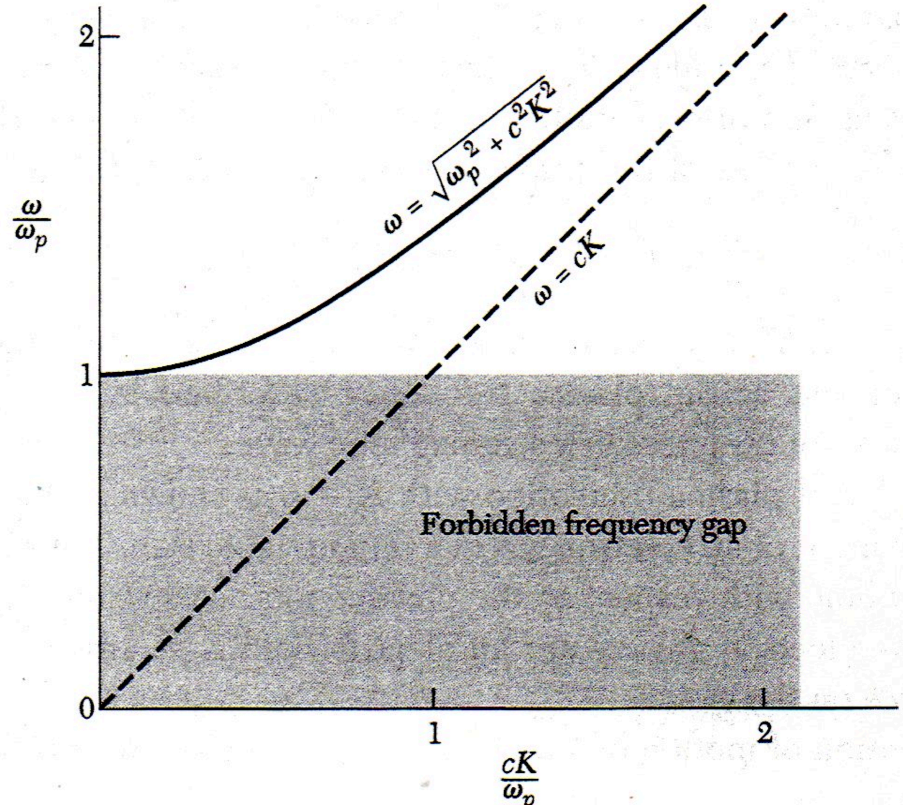
within $1 < \omega < \overline{\omega}_p$ damping Solution exp(-|K|x)

Incident wave does not propagate into the medium, it is totally reflected

For $\omega > \overline{\omega}_p$ DK is positive and real ,

Dispersion relation

$$\omega^2 = \overline{\omega}_p^2 + \frac{K^2}{\mu_0\varepsilon_0\varepsilon(\infty)}$$



