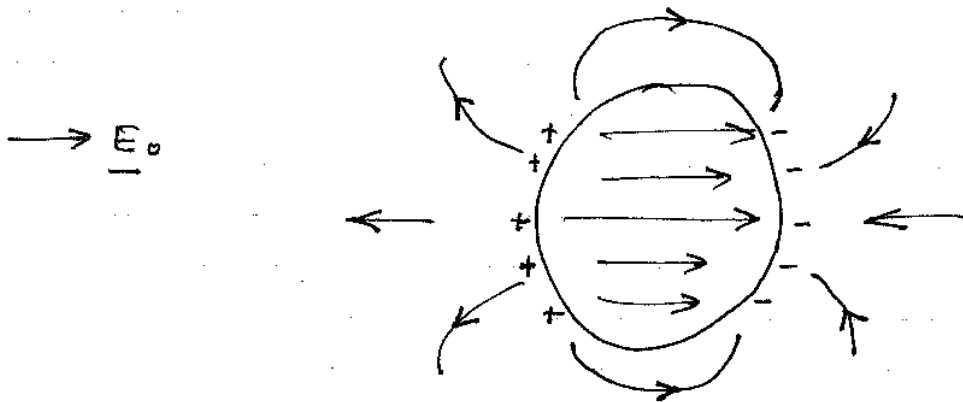


Last time we found that a spherical hole in a dielectric produces an enhancement of E within the hole, compared to its magnitude far from the hole, by a factor

$$\frac{E_{in}}{E_0} = \frac{3\epsilon}{\epsilon_0 + 2\epsilon} > 1 \quad (4.59)$$

Outside the hole, \underline{E} = uniform field + dipole perturbation.

The dipole perturbation reduces the external field near the z axis, increases it near $z=0$ (where $\underline{E}_0 = E_0 \hat{z}$):



normal component of

This means that the electric field \underline{E} (and hence of the polarization \underline{P}) is smaller just outside the hole than at large distances.

What if we instead assume $\underline{P} = P_0 \hat{z}$ (uniform) outside the hole?

This gives a larger polarization charge density ($-\nabla \cdot \underline{P}$) at the edges of the hole, hence a larger enhancement of E inside.

As you will show (in homework problem 1), it gives

$$\frac{E_{in}}{E_0} = 1 + \frac{P_0}{3\epsilon_0 E_0} \quad (4.12)$$

which is larger than (4.59).

In terms of the susceptibility χ_e , (4.12) is

$$\frac{E_{in}}{E_0} = 1 + \chi_e / 3 \quad (4.12)$$

while (4.59) is

$$\frac{E_{in}}{E_0} = \frac{1 + \chi_e}{1 + \frac{2}{3}\chi_e} \quad (4.59)$$

The two factors are the same to first order in χ_e if $\chi_e \ll 1$, but quite different if $\chi_e \gtrsim 1$.

It is worth noting that the electric-field amplification factor (4.12) is independent of the radius of the hole, provided it is large enough to apply the macroscopic description $\underline{P} = N_s \langle \underline{p}_s \rangle$.

To calculate \underline{E} at the location of a specific atom or molecule in a solid, we can imagine a spherical hole surrounding that atom/molecule with macroscopic radius, and use (x4.12) to describe the macroscopic effect of polarization outside the hole. (Since the hole is imaginary, not physical, it is appropriate to use (x4.12), not (4.59).) Then we can add to this the microscopic contribution due to neighboring atoms/molecules within the hole:

$$\underline{E}_{\text{real}}(\underline{x}) = \underline{E}_0 \left(1 + \frac{P_0}{3\epsilon_0 \epsilon_0} \right) + \underline{E}_{\text{near}}(\underline{x}) \quad (\text{x4.13})$$

The remarkable thing about this argument is that $\underline{E}_{\text{near}} \approx 0$ is a good assumption.

For example, if equally-oriented dipoles are placed at the lattice sites of a simple cubic lattice, the resultant \underline{E} at any given lattice site is zero (see Jackson, p. 161). Also, if equally-oriented dipoles are placed randomly on a spherical shell, \underline{E} at the center is ≈ 0 (see homework problem 2). Thus, a good general rule of thumb (although not a rigorously valid statement) is

$$\underline{E}_{\text{near}} \approx 0$$

so (x4.13) gives $\underline{E}_{\text{real}} \approx \underline{E}_0 \left(1 + \frac{P_0}{3\epsilon_0 \epsilon_0} \right)$ (x4.14)

Connection to molecular properties.

The molecular polarizability γ_{mol} is defined by

$$\langle \underline{p}_{mol} \rangle = \epsilon_0 \gamma_{mol} \underline{E}_{real}$$

so

$$\underline{P} \equiv N \langle \underline{p}_{mol} \rangle = N \epsilon_0 \gamma_{mol} \underline{E}_0 \left(1 + \frac{P_0}{3 \epsilon_0 E_0} \right)$$

$$P_0 \left(1 - \frac{N \gamma_{mol}}{3} \right) = N \epsilon_0 E_0 \gamma_{mol}$$

$$P_0 = \frac{N \epsilon_0 \gamma_{mol}}{1 - \frac{N \gamma_{mol}}{3}} E_0$$

$$\text{susceptibility } \chi_e \equiv \frac{P_0}{\epsilon_0 E_0} = \frac{N \gamma_{mol}}{1 - \frac{N \gamma_{mol}}{3}} \quad (4.69)$$

Solving for γ_{mol} gives $\gamma_{mol} = \frac{\chi_e}{N(1 + \frac{\chi_e}{3})}$

Replacing χ_e by $\frac{\epsilon}{\epsilon_0} - 1$ (4.38) gives the Clausius-Mossotti equation

$$\gamma_{mol} = \frac{3 \left(\frac{\epsilon}{\epsilon_0} - 1 \right)}{N \left(\frac{\epsilon}{\epsilon_0} + 2 \right)} \quad (4.70)$$

from which the microscopic parameter γ_{mol} can be deduced from measurements of the macroscopic parameter ϵ .

