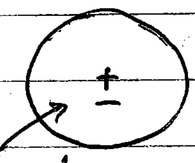
<u>Time dependent polarizeability of an atom</u>



electron cloud

If displace center of electron cloud by a distance $\vec{r}$, there is a restoring force

$$\vec{F}_{rest} = \frac{-e^2\,\vec{r}}{4\pi R^3} \equiv \underset{\substack{\uparrow\\ \text{electron mass}}}{-m}\underset{\substack{\uparrow\\ \text{resonant frequency}}}{\omega_0^2}\,\vec{r}$$

Also, in general there will be a damping force

$$\vec{F}_{damp} = -m\gamma\frac{d\vec{r}}{dt}$$

due to transfer of energy from atom to other degrees of freedom.

In an external electric field $\vec{E}(t)$, the equation of motion for electron cloud is

$$m\frac{d^2\vec{r}}{dt^2} = \vec{F}_{tot} = -e\vec{E}(t) - m\omega_0^2\vec{r} - m\gamma\frac{d\vec{r}}{dt}$$

$$\ddot{\vec{r}} + \gamma\dot{\vec{r}} + \omega_0^2\vec{r} = -\frac{e\vec{E}(t)}{m}$$

assume $\vec{E}$ is spatially constant over atomic distances

For harmonic oscillation $\vec{E}(t) = \vec{E}_0 e^{-i\omega t}$

Assume solution $\vec{r}(t) = \vec{r}_0 e^{-i\omega t}$

(in the end, we will take the real parts)

Substitute into equation of motion

$$-\omega^2\vec{r}_0 - i\omega\gamma_0\vec{r}_0 + \omega_0^2\vec{r}_0 = -\frac{e\vec{E}_0}{m}$$

$$\vec{r}_0 = \frac{-e}{m(\omega_0^2 - \omega^2 - i\omega\gamma)}\vec{E}_0$$

polarization

$$\vec{p} = -e\vec{r} = \vec{p}_0 e^{-i\omega t}$$

$$\vec{p}_0 = \frac{e^2}{m} \frac{1}{(\omega_0^2 - \omega^2 - i\omega\gamma)} \vec{E}_0 = \alpha(\omega) E_0$$

$$\alpha(\omega) = \frac{e^2}{m} \frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma}$$ freq dependent polarizabi

Since α is complex the polarization does not in general oscillate in phase with $\vec{E}$.

If $\alpha(\omega) = |\alpha| e^{i\delta}$ δ is phase of complex α

$$\vec{p}(t) = \alpha(\omega)\vec{E}(t) = |\alpha| e^{i\delta} \vec{E}_0 e^{-i\omega t} = |\alpha| \vec{E}_0 e^{-i(\omega t - \delta)}$$

phase shifted by δ

For a general electric field

$$\vec{E}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \vec{E}_\omega e^{-i\omega t}$$

$$\vec{E}_\omega^* = \vec{E}_{-\omega}$$

$$\vec{p}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} p_\omega e^{-i\omega t} = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \alpha(\omega) \vec{E}_\omega e^{-i\omega t}$$

Substitute in $\vec{E}_\omega = \int_{-\infty}^{\infty} dt' \, E(t') e^{i\omega t'}$ to get

$$\vec{p}(t) = \int_{-\infty}^{\infty} dt' \, \vec{E}(t') \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \alpha(\omega) e^{-i\omega(t-t')}$$

$$\vec{p}(t) = \int_{-\infty}^{\infty} dt' \, \vec{E}(t') \, \tilde{\alpha}(t-t')$$

Fourier transf of $\alpha(\omega)$

$\vec{p}$ at time t is due to $\vec{E}$ at all times t'

non local in time

$\tilde{\chi}(t)$ is the response to $\vec{E}(t) = \delta(t)$

For our simple model

$$\tilde{\alpha}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, e^{-i\omega t}\, \frac{e^2}{m}\, \frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma}$$

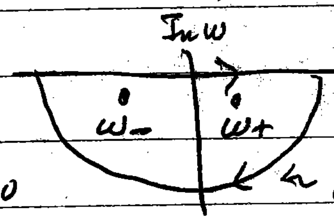
do by contour integration

$$\frac{1}{\omega^2 + i\gamma\omega - \omega_0^2} = \frac{1}{(\omega - \omega_+)(\omega - \omega_-)}$$

$$\omega_\pm = -\frac{i\gamma}{2} \pm \sqrt{\omega_0^2 - \gamma^2/4} = -\frac{i\gamma}{2} \pm \bar{\omega}$$

poles at $\omega_\pm$ are in lower half complex plane.

