DIPOLE MOMENT AND POLARIZABILITY

LECTURE-7

Polarizability

Polarizability allows us to better understand the interactions between nonpolar atoms and molecules and other electrically charged species, such as ions or polar molecules with dipole moments.

Introduction

Neutral nonpolar species have spherically symmetric arrangements of electrons in their electron clouds. When in the presence of an electric field, their electron clouds can be distorted (Figure 1). The ease of this distortion is defined as the **polarizability** of the atom or molecule. The created distortion of the electron cloud causes the originally nonpolar molecule or atom to acquire a dipole moment. This induced dipole moment is related to the polarizability of the molecule or atom and the strength of the electric field by the following equation:

$$\mu_{ind} = \alpha E \tag{1}$$

where E denotes the strength of the electric field and α is the polarizability of the atom or molecule with units of C m^{2}V^{-1}.

Neutral Species

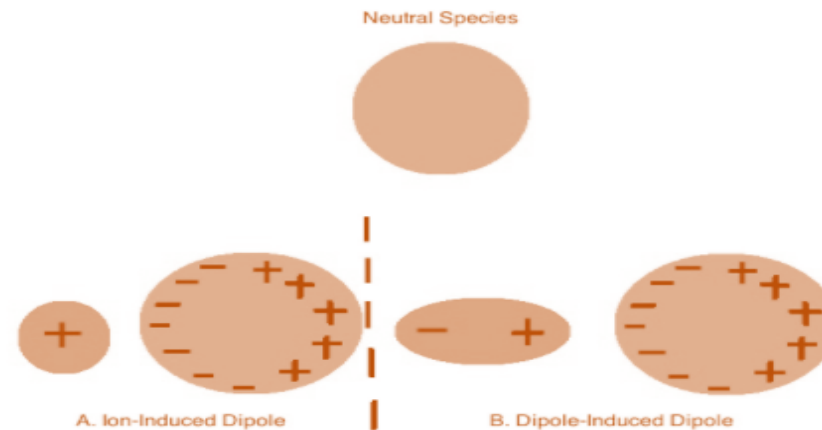A. Ion-Induced Dipole   B. Dipole-Induced Dipole

Figure 1: A neutral nonpolar species's electron cloud is distorted by A.) an Ion and B.) a polar molecule to induce a dipole moment.

In general, polarizability correlates with the interaction between electrons and the nucleus. The amount of electrons in a molecule affects how tight the nuclear charge can control the overall charge distribution. Atoms with fewer electrons will have smaller, denser electron clouds, as there is a strong interaction between the few electrons in the atoms' orbitals and the positively charged nucleus. There is also less shielding in atoms with fewer electrons contributing to the stronger interaction of the outer electrons and the nucleus. With the electrons held tightly in place in these smaller atoms, these atoms are typically not easily polarized by external electric fields. In contrast, large atoms with many electrons, such as negative ions with excess electrons, are easily polarized. These atoms typically have very diffuse electron clouds and large atomic radii that limit the interaction of their external electrons and the nucleus.

Factors that Influence Polarizability

The relationship between polarizability and the factors of electron density, atomic radii, and molecular orientation is as follows:

1. The greater the number of electrons, the less control the nuclear charge has on charge distribution, and thus the increased polarizability of the atom.

2. The greater the distance of electrons from nuclear charge, the less control the nuclear charge has on the charge distribution, and thus the increased polarizability of the atom.

3. Molecular orientation with respect to an electric field can affect polarizibility (labeled Orientation-dependent), except for molecules that are: tetrahedral, octahedral or icosahedral (labeled Orientation-independent). This factor is more important for unsaturated molecules that contain areas of electron-dense regions, such as 2,4-hexadiene. Greatest polarizability in these molecules is achieved when the electric field is applied parallel to the molecule rather than perpendicular to the molecule.

Polarizability Influences Dispersion Forces

The dispersion force is the weakest intermolecular force. It is an attractive force that arises from surrounding temporary dipole moments in nonpolar molecules or species. These temporary dipole moments arise when there are instantaneous deviations in the electron clouds of the nonpolar species. Surrounding molecules are influenced by these temporary dipole moments and a sort of chain reaction results in which subsequent weak, dipole-induced dipole interactions are created. These cumulative dipole- induced dipole interactions create attractive dispersion forces. Dispersion forces are the forces that make nonpolar substances condense to liquids and freeze into solids when the temperature is low enough.

- As polarizability *increases*, the dispersion forces also become *stronger*. Thus, molecules attract one another more *strongly* and melting and boiling points of covalent substances *increase* with *larger* molecular mass.

