

Insulating materials:
dielectrics, ferroelectrics, piezoelectrics

Reading:

- ▶ Kasap: 7.1 - 7.12

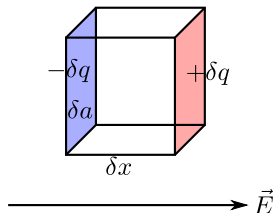
Materials in electric fields

- ▶ All materials composed of charges: electrons and nuclei
- ▶ Charges pulled along/opposite electric field with force $q\vec{E}$
- ▶ Charges separated in each infinitesimal chunk of matter \Rightarrow dipoles
- ▶ Induced dipole moment:

$$\delta\vec{p} = \delta q \delta x \hat{x}$$

- ▶ Polarization is the density of induced dipoles:

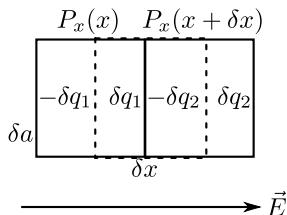
$$\vec{P} = \frac{\delta\vec{p}}{\delta x \delta a} = \frac{\delta q}{\delta a} \hat{x}$$



Bound charge due to polarization

- ▶ Charge density in infinitesimal chunk

$$\begin{aligned}
 \rho_b &= \frac{\delta q_1 - \delta q_2}{\delta a \delta x} \\
 &= \frac{\frac{\delta q_1}{\delta a} - \frac{\delta q_2}{\delta a}}{\delta x} \\
 &= \frac{P_x(x) - P_x(x + \delta x)}{\delta x} \\
 &= -\frac{\partial P_x}{\partial x}
 \end{aligned}$$



- ▶ Similarly accounting for y and z components:

$$\rho_b = -\nabla \cdot \vec{P}$$

Constitutive relations

- ▶ Material determines how \vec{P} (and hence \vec{D}) depends on \vec{E}
- ▶ Material determines how \vec{M} (and hence \vec{H}) depends on \vec{B}
- ▶ Simplest case: linear isotropic dielectric

$$\vec{P} = \chi_e \epsilon_0 \vec{E}$$

$$\vec{M} = \chi_m \vec{H}$$

$$\vec{D} = (1 + \chi_e) \epsilon_0 \vec{E}$$

$$\vec{B} = (1 + \chi_m) \mu_0 \vec{H}$$

$$\epsilon = (1 + \chi_e) \epsilon_0$$

$$\mu = (1 + \chi_m) \mu_0$$

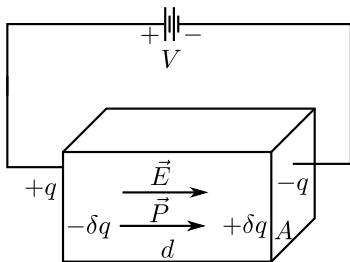
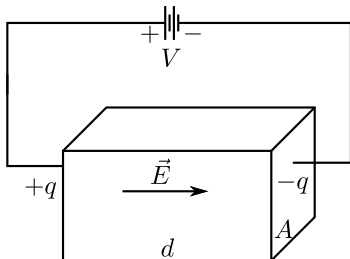
- ▶ Anisotropic dielectric: $\vec{P} = \bar{\chi}_e \cdot \epsilon_0 \vec{E}$ with susceptibility tensor $\bar{\chi}_e$
- ▶ Nonlinear dielectric: $\vec{P} = \chi_e(E) \epsilon_0 \vec{E}$

Capacitance

- ▶ Gauss's law: $E = \frac{q}{\epsilon_0 A}$
- ▶ Potential difference $V = d \cdot E = \frac{qd}{\epsilon_0 A}$
- ▶ Therefore stored charge per potential

$$C \equiv \frac{q}{V} = \frac{\epsilon_0 A}{d}$$

- ▶ Material produces polarization \vec{P}
- ▶ Corresponding bound charge density $\frac{\delta q}{A} = P$ on surface
- ▶ Gauss's law: $E = \frac{q - \delta q}{\epsilon_0 A} = \frac{q}{\epsilon_0 A} - \frac{P}{\epsilon_0}$
- ▶ $q = A(\epsilon_0 E + P) = AD = A\epsilon E = \frac{A\epsilon}{d} V$
- ▶ Therefore $C = \frac{A\epsilon}{d}$ (increases by ϵ/ϵ_0)