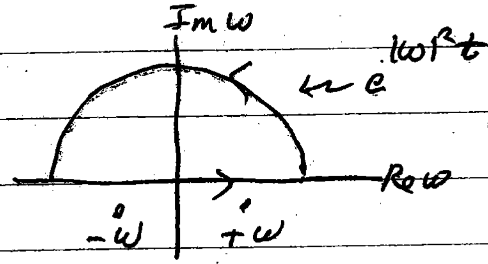
for $t > 0$, close contour in lower half plane



$t > 0$ ← $e^{-|\omega''|t}$ here vanishes for $t > 0$

contour encloses poles & get contribution

for $t < 0$, close contour in upper half plane



← $e^{|\omega''|t}$ vanishes for $t < 0$

contour encloses no poles ⇒ integral vanishes

$\tilde{\chi}(t) = 0 \quad$ for $t < 0$

<u>causal response!</u> No polarization until electric field turns on

For $t > 0$

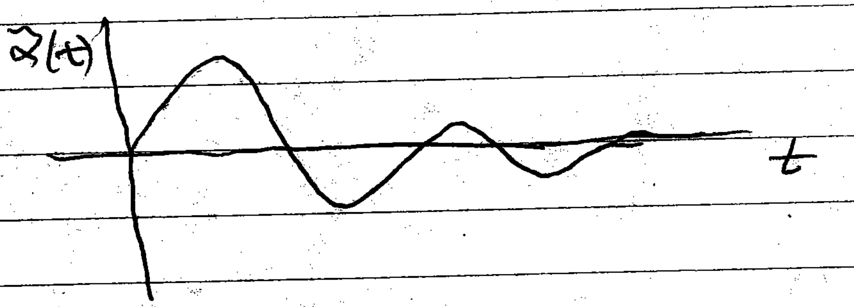
$$\tilde{\alpha}(t) = \int \frac{d\omega}{2\pi}\, e^{-i\omega t}\, \frac{e^2}{m}\, \frac{(-1)}{(\omega-\omega_+)(\omega-\omega_-)}$$

$$= (-2\pi i)\, \frac{e^2}{m}\, \frac{(-1)}{2\pi} \left[\frac{e^{-i\omega_+ t}}{\omega_+ - \omega_-} + \frac{e^{-i\omega_- t}}{\omega_- - \omega_+} \right]$$

from residue theorem

$$= \frac{i e^2}{m} \left[\frac{e^{-\gamma t/2}\, e^{-i\bar{\omega} t}}{2\bar{\omega}} - \frac{e^{-\gamma t/2}\, e^{i\bar{\omega} t}}{2\bar{\omega}} \right]$$

$$\tilde{\alpha}(t) = \begin{cases} \dfrac{e^2}{m}\, \dfrac{e^{-\gamma t/2}}{\bar{\omega}} \sin(\bar{\omega} t) & t > 0 \\ 0 & t < 0 \end{cases}$$



damped oscillation

Polarization density $\vec{P}_\omega = 4\pi \chi(\omega) \vec{E}_\omega$ for harmonic oscillation

$\chi(\omega) \approx M \alpha(\omega)$ for dilute syste

↑ atom density

can use Clausius - Mossotti correction for denser materials

$\Rightarrow \vec{D}_\omega = \varepsilon(\omega) \vec{E}_\omega$ $\qquad \varepsilon(\omega) = 1 + 4\pi \chi(\omega$

