

RAYLEIGH'S RATIO AND TURBIDITY OF IMPERFECT GASES

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General expressions for Rayleigh's ratio and the turbidity are given, containing the molecular constants S_m^{is} and S_m^{anis} of isotropic and anisotropic light scattering. For imperfect gases, the constants S_m^{is} and S_m^{anis} can be expressed as a virial expansion in inverse powers of the molar volume. The second virial coefficients B_S^{is} and B_S^{anis} of isotropic and anisotropic light scattering are calculated for certain molecular models of dipole and quadrupole molecules. The respective quantities are discussed and evaluated numerically for the imperfect gases CO_2 , NH_3 , CH_3F , CH_3CN and COS .

1. Introduction

Kammerlingh-Onnes' equation, which is the equation of state of imperfect gases in terms of an expansion in virial coefficients, represents an important method for the investigation of intermolecular forces. In particular, the second virial coefficient $B(T)$ not only gives insight into the parameters determining the central forces (see, Lennard-Jones 1924), but, moreover, provides information on the non-central intermolecular forces (see, e.g., Stockmayer 1941, Hirschfelder et al. 1942, Rowlinson 1949, Pople 1954, Buckingham and Pople 1955 a).

In recent years, the method of expansion in virial coefficients was applied to the theory of other measurable properties of imperfect gases. Harris and Alder (1953), Buckingham and Pople (1955 b), Hill (1958), and Jansen (1958) proposed virial theories of the dielectric permittivity of imperfect gases. Moreover, Buckingham computed the second virial coefficient for the molecular Kerr constant (1955) and molecular refraction (1956).

Similarly, information on the nature of the forces acting between the molecules can be derived from an investigation of the divergence between light scattering in a compressed and in an ideal gas. To this aim, a theory of the virial coefficients for Rayleigh's ratio S and the turbidity h of imperfect gases is proposed in the present paper. In particular, the second virial coefficient for light scattering on different models of dipole and quadrupole molecules is computed numerically.

2. General formulation of the theory

By statistical-mechanical theory of classical light scattering, Rayleigh's ratio S and the turbidity h are given by (see, Kielich 1960)

$$S = \frac{(n^2 + 2)^2}{9V} (S_m^{\text{is}} + S_m^{\text{anis}}), \quad (2.1)$$

$$h = \frac{16\pi(n^2 + 2)^2}{27V} \left(S_m^{\text{is}} + \frac{5}{13} S_m^{\text{anis}} \right), \quad (2.2)$$

wherein V is the molar volume of the scattering medium of refractive index n . The molecular constants S_m^{is} and S_m^{anis} account for the molecular mechanism of isotropic and anisotropic light scattering. In the case of a scattering medium consisting of N molecules of one kind, whose linear dimensions are small as compared to the light wavelength λ , we have

$$S_m^{\text{is}} = \frac{8\pi^4}{9\lambda^4} \left\langle \sum_{i=1}^N \sum_{j=1}^N \frac{\partial m_\alpha^{(i)}}{\partial E_\alpha} \frac{\partial m_\beta^{(j)}}{\partial E_\beta} \right\rangle, \quad (2.3)$$

$$S_m^{\text{anis}} = \frac{52\pi^4}{45\lambda^4} \left\langle \sum_{i=1}^N \sum_{j=1}^N \left\{ 3 \frac{\partial m_\alpha^{(i)}}{\partial E_\beta} \frac{\partial m_\alpha^{(j)}}{\partial E_\beta} - \frac{\partial m_\alpha^{(i)}}{\partial E_\alpha} \frac{\partial m_\beta^{(j)}}{\partial E_\beta} \right\} \right\rangle, \quad (2.4)$$

wherein $m_\alpha^{(i)}$ is the α -component of the dipole moment induced in the i -th molecule of the medium by the electric field E_α of the light wave. Here, the brackets $\langle \rangle$ are intended to denote the statistical mean value, as defined by the formula

$$\langle X \rangle = \frac{\int \int \dots \int X(\tau) e^{-\frac{U(\tau)}{kT}} d\tau_1 d\tau_2 \dots d\tau_N}{\int \int \dots \int e^{-\frac{U(\tau)}{kT}} d\tau_1 d\tau_2 \dots d\tau_N}; \quad (2.5)$$

k — Boltzmann's constant, T — the Kelvin temperature, $U(\tau)$ — the total potential energy of the system in the configuration τ .

For an anisotropic molecule immersed in the medium, $m_\alpha^{(i)}$ is given by the following expansion due to Buckingham and Stephen (1957):

$$m_\alpha^{(i)} = \alpha_{\alpha\beta}^{(i)} (E_\beta + F_\beta^{(i)}) + \frac{1}{2} \beta_{\alpha\beta\gamma}^{(i)} (E_\beta + F_\beta^{(i)}) (E_\gamma + F_\gamma^{(i)}) + \frac{1}{6} \gamma_{\alpha\beta\gamma\delta}^{(i)} (E_\beta + F_\beta^{(i)}) (E_\gamma + F_\gamma^{(i)}) (E_\delta + F_\delta^{(i)}) + \dots, \quad (2.6)$$

with $\alpha_{\alpha\beta}^{(i)}$ denoting the polarizability tensor of the i -th molecule, and $\beta_{\alpha\beta\gamma}^{(i)}$ and $\gamma_{\alpha\beta\gamma\delta}^{(i)}$ — its hyperpolarizability tensors as discussed by Buckingham and Pople (1955 c). The tensors $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ account for the properties of the isolated molecule, and are symmetrical in all indices α , β , γ and δ . $F_\alpha^{(i)}$ is the α -component of the molecular field at the centre of the i -th molecule due to the charge distributions of all the others, in the presence of the electric field E_α .

The application of the foregoing theory to imperfect gases consists in expanding the molecular constants S_m^{is} and S_m^{anis} in powers of $1/V$:

$$S_m^{\text{is}} = A_S^{\text{is}} + \frac{B_S^{\text{is}}}{V} + \frac{C_S^{\text{is}}}{V^2} + \dots, \quad (2.7)$$

$$S_m^{\text{anis}} = A_S^{\text{anis}} + \frac{B_S^{\text{anis}}}{V} + \frac{C_S^{\text{anis}}}{V^2} + \dots \quad (2.8)$$

The coefficients of the expansions A_S^{is} , A_S^{anis} , B_S^{is} , B_S^{anis} , C_S^{is} , C_S^{anis} , ... are termed the first, second, third, ... virial coefficient of isotropic and anisotropic light scattering, respectively.

The first virial coefficients, A_S^{is} and A_S^{anis} , characterize light scattering in a gas whose molecules do not interact (ideal gas), and, with respect to eqs. (2.3), (2.4) and (2.6), are given by

$$A_S^{\text{is}} = \frac{8\pi^4}{\lambda^4} \alpha^2 N, \quad (2.9)$$

$$A_S^{\text{anis}} = \frac{52\pi^4}{45\lambda^4} (3\alpha_{\alpha\beta} \alpha_{\alpha\beta} - \alpha_{\alpha\alpha} \alpha_{\beta\beta}) N, \quad (2.10)$$

wherein $\alpha = \frac{1}{3} \alpha_{\alpha\alpha}$ is the mean polarizability of an isolated molecule.

The second virial coefficients, B_S^{is} and B_S^{anis} , relate to pairwise interaction between the molecules. The remaining virial coefficients, C_S^{is} , C_S^{anis} etc., account for the interaction of three, four etc. molecules of an imperfect gas. The coefficients yield a measure of the divergence between light scattering in a real gas and in an ideal gas. We shall restrict ourselves to a discussion of the virial coefficients B_S^{is} and B_S^{anis} only, which, for a not too strongly compressed gas, account essentially for the divergence from the ideal gas. By eqs. (2.3), (2.4) and (2.9), (2.10), we have quite generally:

$$B_S^{\text{is}} = -\frac{16\pi^4 \alpha^2 N}{\lambda^4} B(T) + \frac{8\pi^4 N^2}{9\lambda^4 \Omega^2} \iiint (V_{\alpha\alpha, \beta\beta}^{(ij)} - 9\alpha^2) e^{-\frac{U_{ij}}{kT}} d\mathbf{r}_{ij} d\omega_i d\omega_j, \quad (2.11)$$

$$B_S^{\text{anis}} = \frac{52\pi^4 N^2}{45\lambda^4 \Omega^2} \iiint (3V_{\alpha\beta, \alpha\beta}^{(ij)} - V_{\alpha\alpha, \beta\beta}^{(ij)}) e^{-\frac{U_{ij}}{kT}} d\mathbf{r}_{ij} d\omega_i d\omega_j. \quad (2.12)$$

Herein, the tensor

$$V_{\alpha\beta, \gamma\delta}^{(ij)} = \frac{1}{2} \left\{ \left(\frac{\partial m_\alpha^{(i)}}{\partial E_\beta} + \frac{\partial m_\alpha^{(j)}}{\partial E_\beta} \right) \left(\frac{\partial m_\gamma^{(i)}}{\partial E_\delta} + \frac{\partial m_\gamma^{(j)}}{\partial E_\delta} \right) - (\alpha_{\alpha\beta}^{(i)} \alpha_{\gamma\delta}^{(i)} + \alpha_{\alpha\beta}^{(j)} \alpha_{\gamma\delta}^{(j)}) \right\}, \quad (2.13)$$

and the second virial coefficient of the equation of state of the real gas (Pople, 1954)

$$B(T) = -\frac{N}{2\Omega^2} \iiint (e^{-\frac{U_{ij}}{kT}} - 1) d\mathbf{r}_{ij} d\omega_i d\omega_j, \quad (2.14)$$

have been introduced; U_{ij} denotes the total potential energy of interaction of the i -th and j -th molecules, and r_{ij} — the distance between their centres, the variables ω_i, ω_j describing their respective orientations; $\Omega = \int d\omega_i$ is the integral over angular coordinates.

