From electrodynamics to polarization and back

Starting point - Coupled Maxwell - Liouville equations

$$\nabla \times \nabla \times \vec{E}(\vec{r},t) + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{E}(\vec{r},t) = -\frac{4\pi}{c}\frac{\partial^2}{\partial t^2}\vec{P}(\vec{r},t) \qquad (1)$$

$\vec{E}$ and $\vec{P}$ are macroscopic variables - intensity of electric field & polarization

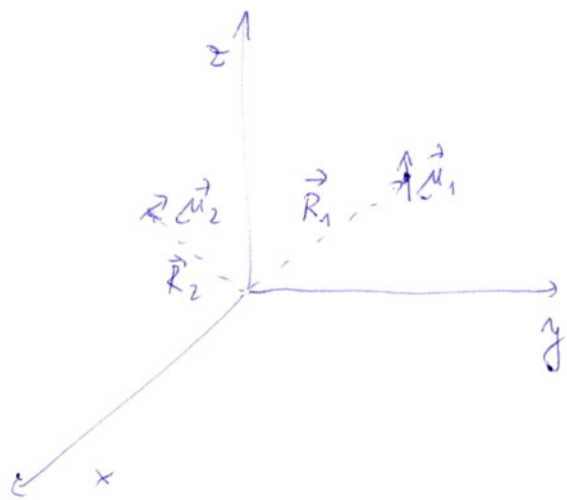
- Polarization describes the material
- We use a microscopic theory to calculate $\vec{P}(\vec{r},t)$

$$\vec{P}(\vec{r},t) = Tr\{\hat{\vec{P}}(\vec{r})\hat{\rho}(t)\} \qquad (2)$$

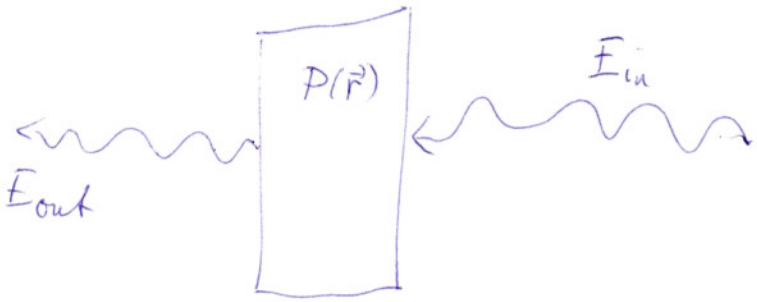
The polarization operator $\hat{\vec{P}}(\vec{r})$ can be expressed as a sum of polarization of individual molecules

$$\hat{\vec{P}}(\vec{r}) = \sum_m \hat{\vec{P}}_m(\vec{r}) \qquad \text{where} \quad \hat{\vec{P}}_m(\vec{r}) = \hat{\vec{\mu}}_m \delta(\vec{r} - \vec{R}_m)$$

↑ position of the molecule m



We assume that our sample takes a limited area in space and is entered by certain coherent electric field from the outside of the sample.



In presence of external field the matter, i.e. $\hat{\rho}(t)$, is brought out of equilibrium and exhibits certain dynamics.

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}\left[\hat{H}_M + \hat{H}_{E-M}^{(t)}, \hat{\rho}(t)\right] \qquad (3)$$

This dynamics influences the $\vec{E}$ $\longleftrightarrow$ That is the source of our information about $\hat{\rho}(t)$

! Important ! In Eq (1), $\vec{P}$ is not the source of $\vec{E}$, it is only a source of its change ! $\vec{E}$ can live happily with $\vec{P} \equiv 0$

Some notes:

$\vec{E} = \vec{E}_\perp$ ... only radiation field

We assume $\vec{E}_\perp$ creates $\vec{P}_\perp$, a perfectly transversal polarization

$\hat{H}_{E-M}^{(t)}$ ... the interaction Hamiltonian will be specified later. It will include the classical field $\vec{E}_\perp$ and will thus be semiclassical.

Linear polarization

Expand the polarization in orders of $\vec{E}$, which generates it

$$\vec{P}(\vec{r},t) = \vec{P}^{(1)}(\vec{r},t) + \vec{P}_{NL}(\vec{r}) \qquad (4)$$

$$\vec{P}^{(2)}(\vec{r}) + \vec{P}^{(3)}(\vec{r}) + \ldots$$

What is the most general possible linear dependence of time and space dependent $\vec{P}^{(1)}$ on the time and space dependent $\vec{E}$?

$$\vec{P}^{(1)}(\vec{r},t) = \int d\vec{r}' \int_0^t dt' \; \underbrace{S^{(1)}(\vec{r}-\vec{r}', t-t')}_{\text{linear response function}} E(\vec{r}',t') \qquad (5)$$

expresses causality

What is a response function?