↑ freq dependent

→ as with $\vec{J}$ and $\vec{E}$, relation between $\vec{D}$ and $\vec{E}$ is <u>non-local</u> in time

$$\vec{D}(t) \neq \varepsilon \vec{E}(t)$$

rather

$$\vec{D}(t) = \int_{-\infty}^{\infty} dt' \, \vec{E}(t') \, \tilde{\varepsilon}(t-t')$$

$\tilde{\varepsilon}$ Fourier transf of $\varepsilon(\omega)$

Ampere's law is

$$\vec{\nabla} \times \vec{H} = 4\pi \vec{J} + \frac{1}{c}\frac{\partial \vec{D}}{\partial t}$$

becomes $$\frac{1}{\mu} \vec{\nabla} \times \vec{B} = 4\pi \vec{J} + \frac{1}{c} \int_{-\infty}^{\infty} dt' \, \vec{E}(t') \frac{d}{dt} \tilde{\varepsilon}(t-t')$$

integro-differential-equation!

Maxwells equations only look simple when expressed in terms of Fourier transforms

$$\vec{E}(\vec{r},t) = \vec{E}_\omega \, e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$
$$\vec{B}(\vec{r},t) = \vec{B}_\omega \, e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$
$$\vec{D}(\vec{r},t) = \vec{D}_\omega \, e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$
$$\vec{H}(\vec{r},t) = \vec{H}_\omega \, e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

Maxwell's Equ for <u>source free</u> system $\rho = \vec{J} = 0$

$$\vec{\nabla}\cdot\vec{D} = 0, \quad \vec{\nabla}\cdot\vec{B} = 0, \quad \vec{\nabla}\times\vec{E} = -\frac{\partial \vec{B}}{c\,\partial t}, \quad \vec{\nabla}\times\vec{H} = \frac{\partial \vec{D}}{c\,\partial t}$$

assume μ is true constant - not freq dependent
dielectric response is $\vec{D}_\omega = \varepsilon(\omega)\vec{E}_\omega$

Then for the Fourier amplitudes of the fields, Maxwell's Equations become

transverse polarized

1) $i\vec{k}\cdot\vec{D}_\omega = i\,\varepsilon(\omega)\,\vec{k}\cdot\vec{E}_\omega = 0 \quad \Rightarrow \boxed{\vec{k}\perp\vec{E}_\omega}$ (unless $\varepsilon(\omega)=$

2) $i\vec{k}\cdot\vec{B}_\omega = 0 \quad \Rightarrow \boxed{\vec{k}\perp\vec{B}_\omega}$

3) $i\vec{k}\times\vec{E}_\omega = i\frac{\omega}{c}\vec{B}_\omega$

4) $i\vec{k}\times\vec{H}_\omega = -i\frac{\omega}{c}\vec{D}_\omega \Rightarrow \frac{i\vec{k}}{\mu}\times\vec{B}_\omega = -\frac{i\omega}{c}\varepsilon(\omega)\vec{E}_\omega$

$$\vec{k}\times(3) = i\vec{k}\times(\vec{k}\times\vec{E}_\omega) = i\frac{\omega}{c}\vec{k}\times\vec{B}_\omega$$

$$\Rightarrow -ik^2\vec{E}_\omega = -i\frac{\omega^2}{c^2}\varepsilon(\omega)\mu\,\vec{E}_\omega \quad \text{using (4)}$$

$$\boxed{k^2 = \frac{\omega^2}{c^2}\varepsilon(\omega)\mu}$$ dispersion relation

Note: $\frac{\omega}{k} = \frac{c}{\sqrt{\varepsilon(\omega)\mu}}$ varies with ω.
There is not a single phase velocity.

