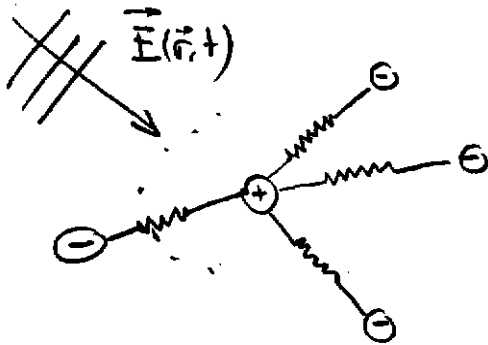


# CLASSICAL ELECTRON THEORY &

## THE LORENTZ ATOM MODEL

①



Lorentz classical model of atom: The  $i$ -th electron is attached to the massive nucleus by a spring with spring constant  $k_i$ , and its motion is damped by the force  $d_i \vec{v}_i$ .

Equation of motion of  $i$ -th electron:

$$m \frac{d^2 \vec{r}_i}{dt^2} + d_i \frac{d \vec{r}_i}{dt} + k_i \vec{r}_i = -e \vec{E}(t) \quad (1)$$

(no retardation: field  $\vec{E}$  at the electron sites is the same as the field at the nucleus

→ dipole approximation)

Parameters:  $\vec{p}_i = -e \vec{r}_i \hat{=} \text{dipole moment of } i\text{-th electron}$

$\omega_i = \sqrt{k_i/m} \hat{=} \text{natural frequency of } i\text{-th electron}$

$\gamma_i = \sqrt{d_i/m} \hat{=} \text{damping coefficient of } i\text{-th electron}$

$$\ddot{\vec{p}}_i + \gamma_i \dot{\vec{p}}_i + \omega_i^2 \vec{p}_i = \frac{e^2}{m} \vec{E}(t) \quad (2)$$

solution for time-harmonic excitation:

$$\vec{E}(t) = \text{Re} \{ \vec{E}_0 e^{-i\omega t} \}$$

$$\vec{p}_n(t) = \text{Re} \left\{ \underbrace{\frac{e^2/m}{(\omega_n^2 - \omega^2) - i\gamma_n \omega}}_{\text{Complex amplitude } \vec{p}_n} \vec{E}_0 e^{-i\omega t} \right\}$$

thus:  $\vec{p}_n = \alpha_n(\omega) \vec{E}_0$

with  $\alpha_n(\omega) = \frac{e^2/m}{\omega_n^2 - \omega^2 - i\gamma_n \omega}$

(3)

total atomic dipole moment:  $\vec{p} = \sum_n \vec{p}_n$

↳ atomic polarizability:  $\alpha(\omega) = \sum_n \frac{e^2/m}{\omega_n^2 - \omega^2 - i\gamma_n \omega} f_n$  (4)

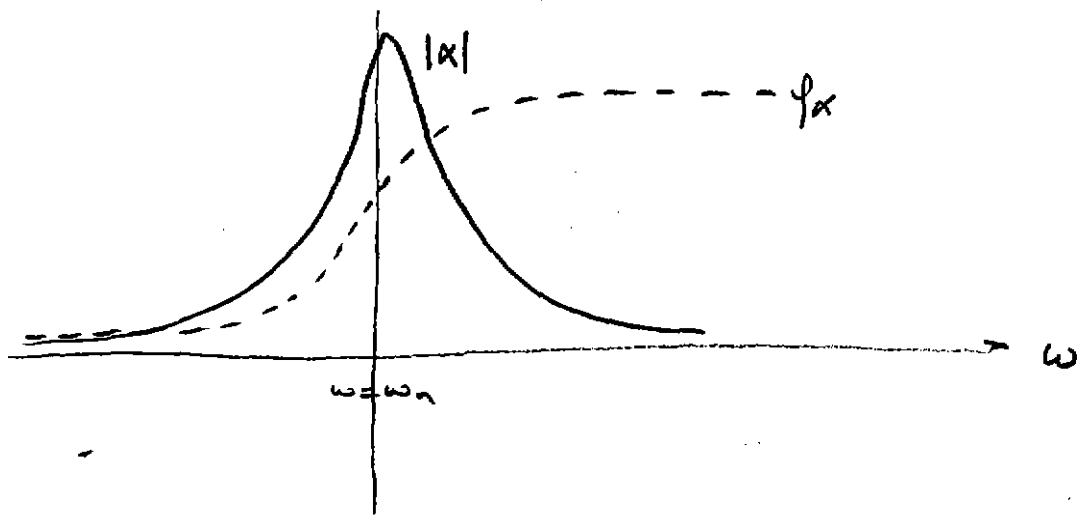
Oscillator strength  $f_n$  has been introduced since not every electron contributes with the same strength. The origin of  $f_n$  is quantum mechanical. It contains the selection rules for promoting an electron from one orbital to another. The oscillator strength is usually a tensor with elements

$$\vec{f} = f_{ij} = \frac{2m\omega_n}{3\hbar e^2} \langle g | \hat{D}_i | e \rangle \langle e | \hat{D}_j | g \rangle$$

ground state
excited state
j-th component of dipole operator

Amplitude and phase of  $\vec{\alpha}(\omega)$  near particular resonance  $\omega = \omega_n$ :  
 $\rightarrow$  set  $\vec{f} = 1$ :  $|\alpha| = \frac{e^2/m f_n}{[(\omega_n^2 - \omega^2)^2 + \gamma_n^2 \omega^2]^{1/2}}$  (5)

$\varphi_n = \arctan \frac{\gamma_n \omega}{\omega_n^2 - \omega^2}$  (6)



Dispersion in gases:  $\vec{P} = N \vec{p}$   
 polarization                      number of atoms (molecules) per unit volume                      atomic (molecular) dipole moment

$$\vec{P} = \epsilon_0 \sum_n \frac{\omega_{pn}^2}{\omega_n^2 - \omega^2 - i\gamma_n \omega} \vec{E}_0$$

