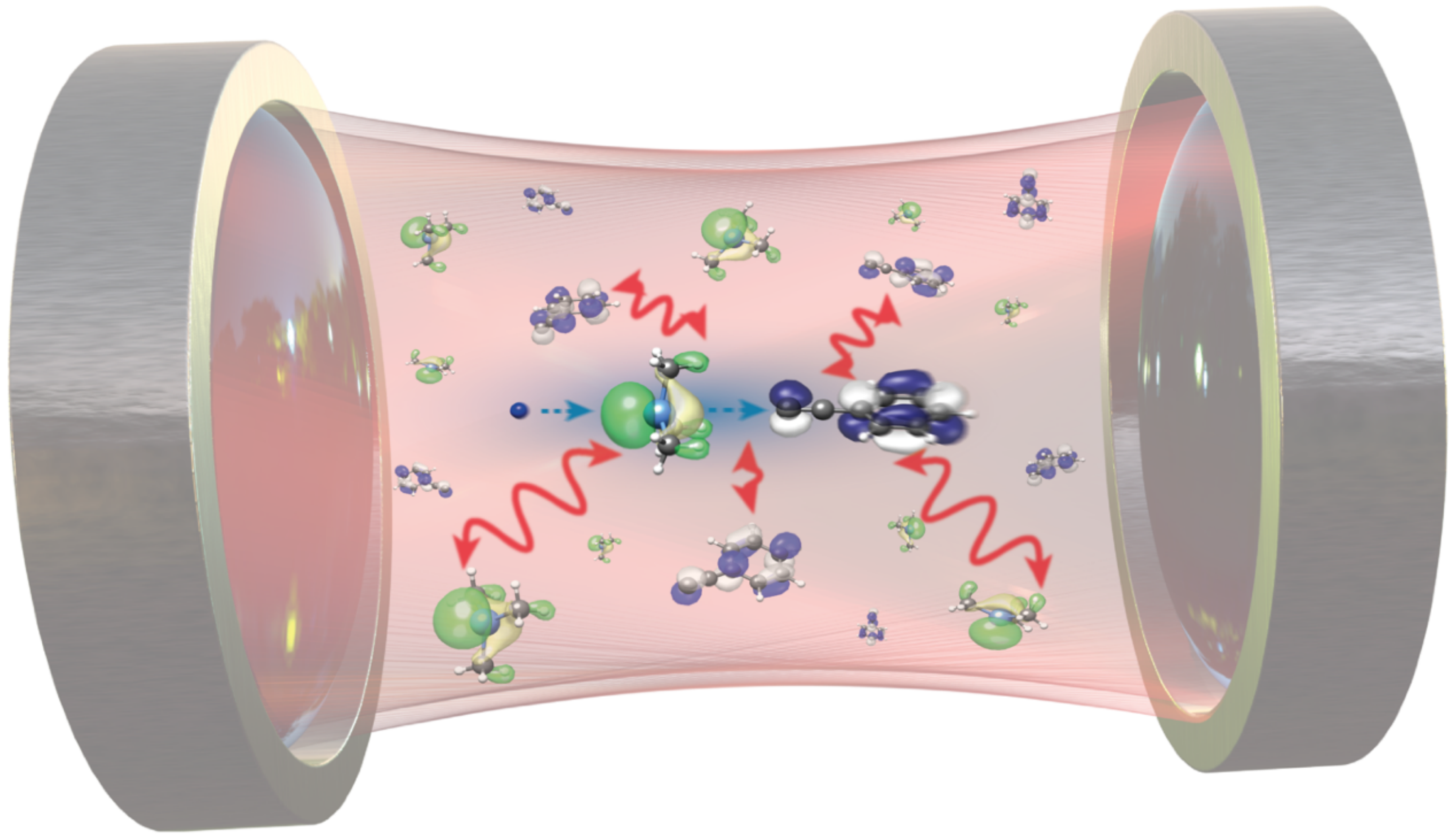
Dominik Sidler, 2025

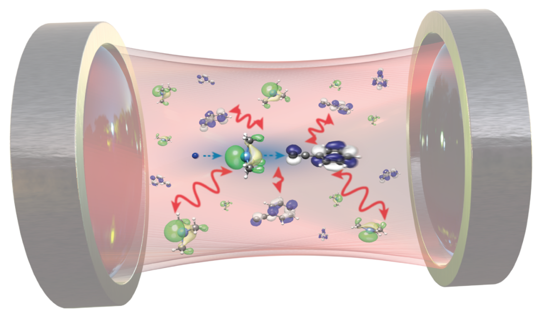
Polaritonic / QED Chemistry

Lecture 3: Macroscopic cavities / Maxwell's equations



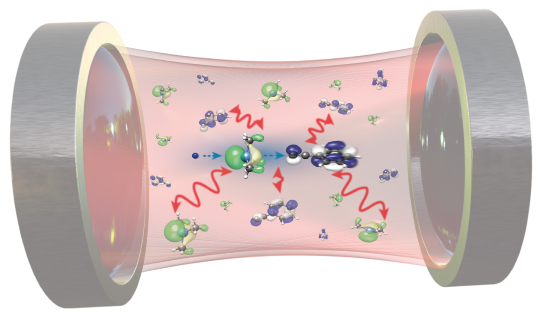
mpsd
Max-Planck-Institut für Struktur und Dynamik der Materie
PSI
University of Zurich UZH

Lecture Outline



1. Introduce **Maxwell's equations to** describe **classical electro-magnetic fields**.
2. Definition of **magnetic vector potential A** and **gauge freedom.**
3. Modeling **response of macroscopic media** to electro-magnetic fields.
4. Drude model for metals.
5. **Boundary conditions** for Maxwell's equations.
6. Relevance for the **design of specific light-matter interactions** in optical cavities.

Introduction to Maxwell's Equations



Microscopic formulation (vacuum) in cartesian coordinates and SI units

$$\nabla \cdot \boldsymbol{E}(x,y,z,t) = \frac{\rho(x,y,z,t)}{\epsilon_0}$$

Gauss's law for electric field

$$\nabla \cdot \boldsymbol{B}(x,y,z,t) = 0$$

Gauss's law for magnetic field

$$\nabla \times \boldsymbol{E}(x,y,z,t) = -\frac{\partial \boldsymbol{B}(x,y,z,t)}{\partial t}$$

Faraday's law of induction

$$\nabla \times \boldsymbol{B}(x,y,z,t) = \mu_0\left(\boldsymbol{J}(x,y,z,t) + \epsilon_0 \frac{\partial \boldsymbol{E}(x,y,z,t)}{\partial t}\right)$$

Ampère's circuital law

Divergence operator $\nabla \cdot \boldsymbol{E} = \frac{\partial \boldsymbol{E}}{\partial x} + \frac{\partial \boldsymbol{E}}{\partial y} + \frac{\partial \boldsymbol{E}}{\partial z}$

Curl operator

$$\nabla \times \boldsymbol{B} = \begin{pmatrix} \frac{\partial B_z}{\partial y} - \frac{\partial B_y}{\partial z} \\ \frac{\partial B_x}{\partial z} - \frac{\partial B_z}{\partial x} \\ \frac{\partial B_y}{\partial x} - \frac{\partial B_x}{\partial y} \end{pmatrix}$$

