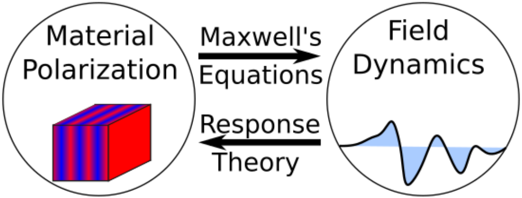
Response Theory

Mike Reppert

October 28, 2022

Previously on CHM676...

In homogeneous dielectric materials, the dynamics of $\boldsymbol{E}$ and $\boldsymbol{B}$ are determined by the polarization density $\boldsymbol{P}$.



Today: How does $\boldsymbol{P}$ respond to the field?

Outline for Today:

1. Physical Guidelines
2. Mathematical Framework
3. Symmetry and Invariance of Response Tensors

Physical Guidelines

Physical Guidelines

We study $\boldsymbol{P}$ as a *functional* of $\boldsymbol{E}$ and $\boldsymbol{B}$:

$$\boldsymbol{P}(\boldsymbol{x}, t) = \boldsymbol{P}[\boldsymbol{E}(\boldsymbol{x}', t'), \boldsymbol{B}(\boldsymbol{x}', t')].$$

Physical Guidelines

We study $\boldsymbol{P}$ as a *functional* of $\boldsymbol{E}$ and $\boldsymbol{B}$:

$$\boldsymbol{P}(\boldsymbol{x}, t) = \boldsymbol{P}[\boldsymbol{E}(\boldsymbol{x}', t'), \boldsymbol{B}(\boldsymbol{x}', t')].$$

Physically, we expect:

- Response to $\boldsymbol{B}$ is negligible

Physical Guidelines

We study $\boldsymbol{P}$ as a *functional* of $\boldsymbol{E}$ and $\boldsymbol{B}$:

$$\boldsymbol{P}(\boldsymbol{x}, t) = \boldsymbol{P}[\boldsymbol{E}(\boldsymbol{x}', t'), \boldsymbol{B}(\boldsymbol{x}', t')].$$

Physically, we expect:

- Response to $\boldsymbol{B}$ is negligible
- Response is *local*: $\boldsymbol{P}(\boldsymbol{x})$ depends only on $\boldsymbol{E}(\boldsymbol{x})$.

Physical Guidelines

We study $\boldsymbol{P}$ as a *functional* of $\boldsymbol{E}$ and $\boldsymbol{B}$:

$$\boldsymbol{P}(\boldsymbol{x}, t) = \boldsymbol{P}[\boldsymbol{E}(\boldsymbol{x}', t'), \boldsymbol{B}(\boldsymbol{x}', t')].$$

Physically, we expect:

- Response to $\boldsymbol{B}$ is negligible
- Response is *local*: $\boldsymbol{P}(\boldsymbol{x})$ depends only on $\boldsymbol{E}(\boldsymbol{x})$.
- Response is *causal*: $\boldsymbol{P}(t)$ depends only on $\boldsymbol{E}(t' \leq t)$.

Physical Guidelines

We study $\boldsymbol{P}$ as a *functional* of $\boldsymbol{E}$ and $\boldsymbol{B}$:

$$\boldsymbol{P}(\boldsymbol{x}, t) = \boldsymbol{P}[\boldsymbol{E}(\boldsymbol{x}', t'), \boldsymbol{B}(\boldsymbol{x}', t')].$$

Physically, we expect:

- Response to $\boldsymbol{B}$ is negligible
- Response is *local*: $\boldsymbol{P}(\boldsymbol{x})$ depends only on $\boldsymbol{E}(\boldsymbol{x})$.
- Response is *causal*: $\boldsymbol{P}(t)$ depends only on $\boldsymbol{E}(t' \leq t)$.
- Response is *stable*:

Physical Guidelines

We study $\boldsymbol{P}$ as a *functional* of $\boldsymbol{E}$ and $\boldsymbol{B}$:

$$\boldsymbol{P}(\boldsymbol{x}, t) = \boldsymbol{P}[\boldsymbol{E}(\boldsymbol{x}', t'), \boldsymbol{B}(\boldsymbol{x}', t')].$$

Physically, we expect:

- Response to $\boldsymbol{B}$ is negligible
- Response is *local*: $\boldsymbol{P}(\boldsymbol{x})$ depends only on $\boldsymbol{E}(\boldsymbol{x})$.
- Response is *causal*: $\boldsymbol{P}(t)$ depends only on $\boldsymbol{E}(t' \leq t)$.
- Response is *stable*:
  - Must exist a time scale δt *below* which $\boldsymbol{P}$ no longer cares about variations in $\boldsymbol{E}(t + \delta t)$

Physical Guidelines

We study $\boldsymbol{P}$ as a *functional* of $\boldsymbol{E}$ and $\boldsymbol{B}$:

$$\boldsymbol{P}(\boldsymbol{x}, t) = \boldsymbol{P}[\boldsymbol{E}(\boldsymbol{x}', t'), \boldsymbol{B}(\boldsymbol{x}', t')].$$

Physically, we expect:

- Response to $\boldsymbol{B}$ is negligible
- Response is *local*: $\boldsymbol{P}(\boldsymbol{x})$ depends only on $\boldsymbol{E}(\boldsymbol{x})$.
- Response is *causal*: $\boldsymbol{P}(t)$ depends only on $\boldsymbol{E}(t' \leq t)$.
- Response is *stable*:
    - Must exist a time scale δt *below* which $\boldsymbol{P}$ no longer cares about variations in $\boldsymbol{E}(t + \delta t)$
    - Must exist a time scale T *beyond* which $\boldsymbol{P}$ doesn't remember $\boldsymbol{E}(t - T)$.

Take-Home Point

Physical constraints:

- locality
- causality
- stability

strongly limit the possible forms for the **mathematical** dependence of P on E.

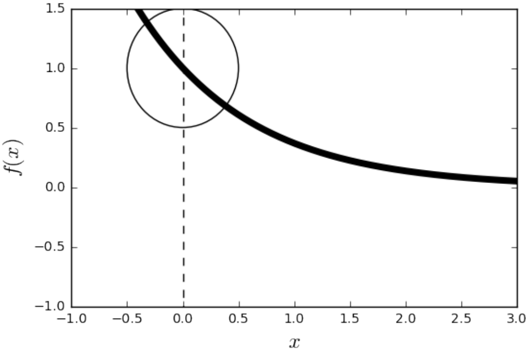
Mathematical Framework

Mathematical Framework

The *response theory* framework is essentially a Taylor series expansion for functionals.

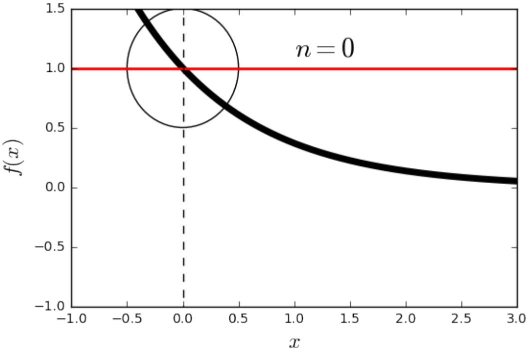
Mathematical Framework

The *response theory* framework is essentially a Taylor series expansion for functionals.



Mathematical Framework

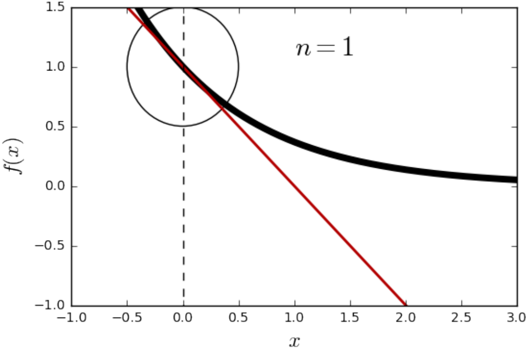
The *response theory* framework is essentially a Taylor series expansion for functionals.



$$f(x) \approx f(0)$$

Mathematical Framework

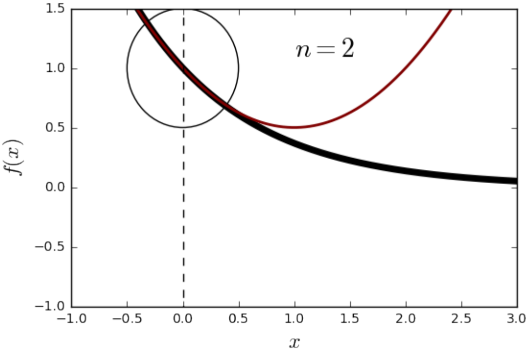
The *response theory* framework is essentially a Taylor series expansion for functionals.