$\chi_e(\omega)$

where  $\omega_{pn}^2 = N \frac{e^2}{m \epsilon_0} f_n$   
 plasma frequency

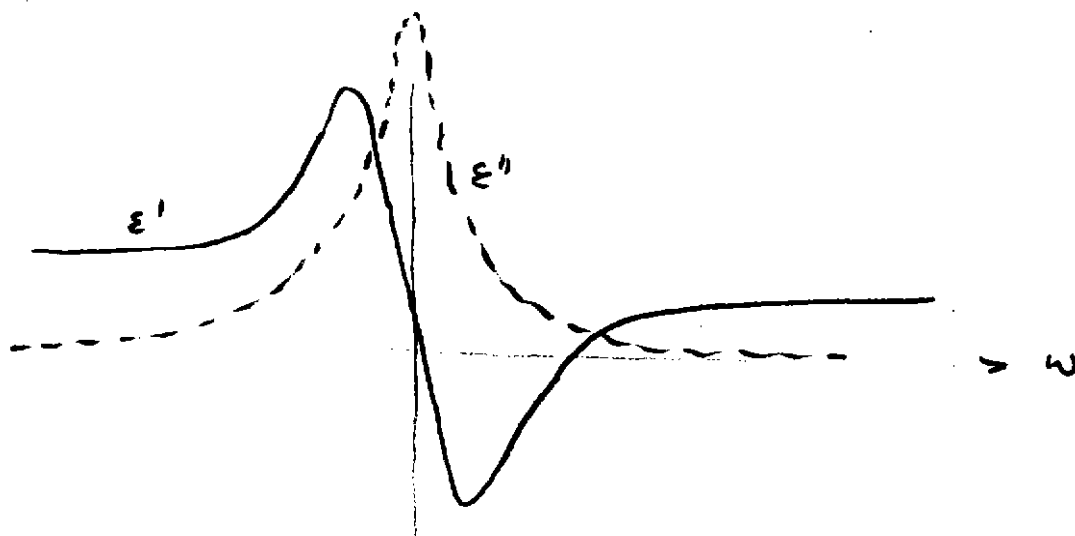
(7)

dielectric constant:

$$\epsilon(\omega) = 1 + \chi_e(\omega) = 1 + \sum_n \frac{\omega_{pn}^2}{\omega_n^2 - \omega^2 - i\gamma_n \omega} \quad (8)$$

real part:  $\epsilon'(\omega) = 1 + \sum_n \frac{\omega_{pn}^2(\omega_n^2 - \omega^2)}{(\omega_n^2 - \omega^2)^2 + \gamma_n^2 \omega^2} \quad (9)$

im. part:  $\epsilon''(\omega) = \sum_n \frac{\omega_{pn}^2 \gamma_n \omega}{(\omega_n^2 - \omega^2)^2 + \gamma_n^2 \omega^2} \quad (10)$



Measurements determine reflectance  $R$ , defined as

$$R = |r|^2 = \left| \frac{E_{ref}}{E_{in}} \right|^2 = \frac{I_{ref}}{I_{in}} = \left| \frac{1 - n(\omega)}{1 + n(\omega)} \right|^2 = \frac{(n' - 1)^2 + n''^2}{(n' + 1)^2 + n''^2} \quad (11)$$

where  $n(\omega) = \sqrt{\epsilon(\omega)}$

Measurements of amplitude and phase of R allow to determine dielectric constant.

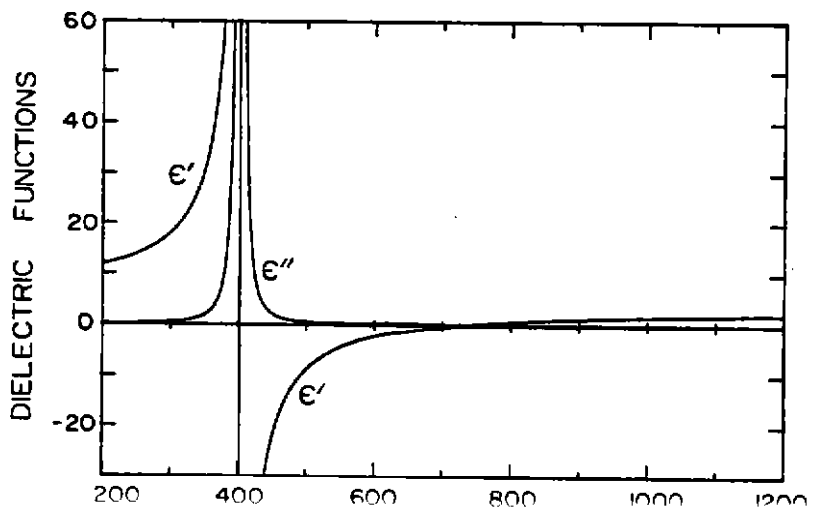
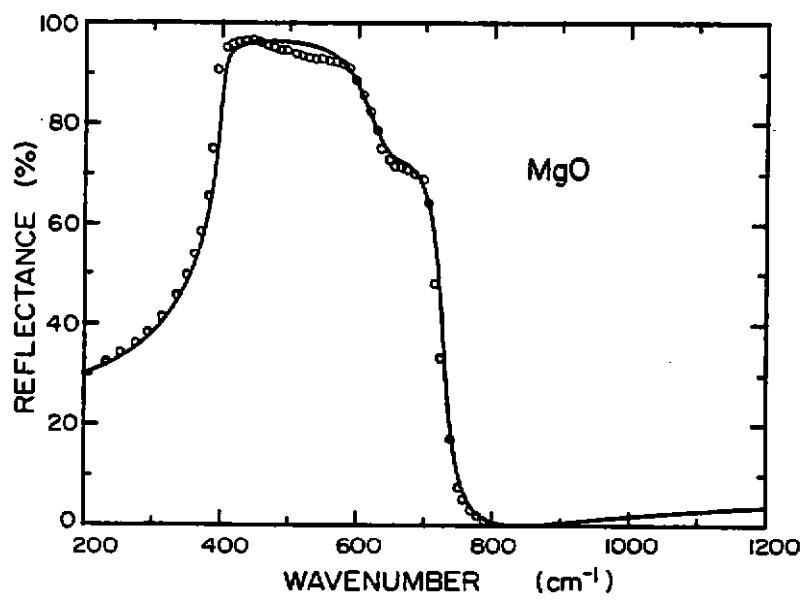
Example: MgO at 295°K (non-gas!)