Sources of polarization

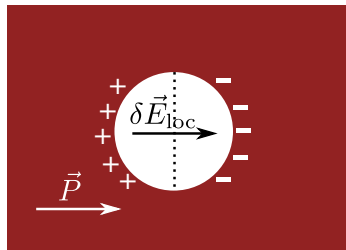
- ▶ Need to know constitutive relation $\vec{P} = \chi_e \epsilon_0 \vec{E}$
- ▶ i.e. need $\chi_e \equiv$ induced dipole / volume per unit field E
- ▶ Various sources:
 - ▶ Electrons bound to atoms (ala HW1): electronic polarizability
 - ▶ Displacement of ions in an ionic solid
 - ▶ Rotations of dipoles in a dipolar material
- ▶ Define polarizability $\alpha \equiv$ dipole moment induced per unit field E in atom / molecule
- ▶ Relation between χ_e and α is $\chi_e \epsilon_0 = N\alpha$, where N is number density of atoms / molecules?
- ▶ Almost, but not quite: local field differs from macroscopic field!

Lorenz equation

- ▶ Each atom / molecule feels effect of field \vec{E}
- ▶ It additionally feels effect of field produced by surrounding atoms / molecules
- ▶ Surrounding molecules have \vec{P} except in a 'cavity' containing the atom
- ▶ For simplicity assume spherical cavity
- ▶ Bound charge due to polarization $\rho_b = -\nabla \cdot \vec{P} = 0$
- ▶ Except at edge of cavity, where it changes abruptly
- ▶ Bound surface charge density $\sigma = -\vec{P} \cdot \hat{n}$
- ▶ Corresponding electric field (at center):

$$\begin{aligned} \delta E_{\text{loc}} &= \int_{-1}^1 \underbrace{2\pi r^2 d \cos \theta}_{dA} \frac{P \cos \theta}{4\pi \epsilon_0 r^2} \cos \theta \\ &= \frac{P}{3\epsilon_0} \end{aligned}$$

- ▶ Net local field $\vec{E}_{\text{loc}} = \vec{E} + \frac{\vec{P}}{3\epsilon_0}$



Clausius-Mossoti relation

- ▶ Induced dipole moment $\vec{p} = \alpha \vec{E}_{\text{loc}}$
- ▶ Polarization density $\vec{P} = N\vec{p} = N\alpha \vec{E}_{\text{loc}}$
- ▶ Relation between χ_e and α :

$$\vec{P} = N\alpha \vec{E}_{\text{loc}} = N\alpha \left(\vec{E} + \frac{\vec{P}}{3\epsilon_0} \right)$$

$$\vec{P} \left(1 - \frac{N\alpha}{3\epsilon_0} \right) = N\alpha \vec{E}$$

$$\chi_e \equiv \frac{\vec{P}}{\epsilon_0 \vec{E}} = \frac{\frac{N\alpha}{\epsilon_0}}{1 - \frac{N\alpha}{3\epsilon_0}} > \frac{N\alpha}{\epsilon_0}$$

i.e. local field enhances response

- ▶ Dielectric constant (Clausius-Mossoti relation):

$$\epsilon = \epsilon_0(1 + \chi_e) = \epsilon_0 \frac{1 + \frac{2N\alpha}{3\epsilon_0}}{1 - \frac{N\alpha}{3\epsilon_0}} \quad \Leftrightarrow \quad \frac{\epsilon - \epsilon_0}{\epsilon + 2\epsilon_0} = \frac{N\alpha}{3\epsilon_0}$$

Electronic / ionic polarization

- ▶ Charges: either electrons or ions in equilibrium position
- ▶ Displacement produces restoring forces: effective spring constant k
- ▶ Equation of motion in electric field:

$$m\ddot{x} = -kx - \gamma\dot{x} + qEe^{-i\omega t}$$

- ▶ Solve in frequency domain:

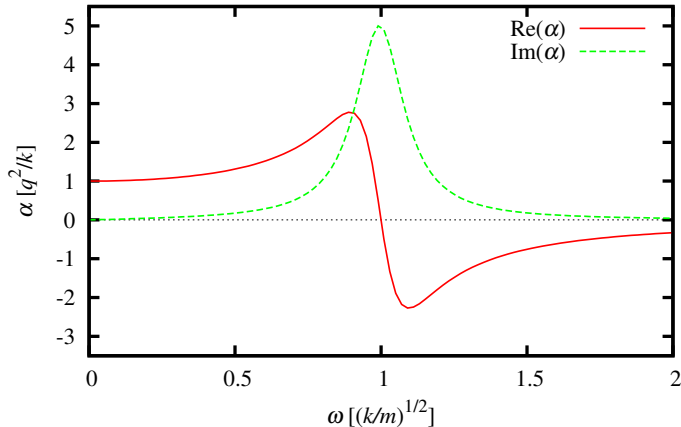
$$x = \frac{qE}{k - i\gamma\omega - m\omega^2}$$

- ▶ Polarizability (Lorentz oscillator model):

$$\alpha = \frac{p}{E} = \frac{qx}{E} = \frac{q^2}{k - i\gamma\omega - m\omega^2}$$

- ▶ Qualitatively similar behavior for electrons and ions
- ▶ Electrons: high k and small $m \Rightarrow$ smaller α over larger ω range
- ▶ Ions: small k and large $m \Rightarrow$ greater α over smaller ω range

Frequency response of polarization



- ▶ Strength of response $\propto q^2/k$
- ▶ Frequency range set by resonant frequency $\omega_0 = \sqrt{k/m}$
- ▶ Width of resonance set by damping γ/m

Dipolar polarization

- ▶ What if molecules in solid have built-in dipole \vec{p} ?
- ▶ In response to field, they can produce additional induced dipole (electronic/ionic)
- ▶ Additionally, they can rotate to align with the field!
- ▶ Without field, dipoles in random direction \Rightarrow average = 0
- ▶ With field, probability of dipole with given $\cos \theta$ with respect to field

$$P(\cos \theta) \propto \exp \frac{-(-\vec{p} \cdot \vec{E})}{k_B T} = \exp \frac{pE \cos \theta}{k_B T}$$

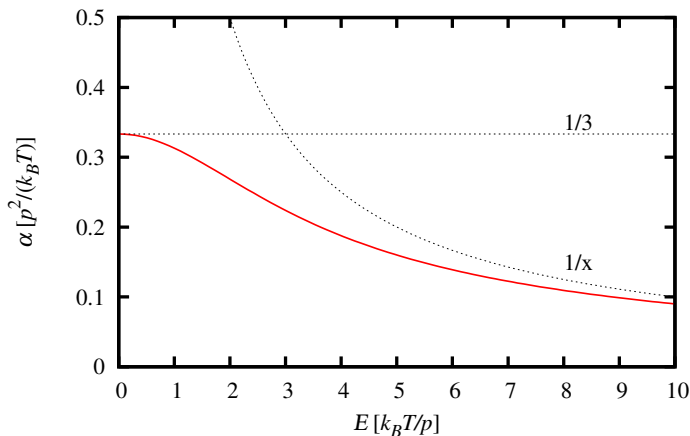
- ▶ Thermal average dipole moment:

$$\begin{aligned} \bar{p} &= \frac{\int_{-1}^1 d \cos \theta P(\cos \theta) p \cos \theta}{\int_{-1}^1 d \cos \theta P(\cos \theta)} = \frac{\int_{-1}^1 d \cos \theta p \cos \theta \exp \frac{pE \cos \theta}{k_B T}}{\int_{-1}^1 d \cos \theta \exp \frac{pE \cos \theta}{k_B T}} \\ &= \frac{k_B T \frac{\partial}{\partial E} \int_{-1}^1 d \cos \theta \exp \frac{pE \cos \theta}{k_B T}}{\int_{-1}^1 d \cos \theta \exp \frac{pE \cos \theta}{k_B T}} = \frac{k_B T \partial}{\partial E} \log \int_{-1}^1 d \cos \theta \exp \frac{pE \cos \theta}{k_B T} \end{aligned}$$

Dipole rotational response

$$\begin{aligned}
 \bar{p} &= k_B T \frac{\partial}{\partial E} \log \int_{-1}^1 d \cos \theta \exp \frac{pE \cos \theta}{k_B T} \\
 &= k_B T \frac{\partial}{\partial E} \log \left[\frac{k_B T}{pE} \left(\exp \frac{pE}{k_B T} - \exp \frac{-pE}{k_B T} \right) \right] \\
 &= k_B T \frac{\partial}{\partial E} \left[\log \sinh \frac{pE}{k_B T} - \log E + \text{const.} \right] \\
 &= k_B T \left[\frac{p}{k_B T} \coth \frac{pE}{k_B T} - \frac{1}{E} \right] \\
 &= E \frac{p^2}{k_B T} \left[\frac{k_B T}{pE} \coth \frac{pE}{k_B T} - \left(\frac{k_B T}{pE} \right)^2 \right] \\
 \alpha &= \frac{p^2}{k_B T} \left[\frac{\frac{pE}{k_B T} \coth \frac{pE}{k_B T} - 1}{\left(\frac{pE}{k_B T} \right)^2} \right]
 \end{aligned}$$