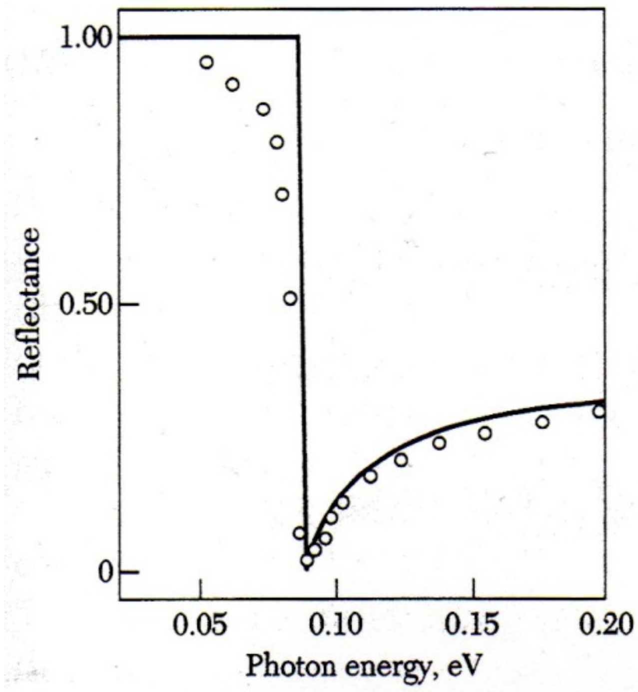
Plasma frequency, plasma wavelength

n, electrons/cm^3	10^{22}	10^{18}	10^{14}	10^{10}
ω_p, s^{-1}	5.7×10^{15}	5.7×10^{13}	5.7×10^{11}	5.7×10^{9}
λ_p, cm	3.3×10^{-5}	3.3×10^{-3}	0.33	33

Simple metals reflect light in visible frequence range and are transparent in UV

InSb n=4 x 10^{18} cm^{-3}

$$\overline{\omega}_p / \hbar = 0.09 eV$$



Longitudinal plasma oscillations

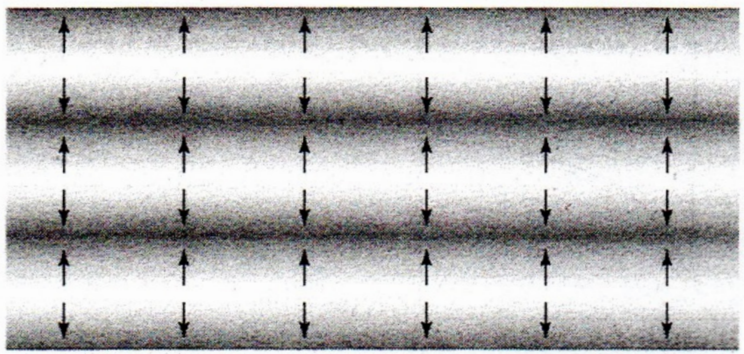
For $$\varepsilon\ (\omega_L) = 1 - \frac{\omega_p^2}{\omega_L^2} = 0$$ near K=0

There is a free longitudinal oscillation mode of electron gas at

$$\omega_{LO} = \overline{\omega}_p$$

$$\omega_p^2 = \frac{ne^2}{\varepsilon_0 m}$$ with amplitude $$u = \frac{\varepsilon_0 E}{ne}$$

In more detail $$\omega = \omega_p (1 + 3k^2 v_F^2 / 10\omega_p^2 + ...$$

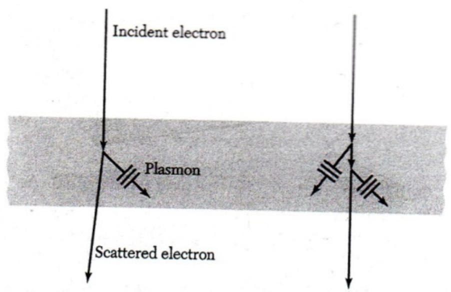


Arrows indicate displacement of electrons

PLASMONS

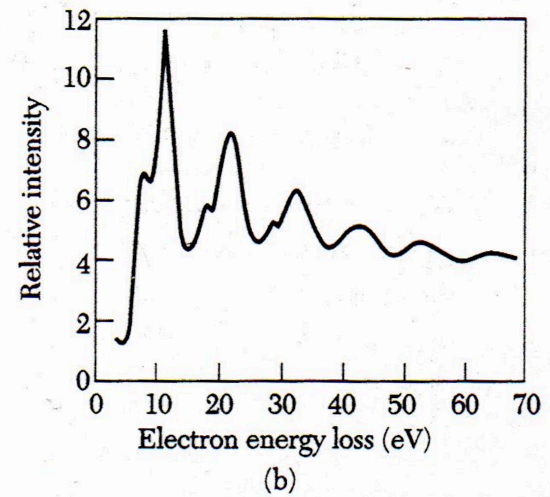
Plasma oscillation in a metal is a collective longitudinal excitation of conduction electron gas
PLASMON is a quantum of a plasma oscillation

Excited by reflecting electrons or photons from a metallic film or by transmission of electrons or photons throughout a film → electron energy loss spectroscopy EELS



