On the Clausius-Mossotti Relation

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1 The Clausius-Mossotti Relation

In this note we review the derivation of the Clausius-Mossotti relation [1, 3] between the molecular polarizability α and the relative dielectric constant $k = \epsilon_r$ of a uniform dielectric medium in a uniform electric field $\mathbf{E}$, and the assumptions on which it is based. In SI units, a common form of the Clausius-Mossotti relation is

$$N\alpha = 3\frac{\epsilon_r - 1}{\epsilon_r + 2} = 3\frac{k-1}{k+2}\,, \tag{1}$$

where N in the number density of molecules in the medium. Equivalently,

$$\epsilon_r = k = \frac{1 + 2N\alpha/3}{1 - N\alpha/3}\,. \tag{2}$$

A step towards eq. (1) is to suppose that the molecules have no intrinsic electric dipole moment $\mathbf{p}$, but take on induced moment

$$\mathbf{p} = \alpha\epsilon_0\mathbf{E}_{\rm other} \tag{3}$$

when in an external electric field $\mathbf{E}_{\rm other}$ due to other sources.[1] In general, eq. (3) can be a tensor relation, with $\mathbf{p}$ not parallel to $\mathbf{E}_{\rm other}$, and the molecular polarizability α can depend on the field strength $E_{\rm other}$.

The induced electric dipole moments contribute to the total field in the medium, and this contribution is nonuniform on an atomic scale. However, for purposes of the Clausius-Mossotti relation we suppose that we can consider the polarization density

$$\mathbf{P} = N\mathbf{p} = N\alpha\epsilon_0\mathbf{E}_{\rm other} \tag{4}$$

as uniform within small volumes containing several molecules (or even just one), with N being the number density of the molecules in this small volume.

We will define $\mathbf{E}_{\rm self}$ as electric field in such a small volume due only to the (polarized) molecules in that volume. The assumption that the polarization density $\mathbf{P}$ is uniform over small volumes implies that $\mathbf{E}_{\rm self}$ is also uniform over a small volume. Then, by considering a small spherical volume we can use the well known result that the electric field inside a uniformly polarized sphere[2] is given by[3]

$$\mathbf{E}_{\rm self} = -\frac{\mathbf{P}}{3\epsilon_0}\,. \tag{5}$$

[1]In a survey of textbooks on electrodynamics in SI units [4]-[10], all gave eq. (3) as the definition of the molecular polarizability α for a linear dielectric medium, except [9] which uses the form $\mathbf{p} = \alpha\mathbf{E}_{\rm other}$ (that is the usual form in Gaussian units).

[2]The case of a cubical volume was considered in sec. 9.13 of [11] (in Gaussian units), where our eq. (11) was given in Purcell's eq. (72). The intricate argument of sec. 9.13 of [11] was not included in later editions ([10], which switched to SI units).

[3]See, for example, eq. (6.17), p. 163 of [8].

The final ingredient in the derivation of the Clausius-Mossotti relation is[4]

$$\mathbf{P} = (\epsilon_r - 1)\epsilon_0 \mathbf{E}, \tag{6}$$

which can be considered as a definition of the relative dielectric constant ϵ_r in terms of the polarization density $\mathbf{P}$ of a dielectric medium in a total electric field $\mathbf{E}$. The latter is the sum of the self field $\mathbf{E}_{\rm self}$ on the polarization density $\mathbf{P}$ in some small volume and the field $\mathbf{E}_{\rm other}$ due to sources outside that volume,

$$\mathbf{E} = \mathbf{E}_{\rm self} + \mathbf{E}_{\rm other}. \tag{7}$$

Then,

$$\mathbf{E}_{\rm other} = \mathbf{E} - \mathbf{E}_{\rm self} = \mathbf{E} + \frac{\mathbf{P}}{3\epsilon_0} = \mathbf{E} + \frac{(\epsilon_r - 1)}{3}\mathbf{E} = \mathbf{E}\frac{\epsilon_r + 2}{3}\,. \tag{8}$$

Using both eqs. (4) and (6), together with eq. (8), we have

$$\mathbf{P} = N\alpha\epsilon_0\mathbf{E}\frac{\epsilon_r + 2}{3} = (\epsilon_r - 1)\epsilon_0\mathbf{E}, \tag{9}$$

from which the Clausius-Mossotti relation (1) follows.

