Selected Topics in Advanced Optics

Week 3 – part 1

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Module 2: Material properties and optical constants

- B.E.A. Saleh & M.C. Teich, Fundamental of photonics 2^{nd} Ed. (Wiley, Hoboken, 2007), Chapters 5 & 6.
- C.F. Bohren & D.R. Huffman, Absorption and scattering of light by small particles (Wiley, New York, 1983).
- Optical Society of America, Handbook of optics,2^{nd} Ed. (Mc Grawn Hill, New York, 1995), Vol. II, Chapter 33.

Maxwell's equations without sources

- This is the form generally used in optics

$$\boxed{\begin{aligned} &\nabla \times \mathbf{E}(\mathbf{r},t) = -\frac{\partial \mathbf{B}(\mathbf{r},t)}{\partial t} && \nabla \cdot \mathbf{D}(\mathbf{r},t) = 0 \\ &\nabla \times \mathbf{H}(\mathbf{r},t) = \frac{\partial \mathbf{D}(\mathbf{r},t)}{\partial t} && \nabla \cdot \mathbf{B}(\mathbf{r},t) = 0 \end{aligned}}$$

- The electric and magnetic properties of the medium are described by the constitutive relations:

$$\boxed{\mathbf{D} = \varepsilon_{\mathbf{0}}\mathbf{E} + \mathbf{P} = \varepsilon_0\mathbf{E} + \varepsilon_0\chi\mathbf{E} = \varepsilon_0(1+\chi)\mathbf{E} = \varepsilon_{\mathbf{0}}\varepsilon_r\mathbf{E}}$$

$$\mathbf{B} = \mu_0\mathbf{H} + \mu_0\mathbf{M} = \mu_0\mu_r\mathbf{H}$$

$\mathbf{P}$: polarization density

$\mathbf{M}$: magnetization density

- $\mathbf{P}$ and $\mathbf{M}$ depend on the applied fields $\mathbf{E}$ and $\mathbf{H}$. This dependence describes the response of the medium
- Although the matter is neutral, it does not mean that charges cannot respond to the applied fields !

Classical theories of optical constants

- Two sets of quantities are used to describe the optical properties: the complex refractive index $N = \tilde{n} = n + jk$
  and the complex dielectric function (or relative permittivity) $\varepsilon_r = \varepsilon' + j\varepsilon''$
- We assume non-magnetic materials $(\mu_r = 1)$
- Both quantities are related:

$$\boxed{\begin{aligned} \varepsilon' &= n^2 - k^2 \\ \varepsilon'' &= 2nk \end{aligned}}$$

$$\boxed{\begin{aligned} n &= \sqrt{\frac{\sqrt{\varepsilon'^2 + \varepsilon''^2} + \varepsilon'}{2}} \\ k &= \sqrt{\frac{\sqrt{\varepsilon'^2 + \varepsilon''^2} - \varepsilon'}{2}} \end{aligned}}$$

Selected Topics in Advanced Optics

Week 3 – part 2

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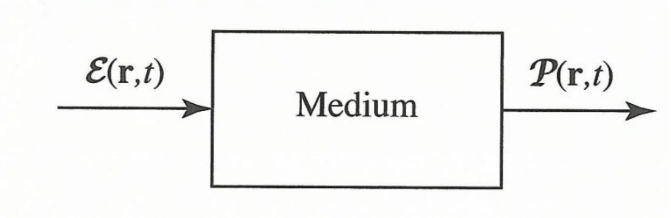
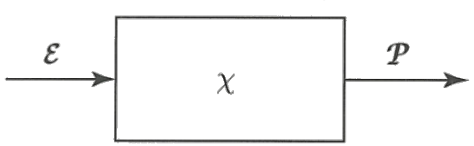
Electromagnetic waves in dielectric media

- Most phenomena relevant to optics concern dielectric materials (i.e. magnetic effects can be neglected)
- In response to an applied electric field $\mathbf{E}$, a dielectric medium creates a polarization density $\mathbf{P}$:



- This response characterizes the medium:
  - Linear (linear relation between $\mathbf{E}$ and $\mathbf{P}$)
  - Nondispersive: instantaneous response
  - Homogeneous: relation between $\mathbf{E}$ and $\mathbf{P}$ independent of the position
  - Isotropic: relation between $\mathbf{E}$ and $\mathbf{P}$ independent of the direction of $\mathbf{E}$, the vectors $\mathbf{E}$ and $\mathbf{P}$ must be parallel
  - Spatially nondispersive: the relation between $\mathbf{E}$ and $\mathbf{P}$ is local; i.e. $\mathbf{P}$ is only influenced by $\mathbf{E}$ at the same point (optically active materials are spatially dispersive).

Linear, nondispersive, homogeneous, isotropic media



- $\mathbf{P}$ and $\mathbf{E}$ are parallel and proportional:

$$\mathbf{P}(\mathbf{r},t) = \varepsilon_0 \chi \mathbf{E}(\mathbf{r},t) \qquad \chi: \text{electric susceptibility}$$

- Maxwell's equations become:

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

$$\boxed{\begin{aligned} \nabla \times \mathbf{E}(\mathbf{r},t) &= -\mu \frac{\partial \mathbf{H}(\mathbf{r},t)}{\partial t} & \qquad \nabla \cdot \mathbf{E}(\mathbf{r},t) &= 0 \\ \nabla \times \mathbf{H}(\mathbf{r},t) &= \varepsilon \frac{\partial \mathbf{E}(\mathbf{r},t)}{\partial t} & \qquad \nabla \cdot \mathbf{H}(\mathbf{r},t) &= 0 \end{aligned}}$$

$$\varepsilon = \varepsilon_0 \varepsilon_r$$

$$\mu = \mu_0 \mu_r$$

- Wave equation for each field component:

$$\nabla^2 u - \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2} = 0 \qquad \text{with } c = \frac{1}{\sqrt{\varepsilon\mu}} \qquad \text{and} \qquad \boxed{n = \frac{c_0}{c} = \sqrt{\frac{\varepsilon\mu}{\varepsilon_0 \mu_0}}}$$

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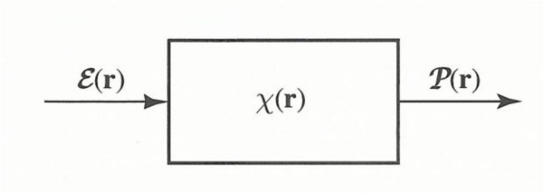
Inhomogeneous media



- Inhomogeneous wave equations:

$$\boxed{\begin{aligned}&\frac{\varepsilon_0}{\varepsilon(\mathbf{r})}\nabla\times\left(\nabla\times\mathbf{E}(\mathbf{r},t)\right)=-\frac{1}{c_0^2}\frac{\partial^2\mathbf{E}(\mathbf{r},t)}{\partial t^2}\\&\nabla\times\left(\frac{\varepsilon_0}{\varepsilon(\mathbf{r})}\nabla\times\mathbf{H}(\mathbf{r},t)\right)=-\frac{1}{c_0^2}\frac{\partial^2\mathbf{H}(\mathbf{r},t)}{\partial t^2}\end{aligned}}$$

- Often the equation for the electric field is written:

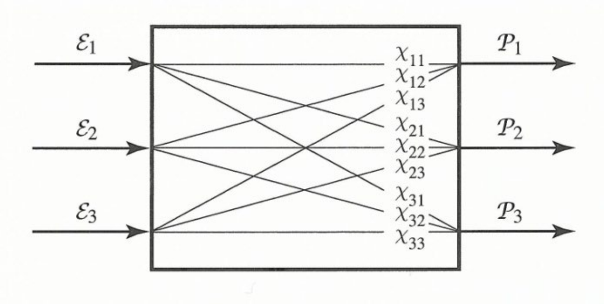
$$\nabla^2\mathbf{E}(\mathbf{r},t)+\nabla\left(\frac{1}{\varepsilon(\mathbf{r})}\nabla\varepsilon(\mathbf{r})\cdot\mathbf{E}(\mathbf{r},t)\right)-\mu_0\varepsilon(\mathbf{r})\frac{\partial^2\mathbf{E}(\mathbf{r},t)}{\partial t^2}=0$$

- For a medium varying slowly in space:

$$\nabla^2\mathbf{E}(\mathbf{r},t)-\mu_0\varepsilon(\mathbf{r})\frac{\partial^2\mathbf{E}(\mathbf{r},t)}{\partial t^2}\simeq 0$$

Anisotropic media

- Tensorial susceptibility and permittivity:



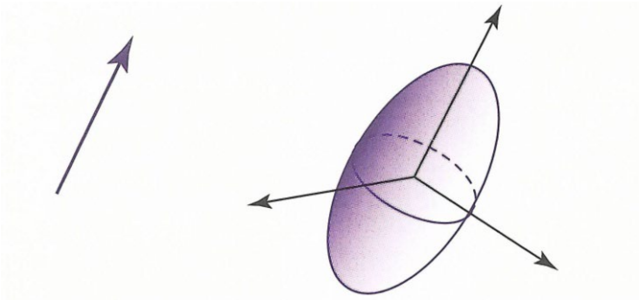
$$P_i = \sum_j \varepsilon_0 \chi_{ij} E_j \qquad D_i = \sum_j \varepsilon_{ij} E_j$$

$$\begin{pmatrix} D_x \\ D_y \\ D_z \end{pmatrix} = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{pmatrix} \cdot \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

- $\mathbf{E}$ and $\mathbf{D}$ are not parallel !
- Most crystals (including semiconductors) are anisotropic

Anisotropic media – Refractive indices

- Permittivity tensor $$D_i = \sum_j \varepsilon_{ij} E_j$$
- Can be represented by an ellipsoid (because it is a symmetric tensor of second rank)



$$\sum_{ij} \varepsilon_{ij} x_i x_j = 1$$ quadratic representation

$$\varepsilon_1 x_1^2 + \varepsilon_2 x_2^2 + \varepsilon_3 x_3^2 = 1$$ in the principal coordinate system

(ε_{ij} is diagonal)

$$D_1 = \varepsilon_{11} E_1 = \varepsilon_1 E_1 \quad D_2 = \varepsilon_{22} E_2 = \varepsilon_2 E_2 \quad D_3 = \varepsilon_{33} E_3 = \varepsilon_3 E_3$$

$$n_1 = \sqrt{\varepsilon_1 / \varepsilon_0} \qquad n_2 = \sqrt{\varepsilon_2 / \varepsilon_0} \qquad n_3 = \sqrt{\varepsilon_3 / \varepsilon_0}$$

principal refractive indexes

Anisotropic media – Refractive indices

- Biaxial crystal: $n_1 \neq n_2 \neq n_3$
- Uniaxial crystal: $n_1 = n_2 \neq n_3$

$n_1 = n_2 = n_o$ ordinary index

$n_3 = n_e$ extraordinary index

positive uniaxial : $n_e > n_o$

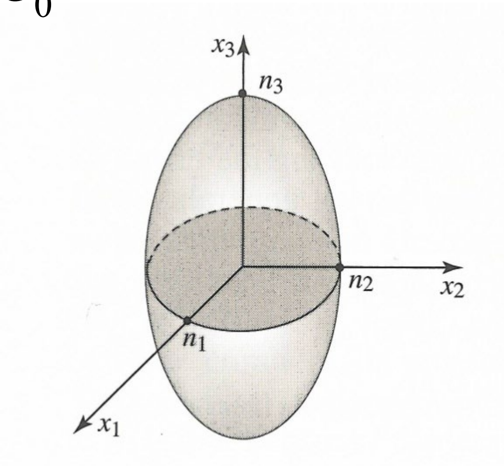
negative uniaxial : $n_e < n_o$

z - axis (n_o for propagation along z) = optical axis

- Isotropic crystal: $n_1 = n_2 = n_3$
- Impermeability tensor: $\mathbf{E} = \boldsymbol{\varepsilon}^{-1} \cdot \mathbf{D} = \frac{1}{\varepsilon_0} \boldsymbol{\eta} \cdot \mathbf{D}$
- Index ellipsoid:

$$\sum_{ij} \eta_{ij} x_i x_j = 1$$

$$\boxed{\frac{x_1^2}{n_1^2} + \frac{x_2^2}{n_2^2} + \frac{x_3^2}{n_3^2} = 1}$$



ellipsoid of revolution for a uniaxial crystal

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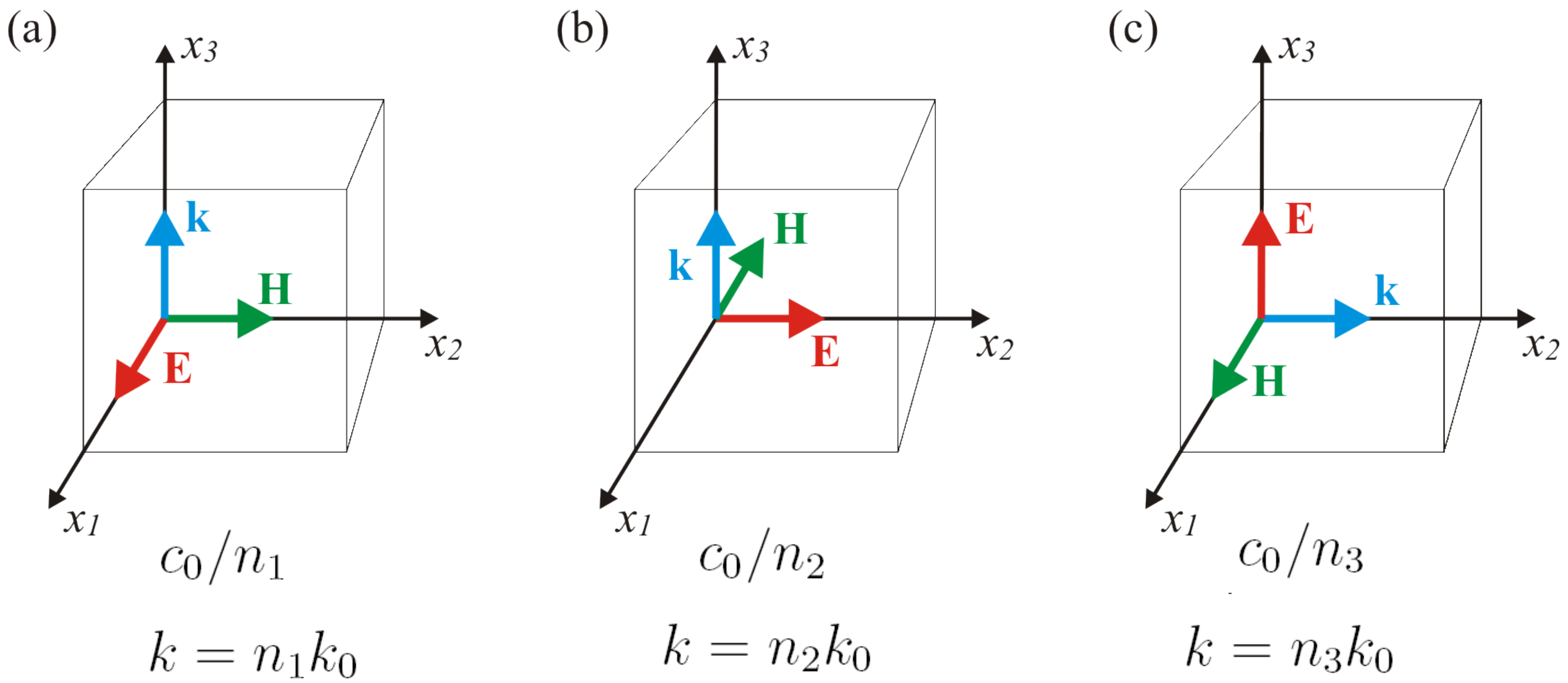
Anisotropic media – Propagation/polarization along the principal axes

