Microscopic Theory of Polarization

↳ The Clausius-Mossotti equation

1st-order perturbation theory in quantum physics can be applied to an atom or molecule placed into an external electric field we will call $\vec{E}_{other}$, to calculate the induced electric dipole moment, written as $\vec{p} = \epsilon_0 \gamma_{mol} \vec{E}_{other}$

where γ_{mol} = molecular polarizability = dimensions = (length)^3

IMPORTANT: $\vec{E}_{other}$ omits the $\vec{E}$-field due to the molecule itself

e.g. For a 1-electron atom or molecule, the perturbation term in the Hamiltonian is

$$H' = e E_{other} z \quad (\text{if } \vec{E}_{other} \text{ is along } \hat{z})$$

Then the 1st-order perturbed wavefunction is

$$|\psi^{(1)}_{gnd}\rangle = |\psi^{(0)}_{gnd}\rangle + \sum_{k \neq gnd} |\psi^{(0)}_k\rangle \frac{\langle \psi^{(0)}_k | e E_{other} z | \psi^{(0)}_{gnd} \rangle}{E^{(0)}_{gnd} - E^{(0)}_k}$$

And the 1st-order electric dipole moment is

$$p_z = -\langle \psi^{(1)}_{gnd} | e z | \psi^{(1)}_{gnd} \rangle$$

or

$$p_z = \left(\frac{2e^2}{\epsilon_0} \sum_{k \neq gnd} \frac{|\langle \psi^{(0)}_k | z | \psi^{(0)}_{gnd} \rangle|^2}{E^{(0)}_k - E^{(0)}_{gnd}} \right) \equiv \gamma_{mol} \epsilon_0 E_{other},$$

⇒ This is the microscopic induced dipole moment.

On the other hand, we have the macroscopic relation in the dielectric, $\vec{P} = \epsilon_0 \chi_e \vec{E}$

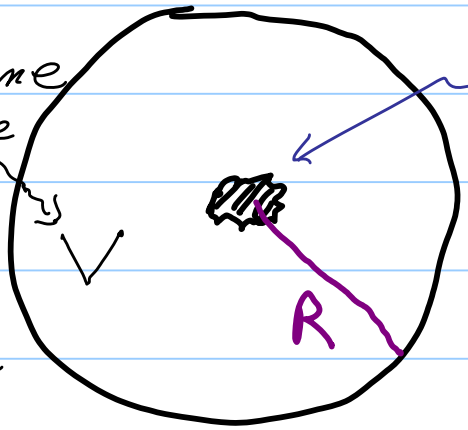
OUR MISSION: relate χ_e to γ_{mol}

Where $\vec{E}$ = the TOTAL macroscopic field

$\Rightarrow$ Let's try to keep separate the 2 contributions by writing $\vec{E} = \vec{E}_{other} + \vec{E}_{self}$

Consider a spherical volume V of radius R that is centered on, and includes, a single molecule

V = average volume per molecule $\equiv \frac{1}{N}$, where N = molecular number density



We need to find out the average field produced by the molecule itself, averaged over its own sphere,

$\Rightarrow$ Call this

$$\vec{E}_{self} = \left\langle \vec{E}^{microscopic}_{self} \right\rangle = \frac{1}{V} \int_V \vec{E}^{microscopic}_{self} \, d^3x$$

$$= \frac{1}{V} \int_V \left(-\frac{\vec{p}_{mol}}{3\epsilon_0} \delta(\vec{x}) \right) d^3x = -\frac{\vec{p}_{mol}}{V} \frac{1}{3\epsilon_0}$$

or $\vec{E}_{self} = -\frac{N}{3\epsilon_0}\vec{p}_{mol} = -\frac{\vec{P}}{3\epsilon_0}$, recalling that POLARIZATION is the average dipole moment per unit volume

Now, at the same time, a linear dielectric obeys $\vec{P} = \epsilon_0 \chi_e \vec{E} = \epsilon_0 \chi_e (\vec{E}_{other} + \vec{E}_{self})$ (*)

$= -3\epsilon_0 \vec{E}_{self}$ "

