The Electric Susceptibility, Dielectric Constant, and Complex Index of Refraction
R. Corn, Winter 2005.

Electric Polarization: $\mathbf{P}(\omega) = \varepsilon_0 \chi(\omega)\mathbf{E}(\omega)$

Electric Displacement: $\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$

$$\mathbf{D} = \varepsilon_0(1+\chi)\mathbf{E} = \varepsilon_0\varepsilon_r(\omega)\mathbf{E} = \varepsilon\mathbf{E}$$

$\chi(\omega)$ = complex frequency dependent electric susceptibility

ε_0 = permittivity of free space
ε = permittivity
$\varepsilon_r(\omega)$ = relative permittivity or complex frequency dependent dielectric constant

$$\chi = \chi' + j\chi''$$
$$\varepsilon_r = 1 + \chi = (1+\chi') + j\chi''$$

EM Plane Wave: $\mathbf{E}(\mathbf{r},t) = \mathbf{E_0}\exp(j\mathbf{k}\cdot\mathbf{r} - j\omega t)$

In free space:
$$k = \omega(\varepsilon_0\mu_0)^{1/2} = \frac{\omega}{c}$$
$$c = (\varepsilon_0\mu_0)^{-1/2}$$

c = speed of light
μ_0 = permeability of free space

In a dielectric:
$$k = \omega(\varepsilon\mu_0)^{1/2} = \omega(\varepsilon_r\varepsilon_0\mu_0)^{1/2} = \frac{n\omega}{c}$$

$$n = \varepsilon_r^{1/2}$$

$$n = \eta + j\kappa$$
$$\varepsilon_r = n^2 = (\eta^2 - \kappa^2) + j(2\eta\kappa)$$

n = complex index of refraction
η = (real) refractive index
κ = extinction coefficient

EM wave in z direction:
$$E(z,t) = E_0 \exp\left(j\omega\left(\frac{\eta z}{c} - t\right) - \frac{\omega\kappa z}{c}\right)$$

Beer's Law:
$$I(z) = I_0\exp(-Kz)$$
$$K = \frac{2\omega\kappa}{c}$$

K = Beer's Law absorption coefficient

Linear Electric Susceptibility Equations.
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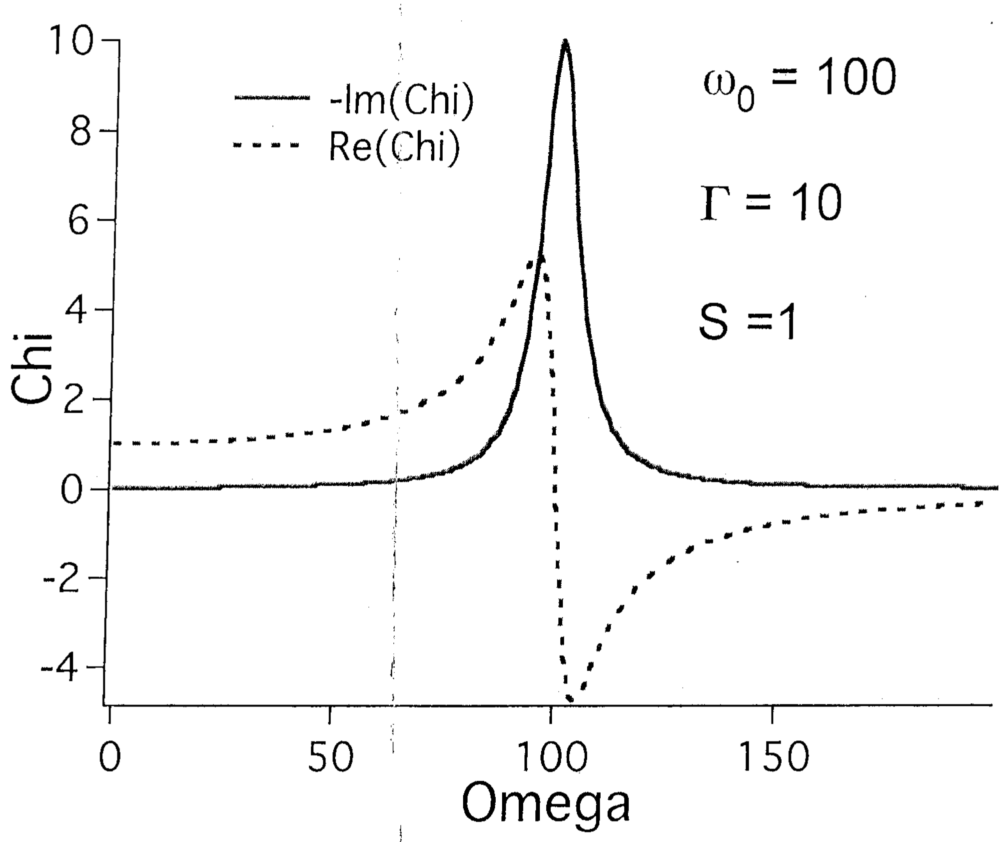
$$\chi(\omega) = \frac{S\omega_0^2}{\omega_0^2 - \omega^2 + j\omega\Gamma}$$

