Linear Response

Mike Reppert

September 28, 2020

Previously on CHM676...

We saw that the polarization of a dielectric material can be expanded in a perturbative series:

$$P_\alpha(t) = \sum_{n=0}^{\infty} P_\alpha^{(n)}(t)$$

Previously on CHM676...

We saw that the polarization of a dielectric material can be expanded in a perturbative series:

$$P_\alpha(t) = \sum_{n=0}^{\infty} P_\alpha^{(n)}(t)$$

where

$$P_\alpha^{(n)}(t) = \sum_{\alpha_1,...,\alpha_n} \int_{-\infty}^{\infty} d\tau_n ... \int_{-\infty}^{\infty} d\tau_1 R^{(n)}_{\alpha_1...\alpha_n\alpha}(\tau_1, ..., \tau_n)$$
$$\times E_{\alpha_1}(t-\tau_1-...-\tau_n)E_{\alpha_2}(t-\tau_2-...-\tau_n)...E_{\alpha_n}(t-\tau_n).$$

$R^{(n)}_{\alpha_1...\alpha_n\alpha}(\tau_1, ..., \tau_n)$ is the n^{th}-order *response function* for the material.

Previously on CHM676...

We saw that the polarization of a dielectric material can be expanded in a perturbative series:

$$P_\alpha(t) = \sum_{n=0}^{\infty} P_\alpha^{(n)}(t)$$

where

$$P_\alpha^{(n)}(t) = \sum_{\alpha_1,\dots,\alpha_n} \int_{-\infty}^{\infty} d\tau_n \dots \int_{-\infty}^{\infty} d\tau_1 R^{(n)}_{\alpha_1\dots\alpha_n\alpha}(\tau_1,\dots,\tau_n) \times E_{\alpha_1}(t-\tau_1-\dots-\tau_n)E_{\alpha_2}(t-\tau_2-\dots-\tau_n)\dots E_{\alpha_n}(t-\tau_n).$$

$R^{(n)}_{\alpha_1\dots\alpha_n\alpha}(\tau_1,\dots,\tau_n)$ is the n^{th}-order *response function* for the material.

Today: First-order – a.k.a. "linear" – response

Outline for Today:

1. Solving Maxwell's Equations

2. Absorption Spectroscopy

Solving Maxwell's Equations

Linear Response Regime

Under **linear response** conditions, the total polarization $\mathbf{P}(t)$ is dominated by the linear response

$$P_{\alpha}^{(1)}(t) = \sum_{\beta} \int_{-\infty}^{\infty} d\tau R_{\alpha\beta}^{(1)}(\tau) E_{\beta}(t-\tau).$$

Linear Response Regime

Under **linear response** conditions, the total polarization $\mathbf{P}(t)$ is dominated by the linear response

$$P_\alpha^{(1)}(t) = \sum_\beta \int_{-\infty}^{\infty} d\tau R_{\alpha\beta}^{(1)}(\tau) E_\beta(t-\tau).$$

The linear response regime is dictated by:

- Field intensity

Linear Response Regime

Under **linear response** conditions, the total polarization $\mathbf{P}(t)$ is dominated by the linear response

$$P_\alpha^{(1)}(t) = \sum_\beta \int_{-\infty}^{\infty} d\tau R_{\alpha\beta}^{(1)}(\tau) E_\beta(t-\tau).$$

The linear response regime is dictated by:

- Field intensity
- Material properties

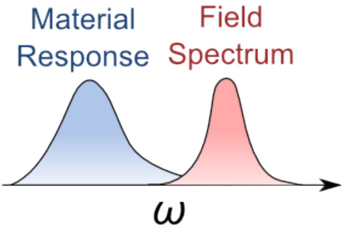
Linear Response Regime

Under **linear response** conditions, the total polarization $\mathbf{P}(t)$ is dominated by the linear response

$$P_\alpha^{(1)}(t) = \sum_\beta \int_{-\infty}^{\infty} d\tau R_{\alpha\beta}^{(1)}(\tau) E_\beta(t-\tau).$$

The linear response regime is dictated by:

- Field intensity
- Material properties
- Field spectrum.