permittivity of free space ϵ_0

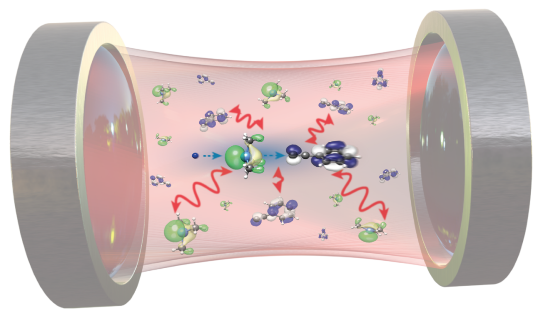
permeability of free space μ_0

charge density $\rho(x,y,z,t)$

current density $\boldsymbol{J}(x,y,z,t)$

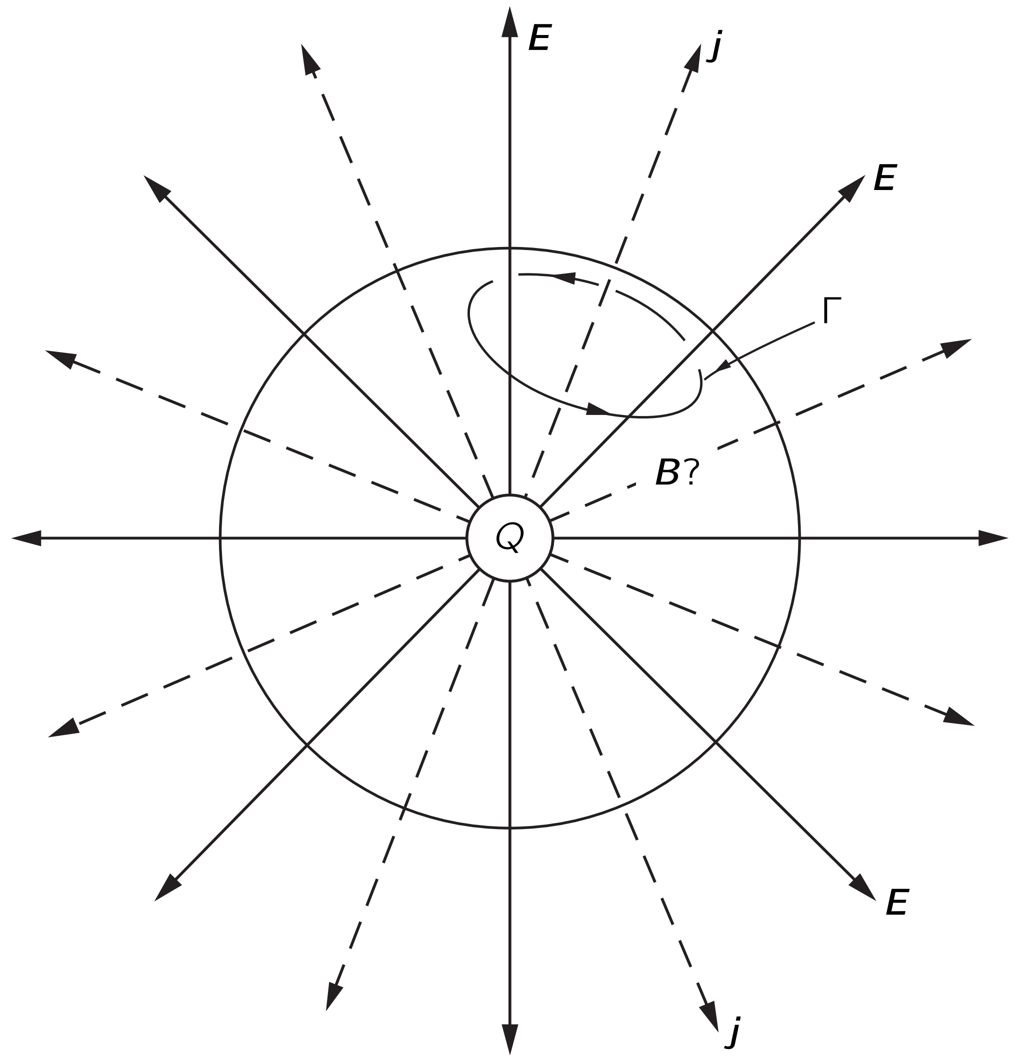
Source terms

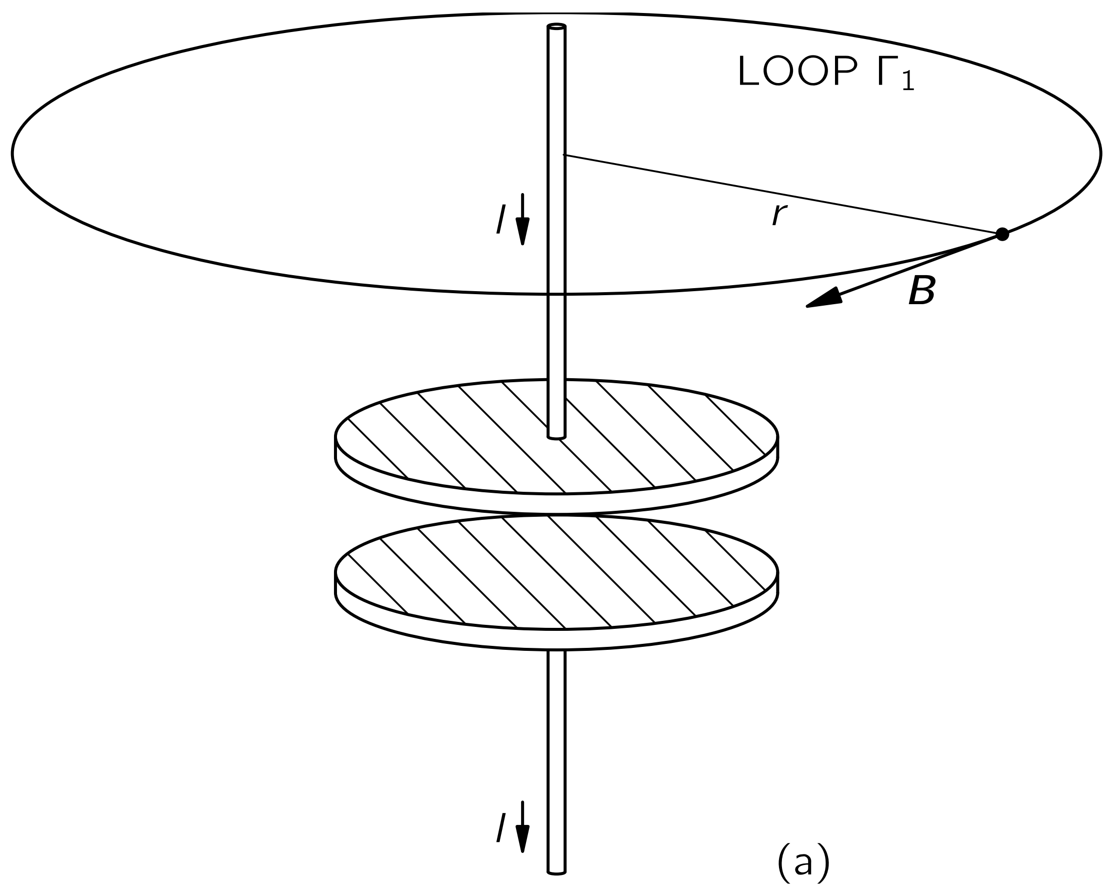
Introduction to Maxwell’s Equations



Interpretation

$\nabla \cdot \boldsymbol{E} = \dfrac{\rho}{\epsilon_0}$	(Flux of $\boldsymbol{E}$ through a closed surface) $= (\text{Charge inside})/\epsilon_0$
$\nabla \times \boldsymbol{E} = -\dfrac{\partial \boldsymbol{B}}{\partial t}$	(Line integral of $\boldsymbol{E}$ round a loop) $= -\dfrac{d}{dt}$(Flux of $\boldsymbol{B}$ through the loop)
$\nabla \cdot \boldsymbol{B} = 0$	(Flux of $\boldsymbol{B}$ through a closed surface) $= 0$
$c^2 \nabla \times \boldsymbol{B} = \dfrac{\boldsymbol{j}}{\epsilon_0} + \dfrac{\partial \boldsymbol{E}}{\partial t}$	c^2(Integral of $\boldsymbol{B}$ around a loop) $= (\text{Current through the loop})/\epsilon_0 + \dfrac{d}{dt}$(Flux of $\boldsymbol{E}$ through the loop)

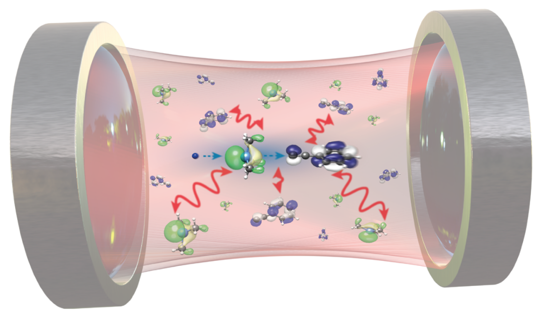




(a)

https://www.feynmanlectures.caltech.edu/II_18.html

Electrodynamics



Simple example: Propagating wave in vacuum

Free space: $\rho = 0,\ \boldsymbol{J} = 0$

Vector identity: $\nabla \times \left(\nabla \times \boldsymbol{F}\right) = \nabla(\nabla \cdot \boldsymbol{F}) - \Delta F$

Speed of light: $c = \sqrt{\mu_0 \epsilon_0}$

Laplace Operator: $\Delta \boldsymbol{E} = \frac{\partial^2 \boldsymbol{E}}{\partial x^2} + \frac{\partial^2 \boldsymbol{E}}{\partial y^2} + \frac{\partial^2 \boldsymbol{E}}{\partial z^2}$

Maxwell's equations turn into wave equations:

$$\frac{1}{c^2}\frac{\partial^2 \boldsymbol{E}}{\partial t^2} - \Delta \boldsymbol{E} = 0 \qquad \boldsymbol{E} \cdot \boldsymbol{B} = \boldsymbol{E} \cdot \boldsymbol{k} = \boldsymbol{B} \cdot \boldsymbol{k} = 0$$

