

Optical properties of Materials

Reading:

- ▶ Kasap: 9.1 - 9.18

Maxwell's equations in free media

- ▶ Linear response of materials described very generally by $\epsilon(\omega)$ and $\mu(\omega)$
- ▶ Maxwell's equations in the absence of free charges and currents

$$\nabla \cdot (\epsilon(\omega)\vec{E}) = 0$$

$$\nabla \times \vec{E} = i\omega\vec{B}$$

$$\nabla \times \frac{\vec{B}}{\mu(\omega)} = -i\omega(\epsilon(\omega)\vec{E})$$

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

- ▶ Substitute second equation in curl of third equation:

$$\frac{\nabla \times (\nabla \times \vec{B})}{\mu(\omega)} = -i\omega\epsilon(\omega)\nabla \times \vec{E} = \omega^2\epsilon(\omega)\vec{B}$$

$$-\nabla^2\vec{B} = \omega^2\epsilon(\omega)\mu(\omega)\vec{B}$$

using $\nabla \cdot \vec{B} = 0$

Electromagnetic waves

- ▶ Write Maxwell's equation in linear media with no free charge or current as:

$$v^2(\omega)\nabla^2\vec{B} = -\omega^2\vec{B}$$

$$v^2(\omega)\nabla^2\vec{E} = -\omega^2\vec{E}$$

where $v(\omega) \equiv 1/\sqrt{\epsilon(\omega)\mu(\omega)}$

- ▶ This is exactly the equation of a wave with speed v

$$v^2\nabla^2 f = -\omega^2 f$$

$$v^2\nabla^2 f = \frac{\partial^2 f}{\partial t^2}$$

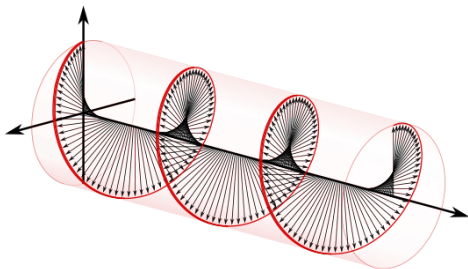
where f is either \vec{E} or \vec{B}

- ▶ Solution to the wave equation with $|\vec{k}| = \omega/v$:

$$f(\vec{r}) = f e^{i\vec{k}\cdot\vec{r}}$$

$$f(\vec{r}, t) = f e^{i(\vec{k}\cdot\vec{r} - \omega t)}$$

Polarization



- ▶ EM wave propagating along x :

$$\vec{E}(\vec{r}, t) = E_0 \hat{y} e^{i(kx - \omega t)} \quad \text{or} \quad \vec{E}(\vec{r}, t) = E_0 \hat{z} e^{i(kx - \omega t)}$$

two field directions \Rightarrow two independent linear polarizations

- ▶ Linearly combine to

$$\vec{E}(\vec{r}, t) = E_0 \frac{\hat{y} + i\hat{z}}{\sqrt{2}} e^{i(kx - \omega t)} \quad \text{or} \quad \vec{E}(\vec{r}, t) = E_0 \frac{\hat{y} - i\hat{z}}{\sqrt{2}} e^{i(kx - \omega t)}$$

\Rightarrow two independent circular polarizations (left/right)

- ▶ Photons: circular polarizations have spin angular momentum $\pm \hbar$ along propagation direction (photons are spin $s = 1$ particles)

Wave speed and refractive index

- ▶ Electromagnetic waves satisfy dispersion relation $\omega = v|\vec{k}|$
- ▶ EM wave velocity $v(\omega) = 1/\sqrt{\epsilon(\omega)\mu(\omega)}$
- ▶ In vacuum, $\epsilon(\omega) = \epsilon_0$ and $\mu(\omega) = \mu_0$, so that speed of light in free space

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

- ▶ In materials, speed of light usually specified by refractive index

$$n(\omega) \equiv \frac{c}{v(\omega)} = \sqrt{\frac{\epsilon(\omega)\mu(\omega)}{\epsilon_0\mu_0}}$$