- Polarazibility also affects dispersion forces through the molecular shape of the affected molecules. Elongated molecules have electrons that are easily moved increasing their polarizability and thus strengthening the dispersion forces, (Figure 2). In contrast, small, compact, symmetrical molecules are less polarizable resulting in weaker dispersion forces.
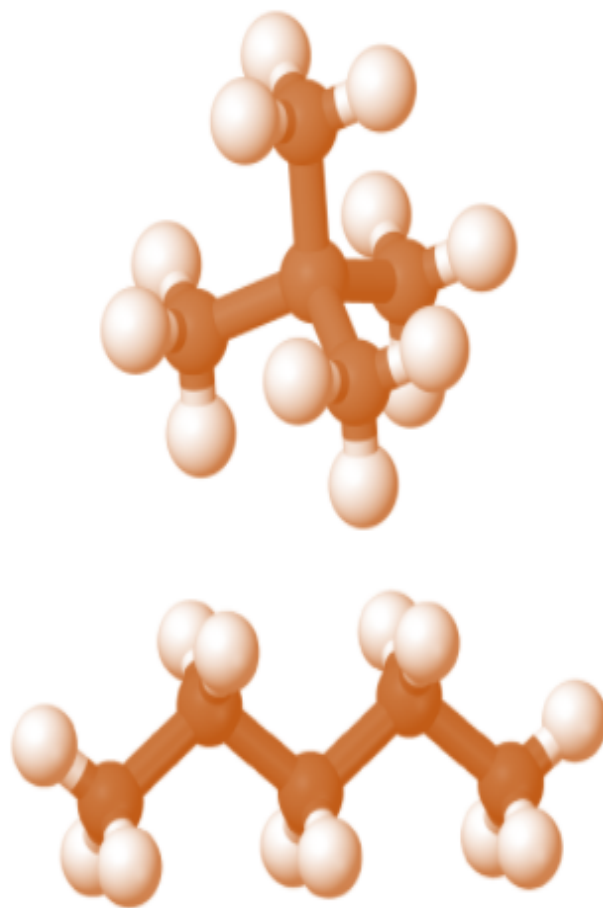

Figure 2: (top) Neopentane, an isomer of n-pentane, is an example of a more compact and less polarizable molecule. (bottom) n-Pentane is an example of an elongated molecule that is more easily polarized.

The relationship between polarizability and dispersion forces can be seen in the following equation, which can be used to quantify the interaction between two like nonpolar atoms or molecules:

$$V = \frac{-3}{4} \frac{\alpha^2 I}{r^6} \tag{2}$$

where

- r is the distance between the atoms or molecules,
- I is the first ionization energy of the atom or molecule, and
- α is the polarizability constant expressed in units of m^3.

This expression of α is related to α' by the following equation:

$$\alpha = \frac{\alpha}{4\pi\epsilon_o} \tag{3}$$

To quantify the interaction between unlike atoms or molecules (A and B) the Equation 2 becomes:

$$V = \frac{-3}{2} \frac{I_A I_B}{I_A + I_B} \frac{\alpha_A \alpha_B}{r^6} \tag{4}$$

Dipole Moments

Dipole moments occur when there is a separation of charge. They can occur between two ions in an ionic bond or between atoms in a covalent bond; dipole moments arise from differences in electronegativity. The larger the difference in electronegativity, the larger the dipole moment. The distance between the charge separation is also a deciding factor into the size of the dipole moment. The dipole moment is a measure of the polarity of the molecule.

Introduction

When atoms in a molecule share electrons unequally, they create what is called a dipole moment. This occurs when one atom is more electronegative than another, resulting in that atom pulling more tightly on the shared pair of electrons, or when one atom has a lone pair of electrons and the difference of electronegativity vector points in the same way. One of the most common examples is the water molecule, made up of one oxygen atom and two hydrogen atoms. The differences

Dipole Moment

When two electrical charges, of opposite sign and equal magnitude, are separated by a distance, an electric dipole is established. The size of a dipole is measured by its dipole moment (μ). Dipole moment is measured in Debye units, which is equal to the distance between the charges multiplied by the charge (1 Debye equals $3.34 \times 10^{-30} \, C\,m$). The dipole moment of a molecule can be calculated by Equation 1:

$$\vec{\mu} = \sum_i q_i \, \vec{r}_i \tag{1}$$

where

- $\vec{\mu}$ is the dipole moment vector
- q_i is the magnitude of the ith charge, and
- $\vec{r}_i$ is the vector representing the position of ith charge.

The dipole moment acts in the direction of the vector quantity. An example of a polar molecule is H_2O. Because of the lone pair on oxygen, the structure of H_2O is bent (via VEPSR theory), which that the vectors representing the dipole moment of each bond do not cancel each other out. Hence, water is polar.
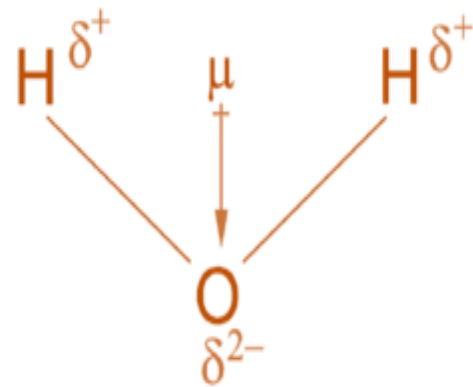

Figure 1: Dipole moment of water. The convention in chemistry is that the arrow representing the dipole moment goes from positive to negative. Physicist tend to use the opposite orientation.

The vector points from positive to negative, on both the molecular (net) dipole moment and the individual bond dipoles. Table A2 shows the electronegativity of some of the common elements. The larger the difference in electronegativity between the two atoms, the more electronegative that bond is. To be considered a polar bond, the difference in electronegativity must be large. The dipole moment points in the direction of the vector quantity of each of the bond electronegativities added together.

It is relatively easy to measure dipole moments; just place a substance between charged plates (Figure 2) and polar molecules increase the charge stored on plates and the dipole moment can be obtained (i.e., via the capacitance of the system). Nonpolar CCl_4 is not deflected; moderately polar acetone deflects slightly; highly polar water deflects strongly. In general, polar molecules will align themselves: (1) in an electric field, (2) with respect to one another, or (3) with respect to ions (Figure 2).