Linear Isotropic Media

Under **linear response** conditions, the total polarization $\mathbf{P}(t)$ is dominated by the linear response

$$P_{\alpha}^{(1)}(t) = \sum_{\beta} \int_{-\infty}^{\infty} d\tau R_{\alpha\beta}^{(1)}(\tau) E_{\beta}(t-\tau).$$

We'll focus on *isotropic media* where symmetry dictates that

$$R_{xx}^{(1)} = R_{yy}^{(1)} = R_{zz}^{(1)} \equiv R^{(1)}.$$

Linear Isotropic Media

Under **linear response** conditions, the total polarization $\mathbf{P}(t)$ is dominated by the linear response

$$P_\alpha^{(1)}(t) = \sum_\beta \int_{-\infty}^{\infty} d\tau R_{\alpha\beta}^{(1)}(\tau) E_\beta(t-\tau).$$

We'll focus on *isotropic media* where symmetry dictates that

$$R_{xx}^{(1)} = R_{yy}^{(1)} = R_{zz}^{(1)} \equiv R^{(1)}.$$

Then

$$\boldsymbol{P}^{(1)}(t) = \int_{-\infty}^{\infty} d\tau R^{(1)}(\tau) \boldsymbol{E}(t-\tau).$$

Solving Maxwell's Equations

The field dynamics are governed by the linear response equation and Maxwell's Equations:

$$\begin{aligned}
\nabla \cdot \boldsymbol{E} &= -4\pi \nabla \cdot \boldsymbol{P}(\boldsymbol{x}, t) \\
\nabla \cdot \boldsymbol{B} &= 0 \\
\nabla \times \boldsymbol{E} + \frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} &= 0 \\
\nabla \times \boldsymbol{B} - \frac{1}{c}\frac{\partial \boldsymbol{E}}{\partial t} &= \frac{4\pi}{c}\frac{\partial \boldsymbol{P}(\boldsymbol{x}, t)}{\partial t}.
\end{aligned}$$

This still looks pretty bad!

The Partially-transformed Field

Life gets much better if we Fourier transform w.r.t. time:

$$\breve{\boldsymbol{E}}(\boldsymbol{x}, \omega) \equiv \int_{-\infty}^{\infty} dt e^{\mathrm{i}\omega t} \boldsymbol{E}(\boldsymbol{x}, t).$$

The Partially-transformed Field

Life gets much better if we Fourier transform w.r.t. time:

$$\breve{\boldsymbol{E}}(\boldsymbol{x},\omega) \equiv \int_{-\infty}^{\infty} dt e^{\mathrm{i}\omega t} \boldsymbol{E}(\boldsymbol{x},t).$$

The linear response relation becomes:

$$\breve{\boldsymbol{P}}^{(1)}(\omega) = \int dt e^{\mathrm{i}\omega t} \boldsymbol{P}^{(1)}(t) = \left(\int d\tau R^{(1)}(\tau) e^{\mathrm{i}\omega\tau} \right) \breve{\boldsymbol{E}}(\omega)$$
$$\equiv \chi(\omega) \breve{\boldsymbol{E}}(\omega).$$

where $\chi(\omega)$ is the **linear susceptibility**.

The Partially-transformed Field

Life gets much better if we Fourier transform w.r.t. time:

$$\breve{\boldsymbol{E}}(\boldsymbol{x},\omega) \equiv \int_{-\infty}^{\infty} dt e^{\mathrm{i}\omega t} \boldsymbol{E}(\boldsymbol{x},t).$$

The linear response relation becomes:

$$\begin{aligned}\breve{\boldsymbol{P}}^{(1)}(\omega) = \int dt e^{\mathrm{i}\omega t} \boldsymbol{P}^{(1)}(t) &= \left(\int d\tau R^{(1)}(\tau) e^{\mathrm{i}\omega\tau}\right) \breve{\boldsymbol{E}}(\omega) \\ &\equiv \chi(\omega) \breve{\boldsymbol{E}}(\omega).\end{aligned}$$

where $\chi(\omega)$ is the **linear susceptibility**.

No more convolution! Fourier transforms are magical!
Fourier transforms convert convolutions to products.