Refractive index: frequency dependence

- ▶ Most materials are non-magnetic $\mu \approx \mu_0$
- ▶ Therefore $n^2(\omega) \approx \epsilon_r \equiv \epsilon(\omega)/\epsilon_0$
- ▶ Several contributions to relative permittivity:

$$n^2 \approx \epsilon_r = 1 + \chi_e^{(\text{free } e^-)} + \chi_e^{(\text{bound } e^-)} + \chi_e^{(\text{ions})} + \chi_e^{(\text{dipoles})}$$

- ▶ Frequency dependence (Drude-Lorentz model):

$$n^2(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} + \sum_{\alpha} \frac{\chi_{0\alpha}\omega_{0\alpha}^2}{\omega_{0\alpha}^2 - i\gamma_{\alpha}\omega - \omega^2}$$

where α includes bound e^- , ions and dipoles

- ▶ First Drude term proportional to free carrier density:
 - ▶ Dominates for metals
 - ▶ Present to varying degrees for doped semiconductors
- ▶ Remaining terms contribute in all materials

Refractive index: wavelength dependence

- ▶ Frequency dependence (Drude-Lorentz model):

$$n^2(\omega) = 1 + \sum_{\alpha} \frac{\chi_{0\alpha} \omega_{0\alpha}^2}{\omega_{0\alpha}^2 - i\gamma_{\alpha}\omega - \omega^2}$$

(Drude term captured by setting $\chi_{0\alpha} \omega_{0\alpha}^2 \rightarrow \omega_p^2$, $\omega_0 \rightarrow 0$ and $\gamma \rightarrow 1/\tau$)

- ▶ Equivalently in terms of wavelength $\lambda = 2\pi c/\omega$:

$$n^2(\lambda) = 1 + \sum_{\alpha} \frac{\chi_{0\alpha} \lambda^2}{\lambda^2 - i\delta_{\alpha}\lambda - \lambda_{0\alpha}^2}$$

where $\lambda_0 = 2\pi c/\omega_0$ and $\delta = 2\pi c\gamma_{\alpha}/\omega_0^2$

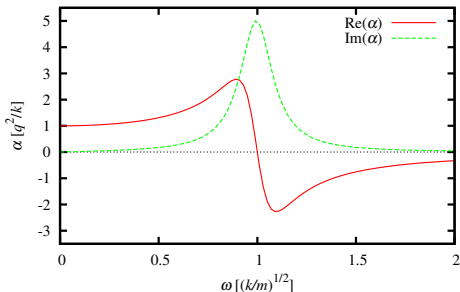
- ▶ Can use a number of α in the empirical Sellmeier relation instead:

$$n^2(\lambda) = 1 + \sum_{\alpha} \frac{A_{\alpha} \lambda^2}{\lambda^2 - i\delta_{\alpha}\lambda - \lambda_{\alpha}^2}$$

Complex refractive index

- ▶ The n^2 we have been working with so far has been implicitly complex (due to the τ and γ 's)
- ▶ Customary to call complex refractive index $N = n + iK$ (where n and K are real)
- ▶ Wave speed $v = \frac{c}{N} = \frac{c}{n+iK}$ is complex
- ▶ Wave vector $k = \frac{\omega}{v} = \frac{\omega}{c}(n + iK) = k_0(n + iK)$ is complex
- ▶ What do the imaginary parts here mean?
- ▶ Wave function (fields) $\propto e^{ikx} = e^{i(nk_0)x} \cdot e^{-(Kk_0)x}$
- ▶ Wave intensity $\propto e^{-(2Kk_0)x}$ (proportional to $|\text{field}|^2$)
- ▶ \Rightarrow Wave attenuates as $e^{-\alpha x}$ with absorption coefficient $\alpha = 2Kk_0$

Kramers-Kronig relations



- ▶ Real and imaginary parts of $\epsilon(\omega)$ (and hence $n(\omega)$) not independent
- ▶ Causality \Rightarrow response functions (eg. $\chi(\omega)$) must be complex analytic functions ($\chi(z)$)
- ▶ Leads to the Kramers-Kronig relations:

$$\text{Re}\chi(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} d\omega' \frac{\text{Im}\chi(\omega')}{\omega' - \omega}, \quad \text{Im}\chi(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} d\omega' \frac{\text{Re}\chi(\omega')}{\omega' - \omega}$$