Figure 2: Polar molecules align themselves in an electric field (left), with respect to one another (middle), and with respect to ions (right)

Equation 1 can be simplified for a simple separated two-charge system like diatomic molecules or when considering a bond dipole within a molecule

$$\mu_{diatomic} = Q \times r \tag{2}$$

This bond dipole is interpreted as the dipole from a charge separation over a distance r between the partial charges Q^+ and Q^- (or the more commonly used terms δ^+ - δ^-); the orientation of the dipole is along the axis of the bond. Consider a simple system of a single electron and proton separated by a fix distance. When proton and electron close together, the dipole moment (degree of polarity) decreases. However, as proton and electron get farther apart, the dipole moment increases. In this case, the dipole moment calculated as (via Equation 2):

$$\mu = Qr$$
$$= (1.60 \times 10^{-19}\, C)(1.00 \times 10^{-10}\, m)$$
$$= 1.60 \times 10^{-29}\, C \cdot m \tag{3}$$

The Debye characterizes size of dipole moment. When a proton & electron 100 pm apart, the dipole moment is 4.80 D:

$$\mu = (1.60 \times 10^{-29}\, C \cdot m)\left(\frac{1\, D}{3.336 \times 10^{-30}\, C \cdot m}\right)$$
$$= 4.80\, D \tag{4}$$

$4.80\ D$ is a key reference value and represents a pure charge of +1 and -1 separated by 100 pm. If the charge separation were increased then the dipole moment increases (linearly):

- If the proton and electron were separated by 120 pm:

$$\mu = \frac{120}{100}(4.80\ D) = 5.76\ D \tag{5}$$

- If the proton and electron were separated by 150 pm:

$$\mu = \frac{150}{100}(4.80\ D) = 7.20\ D \tag{6}$$

- If the proton and electron were separated by 200 pm:

$$\mu = \frac{200}{100}(4.80\ D) = 9.60\ D \tag{7}$$

Example 1: Water

The water molecule in Figure 1 can be used to determine the direction and magnitude of the dipole moment. From the electronegativities of oxygen and hydrogen, the difference is 1.2e for each of the hydrogen-oxygen bonds. Next, because the oxygen is the more electronegative atom, it exerts a greater pull on the shared electrons; it also has two lone pairs of electrons. From this, it can be concluded that the dipole moment points from between the two hydrogen atoms toward the oxygen atom. Using the equation above, the dipole moment is calculated to be 1.85 D by multiplying the distance between the oxygen and hydrogen atoms by the charge difference between them and then finding the components of each that point in the direction of the net dipole moment (the angle of the molecule is 104.5°).

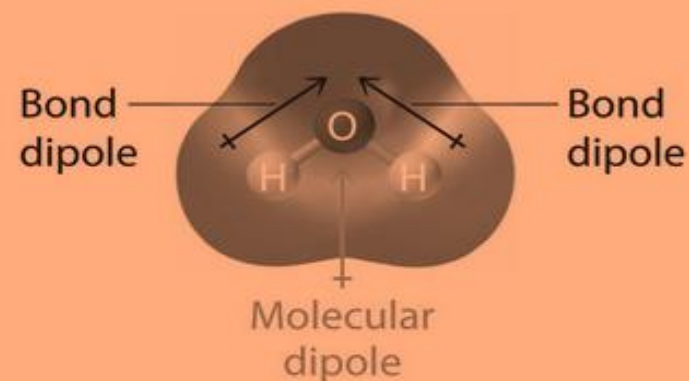The bond moment of O-H bond =1.5 D, so the net dipole moment is

$$\mu = 2(1.5)\cos\left(\frac{104.5^\circ}{2}\right) = 1.84\ D$$

Polarity and Structure of Molecules

The shape of a molecule and the polarity of its bonds determine the OVERALL POLARITY of that molecule. A molecule that contains polar bonds, might not have any overall polarity, depending upon its shape. The simple definition of whether a complex molecule is polar or not depends upon whether its overall centers of positive and negative charges overlap. If these centers lie at the same point in space, then the molecule has no overall polarity (and is non polar). If a molecule is completely symmetric, then the dipole moment vectors on each molecule will cancel each other out, making the molecule nonpolar. A molecule can only be polar if the structure of that molecule is not symmetric.
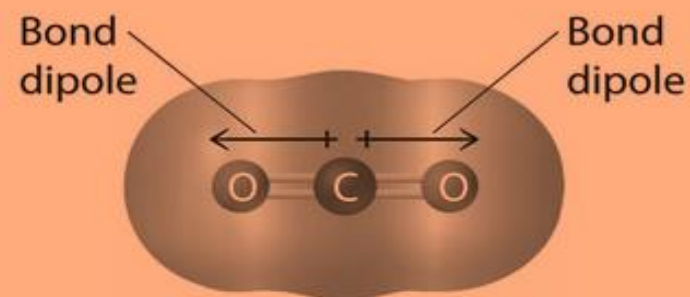
(a) No net dipole moment   (b) Net dipole moment

Figure 3: Charge distributions of CO_2 and H_2O. Blue and red colored regions are negative and positively signed regions, respectively.

A good example of a nonpolar molecule that contains polar bonds is carbon dioxide (Figure 3a). This is a linear molecule and each C=O bond is, in fact, polar. The central carbon will have a net positive charge, and the two outer oxygen atoms a net negative charge. However, since the molecule is linear, these two bond dipoles cancel each other out (i.e. the vector addition of the dipoles equals zero) and the overall molecule has a zero dipole moment ($\mu = 0$).

