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Molecular Theory of the Dielectric Constant of Nonpolar Gases*

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A theory of molecular polarization is developed which applies to nonpolar gases consisting of axially symmetric molecules. The interaction Hamiltonian of the system includes induced dipole and induced and permanent quadrupole contributions. The average induced dipole moment of a molecule is evaluated through third order of perturbation theory, following earlier calculations for hydrogen and helium atoms by Jansen and Mazur. General equations are given for the induced dipole moment in terms of tensors $\mathbf{T}^{(2)}$, $\mathbf{T}^{(3)}$, $\mathbf{T}^{(4)}$, characteristic for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively; and characteristic functions $C_1, C_2, \cdots C_7$, depending upon the molecular charge distributions. It is shown that α in the Clausius-Mossotti equation is in general not equal to the polarizability of a free molecule, but depends on the density of the system.

INTRODUCTION

ACCURATE measurements of the dielectric constant of nonpolar gases have shown[1–3] that the Clausius-Mossotti (C-M) relation,

$$\frac{(\epsilon-1)}{(\epsilon+2)}V=\frac{4}{3}\pi N\alpha,$$

is not strictly valid. The dielectric constant of the gas is ϵ, V is the molar volume, N is Avogadro's number, and α is the polarizability of the molecules. For all gases it has been found that $(\epsilon-1)V/(\epsilon+2)$ with increasing density first increases, reaching a maximum at about 150 to 200 Amagat units, and then decreases, eventually becoming smaller than the value for standard conditions.[4] This density dependence must be explained in terms of the following possibilities:

(1) The time average of the field acting on a specific molecule is not equal to the Lorentz field.

(2) The polarizability, α, of a molecule in interaction with other molecules is no longer a well-defined quantity independent of the medium.

Kirkwood,[5] Yvon,[6] Van Vleck,[7] Brown,[8] and de Boer[9] have discussed the first possibility and have shown that owing to fluctuations in the induced dipole moments of the molecules, the local field averaged over time is actually larger than the Lorentz field at low and moderate densities. This fluctuation can be expressed in the form of a virial expansion in powers of the density of the gas. At low densities the factor $(\epsilon-1)V/(\epsilon+2)$ is larger than $(4/3)\pi N\alpha$ and at very high densities it is smaller, in qualitative agreement with experiments. Although the virial theory cannot be expected to be accurate at high densities it should permit accurate comparison with experiments in the region of low densities. It was found that the initial increase in the C-M function is about one-half of the experimental value for argon and carbon dioxide.

Mazur and one of us[10,11] have investigated the effect of molecular interactions on the polarizability of a molecule, and it was found that the factor α in the C-M function is density-dependent and gives rise to an additional increase in the C-M function at low densities. Numerical results were given for hydrogen atoms with parallel spins and helium atoms; this effect on the polarizability appears to be of the same order of magnitude as the dipole fluctuation effect. Very recently Zwanzig[12] has calculated the dielectric constant for compressed carbon dioxide gas; the effect of molecular interactions on the polarizability was taken into account in an approximate way, following references 10 and 11.

In this and the following paper we will extend the calculations to include the heavy rare gases and also to include gases consisting of some simple diatomic molecules (in general, any axially symmetric molecules). The derivation of an expression for the polarizability in isotropic media involves the calculation of the average induced dipole moment of an atom or molecule. We consider a system of N identical atoms or molecules between the plates of a plane condenser. The external static electric field is $\mathbf{E}_0$, and equal to the electric displacement vector $\mathbf{D}$ between the parallel plates. The

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[2] A. Michels and C. Michels, Trans. Roy. Soc. (London) **A231**, 587 (1933).

[3] A. Michels and L. Kleerekoper, Physica **6**, 586 (1939).

[4] The maximum deviation of $(\epsilon-1)V/(\epsilon+2)$ from its value at zero density amounts to almost one-half of one percent for argon at room temperature and around 200 Amagat units of density; for carbon dioxide it is two percent higher at 48°C, again at about 200 Amagat density.

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[10] L. Jansen and P. Mazur, Physica **21**, 193 (1955).

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calculation of the average induced dipole moment of a molecule will be performed in two steps: (1) a quantum mechanical calculation of the induced dipole moment, $\langle \mathbf{p} \rangle$, for a fixed configuration of molecules in different orders of perturbation theory; (2) a subsequent classical average over a canonical ensemble, $\{\langle \mathbf{p} \rangle\}$. In general we will use a symbol $\langle A \rangle$ for the quantum mechanical expectation value of an operator A for a fixed configuration of molecules; a symbol $\{\langle A \rangle\}$ for the average over a canonical ensemble; and a notation $\langle A \rangle_{\mathrm{or}}$ if the statistical averaging involves only the orientations of the molecular symmetry axes. The molecules are supposed to have no permanent dipole moments, but the effect of permanent and induced quadrupole moments will be taken into account. In general, $\langle \mathbf{p} \rangle$ is the sum of two contributions: a term $\langle \mathbf{p} \rangle_{E_0}$ due directly or indirectly to the external field, and a term $\langle \mathbf{p} \rangle_Q$ due to the quadrupole moments of the surrounding molecules. Thus

$$\langle \mathbf{p}_i \rangle = \langle \mathbf{p}_i \rangle_{E_0} + \langle \mathbf{p}_i \rangle_Q ; \quad i = 1, 2, 3, \cdots N.$$

For isotropic media, however, the statistical average of $\langle \mathbf{p}_i \rangle_Q$ is zero, so that we have only to consider $\langle \mathbf{p}_i \rangle_{E_0}$. The average value, $\{\langle \mathbf{p} \rangle\}$, is generally obtained as a power series in the density of the system. We shall limit ourselves to the term linear in the density, which implies that the density must be so low that simultaneous interactions between more than two molecules may be neglected. In this case the perturbation Hamiltonian may be given as a series of interactions between multipoles of increasing order. The higher multipole terms are difficult to handle if they are expressed explicitly in the angles of orientation of the molecular symmetry axes. We shall therefore give the multipole expansion in a tensor notation.

MULTIPOLE INTEACTIONS IN TENSOR NOTATION

To derive an expression for the electrostatic interaction between two molecules, we consider two arbitrary charge distributions; for convenience we consider these distributions to be continuous, with charge densities $\rho(\mathbf{r}_i)$ and $\rho(\mathbf{r}_j)$. The vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ are measured with respect to a fixed center in each charge distribution. The distance between the two centers is r. Then the potential, $V(r)$, at the center of distribution 2 resulting from all the charges of distribution 1 is

$$\begin{aligned} V(r) &= \int_1 \frac{\rho(\mathbf{r}_i)}{|\mathbf{r}-\mathbf{r}_i|} d\mathbf{r}_i \\ &= \frac{1}{r}\int_1 \rho(\mathbf{r}_i) d\mathbf{r}_i - \nabla\left(\frac{1}{r}\right)\cdot\int_1 \rho(\mathbf{r}_i)\mathbf{r}_i d\mathbf{r}_i \\ &\quad + \tfrac{1}{2}\nabla\nabla\left(\frac{1}{r}\right):\int_1 \rho(\mathbf{r}_i)\mathbf{r}_i\mathbf{r}_i d\mathbf{r}_i + \cdots. \end{aligned} \quad (1)$$

The double dot product (:) of two second rank tensors, A and B, is $\sum_{\alpha\beta} A_{\alpha\beta} B_{\beta\alpha}$. The first integral in Eq. (1) is zero since molecule 1 has no net charge. The other terms can be rewritten with the help of the usual multipole definitions:

$$\text{Dipole moment:} \quad \mathbf{p}_1 = \int_1 \rho(\mathbf{r}_i)\mathbf{r}_i d\mathbf{r}_i;$$

$$\text{Quadrupole moment:} \quad \mathbf{q}_1 = \int_1 \rho(\mathbf{r}_i)\mathbf{r}_i\mathbf{r}_i d\mathbf{r}_i.$$

The definition of higher multipoles, octupoles, etc., is similar. Thus

$$V(r) = -\nabla(1/r)\cdot\mathbf{p}_1 + \tfrac{1}{2}\nabla\nabla(1/r):\mathbf{q}_1 + \cdots.$$

