# The Clausius-Mossotti Equation

Ottaviano Mossotti (1850) and Rudolf Clausius (1879)

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McKinley Group Summer Reading Club
“Familiar Results and Famous Papers”
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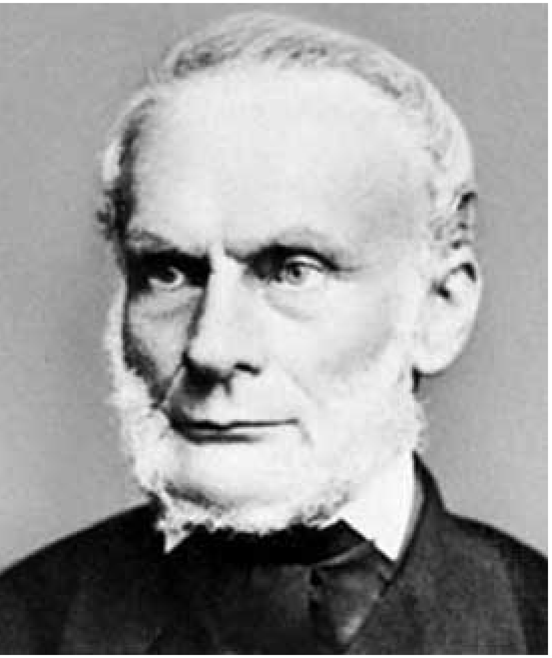
# Ottaviano Fabrizio Mossotti (1791-1863)

- Italian physicist and mathematician
  - Completed studies at University of Pavia in 1811 at age 20
- Contributions in:
  - Astrophysics (Brera Observatory, 1813 – 1823)
  - Molecular physics
- Interesting facts:
  - Part of a secret society against the occupying Austrian government
  - Escaped to London in 1823, then to Buenos Aires, Argentina, until 1835
  - Returned to Italy in 1840, where he taught until his death

http://liberti.dhs.org/liberti/maths-history/mossotti/mossotti.html

# 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

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



http://en.wikipedia.org/wiki/Rudolf_Clausius

Tester, J.W., Modell, M. (1997), *Thermodynamics and Its Applications, 3rd Ed.*, Prentice Hall, New Jersey, p. 681.

# 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 $\left(\frac{A^2 \cdot s^4}{m^3 \cdot kg}\right)$

$\chi =$ bulk dielectric susceptibility

$\alpha =$ molecular polarizability $\left(\frac{A^2 \cdot s^4}{kg}\right)$

$\alpha_V =$ molecular polarizability volume $\left(m^3\right)$

$N =$ Number of dipolar molecules per unit volume

- Relates bulk, macroscopic quantity ($\varepsilon$ or $\chi$) to molecular quantity ($\alpha$)
- Derived independently (supposedly) by Mossotti (1850) and Clausius (1879)

Clausius, R. (1879), *Die Mechanische Wärmetheorie*, **2**, Braunschweig, p. 62 – 97.