$\Rightarrow \vec{E}$ is not in general a solution of a wave equation - different frequencies travel with different speed

Since $\varepsilon(\omega)$ is complex $\quad \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$

$\Rightarrow$ wave vector also complex $\quad$ For $\vec{k} = k\hat{z}$

$$k = k_1 + ik_2 = \pm \frac{\omega}{c}\sqrt{\mu}\sqrt{\varepsilon_1 + i\varepsilon_2}$$

$$\vec{E}(\vec{r},t) = \vec{E}_\omega e^{i(\vec{k}\cdot\vec{r}-\omega t)} = \vec{E}_\omega e^{i[(k_1+ik_2)z - \omega t]}$$
$$= \vec{E}_\omega e^{-k_2 z} e^{i(k_1 z - \omega t)}$$

k_1 determines the oscillation of the wave

k_2 determines the decay or <u>attenuation</u> of the wave as it propagates into the material

<u>phase velocity</u> $\quad v_p = \frac{\omega}{k_1}$

<u>index of refraction</u> $\quad n = \frac{c}{v_p} = \frac{ck_1}{\omega}$

<u>group velocity</u> $v_g \quad \frac{1}{v_g} = \frac{dk_1}{d\omega}$

<u>Magnetic field</u> : $\quad \vec{B}_\omega = \frac{\vec{k}}{\omega} \times \vec{E}_\omega$

for $\vec{k} = k\hat{z}$, $\quad \vec{B}_\omega = \frac{(k_1 + ik_2)}{\omega}\hat{z} \times \vec{E}_\omega$

if $\quad k_1 + ik_2 = \sqrt{k_1^2 + k_2^2}\, e^{i\delta} \qquad \delta = \arctan\left(\frac{k_2}{k_1}\right)$
$$= |k| e^{i\delta}$$

$$\vec{B}_\omega = \frac{|k|}{\omega}\hat{z} \times \vec{E}_\omega e^{i\delta}$$

phase shift

$$\vec{B}(\vec{r},t) = \frac{|k|}{\omega} (\hat{z}\times\vec{E}_\omega) e^{-k_2 z} e^{i(k_1 z - \omega t + \delta)}$$

<u>Physical fields</u> - take real parts

$$\vec{E}(\vec{r},t) = \vec{E}_\omega \, e^{-k_2 z} \cos(k_1 z - \omega t)$$

$$\vec{B}(\vec{r},t) = (\hat{z}\times\vec{E}_\omega)\frac{|k|}{\omega} e^{-k_2 z} \cos(k_1 z - \omega t + \delta)$$

<u>Conclusions</u>

1) $\vec{E}$ and $\vec{B}$ $\perp$ $\vec{k}$ transverse polarized
2) $\vec{E} \perp \vec{B}$
3) amplitude ratio $\frac{|\vec{B}|}{|\vec{E}|} = \frac{|k|}{\omega} = \sqrt{|\varepsilon(\omega)|\mu}$
4) $\vec{B}$ is shifted in phase with respect to $\vec{E}$ by phase shift $\delta = \arctan(k_2/k_1)$
5) waves decay as they propagate $e^{-k_2 z}$

} consequence of ~~complex~~ $\varepsilon(\omega)$

If $\varepsilon_2 = 0$, ie $\varepsilon(\omega)$ is real, <u>and</u> if $\varepsilon > 0$, then $k_2 = 0 \Rightarrow$ no decay, no phase shift

consequences of frequency dependence of $\varepsilon(\omega)$ {

6) $\vec{E}(t)$ and $\vec{D}(t)$ non locally related in time
7) waves of different ω travel with different $v_p = \omega/k$
8) <u>dispersion</u> - wave pulses do <u>not</u> travel with v_p and they spread as the propagate
pulses travel with group velocity $v_g = \frac{d\omega}{dk}$
(see Quantum Mechanics discussion)
$v_g < v_p$ "normal dispersion"
$v_g > v_p$ "anomalous dispersion"

index of refraction

$$\frac{1}{v_g} = \frac{dk_1}{d\omega} = \frac{d}{d\omega}\left[\frac{\omega}{c} n\right]$$

$$\frac{1}{v_g} = \frac{n}{c} + \frac{\omega}{c}\frac{dn}{d\omega} = \frac{1}{v_p} + \frac{\omega}{c}\frac{dn}{d\omega}$$

$$v_g = \frac{v_p}{1 + \frac{v_p}{c}\,\omega\frac{dn}{d\omega}}$$

$$\Rightarrow \text{ when } \begin{cases} \frac{dn}{d\omega} > 0, \quad v_g < v_p & \text{normal dispersion} \\ \frac{dn}{d\omega} < 0, \quad v_g > v_p & \text{anomalous dispersion} \end{cases}$$