$$\begin{aligned} \omega_1 &= 401 \text{ cm}^{-1} & \gamma_1 &= 7.62 \text{ cm}^{-1} & \omega_{p1}^2 &= 6.6 \omega_1^2 \\ \omega_2 &= 640 \text{ cm}^{-1} & \gamma_2 &= 102.4 \text{ cm}^{-1} & \omega_{p2}^2 &= 0.045 \omega_2^2 \\ \epsilon^0 &= 3.01 \end{aligned}$$

$$\epsilon(\omega) = \epsilon^0 + \sum_{n=1}^2 \frac{\omega_{pn}^2}{\omega_n^2 - \omega^2 - i\gamma_n\omega}$$

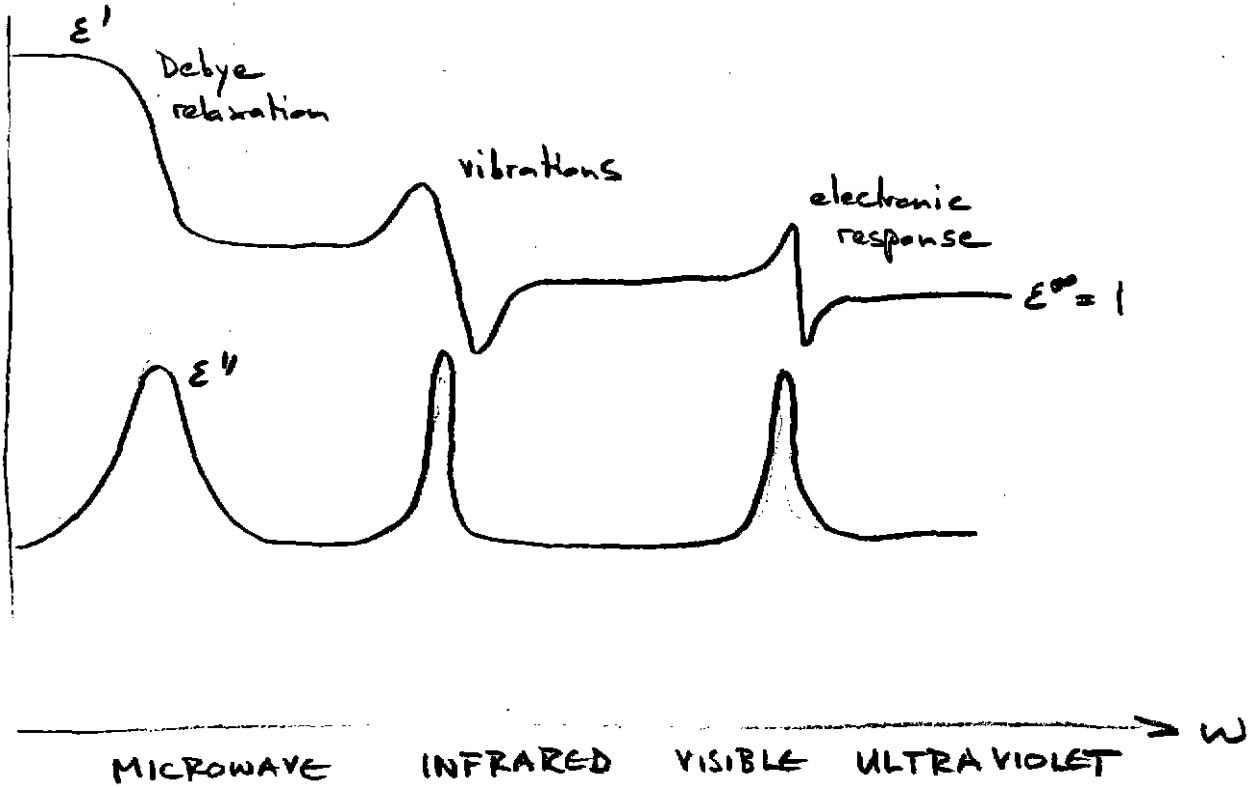
(12)

↑ deviation from 1 because not all oscillators are included in the model!



Across the entire electromagnetic spectrum there are 3 major contributions to the dielectric constant :

- ① Debye relaxation  
→ relaxation of permanent molecular dipoles
- ② Vibrational resonances  
→ resonances associated with vibrational oscillations between nuclei
- ③ Electronic resonances  
→ resonances associated with oscillations of electrons bound to nuclei,



Anisotropic media:  $\vec{D} = \epsilon_0 \vec{\epsilon} \vec{E}$  (7) (13)

In most cases,  $\vec{\epsilon}$  is a symmetric  $3 \times 3$  tensor. Therefore, a coordinate system can be found in which  $\vec{\epsilon}$  is diagonal, i.e.

$$\vec{\epsilon} = \begin{bmatrix} \epsilon_1 & 0 & 0 \\ 0 & \epsilon_2 & 0 \\ 0 & 0 & \epsilon_3 \end{bmatrix} \quad (14)$$

Dielectric constant is generally described by 3 different sets of oscillator parameters appropriate to  $\epsilon_1, \epsilon_2, \epsilon_3$ .