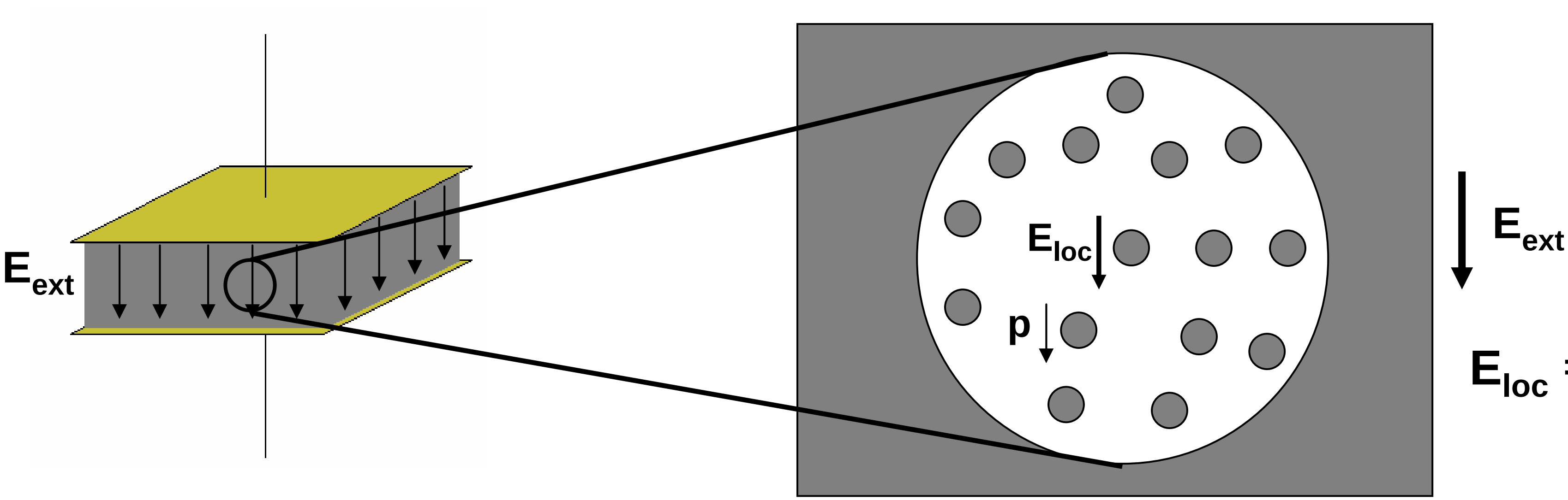
Mossotti, O.F. *Mem. Di Math, e Fisica d. Soc. Italiana d. Scienze*, **24**, 2, (1850), 49.

# What's the big deal?

- Useful
  - Clarifies molecular origin of dielectric constant
  - Allows calculation of molecular polarizability from measurements of $\varepsilon$

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

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



# Derivation Path

$\mathbf{E}_{\mathbf{ext}}$ polarizes dielectric → Relate $\mathbf{E}_{\mathbf{ext}}$ to $\mathbf{E}_{\mathbf{loc}}$ → Plug $\mathbf{E}_{\mathbf{loc}}$ into eqn: → Solve for $\chi$

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

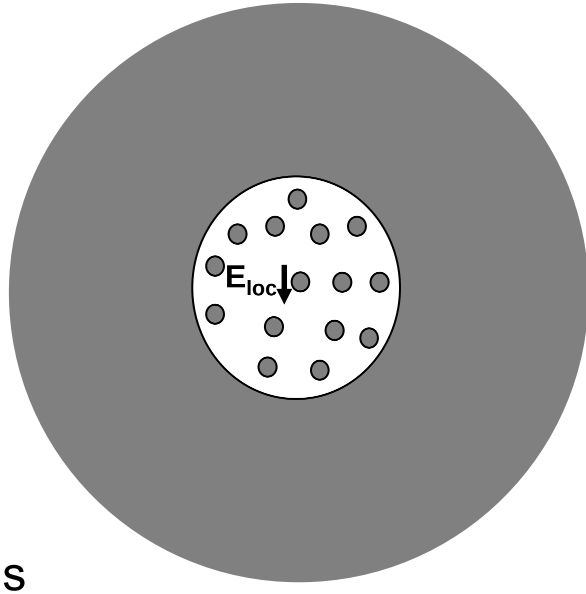
$\mathbf{E}_{\mathbf{ext}}$ polarizes dielectric

↓

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

↓

Split material into discrete and continuum regions → (Relate $\mathbf{E}_{\mathbf{ext}}$ to $\mathbf{E}_{\mathbf{loc}}$)




**<u>Key Assumptions:</u>**

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:

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

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

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

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

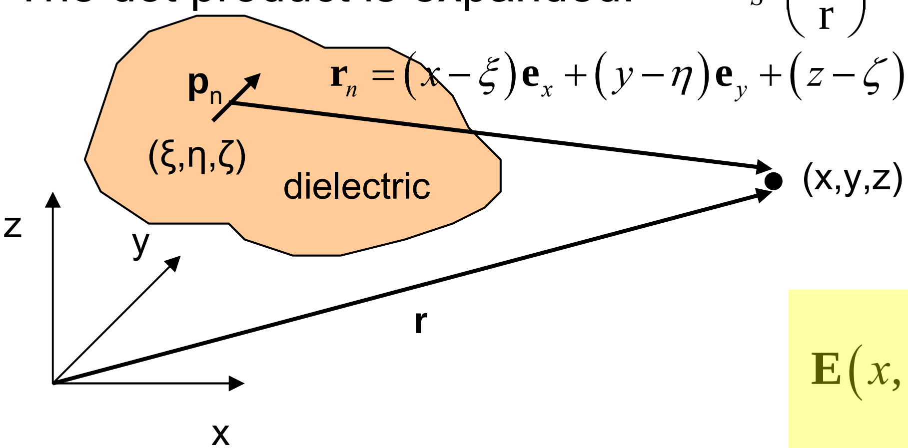
$$\mathbf{E}(\mathbf{R}) = \nabla_1 \int_{body} \frac{\nabla_2 \bullet \mathbf{P}(\mathbf{R}_2)}{4\pi\varepsilon_0 R_{12}} d^3\mathbf{R}_2$$

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

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




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

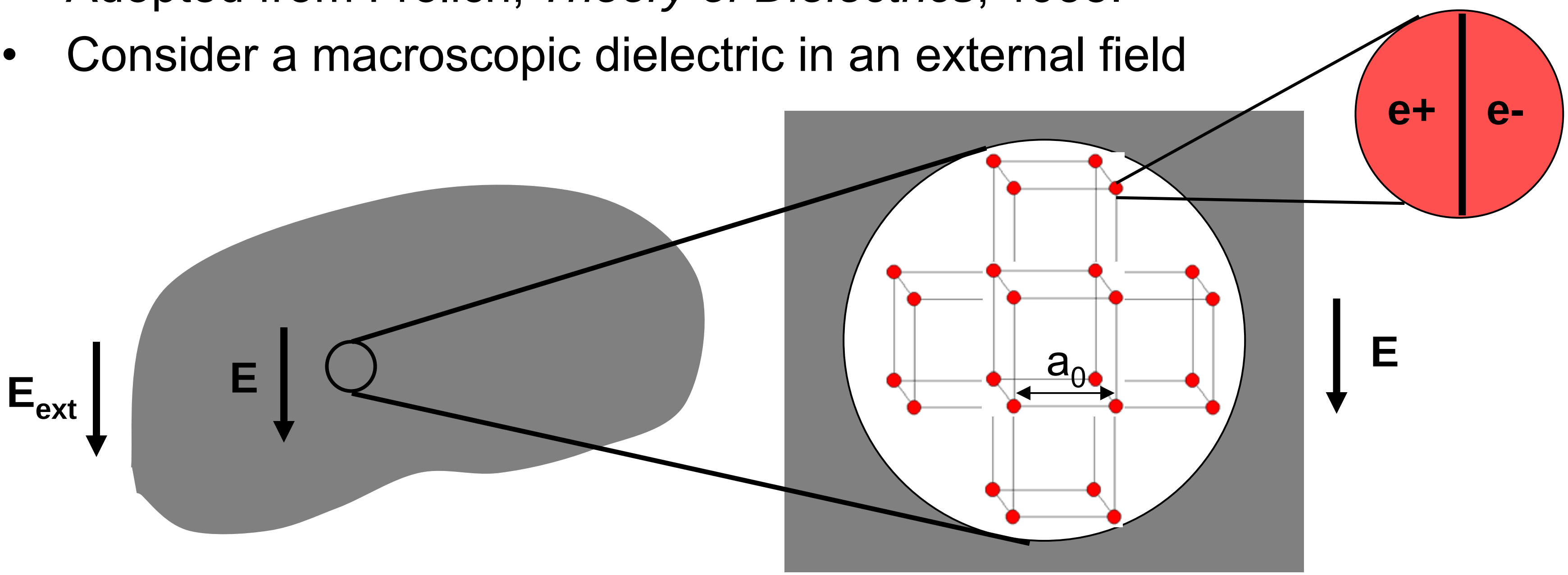
Then use the divergence theorem to get:

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

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

# Finding the Local Field, $E^{loc}$

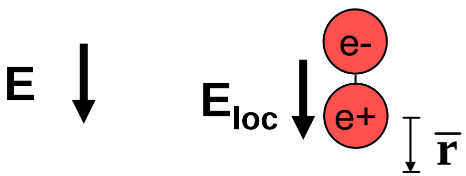
- Adopted from Frölich, *Theory of Dielectrics*, 1958.
- Consider a macroscopic dielectric in an external field




- 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, $\mathbf{E}_{loc}$

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




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

$$\text{Restoring force} = c^2\bar{\mathbf{r}} = e\mathbf{E}_{loc} \quad \rightarrow \quad \mathbf{p} = e\bar{\mathbf{r}} = \left(\frac{e}{c}\right)^2 \mathbf{E}_{loc}$$

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:

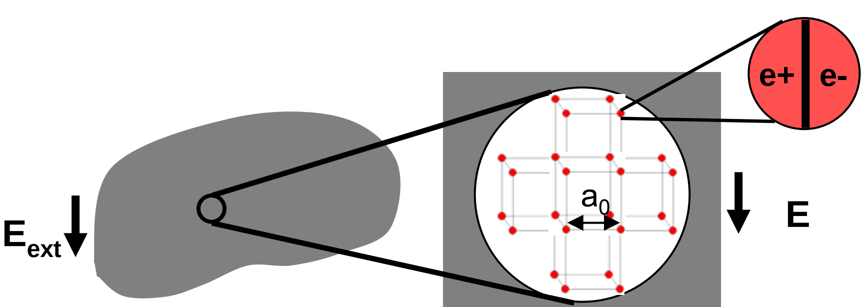
$$\text{Interaction energy between 2 identical point dipoles} = U_{ij} = \frac{p^2}{l_{ij}^3}\left(1 - 3\cos^2\left(\theta_{ij}\right)\right)$$

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

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

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

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

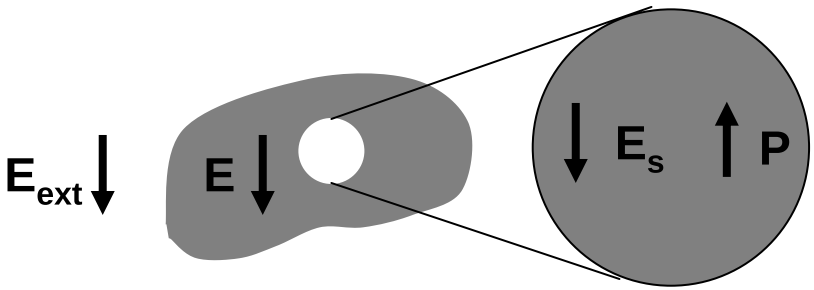


# Finding the Local Field, $\mathbf{E}_{loc}$

$\mathbf{E}_{loc} = \mathbf{E}_{in} + \mathbf{E}_{out}$

Calculate $\mathbf{E}_{out}$ macroscopically

$\mathbf{E}_{out} = \mathbf{E} - \mathbf{E}_s$




$\mathbf{E}_s$ = "self-field" = field at center of a permanently polarized sphere

- Can be found with a standard calculation

$$\mathbf{E}_S = -\frac{4\pi}{3}\mathbf{P}$$

So finally:

$$\mathbf{E}_{loc} = \mathbf{E}_{in} + \mathbf{E}_{out} = \mathbf{E} - \mathbf{E}_S = \mathbf{E} + \frac{4\pi}{3}\mathbf{P}$$

$$\mathbf{E}_{loc} = \frac{\varepsilon + 2}{3}\mathbf{E}$$

"Lorentz formula"

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

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

And the microscopic relation is:

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

Plug into $\mathbf{E}_{loc}$ the microscopic equation

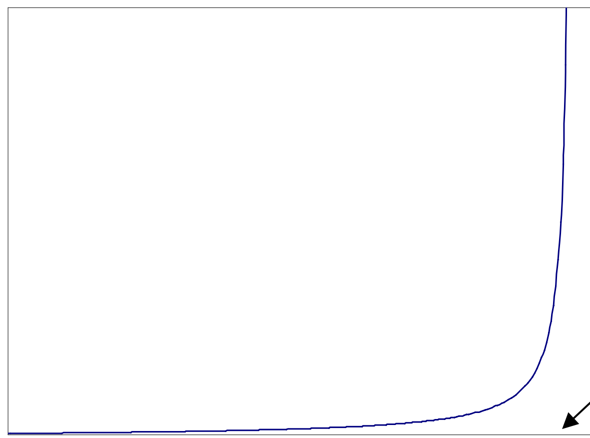
$$\mathbf{P} = N\left(\frac{e}{c}\right)^2 \frac{\varepsilon + 2}{3}\mathbf{E} = \frac{\varepsilon - 1}{4\pi}\mathbf{E} \longrightarrow$$

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

# 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 $N = \dfrac{3}{4\pi\alpha_V}$

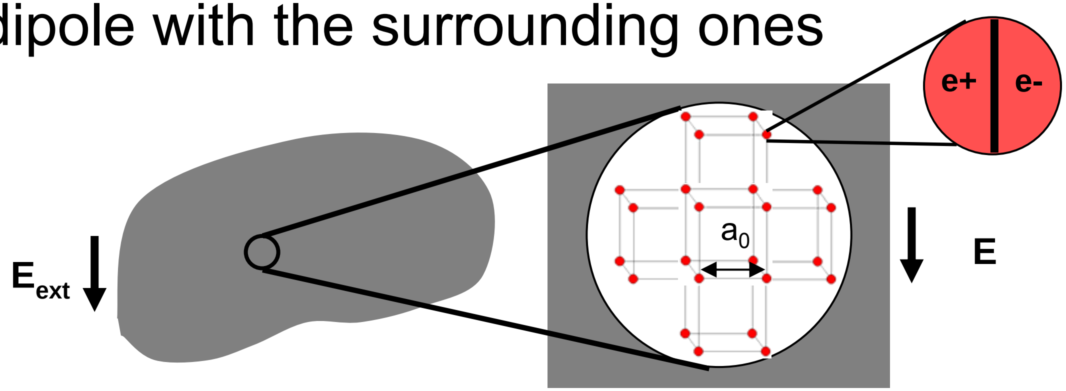
Not observed in experiments

- 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

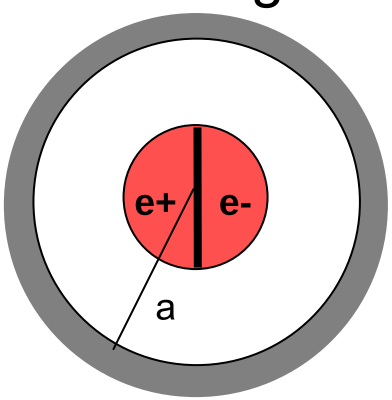
Böttcher, C. J. F. (1952), *Theory of Electric Polarisation*, Elsevier Publishing Co., New York, p. 199 - 212

# Onsager's Correction to Local Field

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




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




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

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:

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

  - 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

S. L. Adler, *Phys. Rev.* **126** (1962) 413.

J.H. Hannay *Eur. J. Phys.* **4** (1983) 141.

Y. Onodera, *Prog. Theo. Phys.*, **49** (1973) 37.

# Applications in Other Areas

- Dispersion properties in optical fibers
  - (P. Melman and R. W. Davies *J. Lightwave Tech.* **3** (1985) 1123.
- Relating molar refractivity to bulk refractive index
  - (Boling, Glass, Owyoung, *IEEE J. Quant. Electronics* **14** (1978) 601.)

# Thank you for your attention!

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

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