3. First Approximation to the Theory

In the first approximation, a molecule of the imperfect gas under consideration is assumed to possess the polarizability of one isolated, i.e. a polarizability independent of the surrounding, neighbouring molecules. In this case, the expansion of eq. (2.6) yields

$$\frac{\partial m_{\alpha}^{(i)}}{\partial E_{\beta}} = \alpha_{\alpha\beta}^{(i)}, \quad (3.1)$$

and the virial coefficients (2.11) and (2.12) assume the form

$$B_S^{\text{is}} = - \frac{16\pi^4 \alpha^2 N}{\lambda^4} B(T) = \frac{8\pi^4 \alpha^2 N^2}{\lambda^4 \Omega^2} \iiint (e^{-\frac{U_{ij}}{kT}} - 1) d\mathbf{r}_{ij} d\omega_i d\omega_j, \\ B_S^{\text{anis}} = \frac{52\pi^4 N^2}{45\lambda^4 \Omega^2} \iiint (3\alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(j)} - \alpha_{\alpha\alpha}^{(i)} \alpha_{\beta\beta}^{(j)}) e^{-\frac{U_{ij}}{kT}} d\mathbf{r}_{ij} d\omega_i d\omega_j. \quad (3.2)$$

Hence, it is seen that the second virial coefficient of isotropic light scattering, B_S^{is} , is accounted for directly by the second virial coefficient $B(T)$ of the equation of state of the imperfect gas only if the molecules exhibit a polarizability that is unaffected by the presence of their neighbours.

The total potential energy U_{ij} consists of the energy $U^{(0)}(r_{ij})$ related to the existence of central forces of attraction and repulsion acting between the molecules, and of the energy $V_{ij} = u(r_{ij}, \omega_i, \omega_j)$ resulting from non-central electric intermolecular forces:

$$U_{ij} = U^{(0)}(r_{ij}) + V_{ij}.$$

The energy V_{ij} will now be considered to represent a perturbation in $U^{(0)}(r_{ij})$, so that the virial coefficients B_S^{is} and B_S^{anis} of eq. (3.2) can be expanded as follows:

$$B_S^{\text{is}} = \text{centr} B_S^{\text{is}} + \frac{8\pi^4 \alpha^2 N^2}{\lambda^4} \sum_{n=1}^{\infty} \frac{1}{n!} \left(-\frac{1}{kT}\right)^n \int \overline{V_{ij}^n} e^{-\frac{U^{(0)}(r_{ij})}{kT}} d\mathbf{r}_{ij}, \quad (3.3)$$

$$B_S^{\text{anis}} = \frac{52\pi^4 N^2}{15\lambda^4} \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{1}{kT}\right)^n \int (\alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(j)} \overline{V_{ij}^n} - 3\alpha_{\alpha\alpha}^{(i)} \alpha_{\beta\beta}^{(j)} \overline{V_{ij}^n}) e^{-\frac{U^{(0)}(r_{ij})}{kT}} d\mathbf{r}_{ij},$$

wherein

$$\text{centr} B_S^{\text{is}} = \frac{8\pi^4 \alpha^2 N^2}{\lambda^4} \int (e^{-\frac{U^{(0)}(r_{ij})}{kT}} - 1) d\mathbf{r}_{ij}, \quad (3.4)$$

is the second virial coefficient of isotropic light scattering, dependent only on the model of central intermolecular forces; the horizontal line is to denote isotropic averaging:

$$\bar{X} = \frac{1}{\Omega^2} \iint X(\omega) d\omega_i d\omega_j,$$

i.e. integration over all possible configurations of either molecule.

The virial coefficients, as given by eq. (3.3), will now be computed for some models of the potential energy V_{ij} of electrostatic interaction between the molecules.

Dipole molecules. The potential energy of electrostatic interaction between two dipole molecules is

$$V_{ij} = \mu_\alpha^{(i)} \mu_\beta^{(j)} T_{\alpha\beta}^{(ij)}, \quad (3.5)$$

wherein $\mu_\alpha^{(i)}$ is the α -component of the permanent dipole moment of the i -th isolated molecule, and

$$T_{\alpha\beta}^{(ij)} = \frac{1}{r_{ij}^5} \{r_{ij}^2 \delta_{\alpha\beta} - 3r_{ij\alpha} r_{ij\beta}\}; \quad i \neq j, \quad (3.6)$$

is the tensor of dipole-dipole interaction.

Substitution of (3.5) in eq. (3.3), with the isotropic mean values $\overline{V_{ij}^n}$ and $\overline{\alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(j)} V_{ij}^n}$ of Appendix B, yields

$$\text{dip} B_S^{\text{is}} = \text{centr} B_S^{\text{is}} + \frac{8\pi^4 \alpha^2 \mu^4 N^2}{3\lambda^4 k^2 T^2} \left\{ \langle r_{ij}^{-6} \rangle + \frac{3\mu^4}{25k^2 T^2} \langle r_{ij}^{-12} \rangle + \dots \right\}, \quad (3.7)$$

$$\text{dip} B_S^{\text{anis}} = \frac{26\pi^4 N^2}{3375 \lambda^4 k^2 T^2} (3\alpha_{\alpha\beta} \mu_\alpha \mu_\beta - \alpha_{\alpha\alpha} \mu_\beta^2) \left\{ \langle r_{ij}^{-6} \rangle + \frac{12\mu^4}{49k^2 T^2} \langle r_{ij}^{-12} \rangle + \dots \right\}, \quad (3.8)$$

wherein

$$\langle r_{ij}^{-n} \rangle = \int r_{ij}^{-n} e^{-\frac{U^{(0)}(r_{ij})}{kT}} d\mathbf{r}_{ij} \quad (3.9)$$

is a quantity that depends solely on the model of central forces.

In the case of a molecule having the axial symmetry, with the axis of symmetry directed along the 3-axis, the following tensor components of μ_α and $\alpha_{\alpha\beta}$ are non-zero:

$$\mu_3 = \mu, \quad \alpha_{11} = \alpha_{22} = \alpha_\perp, \quad \alpha_{33} = \alpha_\parallel;$$

hence,

$$3\alpha_{\alpha\beta} \mu_\alpha \mu_\beta - \alpha_{\alpha\alpha} \mu_\beta^2 = 6\alpha \delta_\alpha \mu^2, \quad (3.10)$$

wherein the quantity

$$\delta_\alpha = \frac{\alpha_\parallel - \alpha_\perp}{3\alpha} = \frac{\alpha_\parallel - \alpha_\perp}{\alpha_\parallel + 2\alpha_\perp} \quad (3.11)$$

accounts for the anisotropy of polarizability of the isolated molecule.

By (3.10), eq. (3.8) reduces to

$$\text{dip} B_S^{\text{anis}} = \frac{104\pi^4 \alpha^2 \delta_\alpha^2 \mu^4 N^2}{375\lambda^4 k^2 T^2} \left\{ \langle r_{ij}^{-6} \rangle + \frac{12\mu^4}{49k^2 T^2} \langle r_{ij}^{-12} \rangle + \dots \right\}, \quad (3.12)$$

valid for axially symmetric molecules.

We shall now proceed a step further, and shall take account of inductive interaction between the dipole molecules. Now, for anisotropically polarizable molecules, we have (see, Appendix A)

$$V_{ij} = \mu_\alpha^{(i)} \mu_\beta^{(j)} T_{\alpha\beta}^{(ij)} - \frac{1}{2} (\alpha_{\alpha\beta}^{(i)} \mu_\gamma^{(j)} \mu_\delta^{(j)} + \alpha_{\alpha\beta}^{(j)} \mu_\gamma^{(i)} \mu_\delta^{(i)}) T_{\alpha\gamma}^{(ij)} T_{\beta\delta}^{(ij)} + \dots, \quad (3.13)$$

wherein, in addition to the first term accounting for dipole-dipole interaction, terms determining the inductive effect of dipole-induced dipole interaction appear.

With the previous expression for V_{ij} , the virial coefficients are now

$$B_S^{\text{is}} = \text{dip} B_S^{\text{is}} + \frac{16\pi^4 \alpha^2 \mu^2 N^2}{\lambda^4 k T} \left\{ \alpha \langle r_{ij}^{-6} \rangle + \frac{2\mu^2}{75k^2 T^2} [15\alpha \mu^2 + 2(3\alpha_{\alpha\beta} \mu_\alpha \mu_\beta - \alpha_{\alpha\alpha} \mu_\beta^2)] \langle r_{ij}^{-12} \rangle + \dots \right\}, \quad (3.14)$$

$$B_S^{\text{anis}} = \text{dip} B_S^{\text{anis}} + \frac{52\pi^4 N^2}{3375 \lambda^4 k T} (3\alpha_{\alpha\beta} \mu_\alpha \mu_\beta - \alpha_{\alpha\alpha} \mu_\beta^2) \left\{ (3\alpha_{\gamma\delta} \alpha_{\gamma\delta} - \alpha_{\gamma\gamma} \alpha_{\delta\delta}) \langle r_{ij}^{-6} \rangle + \frac{12\mu^4}{49k^2 T^2} [4(3\alpha_{\gamma\delta} \alpha_{\gamma\epsilon} - \alpha_{\gamma\gamma} \alpha_{\delta\epsilon}) \mu_\delta \mu_\epsilon + (3\alpha_{\gamma\delta} \mu_\gamma \mu_\delta - \alpha_{\gamma\gamma} \mu_\delta^2) \alpha_{\epsilon\epsilon} + (3\alpha_{\gamma\delta} \alpha_{\gamma\delta} - \alpha_{\gamma\gamma} \alpha_{\delta\delta}) \mu_\epsilon^2] \langle r_{ij}^{-12} \rangle + \dots \right\}, \quad (3.15)$$

wherein the quantities $\text{dip} B_S^{\text{is}}$ and $\text{dip} B_S^{\text{anis}}$ are given by eqs. (3.7) and (3.8).