But we also know that $\vec{E}_{self} = -\frac{1}{V}\frac{1}{3\epsilon_0}\vec{p}_{mol}$ plug in here

and $\vec{p}_{mol} = \epsilon_0 \gamma_{mol} \vec{E}_{other}$

$\Rightarrow \vec{E}_{self} = -\frac{1}{3}\gamma_{mol} N \vec{E}_{other}$

Plugging this last into (*) gives

$\epsilon_0 \chi_e (\vec{E}_{other} - \frac{1}{3}\gamma_{mol} N \vec{E}_{other}) = (-3\epsilon_0)(-\frac{\gamma_{mol}}{3} N)\vec{E}_{other}$

or $\chi_e (1 - \frac{1}{3}\gamma_{mol} N) = \gamma_{mol} N$

giving finally $\chi_e = \dfrac{\gamma_{mol} N}{1 - \frac{1}{3}\gamma_{mol} N}$

or the more common form, called the CLAUSIUS-MOSSOTTI equation, is

$$\gamma_{mol} = \frac{3}{N}\left(\frac{\epsilon/\epsilon_0 - 1}{\epsilon/\epsilon_0 + 2}\right)$$

Although our model/"derivation" was admittedly rather crude, this is not a bad approximation for dilute gases. It is <u>not</u> quantitatively accurate for liquids or solids.

A crude microscopic model of χ_{mol}

A macroscopic polarization can occur via two separate mechanisms:

(I) $\vec{E}_{other}$ distorts the charge distribution in matter and <u>induces</u> dipoles $\vec{p}_{mol}$

or (II) For polar molecules with an <u>intrinsic</u> dipole moment $\vec{p}_0$, when $\vec{E}_{other} = 0$, the dipole orientations are RANDOM, $\Rightarrow \langle \vec{p} \rangle = 0$. But when $\vec{E}_{other} \neq 0$, dipoles tend to orient along $\vec{E}_{other} \Rightarrow \langle \vec{p} \rangle \neq 0$.

Case I <u>Induced dipole moment</u> - a <u>model</u>

Imagine crudely that an atomic or molecular electron is bound in a harmonic oscillator potential, with restoring force $\vec{F} = -m\omega_0^2 \vec{x}$

$\Rightarrow$ In an external field $\vec{E}_0$, the oscillator stretches until the forces balance on $q = -e$.

i.e. $q\vec{E}_0 - m\omega_0^2 \vec{x} = 0$

$$\Rightarrow \vec{p}_{mol} = q\vec{x} = \frac{q^2}{m\omega_0^2}\vec{E}_0$$

But $\vec{p}_{mol} = \epsilon_0 \chi_{mol} \vec{E}_0 \Rightarrow$

$$\boxed{\chi_{mol} = \frac{e^2}{\epsilon_0 m \omega^2}}$$

We can test this against some numerical values:

i.e. for a typical gas molecule an electronic excitation energy might be about

$$\hbar\omega_0 \simeq 4\,eV \times 1.6\times10^{-19}\,\frac{J}{eV} = 6.4\times10^{-19}\,J$$

and $$\omega_0 = \frac{6.4\times10^{-19}\,J}{1.054\times10^{-34}\,J\text{-}s} \simeq 6\times10^{15}\ rad/sec$$

and we would thus predict that in this model,

$$\gamma_{mol} \simeq \frac{(1.6\times10^{-19}\,C)^2}{\left(8.85\times10^{-12}\,\frac{C^2}{N\text{-}m^2}\right)(9.1\times10^{-31}\,kg)\left(6\times10^{15}\,\frac{rad}{s}\right)^2}$$

$$\simeq 8.6\times10^{-29}\,m^3$$

↖ Jackson's numerics give one order of magnitude smaller, in an apparent numerical error — see p. 163.

Or setting $\left(\frac{\gamma_{mol}}{\frac{4}{3}\pi}\right)^{1/3} \simeq R \simeq 5\,\text{Å}$,

we see that γ_{mol} is the right order-of-magnitude to be interpreted as the "molecular volume"

Experiment for χ_e and ϵ/ϵ_0?

Let's use $N \simeq 2.5\times10^{25}\ \frac{molecules}{m^3}$ @ NTP, (20°C, 1 atm)

$\Rightarrow \chi_e \simeq N\gamma_{mol} \simeq 0.0022$ from the Clausius-Mossotti eqn

$\Rightarrow \frac{\epsilon}{\epsilon_0} \simeq 1.0022$, versus expt for air @ NTP, which is $\left.\frac{\epsilon}{\epsilon_0}\right|_{expt} = 1.00054$

On the other hand condensed liquids or solids have densities more like

$$N \simeq 10^{28} - 10^{29}\ m^{-3}$$

$\Rightarrow \chi_e$ can be of order 1 - 10, which is the correct order of magnitude for condensed matter.

