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Optical Spectroscopy in Materials Science

Recommended literature

Kamarás K.: Spektroszkópia és anyagszerkezet. Bevezetés a modern optikába V. kötet, (Műegyetemi Kiadó, 2000.)

D.B. Tanner: Optical Effects in Solids

(Cambridge University Press, Cambridge, 2019.)

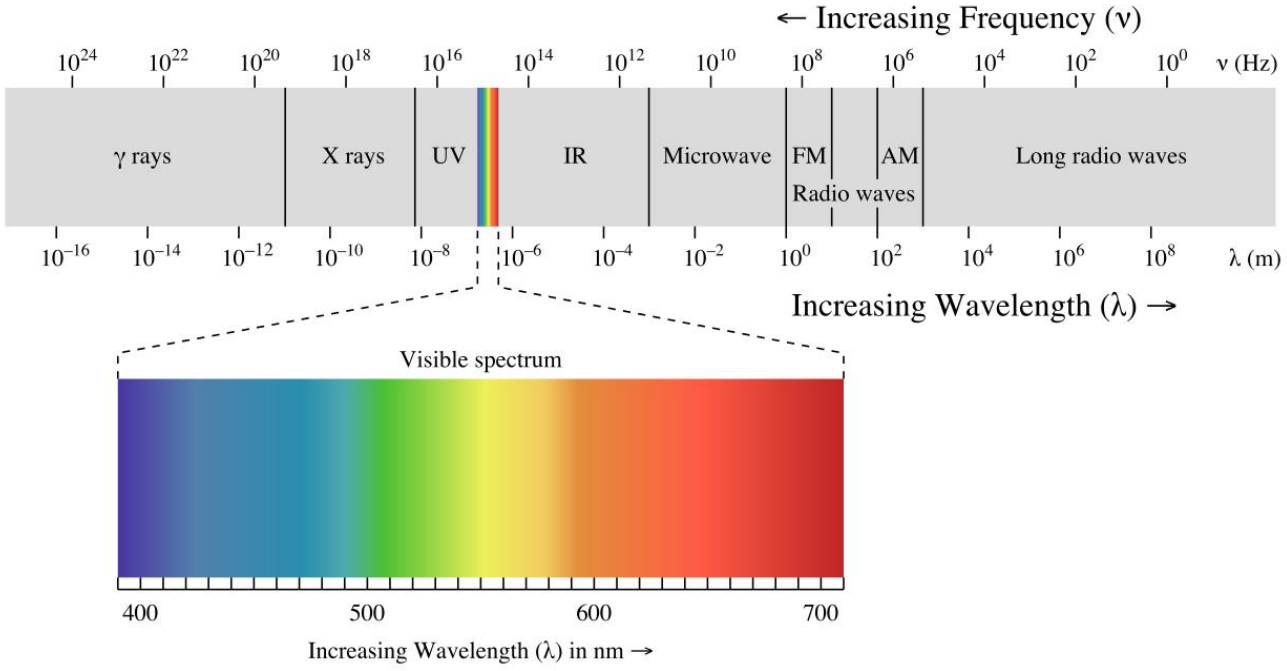
G. Grüner, M. Dressel: Electrodynamics of Solids

(Cambridge University Press, Cambridge, 2003.)

H. Kuzmany: Solid State Spectroscopy, an Introduction

(Springer, Berlin, Heidelberg, 1998.)

Optical spectroscopy: study of light-matter interaction as a function of the frequency of the radiation



Conversion of units: $h\nu = hc \frac{1}{\lambda} = eU = k_B T$ ☠ Wavenumber (hullámszám)

	THz	cm ⁻¹	meV	K
1 THz	1	33.333	4.13	47.96
1 cm ⁻¹	0.03	1	0.124	1.439
1 meV	0.24	8.0655	1	11.6
1 K	0.02086	0.695	0.0862	1

Optical spectroscopy: study of light-matter interaction as a function of the frequency of the radiation

Microscopic model of materials

- Classical equation of motion of charges (magnetic moments): free electron gas, vibrations of molecules
- Quantum mechanics: excitation of electrons in atoms



Linear response theory

Optical response functions

- Refractive index, absorption coefficient, polarizability

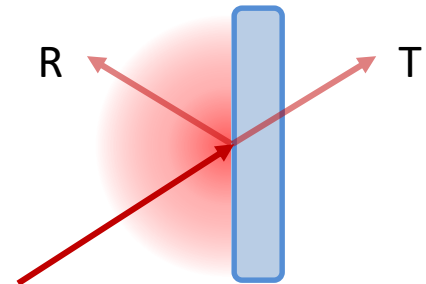


Maxwell's equations

Directly measured quantities

- Reflected, transmitted, scattered intensity

Experimental setups, methods



Electromagnetic wave propagation in vacuum

Maxwell's equations in vacuum:

$$\nabla \cdot \mathbf{E} = \frac{1}{\epsilon_0} \rho$$

$$\nabla \times \mathbf{E} = -\partial_t \mathbf{B}$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{B} = \mu_0 (\mathbf{j} + \epsilon_0 \partial_t \mathbf{E})$$