By eq. (3.10) and the relations

$$3\alpha_{\alpha\beta} \alpha_{\alpha\beta} - \alpha_{\alpha\alpha} \alpha_{\beta\beta} = 18 \alpha^2 \delta_\alpha^2, \\ (3\alpha_{\alpha\beta} \alpha_{\alpha\gamma} - \alpha_{\alpha\alpha} \alpha_{\beta\gamma}) \mu_\beta \mu_\gamma = 6\alpha^2 \delta_\alpha (1 + 2\delta_\alpha) \mu^2, \quad (3.16)$$

eqs. (3.14) and (3.15) yield, for axially symmetric molecules,

$$B_S^{\text{is}} = \text{dip} B_S^{\text{is}} + \frac{16\pi^4 \alpha^3 \mu^2 N^2}{\lambda^4 k T} \left\{ \langle r_{ij}^{-6} \rangle + \frac{2\mu^4}{25k^2 T^2} (5 + 4\delta_\alpha) \langle r_{ij}^{-12} \rangle + \dots \right\}, \quad (3.17)$$

$$B_S^{\text{anis}} = \text{dip} B_S^{\text{anis}} + \frac{208\pi^4 \alpha^3 \delta_\alpha^2 \mu^2 N^2}{125\lambda^4 k T} \left\{ \delta_\alpha \langle r_{ij}^{-6} \rangle + \frac{4\mu^4}{49k^2 T^2} (7 + 11\delta_\alpha) \langle r_{ij}^{-12} \rangle + \dots \right\}. \quad (3.18)$$

Thus, the additional contributions to B_S^{is} and B_S^{anis} from inductive interaction between dipole molecules have been computed.

Quadrupole molecules. For non-dipolar, anisotropically polarizable molecules possessing a quadrupole moment given by the tensor $\Theta_{\alpha\beta}$, the potential energy of electrostatic interaction is (see, Appendix A)

$$V_{ij} = -\frac{1}{6} \Theta_{\alpha\beta}^{(i)} \Theta_{\gamma\delta}^{(j)} T_{\alpha\beta\gamma\delta}^{(ij)} - \frac{1}{18} (\alpha_{\alpha\beta}^{(i)} \Theta_{\gamma\delta}^{(j)} \Theta_{\epsilon\eta}^{(i)} + \alpha_{\alpha\beta}^{(j)} \Theta_{\gamma\delta}^{(i)} \Theta_{\epsilon\eta}^{(j)}) T_{\alpha\gamma\delta}^{(ij)} T_{\beta\epsilon\eta}^{(ij)} + \dots, \quad (3.19)$$

the first term accounting for the energy of quadrupole-quadrupole interaction, whereas the second determines that of quadrupole-induced dipole interaction.

Substitution of the foregoing in eq. (3.3) yields

$$\text{quad}B_S^{\text{is}} = \text{centr}B_S^{\text{is}} + \frac{16\pi^4 \alpha^2 N^2}{15\lambda^4 kT} \Theta_{\alpha\beta} \Theta_{\alpha\beta} \left\{ 15\alpha \langle r_{ij}^{-8} \rangle + \frac{14}{3kT} \Theta_{\gamma\delta} \Theta_{\gamma\delta} \langle r_{ij}^{-10} \rangle + \dots \right\}, \quad (3.20)$$

$$\begin{aligned} \text{quad}B_S^{\text{anis}} = & \frac{208\pi^4 N^2}{4725\lambda^4 kT} (3\alpha_{\alpha\beta} \Theta_{\alpha\gamma} \Theta_{\beta\gamma} - \alpha_{\alpha\alpha} \Theta_{\beta\gamma} \Theta_{\beta\gamma}) \left\{ (3\alpha_{\delta\epsilon} \alpha_{\delta\epsilon} - \alpha_{\delta\delta} \alpha_{\epsilon\epsilon}) \langle r_{ij}^{-8} \rangle + \right. \\ & \left. + \frac{8}{3kT} (3\alpha_{\delta\epsilon} \Theta_{\delta\eta} \Theta_{\epsilon\eta} - \alpha_{\delta\delta} \Theta_{\epsilon\eta} \Theta_{\epsilon\eta}) \langle r_{ij}^{-10} \rangle + \dots \right\}. \end{aligned} \quad (3.21)$$

Herein, the terms in $\langle r_{ij}^{-8} \rangle$ result from quadrupole-induced dipole interaction, whereas those in $\langle r_{ij}^{-10} \rangle$ — from quadrupole-quadrupole interaction.

In the case of molecules exhibiting the axial symmetry, we have

$$\Theta_{\alpha\beta} \Theta_{\alpha\beta} = \frac{3}{2} \Theta^2; \quad 3\alpha_{\alpha\beta} \Theta_{\alpha\gamma} \Theta_{\beta\gamma} - \alpha_{\alpha\alpha} \Theta_{\beta\gamma} \Theta_{\beta\gamma} = \frac{3}{2} \alpha \delta_{\alpha} \Theta^2, \quad (3.22)$$

and the virial coefficients of eqs. (3.20) and (3.21) reduce to

$$\text{quad}B_S^{\text{is}} = \text{centr}B_S^{\text{is}} + \frac{8\pi^4 \alpha^2 \Theta^2 N^2}{5\lambda^4 kT} \left\{ 15\alpha \langle r_{ij}^{-8} \rangle + \frac{7\Theta^2}{kT} \langle r_{ij}^{-10} \rangle + \dots \right\}, \quad (3.23)$$

$$\text{quad}B_S^{\text{anis}} = \frac{208\pi^4 \alpha^2 \delta_{\alpha}^2 \Theta^2 N^2}{175\lambda^4 kT} \left\{ 3\alpha \delta_{\alpha} \langle r_{ij}^{-8} \rangle + \frac{2\Theta^2}{kT} \langle r_{ij}^{-10} \rangle + \dots \right\}, \quad (3.24)$$

with $\Theta = \Theta_{33} = -2\Theta_{11} = -2\Theta_{22}$ denoting the quadrupole moment of the axially symmetric molecule.

Polar molecules. For molecules exhibiting both a dipole and quadrupole moment, the potential energy V_{ij} is given by (see, Appendix A)

$$V_{ij} = \mu_{\alpha}^{(i)} \mu_{\beta}^{(j)} T_{\alpha\beta}^{(ij)} + \frac{1}{6} (\mu_{\alpha}^{(i)} \Theta_{\beta\gamma}^{(j)} - \Theta_{\alpha\beta}^{(i)} \mu_{\gamma}^{(j)}) T_{\alpha\beta\gamma}^{(ij)} - \frac{1}{6} \Theta_{\alpha\beta}^{(i)} \Theta_{\gamma\delta}^{(j)} T_{\alpha\beta\gamma\delta}^{(ij)} + \dots, \quad (3.25)$$

wherein the terms account for dipole-dipole (r_{ij}^{-3}), dipole-quadrupole (r_{ij}^{-4}) and quadrupole-quadrupole (r_{ij}^{-5}) interaction, respectively.

With the foregoing expression, and by the formulas of Appendix B, eq. (3.3) yields

$$B_S^{\text{is}} = \text{dip} B_S^{\text{is}} + \frac{16\pi^4 \alpha^2 N^2}{3\lambda^4 k^2 T^2} \left\{ \mu^2 \Theta_{\alpha\beta} \Theta_{\alpha\beta} \langle r_{ij}^{-8} \rangle - \frac{6}{5kT} (\Theta_{\alpha\beta} \mu_\alpha \mu_\beta)^2 \langle r_{ij}^{-11} \rangle + \dots \right\}, \quad (3.26)$$

$$B_S^{\text{anis}} = \text{dip} B_S^{\text{anis}} + \frac{208\pi^4 N^2}{4725\lambda^4 k^2 T^2} \left\{ (3\alpha_{\alpha\beta} \mu_\alpha \mu_\beta - \alpha_{\alpha\alpha} \mu_\beta^2) (3\alpha_{\gamma\delta} \Theta_{\gamma\epsilon} \Theta_{\delta\epsilon} - \alpha_{\gamma\gamma} \Theta_{\delta\epsilon} \Theta_{\delta\epsilon}) \langle r_{ij}^{-8} \rangle - \right. \\ \left. - \frac{8}{5kT} (3\alpha_{\alpha\beta} \Theta_{\alpha\gamma} \mu_\beta \mu_\gamma - \alpha_{\alpha\beta} \Theta_{\alpha\beta} \mu_\gamma^2 - \alpha_{\alpha\alpha} \Theta_{\beta\gamma} \mu_\beta \mu_\gamma)^2 \langle r_{ij}^{-11} \rangle - \right. \\ \left. - \frac{2\mu^2 \alpha_{\alpha\beta} \Theta_{\alpha\beta}}{5kT} [3\mu^2 \alpha_{\gamma\delta} \Theta_{\gamma\delta} + 4(3\alpha_{\gamma\delta} \Theta_{\gamma\epsilon} - \alpha_{\gamma\gamma} \Theta_{\delta\epsilon}) \mu_\delta \mu_\epsilon] \langle r_{ij}^{-11} \rangle + \dots \right\}, \quad (3.27)$$

wherein the quantities $\text{dip} B_S^{\text{is}}$ and $\text{dip} B_S^{\text{anis}}$ are given by eqs. (3.7) and (3.8).