> *Although a polar bond is a prerequisite for a molecule to have a dipole, not all molecules with polar bonds exhibit dipoles*

For AB_n molecules, where A is the central atom and B are all the same types of atoms, there are certain molecular geometries which are symmetric. Therefore, they will have no dipole even if the bonds are polar. These geometries include linear, trigonal planar, tetrahedral, octahedral and trigonal bipyramid.
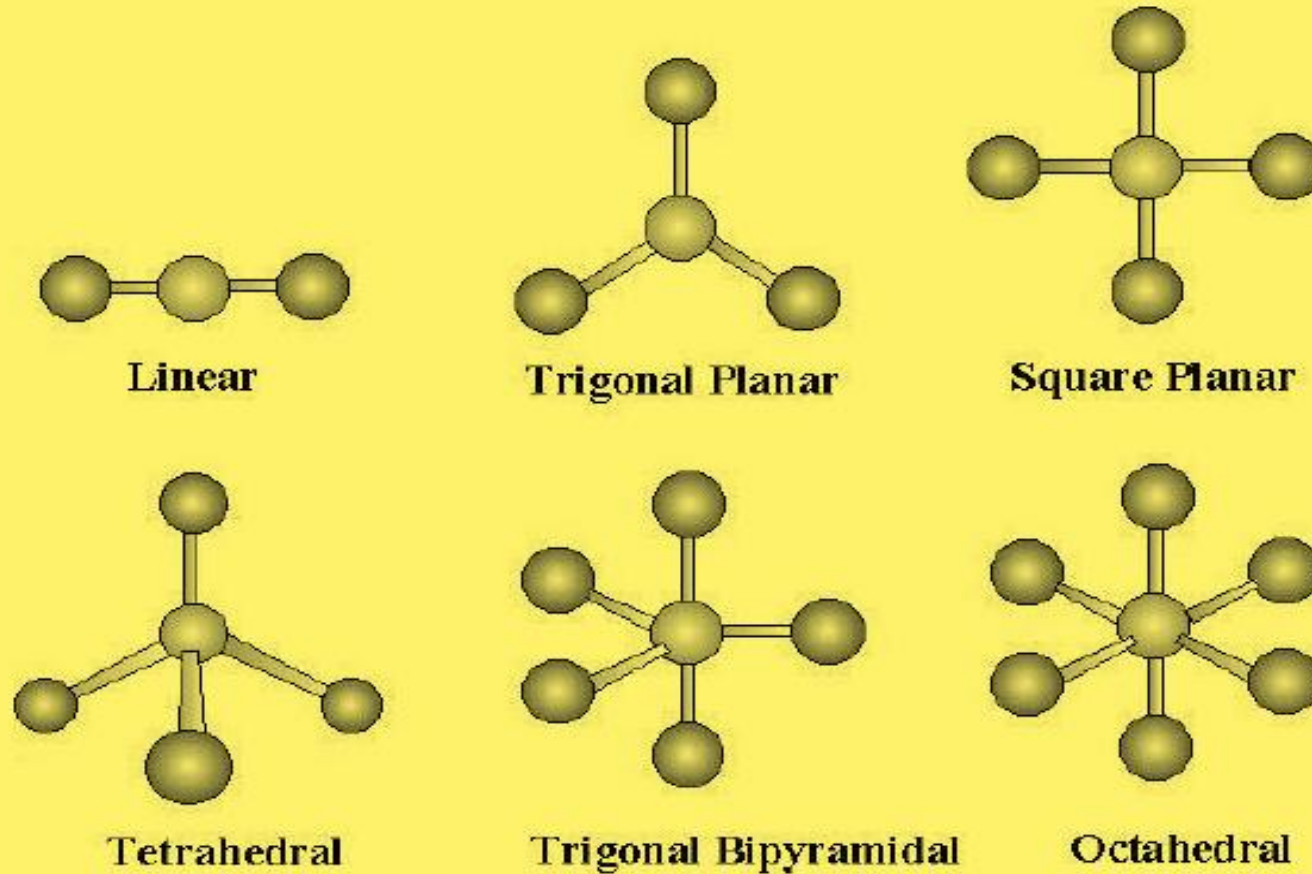

Linear   Trigonal Planar   Square Planar

Tetrahedral   Trigonal Bipyramidal   Octahedral

Figure 4: *Molecular geometries with exact cancellation of polar bonding to generate a non-polar molecule* $(\mu = 0)$

Example 3: C_2Cl_4

Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C=CCl_2$ does not have a net dipole moment.
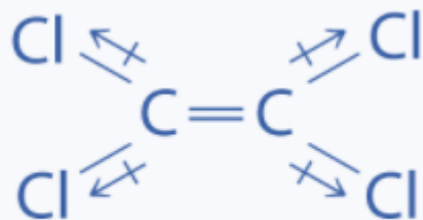
Example 3: CH_3Cl

C-Cl, the key polar bond, is 178 pm. Measurement reveals 1.87 D. From this data, % ionic character can be computed. If this bond were 100% ionic (based on proton & electron),

$$\mu = \frac{178}{100}(4.80\ D)$$
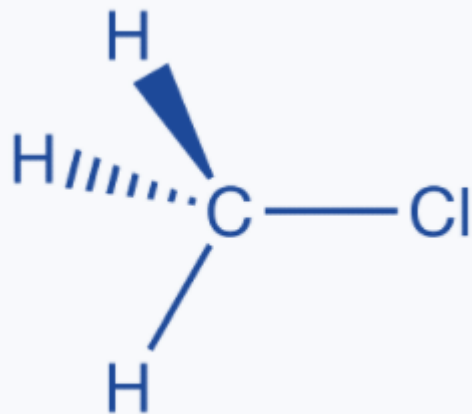
Although the bond length is *increasing*, the dipole is *decreasing* as you move down the halogen group. The electronegativity decreases as we move down the group. Thus, the greater influence is the electronegativity of the two atoms (which influences the *charge* at the ends of the dipole).