If we define a symmetric tensor

$$\mathbf{T}_{12} = 1/r^3[\mathbf{U} - 3\mathbf{r}\mathbf{r}/r^2], \quad \mathbf{T}_{12} = \mathbf{T}_{21}, \quad (2)$$

where $\mathbf{U}$ is the unit second rank tensor, then

$$\nabla\nabla(1/r) = -\mathbf{T}, \quad (3)$$

and

$$V(r) = -\nabla(1/r)\cdot\mathbf{p}_1 - \tfrac{1}{2}\mathbf{T}_{12}:\mathbf{q}_1 + \cdots. \quad (4)$$

The next step is the evaluation of the electrostatic interaction energy between the two charge distributions:

$$H_{\mathrm{el}}' = \int_2 \rho(\mathbf{r}_j) V(\mathbf{r}+\mathbf{r}_j) d\mathbf{r}_j.$$

Now

$$V(\mathbf{r}+\mathbf{r}_j) = V(r) + \nabla V\cdot\mathbf{r}_j + \tfrac{1}{2}\nabla(\nabla V):\mathbf{r}_j\mathbf{r}_j + \cdots,$$

and by defining dipole and quadrupole moments for molecule 2 as for 1 we obtain

$$H_{\mathrm{el}}' = \nabla V\cdot\mathbf{p}_2 + \tfrac{1}{2}\nabla(\nabla V):\mathbf{q}_2 + \cdots.$$

Using expression (4) for $V(r)$, the electrostatic interaction becomes

$$\begin{aligned} H_{\mathrm{el}}' = \mathbf{p}_1\cdot T_{12}\cdot\mathbf{p}_2 &+ \tfrac{1}{2}\mathbf{p}_1\cdot\nabla\mathbf{T}_{12}:\mathbf{q}_2 \\ &- \tfrac{1}{2}\mathbf{p}_2\cdot\nabla\mathbf{T}_{12}:\mathbf{q}_1 - \tfrac{1}{4}\mathbf{q}_1:\nabla\nabla\mathbf{T}_{12}:\mathbf{q}_2 + \cdots. \end{aligned} \quad (5)$$

We make the convention that we always write the interaction between the dipole moment of one molecule (i) and the quadrupole moment of another molecule (k) with the dipole *in front;* thus $\mathbf{p}_i\cdot\nabla\mathbf{T}_{ik}:\mathbf{q}_k$, where $\nabla = \partial/\partial(\mathbf{r}_i - \mathbf{r}_k)$. The total electrostatic interaction energy between all molecules in the gas is then given by the sum

$$\begin{aligned} \tfrac{1}{2}\textstyle\sum_{i,k} \mathbf{p}_i\cdot\mathbf{T}_{ik}\cdot\mathbf{p}_k &+ \tfrac{1}{2}\textstyle\sum_{i,k} \mathbf{p}_i\cdot\nabla\mathbf{T}_{ik}:\mathbf{q}_k \\ &- \tfrac{1}{8}\textstyle\sum_{i,k} \mathbf{q}_i:\nabla\nabla\mathbf{T}_{ik}:\mathbf{q}_k + \cdots. \end{aligned} \quad (6)$$

The tensor characteristic for dipole-dipole interactions is $\mathbf{T}$, that for dipole-quadrupole interactions is $\nabla\mathbf{T}$, and that for quadrupole-quadrupole interactions is $\nabla\nabla\mathbf{T}$. To shorten the notation further we will denote these tensors by $\mathbf{T}^{(2)}$, $\mathbf{T}^{(3)}$, and $\mathbf{T}^{(4)}$; thus

$$\mathbf{T}^{(2)}=\mathbf{T}=-\nabla\nabla(1/r), \tag{7}$$

$$\mathbf{T}^{(3)}=\nabla\mathbf{T}=-\nabla\nabla\nabla(1/r), \tag{8}$$

$$\mathbf{T}^{(4)}=\nabla\nabla\mathbf{T}=-\nabla\nabla\nabla\nabla(1/r). \tag{9}$$

The quadrupole tensor, $\mathbf{q}$, has in general nine coordinates; it is a symmetric tensor and can therefore always be diagonalized by proper choice of coordinates. For diatomic and axially symmetric polyatomic molecules, the quadrupole tensor can be diagonalized by choosing the direction of one of the axes along the line connecting the nuclei. If we call this the z axis, then $q_{xx}=q_{yy}$ and

$$\begin{aligned}\mathbf{T}^{(2)}:\mathbf{q}&=T_{zz}^{(2)}(q_{zz}-q_{xx})+\mathrm{Trace}[\mathbf{T}^{(2)}]q_{xx}\\&=T_{zz}^{(2)}(q_{zz}-q_{xx}),\end{aligned}$$

since

$$\mathrm{Trace}[\mathbf{T}^{(2)}]=0.$$

From this, one sees that only the quantity $Q=(q_{zz}-q_{xx})$ of the quadrupole tensor enters into the interactions between axially symmetric molecules; this quantity is known as the molecular quadrupole moment. (This is zero for spherically symmetric charge distributions.) The z and x axes in the expression for the quadrupole moment lie along the length axis and perpendicular to it, respectively. In transformation formulas, we often meet with the case that we have to evaluate an expression $(q_{z'z'}-q_{x'x'})$, where z' and x' are two axes of an arbitrary Cartesian coordinate system. There is no simple expression connecting $(q_{z'z'}-q_{x'x'})$ and $(q_{zz}-q_{xx})$; on the other hand a simple transformation applies to the quantity $2Q=(2q_{zz}-q_{xx}-q_{yy})$ namely

$$2q_{z'z'}-q_{x'x'}-q_{y'y'}=Q(3\cos^2\theta-1).$$

In this expression θ is the angle between the length axis of the molecule, z, and the z' axis. Whereas the value of the dipole moment of a molecule is independent of the origin of the coordinate system, the quadrupole moment does depend on that choice. We make the convention of taking the center of positive charge of the molecule as the origin of the coordinate system. Of further importance is an expression for the electric field induced at the center of a molecule by the multipole moments of another molecule,

$$\mathbf{F}(r)=-\nabla V=-\mathbf{T}^{(2)}\cdot\mathbf{p}_1+\tfrac{1}{2}\mathbf{T}^{(3)}:\mathbf{q}_1+\cdots. \tag{10}$$

INDUCED DIPOLE MOMENT $\langle p\rangle$ IN VARIOUS ORDERS OF PERTURBATION THEORY

We will now calculate $\langle\mathbf{p}_i\rangle_{E_0}$ in successive orders of approximation with perturbation theory; the zeroth order refers to the free molecules in the absence of an external field. The total Hamiltonian of the system is

$$H=H_0+H',$$

with

$$\begin{aligned}H'=-\textstyle\sum_i\mathbf{p}_i\cdot\mathbf{E}_0+\tfrac{1}{2}\sum_{i,k}\mathbf{p}_i\cdot\mathbf{T}_{ik}^{(2)}\cdot\mathbf{p}_k\\+\tfrac{1}{2}\textstyle\sum_{i,k}\mathbf{p}_i\cdot\mathbf{T}_{ik}^{(3)}:\mathbf{q}_k-\tfrac{1}{8}\sum_{i,k}\mathbf{q}_i:\mathbf{T}_{ik}^{(4)}:\mathbf{q}_k.\end{aligned} \tag{11}$$

The tensors $\mathbf{T}^{(2)}$, $\mathbf{T}^{(3)}$, and $\mathbf{T}^{(4)}$ have been defined in the previous section; $\mathbf{p}$ and $\mathbf{q}$ are the dipole and quadrupole moment operators, respectively. We expand $\langle\mathbf{p}_i\rangle$ in increasing orders of perturbation theory as

$$\langle\mathbf{p}_i\rangle=\langle\mathbf{p}_i\rangle^{(0)}+\langle\mathbf{p}_i\rangle^{(1)}+\langle\mathbf{p}_i\rangle^{(2)}+\langle\mathbf{p}_i\rangle^{(3)}+\cdots. \tag{12}$$

