LECTURE 19: MOLECULAR THEORY OF POLARIZATION Wed Oct 2 2019

0.1 Molecular Theory of Polarization

Recall that for a permanent dipole in a field,

$$W = -\vec{p} \cdot \vec{E}$$

In dielectrics, we see that similarly

$$W = -\int \vec{P}\vec{E}_0 \,\mathrm{d}^3 x$$

The following is a list of interesting phenomena whose derivations are beyond the scope of this class:

- Pyroelectric materials have permanent dipole densities \vec{P}_0 .
- Ferroelectric materials have a strong \vec{P} after a field \vec{E} has been applied. The polarization has a hysteresis (removing the field doesn't remove the polarization).
- Hook's (actual) law:

$$\sigma_{il} = \sum_{k m} \lambda_{ilkm} u_{km}$$

where σ is the stress tensor and

$$u_{ik} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x^k} + \frac{\partial u_k}{\partial x^k} \right)$$

where u_i is the strain.

• Piezoelectricity and electrostriction are results of this. If you write down the free energy of a stressed/strained system, you see that

$$\mathcal{F} = \mathcal{F}_0 + \frac{1}{2} \int \lambda_{iklm} u_{lm} u_{ik} \, \mathrm{d}^3 x + \frac{1}{2} \int \gamma_{ikl} u_{ik} E_l \, \mathrm{d}^3 x + \frac{1}{2} \int \epsilon_{ij} E_i E_j \, \mathrm{d}^3 x$$
$$\sigma_{ik} = \frac{\delta}{\delta \mathcal{F} u^{ik}} = \lambda_{iklm} u_{lm} + \gamma_{ikl} E_l$$

and

$$\mathcal{D}_i = \frac{\delta \mathcal{F}}{\delta E_i} = \gamma_{kli} u_{kl} + \epsilon_{ij} E_j$$

where the ϵ terms are the dielectric constants of the material (not the Levi-Civita symbol). In these sorts of materials, stresses and strains can generate polarizations inside the material.

$$\vec{E} \mapsto \vec{E}_{\text{macro}}$$

is found by averaging over "small" regions. Take a region with a molecule in the center. We divide the electric field into an external (outside our averaging region) and an internal portion, which is

$$\vec{E}(0) = \frac{1}{\frac{4}{3}\pi R^3} \int_{\text{ball}(R)} \vec{E}^{\text{ext}} \, \mathrm{d}^3 x$$

If we consider the nearby charges,

$$-\frac{\vec{P}_T}{3\epsilon_0} = \int_{\text{ball}} \vec{E}^{\text{interior}} \, \mathrm{d}^3 x$$

where \vec{P}_T is the total dipole moment $\int_{\text{ball}} \rho(\vec{x}') \vec{x}' \, d^3 x' \approx \frac{4\pi}{3} R^3 \vec{P}$. Therefore, the macroscopic field of the center is \vec{E}^{ext} — average $+\vec{E}^{\text{int}}_{\text{average}}$. When there is a molecule at the center of the region, we should remove the internal field contribution and introduce some near-field contribution.

$$\vec{E}^{\text{near}} \approx \vec{0}$$

for most uniform crystals and random media. Essentially, for many things, the main contribution to the field is $\vec{E}^{\rm ext}(0) = \vec{E}_{\rm macro} + \frac{\vec{P}}{3\epsilon_0}$ which includes our dipole correction term. What does this mean?

$$\langle ec{p}_{
m mol}
angle = \epsilon_0 \gamma_{
m mol} \left(ec{E}_{
m macro} + rac{ec{P}}{3\epsilon_0}
ight)$$

SO

$$\vec{P} = N \langle \vec{p}_{\text{mol}} \rangle$$

where N is the number density of the molecules. Therefore

$$\vec{P} = \frac{\overbrace{\gamma_{\text{mol}} N}^{\kappa}}{1 - \frac{\gamma N}{3}} \epsilon_0 \vec{E}$$

Mossotti and Classius discovered the relationship

$$\frac{\epsilon/\epsilon_0 - 1}{\epsilon/\epsilon_0 + 2} = 3N\gamma_{\text{mol}}$$

In all of these equations, $\gamma = \frac{\vec{p}}{\epsilon_0}$ We can write a Hamiltonian for a molecule

$$H = \sum \frac{P_i^2}{2m} - \sum_i \frac{(Ze)e}{\|\vec{x}_i\|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{\|\vec{x}_i - \vec{x}_j\|}$$

We can perturb this Hamiltonian by applying an electric field

$$H \to H - eEz_i$$

where the second part is much smaller than the original energy levels. This can be approximated as a harmonic oscillator, which implies that

$$m\omega^2\vec{x} = e\vec{E}$$

where we ignore any $m\vec{x}''$ in the static case, so

$$\vec{x} = \frac{e}{m\omega^2} \vec{E}$$

where $m\omega^2$ is sort of like a spring constant between the atoms in the molecule. Therefore

$$\vec{p} = e\vec{x} = \sum_{i=1}^{n} \frac{e^2}{m\omega_i^2} \vec{E} \propto \gamma_{\text{mol}} \vec{E}$$

In solids, $N \propto 10^{28,30}$ so $\epsilon \propto 10^{0,1}$.

0.1.1 Permanent Dipoles

Some molecules (like water) have permanent dipole moments. There will also be temperature contributions, since the probability of aligning to an external field is $\propto e^{-\vec{p}\cdot\vec{E}/(k_bT)}$.