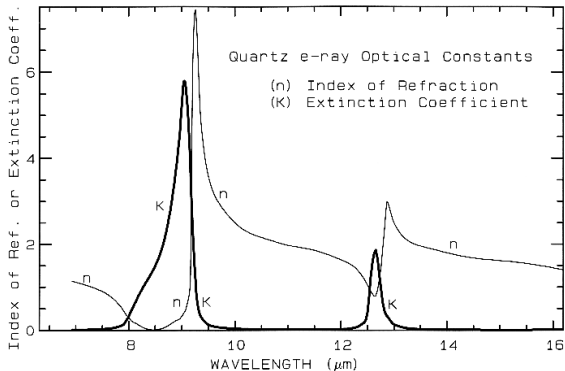
- ▶ Absorption at ω_0 affects n at all ω

Absorption mechanisms

Every polarizability term has a corresponding absorption mechanism:

- ▶ Free electrons: resistive loss in Drude term
 - ▶ Bound electrons: absorption excites electronic transitions
 - ▶ Ions: absorption excites phonons
 - ▶ Dipoles: absorption excites molecular rotations
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- ▶ Simple model so far (Lorentz) assumed single resonant frequency ω_0
 - ▶ Each of the above processes have a band of absorption frequencies instead

Lattice absorption: Reststrahlen band



- ▶ Optical phonons in ionic crystals: charge oscillations \Rightarrow interact with EM (hence the name 'optical' phonons)
- ▶ High DOS for transverse and longitudinal optical phonons
- ▶ Absorption peaks at corresponding wavelengths: Reststrahlen band
- ▶ Typically in the mid-infrared part of the spectrum

Electronic absorption: bound model

- ▶ Simple model for insulators so far: electrons bound by springs
- ▶ In reality: electrons delocalized in insulators / semiconductors too
- ▶ Only no net current in completely filled (or empty) bands
- ▶ Low frequency response is effectively like bound electrons (because $v_d = 0$)
- ▶ Bound model obtained response of form:

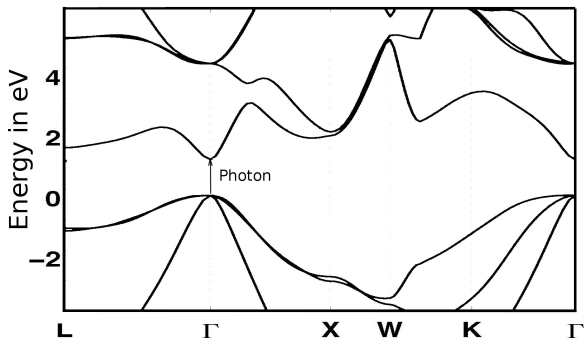
$$\chi(\omega) = \frac{\chi_0 \omega_0^2}{\omega_0^2 - i\gamma\omega - \omega^2}$$

- ▶ Interpretation of behavior near $\omega \sim \omega_0$ needs revision
- ▶ Energy absorbed from light must be taken up by the electrons
- ▶ How can you increase the electronic energy of insulators?
- ▶ Move an electron from the valence to conduction band (leave hole behind)
- ▶ What is the minimum frequency that can do this? $\hbar\omega = E_g$
- ▶ Effectively ω_0 now corresponds to E_g/\hbar

Optical excitation of electrons

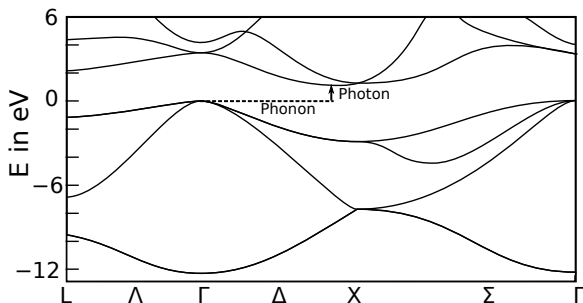
- ▶ Light excites electron in valence band (initial energy $E_i < 0$) to conduction band (final energy $E_j > E_g$)
- ▶ Energy conservation: $E_i + \hbar\omega = E_j \Rightarrow \omega = (E_j - E_i)/\hbar > E_g/\hbar$
- ▶ Momentum conservation $\hbar k_i + \hbar\omega/c = \hbar k_j \Rightarrow k_j - k_i = \omega/c = 2\pi/\lambda$
- ▶ Typical $E_g \sim 1 - 10$ eV with $\lambda \sim 100$ nm - 1 μ m (NIR, visible, UV)
- ▶ Typical $k_i, k_j \sim 2\pi/a$ with $a < 1$ nm
- ▶ \Rightarrow photon momentum is negligible in electronic processes
- ▶ Effectively $k_i = k_j$ (vertical transitions) for optical absorption