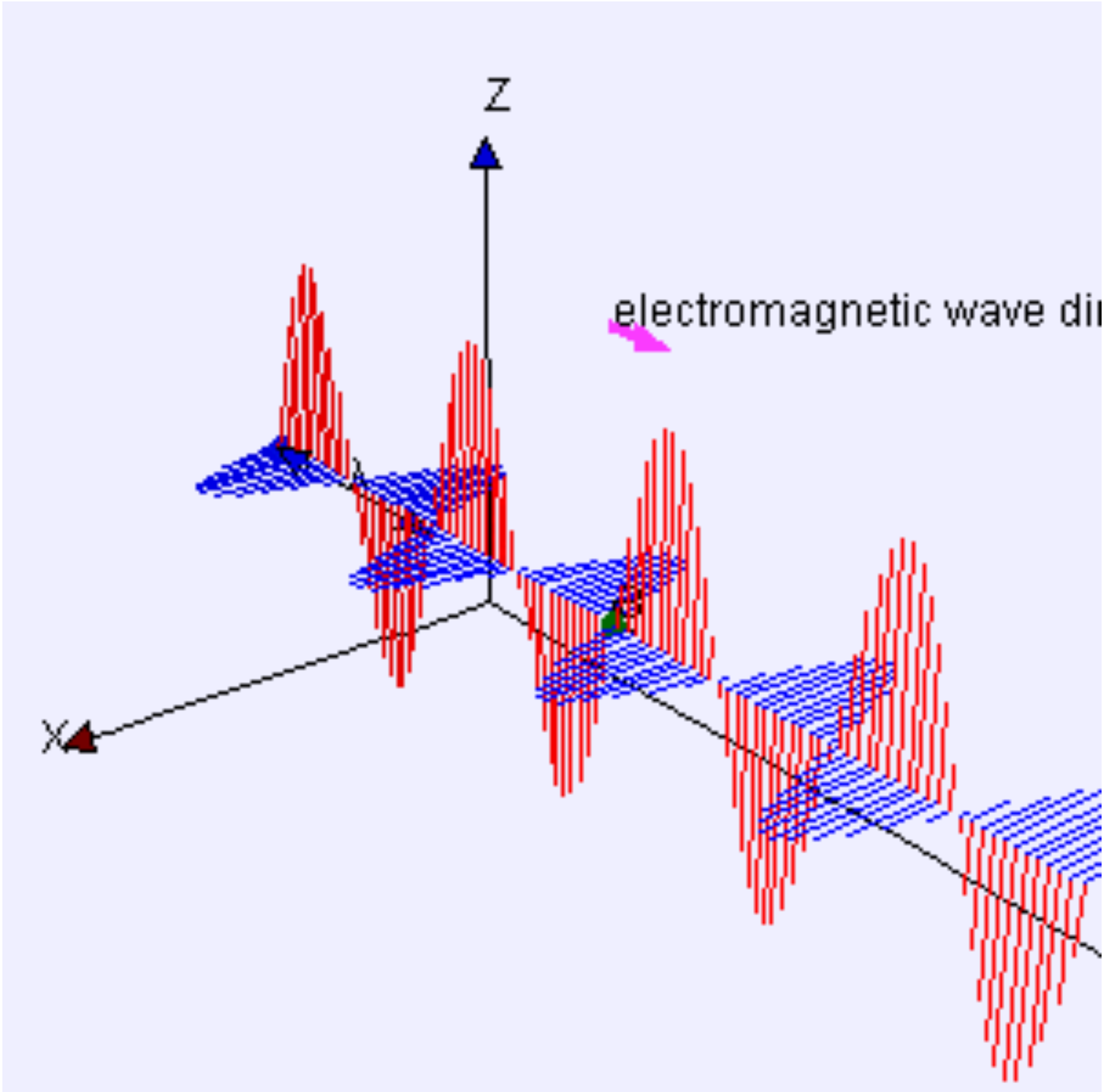
$$\frac{1}{c^2}\frac{\partial^2 \boldsymbol{B}}{\partial t^2} - \Delta \boldsymbol{B} = 0$$

Waves are in phase

Possible solution: Linearly polarized propagating wave along **k**=k_z direction.

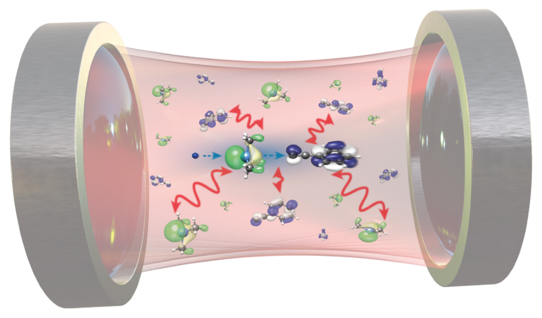
$$\boldsymbol{E}(z,t) = \boldsymbol{E}_x \sin(-\omega t + k_z z)$$

$$\boldsymbol{B}(z,t) = \boldsymbol{B}_y \sin(-\omega t + k_z z)$$



https://en.wikipedia.org/wiki/Maxwell%27s_equations, Jackson, „Classical Electrodynamics, ISBN #9781119770763

Vector Potential and Gauge Freedom



Blackboard

$$\boldsymbol{B}(x, y, z, t) = \nabla \times \boldsymbol{A}(x, y, z, t)$$

magnetic vector potential: $\boldsymbol{A}(x, y, z, t)$

$$\boldsymbol{E}(x, y, z, t) = -\nabla \Phi(x, y, z, t) - \partial_t \boldsymbol{A}(x, y, z, t)$$

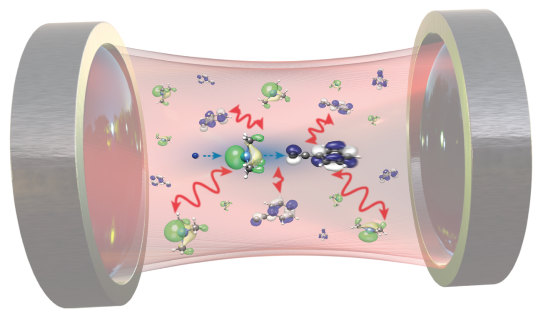
electric scalar potential: $\Phi(x, y, z, t)$

longitudinal electric field (electrostatics)	transverse electric field (dynamics)

Gauge freedom:
$$\boldsymbol{A} \mapsto \boldsymbol{A} + \nabla \varphi$$
$$\Phi \mapsto \Phi - \partial_t \varphi$$

Coulomb gauge choice: $\nabla \cdot \boldsymbol{A} \overset{!}{=} 0$

Macroscopic Maxwell's equation



Presence of materials can be modeled by <u>bound</u> charges and currents

$$\nabla \cdot \boldsymbol{E} = \frac{\rho_{\text{free}} + \rho_{\text{bound}}}{\epsilon_0} = \frac{\rho_{\text{free}} - \nabla \cdot \boldsymbol{P}}{\epsilon_0}$$

Magnetizing field $\boldsymbol{H} = \dfrac{\boldsymbol{B}}{\mu_o} - \boldsymbol{M}$

$$\nabla \times \boldsymbol{B} = \mu_0 \left(\boldsymbol{J}_{\text{free}} + \boldsymbol{J}_{\text{bound}} + \epsilon_0 \frac{\partial \boldsymbol{E}}{\partial t} \right) = \mu_0 \left(\boldsymbol{J}_{\text{free}} + \nabla \times \boldsymbol{M} + \frac{\partial \boldsymbol{P}}{\partial t} + \epsilon_0 \frac{\partial \boldsymbol{E}}{\partial t} \right)$$

Displacement field $\boldsymbol{D} = \epsilon_0 \boldsymbol{E} + \boldsymbol{P}$

Magnetization field **M**

Polarization **P**

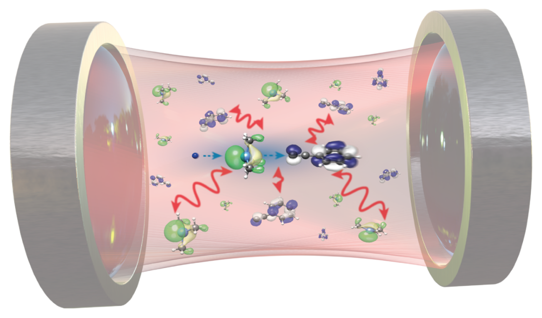
Macroscopic Maxwell's equation:

$$\nabla \cdot \boldsymbol{D} = \rho_{\text{free}}, \ \nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}$$

$$\nabla \cdot \boldsymbol{B} = 0, \ \nabla \times \boldsymbol{H} = \boldsymbol{J}_{\text{free}} + \frac{\partial \boldsymbol{D}}{\partial t}$$

How to describe a material, i.e., bound charges and currents?

Linear Media



How to describe material, i.e., bound charges and currents?

Assume (for the moment) no source terms: $\rho_{\text{free}} = 0,\ \boldsymbol{J}_{\text{free}} = 0$

Time domain:

$$\nabla \cdot \boldsymbol{D} = 0,\ \nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}$$

$$\nabla \cdot \boldsymbol{B} = 0,\ \nabla \times \boldsymbol{H} = \frac{\partial \boldsymbol{D}}{\partial t}$$

Fourier Transform

Frequency domain:

$$\nabla \cdot \boldsymbol{D} = 0,\ \nabla \times \boldsymbol{E} = i\omega \boldsymbol{B}$$

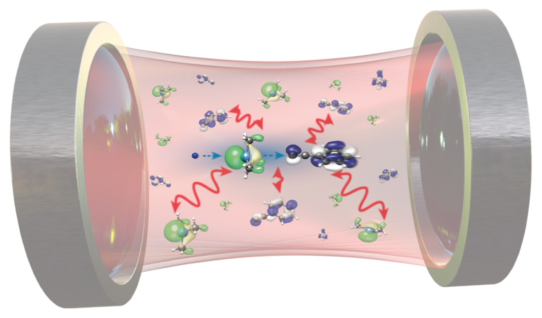
$$\nabla \cdot \boldsymbol{B} = 0,\ \nabla \times \boldsymbol{H} = -i\omega \boldsymbol{D}$$

$$\boldsymbol{P}(\boldsymbol{r}, \omega) = \epsilon_0 \int d\boldsymbol{r}_1 \boxed{\chi_e(\boldsymbol{r}, \boldsymbol{r}_1, \omega)} \boldsymbol{E}(\boldsymbol{r}_1, \omega)$$

Linear media (linear response): **microscopic information about media contained in susceptibility**

$$\boldsymbol{M}(\boldsymbol{r}, \omega) = \mu_0^{-1} \int d\boldsymbol{r}_1 \boxed{\chi_m(\boldsymbol{r}, \boldsymbol{r}_1, \omega)} \boldsymbol{B}(\boldsymbol{r}_1, \omega)$$