It is assumed that the system of N interacting molecules in the external field $\mathbf{E}_0$ is in its ground state, specified by Ψ, an eigenfunction of the total Hamiltonian, H. The energy eigenfunctions of the *unperturbed* system are $\varphi_\kappa(\kappa=0,1,2,\cdots)$, where κ labels the various eigenfunctions. The perturbed wave function Ψ is expanded in successive orders of approximation as

$$\Psi=\Psi^{(0)}+\Psi^{(1)}+\Psi^{(2)}+\Psi^{(3)}+\cdots. \tag{13}$$

The perturbation expressions for the different order wave functions are[13]

$$\Psi^{(0)}=\varphi_0, \tag{14}$$

$$\Psi^{(1)}=\sum_{\kappa\neq0}\frac{\varphi_\kappa H_{\kappa0}'}{(E_0-E_\kappa)}. \tag{15}$$

$$\begin{aligned}\Psi^{(2)}=\sum_{\kappa\neq0}\sum_{\lambda\neq0}\frac{\varphi_\kappa H_{\kappa\lambda}'H_{\lambda0}'}{(E_0-E_\kappa)(E_0-E_\lambda)}-\sum_{\kappa\neq0}\frac{\varphi_\kappa H_{\kappa0}'H_{00}'}{(E_0-E_\kappa)^2}\\-\tfrac{1}{2}\sum_{\kappa\neq0}\frac{\varphi_0H_{0\kappa}'H_{\kappa0}'}{(E_0-E_\kappa)^2},\end{aligned} \tag{16}$$

$$\begin{aligned}\Psi^{(3)}=&\sum_{\kappa\neq0}\sum_{\lambda\neq0}\sum_{\mu\neq0}\frac{\varphi_\kappa H_{\kappa\lambda}'H_{\lambda\mu}'H_{\mu0}'}{(E_0-E_\kappa)(E_0-E_\lambda)(E_0-E_\mu)}\\&-\sum_{\kappa\neq0}\sum_{\lambda\neq0}\frac{\varphi_\kappa H_{\kappa\lambda}'H_{\lambda0}'H_{00}'}{(E_0-E_\kappa)^2(E_0-E_\lambda)}\\&-\sum_{\kappa\neq0}\sum_{\lambda\neq0}\frac{\varphi_\kappa H_{\kappa\lambda}'H_{\lambda0}'H_{00}'}{(E_0-E_\kappa)(E_0-E_\lambda)^2}\\&-\sum_{\kappa\neq0}\sum_{\lambda\neq0}\frac{\varphi_\kappa H_{\kappa0}'H_{0\lambda}'H_{\lambda0}'}{(E_0-E_\kappa)^2(E_0-E_\lambda)}\\&-\tfrac{1}{2}\sum_{\kappa\neq0}\sum_{\lambda\neq0}\frac{\varphi_\kappa H_{\kappa0}'H_{0\lambda}'H_{\lambda0}'}{(E_0-E_\kappa)(E_0-E_\lambda)^2}\\&+\sum_{\kappa\neq0}\frac{\varphi_\kappa H_{\kappa0}'(H_{00}')^2}{(E_0-E_\kappa)^3}.\end{aligned} \tag{17}$$

The difference between the energy eigenvalues of the ground state and the κth excited state of the unperturbed system is (E_0-E_κ). All matrix elements are calculated in the system of eigenfunctions of H_0. In the perturbation scheme we will retain only those terms which are linear in $\mathbf{E}_0$.

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[13] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1953), p. 30 ff.

First and Second Orders in the Dipole Moment

If the density of the gas is sufficiently low, the unperturbed wave function $\Psi^{(0)}$ may be written as a simple product of wave functions for the isolated molecules. For the first order in the dipole moment we then obtain simply

$$\langle\mathbf{p}_i\rangle^{(1)}=-2\sum_{\kappa\neq0}\frac{(\mathbf{p}_i)_{0\kappa}(\mathbf{p}_i)_{\kappa0}\cdot\mathbf{E}_0}{(E_0-E_\kappa)}=\boldsymbol{\alpha}_0\cdot\mathbf{E}_0, \tag{18}$$

where $\boldsymbol{\alpha}_0$, is the polarizability tensor of a free molecule.

The second-order approximation, $\langle\mathbf{p}_i\rangle^{(2)}$, has the following form:

$$\begin{aligned}\langle\mathbf{p}_i\rangle^{(2)}=2\sum_{\kappa\neq0}\sum_{\lambda\neq0}&\frac{(\mathbf{p}_i)_{0\kappa}H_{\kappa\lambda}'H_{\lambda0}'}{(E_0-E_\kappa)(E_0-E_\lambda)}\\&+\sum_{\kappa\neq0}\sum_{\lambda\neq0}\frac{H_{0\kappa}'(\mathbf{p}_i)_{\kappa\lambda}H_{\lambda0}'}{(E_0-E_\kappa)(E_0-E_\lambda)}\\&-2\sum_{\kappa\neq0}\frac{(\mathbf{p}_i)_{0\kappa}H_{\kappa0}'H_{00}'}{(E_0-E_\kappa)^2},\end{aligned} \tag{19}$$

with H' given by Eq. (11). The various sums in Eq. (19) can be evaluated if the wave functions of the free molecules are known with sufficient accuracy. This procedure, however, is unfeasible even in the simplest cases. Instead we will use the centroid assumption implying that all excited energy states of the molecule lie within a narrow region on the energy scale. (The width of the range should be small compared with the average energy of the levels in that band.) If this condition is fulfilled, we may replace each factor of the denominators of Eq. (19) by a multiple of $-U_0$, where U_0 is an "average excitation energy" of the molecule. For instance, if (E_0-E_κ) refers to the difference in energy between the ground state and the κth excited state of two molecules, then (E_0-E_κ) is replaced by $-2U_0$, with U_0 counted positive. With the help of this approximation, the matrix summations in Eq. (19) can be carried out. The result is

$$\begin{aligned}\langle\mathbf{p}_i\rangle^{(2)}=&\frac{3}{2U_0^2}\sum_{k\neq i}(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0\mathbf{q}_i)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_k)_{00}\\&-\frac{3}{2U_0^2}\sum_{k\neq i}(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0)_{00}(\mathbf{q}_i)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_k)_{00}\\&-\frac{4}{U_0^2}\sum_{k\neq i}(\mathbf{p}_i\mathbf{p}_k\cdot\mathbf{E}_0\mathbf{p}_i\cdot\mathbf{T}^{(2)}\cdot\mathbf{p}_k)_{00}.\end{aligned} \tag{20}$$

Third Order in the Dipole Moment

From Eqs. (15), (16), and (17), one obtains the following expression for the third-order dipole moment:

$$\begin{aligned}\langle\mathbf{p}_i\rangle^{(3)}=2\Bigg[&\sum_{\kappa\neq0}\sum_{\lambda\neq0}\sum_{\mu\neq0}\frac{(\mathbf{p}_i)_{0\kappa}H_{\kappa\lambda}'H_{\lambda\mu}'H_{\mu0}'}{(E_0-E_\kappa)(E_0-E_\lambda)(H_0-E_\mu)}\\&-\sum_{\kappa\neq0}\sum_{\lambda\neq0}\frac{(\mathbf{p}_i)_{0\kappa}H_{\kappa\lambda}'H_{\lambda0}'H_{00}'}{(E_0-E_\kappa)^2(E_0-E_\lambda)}\\&-\sum_{\kappa\neq0}\sum_{\lambda\neq0}\frac{(\mathbf{p}_i)_{0\kappa}H_{\kappa\lambda}'H_{\lambda0}'H_{00}'}{(E_0-E_\kappa)(E_0-E_\lambda)^2}\\&-\sum_{\kappa\neq0}\sum_{\lambda\neq0}\frac{(\mathbf{p}_i)_{0\kappa}H_{\kappa0}'H_{0\lambda}'H_{\lambda0}'}{(E_0-E_\kappa)^2(E_0-E_\lambda)}\\&-\tfrac{1}{2}\sum_{\kappa\neq0}\sum_{\lambda\neq0}\frac{(\mathbf{p}_i)_{0\kappa}H_{\kappa0}'H_{0\lambda}'H_{\lambda0}'}{(E_0-E_\kappa)(E_0-E_\lambda)^2}\\&+\sum_{\kappa\neq0}\frac{(\mathbf{p}_i)_{0\kappa}H_{\kappa0}'(H_{00}')^2}{(E_0-E_\kappa)^3}\\&+\sum_{\kappa\neq0}\sum_{\lambda\neq0}\sum_{\mu\neq0}\frac{H_{0\kappa}'(\mathbf{p}_i)_{\kappa\lambda}H_{\lambda\mu}'H_{\mu0}'}{(E_0-E_\kappa)(E_0-E_\lambda)(E_0-E_\mu)}\\&-\sum_{\kappa\neq0}\sum_{\lambda\neq0}\frac{H_{0\kappa}'(\mathbf{p}_i)_{\kappa\lambda}H_{\lambda0}'H_{00}'}{(E_0-E_\kappa)(E_0-E_\lambda)^2}\\&-\tfrac{1}{2}\sum_{\kappa\neq0}\sum_{\lambda\neq0}\frac{H_{0\kappa}'(\mathbf{p}_i)_{\kappa0}H_{0\lambda}'H_{\lambda0}'}{(E_0-E_\kappa)(E_0-E_\lambda)^2}\Bigg],\end{aligned} \tag{21}$$