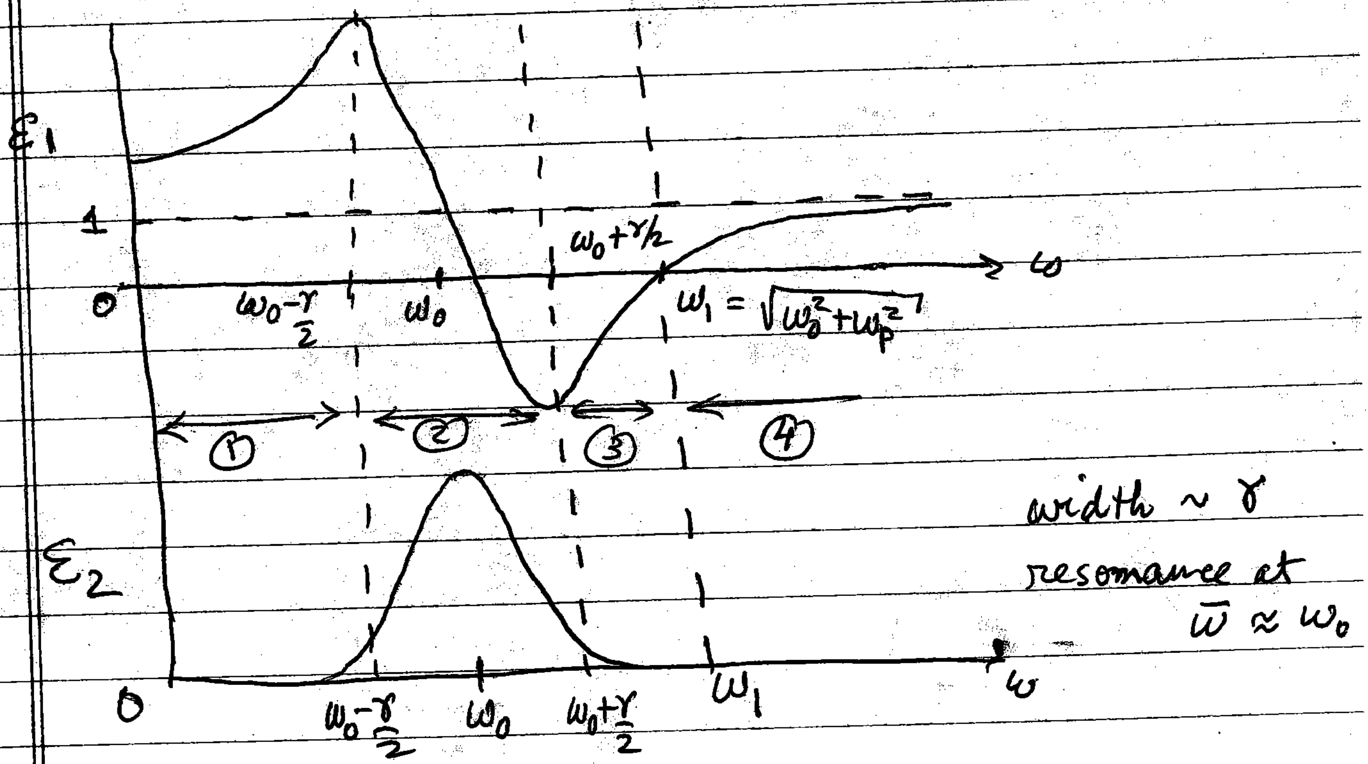
For our simple model: $\varepsilon = 1 + 4\pi\chi \simeq 1 + 4\pi M\alpha$

$$\varepsilon(\omega) = 1 + \frac{4\pi M e^2}{m} \frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma}$$

$$\varepsilon_1 = 1 + \frac{4\pi M e^2}{m} \frac{\omega_0^2 - \omega^2}{(\omega_0^2-\omega^2)^2 + \omega^2\gamma^2}$$

$$\varepsilon_2 = \frac{4\pi M e^2}{m} \frac{\omega\gamma}{(\omega_0^2-\omega^2)^2 + \omega^2\gamma^2}$$