$$\mathrm{Re}\,\chi = \frac{S\omega_0^2\left(\omega_0^2 - \omega^2\right)}{\left(\omega_0^2 - \omega^2\right)^2 + \omega^2\Gamma^2}$$

$$\mathrm{Im}\,\chi = \frac{S\omega_0^2\omega\Gamma}{\left(\omega_0^2 - \omega^2\right)^2 + \omega^2\Gamma^2}$$



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Chemistry 249 Classical Description of The Susceptibility

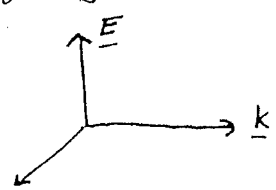
I. Classical Description of Electromagnetic Fields

From Maxwell's equations in free space, one can derive the electric & magnetic fields associated with a plane electromagnetic wave

$$\underline{E}(\underline{r},t) = \underline{E}_0 \exp(i\underline{k}\cdot\underline{r} - i\omega t)$$

$$\underline{H}(\underline{r},t) = \underline{H}_0 \exp(i\underline{k}\cdot\underline{r} - i\omega t)$$

$\underline{E}$ & $\underline{H}$ are oscillating functions of time & space. The EM wave is propagating in the $\underline{k}$ direction. k is called the wavevector:



$|\underline{k}| = \dfrac{\omega}{c}$ free space

$\underline{k}\cdot\underline{E} = \underline{k}\cdot\underline{H} = 0$ $\underline{k}$ is $\perp$ to $\underline{E}$ & $\underline{H}$

$\underline{k}\times\underline{E} = \omega\mu_0\underline{H}_0$

$\underline{k}\times\underline{H} = -\omega\epsilon_0\underline{E}$

$|\underline{H}| = \left(\dfrac{\epsilon_0}{\mu_0}\right)^{1/2}|\underline{E}|$

If $\underline{k}$ is in the $+z$ direction, then both $\underline{E}$ & $\underline{H}$ have the functional form:

$$\exp\left[i\omega\left(\frac{z}{c} - t\right)\right]$$

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When the EM wave is travelling through a dielectric medium, it induces a linear polarization $\underline{P}$:

$$\underline{P} = \epsilon_0 \chi \underline{E}$$

where χ, the proportionality constant, is called the electric susceptibility. χ is related to the wavevector $\underline{k}$ by:

$$\left(\frac{kc}{\omega}\right)^2 = 1 + \chi$$

where χ is a complex quantity.

$$\chi = \chi' + i\chi'' \qquad \text{(Note: some define } \chi = \chi' - i\chi''\text{)}$$

The wavevector is also proportional to η & K

$$kc/\omega = \eta + iK$$

$\eta \equiv$ Refractive index ; $K \equiv$ extinction coefficient.

This is because the time & space varying parts of $\underline{E}$ & $\underline{H}$ now look like:

$$\exp(ikz - \omega t) = \exp\left\{i\omega\left(\frac{\eta z}{c} - t\right) - \frac{\omega K z}{c}\right\}$$

Thus: c/η is the velocity of the EM wave, and the last term $\frac{\omega K z}{c}$ is ~~the~~ an exponentially decaying function with z.

The power of the EM wave is given by the Poynting Vector averaged over one cycle of ω:

$$I(z) = \tfrac{1}{2}\epsilon_0 c \eta \overline{\left| \underline{E}(\underline{r},t) \right|^2}$$

$$= I_0 \exp(-\beta z)$$

where $\beta = \frac{2\omega K}{c}$ is the Beer's law absorption coefficient.

Since

$$(kc/\omega)^2 = 1 + \chi = (\eta + ik)^2$$

then

$$\eta^2 - K^2 = 1 + \chi'$$

$$2\eta K = \chi''$$

Thus χ' & χ'' are related directly to the index of refraction & the extinction coefficient.