(II) Orientation of permanent moments:

In a field $\vec{E}_0$ the energy of a permanent dipole $\vec{p}_0$ is $H = H_0 - \vec{p}_0 \cdot \vec{E}_0$

And according to stat. mech., different configurations occur with relative probabilities governed by the Boltzman factor,

$$f(H) = e^{-H/kT}$$

$$\Rightarrow \langle p_z \rangle = \frac{\int_{-1}^{1} d(\cos\theta)\, p_0 \cos\theta\, e^{p_0 E_0 \cos\theta / kT}}{\int_{-1}^{1} d(\cos\theta)\, e^{p_0 E_0 \cos\theta / kT}}$$

These integrals are readily evaluated, giving

$$\langle p_z \rangle = -\frac{kT}{E_0} + p_0 \coth\left(\frac{p_0 E_0}{kT}\right)$$

$$\xrightarrow[p_0 E_0 << kT]{} \frac{1}{3}\frac{p_0^2 E_0}{kT}$$

(Look at Jackson Fig. 4.10)

Electrostatic Energy in Dielectrics

Recall from elementary physics:

A capacitor connected to a battery at voltage V can store MORE energy if you add a dielectric between its plates, since

$$C \to KC_0 \quad \text{with} \quad K = \frac{\epsilon}{\epsilon_0} = \text{dielectric constant} > 1$$

and

$$W = \frac{1}{2}CV^2 \longrightarrow \frac{1}{2}KC_0V^2$$

We would like to derive this result now, and generalize it, starting from the primitive definition for energy of a charge distribution ρ in free space:

$$W = \frac{1}{2}\int \rho(\vec{x})\,\Phi(\vec{x})\,d^3x$$

where $\rho(\vec{x})$ is the SAME distribution of charges that PRODUCES $\Phi(\vec{x})$

However, it is far from obvious at the outset whether ρ is the TOTAL charge, or FREE charge, or something else.

To analyze this more carefully, consider the change δW in the energy W caused by bringing up a tiny additional FREE charge density $\delta\rho_f$, i.e. determine $W \to W + \delta W$ as $\rho_f \to \rho_f + \delta\rho_f$, and note that Jackson's notation for ρ_f is just ρ.

$$\Rightarrow \delta W = \int \delta\rho_f(\vec{x})\, \Phi(\vec{x})\, d^3x$$

But since $\nabla\cdot\vec{D} = \rho_f \Rightarrow \nabla\cdot\delta\vec{D} = \delta\rho_f$

So we can write $\delta W = \int \Phi\, \nabla\cdot(\delta\vec{D})\, d^3x$

But using the identity $(\nabla\cdot\delta\vec{D})\Phi = \nabla\cdot(\Phi\delta\vec{D}) - \nabla\Phi\cdot\delta\vec{D}$

$$\Rightarrow \delta W = \oint_S \Phi\,\delta\vec{D}\cdot\hat{n}\,da + \int \vec{E}\cdot\delta\vec{D}\, d^3x$$

$\to 0$ if $S \to \infty$

So $\boxed{\delta W = \int_V \vec{E}\cdot\delta\vec{D}\, d^3x}$ is a generally valid result

or $W = \int d^3x \left(\int_0^{\vec{D}} \vec{E}\cdot\delta\vec{D} \right)$

where that last integral MAY depend on path, e.g. if there is hysteresis.

For a LINEAR DIELECTRIC MEDIUM, simpler expression obtain, since then $\vec{D} = \epsilon\vec{E}$ and $\vec{E}\cdot\delta\vec{D} = \frac{1}{2}\delta(\vec{E}\cdot\vec{D})$