Some derivations proceed in a different order, noting that the second equality in eq. (8) permits us to write

$$\mathbf{P} = N\alpha\epsilon_0\mathbf{E}_{\rm other} = N\alpha\epsilon_0\left(\mathbf{E} + \frac{\mathbf{P}}{3\epsilon_0}\right), \tag{10}$$

which can be rearranged to yield the relation

$$\mathbf{P} = \frac{N\alpha}{1 - N\alpha/3}\epsilon_0\mathbf{E}. \tag{11}$$

Then, combining eq. (11) with eq. (6), we again arrive at eq. (1).

2 The Lorentz-Lorenz Relation

Most non-ferromagnetic media have relative magnetic permeability μ_r equal to unity to a very good approximation, in which case the (frequency-dependent) index of refraction n is simply

$$n = \sqrt{\epsilon_r}. \tag{12}$$

Then, eq. (1) can be rewritten as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N\alpha}{3}\,, \tag{13}$$

[4]The dielectric susceptibility χ is defined as $\chi = \epsilon_r - 1$. That is, $\mathbf{P} = \chi\epsilon_0\mathbf{E}$. The Clausius-Mossotti relation (2) can be written (in SI units) in terms of χ as $\chi = N\alpha/(1 - N\alpha/3)$, which is the form given by Clausius in eq. (15), p. 74 of [3] (where his factor of 4π is associated with use of Gaussian units).

where $N\alpha/3$ is proportional to the density of the medium. Similarly, eq. (2) can be rewritten as

$$n^2 = \frac{1 + 2N\alpha/3}{1 - N\alpha/3}. \tag{14}$$

Versions of eq. (13) were given by Lorenz [12, 13] (in Danish, 1869 and 1875) and by Lorentz [15] (in Dutch, 1878) prior to Clausius' work [3] (1879). However, these papers attracted little attention until German versions were published [14, 16] in 1880, after Clausius [3]. For further discussion of this history, see [17].

Our eq. (13) is commonly called the Lorentz-Lorenz relation.

References

[1] O.F. Mossotti, *Discussione analitica sull'influenza che l'azione di un mezzo dielettrico ha sulla distribuzione dell'elettricit alla superficie di pi corpi electrici disseminati in esso*, Mem. Math. Fis. Soc. Ital. Sci. Res. Modena **24** Part 2, 49 (1848).
http://kirkmcd.princeton.edu/examples/EM/mossotti_msis_24_49_48.pdf
Offprint: http://kirkmcd.princeton.edu/examples/EM/mossotti_msis_24_1_46.pdf
For some historical comments on Mossotti, see [2].

[2] G. Pelosi and S. Selleri, *The Pavers of Maxwell's Pathway to His Equations: Ottaviano Fabrizio Mossotti*, Radio Sci. Bull. **355**, 79 (2015).
http://kirkmcd.princeton.edu/examples/EM/pelosi_rsb_355_78_15.pdf

[3] R Clausius, *Die Mechanische Behandlung Der Electricität* (Friedrich Vieweg, Braunschweig, 1879). http://kirkmcd.princeton.edu/examples/EM/clausius_79.pdf
See footnote 4 above regarding Clausius' eq. (15), p. 74. His eq. (54), p. 94, gives our eq. (2) with our k as Clausius' K and our $N\alpha$ as his g.

