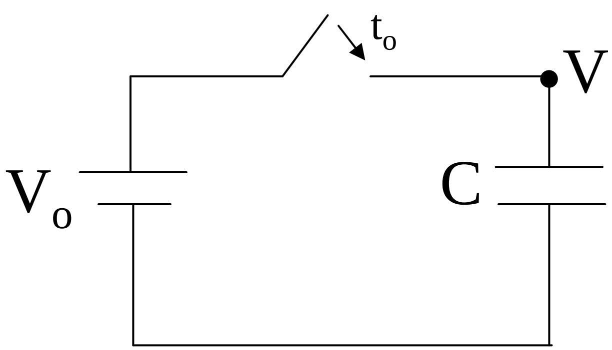
Dielectric and Optical Properties

- As with conductivity, we will start with macroscopic property and connect to the microscopic
- All aspects of free electrons have been covered: only bound electrons left
- Capacitance, Optical properties --> ε,n --> molecules and atoms

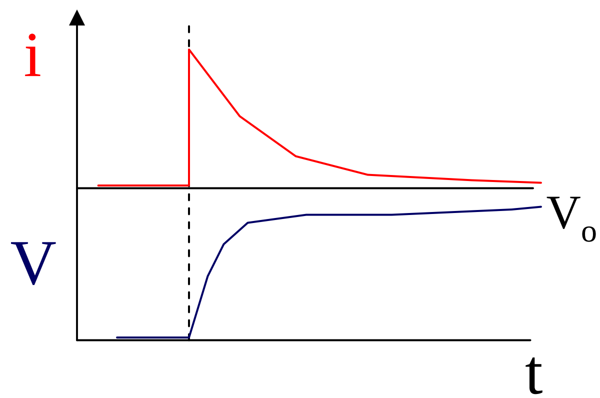
<u>Review of capacitance and connection to dielectric constant</u>

