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ELEMENTARY DERIVATION OF THE DIELECTRIC CONSTANT OF AN IMPERFECT GAS

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ABSTRACT

A general formula for the "second Clausius-Mossotti coefficient" is obtained from elementary considerations of statistical mechanics.

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The static dielectric constant of an imperfect gas in thermal equilibrium can be expressed as a function of density n and temperature θ as follows:

$$\frac{K-1}{K+2} = \frac{4\pi}{3}\left[n\,\alpha_1(\theta) + n^2\,\alpha_2(\theta) + \mathcal{O}(n^3)\right]. \tag{1}$$

In another publication[1] we have applied linked-cluster techniques to the grand partition function, and have derived explicit expressions for α_1, α_2, etc. In this note we present an elementary derivation of the same result, lacking in rigor but appealing to intuition.

We begin by considering a monatomic gas, such that the excitation energy of an atom is large compared to the temperature. For an isolated atom, the polarizability tensor is[2]

$$\underset{\sim}{\alpha}_1 = 2\sum_{\lambda'} \langle\lambda_0|\underset{\sim}{p}|\lambda'\rangle\langle\lambda'|\underset{\sim}{p}|\lambda_0\rangle/(\epsilon' - \epsilon_0), \tag{2}$$

where $\underset{\sim}{p}$ is the dipole-moment operator, ϵ is the energy eigenvalue for the eigenstate $|\lambda\rangle$, and the subscript zero refers to the ground state. Similarly, for two (interacting) atoms with fixed nuclei an interval $\underset{\sim}{r}$ apart, the polarizability tensor is

$$\underset{\sim}{\alpha}_2 (\underset{\sim}{r}) = 2 \sum_{\Lambda'} \langle \Lambda_0 | \underset{\sim}{p}^{(2)} | \Lambda' \rangle \langle \Lambda' | \underset{\sim}{p}^{(2)} | \Lambda_0 \rangle / (\mathcal{E}' - \mathcal{E}_0), \quad (3)$$

where $\underset{\sim}{p}^{(2)}$ is the total dipole-moment operator, and $\mathcal{E}$ is the energy eigenvalue for the eigenstate $|\Lambda\rangle$ of the two-atom Hamiltonian with fixed nuclei. We note that $\mathcal{E}$ and $|\Lambda\rangle$ depend upon $\underset{\sim}{r}$ parametrically.

The polarization $\underset{\sim}{P}$, or mean dipole density, may be found by calculating the mean dipole moment $v\underset{\sim}{P}$ of a spherical volume v, large compared to the volume of an atom but small enough so that nv is much less than one. (Such a v can be found only for a dilute gas.) To terms of order n^2, the probability density that a pair of atoms (with the line of centers $\underset{\sim}{r}$) is in v is

$$\mathcal{P}_2(\underset{\sim}{r}) = \frac{1}{2} n^2 v e^{-\beta\phi(r)}, \quad (4)$$

where the interatomic potential energy is

$$\phi(r) \equiv \mathcal{E}_0(r) - \mathcal{E}_0(\infty). \quad (5)$$

To the same order, the probability that just one atom is in v is

$$\mathcal{P}_1 = n v - n^2 v \int d^3r \, e^{-\beta\phi(r)}, \quad (6)$$

with suitable integration limits. The mean dipole moment of v is thus

$$v\underset{\sim}{P} = [\mathcal{P}_1 \underset{\sim}{\alpha}_1 + \int d^3r \, \mathcal{P}_2(\underset{\sim}{r}) \underset{\sim}{\alpha}_2 (\underset{\sim}{r})] \cdot \underset{\sim}{E}^{eff}, \quad (7)$$

where the effective field in v is[3]

$$\underset{\sim}{E}^{eff} = \underset{\sim}{E} + \frac{4}{3}\pi \underset{\sim}{P} . \tag{8}$$

Using formulas (4) and (6), we obtain

$$\underset{\sim}{P} = \left\{ n \underset{\sim}{\alpha}_1 + n^2 \int d^3r \left[\frac{1}{2} \underset{\sim}{\alpha}_2(\underset{\sim}{r}) - \underset{\sim}{\alpha}_1 \right] e^{-\beta\phi(r)} \right\} \cdot \left(\underset{\sim}{E} + \frac{4}{3}\pi \underset{\sim}{P} \right) . \tag{9}$$

(Since $\underset{\sim}{\alpha}_2(\infty) = 2\underset{\sim}{\alpha}_1$, the integration may be taken over all $\underset{\sim}{r}$).