TABLE I. The distinct terms of $\langle\mathbf{p}_i\rangle^{(3)}$ and their multiplying factors.

Term	Factor $\times U_0^3$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0\mathbf{p}_i\cdot\mathbf{T}^{(2)}\cdot\mathbf{p}_k\mathbf{p}_i\cdot\mathbf{T}^{(2)}\cdot\mathbf{p}_k)_{00}$	$+17/4$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0)_{00}(\mathbf{p}_i\cdot\mathbf{T}^{(2)}\cdot\mathbf{p}_k\mathbf{p}_i\cdot\mathbf{T}^{(2)}\cdot\mathbf{p}_k)_{00}$	$-7/2$
$(\mathbf{p}_i\mathbf{p}_i)_{00}\cdot\mathbf{T}^{(2)}\cdot(\mathbf{p}_k\mathbf{p}_k)_{00}\cdot\mathbf{T}^{(2)}\cdot(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0)_{00}$	$+9/4$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0\mathbf{p}_i\cdot\mathbf{T}^{(3)}:\mathbf{q}_k\mathbf{p}_i\cdot\mathbf{T}^{(3)}:\mathbf{q}_k)_{00}$	$+17/16$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0\mathbf{p}_k\cdot\mathbf{T}^{(3)}:\mathbf{q}_i\mathbf{p}_k\cdot\mathbf{T}^{(3)}:\mathbf{q}_i)_{00}$	$+17/16$
$(\mathbf{p}_i\mathbf{p}_k\cdot\mathbf{E}_0\mathbf{p}_i\cdot\mathbf{T}^{(3)}:\mathbf{q}_k\mathbf{p}_k\cdot\mathbf{T}^{(3)}:\mathbf{q}_i)_{00}$	$-13/8$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0)_{00}(\mathbf{p}_i\cdot\mathbf{T}^{(3)}:\mathbf{q}_k\mathbf{p}_i\cdot\mathbf{T}^{(3)}:\mathbf{q}_k)_{00}$	$-7/8$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0)_{00}(\mathbf{p}_k\cdot\mathbf{T}^{(3)}:\mathbf{q}_i\mathbf{p}_k\cdot\mathbf{T}^{(3)}:\mathbf{q}_i)_{00}$	$-7/8$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0\mathbf{q}_i)_{00}:\mathbf{T}^{(3)}\cdot(\mathbf{p}_k\mathbf{p}_k)_{00}\cdot\mathbf{T}^{(3)}:(\mathbf{q}_i)_{00}$	$+7/8$
$(\mathbf{p}_i\cdot\mathbf{E}_0\mathbf{p}_i)_{00}\cdot\mathbf{T}^{(3)}:(\mathbf{q}_k\mathbf{q}_k)_{00}:\mathbf{T}^{(3)}\cdot(\mathbf{p}_i\mathbf{p}_i)_{00}$	$+9/16$
$(\mathbf{p}_k\cdot\mathbf{E}_0\mathbf{p}_k)_{00}\cdot\mathbf{T}^{(3)}:(\mathbf{q}_i\mathbf{p}_i\mathbf{p}_i)_{00}\cdot\mathbf{T}^{(3)}:(\mathbf{q}_k)_{00}$	$-11/8$
$(\mathbf{p}_i\mathbf{p}_i)_{00}\cdot\mathbf{T}^{(3)}:(\mathbf{q}_k\mathbf{p}_k\cdot\mathbf{E}_0\mathbf{p}_k)_{00}\cdot\mathbf{T}^{(3)}:(\mathbf{q}_i)_{00}$	$-11/8$
$(\mathbf{q}_k)_{00}:\mathbf{T}^{(3)}\cdot(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0\mathbf{p}_i\mathbf{p}_i)_{00}\cdot\mathbf{T}^{(3)}:(\mathbf{q}_k)_{00}$	$+31/16$
$(\mathbf{p}_i\cdot\mathbf{E}_0\mathbf{p}_i)_{00}\cdot\mathbf{T}^{(3)}:(\mathbf{q}_k)_{00}(\mathbf{p}_i\mathbf{p}_i)_{00}\cdot\mathbf{T}^{(3)}:(\mathbf{q}_k)_{00}$	$-73/16$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0)_{00}(\mathbf{q}_k)_{00}:\mathbf{T}^{(3)}\cdot(\mathbf{p}_i\mathbf{p}_i)_{00}\cdot\mathbf{T}^{(3)}:(\mathbf{q}_k)_{00}$	$-9/8$
$(\mathbf{p}_i\mathbf{p}_i)_{00}\cdot\mathbf{T}^{(3)}:(\mathbf{q}_k)_{00}(\mathbf{p}_k\cdot\mathbf{E}_0\mathbf{p}_k)_{00}\cdot\mathbf{T}^{(3)}:(\mathbf{q}_i)_{00}$	$+35/8$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0)_{00}(\mathbf{q}_i)_{00}:\mathbf{T}^{(3)}\cdot(\mathbf{p}_k\mathbf{p}_k)_{00}\cdot\mathbf{T}^{(3)}:(\mathbf{q}_i)_{00}$	$-17/16$
$(\mathbf{p}_i\mathbf{p}_k\cdot\mathbf{E}_0\mathbf{p}_i\cdot\mathbf{T}^{(2)}\cdot\mathbf{p}_k\mathbf{q}_i:\mathbf{T}^{(4)}:\mathbf{q}_k)_{00}$	$-13/8$
$(\mathbf{p}_k\cdot\mathbf{E}_0\mathbf{p}_k)_{00}\cdot\mathbf{T}^{(2)}\cdot(\mathbf{p}_i\mathbf{p}_i\mathbf{q}_i)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_k)_{00}$	$-11/8$
$(\mathbf{p}_i\mathbf{p}_i)_{00}\cdot\mathbf{T}^{(2)}\cdot(\mathbf{p}_k\mathbf{p}_k\cdot\mathbf{E}_0\mathbf{q}_k)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_i)_{00}$	$-11/8$
$(\mathbf{p}_i\mathbf{p}_i)_{00}\cdot\mathbf{T}^{(2)}\cdot(\mathbf{p}_k\mathbf{p}_k\cdot\mathbf{E}_0)_{00}(\mathbf{q}_i)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_k)_{00}$	$+35/8$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0\mathbf{q}_i:\mathbf{T}^{(4)}:\mathbf{q}_k\mathbf{q}_i:\mathbf{T}^{(4)}:\mathbf{q}_k)_{00}$	$+17/64$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0)_{00}(\mathbf{q}_i:\mathbf{T}^{(4)}:\mathbf{q}_k\mathbf{q}_i:\mathbf{T}^{(4)}:\mathbf{q}_k)_{00}$	$-7/32$
$(\mathbf{q}_k)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_i\mathbf{p}_i\cdot\mathbf{E}_0\mathbf{p}_i\mathbf{q}_i)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_k)_{00}$	$+31/64$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0\mathbf{q}_i)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_k\mathbf{q}_k)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_i)_{00}$	$+7/32$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0\mathbf{q}_i)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_k)_{00}(\mathbf{q}_i)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_k)_{00}$	$-55/32$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0)_{00}(\mathbf{q}_k)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_i\mathbf{q}_i)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_k)_{00}$	$-9/32$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0)_{00}(\mathbf{q}_i)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_k\mathbf{q}_k)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_i)_{00}$	$-17/64$
$(\mathbf{p}_i\mathbf{p}_i\cdot\mathbf{E}_0)_{00}(\mathbf{q}_i)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_k)_{00}(\mathbf{q}_i)_{00}:\mathbf{T}^{(4)}:(\mathbf{q}_k)_{00}$	$+97/64$