First, no material in capacitor

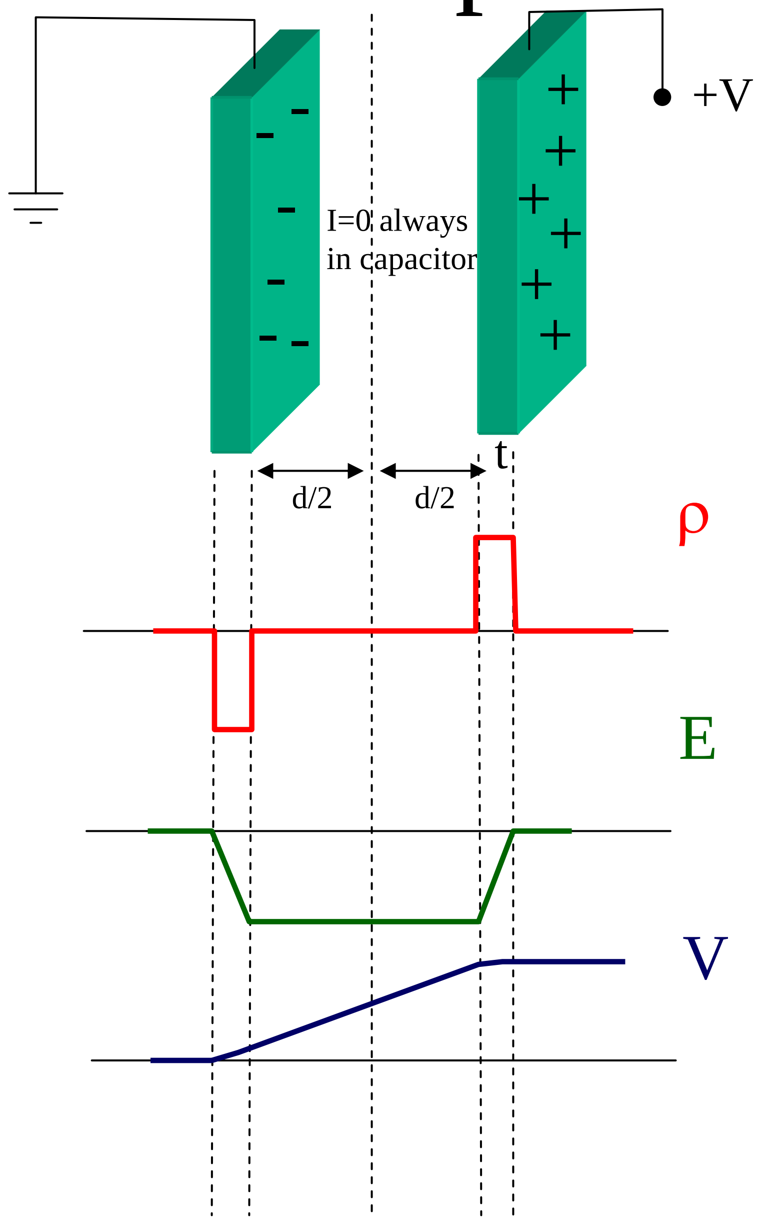


$$Q = CV$$

$$\frac{dq}{dt} = i = C\frac{dV}{dt}$$



The Capacitor



$$\nabla \cdot E = \frac{\rho}{\varepsilon_o}$$

$$E = \int_{\frac{-d}{2}-t}^{\frac{-d}{2}} \frac{\rho}{\varepsilon_o} dx = \frac{\rho t}{\varepsilon_o} = \frac{Q}{A\varepsilon_o}$$

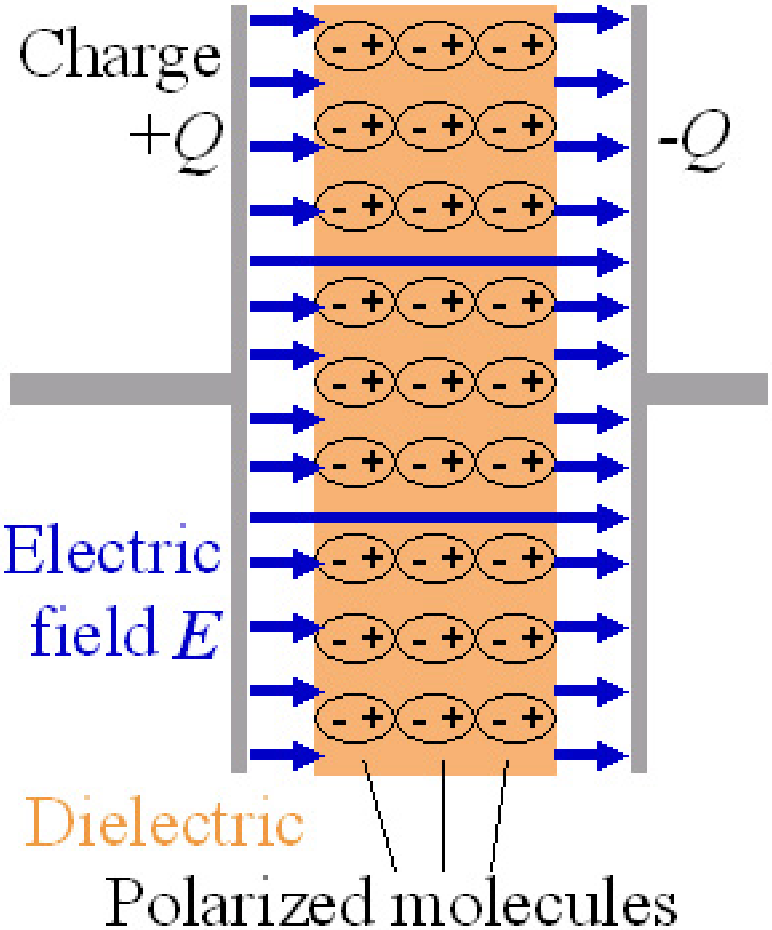
$$V = \int_{\frac{-d}{2}}^{\frac{d}{2}} E dx = \frac{Qd}{A\varepsilon_o}$$