Wave equations with sources:

$$\nabla \times (\nabla \times \mathbf{E}) = -\partial_t (\nabla \times \mathbf{B})$$

$$\nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = -\mu_0 \partial_t \mathbf{j} - \frac{1}{c^2} \partial_t^2 \mathbf{E}$$

$$\nabla^2 \mathbf{E} - \frac{1}{c^2} \partial_t^2 \mathbf{E} = \nabla \frac{\rho}{\epsilon_0} + \mu_0 \partial_t \mathbf{j}$$

$$\nabla \times (\nabla \times \mathbf{B}) = \mu_0 \nabla \times \mathbf{j} + \frac{1}{c^2} \partial_t (\nabla \times \mathbf{E})$$

$$\nabla^2 \mathbf{B} - \frac{1}{c^2} \partial_t^2 \mathbf{B} = -\mu_0 \nabla \times \mathbf{j}$$

Speed of the wave/light:

$$c = \frac{1}{\sqrt{\epsilon_0 \mu_0}}$$

Electromagnetic wave propagation in vacuum

Plane wave solution in free space:

$$\mathbf{E}(\mathbf{r}, t) = \frac{1}{(2\pi)^4} \int d^3\mathbf{q} d\omega \mathbf{E}(\mathbf{q}, \omega) e^{-i(\omega t - \mathbf{q}\mathbf{r})}$$

$$\mathbf{B}(\mathbf{r}, t) = \frac{1}{(2\pi)^4} \int d^3\mathbf{q} d\omega \mathbf{B}(\mathbf{q}, \omega) e^{-i(\omega t - \mathbf{q}\mathbf{r})}$$

$$q^2 \mathbf{E}(\mathbf{q}, \omega) - \frac{\omega^2}{c^2} \mathbf{E}(\mathbf{q}, \omega) = 0$$

Isotropic dispersion relation:

$$\omega = cq$$

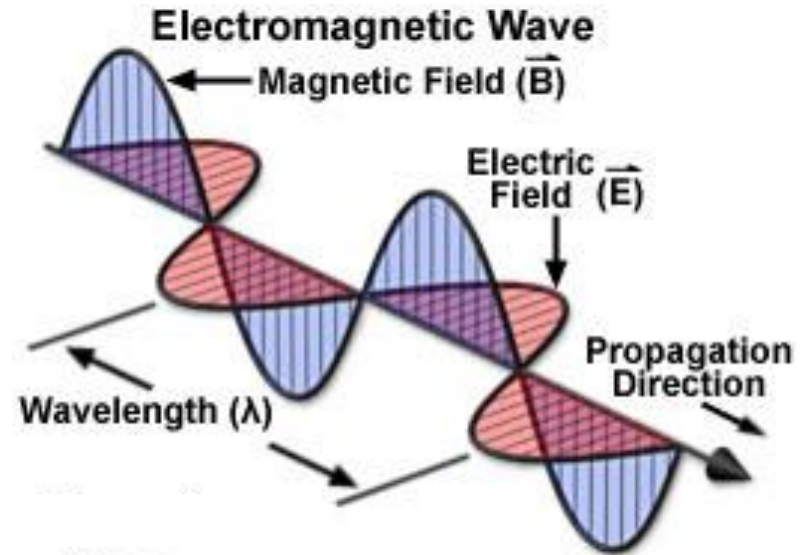
\mathbf{E} , \mathbf{B} and \mathbf{q} are orthogonal to each other:

$$\mathbf{q} \cdot \mathbf{E} = 0$$

$$\mathbf{q} \cdot \mathbf{B} = 0$$

$$\mathbf{q} \times \mathbf{E} = \omega \mathbf{B}$$

$$\mathbf{q} \times \mathbf{B} = -\frac{1}{c^2} \omega \mathbf{E}$$



Characteristic ratio of \mathbf{E} and \mathbf{H} fields:

$$Z_0 = \frac{E}{H} = \sqrt{\frac{\mu_0}{\epsilon_0}} \approx 377\Omega$$

Z_0 vacuum impedance

Energy flux and intensity

From Maxwell's II and IV equations:

$$\mathbf{B} \cdot (\nabla \times \mathbf{E}) = -\frac{1}{2} \partial_t \mathbf{B}^2$$

$$\mathbf{E} \cdot (\nabla \times \mathbf{B}) = \mu_0 \left(\mathbf{E} \cdot \mathbf{j} + \varepsilon_0 \frac{1}{2} \partial_t \mathbf{E}^2 \right)$$

Energy balance:

$$\partial_t \left(\frac{\varepsilon_0 \mathbf{E}^2}{2} + \frac{\mathbf{B}^2}{2\mu_0} \right) = -\nabla \cdot \left(\mathbf{E} \times \frac{\mathbf{B}}{\mu_0} \right) - \mathbf{E} \cdot \mathbf{j}$$

Energy density

Poynting vector

Dissipation by free charges

$$u = \frac{\varepsilon_0 \mathbf{E}^2}{2} + \frac{\mathbf{B}^2}{2\mu_0}$$

$$S = \mathbf{E} \times \frac{\mathbf{B}}{\mu_0} = \mathbf{E} \times \mathbf{H}$$