Dielectric function: $\epsilon(\boldsymbol{r}, \boldsymbol{r}_1, \omega) = 1 + \chi_e(\boldsymbol{r}, \boldsymbol{r}_1, \omega)$



Lorentz Oscillatory Model

Damped harmonic oscillator driven by external electric field E

1. We wrote the equation of motion by comparing bound charges to a mass on a spring.

$$m_e \frac{\partial^2 \vec{r}}{\partial t^2} + m_e \Gamma \frac{\partial \vec{r}}{\partial t} + m_e \omega_0^2 \vec{r} = -q\vec{E}$$

2. We performed a Fourier transform to solve this equation for ***r***.

$$\vec{r}(\omega) = -\frac{q}{m_e} \frac{\vec{E}(\omega)}{\omega_0^2 - \omega^2 - j\omega\Gamma}$$

3. We calculated the electric dipole moment of the charge displaced by ***r***.

$$\vec{\mu}(\omega) = \frac{q^2}{m_e} \frac{\vec{E}(\omega)}{\omega_0^2 - \omega^2 - j\omega\Gamma}$$

4. We calculated the volume averaged dipole moment to derive the material polarization.

$$\vec{P}(\omega) = \tfrac{1}{V}\sum \vec{\mu}_i(\omega) = N\left\langle \vec{\mu}(\omega)\right\rangle = \varepsilon_0 \chi(\omega) \vec{E}(\omega)$$

5. We calculated the material susceptibility.

$$\chi(\omega) = \frac{\omega_p^2}{\omega_0^2 - \omega^2 - j\omega\Gamma} \qquad \omega_p^2 = \frac{Nq^2}{\varepsilon_0 m_e}$$

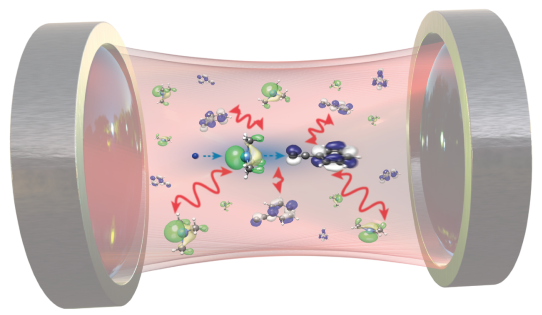
6. We calculated the dielectric function.

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 (1 + \chi_e) \mathbf{E} = \varepsilon_0 \varepsilon_r \mathbf{E}$$

$$\boxed{\tilde{\varepsilon}_r(\omega) = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - j\omega\Gamma}}$$

https://empossible.net/wp-content/uploads/2018/03/Lecture-2-Lorentz-and-Drude-models.pdf

Lorentz Oscillatory Model



Dielectric function and complex refractive index

Complex refractive index: $\tilde{n} = n + j\kappa$

refractive index (bending of light)

extinction coefficient (absorption of light)

relation to **dielectric function**: $\tilde{n}^2 = \tilde{\epsilon}_r = \epsilon_r' + j\epsilon_r''$

store electrical energy

dissipate electrical energy

$$\vec{E}(z) = \vec{E}_0 e^{jkz}$$

$$k = k_0\tilde{n} \qquad k_0 = \frac{2\pi}{\lambda_0}$$

Substituting the complex refractive index into this equation leads to…

$$\vec{E}(z) = \vec{E}_0 e^{jk_0(n+j\kappa)z} = \vec{E}_0 e^{-k_0\kappa z} e^{jk_0 n z}$$

envelope term

Oscillatory term

$$\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P} = \varepsilon_0(1+\chi_e)\mathbf{E} = \varepsilon_0\varepsilon_r\mathbf{E}$$

$$\boxed{\varepsilon_r'(\omega) = 1 + \omega_p^2 \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \omega^2\Gamma^2} \qquad \varepsilon_r''(\omega) = \omega_p^2 \frac{\omega\Gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2\Gamma^2}}$$

https://empossible.net/wp-content/uploads/2018/03/Lecture-2-Lorentz-and-Drude-models.pdf

Lorentz Oscillatory Model

Properties

Transmissive

$$\omega < \omega_0 - \frac{\Gamma}{2}$$

Absorptive

$$\omega_0 - \frac{\Gamma}{2} < \omega < \omega_0 + \frac{\Gamma}{2}$$

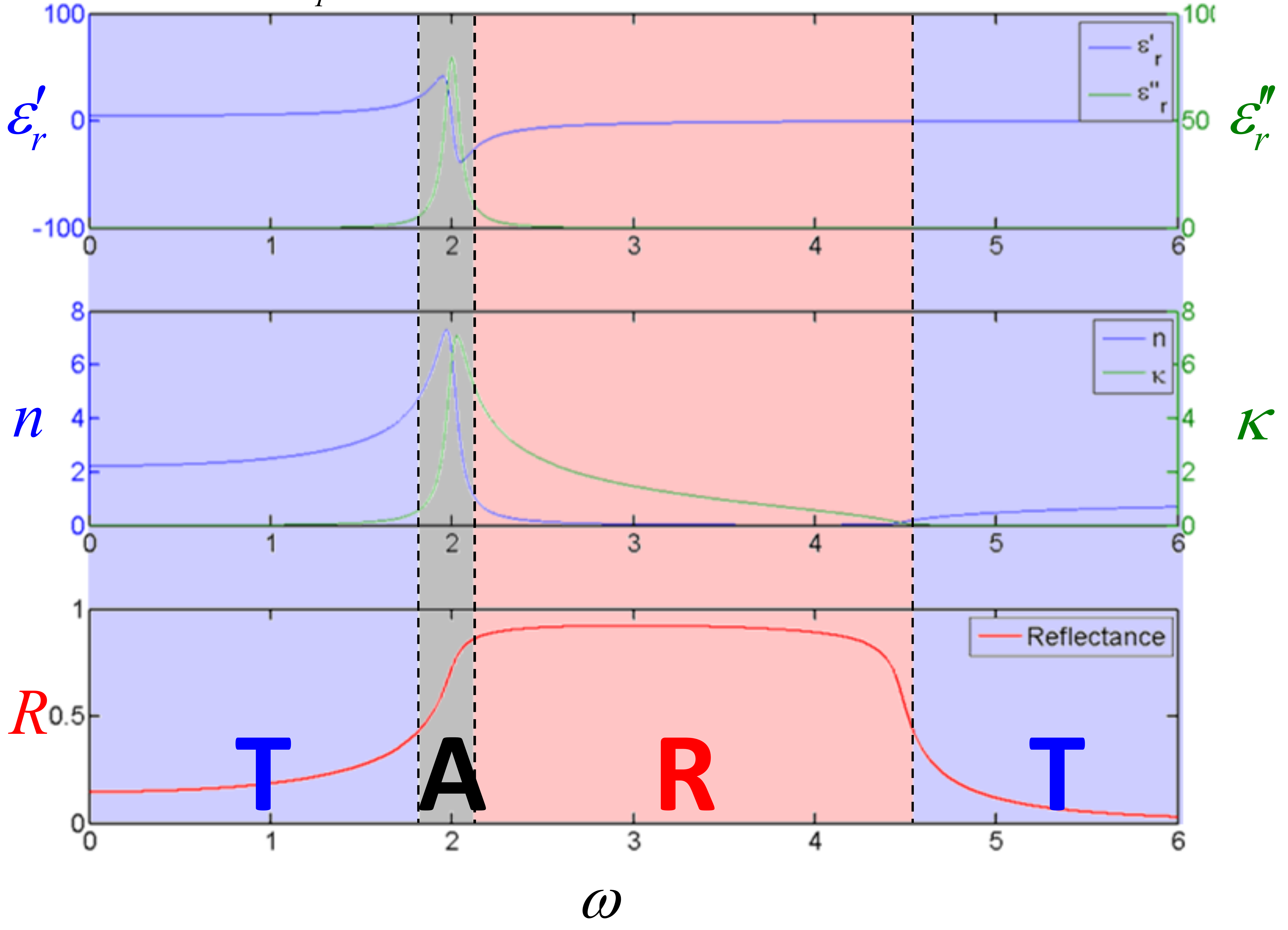
Reflective

$$\omega_0 + \frac{\Gamma}{2} < \omega < \omega_p$$

Transmissive

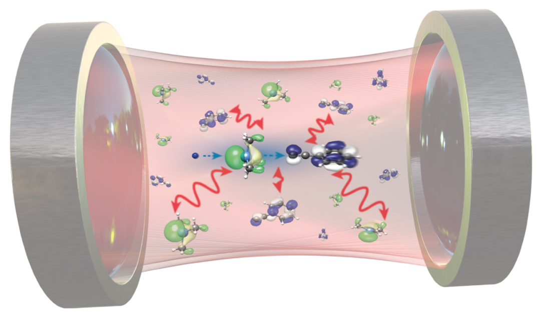
$$\omega > \omega_p$$

$\omega_p = 4$ $\omega_0 = 2$ $\Gamma = 0.1$



https://empossible.net/wp-content/uploads/2018/03/Lecture-2-Lorentz-and-Drude-models.pdf

Drude Model for a Metal



In metals, most electrons are free because they are not bound to a nucleus. For this reason, the restoring force is negligible and there is no natural frequency.