Table **1**: *Relationship between Bond length, Electronegativity and Dipole moments in simple Diatomics*

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

The Clausius-Mossotti Equation

Rudolf Julius Emmanuel Clausius (1822-1888)

- German thermodynamicist extraordinaire
  - Doctoral thesis on atmospheric optics from University of Halle in 1847
  - Taught in Berlin, Würzburg, Bonn, and briefly at ETH Zürich

- A "founding father" of thermodynamics
  - Revised the first and second laws of thermo
  - Mathematically described entropy and coined the term

Famous quotes:

"The energy of the universe is constant"

"The entropy of the universe tends to a maximum"

Clausius-Clapeyron Equation

$$\left[\frac{d \ln(P)}{d(1/T)} \right]_{[L-V]} = -\frac{\Delta H_{vap}}{R}$$

The Equation

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\chi}{\chi + 3} = \frac{N\alpha}{3\varepsilon_0}$$

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\chi}{\chi + 3} = \frac{4}{3}\pi N\alpha_V$$

$\varepsilon =$ bulk dielectric constant

$\varepsilon_0 =$ dielectric permittivity of free space $\left(\dfrac{A^2 \cdot s^4}{m^3 \cdot kg}\right)$

$\chi =$ bulk dielectric susceptibility

$\alpha =$ molecular polarizability $\left(\dfrac{A^2 \cdot s^4}{kg}\right)$
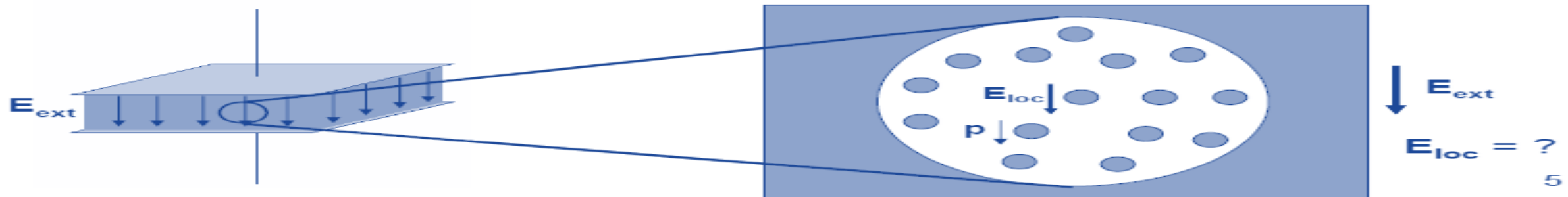
$\alpha_V =$ molecular polarizability volume (m^3)

$N =$ Number of dipolar molecules per unit volume

- Relates bulk, macroscopic quantity (ε or χ) to molecular quantity (α)

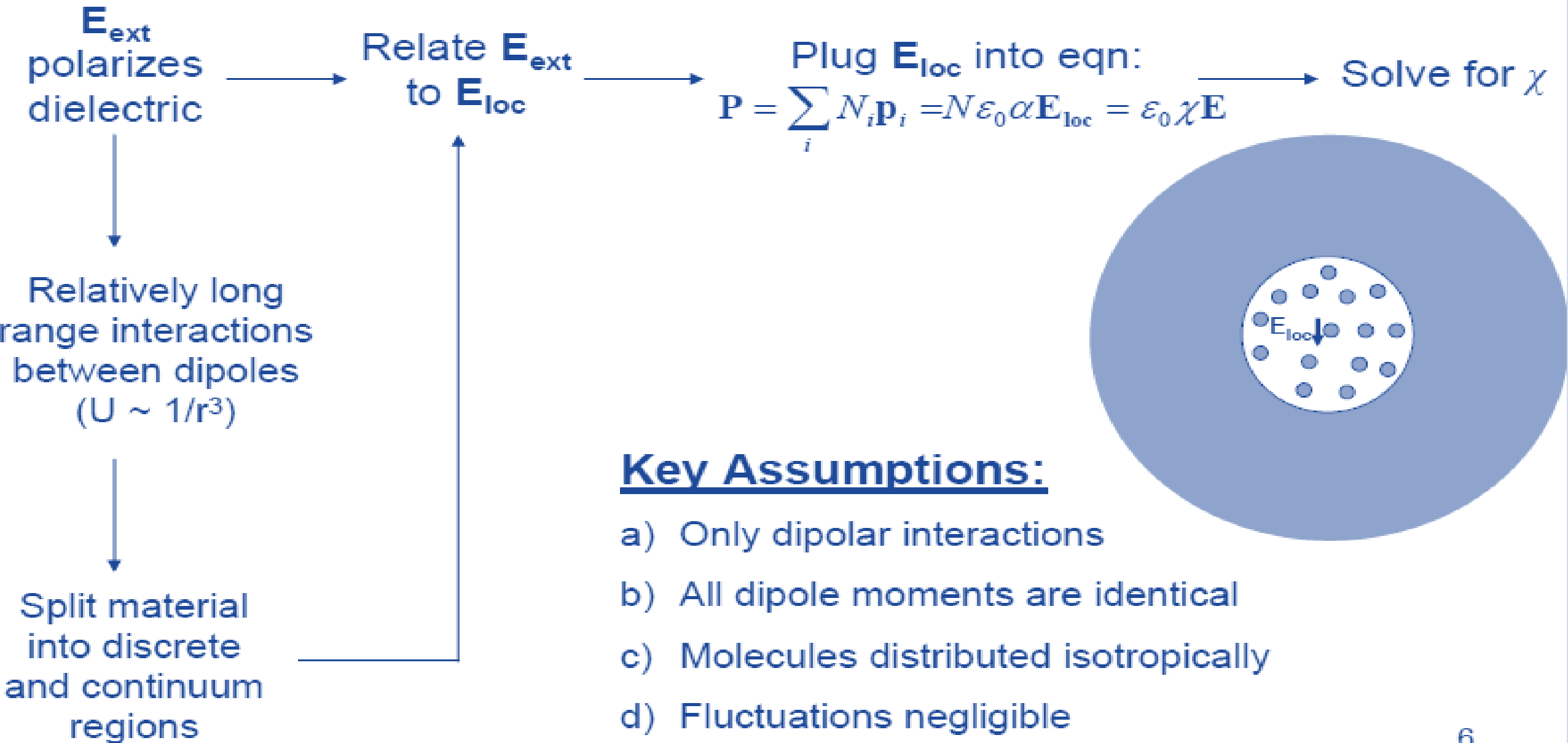- Derived independently (supposedly) by Mossotti (1850) and Clausius (1879)