- Linear polarized plane wave traveling along one of the principal axes (x, y, z) and polarized parallel to another principal axis:



- The polarization direction of the electric field determines the phase velocity
- These 3 waves keep their velocities and polarizations:
  normal modes of the crystal

Nonlinear media

- The relation between $\mathbf{P}$ and $\mathbf{E}$ is nonlinear.
- The superposition principle is not valid anymore !
- For a nonlinear, but homogeneous isotropic medium, one can derive the following wave equation:

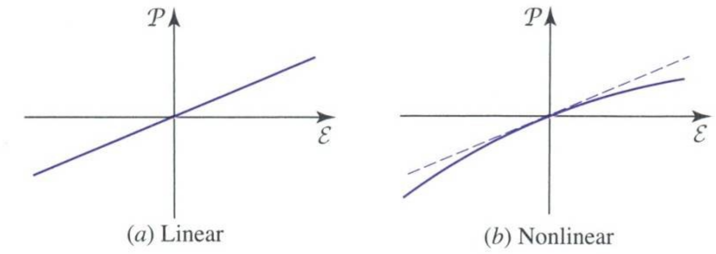
$$\nabla^2 \mathbf{E}(\mathbf{r},t) - \frac{1}{c_0^2}\frac{\partial^2 \mathbf{E}(\mathbf{r},t)}{\partial t^2} = \mu_0 \frac{\partial^2 \mathbf{P}(\mathbf{r},t)}{\partial t^2}$$

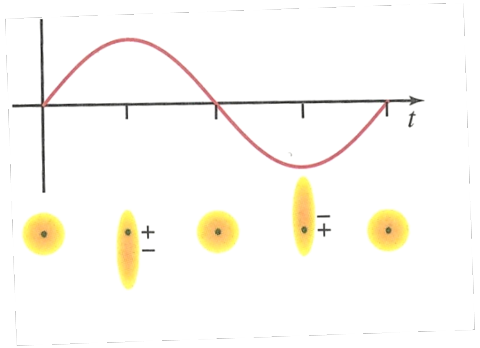
- For nondispersive, nonmagnetic media, the polarization density can be written as a nonlinear function of $\mathbf{E}$; for example:

$$\mathbf{P} = \boldsymbol{\psi}(\mathbf{E}) = a_1 \mathbf{E} + a_2 \mathbf{E}^2$$

$$\nabla^2 \mathbf{E}(\mathbf{r},t) - \frac{1}{c_0^2}\frac{\partial^2 \mathbf{E}(\mathbf{r},t)}{\partial t^2} = \mu_0 \frac{\partial^2 \boldsymbol{\psi}(\mathbf{E})}{\partial t^2}$$

Nonlinear media





- A nonlinear medium is characterized by a nonlinear relation between $\mathbf{P}$ and $\mathbf{E}$
- The relation between $\mathbf{P}$ and $\mathbf{E}$ is linear when the field $\mathbf{E}$ is small, but becomes nonlinear when $\mathbf{E}$ becomes comparable with the interatomic electric field ($\mathbf{E} \sim 10^5 - 10^8$ V/m)
- Macroscopic description: $\mathbf{P}=N\mathbf{p}$ ($\mathbf{p}$: individual dipole moment induced by the applied field); either N or $\mathbf{p}$ can be nonlinear

$$\boxed{P = \varepsilon_0 \left(\chi E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \right)}$$

- In principle the higher order susceptibilities are tensors!

Selected Topics in Advanced Optics

Week 3 – part 3

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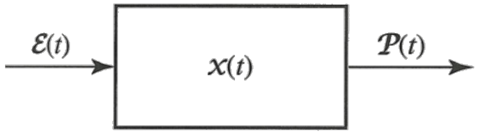
Dispersive media



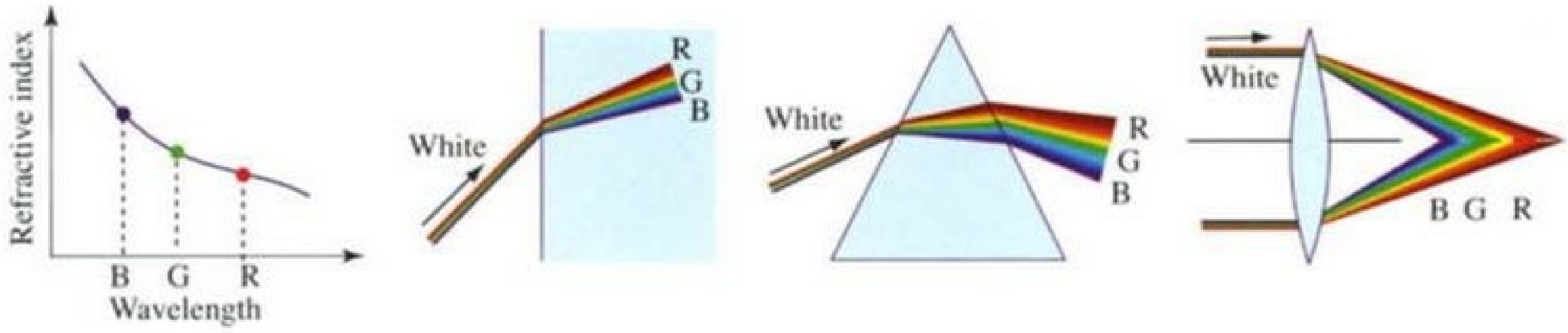
- The relation between $\mathbf{P}$ and $\mathbf{E}$ is not instantaneous, it is dynamic and depends on the history of the system. The polarization density can be expressed as a convolution:

$$\mathbf{P}(t) = \varepsilon_0 \int_{-\infty}^{+\infty} \chi(t - t')\mathbf{E}(t')\,dt'$$

- The function $\varepsilon_0 \chi(t)$ represents the impulse response function of the system.
- Alternatively, one can go to Fourier space and look at the transfer function of the system: $\varepsilon_0 \chi(\nu)$.
- A dispersive medium has a frequency - dependent susceptibility.
- Every material is dispersive!