For molecules exhibiting the axial symmetry,

$$3\alpha_{\alpha\beta} \Theta_{\alpha\gamma} \mu_\beta \mu_\gamma - \alpha_{\alpha\beta} \Theta_{\alpha\beta} \mu_\gamma^2 - \alpha_{\alpha\alpha} \Theta_{\beta\gamma} \mu_\beta \mu_\gamma = 3\alpha \delta_\alpha \mu^2 \Theta, \quad (3.28)$$

and hence the virial coefficients of eqs. (3.26) and (3.27) reduce to

$$B_S^{\text{is}} = \text{dip} B_S^{\text{is}} + \frac{8\pi^4 \alpha^2 \mu^2 \Theta^2 N^2}{\lambda^4 k^2 T^2} \left\{ \langle r_{ij}^{-8} \rangle - \frac{4\mu^2}{5kT} \langle r_{ij}^{-11} \rangle + \dots \right\}, \quad (3.29)$$

$$B_S^{\text{anis}} = \text{dip} B_S^{\text{anis}} + \frac{208\pi^4 \alpha_\alpha^2 \delta_\alpha^2 \mu^2 \Theta^2 N^2}{175\lambda^4 k^2 T^2} \left\{ \langle r_{ij}^{-8} \rangle - \frac{2\mu^2}{kT} \langle r_{ij}^{-11} \rangle + \dots \right\}. \quad (3.30)$$

4. Further approximations to the theory

Further approximations to the theory should account for the fact that, in a sufficiently condensed gas, the polarizability of a molecule is affected by the presence of its neighbours, and that the molecules exhibit the effect of hyperpolarizability. Buckingham and Stephen's expansion as given by eq. (2.6) should now be applied, yielding the following expression for the differential polarizability of the i -th molecule in the absence of an external field:

$$\left(\frac{\partial m_\alpha^{(i)}}{\partial E_x} \right)_{E=0} = \left\{ \alpha_{\alpha\beta}^{(i)} + \beta_{\alpha\beta\gamma}^{(i)} F_\gamma^{(i)} + \frac{1}{2} \gamma_{\alpha\beta\gamma\delta}^{(i)} F_\gamma^{(i)} F_\delta^{(i)} + \dots \right\} \left\{ \delta_{\beta\alpha} + \frac{\partial F_\beta^{(i)}}{\partial E_x} \right\}_{E=0}. \quad (4.1)$$

Neglecting herein the terms in $\frac{\partial F_\beta}{\partial E_x}$, the virial coefficients of eqs. (2.11) and (2.12) are obtained in the form

$$B_S^{\text{is}} = - \frac{16\pi^4 \alpha^2 N}{\lambda^4} B(T) + \frac{8\pi^4 N^2}{9\lambda^4 \Omega^2} \iiint \{ (\alpha_{\alpha\alpha}^{(i)} + \alpha_{\alpha\alpha}^{(j)}) (\beta_{\beta\beta\gamma}^{(i)} F_\gamma^{(i)} + \beta_{\beta\beta\gamma}^{(j)} F_\gamma^{(j)} + \\ + \frac{1}{2} \gamma_{\beta\beta\gamma\delta}^{(i)} F_\gamma^{(i)} F_\delta^{(i)} + \frac{1}{2} \gamma_{\beta\beta\gamma\delta}^{(j)} F_\gamma^{(j)} F_\delta^{(j)} + \dots) + \dots \} e^{-\frac{U_{ij}}{kT}} d\mathbf{r}_{ij} d\omega_i d\omega_j, \quad (4.2)$$

$$\begin{aligned}
B_S^{\text{anis}} = & \frac{52\pi^4 N^2}{45\lambda^4 \Omega^2} \iiint \{3\alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(j)} - \alpha_{\alpha\alpha}^{(i)} \alpha_{\beta\beta}^{(j)} + 3(\alpha_{\alpha\beta}^{(i)} + \alpha_{\alpha\beta}^{(j)}) (\beta_{\alpha\beta\gamma}^{(i)} F_\gamma^{(i)} + \beta_{\alpha\beta\gamma}^{(j)} F_\gamma^{(j)} + \\
& + \frac{1}{2} \gamma_{\alpha\beta\gamma\delta}^{(i)} F_\gamma^{(i)} F_\delta^{(i)} + \frac{1}{2} \gamma_{\alpha\beta\gamma\delta}^{(j)} F_\gamma^{(j)} F_\delta^{(j)} + \dots) - (\alpha_{\alpha\alpha}^{(i)} + \alpha_{\alpha\alpha}^{(j)}) (\beta_{\beta\beta\gamma}^{(i)} F_\gamma^{(i)} + \beta_{\beta\beta\gamma}^{(j)} F_\gamma^{(j)} + \\
& + \frac{1}{2} \gamma_{\beta\beta\gamma\delta}^{(i)} F_\gamma^{(i)} F_\delta^{(i)} + \frac{1}{2} \gamma_{\beta\beta\gamma\delta}^{(j)} F_\gamma^{(j)} F_\delta^{(j)} + \dots) + \dots\} e^{-\frac{U_{ij}}{kT}} d\mathbf{r}_{ij} d\omega_i d\omega_j, \quad (4.3)
\end{aligned}$$

The foregoing expressions will now be discussed separately for quadrupole and dipole molecules.

Quadrupole molecules. Since $\beta_{\alpha\beta\gamma} = 0$ for non-dipolar molecules, and since the electric field at the centre of the i -th molecule due to the quadrupole of the j -th molecule is (see, Appendix A)

$$F_\alpha^{(i)} = \frac{1}{3} T_{\alpha\beta\gamma}^{(ij)} \Theta_{\beta\gamma}^{(j)}, \quad (4.4)$$

eqs. (4.2) and (4.3) yield with respect to (3.19)

$$B_S^{\text{is}} = {}_{\text{quad}}B_S^{\text{is}} + \frac{32\pi^4 \alpha N^2}{9\lambda^4} \gamma_{\alpha\alpha\beta\beta} \Theta_{\gamma\delta} \Theta_{\gamma\delta} \langle r_{ij}^{-8} \rangle + \dots, \quad (4.5)$$

$$\begin{aligned}
B_S^{\text{anis}} = & {}_{\text{quad}}B_S^{\text{anis}} + \frac{104\pi^4 N^2}{945 \lambda^4} \{7(3\alpha_{\alpha\beta} \gamma_{\alpha\beta\gamma\gamma} - \alpha_{\alpha\alpha} \gamma_{\beta\beta\gamma\gamma}) \Theta_{\delta\epsilon} \Theta_{\delta\epsilon} + \\
& + 4\gamma_{\alpha\alpha\beta\beta} (3\alpha_{\gamma\delta} \Theta_{\gamma\epsilon} \Theta_{\delta\epsilon} - \alpha_{\gamma\gamma} \Theta_{\delta\epsilon} \Theta_{\delta\epsilon})\} \langle r_{ij}^{-8} \rangle + \dots, \quad (4.6)
\end{aligned}$$

the quantities ${}_{\text{quad}}B_S^{\text{is}}$ and ${}_{\text{quad}}B_S^{\text{anis}}$ being given by eqs. (3.20) and (3.21).

In the case of axially symmetric molecules, we have the following non-zero tensor components of $\gamma_{\alpha\beta\gamma\delta}$ (see, Buckingham and Stephen, 1957):

$$\gamma_{1111} = \gamma_{2222} = 3\gamma_{1122} = \gamma_{\perp}, \quad \gamma_{1133} = \gamma_{2233} = \frac{1}{6}(\gamma_{\parallel} + \gamma_{\perp}), \quad \gamma_{3333} = \gamma_{\parallel},$$

whence

$$3\alpha_{\alpha\beta} \gamma_{\alpha\beta\gamma\gamma} - \alpha_{\alpha\alpha} \gamma_{\beta\beta\gamma\gamma} = 21\alpha\gamma\delta_{\alpha}\delta_{\gamma}, \quad (4.7)$$

the quantities

$$\delta_{\gamma} = \frac{\gamma_{\parallel} - \gamma_{\perp}}{3\gamma}, \quad \gamma = \frac{1}{3}(\gamma_{\parallel} + 2\gamma_{\perp}), \quad (4.8)$$

yielding a measure of the anisotropy of hyperpolarizability and the mean hyperpolarizability of a non-dipolar molecule, respectively. With respect to eqs. (3.22) and (4.7), the virial coefficients are given by the expressions

$$B_S^{\text{is}} = {}_{\text{quad}}B_S^{\text{is}} + \frac{80\pi^4 \alpha\gamma \Theta^2 N^2}{3\lambda^4} \langle r_{ij}^{-8} \rangle + \dots, \quad (4.9)$$

$$B_S^{\text{anis}} = {}_{\text{quad}}B_S^{\text{anis}} + \frac{52\pi^4 \alpha\gamma \delta_{\alpha} (20 + 49\delta_{\gamma}) \Theta^2 N^2}{105\lambda^4} \langle r_{ij}^{-8} \rangle + \dots, \quad (4.10)$$

which contain terms accounting for the effect of the hyperpolarizability of the molecules on light scattering in an imperfect non-dipolar gas.

Dipole molecules. For simplicity, the terms relating to the tensor $\gamma_{\alpha\beta\gamma\delta}$ will now be omitted in eqs. (4.2) and (4.3) and the problem restricted to one of dipole-dipole interaction. In the present case, in addition to V_{ij} as given by eq. (3.5), account should be taken of the molecular field $F_{\alpha}^{(j)}$ given rise to at the centre of the i -th molecule by the dipole of the j -th one:

$$F_{\alpha}^{(j)} = - T_{\alpha\beta}^{(ij)} \mu_{\beta}^{(j)}; \quad (4.11)$$

thus, by the formulas of Appendix B, eqs. (4.2) and (4.3) yield

$$\begin{aligned} B_S^{\text{is}} &= \text{dip} B_S^{\text{is}} + \frac{64\pi^4 \alpha \mu^2 \beta_{\alpha\alpha\beta} \mu_{\beta} N^2}{9\lambda^4 kT} \left\{ \langle r_{ij}^{-6} \rangle + \frac{6\mu^4}{25k^2 T^2} \langle r_{ij}^{-12} \rangle + \dots \right\}, \quad (4.12) \\ B_S^{\text{anis}} &= \text{dip} B_S^{\text{anis}} + \frac{208\pi^4 N^2}{135\lambda^4 kT} \left\{ (3\alpha_{\alpha\beta} \beta_{\alpha\beta\gamma} - \alpha_{\alpha\alpha} \beta_{\beta\beta\gamma}) \mu_{\gamma} \mu_{\delta}^2 \left(\langle r_{ij}^{-6} \rangle + \right. \right. \\ &+ \left. \frac{6\mu^4}{25k^2 T^2} \langle r_{ij}^{-12} \rangle + \dots \right) + \frac{1}{25} (3\alpha_{\alpha\beta} \mu_{\alpha} \mu_{\beta} - \alpha_{\alpha\alpha} \mu_{\beta}^2) \beta_{\gamma\gamma\delta} \mu_{\delta} \left(\langle r_{ij}^{-6} \rangle + \right. \\ &+ \left. \frac{12\mu^4}{49k^2 T^2} \langle r_{ij}^{-12} \rangle + \dots \right) + \frac{6\mu^2}{1225k^2 T^2} (3\alpha_{\alpha\beta} \mu_{\alpha} \mu_{\beta} - \alpha_{\alpha\alpha} \mu_{\beta}^2) (3\beta_{\gamma\delta\epsilon} \mu_{\gamma} - \\ &\left. - \beta_{\gamma\gamma\delta} \mu_{\epsilon}) \mu_{\delta} \mu_{\epsilon} \langle r_{ij}^{-12} \rangle + \dots \right\}, \quad (4.13) \end{aligned}$$

the virial coefficients $\text{dip} B_S^{\text{is}}$ and $\text{dip} B_S^{\text{anis}}$ being given by the expressions of eqs. (3.7) and (3.8).