Imagine $E(\vec{r}',t') = E_0 \, \delta(\vec{r}'-\vec{R}) \, \delta(t'-T)$

$$\Rightarrow \vec{P}^{(1)}(\vec{r},t) = S^{(1)}(\vec{r}-\vec{R}, t-T) E_0$$

$S^{(1)}$ gives the polarization ~~(the effect or response)~~ at $\vec{r}$ and t as a response to a cause (unity field) acting at $t-T$ before and a point $\vec{R}$.

How is linear response function related to linear changes in the $\vec{E}$?

Let us insert Eq. (5) back into Eq. (1) and move the linear term to the left hand side

$$D \star D \star \vec{E}(\vec{r},t) + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\int d\vec{r}' \int_0^t dt' \, \varepsilon(\vec{r}-\vec{r}', t-t')\,\vec{E}(\vec{r}',t) = -\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\vec{P}_{NL}(\vec{r},t) \qquad (6)$$

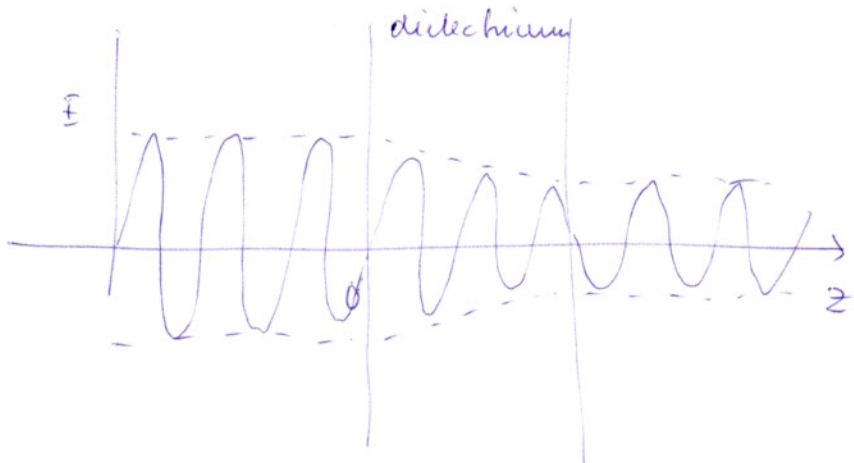
$$\boxed{\varepsilon(\vec{r},t) = \delta(\vec{r})\,\delta(t) + 4\pi\, S^{(1)}(\vec{r},t)} \qquad (7)$$

↑ dielectric function

Let us consider a linear absorption of a plane wave

$$\vec{P}_{NL}(\vec{r},t) \equiv 0$$

$$E(z,t) = E_0\, e^{i\tilde{k}z - i\omega t}$$



$$\nabla \times \vec{F} = \vec{e}_x \left(\frac{\partial F_z}{\partial y} - \frac{\partial F_y}{\partial z}\right) - \vec{e}_y \left(\frac{\partial F_z}{\partial x} - \frac{\partial F_x}{\partial z}\right) + \vec{e}_z \left(\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y}\right)$$

$$\Rightarrow \quad \nabla \times \nabla \times E(z,t) = \nabla \times \left[\left(-\vec{e}_x \frac{\partial E_y}{\partial z}\right) + \vec{e}_y \frac{\partial E_x}{\partial z}\right] \qquad E_z = 0 \text{ anyway}$$

$$= -\frac{\partial^2}{\partial z^2} E_y - \frac{\partial^2}{\partial z^2} E_x = -\frac{\partial^2}{\partial z^2} \vec{E}(z,t)$$

$$\frac{\partial}{\partial t} E_0 e^{i\xi z - i\omega t} = i\xi E(z,t)$$

$$\frac{\partial^2}{\partial z^2} E_0 e^{i\xi z - i\omega t} = -\xi^2 E(z,t)$$

Change of variable in

$$\int_{t_0}^{t} dt' \, \varepsilon(\vec{r} - \vec{r}', t - t') \, \vec{E}(\vec{r}', t)$$

$$t'' = t - t' \quad \Rightarrow \quad t' = t - t''$$

$$dt'' = -dt'$$

$$t''(t_0) = t - t_0$$

$$t''(t) = 0$$

$$-\int_{t-t_0}^{0} dt'' \, \varepsilon(\vec{r} - \vec{r}', t'') \, \vec{E}(\vec{r}', t - t'') = \int_{0}^{t-t_0} dt'' \, \varepsilon(\vec{r} - \vec{r}', t'') \vec{E}(\vec{r}', t - t'')$$

Let us send $t_0 \to -\infty$

$$\Rightarrow \quad \int_{0}^{\infty} dt'' \, \varepsilon(\vec{r} - \vec{r}', t'') \, \vec{E}(\vec{r}', t - t'') =$$

$$\int_0^\infty dt''\, \varepsilon(\vec{r}-\vec{r}', t'')\, E_0\, e^{ikz - i\omega(t-t'')} =$$

$$= E_0\, e^{ikz}\, e^{-i\omega t} \int_0^\infty dt''\, \varepsilon(\vec{r}-\vec{r}', t'')\, e^{i\omega t''}$$

half-sided Fourier transform

The whole time dependence is in here

$$\Rightarrow \frac{1}{c^2}\frac{\partial^2}{\partial t^2} \int d\vec{r}' \int_0^t dt' \ldots = -\frac{\omega^2}{c^2}\, \varepsilon(\vec{k}, \omega)\, E(z,t)$$