Time averaged Poynting vector of a plane wave:

$$\langle S \rangle = \langle \mathbf{E} \times \mathbf{H} \rangle = \left\langle \Re e \left(\mathbf{E} e^{-i\omega t} \right) \times \Re e \left(\mathbf{H} e^{-i\omega t} \right) \right\rangle = \left\langle \frac{\mathbf{E} e^{-i\omega t} + \mathbf{E}^* e^{i\omega t}}{2} \right\rangle \times \left\langle \frac{\mathbf{H} e^{-i\omega t} + \mathbf{H}^* e^{i\omega t}}{2} \right\rangle$$

$$\langle S \rangle = \frac{1}{2} \Re e \left(\mathbf{E} \times \mathbf{H}^* \right)$$

$$[S] = \frac{W}{m^2}$$

Magnitude of typical E and B fields in light

5 mW LASER pointer:

collimated beam
with 1 mm² diameter

$$E_{\omega} \sim \sqrt{Z_0 \frac{P}{A}} \sim \sqrt{Z_0 \frac{5mW}{1mm^2}} \sim 1 \frac{kV}{m} \quad B_{\omega} = \frac{E_{\omega}}{c} \sim 10 \mu T$$

focused to a 1 μm² spot

$$E_{\omega} \sim \sqrt{Z_0 \frac{P}{A}} \sim \sqrt{Z_0 \frac{5mW}{1\mu m^2}} \sim 1 \frac{MV}{m} \quad B_{\omega} = \frac{E_{\omega}}{c} \sim 10 mT$$

Linear optics is applicable below $E < 1 MV/m$

Compare these values to static fields:

- dielectric strength of air: 3 MV/m (lightning)
- Earth's magnetic field: 25 .. 65 μT



Magnitude of typical E and B fields in light

Thermal sources:

$$B_\nu d\nu = h\nu \frac{1}{e^{\beta h\nu} - 1} 2 \frac{\nu^2}{c^2} d\nu$$

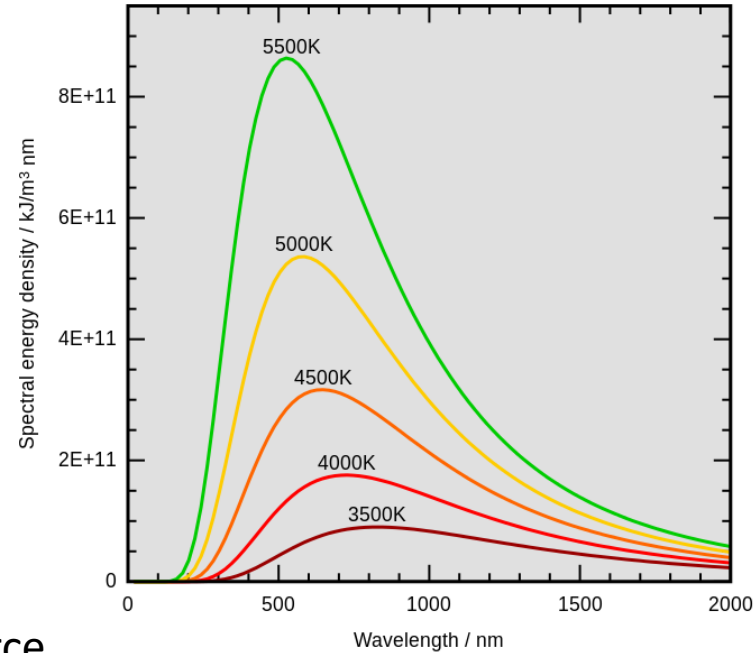
photon energy population photon DOS

Total emitted power per unit area

$$\iint B_\nu d\nu d\Omega = \sigma T^4 \quad \sigma = 5.67 \cdot 10^{-8} \text{ W/m}^2/\text{K}^4$$

Wien's law: $\nu_{\text{max}} \propto T$ high frequencies \rightarrow high T source

Raighly-Jeans (small ν limit): $B_\nu d\nu \approx kT 2 \frac{\nu^2}{c^2} d\nu$ small frequencies \rightarrow high T source



Example: a halogen lamp with $T \sim 3000$ K and area of ~ 1 mm² emits $P \sim 5$ W light over π solid angle

At around 600 nm in a ~ 1 nm broad spectra window the emitted power is ~ 2 mW for this lamp

Maxwell's equations in materials


Maxwell's equations:

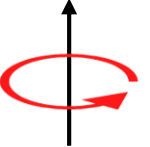
$$\nabla \cdot \mathbf{E} = \frac{1}{\epsilon_0} \rho$$

$$\nabla \times \mathbf{E} = -\partial_t \mathbf{B}$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{B} = \mu_0 (\mathbf{j} + \epsilon_0 \partial_t \mathbf{E})$$

Electric dipole density: $P = \frac{d}{\delta V}$ 

Magnetic dipole density: $M = \frac{m}{\delta V}$ 

Free and bound charges: $\rho = \rho_f + \rho_b = \rho_f - \nabla P$

Free and bound currents: $\mathbf{j} = \mathbf{j}_f + \mathbf{j}_b = \mathbf{j}_f + \partial_t P + \nabla \times M$

