

start

## Lecture 1-4

### Models of the Molecular Polarizability, $\gamma_{\text{mol}}$

Jackson Section 4.6

#### Review the Clausius-Mossotti relation

Let  $\gamma_{\text{mol}}$  = polarizability of a single molecule;

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

The units of  $\gamma = \frac{Cm}{C m^{-2}} = m^3$ .

⇒ Macroscopic parameters

$\chi_e$  = electric susceptibility

$\epsilon$  = permittivity

$N$  = *number density* of the molecules

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

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

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

The results relate a molecular quantity ( $\gamma_{\text{mol}}$ ) to macroscopic quantities ( $\epsilon$  or  $\chi$ , and  $N$ ).

The relation is fairly accurate for gases ( $\leftarrow$  small  $N$ ) but only approximate for condensed matter.

The result is interesting because it gives a way to measure (*or, at least, estimate*)

$\gamma_{\text{mol}}$  from laboratory measurements of  $\epsilon$  and  $N$ .

Now, can we calculate  $\gamma_{\text{mol}}$  using theory?

### Theoretical models for $\gamma_{\text{mol}}$

The best theory would involve quantum mechanics. Here we will only consider classical models.

There are two kinds of molecular polarization:

CASE 1 : If the molecule has an *induced dipole moment* because of the presence of an electric field, which distorts the atomic structure; an example is  $O_2$ .

CASE 2 : If the molecule has a *permanent dipole moment* because of its atomic structure; an example is  $H_2O$ .

### CASE 1: Induced polarization

Here is a reasonable model:

- Treat the negative charge in the molecule as if it is a particle with mass  $m$  and charge  $-e$ . (*These model parameters are not exactly the values for an electron, but should have the same order of magnitude.*)
- Describe a restoring force on the negative charge by  $\vec{F} = -k \vec{x}$ , where  $\vec{x}$  = the displacement from equilibrium.
- Define  $k = m\omega_0^2$  where  $\omega_0$  = an angular frequency characteristic of the molecule.

### Calculation of $\gamma_{\text{mol}}$ for induced polarization

In the presence of an electric field,

$$m \frac{d^2 \vec{x}}{dt^2} = -k \vec{x} - e \vec{E}(\vec{x})$$

So, for a static system,  $m\omega_0^2 \vec{x} = -e \vec{E}(\vec{x})$ .

Then the dipole moment of the molecule is

$$\vec{p}_{\text{mol}} = -e \vec{x} = \frac{e^2}{m\omega_0^2} \vec{E} = \gamma_{\text{mol}} \epsilon_0 \vec{E}$$

Jackson extends this to allow multiple frequencies,

$$\gamma_{\text{mol}} = \frac{1}{\epsilon_0} \sum_j \frac{e^2}{m_j \omega_j^2}$$

*Later, we will use this model for time-dependent electric fields; then there will be a frequency-dependent permittivity.*

### Numerical examples

$$\gamma = \frac{4 \pi}{4 \pi \epsilon_0} \frac{e^2}{m \omega_0^2}$$

Estimate the order of magnitude.

Assume  $e$  = electron charge and  $m$  = electron mass, which should be the right order of magnitude.

Recall the “classical radius of the electron”,

$$r_e = \frac{1}{4 \pi \epsilon_0} \frac{e^2}{m c^2} = 2.82 \times 10^{-15} \text{ m}$$

Then

$$\gamma = \frac{4 \pi r_e c^2}{\omega_0^2}$$

From atomic/molecular physics,

estimate  $\hbar \omega_0 \sim 10 \text{ eV}$  ;

also,  $\hbar c = 197.3 \times 10^{-9} \text{ eV} \cdot \text{m}$  ;

$\therefore \frac{c}{\omega_0} \sim 2 \times 10^{-8} \text{ m}$  .

$$\begin{aligned}\gamma &\sim 4\pi \cdot 3 \times 10^{-15} \cdot 4 \times 10^{-16} \text{ m}^3 \\ &= 150 \times 10^{-31} \text{ m}^3\end{aligned}$$

which makes sense,  $\sim (\text{radius})^3$ .

But what does it imply about the susceptibility,  $\chi_e$ ?

### *Consider an ideal gas at STP*

One mole of an ideal gas will occupy a volume of 22.4 liters at STP (0°C and one atmosphere pressure); that is,

$$N = \frac{6.02 \times 10^{23}}{22.4 \times 10^{-3} \text{ m}^3} = 2.7 \times 10^{25} \text{ m}^{-3}$$

$$\gamma N = 4.05 \times 10^{-4}$$

$$\chi = \frac{N\gamma}{1 - N\gamma/3} = 4.05 \times 10^{-4}$$

$$\epsilon/\epsilon_0 = 1 + \chi_e = 1 + 405 \times 10^{-6}$$

$$\{\epsilon/\epsilon_0 - 1\} \times 10^6 = 405$$

Examples :  $(\epsilon/\epsilon_0 - 1) \times 10^6$

Ar : 555

CO<sub>2</sub> : 990

O<sub>2</sub> : 588

N<sub>2</sub> : 531

Question:

Dielectric constant = relative permittivity

$\kappa = \epsilon / \epsilon_0$  ; for example,  $\kappa = 1.0005$  for air.

How are dielectric constants measured?

Recall, capacitance =  $\frac{\epsilon A}{d}$ .

## Case 2: Molecule with a permanent dipole moment

Dense materials have  $\kappa > 1$  or maybe  $\gg 1$ .

Glasses :  $\kappa$  from 4 to 14

Water :  $\kappa =$  from 35 to 78

BaTiO<sub>3</sub> :  $\kappa$  from 100 to 1250

*dependent on temperature*

“Orientation polarization”

Suppose the permanent dipole moment of the molecule is  $\vec{p}_0$ . Place a sample in an electric field  $\vec{E}$ . The potential energy of the dipole is

$$U = - \vec{p}_0 \cdot \vec{E} = - p_0 E \cos\theta.$$

The distribution of angles is  $C e^{-U/kT}$

(Boltzmann)  $\Rightarrow$  the mean dipole moment is

$$\langle p_0 ( \hat{e}_x \sin\theta \cos\phi + \hat{e}_y \sin\theta \sin\phi + \hat{e}_z \cos\theta ) \rangle$$

$$= p_0 \hat{e}_z \langle \cos\theta \rangle$$

$$\langle \cos\theta \rangle = \frac{\int \cos\theta \exp[-U/kT] \sin\theta d\theta d\phi}{\int \exp[-U/kT] \sin\theta d\theta d\phi}$$

$$= \frac{d}{d\beta} \log \int \exp[\beta \cos\theta] \sin\theta d\theta$$

$$\text{where } \beta = \frac{p_0 E}{kT}$$

$$= \frac{d}{d\beta} \log \left[ \frac{2}{\beta} \text{Sinh}\beta \right]$$

$$= -\frac{1}{\beta} + \coth\beta \approx \frac{\beta}{3} \text{ for small } \beta$$

$$\langle \vec{p} \rangle = p_0 \frac{p_0 E}{3kT} \hat{e}_z = \gamma \epsilon_0 \vec{E}$$

$$\gamma = \frac{p_0^2}{3 \epsilon_0 kT}$$

$$\Rightarrow \chi_e = \frac{N\gamma}{1-N\gamma/3}$$

Exercise: From  $\kappa = 78$  at room temperature, calculate  $p_0$ .