The coefficients of n and n^2 in Eq. (9) are scalar tensors:

$$\alpha_1 \underset{\sim}{I} \equiv \underset{\sim}{\alpha}_1 \tag{10}$$

and

$$\alpha_2(\theta) \underset{\sim}{I} \equiv \int d^3r \left[\frac{1}{2} \underset{\sim}{\alpha}_2 (\underset{\sim}{r}) - \underset{\sim}{\alpha}_1 \right] e^{-\beta\phi(r)} , \tag{11}$$

where $\underset{\sim}{I}$ is the unit tensor. Using the definitions (10) and (11) in Eq. (9), and introducing the dielectric constant K:

$$4\pi \underset{\sim}{P} = (K - 1) \underset{\sim}{E} , \tag{12}$$

we obtain the form (1). (In this case α_1 is independent of temperature.)

The Jansen-Mazur result[4] can be obtained from ours if, in evaluating $\underset{\sim}{\alpha}_2(\underset{\sim}{r})$ from formula (3), one finds $\mathcal{E}$ and $|\Lambda\rangle$ from a second-order perturbation treatment of the two-atom problem, using the dipole-dipole approximation for the interaction energy, with the interaction strength as the perturbation expansion parameter. The Kirkwood approximation[5] replaces the two atoms by harmonic oscillators and also uses the dipole-dipole approximation.

With intuitive concepts, we may generalize our formulas to apply to a molecular gas, for which the excitation energies are not large compared to the temperature. Formula (2) is replaced by[2]

$$\underset{\sim}{\alpha}_1 (\theta) = \sum_{\lambda} e^{-\beta\epsilon} \underset{\sim}{\alpha}_1 (\lambda) / \sum_{\lambda} e^{-\beta\epsilon} , \tag{13}$$

with

$$\underset{\sim}{\alpha}_1(\lambda) \equiv 2 \sum_{\lambda'} \langle\lambda| \underset{\sim}{p} | \lambda'\rangle \langle\lambda'| \underset{\sim}{p} | \lambda\rangle / (\epsilon' - \epsilon), \tag{14}$$

and formula (3) by the analogous form:

$$\underset{\sim}{\alpha}_2 (\underset{\sim}{r}; \theta) = \sum_{\Lambda} e^{-\beta\mathcal{E}} \underset{\sim}{\alpha}_2 (\underset{\sim}{r}; \Lambda) / \sum_{\Lambda} e^{-\beta\mathcal{E}} , \tag{15}$$

with

$$\underset{\sim}{\alpha}_2 (\underset{\sim}{r}; \Lambda) \equiv 2 \sum_{\Lambda'} \langle\Lambda| \underset{\sim}{p}^{(2)} | \Lambda'\rangle \langle\Lambda'| \underset{\sim}{p}^{(2)} | \Lambda\rangle / (\mathcal{E}' - \mathcal{E}). \tag{16}$$

(If expression (14) or (16) involves matrix elements between degenerate states, one may introduce an artificial perturbation[2] to remove the degeneracy, and then in the result (13) or (15) take the limit of vanishing perturbation.) The interaction potential energy $\phi(r)$ is replaced by the interaction free energy $\Phi(r)$:[6]

$$e^{-\beta\Phi(r)} \equiv \sum_{\Lambda} e^{-\beta\mathcal{E}(r)} / \sum_{\Lambda} e^{-\beta\mathcal{E}(\infty)} . \tag{17}$$

Thus Eq. (11) becomes

$$\alpha_2(\theta)\ \underset{\sim}{I} \equiv \int d^3r \left[\frac{1}{2}\ \underset{\sim}{\alpha}_2\ (\underset{\sim}{r};\ \theta) - \underset{\sim}{\alpha}_1\ (\theta)\right] e^{-\beta\Phi(r)}\ , \tag{18}$$

as found in the rigorous approach of reference 1. Various treatments of molecular gases[7] (quadrupole interactions, permanent dipole interactions, etc.) can now be obtained by making suitable models or approximations.

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FOOTNOTES

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1. A. N. Kaufman and K. M. Watson (submitted to Phys. Fluids).

2. J. H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities (Oxford University Press, London, 1932).

3. H. A. Lorentz, Theory of Electrons (Dover Publications, New York, 1952).

4. L. Jansen and P. Mazur, Physica 21, 193, 208 (1955).

5. J. G. Kirkwood, J. Chem. Phys. 4, 592 (1936).

6. R. W. Zwanzig, Phys. Rev. 106, 13 (1957).

7. For a survey, see W. F. Brown, "Dielectrics", in Encyclopedia of Physics, Vol. XVII (Springer-Verlag, Berlin, 1956).

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