We did the same substitution trick with $\vec{r}$

$$\boxed{\varepsilon(\vec{k},\omega) = \int d\vec{r} \int_0^\infty dt\; \varepsilon(\vec{r},t)\, e^{-i\vec{k}\cdot\vec{r} + i\omega t}} \qquad (8)$$

We can define a linear susceptibility $\chi^{(1)}(\vec{k},\omega)$ as

$$\boxed{\varepsilon(\vec{k},\omega) = 1 + 4\pi\chi^{(1)}(\vec{k},\omega)} \qquad (9)$$

Such a relation appears already in high-school text books

The Eq. (6) gives us

$$\boxed{\frac{k^2 c^2}{\omega^2} = \varepsilon(\vec{k},\omega)} \qquad (10)$$

after we eliminated $E(z,t)$

We are looking for so-called dispersion relation

$$\omega \text{ vs. } k$$

Using Eq. (10) we get

$$\frac{k c}{\omega} = \sqrt{\varepsilon(\vec{k}, \omega)} \equiv n(\omega) + i\, \varkappa(\omega) \tag{11}$$

↑ real & imaginary parts of $\sqrt{\varepsilon}$; diffraction index and extinction coefficient

$$k = \frac{\omega}{c} n(\omega) + i \frac{\omega}{c} \varkappa(\omega)$$

Inserting into the definition of our plain wave we obtain

$$E(z,t) = E_0\, e^{i k' z - i\omega t - \frac{\varkappa_a(\omega) z}{2}} \tag{12}$$

The wave vector in the medium is different from vacuum

where we defined

$$k' \equiv \frac{\omega n(\omega)}{c}$$

$$\varkappa_a(\omega) = \frac{2\omega \varkappa(\omega)}{c} \tag{13}$$

this is so-called ~~extinction~~ absorption coefficient. The field is dumped with increasing z

The one-half is due to the fact that we measure decrease in intensity!

$$I(z) \approx |E(z,t)|^2 \quad \Rightarrow$$

$$\boxed{I(z) = I_0 \, e^{-\varkappa_a(\omega) z}} \qquad (14)$$

We now relate $\varkappa_a(\omega)$ to $\chi^{(1)}(\omega)$ and $S^{(1)}(\vec{r},t)$

Let us separate <u>real</u> and <u>imaginary</u> parts of $\chi^{(1)}(\omega)$

$$\boxed{\chi^{(1)}(\omega) = \chi'(\omega) + i\,\chi''(\omega)} \qquad (15)$$

Then

$$\sqrt{\varepsilon(\omega)} = \sqrt{1 + 4\pi\chi' + 4\pi i \chi''} \equiv n(\omega) + i\,\varkappa(\omega)$$

$$1 + 4\pi\chi' + 4\pi i \chi'' = n^2 + 2in\varkappa - \varkappa^2$$

$$\Rightarrow \qquad 4\pi\chi'' = 2n\varkappa$$

$$1 + 4\pi\chi' = n^2 - \varkappa^2$$

$$\boxed{\varkappa(\omega) = \frac{2\pi\chi''(\omega)}{n(\omega)}} \qquad (16)$$

if $4\pi\chi'' \ll 1 + 4\pi\chi'$ $\Rightarrow$ $n^2 + \varkappa^2 \approx 1 + 4\pi\chi'$

$$\Rightarrow \quad n^2 - \varkappa^2 = 1 + 4\pi\chi'$$

$$\Rightarrow \quad 2n^2 = 2(1 + 4\pi\chi')$$

$$\boxed{n(\omega) \approx \sqrt{1 + 4\pi\chi'(\omega)}} \qquad (17)$$

The absorption coefficient then reads

$$\alpha_a(\omega) = \frac{4\pi\omega}{n(\omega)c}\,\chi''(\omega) \tag{18}$$

Using Eq. (7), (8) and (9) we get

$$\chi^{(1)}(\omega) = \int_0^\infty dt\; S^{(1)}(t)\, e^{i\omega t}$$

$$\Rightarrow \quad \alpha_a(\omega) = \frac{4\pi\omega}{n(\omega)c}\,\mathrm{Im}\int_0^\infty dt\; S^{(1)}(t)\, e^{i\omega t} \tag{19}$$

! We droped the $\vec{r}$ dependency of $S^{(1)}$ function and t dependency of the χ function to simplify equations. In the geometry we concidered those dependencies reduced to Eq. (11)

Later our task will be to provide a microscopic theory for $S^{(1)}(t)$ to explain observed absorption spectra $\alpha_a(\omega)$ (20)