$$\frac{Q}{C} = V = \frac{Qd}{A\varepsilon_o}$$

$$C = \frac{\varepsilon_o A}{d}$$

The Capacitor

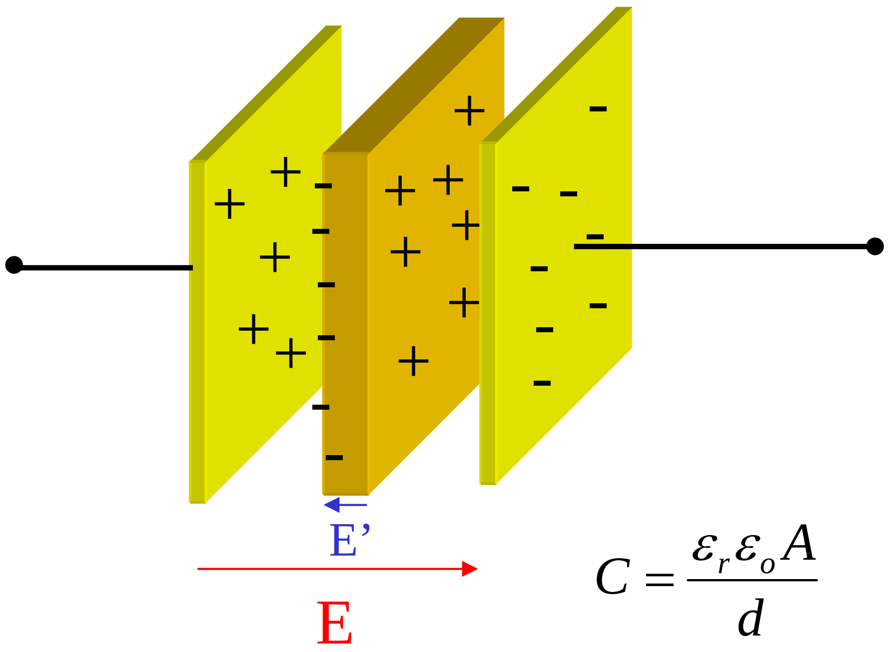
- The air-gap can store energy!
- If we can move charge temporarily without current flow, can store even more
- Bound charge around ion cores in a material can lead to dielectric properties



- Two kinds of charge can create plate charge:
  - surface charge
  - dipole polarization in the volume
- Gauss' law can not tell the difference (only depends on charge per unit area)

Image from Wikimedia Commons, http://commons.wikimedia.org

Material Polarization



$$C = \frac{\varepsilon_r \varepsilon_o A}{d}$$

$$E' = P$$

$$D = \varepsilon_o E + P = \varepsilon E$$

$$\varepsilon = \varepsilon_r \varepsilon_o$$

$$\varepsilon_r = 1 + \frac{P}{\varepsilon_o E} = 1 + \chi$$

P is the Polarization

D is the Electric flux density or the Dielectric displacement

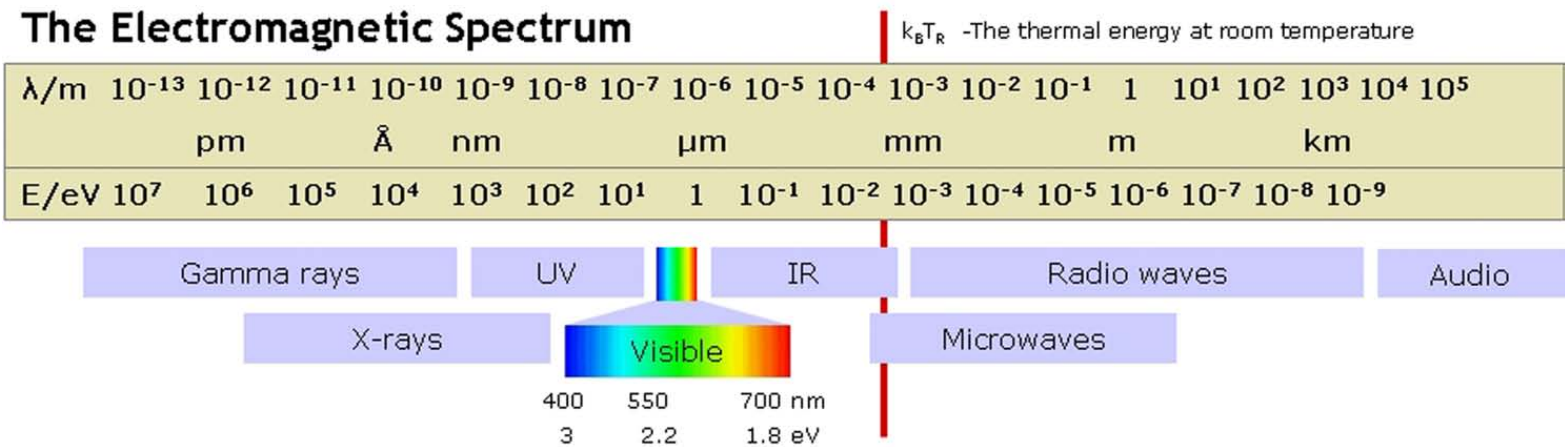
χ is the dielectric or electric susceptibility

All detail of material response is in ε_r and therefore P

Origin of Polarization

- We are interested in the true dipoles creating polarization in materials (not surface effect)
- As with the free electrons, what is the response of these various dipole mechanisms to various E-field frequencies?
- When do we have to worry about controlling
  - molecular polarization (molecule may have non-uniform electron density)
  - ionic polarization (E-field may distort ion positions and temporarily create dipoles)
  - electronic polarization (bound electrons around ion cores could distort and lead to polarization)
- Except for the electronic polarization, we might expect the other mechanisms to operate at lower frequencies, since the units are much more massive
- What are the applications that use waves in materials for frequencies below the visible?