Direct absorption



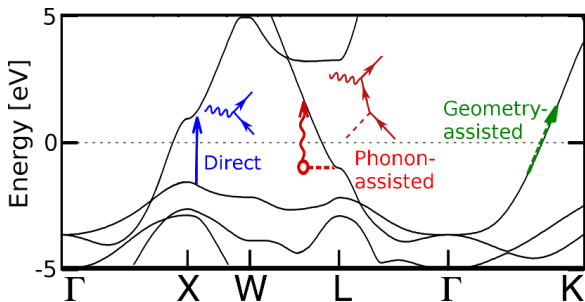
- ▶ Direct band-gap semiconductors (eg. GaAs): VBM and CBM at same k
- ▶ Possible to have $E_j - E_i = E_g$ with $k_i = k_j$
- ▶ Direct absorption: light produces electron-hole pair
- ▶ Allowed here for $\omega \geq E_g/\hbar$

Indirect absorption



- ▶ Indirect band-gap semiconductors (eg. Si): VBM and CBM at different k
- ▶ Not possible to have $E_j - E_i = E_g$ with $k_i = k_j$
- ▶ Indirect absorption: light produces electron-hole pair \pm phonon
- ▶ Conservation: $E_j - E_i \pm \hbar\omega_{\text{ph}} = \hbar\omega$, $k_j \pm k_{\text{ph}} = k_i$
- ▶ Negligible energy in phonon, negligible momentum in photon
- ▶ Direct absorption becomes possible above interband threshold E_t

Absorption in metals (plasmon decay)

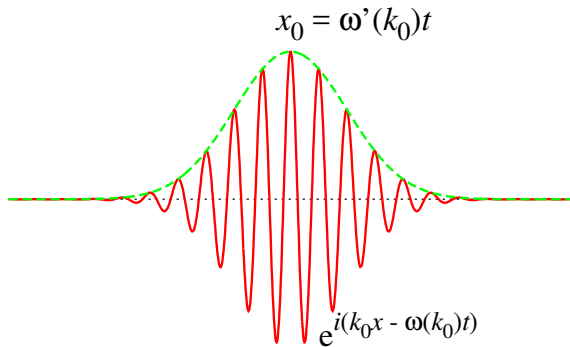


- ▶ Direct interband transitions from d -bands to Fermi level
- ▶ Indirect transitions possible in two ways:
 - ▶ Get momentum from phonons (lattice vibrations)
 - ▶ Geometry effect in nanostructures: uncertainty principle / momentum from surface
- ▶ Additionally resistive losses at all frequencies (dominates at low frequency)

Excitons

- ▶ Photons absorbed to produce electron-hole pairs for $\hbar\omega \geq E_g$
- ▶ This assumes electrons and holes don't interact with each other
- ▶ Instead they attract with potential $V(r) \sim -e^2/(r\epsilon_r)$
- ▶ Corresponding binding energy $E_b = \frac{m_{\text{eff}}}{m\epsilon_r^2}$ Ryd (typically $\sim 0.01 - 0.1$ eV) (similar to the donor/acceptor level estimate)
- ▶ Here $m_{\text{eff}} \sim m_e^* m_h^* / (m_e^* + m_h^*)$ is reduced mass of electron-hole pair
- ▶ Exciton: bound pair of electron and hole
- ▶ Can absorb photons when $\hbar\omega \geq E_g - E_b$ (slightly smaller than band gap)

Wave packets



- ▶ Velocity so far is phase velocity $v(\omega) = \frac{\omega}{k} = \frac{c}{n(\omega)}$
- ▶ Wavepackets travel with group velocity $v_g = \frac{\partial\omega}{\partial k}$
- ▶ Same concept for all waves; only difference: dispersion relation $\omega(k)$