Classification of  $\vec{\epsilon}$ :

① Isotropic (amorphous solids, most liquids, cubic crystals)

$$\epsilon_1 = \epsilon_2 = \epsilon_3 \quad (\text{glass})$$

② Uniaxial crystals (tetragonal, hexagonal, and trigonal crystals)

$$\epsilon_1 = \epsilon_2 \neq \epsilon_3 \quad (\text{quartz})$$

③ Biaxial crystals (orthorhombic, triclinic, and monoclinic crystals)

$$\epsilon_1 \neq \epsilon_2 \neq \epsilon_3$$

Example: Quartz  $\rightarrow$  2 sets of oscillator parameters

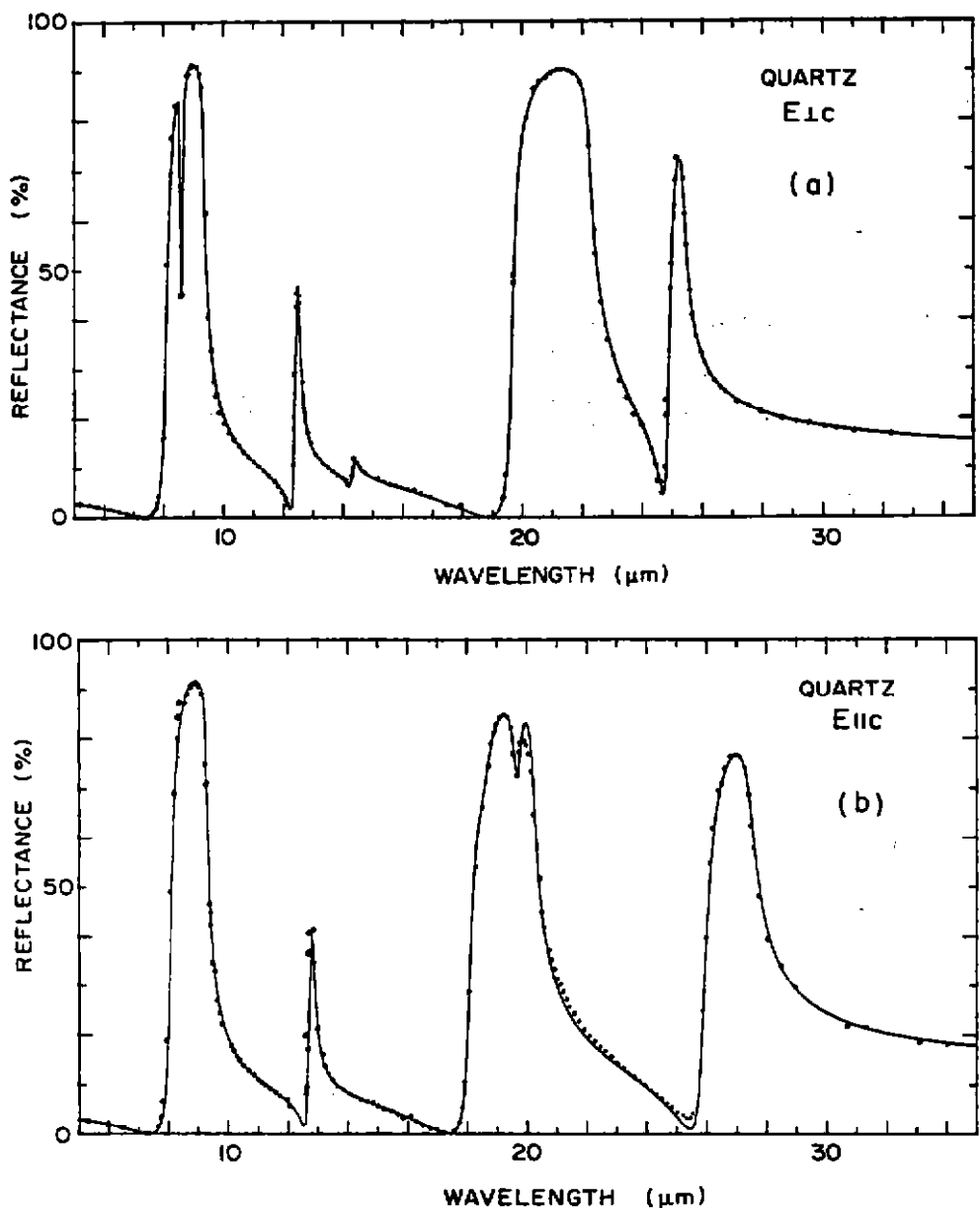


Figure 9.9 Reflectance of quartz for light polarized perpendicular (a) and (b) parallel to the *c* axis. Measurements (dots) and a theoretical fit (solid lines) are from Spitzer and Kleinman (1961).

Table 9.1 Oscillator Parameters Used to Fit the Reflectance Data Shown in Fig. 9.9 (From Spitzer and Kleinman, 1961)

$\omega_j$ (cm <sup>-1</sup> )	$\omega_{pj}^2/\omega_j^2$	$\gamma_j/\omega_j$					
1227	0.009	0.11	Electric field perpendicular to <i>c</i> axis	1220	0.011	0.15	Electric field parallel to <i>c</i> axis
1163	0.01	0.006		1080	0.67	0.0069	
1072	0.67	0.0071		778	0.10	0.010	
797	0.11	0.009		539	0.006	0.04	
697	0.018	0.012		509	0.05	0.014	
450	0.82	0.0090		495	0.66	0.0090	
394	0.33	0.007		364	0.68	0.014	
						$\epsilon_{0e} = 2.383$	





Refractive Index:  $n(\omega) = n'(\omega) + in''(\omega)$

where  $n(\omega) = \sqrt{\epsilon(\omega)} \sqrt{\mu(\omega)}$

$\approx 1$  at optical frequen

→ wave number:  $k(\omega) = \frac{\omega}{c} n(\omega)$

near resonance:  $n^2 = 1 + \frac{\omega_p^2}{\omega_n^2 - \omega^2 - i\gamma_n \omega}$  (ignore other resonances)