We derive the Drude model for metals by assuming ω_0=0.

$$\tilde{\varepsilon}_r(\omega) = 1 + \frac{\omega_p^2}{\cancel{\omega_0^2} - \omega^2 - j\omega\Gamma} \qquad \omega_p^2 = \frac{Nq^2}{\varepsilon_0 m_e}$$

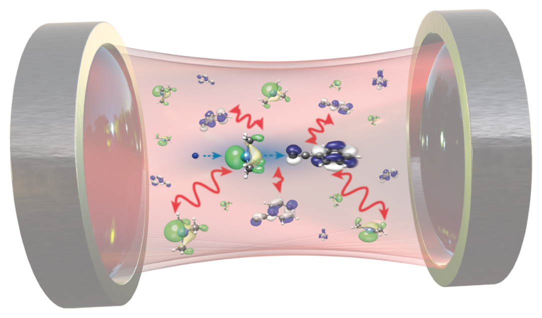
$$\boxed{\tilde{\varepsilon}_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + j\omega\Gamma}}$$

Note, N is now interpreted as electron density N_e.

m_e is the effective mass of the electron.

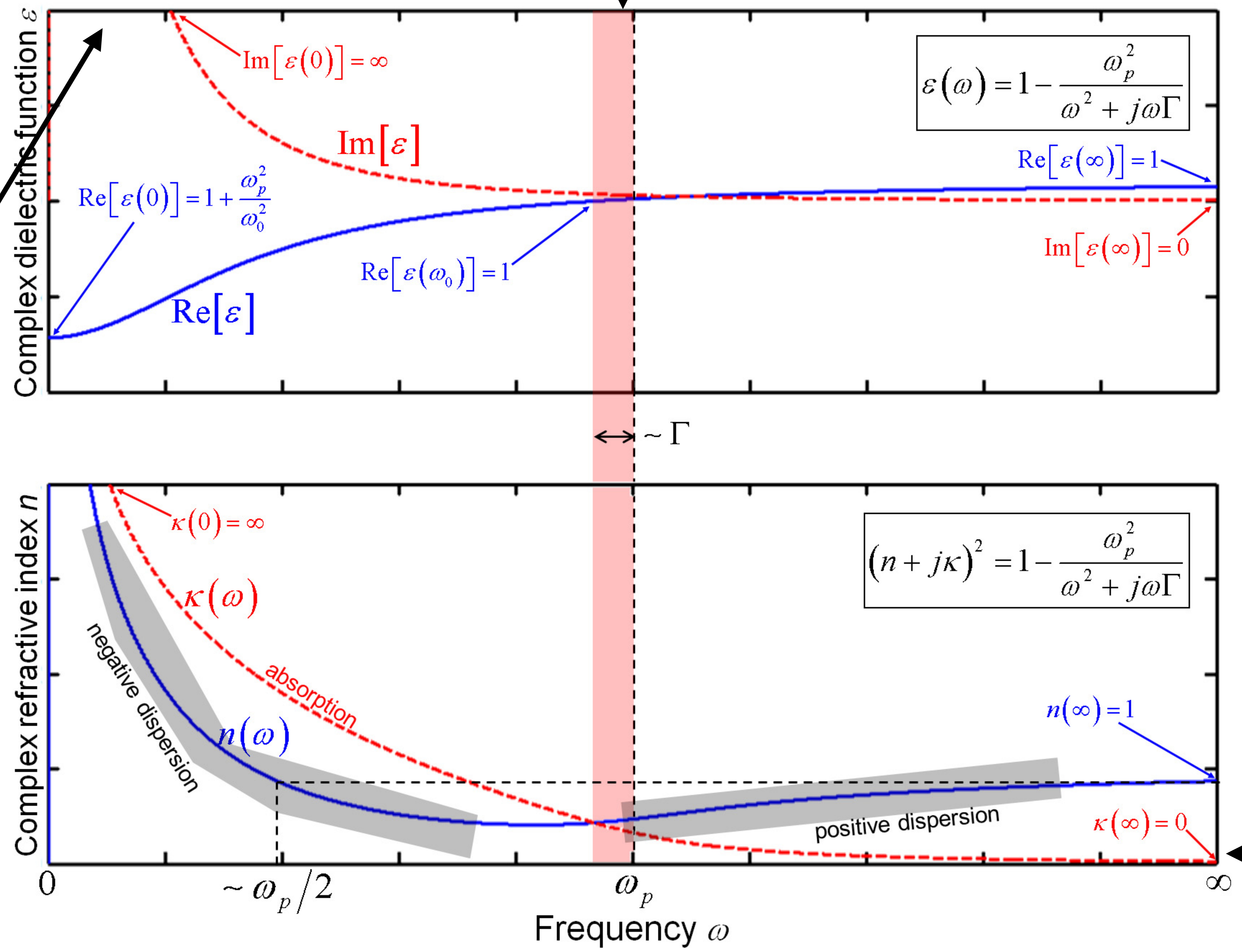
https://empossible.net/wp-content/uploads/2018/03/Lecture-2-Lorentz-and-Drude-models.pdf

Features of Drude Model



Near plasma frequency, real and imaginary parts of permittivity significant. Metal very lossy

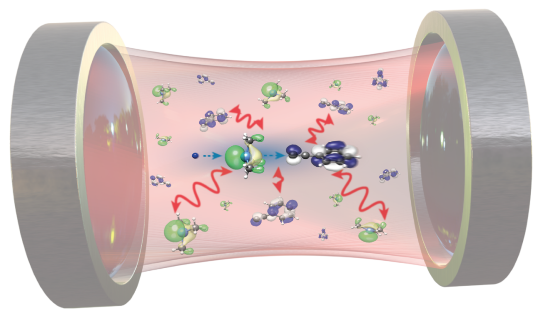
Low frequency, good conductor (dielectric constant mostly imaginary)



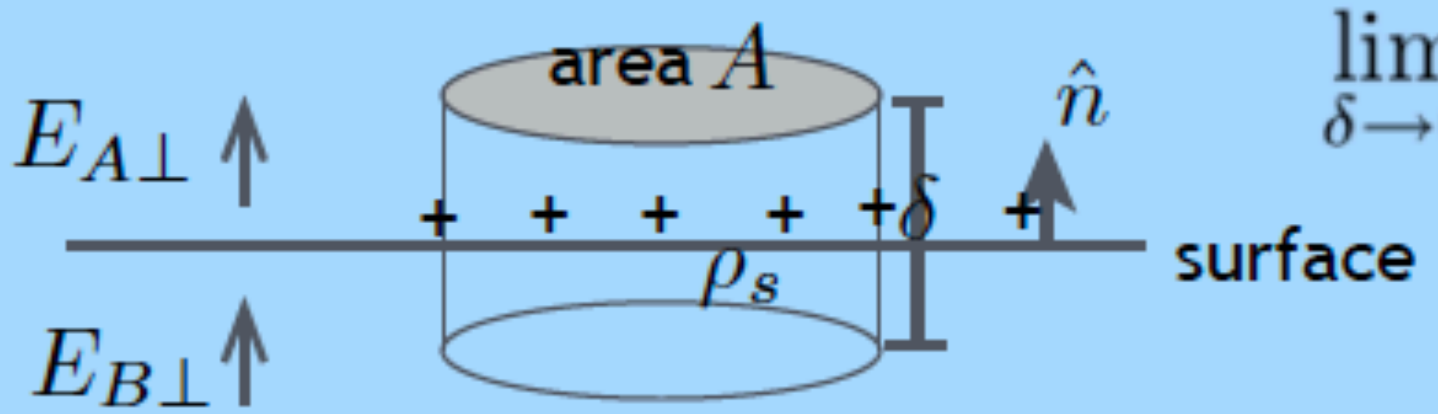
Plasma frequency for typical metals in UV regime -> reflect visible light

High frequency, no losses.
Metal transparent

Maxwell's Equations



Stationary Boundary Conditions for Electric Field

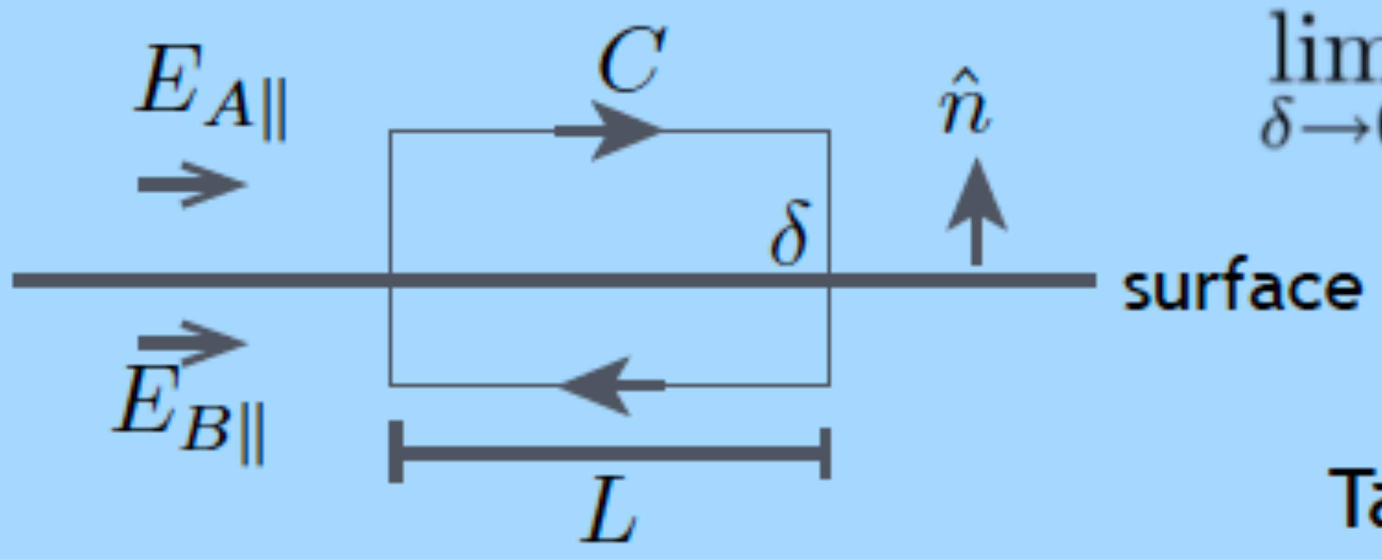


$$\lim_{\delta\to 0} \; Gauss \Rightarrow (\epsilon_0 E_{A\perp} - \epsilon_0 E_{B\perp})A = \rho_s A$$

$$\hat{n}\cdot(\epsilon_0 E_A - \epsilon_0 E_B) = \rho_s$$

Source: Surface charge

Normal $\vec{E}$ is discontinuous at a surface charge.