Group velocity and group index

- ▶ Group velocity

$$\begin{aligned}
 v_g &= \frac{\partial \omega}{\partial k} = \frac{1}{\partial k / \partial \omega} \\
 &= \frac{1}{\partial(\omega n(\omega)/c) / \partial \omega} \\
 &= \frac{c}{n(\omega) + \omega n'(\omega)} \\
 &= \frac{c}{n(\lambda) - \lambda n'(\lambda)}
 \end{aligned}$$

since $\omega \propto \lambda^{-1}$

- ▶ Correspondingly group index:

$$\begin{aligned}
 n_g &\equiv c/v_g = n(\omega) + \omega n'(\omega) \\
 &= n(\lambda) - \lambda n'(\lambda)
 \end{aligned}$$

- ▶ For a non-dispersive medium (constant n), $v_g = v$ and $n_g = n$

Optical energy density and power flux

- ▶ Energy density in electric field = $\frac{\epsilon E^2}{2}$
- ▶ Energy density in magnetic field = $\frac{B^2}{2\mu}$
- ▶ Maxwell's equation $\nabla \times \vec{E} = -\partial \vec{B} / \partial t \Rightarrow |\vec{E}| = v |\vec{B}| = \frac{|\vec{B}|}{\sqrt{\epsilon\mu}}$
- ▶ Therefore energy densities in \vec{E} and \vec{B} are equal
- ▶ Net energy density = ϵE^2
- ▶ Wave moves with velocity v , so power flux is $v\epsilon E^2$
 $= v^2 \epsilon E B = \frac{1}{\mu} E B = E H$
- ▶ More generally, power flux given by Poynting vector $\vec{E} \times \vec{H}$

Interface between media

- ▶ In material with index n_1 , light incident towards interface with n_2
- ▶ Wavevectors: incident \vec{k}_1 , reflected \vec{k}'_1 and transmitted \vec{k}_2
- ▶ At boundary, \vec{E}_{\parallel} , D_{\perp} and \vec{B} continuous (non-magnetic)
- ▶ Frequencies: common ω for all three (phases match for all t)
- ▶ Phase of fields must match at all x and y
- ▶ y -matching implies all three wavevectors in same plane
- ▶ x -matching implies that for all x :

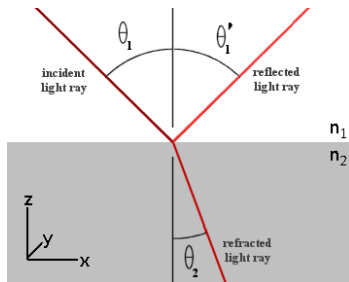
$$e^{ik_1 \sin \theta_1 x} = e^{ik_1 \sin \theta'_1 x} = e^{ik_2 \sin \theta_2 x}$$

$$\Rightarrow k_1 \sin \theta_1 = k_1 \sin \theta'_1$$

- ▶ Therefore $\theta_1 = \theta'_1$ and

$$\frac{\sin \theta_2}{\sin \theta_1} = \frac{k_1}{k_2} = \frac{\omega/v_1}{\omega/v_2} = \frac{c/v_1}{c/v_2} = \frac{n_1}{n_2}$$

(Snell's law)



Fresnel's equations: E in plane (\parallel)

- ▶ Matching conditions:

$$\epsilon_1(E_1 \sin \theta_1 + E'_1 \sin \theta'_1) = \epsilon_2 E_2 \sin \theta_2 \quad (\text{Normal})$$

$$E_1 \cos \theta_1 - E'_1 \cos \theta'_1 = E_2 \cos \theta_2 \quad (\text{Tangential})$$