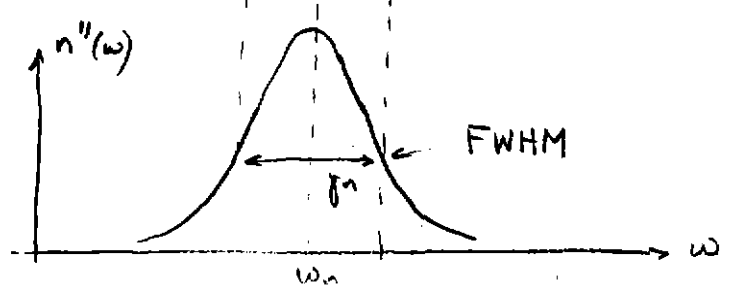
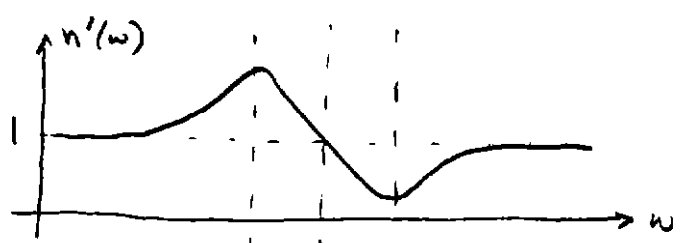
assume  $\frac{\omega_p^2}{\omega_n^2 - \omega^2 - i\gamma_n \omega} < 1$

→  $n = \sqrt{1+x} \approx 1 + \frac{1}{2}x$

$$n'(\omega) = 1 + \frac{\omega_p^2 (\omega_n^2 - \omega^2)}{2 (\omega_n^2 - \omega^2)^2 + \gamma_n^2 \omega^2}$$

$$n''(\omega) = \frac{\omega_p^2}{2} \frac{\gamma_n \omega}{(\omega_n^2 - \omega^2)^2 + \gamma_n^2 \omega^2}$$

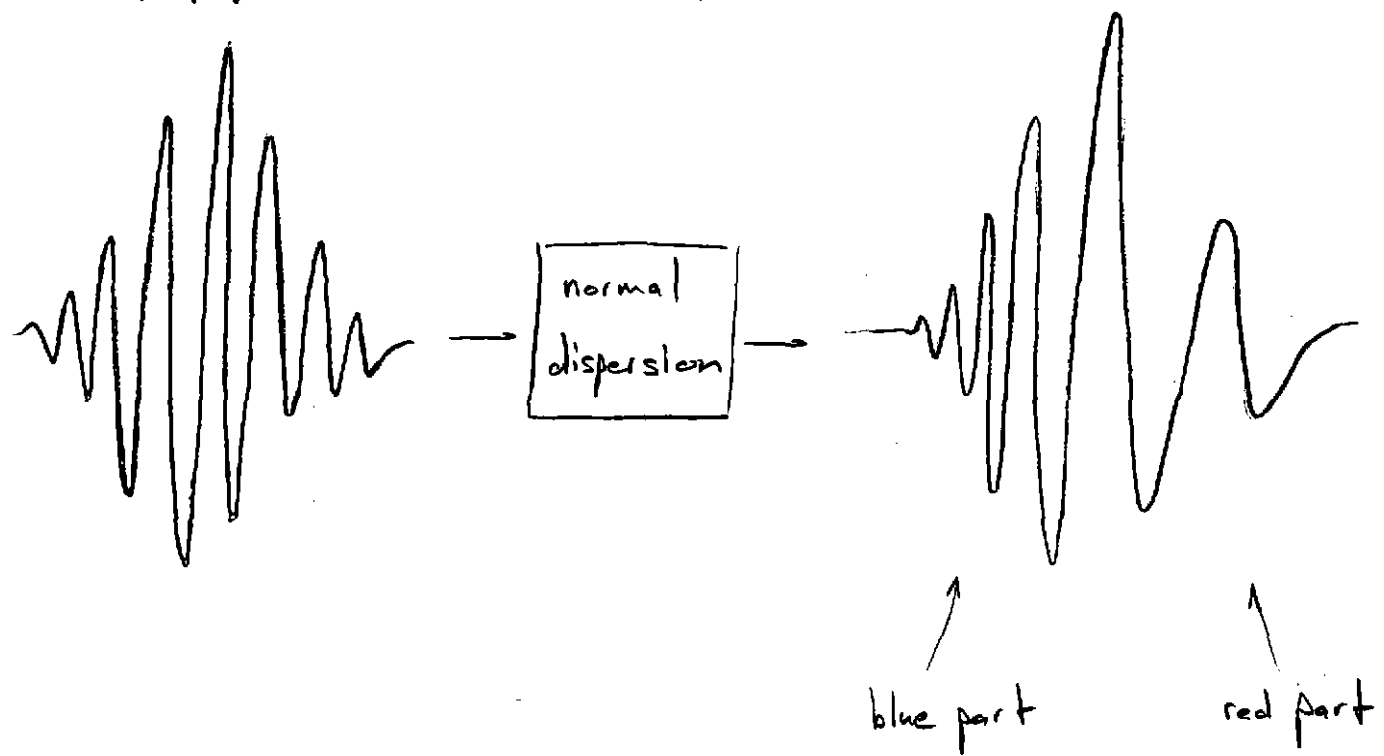
(15) ~~scribble~~



dispersion :  $dn'/d\omega > 0 \rightarrow$  normal dispersion

$dn'/d\omega < 0 \rightarrow$  anomalous dispersion

Anomalous dispersion is usually accompanied by strong absorption. For normal dispersion the red part of the spectrum propagates faster than the blue part.



## Dispersion in dense matter:

So far, it was assumed that the local exciting field of an oscillator corresponds to the illuminating, external field. However, in dense matter the molecules are close enough together that the neighbors affect the field at any one molecule.

The dipole moment  $\vec{p}$  of an arbitrary molecule inside the matter is excited by the exciting local field according to

$$\vec{p} = \alpha \vec{E}_{\text{exc}} \quad (16)$$

$\vec{E}_{\text{exc}}$  is the field due to the incident field  $\vec{E}_0$  and all the partial fields of the other molecules.