with H' again as given by Eq. (11). As was done for the second approximation to the dipole moment, the centroid assumption is used to replace the factors occurring in the denominators of the expression for $\langle \mathbf{p}_i \rangle^{(3)}$ by an "average excitation energy" and then the matrix sums can be evaluated. The total number of terms obtained in this way is approximately 200, of which twenty-nine are distinct. These twenty-nine terms with their corresponding factors are listed in Table I; $\langle \mathbf{p}_i \rangle^{(3)}$ is given by the sum of these terms.

RELATION BETWEEN INDUCED DIPOLE MOMENT AND THE LOCAL FIELD

For the derivation of the Clausius-Mossotti equation it is convenient to establish the relationship between the induced dipole moment, $\langle \mathbf{p}_i \rangle$, and the local field acting on the molecule. To do this we first introduce a tensor $\boldsymbol{\beta}_i$ defined as

$$\langle \mathbf{p}_i \rangle_{E_0} = \boldsymbol{\beta}_i \cdot \mathbf{E}_0, \quad i=1,2,3,\cdots N. \tag{22}$$

The tensor $\boldsymbol{\beta}_i$ can therefore be immediately obtained from the results for $\langle \mathbf{p}_i \rangle_{E_0}$ of the previous section. The local field acting on molecule (i) is

$$\begin{aligned}\mathbf{E}_{\text{local}} &= \mathbf{E}_0 - \sum_{k\neq i} \mathbf{T}_{ik}^{(2)} \cdot \langle \mathbf{p}_k \rangle + \tfrac{1}{2} \sum_{k\neq i} \mathbf{T}_{ik}^{(3)} : \langle \mathbf{q}_k \rangle \\ &= \Big(\mathbf{E}_0 - \sum_{k\neq i} \mathbf{T}_{ik}^{(2)} \cdot \langle \mathbf{p}_k \rangle_{E_0}\Big) \\ &\qquad - \Big(\sum_{k\neq i} \mathbf{T}_{ik}^{(2)} \cdot \langle \mathbf{p}_k \rangle_Q - \tfrac{1}{2} \sum_{k\neq i} \mathbf{T}_{ik}^{(3)} : \langle \mathbf{q}_k \rangle\Big).\end{aligned} \tag{23}$$

The first term in parentheses on the right is that due directly or indirectly to the applied field, $\mathbf{E}_0$, whereas the second term arises from the quadrupole moments of the surrounding molecules. We now introduce a tensor $\boldsymbol{\alpha}_i (i=1,2,3,\cdots N)$ by

$$\langle \mathbf{p}_i \rangle_{E_0} = \boldsymbol{\alpha}_i \cdot \Big(\mathbf{E}_0 - \sum_{k\neq i} \mathbf{T}_{ik}^{(2)} \cdot \langle \mathbf{p}_k \rangle_{E_0}\Big), \quad i=1,2,\cdots N. \tag{24}$$

It will be shown later in this section that this set of Eqs. (24) is consistent. The quantity $\boldsymbol{\alpha}_i$ may be looked upon as the "effective" polarizability of a molecule in the field of its neighbors. It will be found that in general $\boldsymbol{\alpha}_i$ is not equal to the polarizability of an isolated molecule, except in the case of a three-dimensional harmonic oscillator model.[7,10] The tensors $\boldsymbol{\alpha}_i$ can now be expressed in terms of the $\boldsymbol{\beta}_i$ and $\mathbf{T}^{(2)}$ with the help of Eqs. (22) and (24) as

$$\boldsymbol{\beta}_i = \boldsymbol{\alpha}_i \cdot \Big(\mathbf{U} - \sum_{k\neq i} \mathbf{T}_{ik}^{(2)} \cdot \boldsymbol{\beta}_k\Big);$$

or otherwise

$$\boldsymbol{\alpha}_i = \boldsymbol{\beta}_i \cdot \Big(\mathbf{U} - \sum_{k\neq i} \mathbf{T}_{ik}^{(2)} \cdot \boldsymbol{\beta}_k\Big)^{-1}. \tag{25}$$

The term within the parentheses can be expanded as a power series in terms of $\mathbf{T}^{(2)} \cdot \boldsymbol{\beta}$ to give[14]

$$\begin{aligned}\boldsymbol{\alpha}_i = \boldsymbol{\beta}_i + \boldsymbol{\beta}_i \cdot \sum_{k\neq i} \mathbf{T}_{ik}^{(2)} \cdot \boldsymbol{\beta}_k \\ + \boldsymbol{\beta}_i \cdot \sum_{k\neq i} \sum_{l\neq i} \mathbf{T}_{ik}^{(2)} \cdot \boldsymbol{\beta}_k \cdot \mathbf{T}_{il}^{(2)} \cdot \boldsymbol{\beta}_l + \cdots.\end{aligned} \tag{26}$$

In the previous section, we calculated $\langle \mathbf{p}_i \rangle$ or $\boldsymbol{\beta}_i$ in successive orders of approximation with perturbation theory. The corresponding orders of approximation in $\boldsymbol{\alpha}_i$ are

$$\boldsymbol{\alpha}_i^{(0)} = \boldsymbol{\beta}_i^{(0)}, \tag{27}$$

$$\boldsymbol{\alpha}_i^{(1)} = \boldsymbol{\beta}_i^{(1)} + \sum_{k\neq i} \boldsymbol{\beta}_i^{(0)} \cdot \mathbf{T}_{ik}^{(2)} \cdot \boldsymbol{\beta}_k^{(0)}, \tag{28}$$

$$\begin{aligned}\boldsymbol{\alpha}_i^{(2)} = \boldsymbol{\beta}_i^{(2)} + \sum_{k\neq i} \boldsymbol{\beta}_i^{(1)} \cdot \mathbf{T}_{ik}^{(2)} \cdot \boldsymbol{\beta}_k^{(0)} + \sum_{k\neq i} \boldsymbol{\beta}_i^{(0)} \cdot \mathbf{T}_{ik}^{(2)} \cdot \boldsymbol{\beta}_k^{(1)} \\ + \boldsymbol{\beta}_i^{(0)} \cdot \sum_{k\neq i} \sum_{l\neq i} \mathbf{T}_{ik}^{(2)} \cdot \boldsymbol{\beta}_k^{(0)} \mathbf{T}_{il}^{(2)} \cdot \boldsymbol{\beta}_l^{(0)},\end{aligned} \tag{29}$$

etc. Note that $\boldsymbol{\beta}_i^{(0)}$ corresponds to $\langle \mathbf{p}_i \rangle^{(1)}$, $\boldsymbol{\beta}_i^{(1)}$ to $\langle \mathbf{p}_i \rangle^{(2)}$, etc. From Eq. (18), it follows that $\boldsymbol{\alpha}_i^{(0)} = \boldsymbol{\alpha}_0$, the polarizability of a free molecule. The expression for $\boldsymbol{\alpha}_i^{(1)}$ can be obtained directly from Eqs. (20) and (28) as[15]

$$\begin{aligned}\boldsymbol{\alpha}_i^{(1)} = \frac{3}{2U_0^{\,2}} \sum_{k\neq i} \big[(\mathbf{p}_i \mathbf{p}_i \mathbf{q}_i)_{00} : \mathbf{T}^{(4)} : (\mathbf{q}_k)_{00} \\ - (\mathbf{p}_i \mathbf{p}_i)_{00} (\mathbf{q}_i)_{00} : \mathbf{T}^{(4)} : (\mathbf{q}_k)_{00} \big].\end{aligned} \tag{30}$$

It is seen already in this order of approximation that $\boldsymbol{\alpha}_i$ no longer represents the polarizability of an isolated molecule. However, if we average over the orientations of molecule k, then the net effect is zero. This corresponds to the case of atoms with spherical charge distributions.[10]

The second order of approximation, $\boldsymbol{\alpha}_i^{(2)}$, is obtained from Eqs. (20), (21), and (29). The resulting expression is as complicated as the terms in Table I for $\langle \mathbf{p}_i \rangle^{(3)}$ and will therefore not be written down explicitly. In gases we are interested in the averages of $\langle \mathbf{p}_i \rangle$, $\boldsymbol{\alpha}_i$, or $\boldsymbol{\beta}_i$ over the orientation and position coordinates of the molecules. In the following section we will calculate the "effective" polarizability averaged over the molecular symmetry axes.

