

Clausius-Mossotti relation: In linear dielectric, the polarization is $\vec{P} = \epsilon_0 \chi_e \vec{E}$ when the electric field \vec{E} is weak. However, this electric field is the *total* field *i.e.* $\vec{E}_{\text{tot}} = \vec{E}_{\text{ext}} + \vec{E}_{\text{pol}}$, external and that due to polarization. For non-polar material, the induced dipole moment is $\vec{p} = \alpha \vec{E}_{\text{ext}}$, where α is the atomic polarizability. If we are working with weak fields, then we may approximate

$$\vec{P} = N\vec{p} \Rightarrow \epsilon_0 \chi_e \approx N\alpha \rightarrow \chi_e = \frac{N\alpha}{\epsilon_0}, \quad (29)$$

where N is the number of molecules per unit volume and is small. If we consider the non-polar molecule be an uniformly charged sphere of radius R , then $N = 1/(\frac{4}{3}\pi R^3)$.

Next, let us calculate \vec{E}_{pol} when the molecule is placed in \vec{E}_{ext} , using Gauss's law and the way atomic polarizability is calculated in Example 4.1 (Griffiths),

$$E_{\text{pol}} 4\pi r^2 = \frac{\frac{4}{3}\pi r^3 \rho}{\epsilon_0} \Rightarrow \vec{E}_{\text{pol}} = \frac{\rho r \hat{r}}{3\epsilon_0} = \frac{1}{4\pi\epsilon_0} \frac{Q\vec{r}}{R^3} = \frac{\vec{p}}{4\pi\epsilon_0 R^3}.$$

The \vec{E}_{pol} is acting opposite to \vec{E}_{ext} , hence

$$\vec{E}_{\text{pol}} = \frac{-\alpha \vec{E}_{\text{ext}}}{4\pi\epsilon_0 R^3} \Rightarrow \vec{E}_{\text{tot}} = \left(1 - \frac{\alpha}{4\pi\epsilon_0 R^3}\right) \vec{E}_{\text{ext}} = \left(1 - \frac{N\alpha}{3\epsilon_0}\right) \vec{E}_{\text{ext}}. \quad (30)$$

The susceptibility and polarizability get connected by,

$$\vec{P} = N\vec{p} = N\alpha \vec{E}_{\text{ext}} \Rightarrow \frac{N\alpha \vec{E}_{\text{tot}}}{1 - \frac{N\alpha}{3\epsilon_0}} = \epsilon_0 \chi_e \vec{E}_{\text{tot}} \Rightarrow \chi_e = \frac{\frac{N\alpha}{\epsilon_0}}{1 - \frac{N\alpha}{3\epsilon_0}}. \quad (31)$$

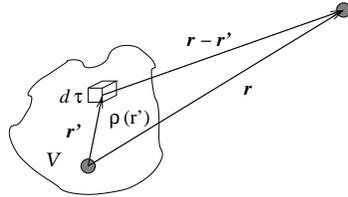
Solving for α , we obtain Clausius-Mossotti relation for non-polar molecule

$$\alpha = \frac{3\epsilon_0}{N} \frac{\chi_e}{3 + \chi_e} = \frac{3\epsilon_0}{N} \frac{K - 1}{K + 2} \quad (32)$$

where, $K = \chi_e + 1$.

Multipole expansion: (*Not in syllabus*) We use *multipole expansion* to determine potential at large distances away from a localized charge distribution, which may or may not be neutral. It is done by expansion of the potential of the charge distribution in powers of $1/r$. Let us first do it in a coordinate independent way, referring to the figure below, we write the potential at \vec{r} as,

$$V(\vec{r}) = \frac{1}{4\pi\epsilon_0} \int_V \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\tau'. \quad (33)$$



Since $|\vec{r} - \vec{r}'| = (r^2 + r'^2 - 2\vec{r} \cdot \vec{r}')^{1/2}$ and $|\vec{r}| \gg |\vec{r}'|$, we have,

$$\begin{aligned} |\vec{r} - \vec{r}'|^{-1} &= (r^2 + r'^2 - 2\vec{r} \cdot \vec{r}')^{-1/2} \\ &= \frac{1}{r} \left[1 - \left(\frac{2\vec{r} \cdot \vec{r}'}{r^2} - \frac{r'^2}{r^2} \right) \right]^{-1/2} \\ &= \frac{1}{r} \left[1 + \frac{1}{2} \left(\frac{2\vec{r} \cdot \vec{r}'}{r^2} - \frac{r'^2}{r^2} \right) + \frac{1}{2} \left(-\frac{1}{2} \right) \left(-\frac{1}{2} - 1 \right) \left(\frac{2\vec{r} \cdot \vec{r}'}{r^2} - \frac{r'^2}{r^2} \right)^2 + \dots \right] \end{aligned}$$

Collecting the terms with same power of r' ,

$$|\vec{r} - \vec{r}'|^{-1} = \frac{1}{r} + \frac{\vec{r} \cdot \vec{r}'}{r^3} + \frac{1}{2} \left(\frac{3(\vec{r} \cdot \vec{r}')^2}{r^5} - \frac{r'^2}{r^3} \right) + \dots \quad (34)$$

Therefore, the potential in Eqn. (33) becomes,

$$V(\vec{r}) = \frac{1}{4\pi\epsilon_0} \int_{\mathcal{V}} \left[\frac{1}{r} + \frac{\vec{r} \cdot \vec{r}'}{r^3} + \frac{1}{2} \left(\frac{3(\vec{r} \cdot \vec{r}')^2}{r^5} - \frac{r'^2}{r^3} \right) + \dots \right] \rho(\vec{r}') d\tau' \quad (35)$$

$$= \frac{1}{4\pi\epsilon_0} \left[\frac{1}{r} \int \rho(\vec{r}') d\tau' + \sum_i \frac{r_i}{r^3} \int r'_i \rho(\vec{r}') d\tau' + \sum_{i,j} \frac{1}{2} \frac{r_i r_j}{r^5} \int [3r'_i r'_j - \delta_{ij} r'^2] \rho(\vec{r}') d\tau' + \dots \right]. \quad (36)$$

The above equation (36) is the desired expansion of potential in $1/r$. To gain some physical insight of the expansion, we define the followings:

$$\text{Monopole : } q = \int_{\mathcal{V}} \rho(\vec{r}') d\tau' \quad (37)$$

$$\text{Dipole moment : } p_i = \int_{\mathcal{V}} r'_i \rho(\vec{r}') d\tau' \quad (38)$$

$$\text{Quadrupole moment : } Q_{ij} = \int_{\mathcal{V}} (3r'_i r'_j - \delta_{ij} r'^2) \rho(\vec{r}') d\tau' \quad (39)$$

In the expression for dipole moment above, Eqn. (38), it is written in component form which, when written in vector notation, is same as before viz.

$$\vec{p} = \int_{\mathcal{V}} \vec{r}' \rho(\vec{r}') d\tau'$$

In polar coordinate, the expression (36) is given by,

$$V(\vec{r}) = \frac{1}{4\pi\epsilon_0} \sum_{n=0}^{\infty} \frac{1}{r^{n+1}} \int_{\mathcal{V}} (r')^n P_n(\cos \theta) \rho(\vec{r}') d\tau' \quad (40)$$

the same as Eqn. 3.95 of Griffiths. This explains the origin of higher moments in potential, Eqn. (15) of a general localized charge distribution. Just for exercise, try to calculate the octopole moment by considering the terms r'^3 in the equations (34, 35).