$$f(x) \approx f(0) + \left.\frac{df}{dx}\right|_{x=0} x$$

Mathematical Framework

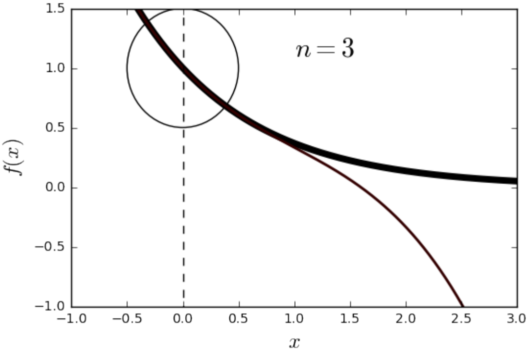
The *response theory* framework is essentially a Taylor series expansion for functionals.



$$f(x) \approx f(0) + \left.\frac{df}{dx}\right|_{x=0} x + \frac{1}{2}\left.\frac{d^2 f}{dx^2}\right|_{x=0} x^2$$

Mathematical Framework

The *response theory* framework is essentially a Taylor series expansion for functionals.



$$f(x) \approx f(0) + \left.\frac{df}{dx}\right|_{x=0} x + \frac{1}{2}\left.\frac{d^2 f}{dx^2}\right|_{x=0} x^2 + \frac{1}{6}\left.\frac{d^3 f}{dx^3}\right|_{x=0} x^3 \ldots$$

Mathematical Framework

The Taylor series of a multi-variable function $g(x_1, ..., x_N)$ looks like:

$$\begin{aligned} g(x_1, ..., x_N) = {} & g(0, ..., 0) \\ & + \frac{\partial g}{\partial x_1}\bigg|_{\boldsymbol{x}=\boldsymbol{0}} x_1 + \frac{\partial g}{\partial x_2}\bigg|_{\boldsymbol{x}=\boldsymbol{0}} x_2 + ... + \frac{\partial g}{\partial x_N}\bigg|_{\boldsymbol{x}=\boldsymbol{0}} x_N \\ & + \frac{1}{2!}\,\frac{\partial^2 g}{\partial x_1^2}\bigg|_{\boldsymbol{x}=\boldsymbol{0}} x_1^2 + \frac{\partial g}{\partial x_1 \partial x_2}\bigg|_{\boldsymbol{v}=\boldsymbol{0}} x_1 x_2 + ... + \frac{1}{2!}\,\frac{\partial^2 g}{\partial x_N^2}\bigg|_{\boldsymbol{x}=\boldsymbol{0}} x_N^2 \\ & + ... \end{aligned}$$

What is the corresponding expansion for a functional like $\boldsymbol{P}[\boldsymbol{E}]$?

Mathematical Framework

Since the response is stable, we can sample $\boldsymbol{E}$ at a finite number of time points:

$$P_I(t) \approx f_I(E_x(t_0), E_y(t_0), E_z(t_0), E_x(t_1), ..., E_z(t_N); t, \delta t, T).$$

Expanding in a Taylor series:

$$\begin{aligned} P_I(t) \approx & f_I(0, ..., 0; t, \delta t, T) \\ & + \left.\frac{\partial f_I}{\partial E_x(t_0)}\right|_{\boldsymbol{E}=\mathbf{0}} E_x(t_0) + ... + \left.\frac{\partial f_I}{\partial E_z(t_N)}\right|_{\boldsymbol{E}=\mathbf{0}} E_z(t_N) \\ & + \frac{1}{2!} \left.\frac{\partial^2 f_I}{\partial [E_x(t_0)]^2}\right|_{\boldsymbol{E}=\mathbf{0}} [E_x(t_0)]^2 + \left.\frac{\partial^2 f_I}{\partial E_x(t_0) \partial E_y(t_0)}\right|_{\boldsymbol{E}=\mathbf{0}} E_x(t_0) E_y(t_0) + ... \end{aligned}$$