TRANSFORMATION EQUATIONS AND AVERAGE "EFFECTIVE" POLARIZABILITY

The process of averaging the different terms of $\langle \mathbf{p}_i \rangle^{(3)}$ over the orientations of the molecular symmetry axes is performed by considering a fixed Cartesian coordinate system $(x'y'z')$ and a rotating (molecular) coordinate system (xyz). The z axis is chosen along the

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[14] We assume that the series in Eq. (25) converges; the determining factor appears to be $\mathbf{T}^{(2)} \cdot \boldsymbol{\beta}$, or β/r^3. Configurations of molecules for which this series diverges will generally have zero probability because of repulsive forces.

[15] We omit subscripts (ik) on tensors $\mathbf{T}$ whenever the expressions are unambiguous.

length axis of the molecule. The x and y axes are chosen such that the y axis lies in the $x'y'$ plane; this may always be done since the molecule has axial symmetry around the z axis. Consequently we need only two Eulerian angles, θ and φ, to indicate the relative orientations of the two coordinate systems. The relation between the coordinates of a vector, for instance the dipole vector $\mathbf{p}$, in the two coordinate systems is given by

$$\mathbf{p}'=\mathbf{G}\cdot\mathbf{p},$$

where

$$\mathbf{G}=G_\theta G_\varphi=\begin{vmatrix}\cos\theta\cos\varphi & -\sin\varphi & \sin\theta\cos\varphi\\ \cos\theta\sin\varphi & \cos\varphi & \sin\theta\sin\varphi\\ -\sin\theta & 0 & \cos\theta\end{vmatrix}. \quad (31)$$

The polarizability tensor $\boldsymbol{\alpha}$, or equivalently $\langle\mathbf{pp}\rangle$, then transforms like

$$\langle\mathbf{p}'\mathbf{p}'\rangle=\langle\mathbf{G}\cdot\mathbf{p}\mathbf{G}\cdot\mathbf{p}\rangle,$$

so that its components are

$$\langle\mathbf{p}'\mathbf{p}'\rangle_{\alpha\beta}=\textstyle\sum_{\gamma\delta}G_{\alpha\gamma}G_{\beta\delta}\langle p_\gamma p_\delta\rangle=\sum_\gamma G_{\alpha\gamma}G_{\beta\gamma}\langle p_\gamma p_\gamma\rangle,$$

since $\langle\mathbf{pp}\rangle$ is diagonal in the molecular coordinate system. The quadrupole tensor $\langle\mathbf{q}\rangle$ of the molecule transforms in the same way as $\langle\mathbf{pp}\rangle$. The transformation of terms like $\langle\mathbf{ppq}\rangle$ involves a fourfold multiplication of matrices G, etc. A general form for the expression of the induced dipole moment $\langle\mathbf{p}_i\rangle^{(3)}$, or equivalently for $\boldsymbol{\beta}_i^{(2)}$, valid for any molecular model can now be worked out by applying the transformation formulas, retaining only those terms which do not vanish upon averaging over the orientations. The following general form of $\boldsymbol{\beta}_i^{(2)}$ is then obtained:

$$\begin{aligned}\boldsymbol{\beta}_i^{(2)}=(C_1+1)\sum_{k\neq i}\mathbf{T}_{ik}^{(2)}\cdot\mathbf{T}_{ik}^{(2)}+C_2\sum_{k\neq i}(\mathbf{T}_{ik}^{(2)}:\mathbf{T}_{ik}^{(2)})\mathbf{U}+C_3\sum_{k\neq i}\mathbf{T}_{ik}^{(3)}:\mathbf{T}_{ik}^{(3)}+C_4\sum_{k\neq i}(\mathbf{T}_{ik}^{(3)}\vdots\mathbf{T}_{ik}^{(3)})\mathbf{U}&\\ +C_5\sum_{k\neq i}\mathbf{T}_{ik}^{(4)}\vdots\mathbf{T}_{ik}^{(4)}+C_6\sum_{k\neq i}(\mathbf{T}_{ik}^{(4)}\vdots\mathbf{T}_{ik}^{(4)})\mathbf{U}+C_7\sum_{k\neq i}\mathbf{T}_{ik}^{(2)}:\mathbf{T}_{ik}^{(4)}.&\quad(32)\end{aligned}$$

The coefficients (C_1+1), C_2, etc. have the following values

$$(C_1+1)U_0^3=(17/6)[\langle p_\alpha^2\rangle][\langle p_\alpha^4\rangle]+(9/4)[\langle p_\alpha^2\rangle][\langle p_\alpha^2\rangle\langle p_\beta^2\rangle]-(19/4)[\langle p_\alpha^2\rangle][\langle p_\alpha p_\beta\rangle\langle p_\alpha p_\beta\rangle]. \quad (33)$$

$$C_2U_0^3=(17/12)[\langle p_\alpha^2\rangle][\langle p_\alpha^4\rangle]-(7/2)[\langle p_\alpha^2\rangle][\langle p_\alpha^2\rangle\langle p_\beta^2\rangle]+(9/4)[\langle p_\alpha^2\rangle][\langle p_\alpha p_\beta\rangle\langle p_\alpha p_\beta\rangle]. \quad (34)$$

$$\begin{aligned}C_3U_0^3=&(17/36)[\langle p_\alpha^4\rangle][\langle q_{\alpha\alpha}^2\rangle]+(17/30)[\langle p_\alpha^2\rangle][\langle p_\alpha^2q_{\alpha\alpha}^2\rangle]-(13/18)[\langle p_\alpha^2q_{\alpha\alpha}\rangle][\langle p_\alpha^2q_{\alpha\alpha}\rangle]\\ &+(31/12)[\langle q_{\beta\gamma}\rangle\langle q_{\beta\gamma}\rangle][\langle p_\alpha^4\rangle]+7[\langle p_\alpha^2\rangle][\langle p_\alpha p_\beta q_{\alpha\gamma}\rangle\langle q_{\beta\gamma}\rangle]-(11/2)[\langle p_\alpha p_\gamma q_{\alpha\gamma}\rangle][\langle p_\beta p_\gamma\rangle\langle q_{\beta\gamma}\rangle]\\ &-(7/2)[\langle q_{\alpha\beta}^2\rangle][\langle p_\alpha p_\beta\rangle\langle p_\alpha p_\beta\rangle]+(35/2)[\langle p_\alpha p_\gamma\rangle\langle q_{\alpha\gamma}\rangle][\langle p_\beta p_\delta\rangle\langle q_{\beta\delta}\rangle]-(9/2)[\langle q_{\delta\gamma}\rangle\langle q_{\delta\gamma}\rangle][\langle p_\alpha p_\beta\rangle\langle p_\alpha p_\beta\rangle]\\ &-(17/2)[\langle p_\alpha^2\rangle][\langle p_\alpha p_\beta\rangle\langle q_{\alpha\gamma}\rangle\langle q_{\beta\gamma}\rangle]+(9/8)[\langle q_{\delta\epsilon}^2\rangle][\langle p_\alpha^2\rangle\langle p_\beta^2\rangle+\langle p_\alpha p_\gamma\rangle\langle p_\alpha p_\gamma\rangle]-(11/2)[\langle p_\beta p_\delta q_{\beta\delta}\rangle]\\ &\times[\langle p_\alpha p_\gamma\rangle\langle q_{\alpha\gamma}\rangle]-7[\langle p_\alpha^2\rangle][\langle p_\alpha p_\beta\rangle\langle q_{\alpha\gamma}q_{\beta\gamma}\rangle]-(73/8)[\langle q_{\delta\epsilon}\rangle\langle q_{\delta\epsilon}\rangle][\langle p_\alpha^2\rangle\langle p_\beta^2\rangle+\langle p_\alpha p_\gamma\rangle\langle p_\alpha p_\gamma\rangle]. \quad (35)\end{aligned}$$