Dispersive media

- Waves of different wavelengths are refracted differently:



- The frequency-dependent speed of light produces different time delays for the different spectral components (e.g. low frequency components travel faster than high frequency ones):

Kramers-Kronig relations

- Absorption and dispersion are related
- A material with a frequency-dependent refractive index must be absorptive (and conversely)… every material is dispersive!
- Kramers-Kronig relate the real and imaginary parts of the susceptibility:

$$\chi(\nu) = \chi'(\nu) + j\chi''(\nu)$$

$$\boxed{\begin{aligned} \chi'(\nu) &= \frac{2}{\pi}\int_0^\infty \frac{s\chi''(s)}{s^2 - \nu^2}\,ds \\ \chi''(\nu) &= \frac{2}{\pi}\int_0^\infty \frac{\nu\chi'(s)}{\nu^2 - s^2}\,ds \end{aligned}}$$

- Hilbert transform pair: $\chi'(\nu)$ and $\chi''(\nu)$ are analytic in the upper complex plane (related to causality)
- The real part can be computed from the imaginary one and vice-versa

Absorption

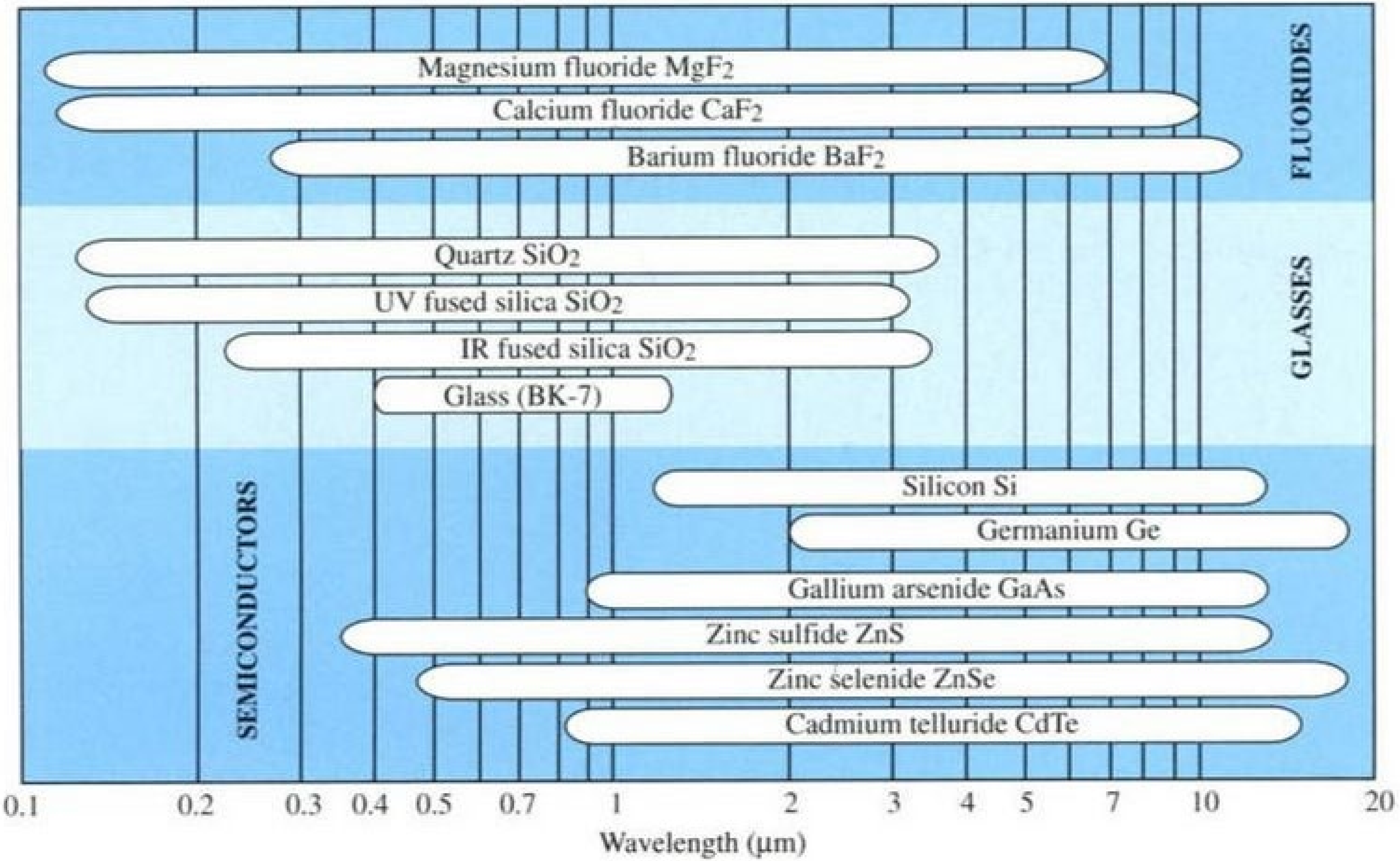
- Complex dielectric susceptibility: $\chi = \chi' + j\chi''$
- Complex permittivity: $\varepsilon = \varepsilon_0 (1+\chi)$
- $\nabla^2 U + k^2 U = 0$ is still valid, but with a complex wavenumber:

$$k = \omega\sqrt{\varepsilon\mu_0} = k_0\sqrt{1+\chi} = k_0\sqrt{1+\chi' + j\chi''}$$

$$\boxed{k = \beta - j\frac{1}{2}\alpha = k_0\sqrt{1+\chi' + j\chi''}}$$

- β : propagation constant of the wave (phase change rate)
- α : absorption coefficient (if α < 0, then γ = -α : gain)
- The sign depends on the convention chosen for $\exp(+j\omega t)$
  a forward propagating wave: $\exp(+j\omega t - jkr)$ will decay if α > 0

Transmission window



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A very useful reference

http://refractiveindex.info

Optical constants of BK7

N-BK7 (SCHOTT)

Wavelength: 0.5876 µm (0.3 – 2.5) line select unit converter

Refractive index [i]

n = 1.5168

Extinction coefficient [i]

k = 9.7525e-9

Other optical constants

Relative permittivity (dielectric constants) [i] [i]
ϵ' = 2.3007
ϵ'' = 2.9585e-8

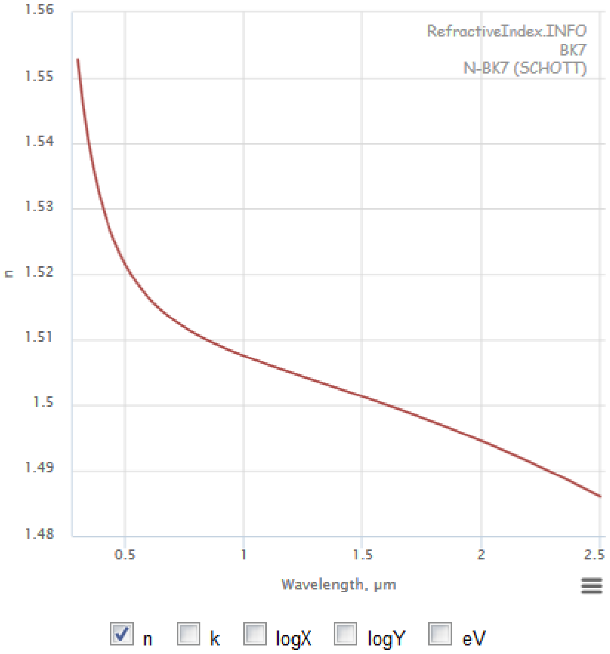
Absorption coefficient [i] [i]
α = 0.0020857 cm^{-1}

Abbe number [i]
V_d = 64.17
Abbe diagram

Chromatic dispersion [i]
$dn/d\lambda$ = -0.041792 µm^{-1}

Group index [i] [i]
n_g = 1.5414

Group velocity dispersion [i] [i] [i]
GVD = 70.372 fs^2/mm
D = -383.92 ps/(nm km)



Dispersion formula [i]

$$n^2 - 1 = \frac{1.03961212\lambda^2}{\lambda^2 - 0.00600069867} + \frac{0.231792344\lambda^2}{\lambda^2 - 0.0200179144} + \frac{1.01046945\lambda^2}{\lambda^2 - 103.560653}$$