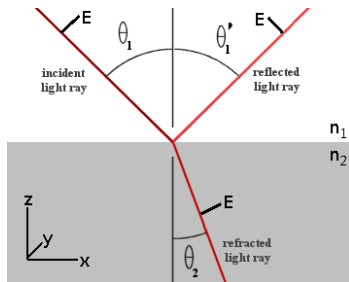
- ▶ Solve for E'_1 and E_2 :

$$r_{\parallel} \equiv \frac{E'_1}{E_1} = \frac{\frac{\epsilon_2 \sin \theta_2}{\epsilon_1 \sin \theta_1} \cos \theta_1 - \cos \theta_2}{\frac{\epsilon_2 \sin \theta_2}{\epsilon_1 \sin \theta'_1} \cos \theta'_1 + \cos \theta_2}$$

$$\Rightarrow r_{\parallel} = \frac{n^2 \cos \theta_1 - \sqrt{n^2 - \sin^2 \theta_1}}{n^2 \cos \theta_1 + \sqrt{n^2 - \sin^2 \theta_1}}$$

$$t_{\parallel} = \frac{2n \cos \theta_1}{n^2 \cos \theta_1 + \sqrt{n^2 - \sin^2 \theta_1}}$$

where $n = n_2/n_1$



Fresnel's equations: E normal to plane (\perp)

- ▶ Matching conditions:

$$\frac{1}{v_1}(E_1 \cos \theta_1 - E'_1 \cos \theta'_1) = \frac{1}{v_2} E_2 \cos \theta_2 \quad (B \text{ tangential})$$

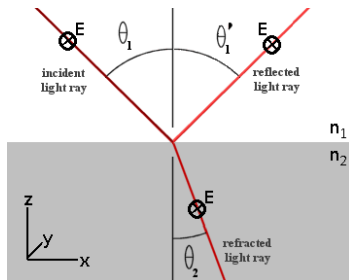
$$E_1 + E'_1 = E_2 \quad (E \text{ Tangential})$$

- ▶ Solve for E'_1 and E_2 :

$$\Rightarrow r_{\perp} = \frac{\cos \theta_1 - \sqrt{n^2 - \sin^2 \theta_1}}{\cos \theta_1 + \sqrt{n^2 - \sin^2 \theta_1}}$$

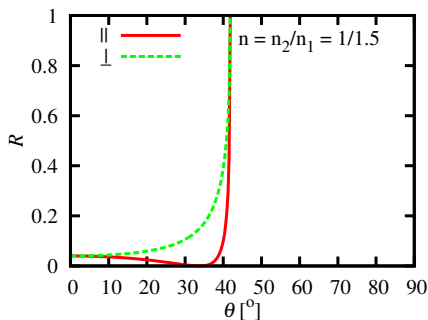
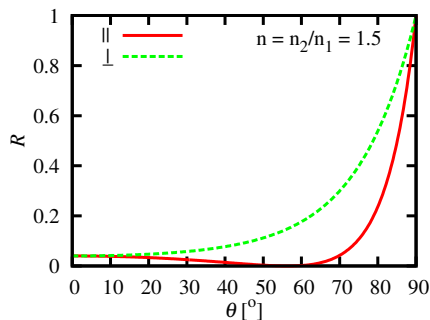
$$t_{\perp} = \frac{2 \cos \theta_1}{\cos \theta_1 + \sqrt{n^2 - \sin^2 \theta_1}}$$

where $n = n_2/n_1$



Reflection and transmission coefficients

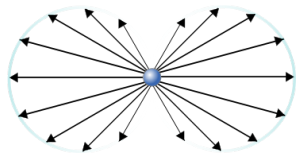
- ▶ Power flow $= v\epsilon|E|^2 = (c/n)n^2|E|^2 \propto n|E|^2$
- ▶ Therefore, $R = |r|^2$ and $T = n|t|^2$ (for each of \parallel and \perp)



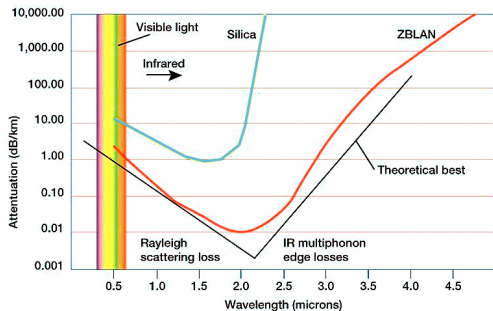
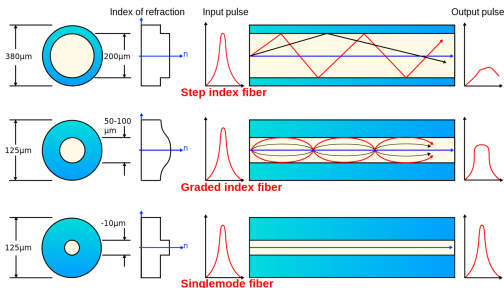
- ▶ R_{\perp} increases monotonically with incidence angle
- ▶ R_{\parallel} goes through zero at Brewster angle $\theta_B = \tan^{-1} n$
- ▶ $R = 1$ beyond $\theta_c = \sin^{-1} n$ when $n < 1$ (total internal reflection)
- ▶ Structures on wavelength scale: interference effects
eg. anti-reflective coatings (see section 9.7)