What's the big deal?

- Useful
  - Clarifies molecular origin of dielectric constant
  - Allows calculation of molecular polarizability from measurements of ε

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\chi}{\chi + 3} = \frac{N\alpha}{3\varepsilon_0}$$

- Derivation is tricky, yet applicable to many physical situations:
  - What is the local electric field of a dielectric on a molecular scale?

E_{ext}

E_{loc}

P

E_{ext}

$E_{loc} = ?$

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Derivation Path

E_{ext} polarizes dielectric → Relate **E_{ext}** to **E_{loc}** → Plug **E_{loc}** into eqn:

$$\mathbf{P} = \sum_i N_i \mathbf{p}_i = N\varepsilon_0\alpha\mathbf{E}_{loc} = \varepsilon_0\chi\mathbf{E}$$

→ Solve for χ

Relatively long range interactions between dipoles ($U \sim 1/r^3$)

Split material into discrete and continuum regions

E_{loc}

Key Assumptions:

a) Only dipolar interactions

b) All dipole moments are identical

c) Molecules distributed isotropically

d) Fluctuations negligible

Clarification and Correction of Eqn 13.2

Electric field from a polarized body:

$$\phi_n(x,y,z) = \frac{\mathbf{p}_n \cdot \mathbf{r}_n}{4\pi\varepsilon_0 \mathbf{r}_n^3}$$

$\mathbf{p}_n$ = dipole moment of molecule n

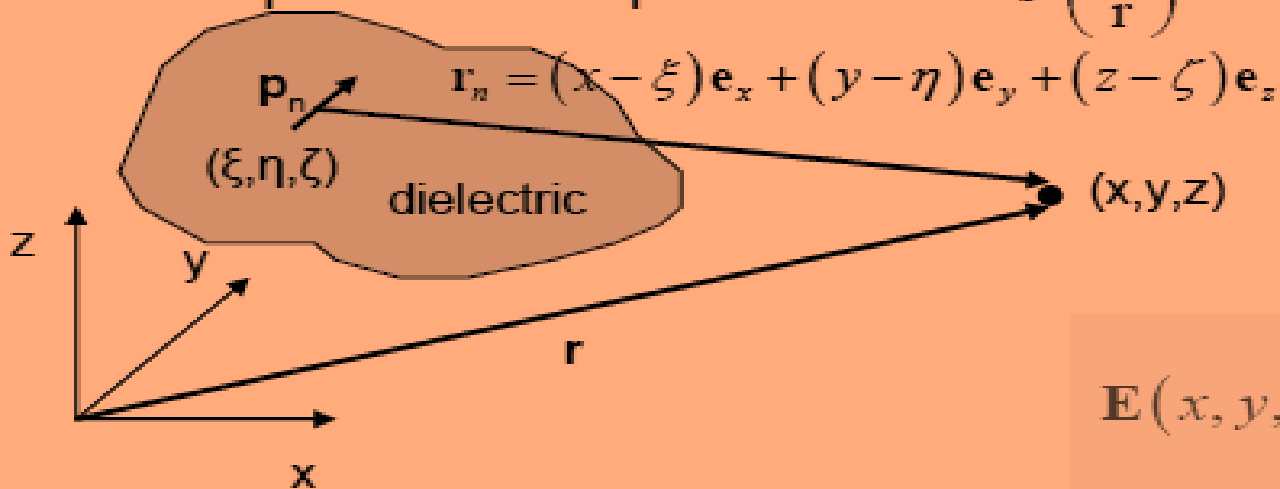$$\mathbf{P}(\xi,\eta,\zeta)dV = \sum_{n=1}^{M}\mathbf{p}_n$$

$$d\phi = \frac{\mathbf{P}\cdot\mathbf{r}}{4\pi\varepsilon_0 \mathbf{r}^3}dV \quad\rightarrow\quad \phi = \int_V \frac{\mathbf{P}(\xi,\eta,\zeta)\cdot\mathbf{r}}{4\pi\varepsilon_0 \mathbf{r}^3}d\xi d\eta d\zeta$$

$$\mathbf{E}(\mathbf{R}) = \nabla_1 \int_{body} \frac{\nabla_2 \cdot \mathbf{P}(\mathbf{R}_2)}{4\pi\varepsilon_0 R_{12}}d^3\mathbf{R}_2$$