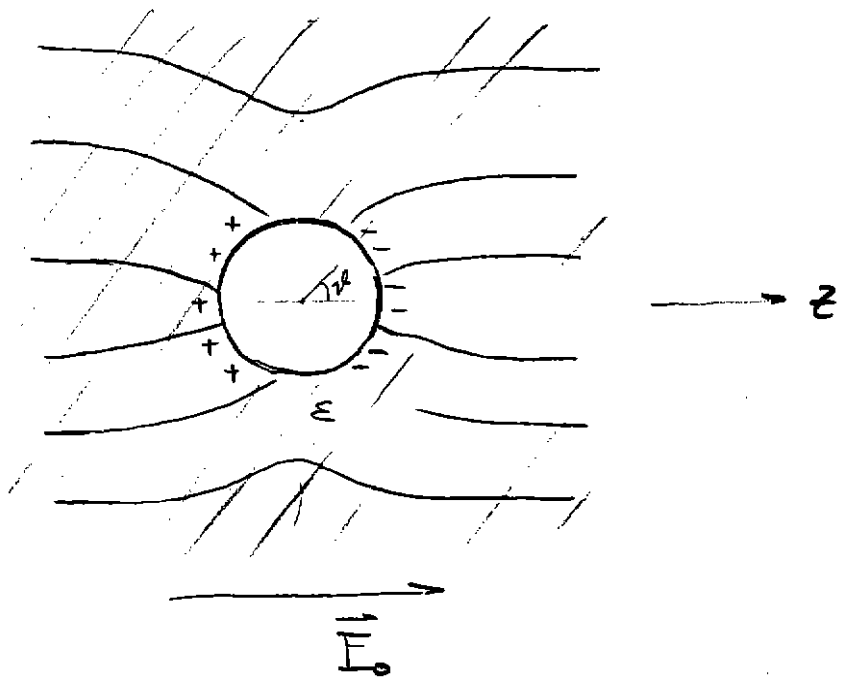
Thus,

$$\vec{E}_{\text{exc}} = \vec{E}_0 + \vec{E}_{\text{molecules}} \quad (17)$$

In order to account for  $\vec{E}_{\text{molecules}}$  we consider a particular molecule inside a spherical cavity surrounded by the macroscopic dielectric made up by the other molecules.

The other molecules are polarized and therefore give rise to a net surface charge density  $\sigma$  which is related to the polarization by (uniform external field)

$$\sigma = -\vec{n} \cdot \vec{P} = -P \cos \theta \quad (18)$$



The charge on a surface element  $da$  is  $q = -\epsilon da$  which gives rise to an electric field  $\vec{E}_i$  inside the cavity

$$\vec{E}_i = \frac{1}{4\pi\epsilon_0} \frac{q}{r^2} \vec{n}_r da = \frac{1}{4\pi\epsilon_0} \frac{P}{r^2} \cos\theta \vec{n}_r da \quad (15)$$

Integrating over the surface gives

$$\vec{E}_i = E_i \vec{n}_z = \frac{1}{4\pi\epsilon_0} P \int_0^\pi \int_0^{2\pi} \frac{\cos^2\theta}{r^2} r^2 \sin\theta d\theta d\phi$$

$\underbrace{\hspace{10em}}_{4\pi/3}$

$$\vec{E}_i = \frac{1}{3\epsilon_0} \vec{P} = \vec{E}_{\text{molecules}} \quad (20)$$

Therefore, the exciting field  $\vec{E}_{\text{exc}}$  of the molecule inside the cavity is

$$\vec{E}_{\text{exc}} = \vec{E}_0 + \frac{1}{3\epsilon_0} \vec{P} \quad (21)$$

The macroscopic polarization is again made by the individual dipole moments  $\vec{p}$  as

$$\vec{P} = N\vec{p} \tag{22}$$

↑  
number of molecules per unit volume

With Eq. (16) we have

$$\vec{P} = N\alpha \vec{E}_{exc} = N\alpha \left( \vec{E}_0 + \frac{1}{3\epsilon_0} \vec{P} \right) \tag{23}$$

$$\rightarrow \vec{P} = \epsilon_0 \frac{3N\alpha}{3\epsilon_0 - N\alpha} \vec{E} \tag{24}$$

In a macroscopic body the polarization  $\vec{P}$  is related to  $\vec{E}$  by

$$\vec{D} = \epsilon_0 \epsilon \vec{E} = \epsilon_0 \vec{E} + \vec{P} \rightarrow \vec{P} = \epsilon_0 (\epsilon - 1) \vec{E} \tag{25}$$

Comparing Eqs. (24) and (25) gives

$$\frac{1}{3\epsilon_0} N\alpha = \frac{\epsilon - 1}{\epsilon + 1}$$

Clausius-Mossotti formula (26)

Clausius-Mossotti formula relates the macroscopic dielectric constant  $\epsilon$  of the medium to the microscopic polarizability  $\alpha$  of the constituent molecules.

Solving for  $\epsilon$ :

$$\epsilon(\omega) = n^2(\omega) = \frac{3 + 2N\alpha(\omega)/\epsilon_0}{3 - N\alpha(\omega)/\epsilon_0} \quad (27)$$

with

$$N\alpha(\omega)/\epsilon_0 = \sum_n \frac{\omega_{pn}^2}{(\omega_n^2 - \omega^2) - i\gamma_n\omega} \quad (28)$$

## THE UNDRIVEN LORENTZ OSCILLATOR

Coherent processes such as scattering follow the frequency of the driving field. Incoherent processes are activated by the external driving field but then oscillate on their own. Fluorescence (spontaneous emission) is such a process. Thus,

$$\ddot{\vec{p}}_n + \gamma_n \dot{\vec{p}}_n + \omega_n^2 \vec{p}_n = 0 \quad (29)$$

What is  $\gamma_r$ ?

Even if there is no intrinsic damping in the oscillator, the oscillation will die out due to energy dissipation associated with radiation.

thus:  $m\ddot{\vec{r}} + k\vec{r} = \vec{F}_r$  (3)

$\vec{F}_r$  is the reaction force due to radiation.