For molecules exhibiting the axial symmetry,

$$\mu_3 = \mu, \quad \beta_{333} = \beta_{\parallel}, \quad \beta_{113} = \beta_{223} = \beta_{\perp},$$

whence

$$\begin{aligned} 3\alpha_{\alpha\beta} \beta_{\alpha\beta\gamma} \mu_{\gamma} - \alpha_{\alpha\alpha} \beta_{\beta\beta\gamma} \mu_{\gamma} &= 18\alpha\beta \delta_{\alpha} \delta_{\beta} \mu, \\ (3\beta_{\alpha\beta\gamma} \mu_{\alpha} - \beta_{\alpha\alpha\beta} \mu_{\gamma}) \mu_{\beta} \mu_{\gamma} &= 6\beta\delta_{\beta} \mu^3, \end{aligned} \quad (4.14)$$

wherein the quantities

$$\delta_{\beta} = \frac{\beta_{\parallel} - \beta_{\perp}}{3\beta}, \quad \beta = \frac{1}{3} (\beta_{\parallel} + 2\beta_{\perp}) \quad (4.15)$$

yield a measure of the anisotropy of hyperpolarizability and the mean hyperpolarizability of a dipolar molecule, respectively.

Substitution of (3.10) and (4.14) in eqs. (4.12) and (4.13) yields the virial coefficients for axially symmetric, hyperpolarizable dipole molecules as follows:

$$B_S^{\text{is}} = \text{dip} B_S^{\text{is}} + \frac{64\pi^4 \alpha\beta\mu^3 N^2}{3\lambda^4 kT} \left\{ \langle r_{ij}^{-6} \rangle + \frac{6\mu^4}{25k^2 T^2} \langle r_{ij}^{-12} \rangle + \dots \right\}, \quad (4.16)$$

$$B_S^{\text{anis}} = \text{dip} B_S^{\text{anis}} + \frac{416\pi^4 \alpha\beta\delta_\alpha \mu^3 N^2}{375\lambda^4 kT} \left\{ (1 + 25\delta_\beta) \langle r_{ij}^{-6} \rangle + \frac{6\mu^4}{49k^2 T^2} (2 + 51\delta_\beta) \langle r_{ij}^{-12} \rangle + \dots \right\}. \quad (4.17)$$

Dipole molecules of variable polarizability. In the present section the terms previously neglected, relating to the derivatives $\frac{\partial F_\alpha}{\partial E_\beta}$ of the molecular field and yielding additional contributions to the constant polarizability $\alpha_{\alpha\beta}$ of the isolated molecule, will be considered. However, in order to avoid further complicating the calculations, the hyperpolarizability terms of eq. (4.1) will be dropped; Kirkwood's method (1936) now yields, for anisotropically polarizable molecules,

$$\left(\frac{\partial m_\alpha^{(i)}}{\partial E_\lambda} \right)_{E=0} = \alpha_{\alpha\lambda}^{(i)} - \alpha_{\alpha\beta}^{(i)} T_{\beta\gamma}^{(ij)} \alpha_{\gamma\lambda}^{(j)} + \alpha_{\alpha\beta}^{(i)} T_{\beta\gamma}^{(ij)} \alpha_{\gamma\delta}^{(j)} T_{\delta\epsilon}^{(ij)} \alpha_{\epsilon\lambda}^{(i)} - \dots, \quad (4.18)$$

and the virial coefficients of eqs. (2.11) and (2.12) can be represented in the form

$$B_S^{\text{is}} = - \frac{16\pi^4 \alpha^2 N}{\lambda^4} B(T) + \frac{16\pi^4 N^2}{9\lambda^4 \Omega^2} \iiint \left\{ - \alpha_{\alpha\alpha}^{(i)} \alpha_{\beta\gamma}^{(i)} \alpha_{\beta\delta}^{(j)} T_{\gamma\delta}^{(ij)} - \alpha_{\alpha\alpha}^{(i)} \alpha_{\beta\gamma}^{(j)} \alpha_{\beta\delta}^{(i)} T_{\gamma\delta}^{(ij)} + \dots \right\} e^{-\frac{U_{ij}}{kT}} d\mathbf{r}_{ij} d\omega_i d\omega_j, \quad (4.19)$$

$$B_S^{\text{anis}} = \frac{52\pi^4 N^2}{45\lambda^4 \Omega^2} \iiint \left\{ 3\alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(j)} - \alpha_{\alpha\alpha}^{(i)} \alpha_{\beta\beta}^{(j)} - 2(3\alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\gamma}^{(i)} - \alpha_{\alpha\alpha}^{(i)} \alpha_{\beta\gamma}^{(i)}) \alpha_{\beta\gamma}^{(j)} T_{\gamma\delta}^{(ij)} - 2(3\alpha_{\alpha\beta}^{(j)} \alpha_{\alpha\gamma}^{(j)} - \alpha_{\alpha\alpha}^{(j)} \alpha_{\beta\gamma}^{(j)}) \alpha_{\beta\delta}^{(i)} T_{\gamma\delta}^{(ij)} + \dots \right\} e^{-\frac{U_{ij}}{kT}} d\mathbf{r}_{ij} d\omega_i d\omega_j. \quad (4.20)$$

Substitution of (3.5) yields

$$B_S^{\text{is}} = \text{dip} B_S^{\text{is}} + \frac{16\pi^4 \alpha N^2}{675\lambda^4 k^2 T^2} \{ 60\alpha \mu^2 - (3\alpha_{\alpha\beta} \mu_\alpha \mu_\beta - \alpha_{\alpha\alpha} \mu_\beta^2) \} (3\alpha_{\gamma\delta} \mu_\gamma \mu_\delta - \alpha_{\gamma\gamma} \mu_\delta^2) \langle r_{ij}^{-9} \rangle + \dots, \quad (4.21)$$

$$B_S^{\text{anis}} = \text{dip} B_S^{\text{anis}} + \frac{104\pi^4 N^2}{10125\lambda^4 k^2 T^2} \{ 10(3\alpha_{\alpha\beta} \alpha_{\alpha\beta} - \alpha_{\alpha\alpha} \alpha_{\beta\beta}) (3\alpha_{\gamma\delta} \mu_\gamma \mu_\delta - \alpha_{\gamma\gamma} \mu_\delta^2) \mu^2 + [30\alpha \mu^2 - (3\alpha_{\alpha\beta} \mu_\alpha \mu_\beta - \alpha_{\alpha\alpha} \mu_\beta^2)] [3(3\alpha_{\gamma\delta} \alpha_{\gamma\epsilon} - \alpha_{\gamma\gamma} \alpha_{\delta\epsilon}) \mu_\delta \mu_\epsilon - (3\alpha_{\gamma\delta} \alpha_{\gamma\delta} - \alpha_{\gamma\gamma} \alpha_{\delta\delta}) \mu^2] \} \langle r_{ij}^{-9} \rangle + \dots \quad (4.22)$$

Hence, by eqs. (3.10) and (3.16), we have, for axially symmetric molecules

$$B_S^{\text{is}} = \text{dip} B_S^{\text{is}} + \frac{64\pi^4 \alpha^3 \delta_\alpha (10 - \delta_\alpha) \mu^4 N^2}{75\lambda^4 k^2 T^2} \langle r_{ij}^{-9} \rangle + \dots, \quad (4.23)$$

$$B_S^{\text{anis}} = \text{dip} B_S^{\text{anis}} + \frac{416\pi^4 \alpha^3 \delta_\alpha (5 + 4\delta_\alpha + 9\delta_\alpha^2) \mu^4 N^2}{375\lambda^4 k^2 T^2} \langle r_{ij}^{-9} \rangle + \dots \quad (4.24)$$

5. Discussion and conclusions

In computing the virial coefficients B_S^{is} and B_S^{anis} in sections 3 and 4, no assumptions were made as to the form of the potential energy of central interaction between the molecules. It will be remembered that Lennard-Jones (1924) proposed the following general expression for $U^{(0)}(r_{ij})$:

$$U^{(0)}(r_{ij}) = -\frac{\lambda_n}{r_{ij}^n} + \frac{\lambda_m}{r_{ij}^m}; \quad m > n, \quad (5.1)$$

the first term accounting for the energy of attraction and the second — for that of repulsion between the molecules. The constants λ_n and λ_m and the exponents n and m can be determined experimentally.

To simplify, the Lennard-Jones potential will henceforth be applied in the form (see, Pople 1954)

$$U^{(0)}(r_{ij}) = 4\epsilon \left\{ \left(\frac{r_0}{r_{ij}} \right)^{12} - \left(\frac{r_0}{r_{ij}} \right)^6 \right\}, \quad (5.2)$$

wherein ϵ represents the negative value of the lowest potential energy and r_0 is the intermolecular distance r_{ij} at which the attractive and repulsive energies exactly balance.