Define $\omega_p = \sqrt{\frac{4\pi M e^2}{m}}$ the "plasma frequency"



$$k = k_1 + ik_2 = \pm \frac{\omega}{c}\sqrt{\mu}\sqrt{\varepsilon_1 + i\varepsilon_2}$$

$$k^2 = k_1^2 - k_2^2 + 2ik_1k_2 = \frac{\omega^2}{c^2}\mu(\varepsilon_1 + i\varepsilon_2)$$

equate real and imaginary pieces and solve for k_1 and k_2

$$k_1 = \pm \frac{\omega}{c}\sqrt{\mu}\left[\frac{1}{2}\sqrt{\varepsilon_1^2+\varepsilon_2^2} + \frac{1}{2}\varepsilon_1\right]^{1/2}$$

$$k_2 = \pm \frac{\omega}{c}\sqrt{\mu}\left[\frac{1}{2}\sqrt{\varepsilon_1^2+\varepsilon_2^2} - \frac{1}{2}\varepsilon_1\right]^{1/2}$$

<u>Regions of different behavior</u>

<u>Regions ① and ④</u> – transparent propagation

$\varepsilon_1 > 0$, $\varepsilon_1 \gg \varepsilon_2$

$$k_1 \simeq \pm \frac{\omega}{c}\sqrt{\mu}\left[\frac{1}{2}\varepsilon_1\left(1+\frac{1}{2}\left(\frac{\varepsilon_2}{\varepsilon_1}\right)^2\right) + \frac{1}{2}\varepsilon_1\right]^{1/2}$$

$$\simeq \pm \frac{\omega}{c}\sqrt{\mu}\left[\varepsilon_1 + \frac{1}{4}\frac{\varepsilon_2^2}{\varepsilon_1}\right]^{1/2}$$

$$\simeq \pm \frac{\omega}{c}\sqrt{\mu\varepsilon_1} \quad + \text{ small correction}$$

$$k_2 \simeq \pm \frac{\omega}{c}\sqrt{\mu}\left[\frac{1}{2}\varepsilon_1\left(1+\frac{1}{2}\left(\frac{\varepsilon_2}{\varepsilon_1}\right)^2\right) - \frac{1}{2}\varepsilon_1\right]^{1/2}$$

$$\simeq \pm \frac{\omega}{c}\sqrt{\mu}\left[\frac{1}{4}\frac{\varepsilon_2^2}{\varepsilon_1}\right]^{1/2} = k_1\left(\frac{\varepsilon_2}{2\varepsilon_1}\right) \ll k_1$$

So $k_2 \ll k_1$ small attenuation

$\Rightarrow$ medium is transparent

<u>Note:</u> $v_p = \frac{\omega}{k_1} = \frac{c}{n} = \frac{c}{\sqrt{\varepsilon_1\mu}}$

in region ①, $\varepsilon_1 > 1 \Rightarrow v_p < c$

in region ④, $\varepsilon_1 < 1 \Rightarrow v_p > c$!

but $v_g < c$ always!

Region (2) $\omega \approx \omega_0$ resonant absorption

$$\varepsilon_2 \approx \frac{\omega_p^2}{\omega_0 \gamma} = \left(\frac{\omega_p}{\omega_0}\right)^2 \left(\frac{\omega_0}{\gamma}\right)^2 \gg 1$$ for a sharp resonance with $\gamma \ll \omega_0$

$$\varepsilon_1 \approx 1$$

So $\varepsilon_2 \gg \varepsilon_1$

$$k_1 \simeq \pm \frac{\omega}{c}\sqrt{\mu}\left[\frac{1}{2}\varepsilon_2\left(1 + \frac{1}{2}\left(\frac{\varepsilon_1}{\varepsilon_2}\right)^2\right) + \frac{1}{2}\varepsilon_1\right]^{1/2}$$