Application for different E-M Frequencies



Courtesy of the Opensource Handbook of Nanoscience and Nanotechnology,
http://en.wikibooks.org/wiki/Nanotechnology

In communications, many E-M waves travel in insulating materials: What is the response of the material (ε_r) to these waves?

Wave Eqn. With Insulating Material and Polarization

$$\nabla x\vec{E} = -\frac{\partial \vec{B}}{\partial t}$$

$$\nabla x\vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t} \xrightarrow{nonmag} \nabla x\vec{B} = \vec{J} + \frac{\partial\left(\varepsilon_o \vec{E} + \vec{P}\right)}{\partial t} \xrightarrow{insulating} \nabla x\vec{B} = \varepsilon \frac{\partial \vec{E}}{\partial t}$$

$$(\vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon \vec{E})$$

$$\nabla^2 E = \mu_0 \varepsilon_0 \varepsilon_r \frac{\partial^2 E}{\partial t^2} = \frac{\varepsilon_r}{c^2} \frac{\partial^2 E}{\partial t^2}$$

$$E = E_0 e^{i(k \bullet r - \varpi t)} = E_0 e^{ik \bullet r} e^{-i\varpi t} = E(r) e^{-i\varpi t}$$

$$\nabla^2 E(r) = -\frac{\omega^2 \varepsilon_r E(r)}{c^2}$$

$$\omega^2 = \frac{c^2}{\varepsilon_r} k^2$$

$$\omega = \frac{c}{\sqrt{\varepsilon_r}} k \xrightarrow{optical} \frac{c}{n} k$$

So polarization slows down the velocity of the wave in the material

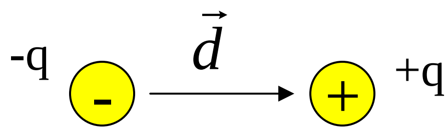
Compare Optical (index of refraction) and Electrical Measurements of ε

Material	Optical, n^2	Electrical, ε	
diamond	5.66	5.68	Only electrical polariztion
NaCl	2.25	5.9	Electrical and ionic polariztion
H_2O	1.77	80.4	Electrical, ionic, and molecular polariztion

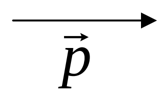
Polarization that is active depends on material and frequency

Microscopic Frequency Response of Materials

- Bound charge can create dipole through charge displacement
- Hydrodynamic equation (Newtonian representation) will now have a restoring force
- Review of dipole physics:



Dipole moment: $\vec{p} = q\vec{d}$



Applied E-field rotates dipole to align with field:

Torque $\vec{\tau} = \vec{p} x \vec{E}$

Potential Energy $U = -\vec{p} \cdot \vec{E} = \left|\vec{p}\right|\left|\vec{E}\right| \cos\theta$

Microscopic Frequency Response of Materials

- For a material with many dipoles:

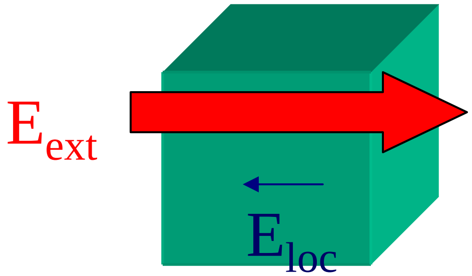
$$\vec{P} = N\vec{p} = N\alpha\vec{E} \; (\vec{p} = \alpha\vec{E})$$

(polarization=(#/vol)*dipole polarization)
α=polarizability

$$\chi = \frac{|\vec{P}|}{\varepsilon_o |\vec{E}|}, \text{ so } \chi = N\alpha$$

$\vec{p} = \alpha\vec{E}$ Actually works well only for low density of dipoles, i.e. gases: little screening