Typical plasmon energies (eV)

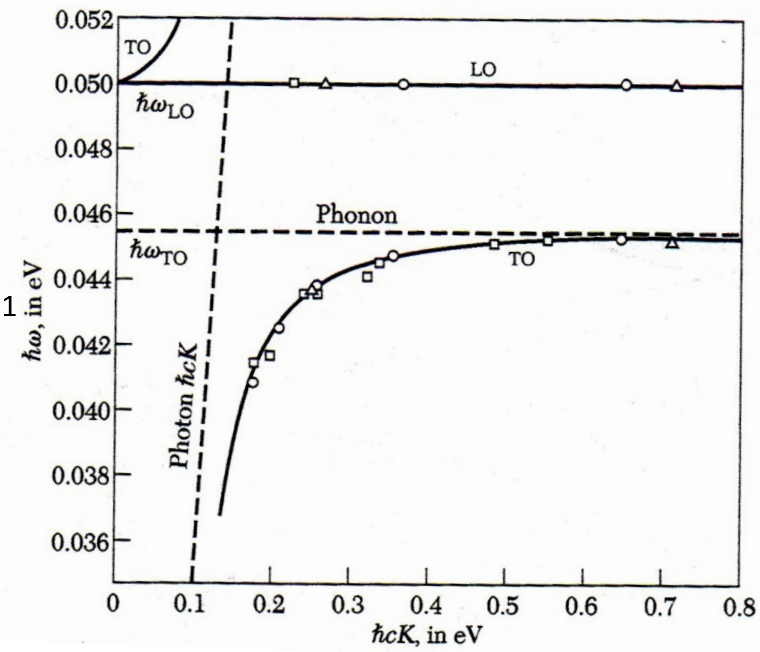
Material	Observed	Calculated $\hbar\omega_p$	Calculated $\hbar\bar{\omega}_p$
Metals			
Li	7.12	8.02	7.96
Na	5.71	5.95	5.58
K	3.72	4.29	3.86
Mg	10.6	10.9	
Al	15.3	15.8	
Dielectrics			
Si	16.4–16.9	16.0	
Ge	16.0–16.4	16.0	
InSb	12.0–13.0	12.0	



EELS spectrum of Mg,
combination of surface plasmon at 7.1eV and volume plasmon at 10.6 eV

Phonon – photon coupling : POLARITONS

Transverse optical phonons are coupling with transverse electromagnetic waves if both frequencies and wave vectors are approximately equal.
Crossover at c k(photon)=ω(phonon)≈10^{13}/s , k ≈ 300cm^{-1}



Coupling of electric field E of photon with dielectric polarization of TO phonon is described by wave equation

$$c^2 K^2 E = \omega^2 (E + \frac{P}{\varepsilon_0})$$

At low K, ω_{TO} is in dependent from K, Polarization is proportional to displacement of ions, u, written as P=N q u

$$-\omega^2 P + \omega_{TO}^2 P = (Nq^2 / \mu) E$$

N number of ion pairs,
q- charge, μ reduced mass

solving
$$\begin{vmatrix} \omega^2 - c^2 K^2 & \omega^2 / \varepsilon_0 \\ Nq / \mu & \omega^2 - \omega_{TO}^2 \end{vmatrix} = 0$$