$$\begin{aligned}C_4U_0^3=&(17/72)[\langle p_\alpha^4\rangle][\langle q_{\alpha\alpha}^2\rangle]+(17/120)[\langle p_\alpha^2\rangle][\langle p_\alpha^2q_{\alpha\alpha}^2\rangle]-(7/4)[\langle p_\alpha^2\rangle][\langle p_\alpha^2\rangle\langle q_{\beta\gamma}^2\rangle]\\ &+(31/24)[\langle q_{\beta\gamma}\rangle\langle q_{\beta\gamma}\rangle][\langle p_\alpha^4\rangle]+(7/4)[\langle p_\alpha^2\rangle][\langle p_\alpha^2q_{\beta\gamma}\rangle\langle q_{\beta\gamma}\rangle]-(7/4)[\langle q_{\gamma\delta}^2\rangle][\langle p_\alpha^2\rangle\langle p_\beta^2\rangle]\\ &-(9/4)[\langle q_{\gamma\delta}\rangle\langle q_{\gamma\delta}\rangle][\langle p_\alpha^2\rangle\langle p_\beta^2\rangle]-(17/8)[\langle p_\alpha^2\rangle][\langle p_\alpha^2\rangle\langle q_{\beta\gamma}\rangle\langle q_{\beta\gamma}\rangle]\\ &+(9/8)[\langle q_{\gamma\delta}^2\rangle][\langle p_\alpha p_\beta\rangle\langle p_\alpha p_\beta\rangle]-(73/8)[\langle q_{\gamma\delta}\rangle\langle q_{\gamma\delta}\rangle][\langle p_\alpha p_\beta\rangle\langle p_\alpha p_\beta\rangle]. \quad (36)\end{aligned}$$

$$\begin{aligned}C_5U_0^3=&(17/180)[\langle q_{\alpha\alpha}^2\rangle][\langle p_\alpha^2q_{\alpha\alpha}^2\rangle]+(31/60)[\langle q_{\beta\gamma}\rangle\langle q_{\beta\gamma}\rangle][\langle p_\alpha^2\rangle\langle q_{\alpha\alpha}^2\rangle]-(55/2)[\langle q_{\delta\epsilon}\rangle\langle q_{\delta\epsilon}\rangle][\langle p_\alpha p_\beta q_{\alpha\gamma}\rangle\langle q_{\beta\gamma}\rangle]\\ &+(7/2)[\langle q_{\delta\epsilon}^2\rangle][\langle p_\alpha p_\beta q_{\alpha\gamma}\rangle\langle q_{\beta\gamma}\rangle]-(9/2)[\langle q_{\delta\epsilon}\rangle\langle q_{\delta\epsilon}\rangle][\langle p_\alpha p_\beta\rangle\langle q_{\alpha\gamma}q_{\beta\gamma}\rangle]-(17/4)[\langle q_{\delta\epsilon}^2\rangle]\\ &\times[\langle p_\alpha p_\beta\rangle\langle q_{\alpha\gamma}\rangle\langle q_{\beta\gamma}\rangle]-(7/2)[\langle q_{\delta\epsilon}^2\rangle][\langle p_\alpha p_\beta\rangle\langle q_{\alpha\gamma}q_{\beta\gamma}\rangle]+(97/4)[\langle q_{\delta\epsilon}\rangle\langle q_{\delta\epsilon}\rangle][\langle p_\alpha p_\beta\rangle\langle q_{\alpha\lambda}\rangle\langle q_{\beta\lambda}\rangle]. \quad (37)\end{aligned}$$

$$\begin{aligned}C_6U_0^3=&(17/720)[\langle q_{\alpha\alpha}^2\rangle][\langle p_\alpha^2q_{\alpha\alpha}^2\rangle]-(7/8)[\langle q_{\delta\epsilon}^2\rangle][\langle p_\alpha^2\rangle\langle q_{\beta\gamma}^2\rangle]+(31/240)[\langle q_{\beta\gamma}\rangle\langle q_{\beta\gamma}\rangle][\langle p_\alpha^2q_{\alpha\alpha}^2\rangle]\\ &-(55/8)[\langle q_{\delta\epsilon}\rangle\langle q_{\delta\epsilon}\rangle][\langle p_\alpha^2q_{\beta\gamma}\rangle\langle q_{\beta\gamma}\rangle]+(7/8)[\langle q_{\delta\epsilon}^2\rangle][\langle p_\alpha^2q_{\beta\gamma}\rangle\langle q_{\beta\gamma}\rangle]-(9/8)[\langle q_{\delta\epsilon}\rangle\langle q_{\delta\epsilon}\rangle][\langle p_\alpha^2\rangle\langle q_{\beta\gamma}^2\rangle]\\ &-(17/16)[\langle q_{\delta\epsilon}^2\rangle][\langle p_\alpha^2\rangle\langle q_{\beta\gamma}\rangle\langle q_{\beta\gamma}\rangle]+(97/16)[\langle q_{\delta\epsilon}\rangle\langle q_{\delta\epsilon}\rangle][\langle p_\alpha^2\rangle\langle q_{\gamma\lambda}\rangle\langle q_{\gamma\lambda}\rangle]. \quad (38)\end{aligned}$$

$$C_7U_0^3=-(13/2)[\langle p_\alpha p_\beta q_{\alpha\beta}\rangle][\langle p_\alpha p_\beta q_{\alpha\beta}\rangle]-11[\langle p_\alpha p_\beta q_{\alpha\beta}\rangle][\langle p_\alpha p_\beta\rangle\langle q_{\alpha\beta}\rangle]+(35/2)[\langle p_\alpha p_\beta\rangle\langle q_{\alpha\beta}\rangle][\langle p_\alpha p_\beta\rangle\langle q_{\alpha\beta}\rangle]. \quad (39)$$

In this formalism, averaging with respect to orientations extends simultaneously over all factors occurring within the [ ] brackets; the usual quantum mechanical averages are implied by the ⟨ ⟩ brackets. The components p_α, $q_{\beta\gamma}$, etc., refer to the fixed coordinate system $(x'y'z')$; for the averaging over the orientations of the molecular symmetry axes α, β, γ, $\cdots$ are arbitrary indices. However, they must be taken as different whenever they are indicated as different subscripts. Equation (32) for $\boldsymbol{\beta}_i^{(2)}$ is quite general; i.e., it is valid for any molecular model. It also shows, when combined with (30) and (26), that the set of Eqs. (24) for the "effective" polarizability is consistent, at least up to third order of perturbation theory.

