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

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

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

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

The Equation

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

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\chi}{\chi + 3} = \frac{4\pi N\alpha_v}{3}
\]

\( \varepsilon \) = 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)


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

\( \mathbf{E}_{\text{ext}} \) polarizes dielectric → Relate \( \mathbf{E}_{\text{ext}} \) to \( \mathbf{E}_{\text{loc}} \) → Plug \( \mathbf{E}_{\text{loc}} \) into eqn:

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

Solve for \( \chi \)

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:

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

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

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

Define two different gradient operators for the two coordinates:

\( \mathbf{\nabla}_F = \frac{\partial}{\partial x} \mathbf{e}_x + \frac{\partial}{\partial y} \mathbf{e}_y + \frac{\partial}{\partial z} \mathbf{e}_z \quad \mathbf{\nabla}_S = \frac{\partial}{\partial \xi} \mathbf{e}_x + \frac{\partial}{\partial \eta} \mathbf{e}_y + \frac{\partial}{\partial \zeta} \mathbf{e}_z \)

We now recognize:

\[ \mathbf{\nabla}_s \left( \frac{1}{r} \right) = \frac{\mathbf{r}}{r^3} \quad \rightarrow \quad \phi(x, y, z) = \frac{1}{4\pi\varepsilon_0} \int_V \mathbf{P} \cdot \left[ \mathbf{\nabla}_s \left( \frac{1}{r} \right) \right] \, dV \]

The dot product is expanded:

\[ \mathbf{\nabla}_s \cdot \left( \frac{\mathbf{P}}{r} \right) = \frac{\mathbf{\nabla}_s \cdot \mathbf{P}}{r} + \frac{\mathbf{P} \cdot \mathbf{\nabla}_s \left( \frac{1}{r} \right)}{r} \]

Then use the divergence theorem to get:

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

\[ \mathbf{E}(x, y, z) = -\mathbf{\nabla}_F \left[ \int_S \frac{\mathbf{P} \cdot d\mathbf{S}}{4\pi\varepsilon_0 r} + \int_V \left( -\mathbf{\nabla}_s \cdot \mathbf{P} \right) \, dV \right] \]
Finding the Local Field, $E^{\text{loc}}$

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

- Assume that applying $\mathbf{E}$ polarizes each lattice site the same amount:

$$\mathbf{E} \downarrow \quad \mathbf{E}_{\text{loc}} \downarrow \quad \mathbf{r}$$

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

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

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

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

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 $\mathbf{E}_{\text{in}} = 0$!
Finding the Local Field, $E_{\text{loc}}$

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

Calculate $E_{\text{out}}$ macroscopically

$E_{\text{out}} = E - E_s$

$E_s = \text{"self-field"} = \text{field at center of a permanently polarized sphere}$

- Can be found with a standard calculation

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

$E_{\text{loc}} = \frac{\varepsilon + 2}{3}E$ \hspace{1cm} \text{"Lorentz formula"}$

So finally:

$\varepsilon - 1 \ \ 4\pi$

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

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

$\varepsilon - 1 \ \ 4\pi$

$\varepsilon + 2 \ \ 3$

$\varepsilon - 1 \ \ 4\pi$

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

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 $E_{\text{loc}}$, we neglected the coupling of the center dipole with the surrounding ones.

Onsager corrected this: $E_{\text{corr}} = E_{\text{loc}} - E_{\text{reaction}}$

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

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:
    \[
    E = \frac{3(p \cdot r) r}{r^5} - \frac{p}{r^3} - \frac{4\pi}{3} p \delta(r)
    \]
  - 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.
Applications in Other Areas

- Dispersion properties in optical fibers

- Relating molar refractivity to bulk refractive index
Thank you for your attention!

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