Two solutions

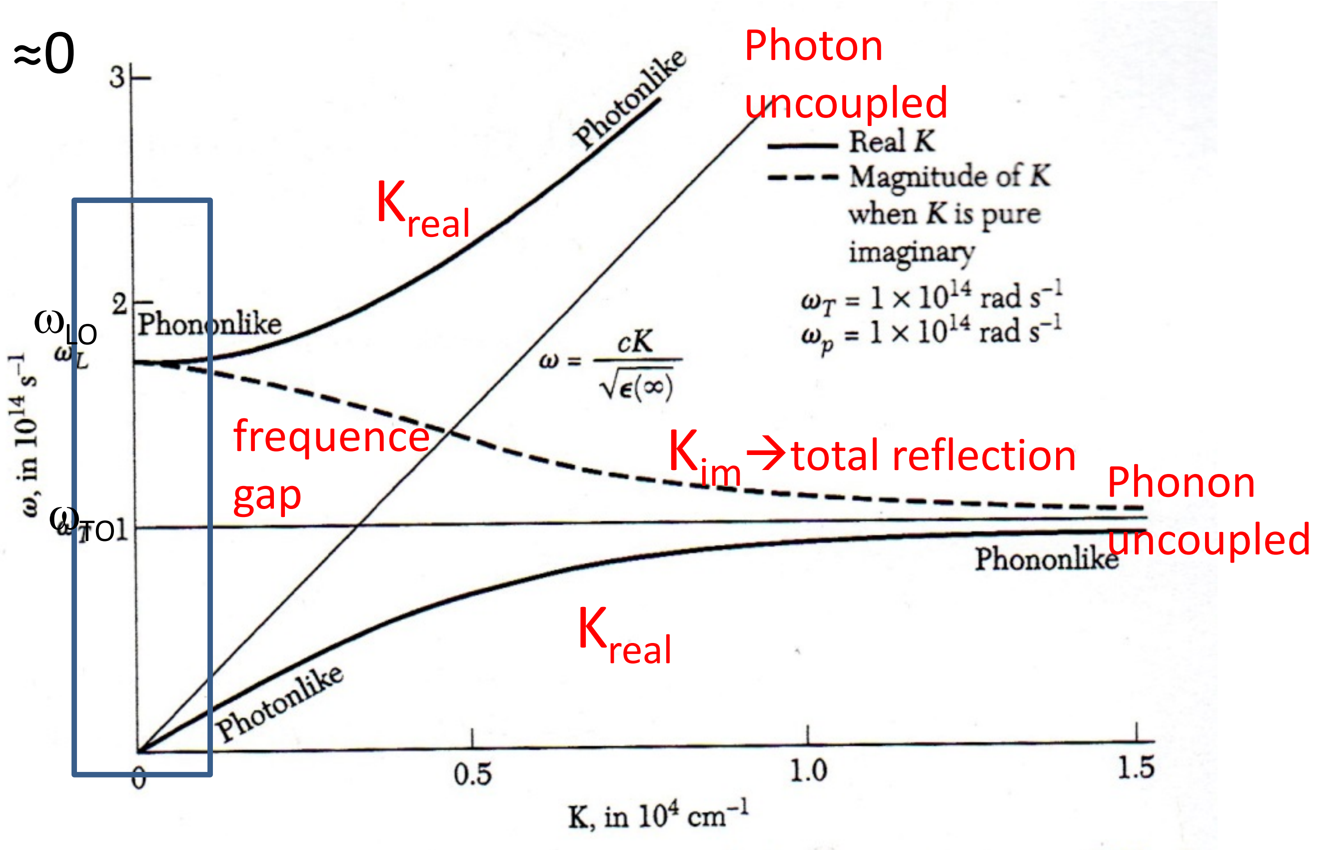
$$\omega = 0$$ For Photons

$$\omega^2 = \omega_{TO}^2 + \frac{Nq^2}{\varepsilon_0 \mu}$$ For Polariton

Two solutions for K ≈0

$$\omega = 0$$

$$\omega^2 = \omega_{TO}^2 + \frac{Nq^2}{\varepsilon_0 \mu}$$



For K >0 two branches

$$\omega^2 = \frac{1}{2}(\omega_{TO}^2 + \frac{c^2K^2}{\varepsilon(\infty)}) \pm [\frac{1}{4}(\omega_{LO}^2 + \frac{c^2K^2}{\varepsilon(\infty)})^2 - (\frac{c^2K^2\omega_{TO}^2}{\varepsilon(\infty)})^2]^{1/2}$$