$$\simeq \pm \frac{\omega}{c}\sqrt{\mu}\left[\frac{1}{2}\varepsilon_2 + \frac{1}{4}\frac{\varepsilon_1^2}{\varepsilon_2} + \frac{1}{2}\varepsilon_1\right]^{1/2}$$

$$k_1 \simeq \pm \frac{\omega}{c}\sqrt{\mu}\sqrt{\tfrac{1}{2}\varepsilon_2}$$

$$k_2 \simeq \pm \frac{\omega}{c}\sqrt{\mu}\left[\frac{1}{2}\varepsilon_2\left(1 + \frac{1}{2}\left(\frac{\varepsilon_1}{\varepsilon_2}\right)^2\right) - \frac{1}{2}\varepsilon_1\right]^{1/2}$$

$$\simeq \pm \frac{\omega}{c}\sqrt{\mu}\left[\frac{1}{2}\varepsilon_2 + \frac{1}{4}\frac{\varepsilon_1^2}{\varepsilon_2} - \frac{1}{2}\varepsilon_1\right]^{1/2}$$

$$\simeq \pm \frac{\omega}{c}\sqrt{\mu}\sqrt{\tfrac{1}{2}\varepsilon_2}$$

$k_1 \approx k_2$ strong attenuation

wave excites atoms at resonance $\Rightarrow$ large atomic displacements $\rightarrow$ media absorbs most energy from the wave $\Rightarrow$ wave decays rapidly, decreases factor $\frac{1}{e}$ within one wavelength of propagation.

Region 3 $\quad \varepsilon_1 < 0, \quad |\varepsilon_1| \gg \varepsilon_2$

total reflection

width of region 4 is

$$\omega_1 - \omega_0 = \sqrt{\omega_0^2 + \omega_p^2} - \omega_0 \sim \omega_p \sim \sqrt{N}$$

increases with atomic density $\quad$ as $\omega_p \gg \omega_0$

$$k_1 \simeq \pm \frac{\omega}{c}\sqrt{\mu}\left[\frac{1}{2}|\varepsilon_1| + \frac{1}{4}\frac{\varepsilon_2^2}{|\varepsilon_1|} + \frac{1}{2}\varepsilon_1\right]^{1/2}$$

cancel as $|\varepsilon_1| = -\varepsilon_1$

$$k_1 \simeq \pm \frac{\omega}{c}\sqrt{\mu|\varepsilon_1|}\;\frac{\varepsilon_2}{2|\varepsilon_1|}$$

$$k_2 \simeq \pm \frac{\omega}{c}\sqrt{\mu}\left[\frac{1}{2}|\varepsilon_1| + \frac{1}{4}\frac{\varepsilon_2^2}{|\varepsilon_1|} - \frac{1}{2}\varepsilon_1\right]^{1/2}$$