Mathematical Framework

As our sampling points get closer together, the sums converge to integrals:

$$\boldsymbol{P}(t) = \sum_{n=0}^{\infty} \sum_{\alpha_1,\ldots,\alpha_n} \int_{-\infty}^{t} dt_n \int_{-\infty}^{t_n} dt_{n-1} \ldots \int_{-\infty}^{t_2} dt_1 \times E_{\alpha_1}(t_1) E_{\alpha_2}(t_2) \ldots E_{\alpha_n}(t_n) \times R^{(n)}_{\alpha_1 \ldots \alpha_n \alpha}(t, t_n, t_{n-1}, \ldots, t_1)$$

where $R^{(n)}_{\alpha_1 \ldots \alpha_n \alpha}(t, t_n, t_{n-1}, \ldots, t_1)$ is the n^{th}-order *response function** – the target of n^{th}-order spectroscopies.

*Almost. Actually $R^{(n)}$ depends only on time *differences*. Stay tuned!

Symmetry and Invariance of Response Tensors

Time-translation Invariance

All systems we study will satisfy **time-translation invariance**: Only time *differences* matter!

$$R^{(n)}_{\alpha_1 \dots \alpha_n \alpha}(t, t_n, t_{n-1}, \dots, t_1) \Rightarrow R^{(n)}_{\alpha_1 \dots \alpha_n \alpha}(t - t_n, t_n - t_{n-1}, \dots, t_2 - t_1)$$

Time-translation Invariance

All systems we study will satisfy **time-translation invariance**: Only time *differences* matter!

$$R^{(n)}_{\alpha_1 \ldots \alpha_n \alpha}(t, t_n, t_{n-1}, \ldots, t_1) \Rightarrow R^{(n)}_{\alpha_1 \ldots \alpha_n \alpha}(t - t_n, t_n - t_{n-1}, \ldots, t_2 - t_1)$$

Rearranging:

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

Time-translation Invariance

All systems we study will satisfy **time-translation invariance**: Only time *differences* matter!

$$R^{(n)}_{\alpha_1 \ldots \alpha_n \alpha}(t, t_n, t_{n-1}, \ldots, t_1) \Rightarrow R^{(n)}_{\alpha_1 \ldots \alpha_n \alpha}(t - t_n, t_n - t_{n-1}, \ldots, t_2 - t_1)$$

Rearranging:

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

Causality dictates that $R^{(n)}_{\alpha_1, \ldots, \alpha_n, \alpha}$ is non-zero only for *positive time delays*.

Spatial Symmetries

Neumann's Principle: Spatial symmetries of the material *must* be reflected in the response tensor.

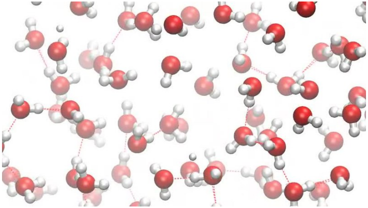
This **dramatically** simplifies the analysis of nonlinear experiments!

Spatial Symmetries

Neumann's Principle: Spatial symmetries of the material *must* be reflected in the response tensor.

This **dramatically** simplifies the analysis of nonlinear experiments!

NB: Only *macroscopic* symmetry is relevant!

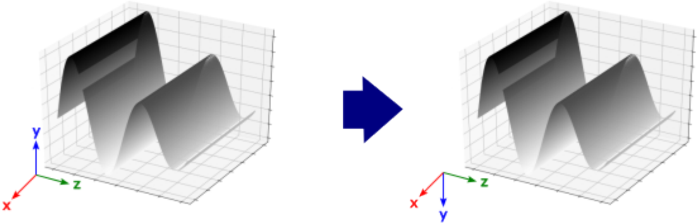


https://commons.wikimedia.org/wiki/File:A_Molecular_Dynamics_Simulation_of_Liquid_Water_at_298_K.webm

Spatial Symmetries

Example: $R_{xy}^{(1)}$ in an isotropic sample

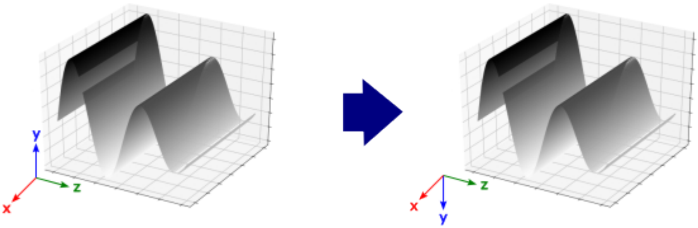
Suppose $\boldsymbol{E}$ is polarized along the y-axis. What happens to $P_x^{(1)}$ when we invert the y-axis?