Dielectric function is

$$\varepsilon(\omega) = \varepsilon(\infty) + \frac{Nq^2/\mu}{\varepsilon_0(\omega_{TO}^2 - \omega^2)}$$

Set:

$$\varepsilon(0) = \varepsilon(\infty) + \frac{Nq^2}{\mu\varepsilon_0\omega_{TO}^2}$$

$$\varepsilon(\omega) = \varepsilon(\infty) + [\varepsilon(0) - \varepsilon(\infty)]\frac{\omega_{TO}^2}{\omega_{TO}^2 - \omega^2}$$

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

With lattice absorption

$$\varepsilon(\omega) = \varepsilon(\infty)\frac{\omega_{LO}^2 - \omega^2 - i\omega\Gamma}{\omega_{TO}^2 - \omega^2 - i\omega\Gamma}$$

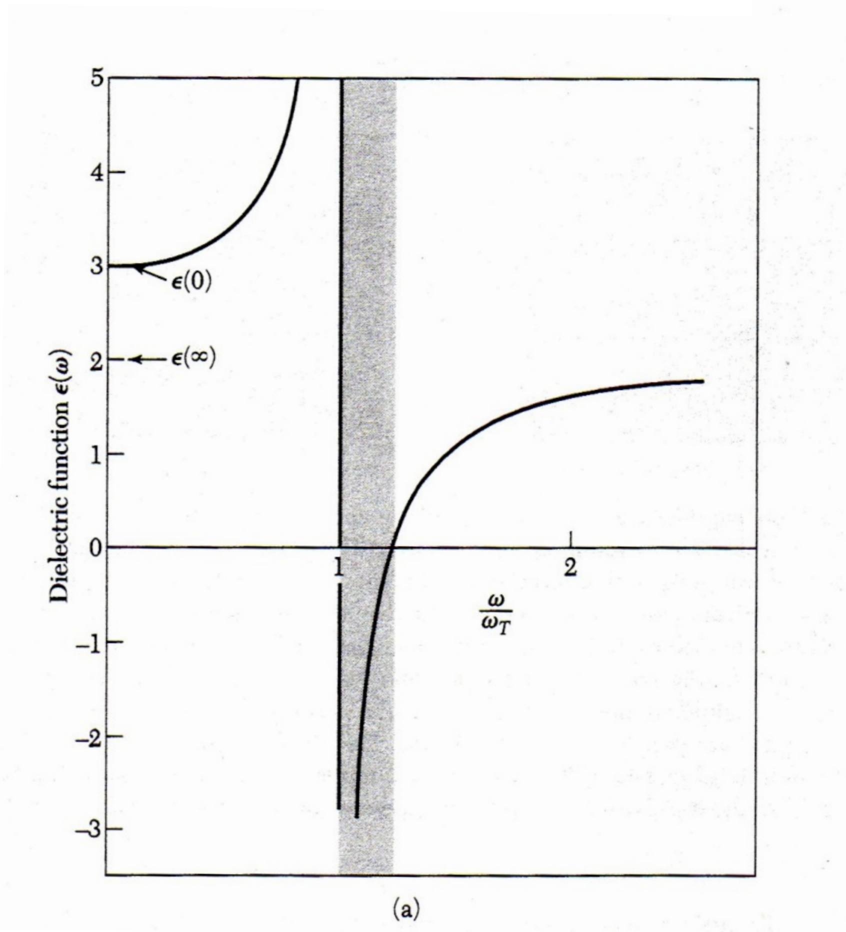
This gives

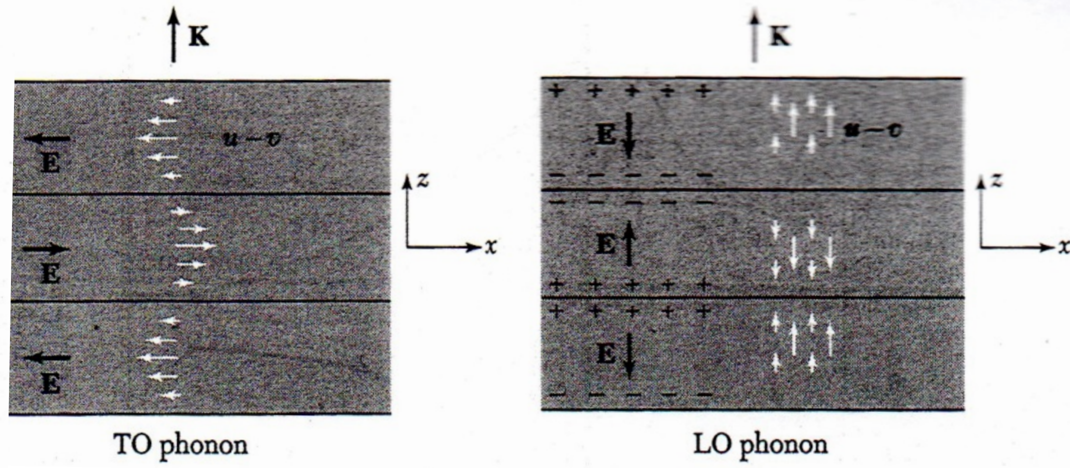
$$\varepsilon(\infty)\omega_{LO}^2 = \varepsilon(0)\omega_{TO}^2$$

$\varepsilon(\omega)$ defines ω_{LO} and pole of $\varepsilon(\omega)$ defines ω_{TO}

$$\boxed{\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\varepsilon(0)}{\varepsilon(\infty)}}$$

Lyddane-Sachs-Teller relation





Relative dispacement of positive and negative ions for a wave travelling along z-axis
For TO phonon ionic displacement and E-vector are perpendicular to K vector; For LO phonon ionic displacement and E-vector are parallel to K