Selected Topics in Advanced Optics

Week 3 – part 4

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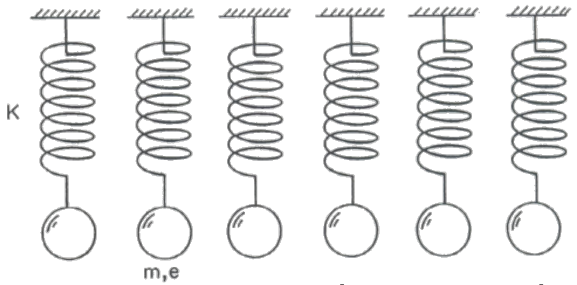
Lorentz model

(book by Bohren and Huffman)



- Now we assume the following time-dependence: $\exp(-j\omega t)$
- The electrons and ions in matter are treated as simple harmonic oscillators (springs)
- The applied force is given by the local electric field
- Equation of motion:

$$m\ddot{\mathbf{x}} + b\dot{\mathbf{x}} + K\mathbf{x} = e\mathbf{E}$$

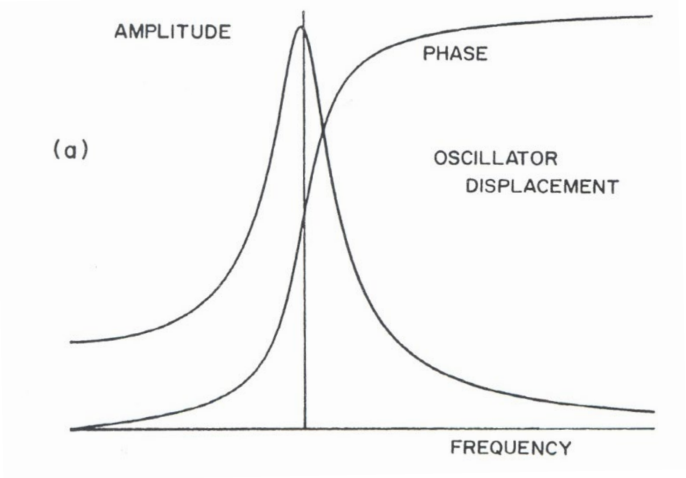
- Solution (oscillatory part):

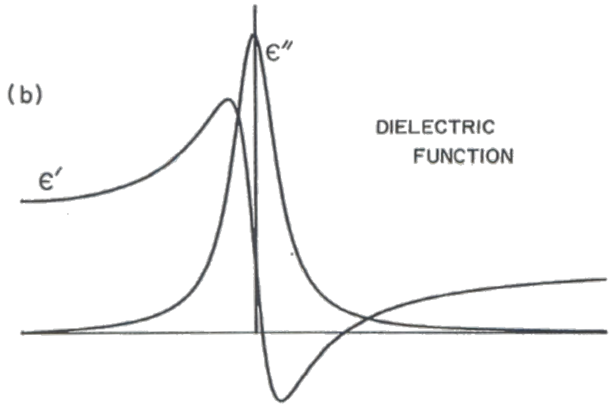
$$\mathbf{x} = \frac{(e/m)\mathbf{E}}{\omega_0^2 - \omega^2 - j\gamma\omega} \qquad \omega_0^2 = K/m \quad \gamma = b/m$$

- If $\gamma \neq 0$, the proportionality factor between $\mathbf{x}$ and $\mathbf{E}$ is complex
  → the displacement and field are usually not in phase

$$\mathbf{x} = (e/m)\mathbf{E}Ae^{j\Theta} \text{ with } A = \frac{1}{\sqrt{\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2}} \qquad \Theta = \arctan\left(\frac{\gamma\omega}{\omega_0^2 - \omega^2}\right)$$

Lorentz model



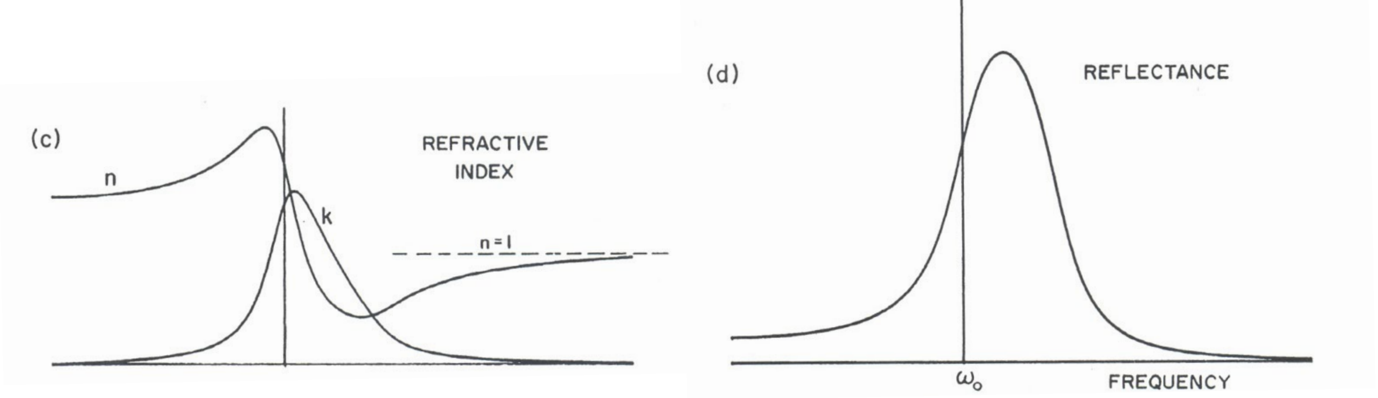


- The amplitude is maximum for $\omega = \omega_0$ and the width inversely proportional to γ
- At low frequency the oscillator is in-phase $(\Theta = 0)$ and at high frequency it is out of phase by 180°. The change occurs at $\omega \simeq \omega_0$
- The induced dipole moment of a single oscillator is $\mathbf{p} = e\mathbf{x}$
- For a collection of n oscillators per volume unit, the polarization is $\mathbf{P} = ne\mathbf{x}$

$$\mathbf{P} = \frac{\omega_p^2}{\omega_0^2 - \omega^2 - j\gamma\omega}\varepsilon_0\mathbf{E} \quad \text{plasma frequency}: \omega_p^2 = ne^2 / m\varepsilon_0$$

- Since $\mathbf{P} = \varepsilon_0 \chi \mathbf{E} \rightarrow \boxed{\varepsilon_r = 1 + \chi = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - j\gamma\omega}}$

Lorentz model



- The real part and the imaginary part of the permittivity are then

$$\varepsilon' = 1 + \chi' = 1 + \frac{\omega_p^2\left(\omega_0^2 - \omega^2\right)}{\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2} \qquad \varepsilon'' = \chi'' = \frac{\omega_p^2\gamma\omega}{\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2}$$

- A region of anomalous dispersion exists around the resonance
- High frequency limits:

$$\left(\omega \gg \omega_0\right) \quad \varepsilon' \simeq 1 - \frac{\omega_p^2}{\omega^2} \quad \varepsilon'' \simeq \frac{\gamma\omega_p^2}{\omega^3}$$

$$n \simeq \sqrt{\varepsilon'} \simeq 1 - \frac{\omega_p^2}{2\omega^2} \quad k \simeq \frac{\varepsilon''}{2} \simeq \frac{\gamma\omega_p^2}{2\omega^3}$$

- Low frequency limits:

$$\left(\omega \ll \omega_0\right) \quad \varepsilon' \simeq 1 + \frac{\omega_p^2}{\omega_0^2} \quad \varepsilon'' \simeq \frac{\gamma\omega_p^2\omega}{\omega_0^4}$$

