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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:

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

In another publication¹ 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 is²

$$\alpha_1 = 2 \sum_{\lambda'} \frac{\langle \lambda_0 | \underline{p} | \lambda' \rangle \langle \lambda' | \underline{p} | \lambda_0 \rangle}{\epsilon' - \epsilon_0}, \quad (2)$$

where $\underline{p}$ 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 $\underline{r}$ apart, the polarizability tensor is

$$\alpha_2(\underline{r}) = 2 \sum_{\Lambda'} \langle \Lambda_0 | \underline{p}^{(2)} | \Lambda' \rangle \langle \Lambda' | \underline{p}^{(2)} | \Lambda_0 \rangle / (\mathcal{E}' - \mathcal{E}_0), \quad (3)$$

where $\underline{p}^{(2)}$ 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 $\underline{r}$ parametrically.

The polarization $\underline{P}$, or mean dipole density, may be found by calculating the mean dipole moment $v\underline{P}$ 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 $\underline{r}$) is in v is

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

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

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

where the effective field in v is³

$$\underline{\underline{E}}^{\text{eff}} = \underline{\underline{E}} + \frac{4}{3} \pi \underline{\underline{P}}. \quad (8)$$

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

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

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

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

$$\underline{\underline{\alpha}}_1 \underline{\underline{I}} \equiv \underline{\underline{\alpha}}_1 \quad (10)$$

and

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

where $\underline{\underline{I}}$ is the unit tensor. Using the definitions (10) and (11) in Eq.

(9), and introducing the dielectric constant K :

$$4\pi \underline{\underline{P}} = (K - 1) \underline{\underline{E}}, \quad (12)$$

we obtain the form (1). (In this case $\underline{\underline{\alpha}}_1$ is independent of temperature.)

The Jansen-Mazur result⁴ can be obtained from ours if, in evaluating $\underline{\underline{\alpha}}_2(r)$ 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 approximation⁵ 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 by²

$$\alpha_1(\theta) = \sum_{\lambda} e^{-\beta \epsilon} \alpha_1(\lambda) / \sum_{\lambda} e^{-\beta \epsilon}, \quad (13)$$

with

$$\alpha_1(\lambda) \equiv 2 \sum_{\lambda'} \langle \lambda | \underline{p} | \lambda' \rangle \langle \lambda' | \underline{p} | \lambda \rangle / (\epsilon' - \epsilon), \quad (14)$$

and formula (3) by the analogous form:

$$\alpha_2(\underline{r}; \theta) = \sum_{\Lambda} e^{-\beta \mathcal{E}} \alpha_2(\underline{r}; \Lambda) / \sum_{\Lambda} e^{-\beta \mathcal{E}}, \quad (15)$$

with

$$\alpha_2(\underline{r}; \Lambda) \equiv 2 \sum_{\Lambda'} \langle \Lambda | \underline{p}^{(2)} | \Lambda' \rangle \langle \Lambda' | \underline{p}^{(2)} | \Lambda \rangle / (\mathcal{E}' - \mathcal{E}). \quad (16)$$

(If expression (14) or (16) involves matrix elements between degenerate states, one may introduce an artificial perturbation² 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

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

Thus Eq. (11) becomes

$$\alpha_2(\theta) \bar{I} \equiv \int d^3r \left[\frac{1}{2} \alpha_2(\underline{r}; \theta) - \alpha_1(\theta) \right] e^{-\beta\Phi(r)}, \quad (18)$$

as found in the rigorous approach of reference 1. Various treatments of molecular gases⁷ (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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 2. J. H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities (Oxford University Press, London, 1932).
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 7. For a survey, see W. F. Brown, "Dielectrics", in Encyclopedia of Physics, Vol. XVII (Springer-Verlag, Berlin, 1956).

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