Electric displacement: $D = \epsilon_0 E + P$ Magnetic induction: $B = \mu_0 (H + M)$

$$\nabla \cdot \mathbf{D} = \rho_f$$

$$\nabla \times \mathbf{E} = -\partial_t \mathbf{B}$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{H} = \mathbf{j}_f + \partial_t \mathbf{D}$$

Electromagnetic wave propagation in linear materials

Linear response for $\mathbf{P}(\mathbf{E})$ and $\mathbf{M}(\mathbf{H})$:

$$P_{\alpha} = \chi_{\alpha\beta}^{ee} E_{\beta}$$

$$M_{\alpha} = \chi_{\alpha\beta}^{mm} H_{\beta}$$

Further response functions:

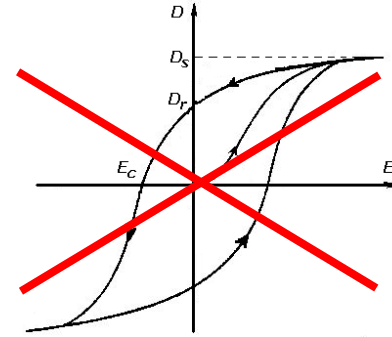
$$D_{\alpha} = \varepsilon_0 \varepsilon_{\alpha\beta} E_{\beta} = \varepsilon_0 (1 + \chi_{\alpha\beta}^{ee}) E_{\beta}$$

$$j_{\alpha} = \sigma_{\alpha\beta} E_{\beta}$$

$$B_{\alpha} = \mu_0 \mu_{\alpha\beta} H_{\beta} = \mu_0 (1 + \chi_{\alpha\beta}^{mm}) H_{\beta}$$

$$iq \cdot (\varepsilon_0 \varepsilon \mathbf{E}) = \rho_f = \frac{1}{\omega} q \cdot (\sigma \mathbf{E})$$

$$iq \cdot \left(\varepsilon \mathbf{E} + i \frac{\sigma \mathbf{E}}{\varepsilon_0 \omega} \right) = 0$$



Charge conservation:

$$\partial_t \rho_f = -\nabla \cdot \mathbf{j}_f$$

$$\omega \rho_f = q \cdot \mathbf{j}_f = q_{\alpha} \sigma_{\alpha\beta} E_{\beta}$$

$$q \times \mathbf{H} = \mathbf{j}_f + \partial_t \mathbf{D} = -i \sigma \mathbf{E} - \omega \varepsilon_0 \varepsilon \mathbf{E}$$

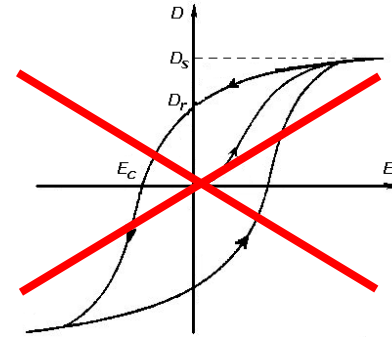
$$q \times \mathbf{H} = \mathbf{j}_f + \partial_t \mathbf{D} = -\varepsilon_0 \omega \left(\varepsilon \mathbf{E} + i \frac{\sigma \mathbf{E}}{\varepsilon_0 \omega} \right)$$

Electromagnetic wave propagation in linear materials

Linear response for $\mathbf{P}(\mathbf{E})$ and $\mathbf{M}(\mathbf{H})$:

$$P_{\alpha} = \chi_{\alpha\beta}^{ee} E_{\beta}$$

$$M_{\alpha} = \chi_{\alpha\beta}^{mm} H_{\beta}$$



Further response functions:

$$D_{\alpha} = \varepsilon_0 \varepsilon_{\alpha\beta} E_{\beta} = \varepsilon_0 (1 + \chi_{\alpha\beta}^{ee}) E_{\beta}$$

$$j_{\alpha} = \sigma_{\alpha\beta} E_{\beta}$$

$$B_{\alpha} = \mu_0 \mu_{\alpha\beta} H_{\beta} = \mu_0 (1 + \chi_{\alpha\beta}^{mm}) H_{\beta}$$

Charge conservation:

$$\partial_t \rho_f = -\nabla \cdot j_f$$

$$\omega \rho_f = q \cdot j_f = q_{\alpha} \sigma_{\alpha\beta} E_{\beta}$$

$$iq \cdot \left(\varepsilon \mathbf{E} + i \frac{\sigma \mathbf{E}}{\varepsilon_0 \omega} \right) = 0$$

$$q \times \mathbf{E} = \omega \mathbf{B}$$

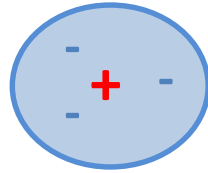
$$q \cdot \mathbf{B} = 0$$

$$q \times \mathbf{H} = j_f + \partial_t \mathbf{D} = -\varepsilon_0 \omega \left(\varepsilon \mathbf{E} + i \frac{\sigma \mathbf{E}}{\varepsilon_0 \omega} \right)$$