Multiple oscillator model

- The Lorentz model can be extended for a broad range of materials by considering several resonances (i.e. several oscillators):

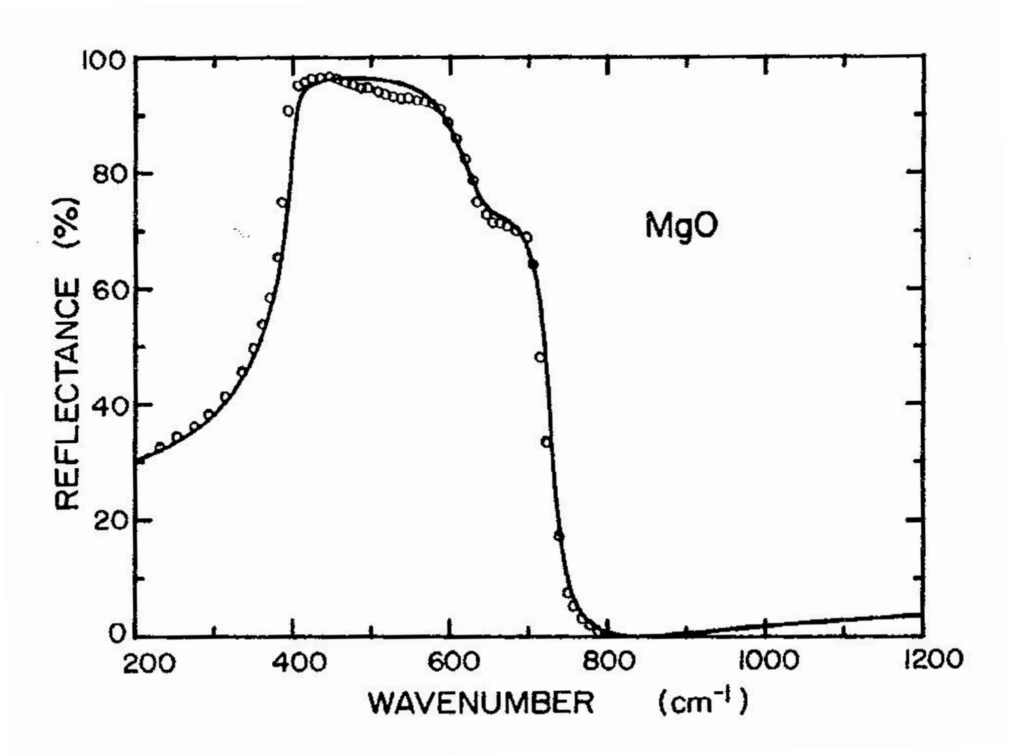
$$\varepsilon_r = \varepsilon_\infty + \sum_j \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 - j\gamma_j\omega}$$

- ε_∞ represents the effect of all oscillators at high frequency, if all oscillators are included in the summation, then $\varepsilon_\infty = 1$

Multiple oscillator model

- MgO crystal: reflectance data are well fitted using two oscillators (in this spectral region)

$$\varepsilon_r = \varepsilon_\infty + \sum_j \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 - j\gamma_j\omega}$$



$$\varepsilon_\infty = 3.01$$

$$\omega_1 = 401\,\text{cm}^{-1} \quad \gamma_1 = 7.62\,\text{cm}^{-1} \quad \omega_{p1}^2 / \omega_1^2 = 6.6$$

$$\omega_2 = 640\,\text{cm}^{-1} \quad \gamma_2 = 102.4\,\text{cm}^{-1} \quad \omega_{p2}^2 / \omega_2^2 = 0.045$$

Multiple oscillator model

- The permittivity of hemoglobin depends on the oxygen level

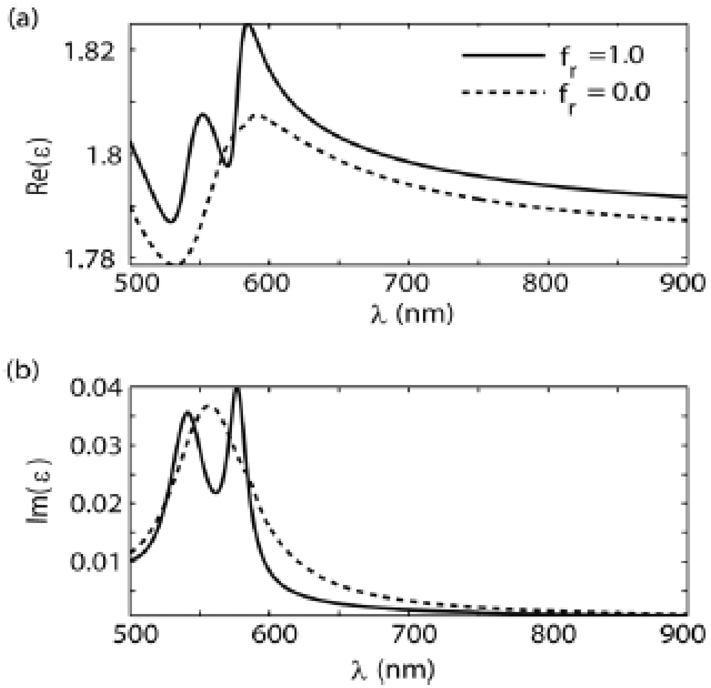


FIG. 2. (a) Real and (b) imaginary parts of the dielectric function of Hb at a concentration of 25 mM, in the oxygenated ($f_r = 1$) and deoxygenated ($f_r = 0$) states.

JOURNAL OF APPLIED PHYSICS **110**, 044701 (2011)

Strongly coupled bio-plasmonic system: Application to oxygen sensing

Shourya Dutta-Gupta and Olivier J. F. Martin[a)]
Nanophotonics and Metrology Laboratory (NAM), EPFL, Lausanne (CH - 1015), Switzerland

Multiple oscillator model

- A simple model with three oscillators reproduces this permittivity very well, but the oscillators are different for the oxygenated and de-oxygenated states:

$$\varepsilon_\alpha = \varepsilon_w + \frac{\nu_{p1}^2}{\nu_{01}^2 - \nu^2 - i\gamma_{01}\nu} + \frac{\nu_{p2}^2}{\nu_{02}^2 - \nu^2 - i\gamma_{02}\nu} + \frac{\nu_{p3}^2}{\nu_{03}^2 - \nu^2 - i\gamma_{03}\nu},$$

TABLE I. Values of the various parameters used to fit the permittivity of Hb.