giving

$$\delta W = \delta\left[\frac{1}{2}\int \vec{E}\cdot\vec{D}\, d^3x\right]$$

and

$$\boxed{W = \frac{1}{2}\int \vec{E}\cdot\vec{D}\, d^3x}$$

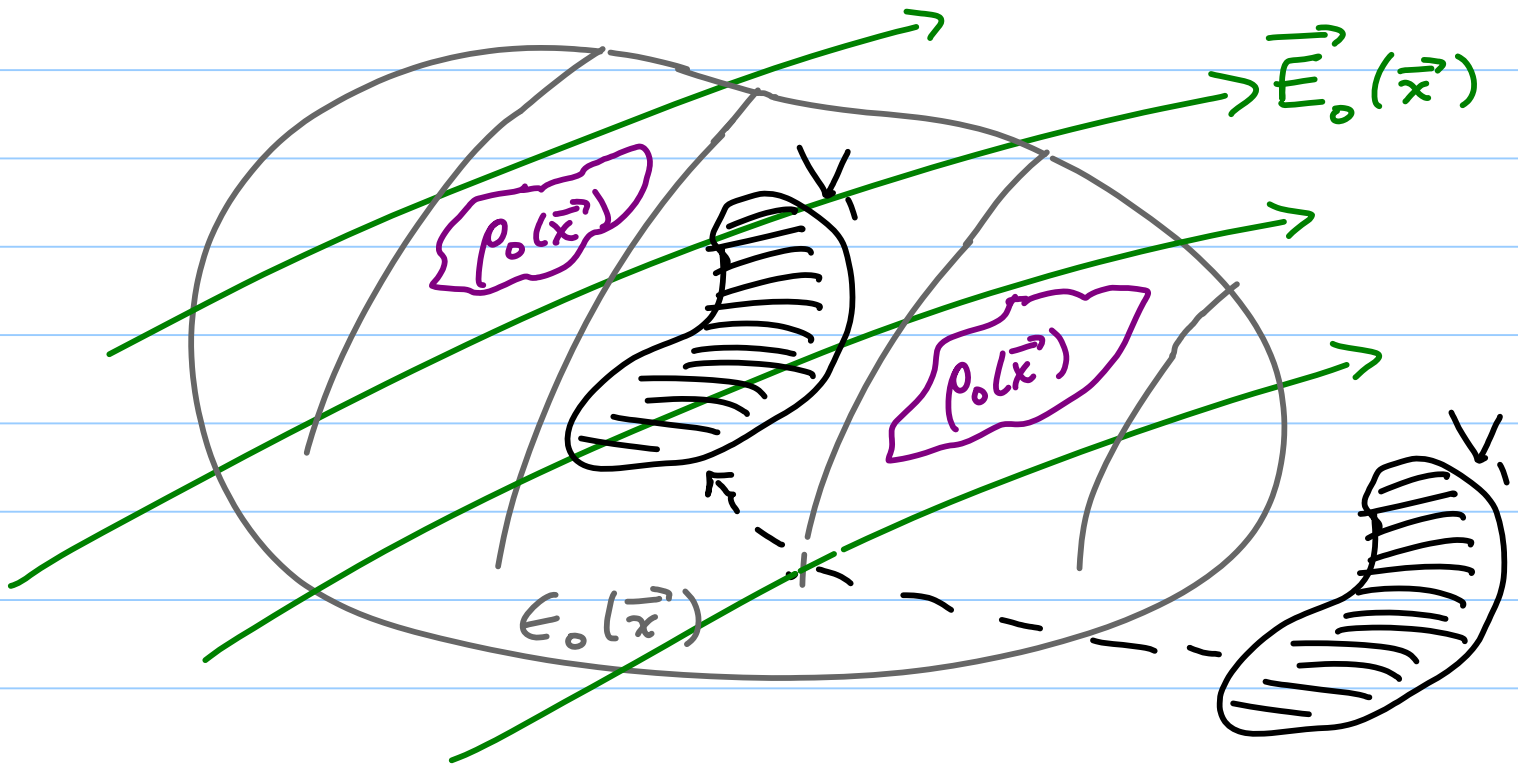
← FOR LINEAR MEDIA ONLY!

Next, consider the change in energy when a dielectric is placed into an electric field created by fixed sources.

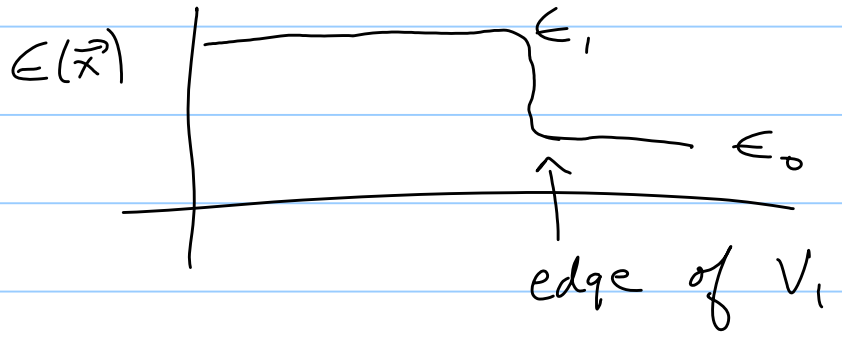
⇒ Suppose a field $\vec{E}_0(\vec{x})$ is produced by some charge distribution $\rho_0(\vec{x})$ in a medium of dielectric constant $\epsilon_0(\vec{x})$ not necessarily vacuum.