By the Lennard-Jones method (1924), with respect to eq. (5.2), we have (see, Buckingham and Pople 1955 a)

$$\int_0^\infty \left(e^{-\frac{U^{(0)}(r_{ij})}{kT}} - 1 \right) dr_{ij} = \frac{2\pi r_0^3}{3y^2} \{H_6(y) - 2H_{12}(y)\}, \quad (5.3)$$

$$\langle r_{ij}^{-n} \rangle = \int_0^\infty r_{ij}^{-n} e^{-\frac{U^{(0)}(r_{ij})}{kT}} dr_{ij} = \frac{\pi r_0^{3-n}}{3y^4} H_n(y), \quad (5.4)$$

wherein

$$H_n(y) = y^{\frac{27-n}{6}} \sum_{m=0}^\infty \Gamma\left(\frac{6m+n-3}{12}\right) \frac{y^m}{m!}; \quad y^2 = \frac{4\epsilon}{kT}; \quad (5.5)$$

are functions introduced by Pople (1954); these have been discussed and their values tabulated by Buckingham and Pople (1955 a).

Eqs. (5.3) and (5.4) can serve for putting the virial coefficients B_S^{is} and B_S^{anis} , as calculated previously, in a form adapted to numerical evaluations, provided the central force parameters ϵ and r_0 as well as other molecular parameters, such as α and μ , whose values for some gases are assembled in Table I, are known.

Table I. Numerical values of the molecular parameters and of A_S^{is} and A_S^{anis} ($\lambda = 4358 \text{ \AA}$) for some imperfect gases.

Gases	CO ₂	NH ₃	CH ₃ F	CH ₃ CN	COS
$\mu \times 10^{18}$ e.s.u.	0	1.47	1.82	3.50	0.72
$\alpha_{\parallel} \times 10^{24}$ cm ³	4.49 ¹⁾	2.42 ¹⁾	3.16 ²⁾	5.43 ²⁾	9.62 ³⁾
$\alpha_{\perp} \times 10^{24}$ cm ³	2.14 ¹⁾	2.18 ¹⁾	2.32 ²⁾	3.70 ²⁾	3.73 ³⁾
$\alpha \times 10^{24}$ cm ³	2.92	2.26	2.6	4.27	5.69
δ_{α}	0.27	0.04	0.11	0.13	0.34
$r_0 \times 10^8$ cm	3.995 ⁴⁾	2.60 ⁵⁾	3.33 ⁶⁾	4.02 ⁷⁾	4.13 ⁸⁾
ϵ/k °K	190.0 ⁴⁾	320.0 ⁵⁾	205.0 ⁶⁾	400.0 ⁷⁾	335.0 ⁸⁾
$A_S^{\text{is}} \left(\frac{\text{cm}^2}{\text{mol}} \right) \times 10^4$	11.03	6.62	8.75	24.25	42.04
$A_S^{\text{anis}} \left(\frac{\text{cm}^2}{\text{mol}} \right) \times 10^4$	2.04	0.03	0.28	1.11	12.61

¹⁾ Stuart, H. A., *Die Struktur des freien Moleküls*, Berlin, 1952.

²⁾ Le Fevre, C. G. and Le Fevre, R. J. W., *Revs. Pure and Appl. Chem.* **5**, 261 (1955).

³⁾ Computed from polarizability of the C = O and C = S bonds.

⁴⁾ Johnston, H. L. and Mc Closkey, K. E., *J. Phys. Chem.*, **44**, 1038 (1940).

⁵⁾ Keys F. G., *J. Amer. Chem. Soc.*, **60**, 1761 (1938).

⁶⁾ Buckingham A. D. and Pople J. A., *Trans. Faraday Soc.*, **51**, 1173 (1955).

⁷⁾ Lambert, Roberts, Rowlinson and Wilkinson, *Proc. Roy. Soc.*, **A 196**, 113 (1949).

⁸⁾ Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, Springer.

(i) *Quadrupole molecules.* For anisotropic molecules possessing a quadrupole moment, eqs. (3.23) and (3.24) yield for the Lennard-Jones model

$$\text{quad}B_S^{\text{is}} = \text{centr}B_S^{\text{is}} + \frac{\pi^5 \alpha^2 \Theta^2 N^2}{30\lambda^4 r_0^2 \epsilon} \left\{ \frac{60\alpha}{r_0^3 y^2} H_8(y) + \frac{7\Theta^2}{r_0^5 \epsilon} H_{10}(y) \right\}, \quad (5.6)$$

$$\text{quad}B_S^{\text{anis}} = \frac{26\pi^5 \alpha^2 \delta_{\alpha}^2 \Theta^2 N^2}{525\lambda^4 r_0^2 \epsilon} \left\{ \frac{6\alpha\delta_{\alpha}}{r_0^3 y^2} H_8(y) + \frac{\Theta^2}{r_0^5 \epsilon} H_{10}(y) \right\}, \quad (5.7)$$

$$\text{centr}B_S^{\text{is}} = \frac{16\pi^5 \alpha^2 r_0^3 N^2}{3\lambda^4 y^2} \{H_6(y) - 2H_{12}(y)\} = -\frac{16\pi^4 \alpha^2 N}{\lambda^4} B^{(0)}(T). \quad (5.8)$$

Assuming a value of $\Theta = 5.29 \times 10^{-26}$ e.s.u. for the carbon dioxide molecule (see, Buckingham and Pople 1955 b) in addition of the data of Table I, the foregoing formulas yield, at $T = 300^\circ\text{K}$,

$$\text{quad}B_S^{\text{is}} = (31.79 + 1.86 + 9.59) \times 10^{-2} \frac{\text{cm}^5}{\text{mol}^2} = 43.24 \times 10^{-2} \frac{\text{cm}^5}{\text{mol}^2},$$

$$\text{quad}B_S^{\text{anis}} = (0.14 + 14.4) \times 10^{-4} \frac{\text{cm}^5}{\text{mol}^2} = 0.15 \times 10^{-2} \frac{\text{cm}^5}{\text{mol}^2}.$$

Thus, in the case of isotropic light scattering, the contribution from non-central intermolecular forces, $(1.86 + 9.59) \times 10^{-2} \frac{\text{cm}^5}{\text{mol}^2}$, is seen to amount to 26% of the total value of $\text{quad}B_S^{\text{is}}$, one fifth thereof resulting from quadrupole-induced dipole interaction, and the remaining four fifths — from the quadrupole-quadrupole interaction predominating in the case under consideration. The second virial coefficient of anisotropic light scattering, $\text{quad}B_S^{\text{anis}}$, yields a contribution that is barely 0.4% of that of $\text{quad}B_S^{\text{is}}$, and so plays practically no part at all here.

By eqs. (5.3) and (5.4), the effect of hyperpolarizability on light scattering as given by eqs. (4.9) and (4.10) assumes the form

$$B_S^{\text{is}} = \text{quad}B_S^{\text{is}} + \frac{80\pi^5 \alpha \gamma \Theta^2 N^2}{9\lambda^4 r_0^5 y^4} H_8(y) + \dots, \quad (5.9)$$

$$B_S^{\text{anis}} = \text{quad}B_S^{\text{anis}} + \frac{52\pi^5 \alpha \gamma \delta_\alpha (20 + 49\delta_\gamma) \Theta^2 N^2}{315\lambda^4 r_0^5 y^4} H_8(y) + \dots \quad (5.10)$$

Assuming a value of $\gamma = 25 \times 10^{-26}$ e.s.u. for the CO_2 molecule, eq. (5.9) yields

$$B_S^{\text{is}} = \text{quad}B_S^{\text{is}} + 0.25 \times 10^{-2} \frac{\text{cm}^5}{\text{mol}^2};$$

thus, the effect of the hyperpolarizability of non-dipolar molecules on B_S^{is} is quite unimportant in the present case.

(ii) *Dipole molecules.* By (5.3) and (5.4), the expressions of eqs. (3.7) and (3.12) now assume the form

$$\text{dip}B_S^{\text{is}} = \text{centr}B_S^{\text{is}} + \frac{\pi^5 \alpha^2 \mu^4 N^2}{18\lambda^4 r_0^3 \epsilon^2} \left\{ H_6(y) + \frac{3\mu^4 y^4}{400 r_0^6 \epsilon^2} H_{12}(y) + \dots \right\}, \quad (5.11)$$

$$\text{dip}B_S^{\text{anis}} = \frac{13\pi^5 \alpha^2 \delta_\alpha^2 \mu^4 N^2}{2250\lambda^4 r_0^3 \epsilon^2} \left\{ H_6(y) + \frac{3\mu^4 y^4}{196 r_0^6 \epsilon^2} H_{12}(y) + \dots \right\}. \quad (5.12)$$

The expressions of eqs. (3.17) and (3.18) which, in addition to dipole-dipole interaction, account for dipole-induced dipole interaction, can now be written as

follows:

$$B_S^{\text{is}} = \text{dip} B_S^{\text{is}} + \frac{4\pi^5 \alpha^3 \mu^2 N^2}{3\lambda^4 r_0^3 \epsilon y^2} \left\{ H_6(y) + \frac{\mu^4 y^4}{200r_0^6 \epsilon^2} (5 + 4\delta_\alpha) H_{12}(y) + \dots \right\}, \quad (5.13)$$

$$B_S^{\text{anis}} = \text{dip} B_S^{\text{anis}} + \frac{52\pi^5 \alpha^3 \delta_\alpha^2 \mu^2 N^2}{375\lambda^4 r_0^3 \epsilon y^2} \left\{ \delta_\alpha H_6(y) + \frac{\mu^4 y^4}{196r_0^6 \epsilon^2} (7 + 11\delta_\alpha) H_{12}(y) + \dots \right\}. \quad (5.14)$$

Table II. Theoretical values of virial coefficients B_S^{is} and B_S^{anis} of light scattering, in cm^5/mol^2 .

		central-forces potential	dipole-induced dipole inter- action	dipole-dipole interaction	total
NH ₃	$B_S^{\text{is}} \times 10^2$	7.36	6.63	32.11	46.10
$T = 320^\circ \text{K}$	$B_S^{\text{anis}} \times 10^4$	0	0.003	0.45	0.453
CH ₃ F	$B_S^{\text{is}} \times 10^2$	9.06	4.53	20.83	34.42
$T = 320^\circ \text{K}$	$B_S^{\text{anis}} \times 10^4$	0	0.02	3.04	3.06
CH ₃ CN	$B_S^{\text{is}} \times 10^2$	153.72	67.64	707.11	928.47
$T = 400^\circ \text{K}$	$B_S^{\text{anis}} \times 10^4$	0	0.2	113.0	113.20

In Table II, the numerical values of the virial coefficients B_S^{is} and B_S^{anis} computed from the foregoing formulas for the dipole gases NH₃, CH₃F and CH₃CN are assembled. Each of the respective values is split in three parts, the first accounting for the contribution from light scattering due solely to the presence of central forces. The second and third parts are contributions arising from the fact that, in addition to central forces, also forces of electrostatic i.e. dipole-induced dipole and dipole-dipole interaction are present. The data in Table II prove immediately that the principal contribution to the total value of B_S^{is} is related to the non-central forces, the inductive effect playing a lesser part as compared with the considerable dipole-dipole interaction. As to the second virial coefficient of anisotropic light scattering, its contribution to the total is negligible. The latter conclusion was reached earlier by Benoit and Stockmayer (1956) in their theory of the degree of depolarisation of imperfect gases.