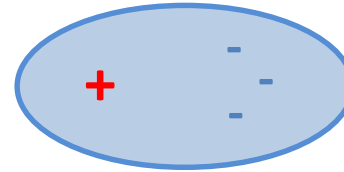
Complex response functions

At finite frequencies charge susceptibility and conductivity appears similarly:

$$\chi_{\alpha\beta}^{ee} = \frac{i\sigma_{\alpha\beta}}{\epsilon_0\omega}$$



t



t+dt

Further response functions:

$$\epsilon_{\alpha\beta} = 1 + \chi_{\alpha\beta}^{ee} = 1 + \frac{i\sigma_{\alpha\beta}}{\epsilon_0\omega}$$

$$\epsilon_0 = 8.85...10^{-8} \text{ s}\Omega^{-1}\text{m}^{-1}$$

Electromagnetic wave propagation in isotropic materials

Isotropic, linear materials: $\epsilon_{\alpha\beta} = \epsilon\delta_{\alpha\beta}$

$$\mathbf{q} \cdot \epsilon_0 \epsilon \mathbf{E} = 0$$

$$\mathbf{q} \times \mathbf{E} = \omega \mu_0 \mu \mathbf{H}$$

$$\mathbf{q} \cdot \mu_0 \mu \mathbf{H} = 0$$

$$\mathbf{q} \times \mathbf{H} = -\omega \epsilon_0 \epsilon \mathbf{E}$$

$$\mathbf{q} \times (\mathbf{q} \times \mathbf{E}) = \omega \mu_0 \mu (\mathbf{q} \times \mathbf{H})$$

$$\mathbf{q} \cdot (\mathbf{q} \cdot \mathbf{E}) - q^2 \mathbf{E} = -\frac{\omega^2}{c^2} \epsilon \mu \mathbf{E}$$

To satisfy Maxwell I, either $\epsilon=0$ (comes latter), or $\mathbf{q} \cdot \mathbf{E}=0$ (transverse solution)

$$q^2 \mathbf{E} = \frac{\omega^2}{c^2} \epsilon \mu \mathbf{E}$$

Isotropic dispersion relation with renormalized speed of light:

$$\omega = \frac{c}{N} q$$

refractive index $N = \sqrt{\epsilon \mu} = n + i\kappa$

Ratio of \mathbf{E} and \mathbf{H} fields:

$$\frac{\mathbf{E}}{\mathbf{H}} = \sqrt{\frac{\mu_0}{\epsilon_0}} \sqrt{\frac{\mu}{\epsilon}} = Z_0 Z$$

Electromagnetic wave propagation in isotropic materials

Isotropic, linear materials: $\epsilon_{\alpha\beta} = \epsilon\delta_{\alpha\beta}$

$$\mathbf{q} \cdot \epsilon_0 \epsilon \mathbf{E} = 0$$

$$\mathbf{q} \times \mathbf{E} = \omega \mu_0 \mu \mathbf{H}$$

$$\mathbf{q} \cdot \mu_0 \mu \mathbf{H} = 0$$

$$\mathbf{q} \times \mathbf{H} = -\omega \epsilon_0 \epsilon \mathbf{E}$$

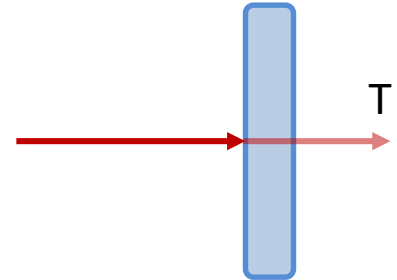
$$\mathbf{q} \times (\mathbf{q} \times \mathbf{E}) = \omega \mu_0 \mu (\mathbf{q} \times \mathbf{H})$$

$$\mathbf{q} \cdot (\mathbf{q} \cdot \mathbf{E}) - q^2 \mathbf{E} = -\frac{\omega^2}{c^2} \epsilon \mu \mathbf{E}$$

Propagation along the z direction

$$\mathbf{E} = E_0 e^{-i(\omega t - qz)} = E_0 e^{i\frac{n\omega}{c}z} e^{-i\omega t} = E_0 e^{i\frac{n\omega}{c}z} e^{-\frac{\kappa\omega}{c}z} e^{-i\omega t}$$

phase shift attenuation



Intensity

$$I(z) = \langle S \rangle = \langle \Re e(\mathbf{E}) \times \Re e(\mathbf{H}) \rangle = \frac{1}{2} \frac{|E_0|^2}{Z_0 Z^*} e^{-\frac{2\kappa\omega}{c}z} = I(0) e^{-\frac{2\kappa\omega}{c}z}$$