Scattering

- ▶ Index change due to impurity, defect or particles (in a suspension / composite)
- ▶ Scattered light output in all directions (cannot separate reflected / transmitted)
- ▶ Contributes to attenuation α (along with absorption)
- ▶ Rayleigh scattering: scatterer size $\ll \lambda$ (wave limit)
- ▶ Scattering cross section $\propto \lambda^{-4}$
- ▶ Angular distribution $\propto (1 + \cos^2 \theta)$
- ▶ Mie theory: general case of spherical particles $<, \sim, > \lambda$
- ▶ Used to determine particle sizes from diffraction measurements
- ▶ Scatter size $\gg \lambda$ (particle limit)
- ▶ Scattering cross section $\sim \pi r^2$ (constant in λ)
- ▶ Why is the sky blue, but clouds white/grey?



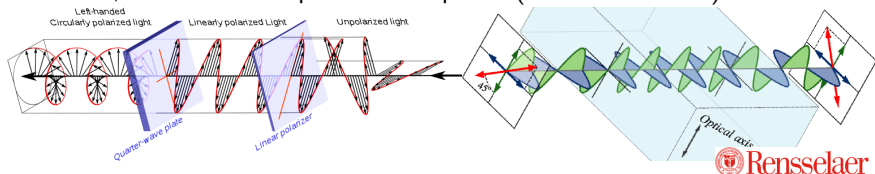
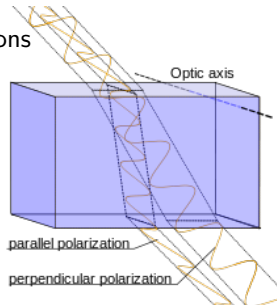
Optical fibers



- ▶ Higher n core surrounded by lower n sheath
- ▶ Channel light using total internal reflection
- ▶ Pulse shape distortion due to angle distribution
- ▶ Rectify / minimize using graded index / single mode fibers
- ▶ Attenuation: scattering at low λ , lattice absorption at high λ
- ▶ Alternate glasses like heavy metal fluorides (expensive) eg. ZBLAN (Zr-Ba-La-Al-Na-F)

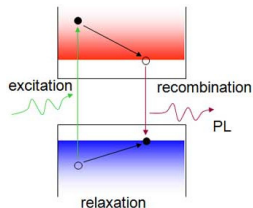
Anisotropic media

- ▶ In crystals, $n^2 = \epsilon$ is a tensor
- ▶ In general, values n_1, n_2, n_3 along principal directions
- ▶ Isotropic: $n_1 = n_2 = n_3$ eg. cubic
- ▶ Uniaxial: $n_1 = n_2 \neq n_3$ eg. tetragonal, hexagonal
- ▶ Biaxial: $n_1 \neq n_2 \neq n_3$ eg. orthorhombic, triclinic
- ▶ Optic axis: direction along which n_{\perp} is isotropic
- ▶ Uniaxial: single optic axis (direction 3 above)
- ▶ Biaxial: two optic axes (not along 1, 2 or 3)
- ▶ Consequence: two polarizations have different n for same direction
- ▶ Refracted waves in different directions (birefringence)
- ▶ Commonly used material: calcite (rhombohedral)
- ▶ Polarizers, half-wave and quarter-wave plates (Read 9.15 - 9.17)