Spatial Symmetries

Example: $R^{(1)}_{xy}$ in an isotropic sample

Suppose $\boldsymbol{E}$ is polarized along the y-axis. What happens to $P^{(1)}_x$ when we invert the y-axis?



Nothing!

Spatial Symmetries

Under y-axis inversion:

- $y \to -y$
- $E_y \to -E_y$
- $P_x^{(1)} \to P_x^{(1)}$
- $R_{xy} \to R_{xy}$

Spatial Symmetries

Under y-axis inversion:

- $y \rightarrow -y$
- $E_y \rightarrow -E_y$
- $P_x^{(1)} \rightarrow P_x^{(1)}$
- $R_{xy} \rightarrow R_{xy} \Leftarrow$ Neumann's Principle

Spatial Symmetries

Under y-axis inversion:

- $y \to -y$
- $E_y \to -E_y$
- $P_x^{(1)} \to P_x^{(1)}$
- $R_{xy} \to R_{xy} \Leftarrow$ Neumann's Principle

But response theory says:

$$P_x^{(1)}(t) = \int_{-\infty}^{\infty} d\tau_1 R_{xy}^{(1)}(\tau_1) E_y(t-\tau_1) = -P_x^{(1)}(t).$$

Spatial Symmetries

Under y-axis inversion:

- $y \to -y$
- $E_y \to -E_y$
- $P_x^{(1)} \to P_x^{(1)}$
- $R_{xy} \to R_{xy} \Leftarrow$ Neumann's Principle

But response theory says:

$$P_x^{(1)}(t) = \int_{-\infty}^{\infty} d\tau_1 R_{xy}^{(1)}(\tau_1) E_y(t-\tau_1) = -P_x^{(1)}(t).$$

The only possible conclusion is that $R_{xy}^{(1)} = 0$!

Spatial Symmetries

More generally: In isotropic media

- All tensor elements with an odd number *of any index* vanish (e.g., $R^{(3)}_{xxxy} = 0$)

Spatial Symmetries

More generally: In isotropic media

- All tensor elements with an odd number *of any index* vanish (e.g., $R^{(3)}_{xxxy} = 0$)
- Corollary: all even-order response functions vanish(!)

Spatial Symmetries

More generally: In isotropic media

- All tensor elements with an odd number *of any index* vanish (e.g., $R^{(3)}_{xxxy} = 0$)
- Corollary: all even-order response functions vanish(!)
- Response tensor elements are symmetry-related (e.g., $R^{(3)}_{xxyy} = R^{(1)}_{yyxx}$)

Even-Order Spectroscopies

But remember: Not all materials are isotropic

Even-Order Spectroscopies

But remember: Not all materials are isotropic

Even-order spectroscopies are *specifically sensitive* to material boundaries

Even-Order Spectroscopies

But remember: Not all materials are isotropic

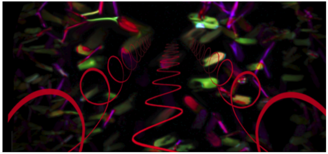
Even-order spectroscopies are *specifically sensitive* to material boundaries
$\Rightarrow$ Imaging!

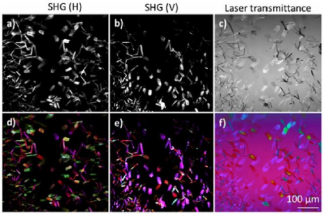
Even-Order Spectroscopies

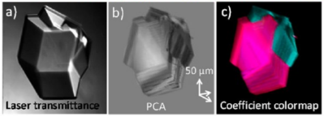
But remember: Not all materials are isotropic

Even-order spectroscopies are *specifically sensitive* to material boundaries
$\Rightarrow$ Imaging!

Garth Simpson







Take-Home Points

Time-translation invariance and **causality** dictate that response functions depend only on *positive time delays* between interactions.

Spatial symmetries in the material must be reflected in the response tensors.

In **isotropic media**:

- Response elements with unpaired axes vanish
- Surviving elements are symmetry-related
- Even-order spectroscopies are forbidden – hence useful for detecting defects