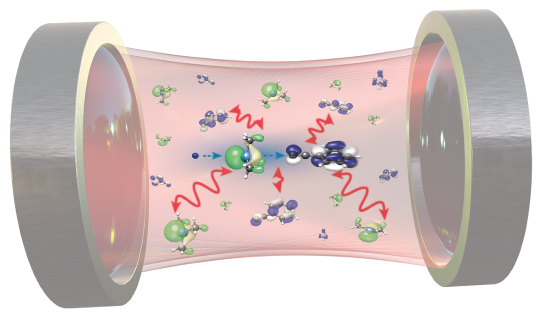
$$\lim_{\delta\to 0} \; Faraday \Rightarrow (E_{A\|} - E_{B\|})L = 0$$

$$\hat{n}\times(E_A - E_B) = 0$$

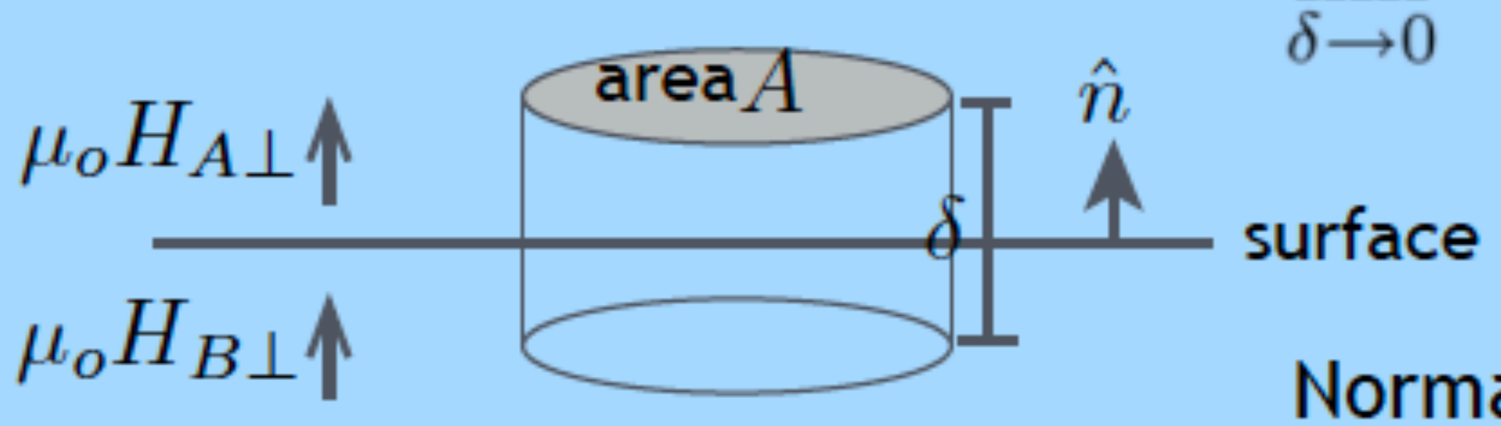
Tangential $\vec{E}$ is continuous at a surface.

https://ocw.mit.edu/courses/6-007-electromagnetic-energy-from-motors-to-lasers-spring-2011

Maxwell's Equations



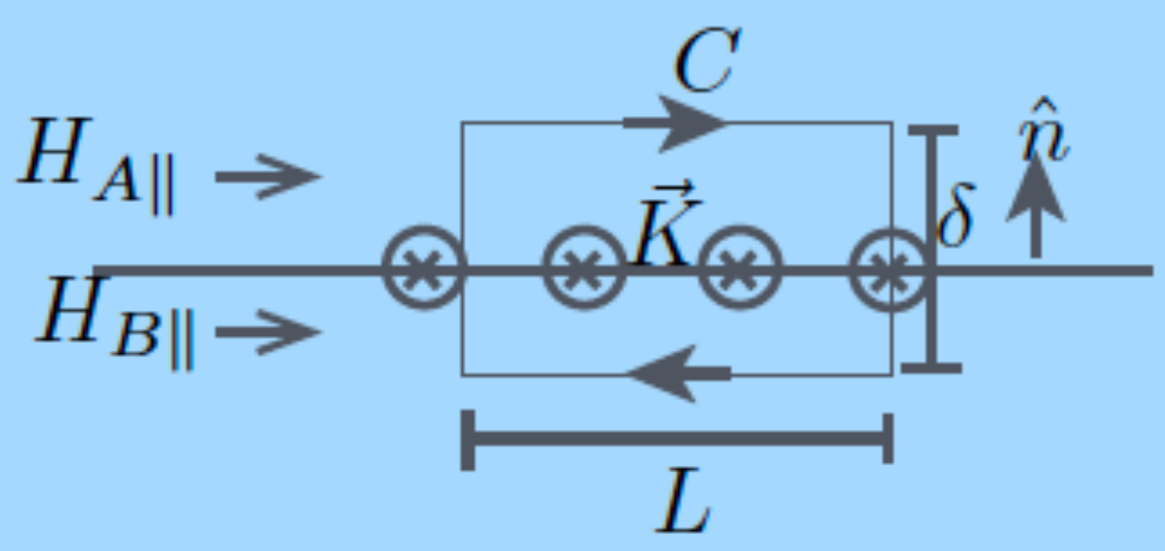
Stationary Boundary Conditions for Magnetic Field



$$\lim_{\delta \to 0} \; Gauss \Rightarrow (\mu_0 H_{A\perp} - \mu_0 H_{B\perp})A = 0$$

$$\hat{n} \cdot (\mu_0 H_A - \mu_0 H_B) = 0$$

Normal $\mu_o \vec{H}$ is continuous at a surface.



$$\lim_{\delta \to 0} \; Ampere \Rightarrow (H_{A\|} - H_{B\|})L = K\,L$$

$$\hat{n} \times (H_A - H_B) = \vec{K}$$

Tangential $\vec{H}$ is discontinuous at a surface current $\vec{K}$.

Source: Surface currents

https://ocw.mit.edu/courses/6-007-electromagnetic-energy-from-motors-to-lasers-spring-2011

Sources and Radiation

With a source current, Helmholtz equation for the electric field reads,

$$\left[\nabla\times\kappa(\mathbf{r},\omega)\nabla\times-\frac{\omega^2}{c^2}\epsilon(\mathbf{r},\omega)\right]\mathbf{E}(\mathbf{r},\omega)=i\omega\mu_0\,\mathbf{J}(\mathbf{r},\omega)$$

In the presence of a time dependent current, electromagnetic radiation can form. The simplest form is dipole radiation,