Simple Models of Molecular Polarizability

A. Induced dipole moments.

Assume charges are bound to lattice sites in simple harmonic oscillator potentials

$$\underline{F} = -m\omega_0^2 \underline{x} \quad (4.71)$$

An imposed field \underline{E} produces a displacement

$$\underline{x} = e\underline{E} / m\omega_0^2$$

and a dipole moment

$$\underline{p} = e\underline{x} = \frac{e^2}{m\omega_0^2} \underline{E} \quad (4.72)$$

Summing over species j :

$$\chi_{\text{mol}} = \frac{P}{\epsilon_0 E} = \sum_j \frac{e_j^2}{\epsilon_0 m_j \omega_{0j}^2} \quad (4.73)$$

If we assume $\hbar\omega_{0j} \sim 4 \text{ eV}$,

$$\omega_{0j} \sim \frac{4 \times 1.6 \times 10^{-19} \text{ J}}{1.1 \times 10^{-34} \text{ J-s}} \sim 6 \times 10^{15} \text{ s}^{-1} \quad (\text{optical range})$$

$$\begin{aligned} \chi_{\text{mol}} &\sim \frac{(1.6 \times 10^{-19})^2}{(9 \times 10^{-12})(9 \times 10^{-31})(6 \times 10^{15})^2} \\ &\sim 9 \times 10^{-30} \text{ m}^3 \sim (3 \text{ \AA})^3 \end{aligned}$$

consistent with volume of a lattice site.

For a solid, $NY \sim 1$ so $\frac{\epsilon}{\epsilon_0} - 1 \sim 1$

For a gas at STP, $N \sim 2.7 \times 10^{25} / \text{m}^3$ so

$$\chi_e \sim NY_{\text{mol}} \sim \text{few} \times 10^{-4} \rightarrow \epsilon \approx \epsilon_0.$$

B. Alignment of permanent dipole moments.

Assume each molecule (e.g. H_2O) has a permanent dipole moment p_0 that is randomly oriented for $\underline{E} = 0$. With $\underline{E} \neq 0$, the Hamiltonian

$$H = H_0 - \underline{p}_0 \cdot \underline{E} \quad (4.79)$$

Assume the probability distribution is

$$f(H) \propto e^{-H/kT} \quad (4.74)$$

(the Boltzmann factor). Then

$$\langle p_{\text{mol}} \rangle = \frac{\int d\Omega p_0 \cos\theta \exp\left(\frac{p_0 E \cos\theta}{kT}\right)}{\int d\Omega \exp\left(\frac{p_0 E \cos\theta}{kT}\right)} \quad (4.80)$$

where $\hat{z} = \underline{E} / E_0$, and $\int d\Omega [] = 2\pi \int_0^\pi [] \sin\theta d\theta$.

Assuming $\frac{p_0 E}{kT} \ll 1$ (true for "ordinary" temperatures), expand the exponential \rightarrow

$$\langle p_{\text{mol}} \rangle = \frac{p_0^2 E}{3kT} \quad (4.81)$$

$$\text{so } \gamma_{\text{mol}} = \frac{\langle p_{\text{mol}} \rangle}{\epsilon_0 E} = \frac{p_0^2}{3\epsilon_0 kT}$$

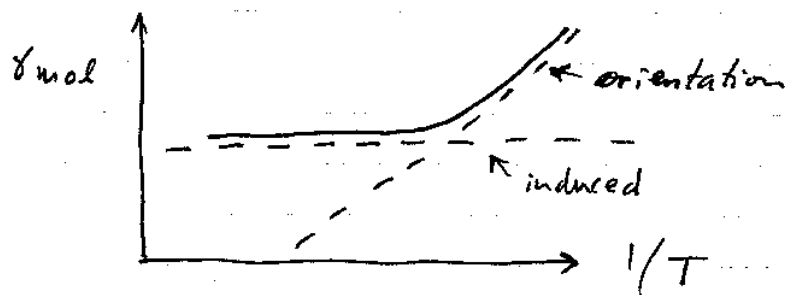
for alignment of permanent moments p_0 .

Combining both types of polarization (induced + orientation) gives

$$\gamma_{\text{mol}} \approx \gamma_i + \frac{p_0^2}{3\epsilon_0 kT} \quad (4.82)$$

where $\gamma_i = \gamma_{\text{mol}}$ (induced) calculated above,

which is independent of temperature to first order. So a set of measurements of γ_{mol} vs. T^{-1} might look like



The slope of the portion of $1/T$ gives a determination of p_0 . Empirically, for polar molecules (e.g., H_2O , HCl), this gives

$$p_0 \sim e \times (1 \text{ \AA})$$

which makes sense.

End of electrostatics.