Eqs. (4.16) and (4.17), which accounted for the effect of the hyperpolarizability of the molecules on light scattering in a dipole gas, now assume the form

$$B_S^{\text{is}} = \text{dip} B_S^{\text{is}} + \frac{16\pi^5 \alpha \beta \mu^3 N^2}{9\lambda^4 r_0^3 \epsilon y^2} \left\{ H_6(y) + \frac{3\mu^4 y^4}{200r_0^6 \epsilon^2} H_{12}(y) + \dots \right\}, \quad (5.15)$$

$$B_S^{\text{anis}} = \text{dip} B_S^{\text{anis}} + \frac{104\pi^5 \alpha \beta \delta_\alpha \mu^3 N^2}{1125\lambda^4 r_0^3 \epsilon y^2} \left\{ (1 + 25\delta_\beta) H_6(y) + \frac{3\mu^4}{392r_0^6 \epsilon^2} (2 + 51\delta_\beta) H_{12}(y) + \dots \right\}. \quad (5.16)$$

To exemplify, in the case of CH_3F , with the data of Table I and a value of $\beta = 10 \times 10^{-30}$ e.s.u. (see, Buckingham 1956), eq. (5.15) yields

$$B_S^{\text{is}} = \text{dip}B_S^{\text{is}} + 20.5 \times 10^{-2} \frac{\text{cm}^5}{\text{mol}^2}.$$

Thus, the contribution due to the effect of the hyperpolarizability of the dipole molecules is seen to amount to 60% of the value of $\text{dip}B_S^{\text{is}} = 34.42 \times 10^{-2} \frac{\text{cm}^5}{\text{mol}^2}$. This points to the possibility of a quite considerable effect of the hyperpolarizability of the molecules on light scattering in a dipole imperfect gas, and the situation resembles the one found to exist in a dipole liquid by Buckingham and Stephen (1957).

By eqs. (5.3) and (5.4), eqs. (4.23) and (4.24) can be rewritten as follows:

$$B_S^{\text{is}} = \text{dip}B_S^{\text{is}} + \frac{4\pi^5 \alpha^3 \delta_\alpha (10 - \delta_\alpha) \mu^4 N^2}{225 \lambda^4 r_0^6 \varepsilon^2} H_9(y) + \dots, \quad (5.17)$$

$$B_S^{\text{anis}} = \text{dip}B_S^{\text{anis}} + \frac{26\pi^5 \alpha^3 \delta_\alpha (5 + 4\delta_\alpha + 9\delta_\alpha^2) \mu^4 N^2}{1125 \lambda^4 r_0^6 \varepsilon^2} H_9(y) + \dots \quad (5.18)$$

The contribution to isotropic light scattering resulting from the effect of the molecular field on the polarizability of the molecules is very small, amounting to barely 0.3% in CH_3F , and to 1% in CH_3CN .

(ii) *Dipole-quadrupole molecules.* With the Lennard-Jones model, eqs. (3.29) and (3.30) can be rewritten as follows:

$$B_S^{\text{is}} = \text{dip}B_S^{\text{is}} + \frac{\pi^5 \alpha^2 \mu^2 \Theta^2 N^2}{6 \lambda^4 r_0^5 \varepsilon^2} \left\{ H_8(y) - \frac{\mu^2 y^2}{5 r_0^3 \varepsilon} H_{11}(y) + \dots \right\}, \quad (5.19)$$

$$B_S^{\text{anis}} = \text{dip}B_S^{\text{anis}} + \frac{13\pi^5 \alpha^2 \delta_\alpha^2 \mu^2 \Theta^2 N^2}{525 \lambda^4 r_0^5 \varepsilon^2} \left\{ H_8(y) - \frac{\mu^2 y^2}{2 r_0^3 \varepsilon} H_{11}(y) + \dots \right\}, \quad (5.20)$$

the quantities $\text{dip}B_S^{\text{is}}$ and $\text{dip}B_S^{\text{anis}}$ being given by eqs. (5.11) and (5.12).

For COS, we have $\mu = 0.72 \times 10^{-18}$ e.s.u. and $\Theta = 2.9 \times 10^{-26}$ e.s.u. (see, Gordy et al. 1953) in addition to the figures of Table I, and eq. (5.19) yields, for $T = 335^\circ\text{K}$,

$$B_S^{\text{is}} = (189.5 + 1.21 + 2.48) \times 10^{-2} \frac{\text{cm}^5}{\text{mol}^2}.$$

Here, the contributions of dipole-dipole interaction (the second figure in the brackets) and dipole-quadrupole interaction (the third value) to B_S^{is} are very small, as compared with the value of $189.5 \times 10^{-2} \frac{\text{cm}^5}{\text{mol}^2}$ resulting from the central forces alone. Clearly, this is due to the small numerical value of the dipole moment of the COS molecule. In the present case, dipole-induced dipole interaction plays a greater part; by eq.

(5.13), it contributes to B_S^{is} to the amount of $3.95 \times 10^{-2} \frac{\text{cm}^5}{\text{mol}^2}$. The same is true of quadrupole-quadrupole and quadrupole-induced dipole interaction; by eq. (5.6), their contribution is $6.5 \times 10^{-2} \frac{\text{cm}^5}{\text{mol}^2}$. Thus, the entire contribution resulting from electrostatic interaction forces amounts to $14.14 \times 10^{-2} \frac{\text{cm}^5}{\text{mol}^2}$, which is 8% of that of the forces of central interaction.

The immediate conclusion from the examples discussed above is that, in principle, divergences between light scattering by an imperfect gas and by a perfect gas should be expected to reside only in the isotropic light scattering, accessible to investigation in the quantity B_S^{is} . For molecules having a constant polarizability, B_S^{is} is given directly by the second virial coefficient $B(T)$ of the equation of state of imperfect gases. In the general case the mean hyperpolarizability of the dipole or quadrupole molecules can be determined from the experimental values of B_S^{is} and $B(T)$. Hence, parallel theoretical and experimental investigation of light scattering in imperfect gases should provide new and valuable information on the intermolecular forces and, moreover, on the effect of hyperpolarizability of the molecules.

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Appendix A.

Potential energy of electrostatic interaction between two molecules. The potential of the field at the centre of the i -th molecule due to the electric charges of the j -th molecule can be represented by the expansion

$$\varphi_i = \frac{e^{(j)}}{r} - \mu_\alpha^{(j)} \nabla_\alpha \left(\frac{1}{r} \right) + \frac{1}{2} q_{\alpha\beta}^{(j)} \nabla_\alpha \nabla_\beta \left(\frac{1}{r} \right) - \frac{1}{6} l_{\alpha\beta\gamma}^{(j)} \nabla_\alpha \nabla_\beta \nabla_\gamma \left(\frac{1}{r} \right) + \dots, \quad (\text{A.1})$$

wherein the quantities

$$\begin{aligned} e^{(j)} &\equiv \sum_n e_n^{(j)}, \\ \mu_\alpha^{(j)} &\equiv \sum_n e_n^{(j)} r_{n\alpha}^{(j)}, \\ q_{\alpha\beta}^{(j)} &\equiv \sum_n e_n^{(j)} r_{n\alpha}^{(j)} r_{n\beta}^{(j)}, \\ l_{\alpha\beta\gamma}^{(j)} &\equiv \sum_n e_n^{(j)} r_{n\alpha}^{(j)} r_{n\beta}^{(j)} r_{n\gamma}^{(j)}, \dots, \end{aligned} \quad (\text{A.2})$$

account respectively for the electric unipole, dipole, quadrupole, octupole, ... 2^n -pole moments; $e_n^{(j)}$ — is the n -th electric charge of the j -th molecule, $r_n^{(j)}$ — its radius vector, $\mathbf{r} = \mathbf{r}_{ij}$ — the vector connecting the centres of both molecules, and $\nabla_\alpha \equiv \frac{\partial}{\partial r_\alpha}$ — Hamilton's differential operator.

By (A. 1), the potential energy of electrostatic interaction between two neutral molecules is obtained in the form (see, Pople 1952; Jansen 1958)

$$V_{ij} = \mu_{\alpha}^{(i)} \mu_{\beta}^{(j)} T_{\alpha\beta}^{(ij)} + \frac{1}{2} (\mu_{\alpha}^{(i)} q_{\beta\gamma}^{(j)} - q_{\alpha\beta}^{(i)} \mu_{\gamma}^{(j)}) T_{\alpha\beta\gamma}^{(ij)} + \\ + \frac{1}{12} (2 \mu_{\alpha}^{(i)} l_{\beta\gamma\delta}^{(j)} - 3 q_{\alpha\beta}^{(i)} q_{\gamma\delta}^{(j)} + 2 l_{\alpha\beta\gamma}^{(i)} \mu_{\delta}^{(j)}) T_{\alpha\beta\gamma\delta}^{(ij)} + \dots \quad (\text{A.3})$$

wherein the tensors

$$T_{\alpha\beta}^{(ij)} \equiv - \nabla_{\alpha} \nabla_{\beta} \left(\frac{1}{r_{ij}} \right), \quad T_{\alpha\beta\gamma}^{(ij)} \equiv - \nabla_{\alpha} \nabla_{\beta} \nabla_{\gamma} \left(\frac{1}{r_{ij}} \right), \\ T_{\alpha\beta\gamma\delta}^{(ij)} \equiv - \nabla_{\alpha} \nabla_{\beta} \nabla_{\gamma} \nabla_{\delta} \left(\frac{1}{r_{ij}} \right), \dots, \quad (\text{A.4})$$

account respectively for dipole-dipole, dipole-quadrupole, quadrupole-quadrupole etc. interaction; these are to be found in explicit form in Pople's paper (1952).