Luminescence

- ▶ Reverse of electronic absorption: electron de-excitation emits light (de-excitation includes electron-hole recombination in semiconductors)
- ▶ Electrons in excited states for multiple reasons:
 - ▶ Optical excitation: photoluminescence (PL)
 - ▶ Electronic excitation: cathodoluminescence
 - ▶ Thermal excitation: thermoluminescence
- ▶ Includes fluorescence and phosphorescence (slowed by forbidden transitions)
- ▶ Phosphors: materials used for their luminescence
- ▶ Example: Cr^{3+} in corundrum Al_2O_3 emits in red (ruby)
- ▶ Traps / dopants in semiconductors: radiative recombination
- ▶ Applications:
 - ▶ Defunct display technologies (CRT)
 - ▶ Down-conversion: white LEDs generate red components from blue
 - ▶ Time-resolved PL: analysis of trap levels and lifetimes



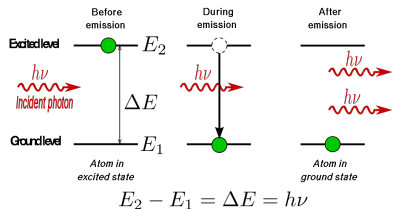
Stimulated emission

- ▶ Consider two level system with populations N_1 and N_2
- ▶ Incident light with intensity I : absorb to excite $1 \rightarrow 2$

$$-\dot{N}_1 = \dot{N}_2 = B_{12}IN_1$$

- ▶ Emission in presence of light:

$$\dot{N}_1 = -\dot{N}_2 = \underbrace{AN_2}_{\text{spontaneous}} + \underbrace{B_{21}IN_2}_{\text{stimulated}}$$

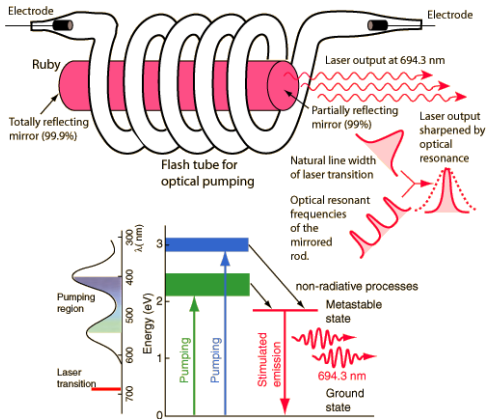


- ▶ Einstein's theorem: $B_{12} = B_{21}$ for detailed balance / microscopic reversibility
- ▶ Basically, matrix element for forward and reverse process
- ▶ Net result:

$$\dot{N}_1 = -\dot{N}_2 = AN_2 + BI(N_2 - N_1)$$

- ▶ Important: stimulated emission in same quantum state as incident (Bosonic effect)

Lasers



- ▶ Basic idea: a synchronized photoluminescence using stimulated emission
- ▶ Population inversion ($N_2 > N_1$) by optical pumping
- ▶ Need long-lived metastable state to hold N_2 (small A)
- ▶ Resonant cavity: light reflects back and forth
- ▶ Stimulated emission enhances intensity (amplification)
- ▶ Light output through slightly transmitting mirror
- ▶ Coherence: light with single wavelength and phase (line narrowing)

Electro- and magneto-optic effects

- ▶ Nonlinearity of ϵ and hence n with respect to \vec{E}

$$n(\vec{E}) = n_0 + \underbrace{\vec{a}_1 \cdot \vec{E}}_{\text{Pockel}} + \underbrace{\vec{E} \cdot \vec{a}_2 \cdot \vec{E}}_{\text{Kerr}} + \dots$$

- ▶ Kerr effect: present in all materials to varying degrees
- ▶ Pockel's effect: present only in materials that are non-centrosymmetric (symmetry breaking needed to give \vec{a}_1 a direction)
- ▶ Note: n must be tensorial for such materials
- ▶ Similarly, magneto-optic effect: nonlinearity in \vec{B}
- ▶ Faraday rotation: magnetic field along propagation direction rotates polarization
- ▶ Relative permeability of iron $\sim 2 \times 10^5 \Rightarrow n = \sqrt{\epsilon\mu} \sim 450$
- ▶ Relative permeability of ferrite $\sim 640 \Rightarrow n = \sqrt{\epsilon\mu} \sim 25$
- ▶ Much higher than any dielectric: why are these not used in optics?