Comparing with the Beer-Lambert law

$$\alpha = \frac{2\omega\kappa}{c}$$

Electromagnetic wave propagation in isotropic materials

Isotropic, linear materials: $\epsilon_{\alpha\beta} = \epsilon\delta_{\alpha\beta}$

$$\mathbf{q} \cdot \epsilon_0 \epsilon \mathbf{E} = 0$$

$$\mathbf{q} \times \mathbf{E} = \omega \mu_0 \mu \mathbf{H}$$

$$\mathbf{q} \cdot \mu_0 \mu \mathbf{H} = 0$$

$$\mathbf{q} \times \mathbf{H} = -\omega \epsilon_0 \epsilon \mathbf{E}$$

$$\mathbf{q} \times (\mathbf{q} \times \mathbf{E}) = \omega \mu_0 \mu (\mathbf{q} \times \mathbf{H})$$

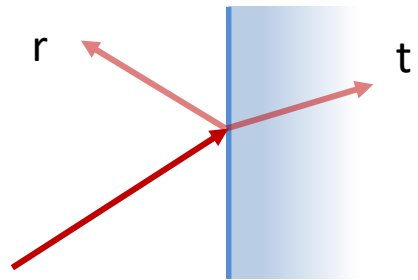
$$\mathbf{q} \cdot (\mathbf{q} \cdot \mathbf{E}) - q^2 \mathbf{E} = -\frac{\omega^2}{c^2} \epsilon \mu \mathbf{E}$$

(Near) normal incidence reflection from semi-infinite sample:

match fields at the boundary

$$E_i + E_r = E_t$$

$$H_i - H_r = H_t \rightarrow \frac{E_i}{Z_0} - \frac{E_r}{Z_0} = \frac{E_t}{Z_0 Z}$$



$$r = \frac{E_r}{E_i} = \frac{Z - 1}{Z + 1} \approx \frac{1 - N}{1 + N}$$

$$R = \frac{I_r}{I_i} = \left| \frac{E_r}{E_i} \right|^2 = \left| \frac{Z - 1}{Z + 1} \right|^2$$

$$R \approx \left| \frac{1 - N}{1 + N} \right|^2$$

(far from spin resonances)

Electromagnetic wave propagation in isotropic materials

Isotropic, linear materials: $\epsilon_{\alpha\beta} = \epsilon\delta_{\alpha\beta}$

$$\mathbf{q} \cdot \epsilon_0 \epsilon \mathbf{E} = 0$$

$$\mathbf{q} \times \mathbf{E} = \omega \mu_0 \mu \mathbf{H}$$

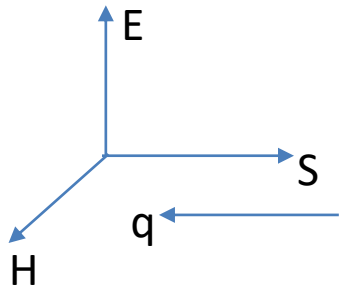
$$\mathbf{q} \cdot \mu_0 \mu \mathbf{H} = 0$$

$$\mathbf{q} \times \mathbf{H} = -\omega \epsilon_0 \epsilon \mathbf{E}$$

$$\mathbf{q} \times (\mathbf{q} \times \mathbf{E}) = \omega \mu_0 \mu (\mathbf{q} \times \mathbf{H})$$

$$\mathbf{q} \cdot (\mathbf{q} \cdot \mathbf{E}) - q^2 \mathbf{E} = -\frac{\omega^2}{c^2} \epsilon \mu \mathbf{E}$$

Both ϵ and μ are negative (for simplicity real as well)

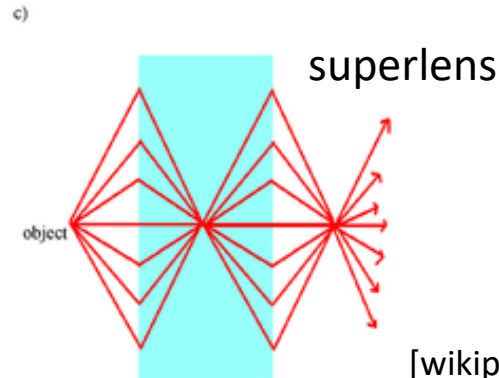
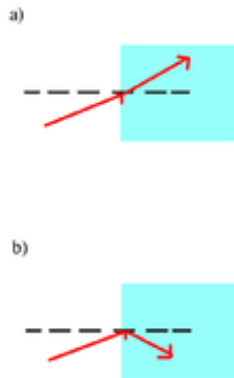


$$\mathbf{S} = \mathbf{E} \times \mathbf{H}$$

Refractive index is negative!

$$\mathbf{E} = E_0 e^{-i(\omega t - qz)} = E_0 e^{i \frac{n\omega}{c} z} e^{-i\omega t} \quad n = -\sqrt{\epsilon \mu}$$

Snell's law in (a) ordinary and (b) negativ index or left-handed materials:



[wikipedia]

Complex response functions

Summary of response functions:

$$\epsilon_{\alpha\beta} = 1 + \chi_{\alpha\beta}^{ee} = 1 + \frac{i\sigma_{\alpha\beta}}{\epsilon_0\omega}$$

$$\mu_{\alpha\beta} = 1 + \chi_{\alpha\beta}^{mm} \approx 1$$

$$N = \sqrt{\epsilon\mu} \approx \sqrt{\epsilon}$$

$$\alpha = \frac{2\omega\kappa}{c}$$

(far from spin resonances)