II. The Frequency-Dependent Susceptibility

χ can in general be thought of as a function of ω. This can be described in terms of the Fourier components of a general electric field $E(t)$ (in lieu of the specific plane wave form of EM radiation):

$$E(t) = \int_{-\infty}^{\infty} E(\omega) \exp(-i\omega t)\, d\omega$$

And, by the inverse FT:

$$E(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} E(t) \exp(i\omega t)\, dt$$

(Since $E(t)$ is real, $E(-\omega) = E^*(\omega)$)

The polarization induced by $E(t)$ is $P(t)$:

$$P(t) = \int_{-\infty}^{\infty} P(\omega) \exp(-i\omega t)\, d\omega.$$

And the frequency-dependent susceptibility is now defined as:

$$P(\omega) = \epsilon_0 \chi(\omega) E(\omega)$$

Because $P(t)$ is real, we require that

$$\chi(-\omega) = \chi^*(\omega)$$

which means that:

$$\chi'(-\omega) = \chi'(\omega)$$
$$\chi''(-\omega) = -\chi''(\omega)$$

These "crossing relations" show that we only need $\chi(\omega)$ for $\omega > 0$, for $E(\omega)\exp(-i\omega t)$.

III. Classical Theory of the Susceptibility

Consider the system to be N damped harmonic oscillators at the resonant frequency ω_0:

$$m(\ddot{x} + \Gamma x + \omega_0^2 x) = -eE = -eE_0 \exp(-i\omega t)$$

The damping in this oscillator is that phenomenological damping that we included in the density matrix derivation.

We can solve this equation by seeking homogeneous solutions & plugging in the driving fields to get:

$$x(t) = \frac{-e\,E(t)}{m(\omega_0^2-\omega^2-i\omega\Gamma)} \qquad E(t)=E_0\exp(-i\omega t)$$

The polarization induced in this collection of N oscillators is given by:

$$P = NeX = \frac{Ne^2 E_0 \exp(-i\omega t)}{m(\omega_0^2-\omega^2-i\omega\Gamma)}$$

The susceptibility $\chi(\omega)$ is therefore given by:

$$\chi(\omega) = \frac{Ne^2/\epsilon_0 m}{\omega_0^2-\omega^2-i\omega\Gamma}$$

This eqn. results in the same form for χ'' & χ' as we derived quantum mechanically:

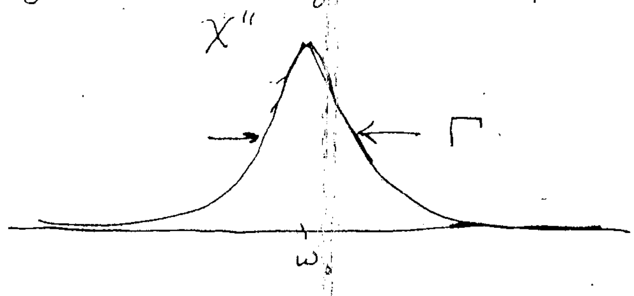
$$\chi'' = 2\eta\kappa \propto \frac{\frac{Ne}{m}\cdot\omega_0^2\,\omega\Gamma}{(\omega_0^2-\omega^2)^2+\omega^2\Gamma^2}$$

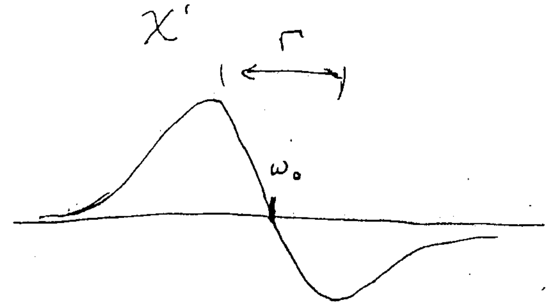
$$1+\chi' = \eta^2-\kappa^2 \propto 1 + \frac{\frac{Ne}{m}\cdot\omega_0^2(\omega_0^2-\omega^2)}{(\omega_0^2-\omega^2)^2+\omega^2\Gamma^2}$$

If $\Gamma \ll \omega_0$, & ω is close to ω_0, then

$$\chi'' \approx \frac{\frac{Ne}{m}\,\omega_0\cdot\frac{\Gamma}{4}}{(\omega_0-\omega)^2+\left(\frac{\Gamma}{2}\right)^2} \qquad \Gamma \ll \omega_0$$

This is once again the Lorentzian lineshape w/ width Γ:





In general, note that κ & β are distorted by the frequency-dependent refractive index η. ($\kappa = \frac{\chi''}{2\eta}$). This is sometimes called a dispersion effect. If η doesn't change too much (i.e. when $\frac{\omega_0 N e}{m\Gamma} << 1$) then κ is a Lorentzian as well as χ''.

As a final note, the $\chi''(\omega)$ and $\chi'(\omega)$ are related to each other by the "Kramers - Kronig" relations":

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

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

where P denotes the principal part of the integral. For a derivation of these relations, see either Born & Wolf, Optics, or R. Loudon, The Quantum Theory of Light.