For solids where there can be a high density: local field



For a spherical volume inside (theory of local field),

$$\vec{E}_{loc} = \vec{E}_{ext} + \frac{\vec{P}}{3\varepsilon_o}$$

Microscopic Frequency Response of Materials

- We now need to derive a new relationship between the dielectric constant and the polarizability

$$D = \varepsilon_r \varepsilon_o E_{ext} = \varepsilon_o E_{ext} + P$$

$$P = \varepsilon_r \varepsilon_o E_{ext} - \varepsilon_o E_{ext}$$

$$E_{loc} = E_{ext}\left(\frac{2+\varepsilon_r}{3}\right)$$

Plugging into $P = N\alpha E_{loc}$:

$$\varepsilon_r \varepsilon_o E_{ext} - \varepsilon_o E_{ext} = N\alpha \frac{(\varepsilon_r + 2)}{3} E_{ext}$$

$$(\varepsilon_r - 1)\varepsilon_o = \frac{N\alpha}{3}(\varepsilon_r + 2)$$

Clausius-Mosotti Relation:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N\alpha}{3\varepsilon_o} = \frac{\alpha}{3v\varepsilon_o}$$

Where v is the volume per dipole (1/N)

Macro Micro

Different Types of Polarizability

Highest natural frequency ↕ Lowest natural frequency

- Atomic or electronic, α_e
- Displacement or ionic, α_i
- Orientational or dipolar, α_o

Lightest mass ↕ Heaviest mass

$$\alpha = \alpha_e + \alpha_i + \alpha_o$$

As with free e-, we want to look at the time dependence of the E-field: $E = E_o e^{-i\omega t}$

$$m\frac{\partial^2 x}{\partial t^2} = \frac{m}{\tau}\frac{\partial x}{\partial t} - eE - Kx$$

Response, Drag, Driving Force, Restoring Force

$$m\ddot{x} = -eE - Kx$$

$$x = x_o e^{-i\omega t}$$

$$m(-\omega^2)x_o = -eE_o - Kx_o$$

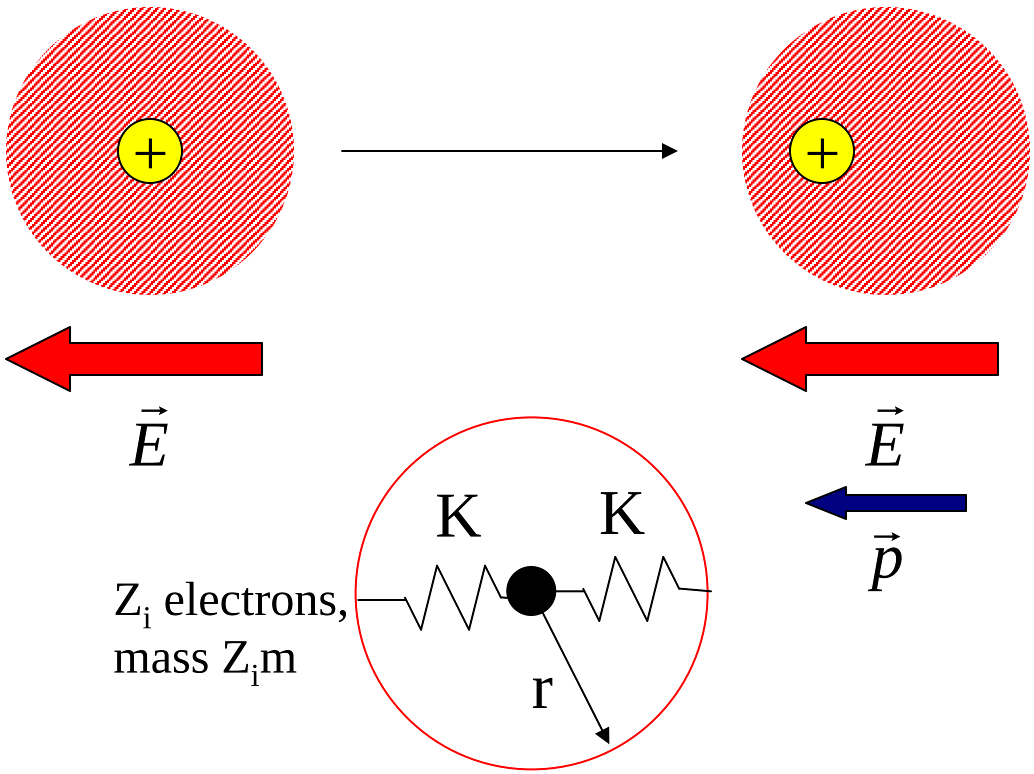
$$x_o = \frac{eE_o}{m\left(\omega^2 - \frac{K}{m}\right)} = \frac{eE_o}{m\left(\omega^2 - \omega_o^2\right)}$$