Maxwell's Equations in the Fourier Domain

Transforming Maxwell's equations and inserting the transformed linear response relation we get:

$$\begin{aligned}(1+4\pi\chi)\,\nabla\cdot\breve{\boldsymbol{E}}&=0\\ \nabla\cdot\breve{\boldsymbol{B}}&=0\\ \nabla\times\breve{\boldsymbol{E}}-\frac{\mathrm{i}\omega}{c}\breve{\boldsymbol{B}}&=0\\ \nabla\times\breve{\boldsymbol{B}}+\frac{\mathrm{i}\omega}{c}(1+4\pi\chi)\,\breve{\boldsymbol{E}}&=0.\end{aligned}$$

Maxwell's Equations in the Fourier Domain

Transforming Maxwell's equations and inserting the transformed linear response relation we get:

$$
\begin{aligned}
(1 + 4\pi\chi)\, \nabla \cdot \breve{\boldsymbol{E}} &= 0 \\
\nabla \cdot \breve{\boldsymbol{B}} &= 0 \\
\nabla \times \breve{\boldsymbol{E}} - \frac{\mathrm{i}\omega}{c} \breve{\boldsymbol{B}} &= 0 \\
\nabla \times \breve{\boldsymbol{B}} + \frac{\mathrm{i}\omega}{c} (1 + 4\pi\chi)\, \breve{\boldsymbol{E}} &= 0.
\end{aligned}
$$

It's convenient to define the **electric permittivity**:

$$\varepsilon(\omega) \equiv 1 + 4\pi\chi(\omega).$$

Attenuated Wave Equation

Rearranging Maxwell's Equations (the usual!) gives a modified wave equation

$$\nabla^2 \breve{\boldsymbol{E}} + \frac{\omega^2}{c^2} \varepsilon \breve{\boldsymbol{E}} = 0$$

with solutions of the form

$$\breve{\boldsymbol{E}}(\boldsymbol{x}, \omega) = \tilde{\boldsymbol{A}}(\omega) \mathrm{e}^{\mathrm{i} \frac{\omega}{c} \sqrt{\varepsilon} \hat{\boldsymbol{s}} \cdot \boldsymbol{x}},$$

where $\hat{\boldsymbol{s}}$ is a real unit vector.

Attenuated Wave Equation

Rearranging Maxwell's Equations (the usual!) gives a modified wave equation

$$\nabla^2 \breve{\boldsymbol{E}} + \frac{\omega^2}{c^2}\varepsilon \breve{\boldsymbol{E}} = 0$$

with solutions of the form

$$\breve{\boldsymbol{E}}(\boldsymbol{x}, \omega) = \tilde{\boldsymbol{A}}(\omega) \mathrm{e}^{\mathrm{i}\frac{\omega}{c}\sqrt{\varepsilon}\hat{\boldsymbol{s}}\cdot\boldsymbol{x}},$$

where $\hat{\boldsymbol{s}}$ is a real unit vector.

NB: The complete solution is a linear combination of such solutions that satisfies the *boundary conditions* of the problem!

Take-Home Point

Linear Response: $\boldsymbol{R}^{(1)}$ dominates.

In **isotropic media** linear response is governed by *scalar* quantities:

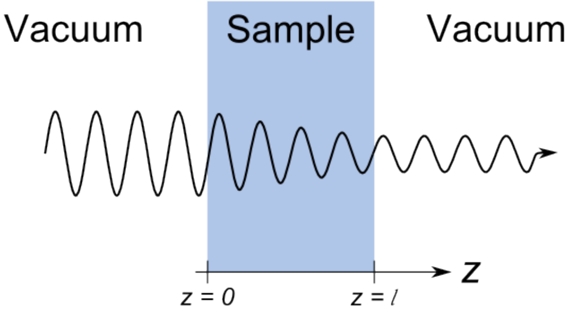
- The response function $R^{(1)}(\tau)$ **or**
- the *susceptibility* $\chi(\omega) = \int d\tau R^{(1)}(\tau) e^{\mathrm{i}\omega\tau}$ **or**
- the *permittivity* $\varepsilon(\omega) \equiv 1 + 4\pi\chi(\omega)$

Under linear response, solutions to MEs resemble propagating waves with **attenuated amplitude** and **shifting phase** due to $\varepsilon(\omega)$.