Frequency response of polarization



- ▶ At low fields $\alpha = \frac{p^2}{k_B T}$
- ▶ Response decays due to saturation at fields $\sim \frac{k_B T}{p}$
- ▶ Maximum induced dipole = p (complete alignment)!

Sources of polarization summary

- ▶ Single material would have multiple contributions which add together
- ▶ Electronic
 - ▶ Typically weakest response
 - ▶ Extends to highest frequency (visible/ultraviolet)
- ▶ Ionic
 - ▶ Stronger than electronic
 - ▶ Extends to vibrational frequency range (infrared)
- ▶ Dipole
 - ▶ Stronger than ionic for dipolar molecular materials
 - ▶ Extends to rotational frequency range (microwave/IR)
- ▶ Interfacial / defect charges
 - ▶ Slowest response (if present)
- ▶ (See Fig. 7.15 in Kasap)

Insulation

- ▶ Metals: high conductivity
- ▶ Semiconductors: lower, but controllable conductivity
- ▶ Insulators: minimize conductivity

Substance	ρ [Ωm]	σ [$(\Omega\text{m})^{-1}$]
Silver	1.59×10^{-8}	6.30×10^7
Copper	1.68×10^{-8}	5.96×10^7
Tungsten	5.6×10^{-8}	1.79×10^7
Lead	2.2×10^{-7}	4.55×10^6
Titanium	4.2×10^{-7}	2.38×10^6
Stainless steel	6.9×10^{-7}	1.45×10^6
Mercury	9.8×10^{-7}	1.02×10^6
Carbon (amorph)	$5 - 8 \times 10^{-4}$	$1 - 2 \times 10^3$
Germanium	4.6×10^{-1}	2.17
Silicon	6.4×10^2	1.56×10^{-3}
Diamond	1.0×10^{12}	1.0×10^{-12}
Quartz	7.5×10^{17}	1.3×10^{-18}
Teflon	$10^{23} - 10^{25}$	$10^{-25} - 10^{-23}$

Insulators: band structure criteria

- ▶ What do we need to minimize conductivity?
- ▶ Large band gap ($\gtrsim 100k_B T$) to reduce intrinsic conductivity

$$\sigma_i = e(\mu_e + \mu_h)n_i = e(\mu_e + \mu_h)\sqrt{N_c N_v} \exp \frac{-E_g}{2k_B T}$$

(mobilities and $N_{c/v}$ change only by one-two orders)

- ▶ Few ionizable dopants or defects to produce free carriers ($\sigma \propto N_a, N_d$)
- ▶ First metric for insulator: small σ
- ▶ Second metric: dielectric breakdown strength \mathcal{E}_{br}
- ▶ Field beyond which material starts conducting (a nonlinear response)

Electronic breakdown: perfect crystals

- ▶ Perfect material: still few intrinsic carriers
- ▶ Apply electric field \mathcal{E} , carrier can pick up energy $e\mathcal{E}\lambda$ before scattering
- ▶ If $e\mathcal{E}\lambda > E_g$, carrier has enough energy to produce more electron-hole pairs
- ▶ New electron-hole pairs accelerated by field, produce further e-h pairs \Rightarrow cascade / avalanche
- ▶ Characteristic field scale: $\lambda \sim 50$ nm, $E_g \sim 5$ eV $\Rightarrow \mathcal{E} \gtrsim 10^8$ V/m.
- ▶ Additional sources of free carriers for breakdown:
 - ▶ Injection from surfaces
 - ▶ Photo-ionization by light / radiation / cosmic rays