For velocities  $\dot{\vec{r}} \ll c$ ,  $\vec{F}_r$  can be related to Larmor's formula as

$$\frac{dW}{dt} = \vec{F}_r \cdot \dot{\vec{r}} = -\frac{1}{4\pi\epsilon_0} \frac{2q^2}{3c^2} |\ddot{\vec{r}}|^2 = -\frac{1}{4\pi\epsilon_0} \frac{2q^2}{3c^2} (\ddot{\vec{r}} \cdot \ddot{\vec{r}}) \quad (3)$$

Integrate over short interval of time  $[t_1, t_2]$  :

$$\int_{t_1}^{t_2} \vec{F}_r \cdot \dot{\vec{r}} dt = -\frac{1}{4\pi\epsilon_0} \frac{2q^2}{3c^2} \int_{t_1}^{t_2} \ddot{\vec{r}} \cdot \ddot{\vec{r}} dt$$
$$\ddot{\vec{r}} \cdot \ddot{\vec{r}} \Big|_{t_1}^{t_2} - \int_{t_1}^{t_2} \ddot{\vec{r}} \cdot \ddot{\vec{r}} dt$$

If  $(t_2 - t_1)$  is very small:  $\ddot{\vec{r}} \cdot \ddot{\vec{r}} \Big|_{t_1}^{t_2} \approx 0$

$$\int_{t_1}^{t_2} \left( \vec{F}_r - \frac{1}{4\pi\epsilon_0} \frac{2q^2}{3c^2} \ddot{\vec{r}} \right) \cdot \dot{\vec{r}} dt \approx 0$$

or:

$$\ddot{\vec{r}} = \frac{1}{4\pi\epsilon_0} \frac{2q^2}{3c^3} \frac{d^3 \vec{r}(t)}{dt^3} \quad (33)$$

Abraham-Lorentz formula for radiation reaction force

In most situations  $\ddot{\vec{r}}$  is small and it can be neglected in a first approximation. In this case, the solution of Eq. (30) is

$$\vec{r}(t) = \text{Re} \left\{ \vec{r}_0 e^{-i\omega_0 t} \right\} \quad \text{where } \omega_0^2 = \frac{k}{m} \quad (34)$$

Insert into Eq. (33):

$$\ddot{\vec{r}} \approx \text{Re} \left\{ \frac{1}{4\pi\epsilon_0} \frac{2q^2}{3c^3} i\omega_0^3 \vec{r}_0 e^{-i\omega_0 t} \right\} \quad (35)$$

Use:  $q = -e$  and  $\vec{p}(t) = \text{Re} \left\{ \vec{p}_0 e^{-i\omega_0 t} \right\}$  with  $\vec{p}_0 = -e\vec{r}_0$  (36)

$$\ddot{\vec{r}} = \frac{1}{4\pi\epsilon_0} \frac{2e}{3c^3} \omega_0^2 \frac{d}{dt} \vec{p}(t) \quad (37)$$

and insert back into Eq. (30):

$$\ddot{\vec{p}} + \gamma_0 \dot{\vec{p}} + \omega_0^2 \vec{p} = 0 \quad \text{where } \gamma_0 = \frac{1}{4\pi\epsilon_0} \frac{2e^2 \omega_0^2}{3mc^3} \quad (38)$$

→ compare with Eq. (29)



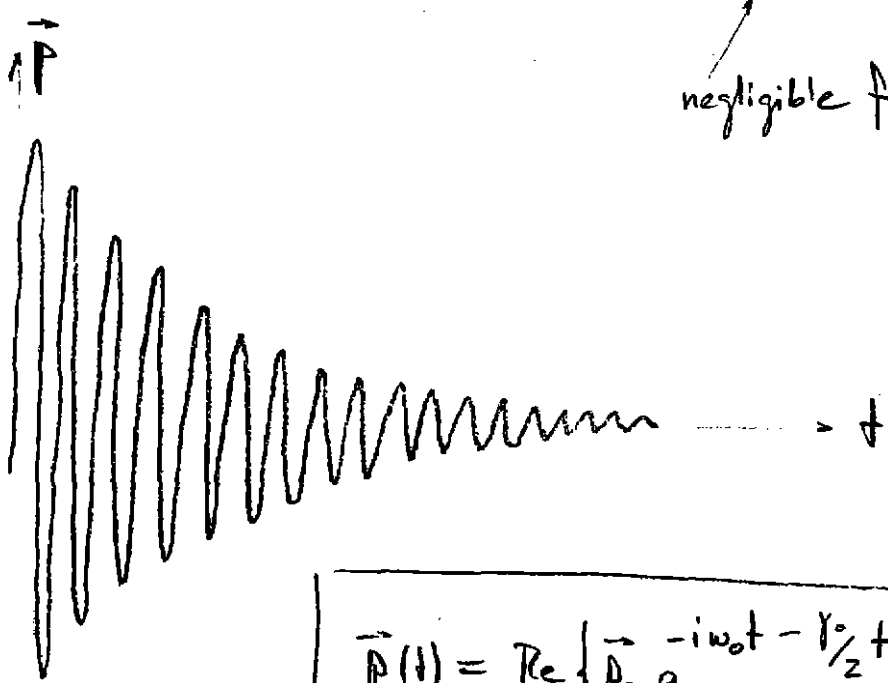
Comparison of  $\gamma_0$  and  $\omega_0$ :

$$\frac{\gamma_0}{\omega_0} = \frac{e^2 \omega_0}{6\pi \epsilon_0 m c^3} \approx \begin{cases} 2 \cdot 10^{-8} & (\lambda = 500 \text{ nm}) \\ 1 & (\lambda = 12 \text{ fm}) \end{cases}$$

At visible wavelengths  $\omega_0 \gg \gamma_0$  and  $\gamma_0$  is in the range of  $10^8 \text{ Hz}$  (radio frequencies  $\approx 100 \text{ MHz}$  — FM radio)

Solution of Eq. (38):  $\vec{p}(t) = \text{Re} \left\{ \vec{p}_0 e^{-i\Omega t} \right\}$

where  $\Omega = \pm \omega_0 \left( 1 - \frac{\gamma_0^2}{8\omega_0^2} \right) - i\gamma_0/2$  (39)



negligible frequency shift

$$\vec{p}(t) = \text{Re} \left\{ \vec{p}_0 e^{-i\omega_0 t - \gamma_0/2 t} \right\}$$

To derive the fields of the attenuated oscillating dipole  $\vec{p}(t)$  replace  $\omega$  by the complex frequency  $\Omega$ !