Absorption Spectroscopy

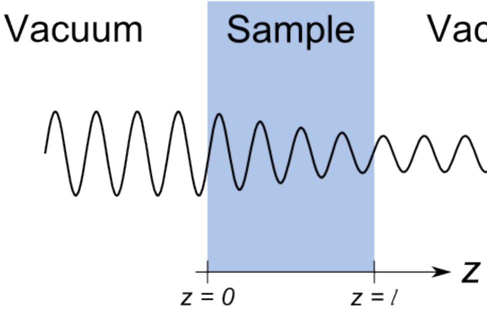
Absorption Spectroscopy

Let's think about a specific set of boundary conditions:



Absorption Spectroscopy

Let's think about a specific set of boundary conditions:

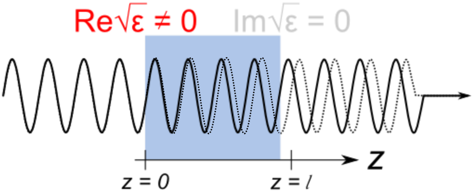


Then

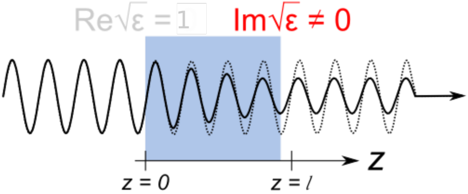
$$\breve{\boldsymbol{E}}(\boldsymbol{x},\omega) = \tilde{\boldsymbol{A}}(\omega)\cdot\begin{cases} e^{i\frac{\omega}{c}z}, & z<0 \\ e^{i\frac{\omega}{c}\sqrt{\varepsilon(\omega)}z}, & 0\le z\le \ell \\ e^{i\frac{\omega}{c}\left(\sqrt{\varepsilon(\omega)}\ell+z\right)}, & z>\ell \end{cases}$$

Linear Processes

$$\boldsymbol{E}(\boldsymbol{x},t) \propto \mathrm{e}^{\mathrm{i}\omega\left(\frac{z}{c}\sqrt{\varepsilon(\omega)}-t\right)}$$



The *refractive index* $n(\omega) \equiv \mathrm{Re}\sqrt{\varepsilon(\omega)}$ decreases the wavelength.



The *extinction coefficient* $\kappa(\omega) \equiv \mathrm{Im}\sqrt{\varepsilon(\omega)}$ decreases the amplitude.

Absorption Spectroscopy

Experimentally, we monitor the *transmittance*

$$T(\omega) = \frac{I(\omega)}{I_o(\omega)} = \frac{\left\|\tilde{A}(\omega)\right\|^2 \mathrm{e}^{-\frac{2\omega}{c}\mathrm{Im}\sqrt{\varepsilon(\omega)}\ell}}{\left\|\tilde{A}(\omega)\right\|^2} = \mathrm{e}^{-\frac{2\omega}{c}\kappa(\omega)\ell}$$

or the *absorbance*

$$A(\omega) = -\mathrm{log} T(\omega) = \frac{2\omega\ell}{c\ln 10}\kappa(\omega).$$

Absorption Spectroscopy

Note that if $\mathrm{Im}\chi^{(1)}(\omega) \ll 1$:

$$n(\omega) \approx \sqrt{1 + 4\pi \mathrm{Re}\chi}$$
$$\kappa(\omega) \approx \frac{2\pi \mathrm{Im}\chi}{n(\omega)}$$

and

$$A(\omega) = \frac{4\pi\omega\ell}{cn(\omega)\ln 10}\mathrm{Im}\chi(\omega).$$

Absorption spectroscopy probes $\mathrm{Im}\chi^{(1)}$*!*

Take-Home Points

In isotropic media linear response is characterized by *scalar quantities*:

- Response function $R^{(1)}(\tau)$
- *Susceptibility* $\chi^{(1)}(\omega) = \int d\tau R^{(1)}(\tau) e^{i\omega\tau}$
- *Permittivity* $\varepsilon(\omega) \equiv 1 + 4\pi\chi(\omega)$
- *Extinction coefficient:* $\kappa(\omega) \equiv \text{Im}\sqrt{\varepsilon(\omega)}$
- *Refractive index:* $n(\omega) \equiv \text{Re}\sqrt{\varepsilon(\omega)}$

Absorption spectroscopy monitors $\kappa(\omega) \approx \text{Im}\chi^{(1)}$.