	ν_{p1} (THz)	ν_{p2} (THz)	ν_{p3} (THz)	γ_{01} (THz)	γ_{02} (THz)	γ_{03} (THz)	λ_{01} (nm)	λ_{02} (nm)	λ_{03} (nm)
Oxygenated Hb	23.5	15.8	87.0	32.5	15.0	39.0	541.0	577.0	415.0
Deoxygenated Hb	35.5	3.0	64.5	66.0	10.0	20.0	556.0	586.0	434.0

$$\boxed{\varepsilon_{eff} = f_r \varepsilon_{oxy} + (1 - f_r)\varepsilon_{deoxy}.}$$

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Drude model (for metals)

- The spring constant is set to zero $K = 0$
- As a result: $\omega_0 = 0$

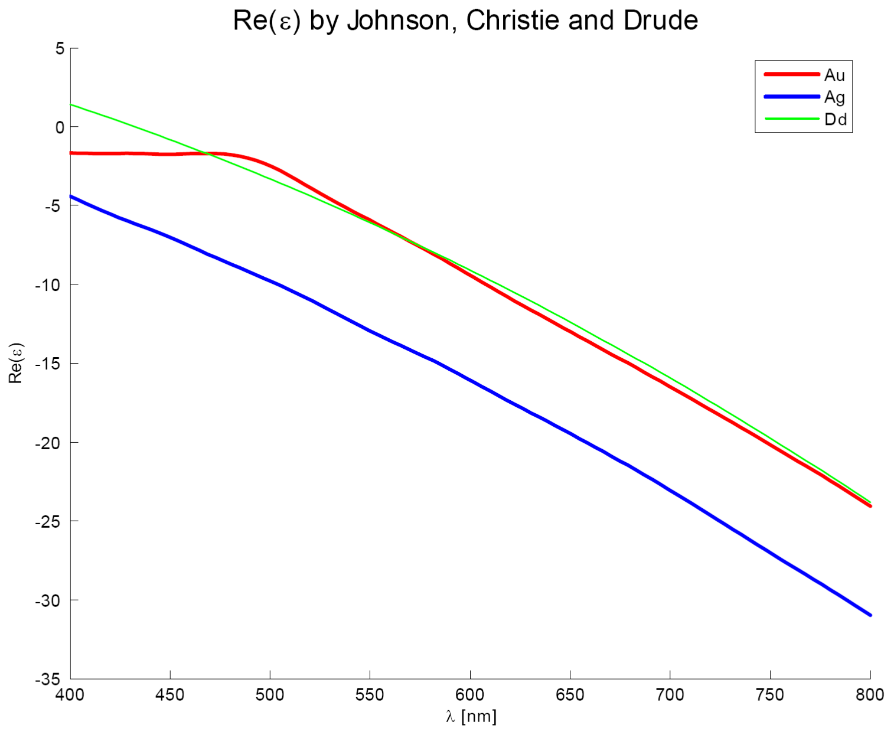
$$\boxed{\varepsilon_r = 1 - \frac{\omega_p^2}{\omega^2 + j\gamma\omega}}$$

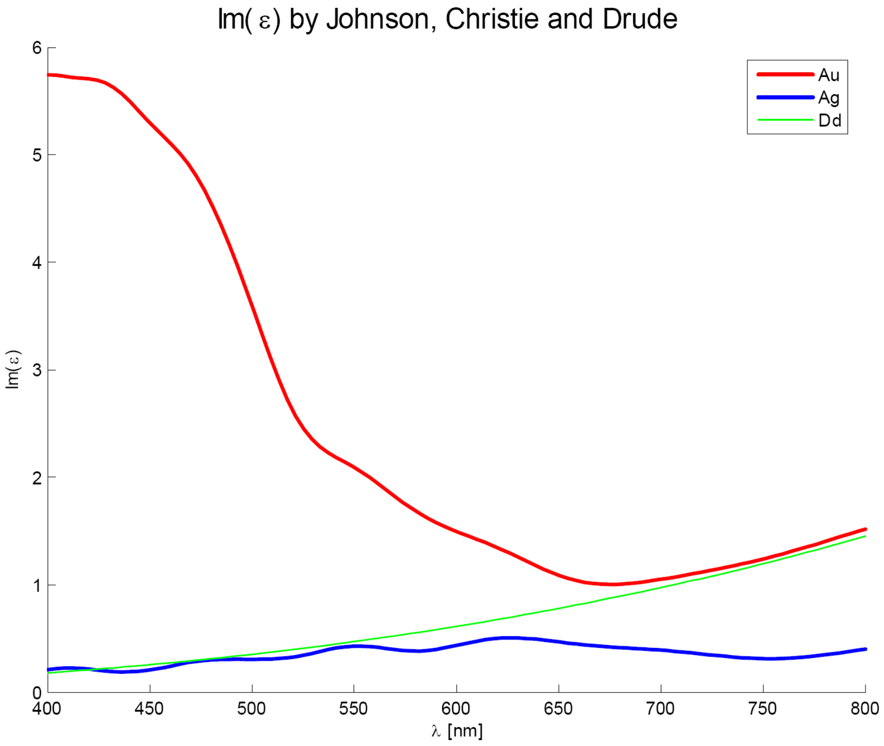
$$\varepsilon' = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} \qquad \varepsilon'' = \frac{\omega_p^2 \gamma}{\omega\left(\omega^2 + \gamma^2\right)}$$

- The real part of the permittivity is negative !
- The following website gathers parameters for the Drude model for many metals:
  http://www.wave-scattering.com/drudefit.html
- For one metal, there are often different possible fits, depending on the wavelength range of interest !

Plasmonic metals

- Coinage metals (noble metals, group 11): Cu, Ag, Au
- The plasma frequency determines the optical range where plasmonic effects can be excited
- Further plasmonic metals include Al, W, Pt





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Selected Topics in Advanced Optics

Week 3 – part 5

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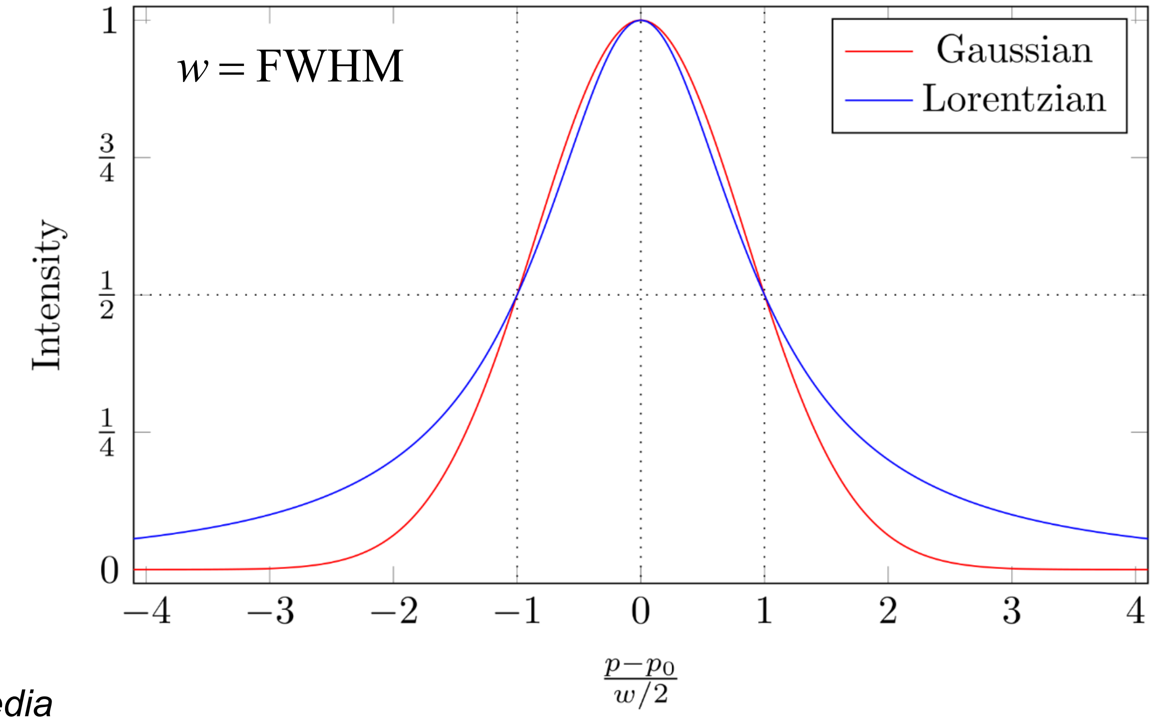
Spectral line shapes