(isotropic materials)

General linear response function:

$$\langle A(r, t) \rangle = \int dr' dt' \chi(r, r', t, t') B(r', t')$$

Homogenous in material and time-independent:

$$\langle A(r, t) \rangle = \int dr' dt' \chi(r - r', t - t') B(r', t')$$

Fourier space

$$\langle A(q, \omega) \rangle = \chi(q, \omega) B(q, \omega)$$

Long-wavelength limit ($a \ll \lambda$), $q=0$

$$\langle A(\omega) \rangle = \chi(\omega) B(\omega)$$

Complex response functions

If $\chi(t)$ is real then $\chi(\omega) = \chi(-\omega)^*$

$$\chi(t) = \chi(t)^*$$

$$\chi(t) = \int \chi(\omega) e^{-i\omega t} \frac{d\omega}{2\pi}$$

$$\chi(t)^* = \int \chi(\omega)^* e^{i\omega t} \frac{d\omega}{2\pi} = \int \chi(-\omega)^* e^{-i\omega t} \frac{d\omega}{2\pi}$$

$$\chi = \chi' + i\chi''$$

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

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

If a response is causal $\chi(\omega)'$ and $\chi(\omega)''$ are connected by the Kramers-Kronig relation

$$\chi(t) = p(t) + q(t)$$

$$p(t) = p(-t)$$

$$q(t) = -q(-t)$$

$$\chi(\omega) = \int \chi(t) e^{i\omega t} dt = \underbrace{\int p(t) e^{i\omega t} dt}_{\chi'(\omega)} + \underbrace{\int q(t) e^{i\omega t} dt}_{\chi''(\omega)}$$

Causality: $\chi(t) = 0$ if $t < 0$, thus $p(t) = \text{sgn}(t)q(t)$

$$F[p(t)] = F[\text{sgn}(t)q(t)]$$

$$F[p(t)] = F[\text{sgn}(t)]^* F[q(t)]$$

Complex response functions

If $\chi(t)$ is real then $\chi(\omega) = \chi(-\omega)^*$

$$\begin{aligned} \chi(t) &= \chi(t)^* & \chi &= \chi' + i\chi'' \\ \chi(t) &= \int \chi(\omega) e^{-i\omega t} \frac{d\omega}{2\pi} & \longrightarrow & \chi'(\omega) = \chi'(-\omega) \\ \chi(t)^* &= \int \chi(\omega)^* e^{i\omega t} \frac{d\omega}{2\pi} = \int \chi(-\omega)^* e^{-i\omega t} \frac{d\omega}{2\pi} & \chi''(\omega) &= -\chi''(-\omega) \end{aligned}$$

If a response is causal $\chi(\omega)'$ and $\chi(\omega)''$ are connected by the Kramers-Kronig relation

$$F[\text{sgn}(t)] = \frac{2i}{\omega}$$

$$\chi'(\omega) = \frac{1}{\pi} \wp \int \frac{\chi''(\omega')}{\omega' - \omega} d\omega'$$

$$\chi''(\omega) = -\frac{1}{\pi} \wp \int \frac{\chi'(\omega')}{\omega' - \omega} d\omega'$$

Kramers-Kronig transformation

Often only positive frequencies are known (absorption is measured)

$$\chi'(\omega) = \frac{1}{\pi} \wp \int \frac{\omega'+\omega}{\omega'+\omega} \frac{\chi''(\omega')}{\omega'-\omega} d\omega' = \frac{1}{\pi} \wp \int \frac{\omega'}{\omega'^2-\omega^2} \chi''(\omega') d\omega' + \frac{1}{\pi} \wp \int \frac{\omega}{\omega'^2-\omega^2} \chi''(\omega') d\omega'$$

even in ω'
odd in ω'

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

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

For numerical evaluation we should remove divergences by adding $\int_0^\infty \frac{\omega \chi''(\omega)}{\omega'^2 - \omega^2} d\omega' = 0$

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

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

Kramers-Kronig transformation

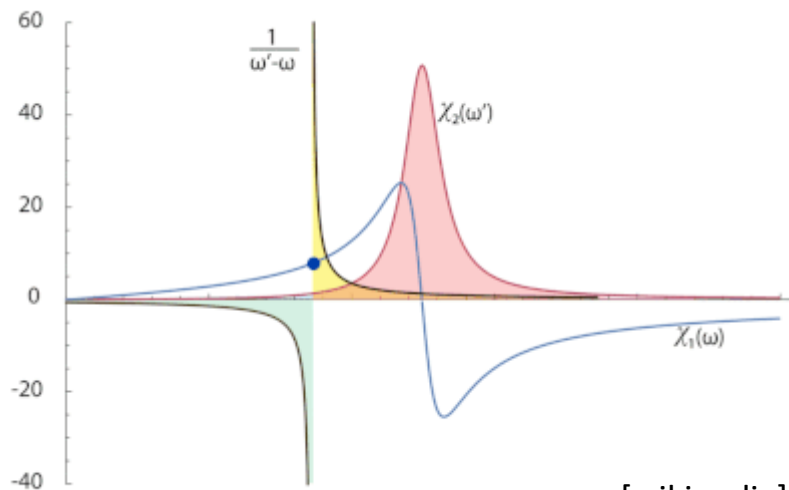
Titchmarsh theorem:

The following statements are equivalent

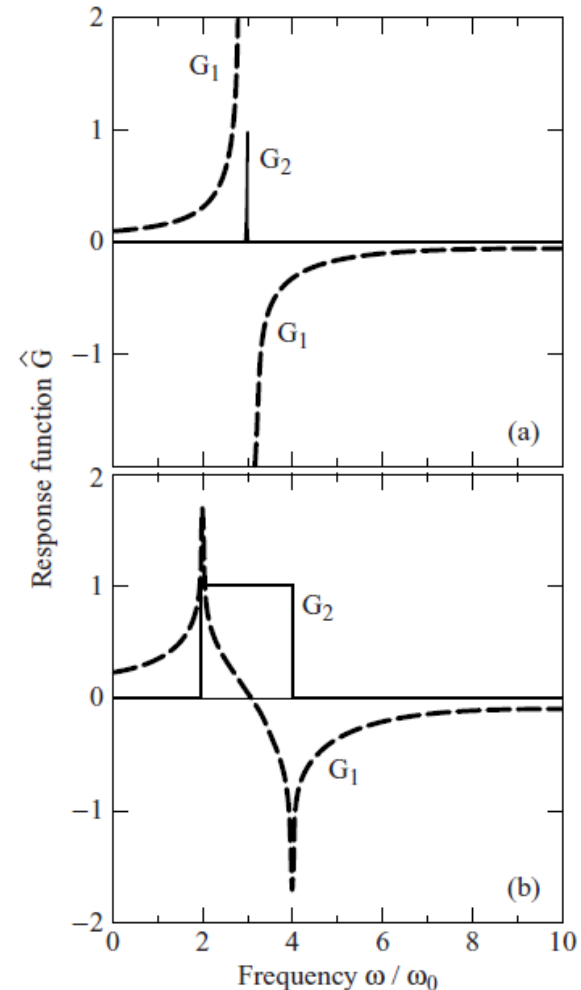
- The real and imaginary part of $\chi(\omega)$ are related by Kramers-Kronig transformation
- $\chi(\omega)$ is causal ($\chi(t)=0$ if $t<0$)
- $\chi(\omega)$ is analytic in the complex upper half-plane

$$\chi'(\omega) = \frac{1}{\pi} \wp \int \frac{\chi''(\omega')}{\omega' - \omega} d\omega'$$

$$\chi''(\omega) = -\frac{1}{\pi} \wp \int \frac{\chi'(\omega')}{\omega' - \omega} d\omega'$$



[wikipedia]



[Grüner&Dressel]

Kramers-Kronig transformation: applications

No strong static response without high-frequency losses:

$$\chi'(0) = \frac{2}{\pi} \wp \int_0^{\infty} \frac{\chi''(\omega')}{\omega'} d\omega'$$

Restore phase, ϕ in the measurement of normal incidence reflectivity:

$$E_r = rE_i$$

$$R = \rho^2$$

$$r = \rho e^{i\phi}$$

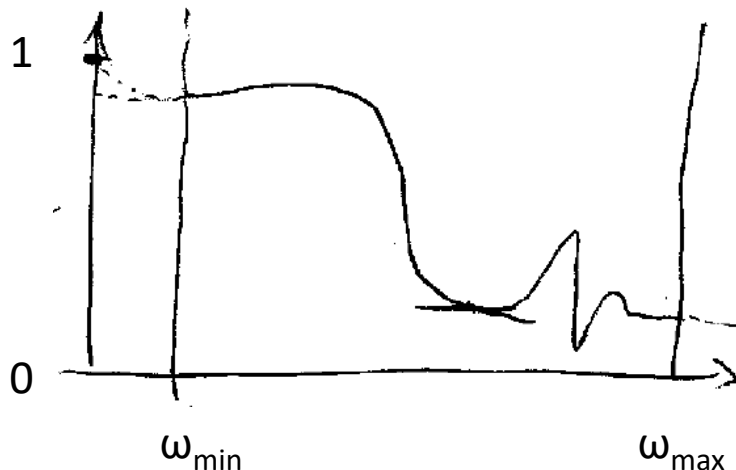
$$\ln(r) = \frac{\ln(R)}{2} + i\phi$$

$$\phi(\omega) = -\frac{\omega}{\pi} \wp \int_0^{\infty} \frac{\ln(R(\omega'))}{\omega'^2 - \omega^2} d\omega'$$

$$\ln(r) = \ln(\rho) + i\phi$$

Then the complex refractive index can be deduced

$$r = \frac{1-N}{1+N} \quad N = \frac{1 - \sqrt{Re}^{i\phi}}{1 + \sqrt{Re}^{i\phi}}$$



Cook book for practical Kramers-Kronig:

- Reflectivity should be measured in a broad frequency range
- Join spectra in the different ranges
- Extrapolate below ω_{\min} and above ω_{\max} using plausible models

