Lecture 1—3 (Fri, Sept 6)

Molecular Polarizability (γ_{mol}) and Electric Susceptibility (χ_e) and Permittivity (ϵ).

Jackson Section 4.5

Review χ_e and ϵ

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P} \quad \text{and} \quad \vec{P} = \chi_e \, \epsilon_0 \, \vec{E}$$

$$\vec{D} = \epsilon \vec{E} \quad \text{and} \quad \epsilon = (1 + \chi_e) \, \epsilon_0$$

Now derive the ***Clausius-Mossotti formula***

$$\chi_e = \frac{N \, \gamma_{mol}}{1 - \frac{1}{3} N \, \gamma_{mol}} \qquad [CM.1]$$

or,

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

It relates a molecular quantity γ_{mol}, to a macroscopic quantity ϵ.

I'll show you the simplest derivation of these results, but not the best justified. Jackson has a more complete derivation, but it gives the same results.

Derivation

We have defined χ_e by these equations

$$\vec{P}(\vec{x}) = \vec{N}(\vec{x})\,\langle\vec{p}_{mol}\rangle_{\vec{x}}$$

$$\vec{P}(\vec{x}) = \chi_e\,\epsilon_0\,\vec{E}(\vec{x})$$

Here $\vec{E}(\vec{x})$ is the macroscopic field, i.e., averaged over $\Delta V \gg$ molecule.

A first guess is $\vec{p}_{mol,x} = \chi_e\,\epsilon_0\,\vec{E}(\vec{x})$, but that is not quite good enough,

We need a better calculation of $\vec{p}$ molecule.

■ The macroscopic field may be called an "external" field, because it comes from external sources—charge outside the region of the single molecule that we are considering.

$\vec{E}(\vec{x})$ is the average due to a large number ($\sim 10^{23}$) of molecules in some macroscopic (but small) ΔV around $\vec{x}$.

■ But there is also an "internal" field, coming from nearby sources. For nearby molecules we should not just average over large numbers. Their field will also affect $\vec{p}_{\text{mol}}$.

So, we should write

$$\vec{p}_{\text{mol}} = \gamma_{\text{mol}}\, \epsilon_0\, \vec{E}_{\text{mol}}$$

$$\text{where}\quad \vec{E}_{\text{mol}} = \vec{E}_{\text{ext}} + \vec{E}_{\text{int}}$$

The parameter $\gamma_{\text{mol}} \equiv$ *molecular polarizability*—a property of a single molecule.

Estimating the local field $\vec{E}_{\text{mol}}$

Ideally we would use a full quantum theory for the molecules. Clausius (1850) and Mossotti (1979) used a classical theory.

■ Imagine a microscopic sphere of radius R enclosing the molecule, and estimate the field at the center of the sphere.

■ Treat the sphere as a cavity in the dielectric $\Longrightarrow$ Example 3 from last time. (See Jackson page 161: "it is a good working assumption that $\vec{E}_{\text{near}} \approx 0$ for most materials.)

$$\boxed{\vec{E}_{mol}}$$

Recall from Example 3, we had

$$\vec{E}_{in} = \frac{3\,\epsilon}{2\,\epsilon + \epsilon_0}\, E_0\, \hat{e}_z$$

and $\quad \vec{E}_{out} = E_0\, \hat{e}_z - \nabla\left(\frac{\vec{p} \cdot \vec{x}}{4\,\pi\,\epsilon_0\, r^3}\right)$

where the distant field is $E_0\, \hat{e}_z$.

■ Approximate

$$\vec{E}_{macro} \approx E_0\, \hat{e}_z \quad \text{and} \quad \vec{E}_{mol} \approx \vec{E}_{in}$$

■ Now we have the following calculation …

$$\vec{P} = \epsilon_0\, \chi\, \vec{E}_{macro} \qquad \text{(def.)}$$

$$\vec{P} = N\, \vec{p}_{mol} = N\, \gamma\, \epsilon_0\, \vec{E}_{mol}$$

$$\vec{E}_{mol} = \frac{3\,\epsilon}{2\,\epsilon + \epsilon_0}\, \vec{E}_0 = \frac{3\,\epsilon_0\,(1+\chi)}{2\,\epsilon_0\,(1+\chi)+\epsilon_0}\, \vec{E}_0$$

$$= \frac{3+3\,\chi}{3+2\,\chi}\, \vec{E}_0 = \left(1 + \frac{\chi}{3+2\,\chi}\right)\vec{E}_0$$

$$\approx \left(1 + \frac{\chi}{3}\right)\vec{E}_{macro}$$

$$\therefore\ \epsilon_0\, \chi\, E_{macro} = N\, \gamma\, \epsilon_0\,\left(1 + \frac{\chi}{3}\right) E_{macro}$$

$$\chi = \frac{N\gamma}{1 - \frac{1}{3}\,N\gamma} \qquad \text{(CM−1)}$$

Or, rewriting the formula in terms of $\epsilon \equiv \epsilon_0\,(1+\chi)$,

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

So this relates a microscopic parameter γ_{mol} to a macroscopic parameter $\epsilon/\epsilon_0 \equiv$

κ = the dielectric constant.

Clausius and Mossotti: for any dielectric material, the quantity $(\kappa-1)/(\kappa+2)$ is proportional to the density.

Example: Jackson Problem 4.11 ; Pentane @ 303 K

```
In[*]:= tb = {{"density", "κ=ϵ/ϵ₀"}, {0.613, 1.82}, {0.701, 1.96},
       {0.796, 2.12}, {0.865, 2.24}, {0.907, 2.33}};
    tb // TableForm
```

density	$\kappa=\epsilon/\epsilon_0$
0.613	1.82
0.701	1.96
0.796	2.12
0.865	2.24
0.907	2.33

```
In[*]:= t2 = Table[
       {tb[[i, 1]], (tb[[i, 2]] - 1) / (tb[[i, 2]] + 2)}, {i, 2, 6}];
    ListPlot[t2, PlotStyle → {Red, PointSize[0.025]},
     BaseStyle → ff,
     Frame → True, FrameLabel → {"ρ", "(κ-1)/(κ+2)"},
     ImageSize → 520]
```