For atoms or molecules with spherical charge distribution, only the first two terms of (C_1+1) are nonzero. The same applies to the first two terms of C_2, the first three of C_3, and the first three of C_4. Of the terms in C_5 all vanish except the first, of C_6 all except the first two, and of C_7 only the first term is nonzero. To obtain values for the coefficients C, we have to make use of a specific molecular model except for a few terms which can be determined directly from experimental measurements. If we denote the molecular quadrupole moment by Q, and introduce an anisotropy factor κ of the polarizability given by

$$\kappa=\langle p_{\shortparallel}{}^2-p_{\perp}{}^2\rangle/3\langle p^2\rangle_{\mathrm{or}},\quad \langle p^2\rangle_{\mathrm{or}}=\tfrac{1}{3}\langle 2p_{\perp}{}^2+p_{\shortparallel}{}^2\rangle;$$

then

$$\begin{aligned}
[\langle q_{\beta\gamma}\rangle\langle q_{\beta\gamma}\rangle]_{\mathrm{or}}&=Q^2/15,\\
[\langle p_\alpha p_\beta\rangle\langle p_\alpha p_\beta\rangle]_{\mathrm{or}}&=\langle p_{\shortparallel}{}^2-p_{\perp}{}^2\rangle^2/15=\tfrac{3}{5}\kappa^2\langle p^2\rangle_{\mathrm{or}}{}^2,\\
[\langle p_\alpha p_\alpha\rangle\langle p_\beta p_\beta\rangle]_{\mathrm{or}}&=[\tfrac{1}{3}\langle 2p_{\perp}{}^2+p_{\shortparallel}{}^2\rangle]^2\\
&\quad-(2/45)[\langle p_{\shortparallel}{}^2-p_{\perp}{}^2\rangle]^2\\
&=\langle p^2\rangle_{\mathrm{or}}{}^2\cdot[1-\tfrac{2}{5}\kappa^2],\\
[\langle p_\alpha p_\beta\rangle\langle q_{\alpha\gamma}\rangle\langle q_{\beta\gamma}\rangle]_{\mathrm{or}}&=(Q^2/105)\langle p_{\shortparallel}{}^2-p_{\perp}{}^2\rangle\\
&=(Q^2/35)\kappa\langle p^2\rangle_{\mathrm{or}}.
\end{aligned}$$

For the part of $\boldsymbol{\beta}_i{}^{(2)}$ involving only dipole-dipole interactions, the only quantity which has to be computed from a molecular model is $\langle p_\alpha{}^4\rangle_{\mathrm{or}}/\langle p^2\rangle_{\mathrm{or}}{}^2$; by using the identity $\alpha_0=2\langle p^2\rangle_{\mathrm{or}}/U_0$ for the average polarizability of a free molecule one obtains the following expression (we will again omit subscripts on the tensors $\mathbf{T}$ and also the summation sign.)

$$\begin{aligned}
&[\boldsymbol{\beta}_i{}^{(2)}{}_{\text{dip-dip}}]_{\mathrm{or}}\\
&=\frac{\alpha_0{}^3}{32}\left\{\left[\frac{34}{3}\left(\frac{\langle p_\alpha{}^4\rangle_{\mathrm{or}}}{\langle p^2\rangle_{\mathrm{or}}{}^2}\right)+9-15\kappa^2\right]\mathbf{T}^{(2)}\cdot\mathbf{T}^{(2)}\right.\\
&\qquad\left.+\left[\frac{17}{3}\left(\frac{\langle p_\alpha{}^4\rangle_{\mathrm{or}}}{\langle p^2\rangle_{\mathrm{or}}{}^2}\right)-14+11\kappa^2\right]\mathbf{T}^{(2)}\cdot\mathbf{T}^{(2)}\mathbf{U}\right\}. \qquad (40)
\end{aligned}$$

This equation simplifies further if the charge distribution has spherical symmetry. For hydrogen atoms, $\langle p_\alpha{}^4\rangle_{\mathrm{or}}/\langle p^2\rangle_{\mathrm{or}}{}^2$ is equal to 9/2; for helium atoms, if one uses Slater wave functions, this ratio is 15/4. For heavier atoms, we take a Gaussian charge distribution function:

$$\rho(r)=(b^3/\pi^{\frac{3}{2}})\exp(-b^2r^2). \qquad (41)$$

Then the above ratio is equal to 3, independent of b. The final formula for $\boldsymbol{\beta}_i{}^{(2)}{}_{\text{dip-dip}}$ based on a Gaussian distribution is

$$\begin{aligned}
\boldsymbol{\beta}_i{}^{(2)}{}_{\text{dip-dip}}=\alpha_0{}^3[&(43/32)\mathbf{T}^{(2)}\cdot\mathbf{T}^{(2)}\\
&+(3/32)\mathbf{T}^{(2)}:\mathbf{T}^{(2)}\mathbf{U}]. \qquad (42)
\end{aligned}$$

From Eqs. (27), (28), and (29) connecting tensors $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$, we can also obtain average values for the "effective" polarizability of a molecule. The following results apply for *unweighted* averages over the orientations

$$[\boldsymbol{\alpha}_i{}^{(1)}]_{\mathrm{or}}=0, \qquad (43)$$

$$\begin{aligned}
[\boldsymbol{\alpha}_i{}^{(2)}]_{\mathrm{or}}&=[\boldsymbol{\beta}_i{}^{(2)}]_{\mathrm{or}}-\alpha_0{}^3[1+\tfrac{1}{5}\kappa^2]\mathbf{T}^{(2)}\cdot\mathbf{T}^{(2)}\\
&\quad+\tfrac{3}{5}\kappa Q\alpha_0{}^3\left[\frac{\langle p_\alpha p_\beta q_{\alpha\beta}\rangle_{\mathrm{or}}}{\langle p^2\rangle_{\mathrm{or}}{}^2}-\frac{\kappa Q}{5\langle p^2\rangle_{\mathrm{or}}}\right]\mathbf{T}^{(2)}:\mathbf{T}^{(4)}. \qquad (44)
\end{aligned}$$

The expression for $[\boldsymbol{\alpha}_i{}^{(2)}]_{\mathrm{or}}$ is very much simpler for spherical atoms; by combining Eqs. (42) and (44) we obtain in this case for the dipole part of $\boldsymbol{\alpha}_i{}^{(2)}$:

$$\begin{aligned}
\boldsymbol{\alpha}_i{}^{(2)}{}_{\text{dip-dip}}=\alpha_0{}^3[&(11/32)\mathbf{T}^{(2)}\cdot\mathbf{T}^{(2)}\\
&+(3/32)\mathbf{T}^{(2)}:\mathbf{T}^{(2)}\mathbf{U}]. \qquad (45)
\end{aligned}$$

When we consider the problem of two spherical charge distributions at a distance r between their centers and interacting through induced dipole forces, then Eq. (45) shows that the "effective" polarizability differs from the polarizability of a free molecule by $(31/16)(\alpha_0/r^3)^2\alpha_0$ along the line joining the centers and by $(29/32)(\alpha_0/r^3)^2\alpha_0$ in a direction perpendicular to it. This illustrates that $\boldsymbol{\alpha}_i$ is dependent on the density of the medium. The remaining terms in $\boldsymbol{\alpha}_i{}^{(2)}$, *viz.*, those due to dipole-quadrupole and quadrupole-quadrupole interactions, can also be calculated easily using Eq. (41). The results are

$$\begin{aligned}
\boldsymbol{\alpha}_{i\,\text{dip-quad}}{}^{(2)}=\alpha_0{}^3\bigg[&\frac{25}{64b^2}\mathbf{T}^{(3)}:\mathbf{T}^{(3)}+\frac{5}{32b^2}\mathbf{T}^{(3)}\vdots\mathbf{T}^{(3)}\mathbf{U}\\
&-\frac{13}{32b^2}\mathbf{T}^{(2)}:\mathbf{T}^{(4)}\bigg], \qquad (46)
\end{aligned}$$

$$\boldsymbol{\alpha}_{i\,\text{quad-quad}}{}^{(2)}=\alpha_0{}^3\left[\frac{17}{128b^4}\mathbf{T}^{(4)}\vdots\mathbf{T}^{(4)}+\frac{3}{512b^4}\mathbf{T}^{(4)}\vdots\mathbf{T}^{(4)}\mathbf{U}\right]. \qquad (47)$$

The values for the parameter b in the Gaussian distribution can be determined, for example, by calculating first the London dipole forces between two Gaussian atoms and then equating the expression to an empirically known quantity, for instance, the $1/r^6$ part of the Lennard-Jones (6–12) potential.[16]

In a subsequent paper we will evaluate the expressions involving the higher multipoles and give a derivation of the Clausius-Mossotti function for gases consisting of axially symmetric molecules.

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[16] L. Jansen and R. T. McGinnies, Phys. Rev. **104**, 961 (1956).