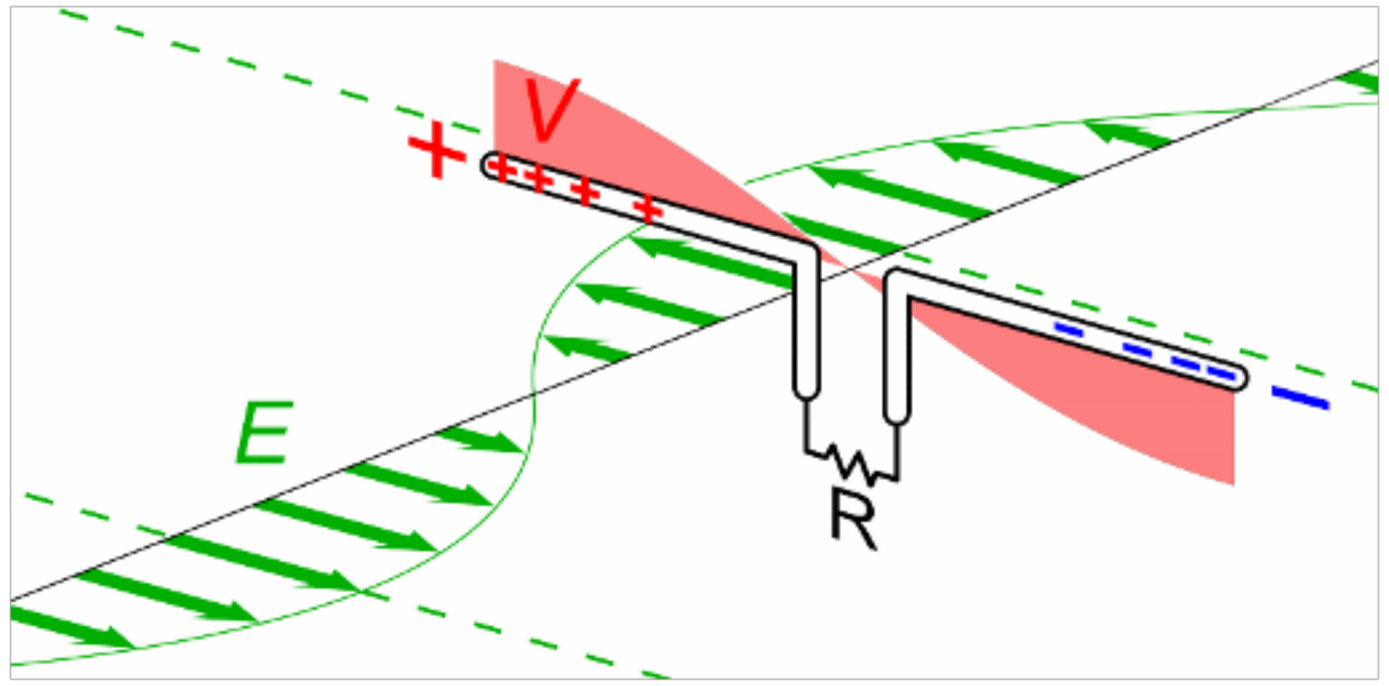


Figure from Wikipedia: https://en.wikipedia.org/wiki/Dipole_antenna (16/4-2024)

To solve for general current sources, it makes sense to define the so called Dyadic Green's function

$$\left[\nabla\times\kappa(\mathbf{r},\omega)\nabla\times-\frac{\omega^2}{c^2}\epsilon(\mathbf{r},\omega)\right]\mathbf{G}(\mathbf{r},\mathbf{r}',\omega)=\mathbf{I}\delta(\mathbf{r}-\mathbf{r}')$$

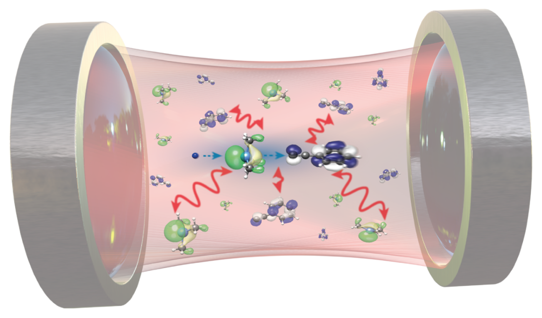
Using the Dyadic Green's Function, we can solve for a general current distribution using the superposition principle

$$\mathbf{E}(\mathbf{r},\omega)=i\omega\mu_0\int d\mathbf{r}'\mathbf{G}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{j}(\mathbf{r},\omega)$$

Physically, the Dyadic Green's Function is the **field response function** to the presence of a point dipole,

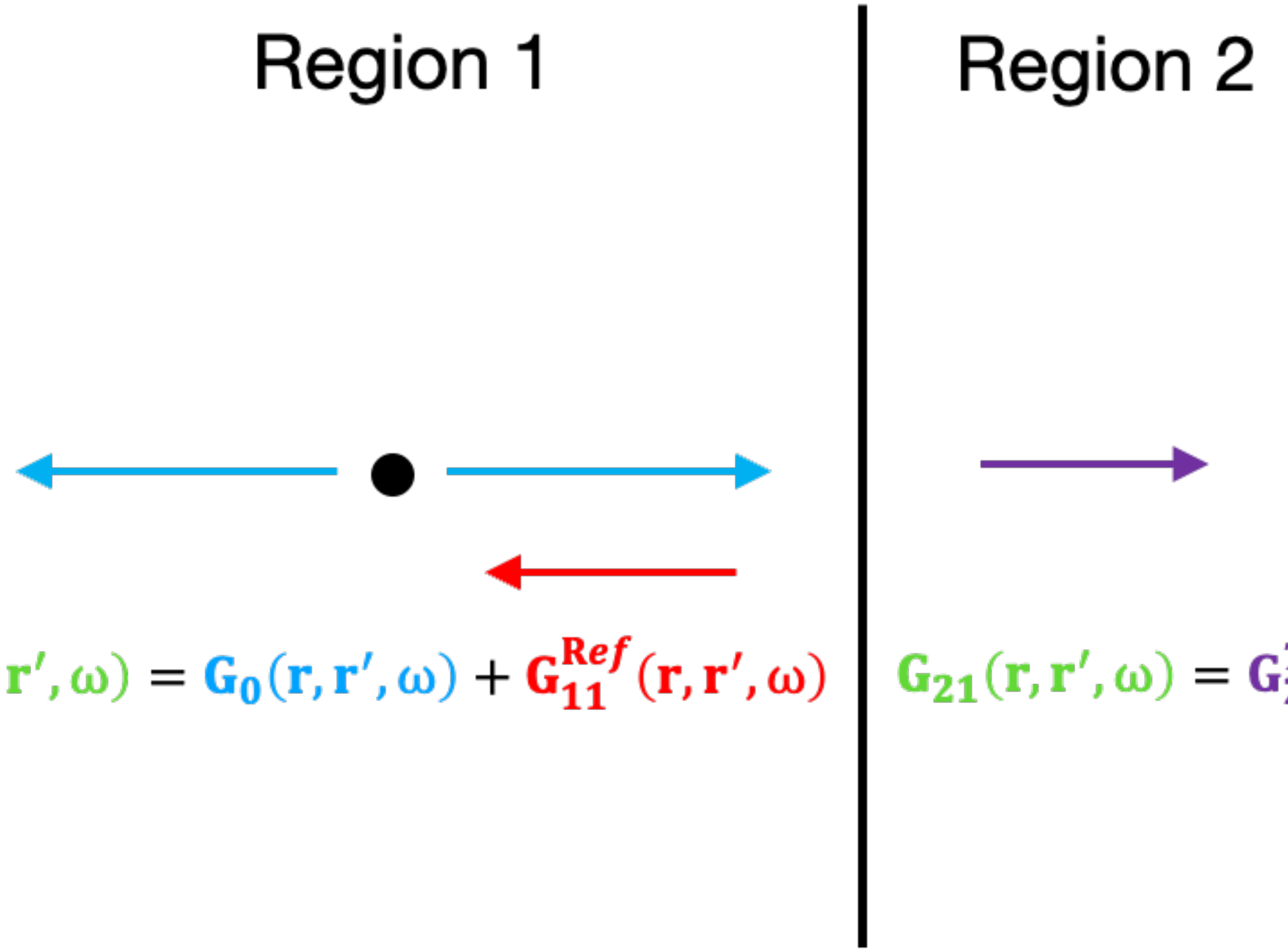
$$\mathbf{E}(\mathbf{r},\omega)=\omega^2\mu_0\mathbf{G}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{d}$$

Calculating the Dyadic Green's Function



The full DGF is a superposition of the bare dipole fields, and the fields that result from reflection

$$\mathbf{G}_{nm}(\mathbf{r},\mathbf{r}',\omega) = \mathbf{G}_0(\mathbf{r},\mathbf{r}',\omega)\delta_{nm} + \mathbf{G}_{nm}^{R/T}(\mathbf{r},\mathbf{r}',\omega)$$



$$\mathbf{G}_{11}(\mathbf{r},\mathbf{r}',\omega) = \mathbf{G}_0(\mathbf{r},\mathbf{r}',\omega) + \mathbf{G}_{11}^{Ref}(\mathbf{r},\mathbf{r}',\omega)$$

$$\mathbf{G}_{21}(\mathbf{r},\mathbf{r}',\omega) = \mathbf{G}_{21}^{Trans}(\mathbf{r},\mathbf{r}',\omega)$$

In practice, the DGF can be calculated by expanded in suitlable basis functions **(Exercise).**

Planarly layered geometry:

- Plane waves

Spherically layered media:

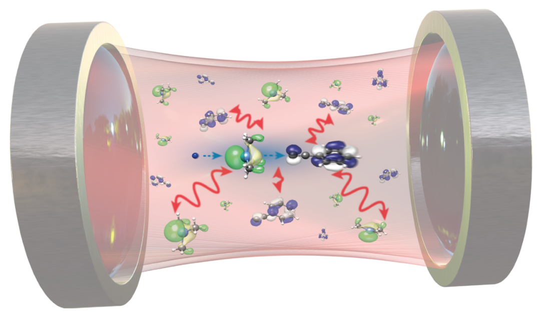
- Vector spherical harmonics

General setups:

- Finite element simulations

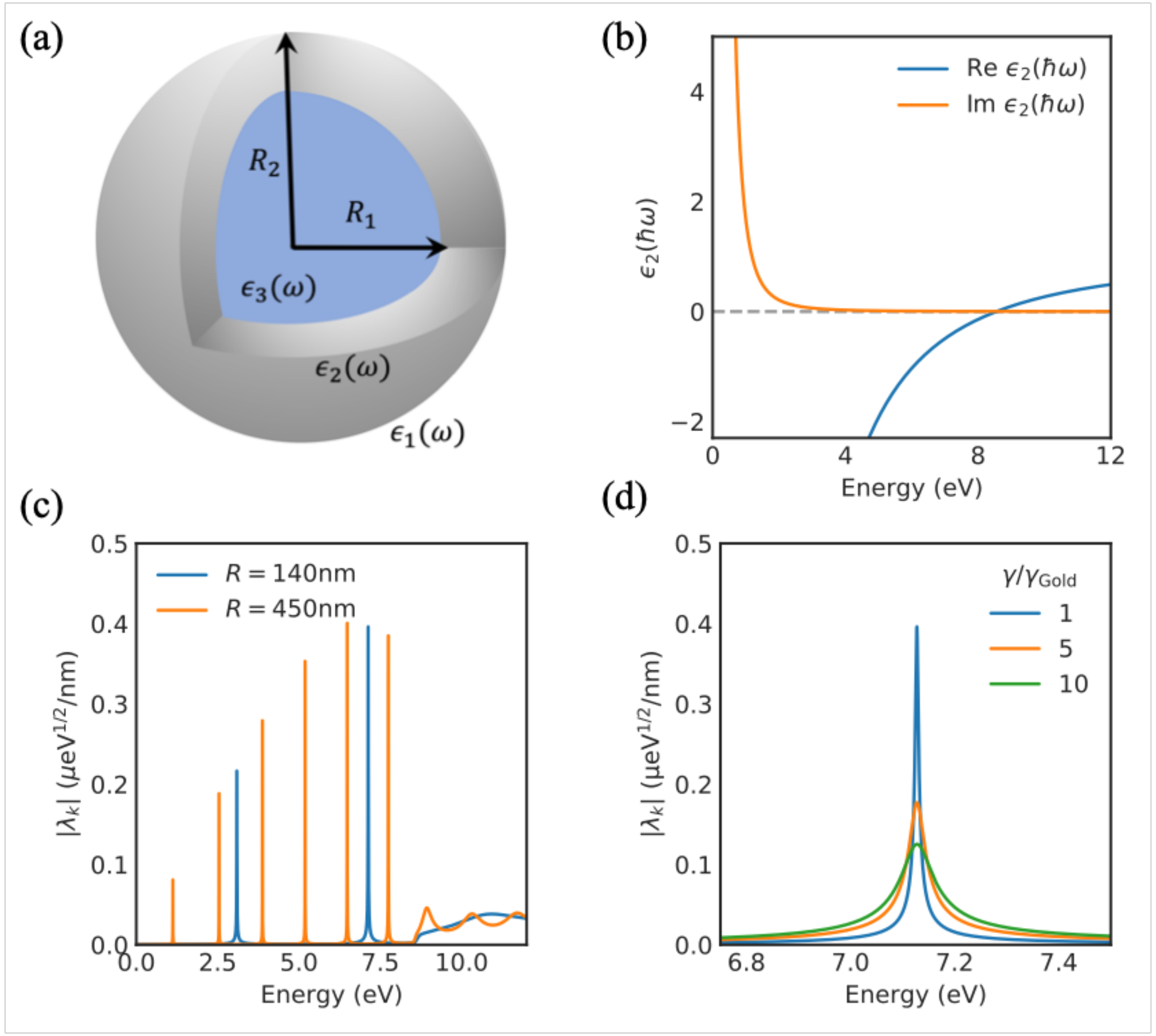
CECAM lecture Mark Svendsen, Frieder Lindel

Exercise 2



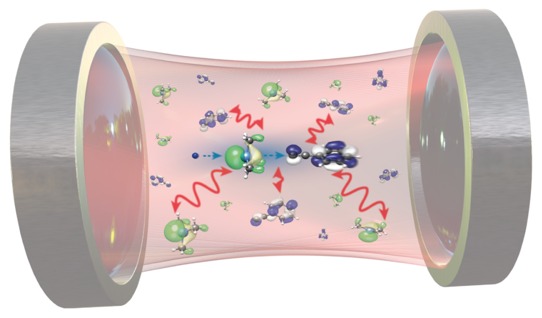
Drude model for spherical Cavity

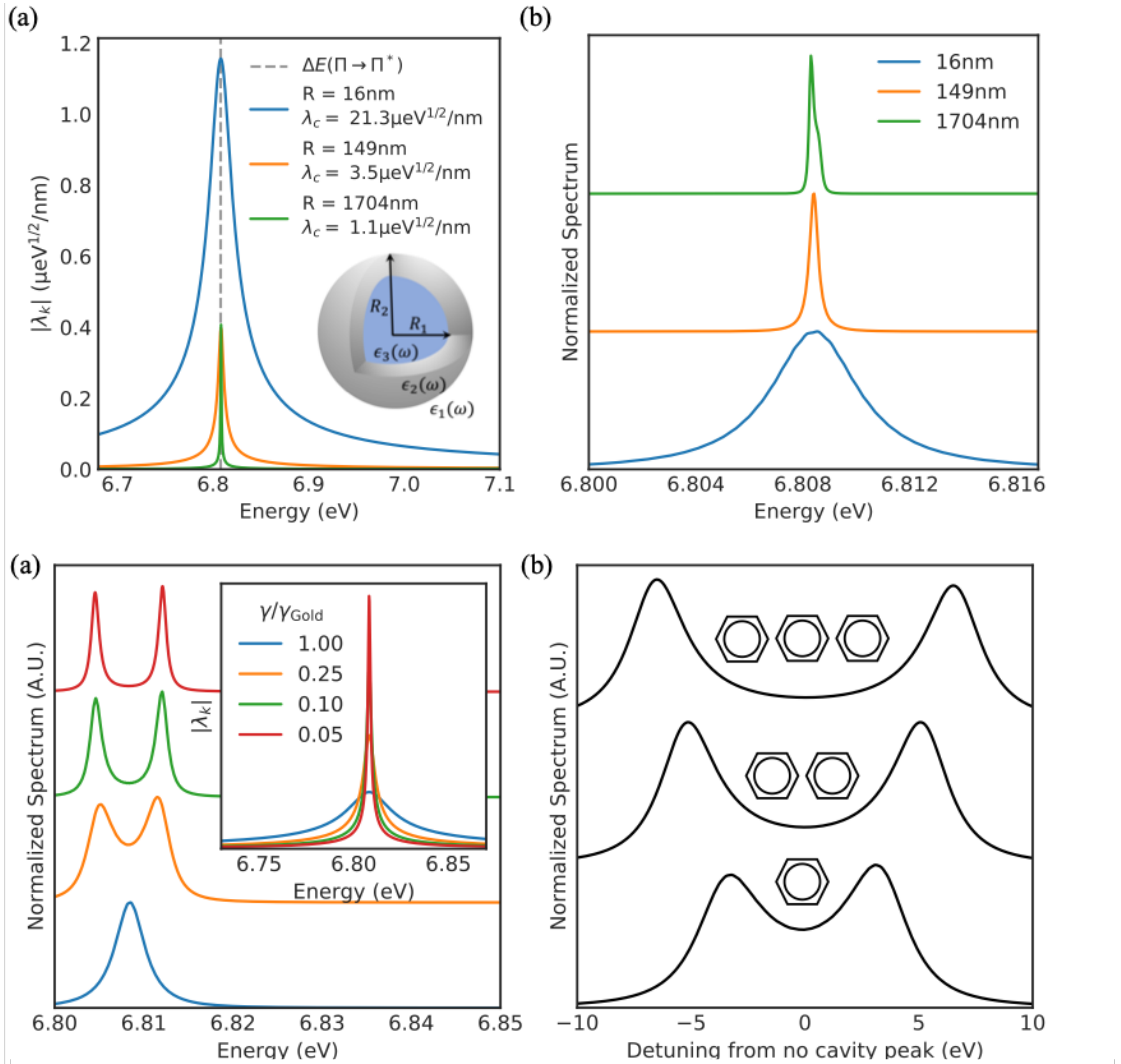
Realistic Spherical Cavity



Svendsen, Mark Kamper, et al. "Ab Initio Calculations of Quantum Light–Matter Interactions in General Electromagnetic Environments." *Journal of Chemical Theory and Computation* 20.2 (2024): 926-936.

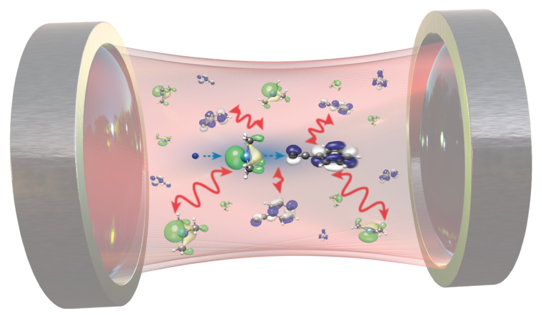
Coupling to Matter: Benzene in Realistic Spherical Cavity





Svendsen, Mark Kamper, et al. "Ab Initio Calculations of Quantum Light–Matter Interactions in General Electromagnetic Environments." *Journal of Chemical Theory and Computation* 20.2 (2024): 926-936.

Summary



1. Maxwell's equations describe **classical electro-magnetic fields (statics and dynamics)**.
2. The magnetic field B can be expressed in terms of a **magnetic vector potential A**. This provides an **ambiguity** in the mathematical description, which is fixed by a specific **gauge choice** (typically Coulomb). Remark: A-field will be **important for quantized light-matter interaction**.
3. **Macroscopic Maxwell's equations** model optical **response of (macroscopic) media** in terms of magnetizing and displacement field.
4. **Boundary conditions** of Maxwell's equations are crucial to determine the electro-magnetic fields.
5. **Material properties** (e.g. **Drude-model** for the metal mirrors) and **shape** of a cavity allow to **design** specific **light-matter interactions**.