$\varepsilon(\omega) < 0$ between ω_{TO} and $\omega_{LO} = \omega/\omega_{TO} = 1.224$
In shadowed region wave cannot propagate in medium, becomes totally reflected, because K is imaginary

Crystal	Static dielectric constant $\epsilon(0)$	Optical dielectric constant $\epsilon(\infty)$	ω_{TO} ω_T, in $10^{13}\ s^{-1}$ experimental	ω_{LO} ω_L, in $10^{13}\ s^{-1}$ LST relation
LiH	12.9	3.6	11.	21.
LiF	8.9	1.9	5.8	12.
LiCl	12.0	2.7	3.6	7.5
LiBr	13.2	3.2	3.0	6.1
NaF	5.1	1.7	4.5	7.8
NaCl	5.9	2.25	3.1	5.0
NaBr	6.4	2.6	2.5	3.9
KF	5.5	1.5	3.6	6.1
KCl	4.85	2.1	2.7	4.0
KI	5.1	2.7	1.9	2.6
RbF	6.5	1.9		
RbI	5.5	2.6		
CsCl	7.2	2.6		
CsI	5.65	3.0		
TlCl	31.9	5.1	1.2	3.0
TlBr	29.8	5.4	0.81	1.9
AgCl	12.3	4.0	1.9	3.4
AgBr	13.1	4.6	1.5	2.5
MgO	9.8	2.95	7.5	14.
GaP	10.7	8.5	6.9	7.6
GaAs	13.13	10.9	5.1	5.5
GaSb	15.69	14.4	4.3	4.6
InP	12.37	9.6	5.7	6.5
InAs	14.55	12.3	4.1	4.5
InSb	17.88	15.6	3.5	3.7
SiC	9.6	6.7	14.9	17.9
C	5.5	5.5	25.1	25.1
Si	11.7	11.7	9.9	9.9
Ge	15.8	15.8	5.7	5.7

	NaI	KBr	GaAs
ω_L/ω_T	1.44 ± 0.05	1.39 ± 0.02	1.07 ± 0.02
$[\epsilon(0)/\epsilon(\infty)]^{1/2}$	1.45 ± 0.03	1.38 ± 0.03	1.08

LST relation

$$\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\varepsilon(0)}{\varepsilon(\infty)}$$