[4] A. Sommerfeld, *Electrodynamics* (Academic Press, New York, 1952). See pp. 74-75.
http://kirkmcd.princeton.edu/examples/EM/sommerfeld_em_52.pdf

[5] W.K.H. Panofsky and M. Phillips, *Classical Electricity and Magnetism*, 2nd ed. (Addison-Wesley, 1962). See sec. 2-4.
kirkmcd.princeton.edu/examples/EM/panofsky-phillips.pdf

[6] R.P. Feynman, R.B. Leighton and M. Sands, *The Feynman Lectures on Physics*, Vol. 2 (Addison-Wesley, 1964). See secs. 11-4,5.
https://www.feynmanlectures.caltech.edu/II_11.html

[7] J.D. Jackson, *Classical Electrodynamics*, 3rd ed. (Wiley, 1999). See secs. 4.5-6.
http://kirkmcd.princeton.edu/examples/EM/jackson_ce3_99.pdf

[8] A. Zangwill, *Modern Electrodynamics* (Cambridge U. Press, 2012), See sec. 6.6.
http://kirkmcd.princeton.edu/examples/EM/zangwill_em_12.pdf

[9] D.J. Griffiths, *Introduction to Electrodynamics*, $4^{\rm th}$ ed. (Addison-Wesley, 2012). See prob. 4.41. http://kirkmcd.princeton.edu/examples/EM/griffiths_em4.pdf
http://kirkmcd.princeton.edu/examples/EM/griffiths_em4_sol_4.41.pdf
Griffiths (private communication) says that the $6^{\rm th}$ edition will use $\mathbf{p} = \alpha\epsilon_0\mathbf{E}$.

[10] E.M. Purcell and D.J. Morin, *Electricity and Magnetism*, $3^{\rm rd}$ ed. (Cambridge U. Press, 2013). See sec. 10.12. http://kirkmcd.princeton.edu/examples/EM/purcell_em_13.pdf
Equation (10.29), p. 480, states that $\mathbf{p} = \alpha\mathbf{E}$, but p. 481 then argues this really should be $\mathbf{p} = 4\pi\alpha\epsilon_0\mathbf{E}$ or perhaps just $\alpha\epsilon_0\mathbf{E}$.

[11] E.M. Purcell, *Electricity and Magnetism* (McGraw-Hill, 1963). See sec. 9.13.
http://kirkmcd.princeton.edu/examples/EM/purcell_em_63_sec9.13.pdf

[12] L. Lorenz, *Experimentale og theoretiske Undersøgelser over Legemernes Brydnings-forhold*, Vidensk. Selsk. Sckrifter **8**, 205 (1870).
http://kirkmcd.princeton.edu/examples/EM/lorenz_kdvss_8_203_70.pdf
On p. 35, Lorenz inferred (but did not derive) that $(n^2-1)/(n^2+2)$ is proportional to the density of an optical medium. The index of refraction n was called A by Lorenz.

[13] L. Lorenz, *Experimentale og theoretiske Undersøgelser over Legemernes Brydnings-forhold*, Vidensk. Selsk. Sckrifter **10**, 483 (1875).
http://kirkmcd.princeton.edu/examples/EM/lorenz_kdvss_10_483_75.pdf

[14] L. Lorenz, *Ueber die Refractionsconstante*, Ann. d. Phys. **11**, 70 (1880).
http://kirkmcd.princeton.edu/examples/EM/lorenz_ap_11_70_80.pdf

[15] H.A. Lorentz, *Concerning the Relation between the Velocity of Propagation of Light and the Density and Composition of Media* (original in Dutch), Verh. Kon. Akad. Wetensch. Amesterdam **18** (1878). Translation on p. 1 of *H.A. Lorentz Collected Papers*, Vol. 2. (Springer, 1936). http://kirkmcd.princeton.edu/examples/EM/lorentz_papers_v2.pdf
On p. 57, eq. (D) states that $(n^2-1)/(n^2+2) = kd$ for the index of refraction n of a medium of density d, where k is a constant.

[16] H.A. Lorentz, *Ueber die Beziehung zwischen der Fortpflanzungsgeschwindigkeit des Lichtes und der Körperdichte*, Ann. d. Phys. **12**, 127 (1881). See eq. (1).
http://kirkmcd.princeton.edu/examples/EM/lorentz_ap_12_127_81.pdf

[17] H. Kragh, *The Lorenz-Lorentz Formula: Origin and Early History*, Substantia **2**(2), 7 (2018). http://kirkmcd.princeton.edu/examples/EM/kragh_substantia_2-2_7_18.pdf