⇒ the initial energy is

$$W_0 = \frac{1}{2}\int \vec{E}_0\cdot\vec{D}_0\, d^3x$$



Now bring in an object of volume V_1 having dielectric constant $\epsilon_1(\vec{x}) = \begin{cases} \epsilon_1(\vec{x}) & \text{inside } V_1 \\ \epsilon_0(\vec{x}) & \text{outside } V_1 \end{cases}$



Then the new energy is $W_1 = \frac{1}{2}\int \vec{E}\cdot\vec{D}\, d^3x$ with $\vec{D} = \epsilon\vec{E}$. And the energy change is

$$\Delta W = W_1 - W_0 = \frac{1}{2}\int (\vec{E}\cdot\vec{D} - \vec{E}_0\cdot\vec{D}_0)\, d^3x$$

$$= \frac{1}{2}\int (\vec{E}\cdot\vec{D}_0 - \vec{D}\cdot\vec{E}_0)\, d^3x + \frac{1}{2}\int (\vec{E}+\vec{E}_0)\cdot(\vec{D}-\vec{D}_0)\, d^3x$$

$$= -\frac{1}{2}\int [\nabla(\Phi+\Phi_0)\cdot(\vec{D}-\vec{D}_0)]\, d^3x$$

↓ now integrate by parts, and assume surface terms → 0

$$= \frac{1}{2}\int (\Phi+\Phi_0)\,\nabla\cdot(\vec{D}-\vec{D}_0)\, d^3x$$

$= 0$ since the sources of free change were assumed not to change.

$$\Rightarrow \Delta W = \frac{1}{2}\int_{\text{all space}} (\vec{E}\cdot\vec{D}_0 - \vec{D}\cdot\vec{E}_0)\, d^3x$$

And since the integrand vanishes outside the dielectric (V_1), we can write this as

$$\Delta W = \frac{1}{2}\int_{V_1} (\vec{E}\cdot\vec{D}_0 - \vec{D}\cdot\vec{E}_0)\, d^3x$$

$$= -\frac{1}{2}\int_{V_1} (\epsilon_1 - \epsilon_0)\vec{E}\cdot\vec{E}_0\, d^3x$$

and if the original dielectric was actually free space, then $(\epsilon_1 - \epsilon_0)\vec{E} = \epsilon_0 \chi_0 \vec{E} = \vec{P}$

whereby $\Delta W = -\frac{1}{2}\int_{V_1} \vec{P}\cdot\vec{E}_0\, d^3x$

This leads us to interpret the energy density of a dielectric placed into an $\vec{E}$-field with fixed sources is $w = -\frac{1}{2}\vec{P}\cdot\vec{E}_0$

Thus the energy is LOWERED when the dielectric is present

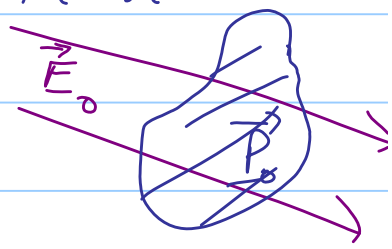
$\Rightarrow$ a dielectric with $\epsilon_1 > \epsilon_0$ is attracted inward

(analogously, $W = \frac{Q^2}{2C} < \frac{Q^2}{2C_0}$ since $C = \kappa C_0 > C_0$)

Note: there is an important energy difference between induced versus permanent dipoles in a field:

Recall that a single permanent dipole in an electric field $\vec{E}_0$ has energy $W = -\vec{p}_0 \cdot \vec{E}_0$

$\Rightarrow$ The energy of a macroscopic body having PERMANENT polarization $\vec{P}_0$ in an $\vec{E}$-field $\vec{E}_0$ would be



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

or the corresponding energy density would be

$$\boxed{W = -\vec{P}_0 \cdot \vec{E}_0}$$

This is a universal factor of $\frac{1}{2}$ for the energy of an induced rather than permanent dipole.

This is also the case for a single atom or molecule, e.g.

$$W = -\vec{p}_0 \cdot \vec{E}_0 \quad \text{for a } \underline{\text{permanent dipole}}$$

whereas for an induced dipole, if $\vec{p} \to \vec{p} + \delta\vec{p}$

$\Rightarrow \delta W = -\delta\vec{p} \cdot \vec{E}$, where $\delta\vec{p} = \epsilon_0 \gamma_{mol} \delta\vec{E}$

$\Rightarrow \delta W = -\epsilon_0 \gamma_{mol} \vec{E} \cdot \delta\vec{E}$ and $W = -\frac{1}{2}\epsilon_0 \gamma_{mol} E^2$

i.e. $\boxed{W = -\frac{1}{2}\vec{p}(E) \cdot \vec{E}}$ for an induced dipole