Define two different gradient operators for the two coordinates:

$$\nabla_F = \frac{\partial}{\partial x}\mathbf{e}_x + \frac{\partial}{\partial y}\mathbf{e}_y + \frac{\partial}{\partial z}\mathbf{e}_z \qquad \nabla_S = \frac{\partial}{\partial \xi}\mathbf{e}_x + \frac{\partial}{\partial \eta}\mathbf{e}_y + \frac{\partial}{\partial \zeta}\mathbf{e}_z$$

We now recognize: $\nabla_S\left(\frac{1}{\mathbf{r}}\right) = \frac{\mathbf{r}}{\mathbf{r}^3}$ $\longrightarrow$ $\phi(x,y,z) = \frac{1}{4\pi\varepsilon_0}\int_V \mathbf{P}\cdot\left[\nabla_S\left(\frac{1}{\mathbf{r}}\right)\right]dV$

The dot product is expanded: $\nabla_S\cdot\left(\frac{\mathbf{P}}{\mathbf{r}}\right) = \frac{\nabla_S\cdot\mathbf{P}}{\mathbf{r}} + \mathbf{P}\cdot\left[\nabla_S\left(\frac{1}{\mathbf{r}}\right)\right]$

$$\mathbf{r}_n = (x-\xi)\mathbf{e}_x + (y-\eta)\mathbf{e}_y + (z-\zeta)\mathbf{e}_z$$

$\mathbf{p}_n$
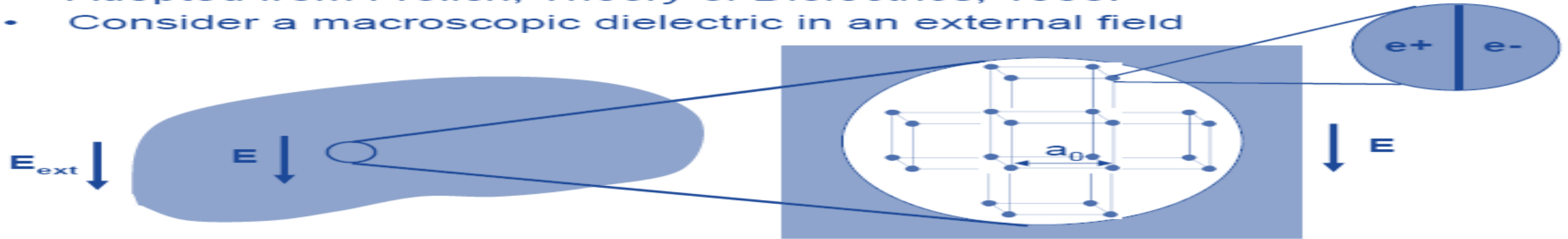(ξ,η,ζ) dielectric
(x,y,z)
z
y
r
x

Then use the divergence theorem to get:

$$\phi(x,y,z) = \int_S \frac{\mathbf{P}\cdot d\mathbf{S}}{4\pi\varepsilon_0 \mathbf{r}} + \int_V \frac{(-\nabla_S\cdot\mathbf{P})dV}{4\pi\varepsilon_0 \mathbf{r}}$$

$$\mathbf{E}(x,y,z) = -\nabla_F\left[\int_S \frac{\mathbf{P}\cdot d\mathbf{S}}{4\pi\varepsilon_0 \mathbf{r}} + \int_V \frac{(-\nabla_S\cdot\mathbf{P})dV}{4\pi\varepsilon_0 \mathbf{r}}\right]$$

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Finding the Local Field, E^{loc}

- Adopted from Frölich, *Theory of Dielectrics*, 1958.
- Consider a macroscopic dielectric in an external field

E_{ext} ↓ E ↓ a_0 E ↓   e+ | e-

- Consider a cubic lattice of dipoles
- Assumptions:
  - Charge separation $<< a_0$
  - Properties in sphere are same as bulk, fluctuations negligible
  - Only dipolar interactions

Finding the Local Field, E_{loc}

- Assume that applying **E** polarizes each lattice site the same amount:

Restoring force $\sim \bar{r}$ balances the force from $\mathbf{E}_{loc}$

Restoring force $= c^2\bar{r} = e\mathbf{E}_{loc}$ → $\mathbf{p} = e\bar{r} = \left(\dfrac{e}{c}\right)^2 \mathbf{E}_{loc}$

E ↓ E_{loc} ↓   e-   e+   ↕ r

Separate contributions of $\mathbf{E}_{loc}$ into inside and outside of sphere: $\mathbf{E}_{loc} = \mathbf{E}_{in} + \mathbf{E}_{out}$

Find $\mathbf{E}_{in}$ by summing each dipole interaction in the sphere:

Interaction energy between 2 identical point dipoles $= U_{ij} = \dfrac{p^2}{l_{ij}^3}\left(1 - 3\cos^2\left(\theta_{ij}\right)\right)$

$l_{ij} = $ Distance between dipoles i and j

Since dipoles are in lattice, $l_{ij} = (ma_0, na_0, qa_0)$ where m, n, q are integers

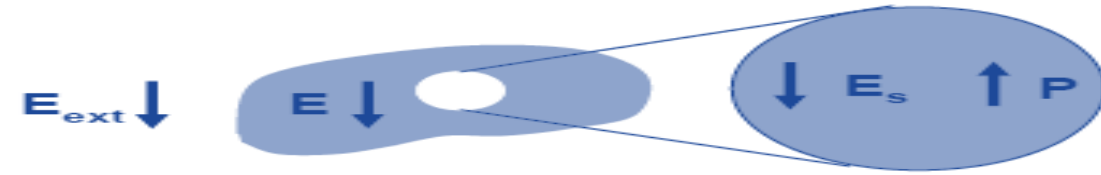$$U = \sum U_{ij} = \frac{p^2}{a_0^3}\sum_{m,n,q}\frac{m^2 + n^2 - 2q^2}{\left(m^2 + n^2 + q^2\right)^{5/2}} = 0$$

E_{ext} ↓   e+ | e- a_0 ↓ E

So $\mathbf{E}_{in} = 0$!