Radiation fields:

$$\vec{E}_\theta(\vec{r}, t) = \frac{\sin\theta}{4\pi\epsilon_0} \frac{1}{c^2 r} \frac{d^2}{dt^2} p(t - r/c) \approx - \frac{\sin\theta}{4\pi\epsilon_0} \frac{\omega_0^2}{c^2 r} p_0 \cos[\omega_0(t - r/c)] e^{-\gamma/2 [t - r/c]} \quad (41)$$

$$H_\phi(\vec{r}, t) = \sqrt{\frac{\epsilon_0}{\mu_0}} \vec{E}_\theta(t) \quad (42)$$

Radiated power (cycle averaged):

$$\boxed{\bar{P} = \frac{|\vec{p}_0|^2}{4\pi\epsilon_0} \frac{\omega_0^4}{3c^3} e^{-\gamma(t - r/c)}} \quad (43)$$

damping term

Spectrum of radiated  $\vec{E}$  field:

$$\hat{\vec{E}}(\vec{r}, \omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \vec{E}(\vec{r}, t) e^{i\omega t} dt = \frac{1}{\sqrt{2\pi}} \int_{r/c}^{\infty} E_\theta(\vec{r}, t) e^{i\omega t} dt \vec{n}_\theta$$

since  $\vec{E}(\vec{r}, t) = 0$  for  $t < r/c$

$$\text{integrating Eq. (41): } \vec{E}(\vec{r}, \omega) = \frac{1}{\sqrt{2\pi}} \frac{p_0 \sin\theta \omega_0^2}{4\pi\epsilon_0 c^2 r} \frac{1}{2} \left[ \frac{e^{i\omega r/c}}{i(\omega + \omega_0) - \frac{\gamma_0}{2}} + \frac{e^{i\omega r/c}}{i(\omega - \omega_0) - \frac{\gamma_0}{2}} \right] \quad (44)$$

Intensity :

$$I(\vec{r}, t) = \vec{S}(\vec{r}, t) \cdot \vec{n}_r = [\vec{E} \times \vec{H}] \cdot \vec{n}_r = \sqrt{\frac{\epsilon_0}{\mu_0}} |\vec{E}(\vec{r}, t)|^2 \quad (45)$$

radiation fields

Total energy radiated into unit solid angle  $d\Omega = \sin\theta d\theta d\phi$  :

$$\frac{dW}{d\Omega} = \int_{-\infty}^{\infty} I(\vec{r}, t) r^2 dt \quad (46)$$

Using Parseval's theorem :

$$\frac{dW}{d\Omega} = r^2 \sqrt{\frac{\epsilon_0}{\mu_0}} \int_{-\infty}^{\infty} |\vec{E}(\vec{r}, t)|^2 dt = r^2 \sqrt{\frac{\epsilon_0}{\mu_0}} 2 \int_0^{\infty} |\hat{\vec{E}}(\vec{r}, \omega)|^2 d\omega \quad (47)$$

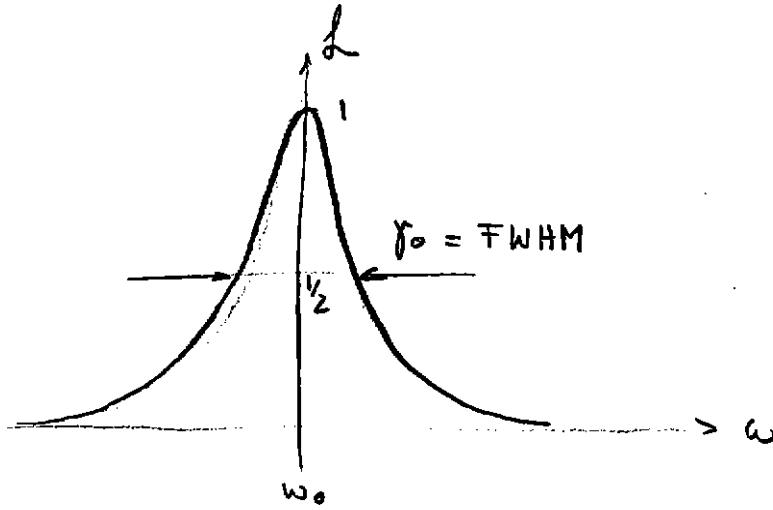
Total energy per unit solid angle per frequency interval  $d\omega$  :

$$\frac{dW}{d\Omega d\omega} = 2 \sqrt{\frac{\epsilon_0}{\mu_0}} r^2 |\hat{\vec{E}}(\vec{r}, \omega)|^2 \quad (48)$$

$$\rightarrow \left[ \frac{dW}{d\Omega d\omega} = \frac{1}{4\pi \epsilon_0} \frac{p_0^2 \omega_0^4 \sin^2 \theta}{16\pi^2 c^3} \left[ \frac{1}{(\omega - \omega_0)^2 + \gamma_0^2/4} \right] \right] \quad (49)$$

Lorentzian lineshape function

write:  $\frac{dW}{d\Omega d\omega} = A \mathcal{L}(\omega)$  where  $\mathcal{L}(\omega) = \frac{\gamma_0^2/4}{(\omega - \omega_0)^2 + \gamma_0^2/4}$  (50)



remember:  $\gamma_0/\omega_0 \ll 1$