$$\omega_o = \sqrt{\frac{K}{m}}$$

So lighter mass will have a higher critical frequency

Classical Model for Electronic Polarizability

- Electron shell around atom is attached to nucleus via springs



$$Z_i m\ddot{r} = -Kr - Z_i e E_{loc}, \text{ assume } r = r_o e^{-i\omega t}$$

Electronic Polarizability

$$r_o = \frac{eE_o}{m\left(\omega^2 - \frac{K}{mZ_i}\right)}$$

$$r_o = \frac{eE_o}{m\left(\omega^2 - \omega_{oe}^2\right)}; \;\; \omega_{oe} = \sqrt{\frac{K}{mZ_i}}$$

$$p = qd = -Z_i er; \;\; p = p_o e^{-i\omega t}$$

$$p_o = \frac{Z_i e^2}{m\left(\omega^2 - \omega_o^2\right)} E_o = \alpha_e E_o$$

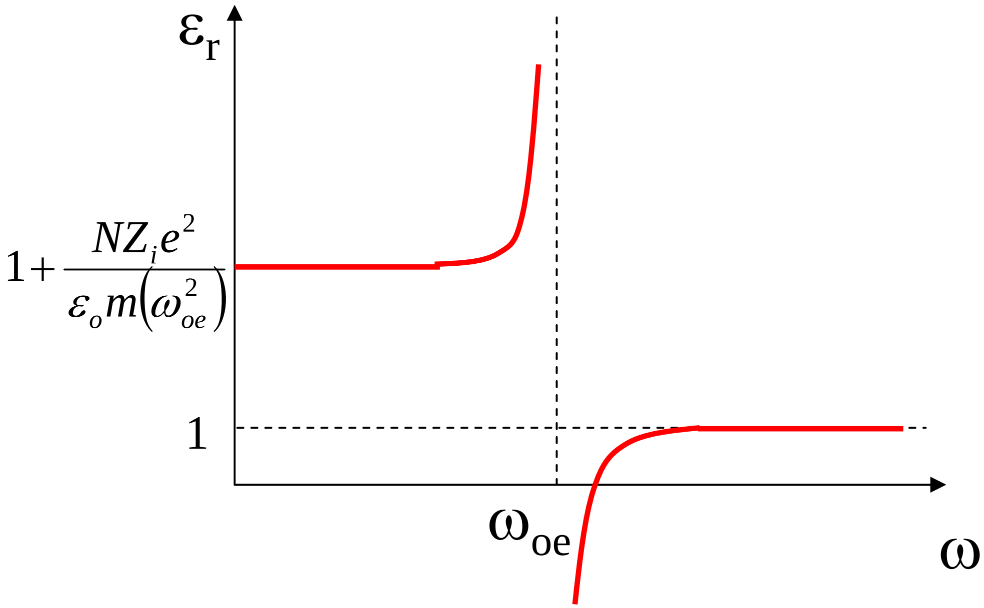
$$\alpha_e = \frac{Z_i e^2}{m\left(\omega^2 - \omega_{oe}^2\right)}$$

$$\omega >> \omega_{oe}, \;\; \alpha_e = 0$$

$$\omega << \omega_{oe}, \;\; \alpha_e = \frac{Z_i e^2}{m\omega_{oe}^2}$$

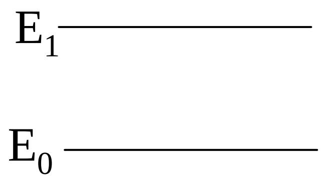
If no Clausius-Mosotti,

$$\varepsilon_r = 1 + \frac{N\alpha_e}{\varepsilon_o} = 1 + \frac{NZ_i e^2}{\varepsilon_o m\left(\omega^2 - \omega_{oe}^2\right)} = n^2$$



QM Electronic Polarizability

- At the atomic electron level, QM expected: electron waves
- QM gives same answer qualitatively
- QM exact answer very difficult: many-bodied problem



$$\alpha_e(\omega) = \frac{e^2}{m}\frac{f_{10}}{\omega_{10}^2 - \omega^2}; \quad \omega_{10} = \frac{E_1 - E_0}{\hbar}$$