Breakdown mechanisms: materials with defects

- ▶ Thermal breakdown
 - ▶ Field amplified near some defects in material
 - ▶ Small conduction / high-frequency losses \Rightarrow local heating
 - ▶ Increased temperature \Rightarrow higher conductivity
 - ▶ More current, more heating \Rightarrow thermal runaway
- ▶ Electromechanical breakdown
 - ▶ Electric field produces stresses
 - ▶ Stresses enough to cause mechanical breakdown
 - ▶ Current pathways open up through cracks / physical contact across thin films
- ▶ Discharges in porous materials
 - ▶ Air gaps in material: lower dielectric strength
 - ▶ Discharge in the gas: current pathway bypassing solid
- ▶ (See Kasap 7.6 for more details)

Capacitor materials

- ▶ Get high capacitance by
 - ▶ High area
 - ▶ Small plate separation
 - ▶ High dielectric constant
- ▶ Ceramic capacitors: film of high-dielectric ceramics (MHz)
 - ▶ Small capacitances than types below
 - ▶ High breakdown voltage (KV) and frequency response
- ▶ Electrochemical capacitors:
 - ▶ High capacitance due to small separation (~ 1 nm between electrode and electrolyte)
 - ▶ Lower breakdown voltage (10-100 V) and frequency response (KHz)
- ▶ Supercapacitors:
 - ▶ Electrochemical capacitor in pseudocapacitance regime
 - ▶ Store charge by reversible redox reaction of surface species
 - ▶ Even smaller breakdown voltage (< 10 V) and frequency response (10 Hz)
- ▶ (See Kasap 7.7 for more details)

Piezo-electricity

- ▶ Centro-symmetric ($\vec{r} \rightarrow -\vec{r}$) crystals: no built-in dipole moment
- ▶ Non centro-symmetric crystals: can have built-in dipole per unit cell
- ▶ Strain symmetric material: no net dipole
- ▶ Broken symmetry: induced dipole
- ▶ Piezoelectric coefficients for induced dipole

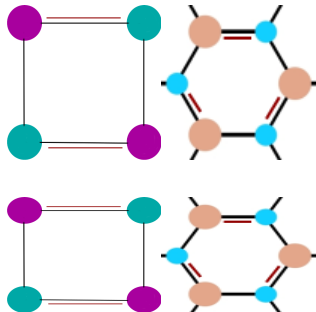
$$P_i = d_{ij} \underbrace{T_j}_{\text{Stress}}$$

- ▶ Converse: applied field produces strain

$$S_j = d_{ij} E_i$$

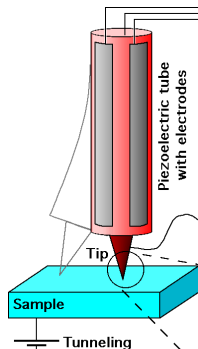
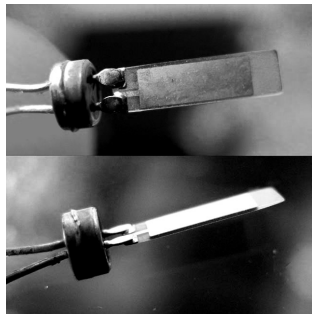
- ▶ Same coefficients in both equations: why?

$$\underbrace{\frac{1}{2} E_i \cdot P_i}_{\Delta E_{\text{diel}}} = \underbrace{\frac{1}{2} T_j \cdot S_j}_{\Delta E_{\text{mech}}}$$



Piezoelectric applications

- ▶ Spark generators: induce high field using stress
- ▶ Crystal oscillators
 - ▶ Electric field coupled to mechanical oscillations
 - ▶ Design quartz crystal dimensions to set resonant frequency
 - ▶ Pickup oscillations as voltage with same frequency
 - ▶ Use electronic circuit to amplify
 - ▶ Stable sharp frequencies compared to electrical (LC) oscillators
- ▶ Precise motion at the atomic scale: use piezo-strain for STM / AFM tip motion



Ferroelectricity and pyroelectricity

- ▶ Non-centrosymmetric crystals: built in \vec{P} per unit cell
- ▶ Crystal grains could have \vec{P} in random directions: dielectric
- ▶ Ferroelectric phase transition with critical temperature T_c
- ▶ Below T_c , crystal grains (domains) align: finite \vec{P} without applied \vec{E}
- ▶ Non-centrosymmetric \Rightarrow must also be piezoelectric
- ▶ Analogous to ferromagnetic materials (discussed in more detail next)
- ▶ Potential applications as electronic memory devices
- ▶ Dipole of ferroelectric material changes with T
- ▶ Pyroelectric coefficient dP/dT