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Finding the Local Field, E_{loc}

$E_{loc} = E_{in} + E_{out}$

Calculate E_{out} macroscopically

$E_{out} = E - E_s$

E_s = "self-field" = field at center of a permanently polarized sphere

- Can be found with a standard calculation

$$E_S = -\frac{4\pi}{3}P$$

So finally:

$$E_{loc} = E_{in} + E_{out} = E - E_S = E + \frac{4\pi}{3}P$$

$$E_{loc} = \frac{\varepsilon+2}{3}E \qquad \text{"Lorentz formula"}$$

Plug into E_{loc} the microscopic equation

Here the macroscopic relation between **P** and **E** is:

$$P = \frac{\varepsilon-1}{4\pi}E$$

And the microscopic relation is:

$$p = \frac{1}{N}P = \left(\frac{e}{c}\right)^2 E_{loc}$$

$$P = N\left(\frac{e}{c}\right)^2 \frac{\varepsilon+2}{3}E = \frac{\varepsilon-1}{4\pi}E \longrightarrow \boxed{\frac{\varepsilon-1}{\varepsilon+2} = \frac{4\pi}{3}N\left(\frac{e}{c}\right)^2 = \frac{4}{3}\pi N\alpha_V}$$

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Limitations of the Equation

- Condensed systems (high density)
  - van der Waals and multipole forces can become significant
  - If we rearrange the C-M eqn, we get:

$$\varepsilon = \frac{3+8\pi N\alpha_V}{3-4\pi N\alpha_V}$$
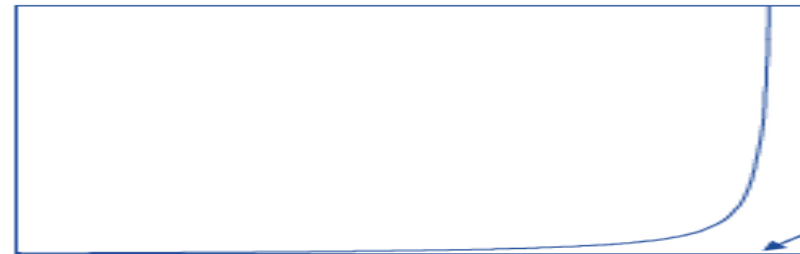
Critical density at $N = \dfrac{3}{4\pi\alpha_V}$

Not observed in experiments
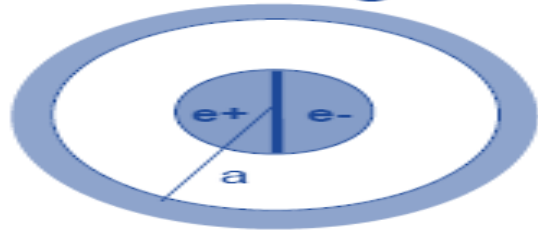
- Systems of permanently polar molecules
  - The derivation assumes that all polarity is induced
  - Permanent dipoles require a correction to the local field, as will be seen

Onsager's Correction to Local Field

- When calculating $\mathbf{E}_{loc}$, we neglected the coupling of the center dipole with the surrounding ones

- Onsager corrected this: $\mathbf{E}_{corr} = \mathbf{E}_{loc} - \mathbf{E}_{reaction}$

$$\mathbf{E}_{reaction} = \frac{2\chi}{3 + 2\chi} \frac{\mathbf{p}}{4\pi\varepsilon_0 a^3}$$

This yields:

$$N\alpha = \frac{\chi\left(1 + \frac{2}{3}\chi\right)}{1 + \chi}$$

$$\chi = \frac{3}{4}\left(N\alpha - 1 + \sqrt{1 + \frac{2}{3}N + N^2\alpha^2}\right)$$

Goes to C-M eqn in low density limit

Alternative Derivations Abound

- Hannay gives a derivation which involves no splitting into inner and outer parts
  - Uses the full expression for field of a dipole:

$$\mathbf{E} = \frac{3(\mathbf{p}\cdot\mathbf{r})\mathbf{r}}{r^5} - \frac{\mathbf{p}}{r^3} - \frac{4\pi}{3}\mathbf{p}\,\delta(\mathbf{r})$$

  - Local field correction results naturally
- Other derivations based on quantum mechanics
  - Attempt to account for non-localization of electrons at lattice points and other more complex phenomena
  - Eg, Adler, Onodera

Applications in Other Areas

- Dispersion properties in optical fibers
- Relating molar refractivity to bulk refractive index

$$\frac{\varepsilon-1}{\varepsilon+2} = \frac{\chi}{\chi+3} = \frac{4}{3}\pi N\alpha_V$$

$$\frac{\varepsilon-1}{\varepsilon+2} = \frac{\chi}{\chi+3} = \frac{N\alpha}{3\varepsilon_0}$$