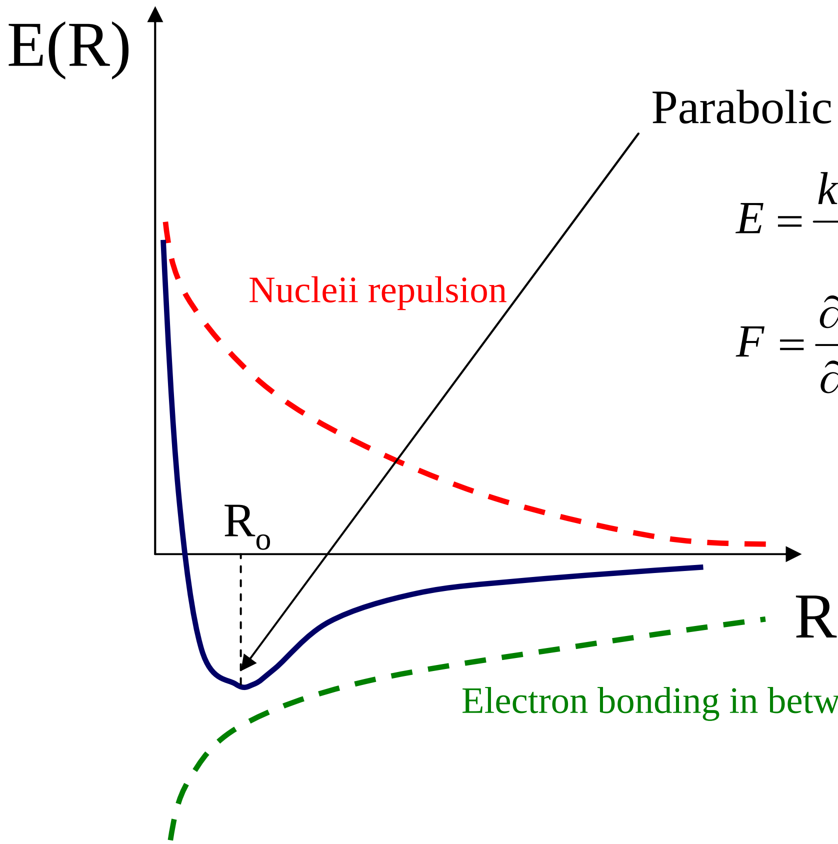
f_{10} is the oscillator strength of the transition (ψ_1 couples to ψ_o by E-field)

For an atom with multiple electrons in multiple levels:

$$\alpha_e(\omega) = \frac{e^2}{m}\sum_{j\neq 0}\frac{f_{j0}}{j_{10}^2 - \omega^2}; \quad \omega_{j0} = \frac{E_j - E_0}{\hbar}$$

Ionic Polarizability

- Problem reduces to one similar to the electronic polarizability
- Critical frequency will be less than electronic since ions are more massive
- The restoring force between ion positions is the interatomic potential



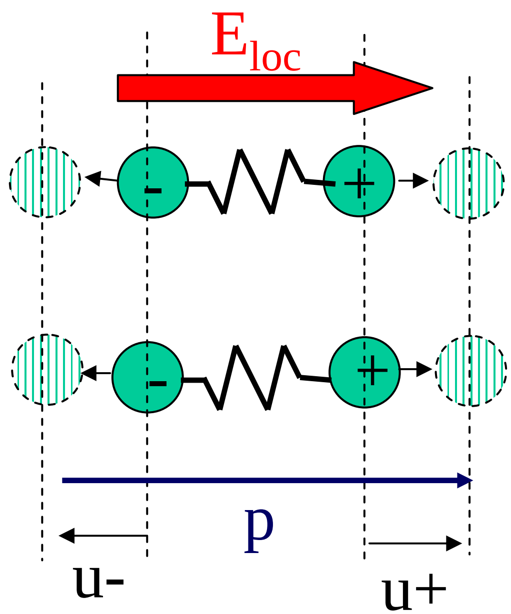
Parabolic at bottom near R_o

$$E = \frac{k(R - R_o)^2}{2}$$

$$F = \frac{\partial E}{\partial R} = k(R - R_o)$$

$$F = kx \Rightarrow \sigma_{ij} = C_{ijkl}\varepsilon_{kl}$$

Ionic Polarizability



- 2 coupled differential eqn's
  - 1 for + ions
  - 1 for - ions

$$w = u_+ - u_-,\ \ddot{w} = \ddot{u}_+ - \ddot{u}_-$$

$$M = \frac{1}{\frac{1}{M_+} + \frac{1}{M_-}}$$

$$M\ddot{w} = -2Kw + eE_{loc}$$

$$E_{loc} = E_o e^{-i\omega t}, w = w_o e^{-i\omega t}$$

$$w_o = \frac{eE_o}{M\left(\omega_{oi}^2 - \omega^2\right)},\ \omega_{oi} = \sqrt{\frac{2K}{M}}$$

$$p_o = ew_o = \alpha_i E_o$$

$$\alpha_i = \frac{e^2}{M\left(\omega_{oi}^2 - \omega^2\right)}$$

Ionic materials always have ionic and electronic polarization, so:

$$\alpha_{tot} = \alpha_i + \alpha_e = \alpha_+ + \alpha_- + \frac{e^2}{M\left(\omega_{oi}^2 - \omega^2\right)}$$