$$\simeq \pm \frac{\omega}{c}\sqrt{\mu|\varepsilon_1|}$$

$$\frac{k_2}{k_1} = \frac{2|\varepsilon_1|}{\varepsilon_2} \gg 1$$

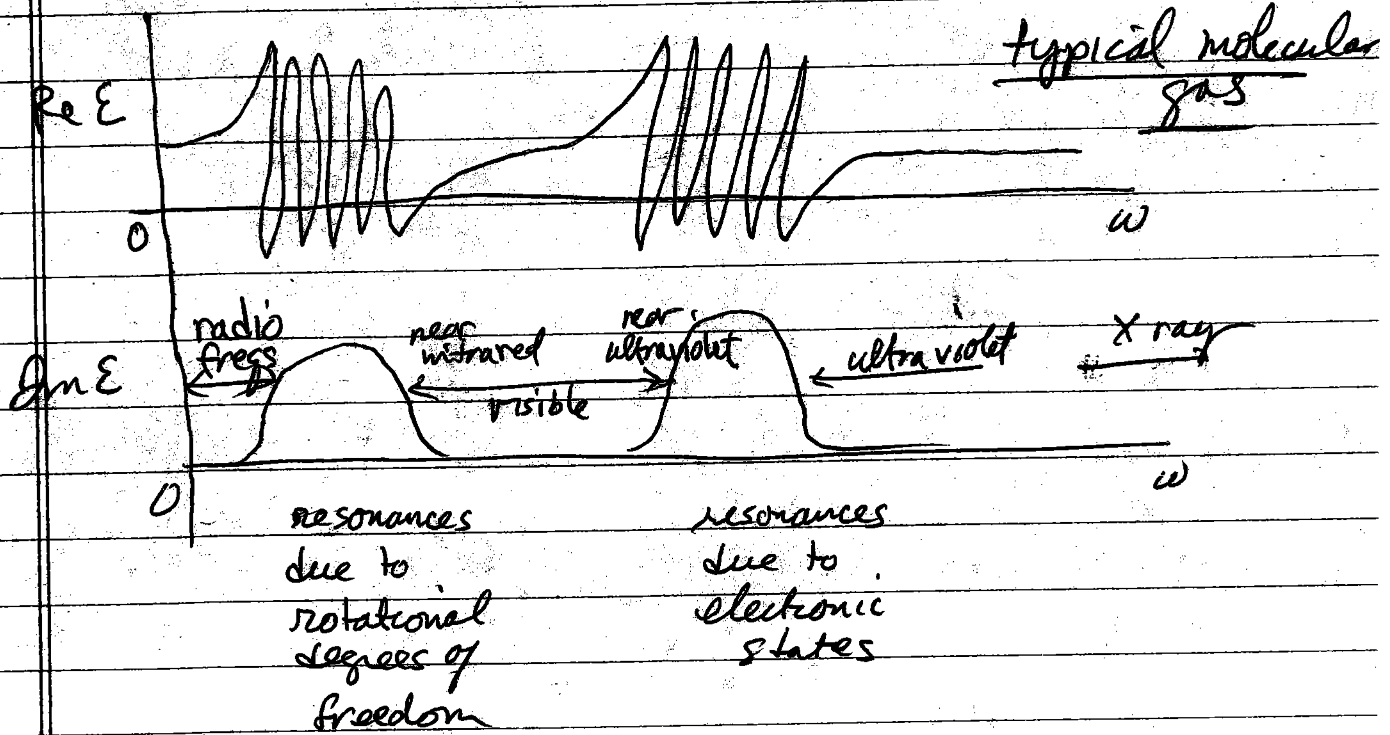
wave vector is almost pure imaginary
wave decays exponentially to zero in much less than one wavelength.

we will see this corresponds to total reflection
Since $\omega \gg \omega_0$, we are not at resonance, so material is not absorbing much energy from wave. The strong attenuation is due to the destructive interference between the wave and the induced fields of the polarized atoms

Our single model had a single resonance at ω_0. A more realistic model for molecules has many bands of resonances due to rotational, vibrational, and electronic modes of excitation

$$\epsilon(\omega) = 1 + \omega_p^2 \sum_i \frac{f_i}{\omega_i^2 - \omega^2 - i\omega\gamma_i}$$

where $\hbar\omega_i$ are spacings between energy levels with allowed electric dipole transitions



$$\omega_p = \sqrt{\frac{4\pi n e^2}{m}}$$

$$= 4.4\times10^{16}\sqrt{\frac{n}{n_A}}\ \sec^{-1}, \quad n_A = 6\times10^{23}/\text{cm}^3$$

~~For H_2O $\frac{n}{n_A}$~~

$$\Rightarrow \hbar\omega_p = 185\sqrt{\frac{n}{n_A}}\ \text{eV}$$

For H_2O $\quad \frac{n}{n_A} \sim 0.05$

$$\hbar\omega_p \sim 40\ \text{eV}$$

For typical metal $\quad \frac{n}{n_A} \sim 0.1$

$$\hbar\omega_p \sim 58\ \text{eV}$$

compared to $\hbar\omega_0 \sim \text{eV}$