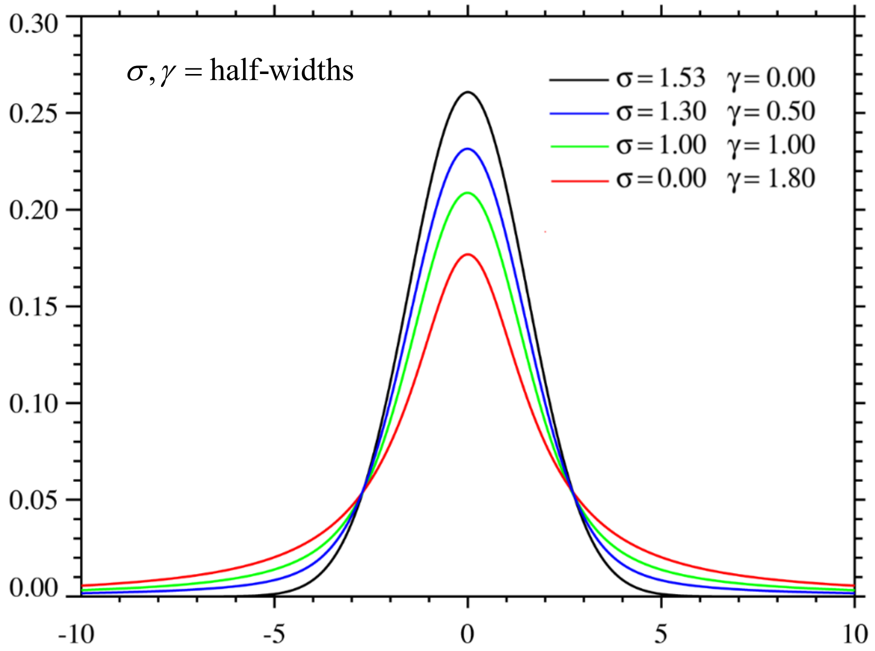
- It is often useful to fit a function on the spectral response of a system
- There are three such main functions
  - Lorentzian:
  - Gaussian:
  - Voigt:

$$L(x) = \frac{1}{1+x^2} \qquad x = \frac{p-p_0}{w/2}$$

$$G(x) = e^{-(\ln 2)x^2}$$

$$V(x;\sigma,\gamma) = \int_{-\infty}^{\infty} G(x';\sigma)\, L(x-x';\gamma)\, dx'$$





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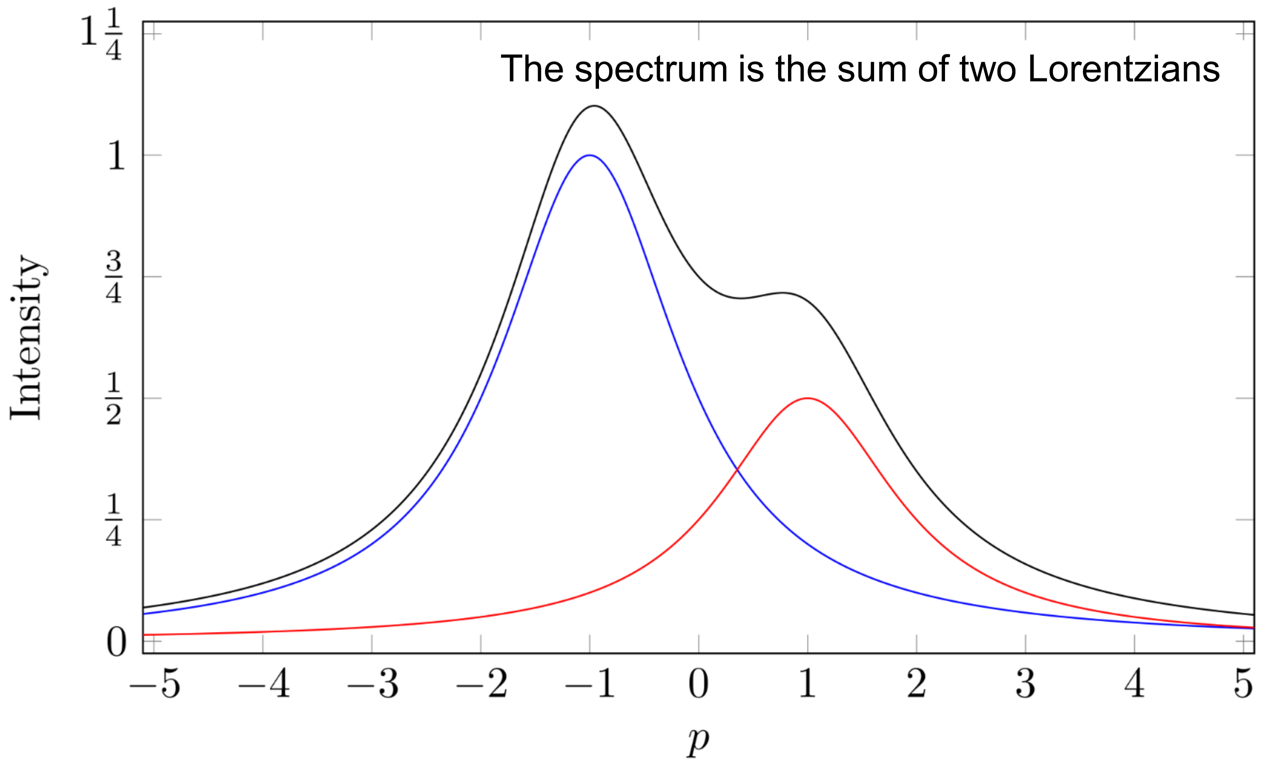
Spectral line shapes

- In most cases, on can safely use a Lorentzian curve
- A complex spectrum can be decomposed into a collection of simple lines



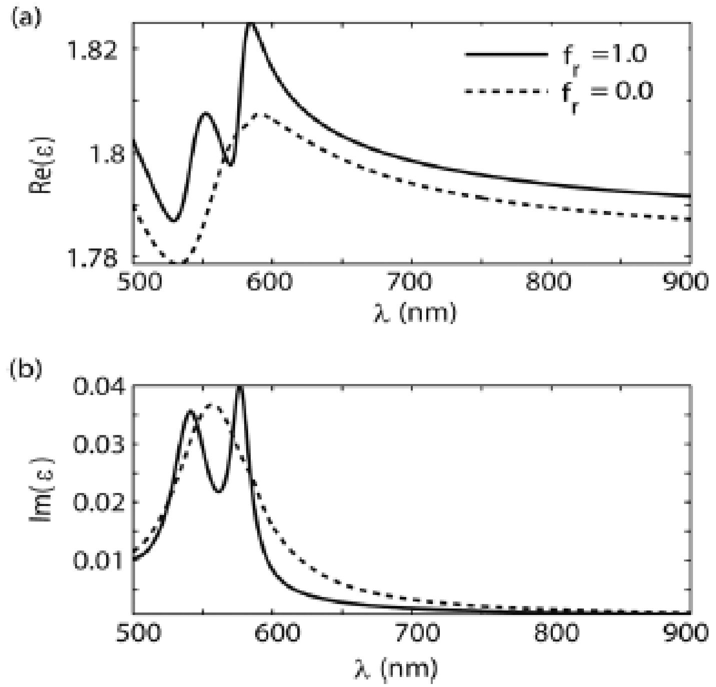


FIG. 2. (a) Real and (b) imaginary parts of the dielectric function of Hb at a concentration of 25 mM, in the oxygenated ($f_r = 1$) and deoxygenated ($f_r = 0$) states.

wikipedia