Ionic Polarizability

- Usually Clausius-Mosotti necessary due to high density of dipoles

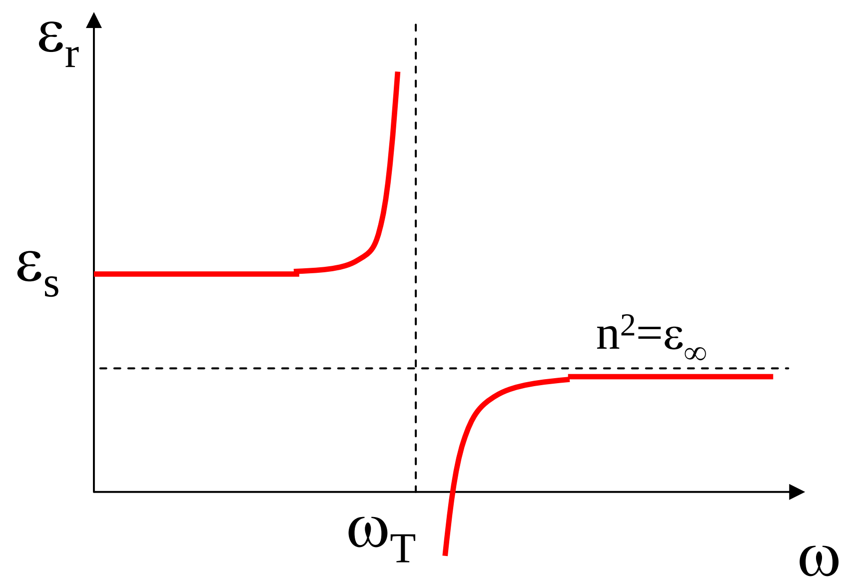
$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N\alpha_{tot}}{3\varepsilon_o} = \frac{1}{3\varepsilon_o v}\left[\alpha_+ + \alpha_- + \frac{e^2}{M\left(\omega_{oi}^2 - \omega^2\right)}\right]$$

By convention, things are abbreviated by using ε_s and ε_∞:

$$\omega << \omega_{oi}, \quad \frac{\varepsilon_s - 1}{\varepsilon_s + 2} = \frac{1}{3\varepsilon_o v}\left[\alpha_+ + \alpha_- + \frac{e^2}{M\left(\omega_{oi}^2\right)}\right]$$

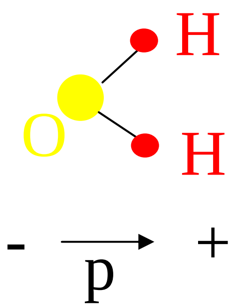
$$\omega >> \omega_{oi}, \quad \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{n^2 - 1}{n^2 + 2} = \frac{1}{3\varepsilon_o v}\left[\alpha_+ + \alpha_-\right]$$

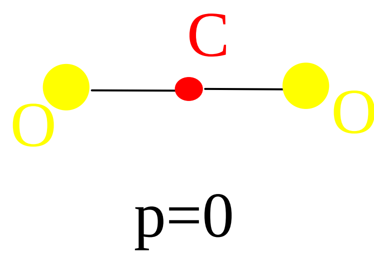
$$\therefore \ \varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_\infty - \varepsilon_s}{\frac{\omega^2}{\omega_T^2} - 1}, \quad \omega_T^2 = \omega_{oi}^2\left(\frac{\varepsilon_\infty + 2}{\varepsilon_s + 2}\right)$$

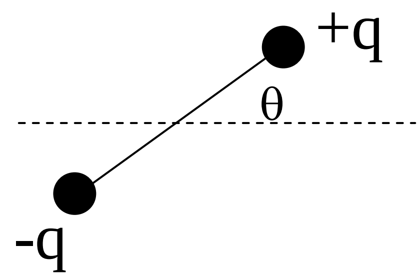


Orientational Polarizability

- No restoring force: analogous to conductivity







For a group of many molecules at some temperature:

$$f = e^{\frac{-U}{k_b T}} = e^{\frac{pE\cos\theta}{k_b T}}$$

After averaging over the polarization of the ensemble molecules (valid for low E-fields):

$$\alpha_{DC} \sim \frac{p^2}{3k_b T}$$

Analogous to conductivity, the molecules collide after a certain time t, giving:

$$\alpha = \frac{\alpha_{DC}}{1-i\omega\tau}$$