With regard to Laplace's equation, the following tensors of the quadrupole and octupole moments of the molecule appear (see, Buckingham, 1959):

$$\Theta_{\alpha\beta}^{(j)} = \frac{1}{2} (3q_{\alpha\beta}^{(j)} - q_{\gamma\gamma} \delta_{\alpha\beta}), \\ \Omega_{\alpha\beta\gamma}^{(j)} = \frac{1}{2} (5l_{\alpha\beta\gamma}^{(j)} - l_{\alpha\delta\delta}^{(j)} \delta_{\beta\gamma} - l_{\beta\delta\delta}^{(j)} \delta_{\gamma\alpha} - l_{\gamma\delta\delta}^{(j)} \delta_{\alpha\beta}), \quad (\text{A.5})$$

and eq. (A.3) can now be rewritten in the form

$$V_{ij} = \mu_{\alpha}^{(i)} \mu_{\beta}^{(j)} T_{\alpha\beta}^{(ij)} + \frac{1}{3} (l_{\alpha}^{(i)} \Theta_{\beta\gamma}^{(j)} - \Theta_{\alpha\beta}^{(i)} \mu_{\gamma}^{(j)}) T_{\alpha\beta\gamma}^{(ij)} + \\ + \frac{1}{15} (3\mu_{\alpha}^{(i)} \Omega_{\alpha\gamma\delta}^{(j)} - 5\Theta_{\alpha\beta}^{(i)} \Theta_{\gamma\delta}^{(j)} + 3\Omega_{\alpha\beta\gamma}^{(i)} \mu_{\delta}^{(j)}) T_{\alpha\beta\gamma\delta}^{(ij)} + \dots, \quad (\text{A.6})$$

where the multipole moment tensors are symmetric in all indices.

By the expansion of eq. (A.1) and the definitions of eqs. (A.4), and (A.5), the electric field due to the charge distribution of the j -th molecule at the centre of the i -th molecule is

$$F_{\alpha}^{(i)} = - \nabla_{\alpha} \varphi_i = - T_{\alpha\beta}^{(ii)} \mu_{\beta}^{(j)} + \frac{1}{3} T_{\alpha\beta\gamma}^{(ii)} \Theta_{\beta\gamma}^{(j)} - \frac{1}{15} T_{\alpha\beta\gamma\delta}^{(ii)} \Omega_{\beta\gamma\delta}^{(j)} + \dots \quad (\text{A.7})$$

For polarizable molecules, account should also be taken of the potential energy related to the effect of induction; this energy is, quite generally, given by

$$V_{ij}^{\text{ind}} = - \frac{1}{2} (\alpha_{\alpha\beta}^{(i)} F_{\alpha}^{(i)} F_{\beta}^{(i)} + \alpha_{\alpha\beta}^{(j)} F_{\alpha}^{(j)} F_{\beta}^{(j)}). \quad (\text{A.8})$$

Substitution of (A.7) herein yields

$$V_{ij}^{\text{ind}} = - \frac{1}{2} (\alpha_{\alpha\beta}^{(i)} \mu_{\gamma}^{(j)} \mu_{\delta}^{(j)} + \alpha_{\alpha\beta}^{(j)} \mu_{\gamma}^{(i)} \mu_{\delta}^{(i)}) T_{\alpha\gamma}^{(ij)} T_{\beta\delta}^{(ij)} + \\ + \frac{1}{3} (\alpha_{\alpha\beta}^{(i)} \mu_{\gamma}^{(j)} \Theta_{\delta\epsilon}^{(j)} + \alpha_{\alpha\beta}^{(j)} \mu_{\gamma}^{(i)} \Theta_{\delta\epsilon}^{(i)}) T_{\alpha\gamma}^{(ij)} T_{\beta\delta\epsilon}^{(ij)} - \\ - \frac{1}{15} (\alpha_{\alpha\beta}^{(i)} \Theta_{\gamma\delta}^{(j)} \Theta_{\epsilon\eta}^{(j)} + \alpha_{\alpha\beta}^{(j)} \Theta_{\gamma\delta}^{(i)} \Theta_{\epsilon\eta}^{(i)}) T_{\alpha\gamma\delta}^{(ij)} T_{\beta\epsilon\eta}^{(ij)} + \\ + \frac{1}{15} (\alpha_{\alpha\beta}^{(i)} \mu_{\gamma}^{(j)} \Omega_{\delta\epsilon\eta}^{(j)} + \alpha_{\alpha\beta}^{(j)} \mu_{\gamma}^{(i)} \Omega_{\delta\epsilon\eta}^{(i)}) T_{\alpha\gamma}^{(ij)} T_{\beta\delta\epsilon\eta}^{(ij)} - + \dots \quad (\text{A.9})$$

Appendix B.

Isotropic averages. With the potential energy of electrostatic molecular interaction of eq. (A.6), the following mean isotropic values result:

$$\begin{aligned}
 \overline{V_{ij}} &= 0, & \overline{\alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(j)} V_{ij}} &= 0, \\
 \overline{V_{ij}^2} &= \frac{1}{9} \mu^4 T_{\sigma\tau}^{(ij)} T_{\sigma\tau}^{(ij)} + \frac{2\mu^2}{135} \Theta_{\alpha\beta} \Theta_{\alpha\beta} T_{\sigma\tau\nu}^{(ij)} T_{\sigma\tau\nu}^{(ij)} + \frac{1}{2025} (\Theta_{\alpha\beta} \Theta_{\alpha\beta})^2 T_{\sigma\tau\nu\varrho}^{(ij)} T_{\sigma\tau\nu\varrho}^{(ij)}, \\
 \overline{V_{ij}^3} &= -\frac{1}{75} (\Theta_{\alpha\beta} \mu_{\alpha} \mu_{\beta})^2 (T_{\sigma\tau}^{(ij)} T_{\nu\varrho}^{(ij)} T_{\sigma\tau\nu\varrho}^{(ij)} + 2 T_{\sigma\tau}^{(ij)} T_{\sigma\nu\varrho}^{(ij)} T_{\tau\nu\varrho}^{(ij)}), \\
 \overline{V_{ij}^3} &= -\frac{1}{75} (\Theta_{\alpha\beta} \mu_{\alpha} \mu_{\beta})^2 (T_{\sigma\tau}^{(ij)} T_{\nu\varrho}^{(ij)} T_{\sigma\tau\nu\varrho}^{(ij)} + 2 T_{\sigma\tau}^{(ij)} T_{\sigma\nu\varrho}^{(ij)} T_{\tau\nu\varrho}^{(ij)}), \\
 \overline{V_{ij}^4} &= \frac{1}{75} \mu^8 (T_{\sigma\tau}^{(ij)} T_{\sigma\tau}^{(ij)} T_{\nu\varrho}^{(ij)} T_{\nu\varrho}^{(ij)} + 2 T_{\sigma\tau}^{(ij)} T_{\tau\nu}^{(ij)} T_{\nu\varrho}^{(ij)} T_{\varrho\sigma}^{(ij)}), \\
 \overline{\alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(j)} V_{ij}^2} &= \frac{1}{1350} \{450\alpha^2 \mu^4 + (3\alpha_{\alpha\beta} \mu_{\alpha} \mu_{\beta} - \alpha_{\alpha\alpha} \mu_{\beta}^2)^2\} T_{\sigma\tau}^{(ij)} T_{\sigma\tau}^{(ij)} + \\
 &+ \frac{2}{14175} \{315\alpha^2 \mu^2 \Theta_{\alpha\beta} \Theta_{\alpha\beta} + 2(3\alpha_{\alpha\beta} \Theta_{\alpha\gamma} \Theta_{\beta\gamma} - \alpha_{\alpha\alpha} \Theta_{\beta\gamma} \Theta_{\beta\gamma}) (3\alpha_{\delta\epsilon} \mu_{\delta} \mu_{\epsilon} - \\
 &- \alpha_{\delta\delta} \mu_{\epsilon}^2)\} T_{\sigma\tau\nu}^{(ij)} T_{\sigma\tau\nu}^{(ij)} + \frac{1}{297675} \{441\alpha^2 (\Theta_{\alpha\beta} \Theta_{\alpha\beta})^2 + 8(3\alpha_{\alpha\beta} \Theta_{\alpha\gamma} \Theta_{\beta\gamma} - \\
 &- \alpha_{\alpha\alpha} \Theta_{\beta\gamma} \Theta_{\beta\gamma})^2\} T_{\sigma\tau\nu\varrho}^{(ij)} T_{\sigma\tau\nu\varrho}^{(ij)}, \tag{B.1} \\
 \overline{\alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(j)} V_{ij}^3} &= -\frac{1}{11025} \{441\alpha^2 (\Theta_{\alpha\beta} \mu_{\alpha} \mu_{\beta})^2 + 8(3\alpha_{\alpha\beta} \Theta_{\alpha\gamma} \mu_{\beta} \mu_{\gamma} - \\
 &- \alpha_{\alpha\beta} \Theta_{\alpha\beta} \mu_{\gamma}^2 - \alpha_{\alpha\alpha} \Theta_{\beta\gamma} \mu_{\beta} \mu_{\gamma})^2\} \{T_{\sigma\tau}^{(ij)} T_{\nu\varrho}^{(ij)} T_{\sigma\tau\nu\varrho}^{(ij)} + 2 T_{\sigma\tau}^{(ij)} T_{\sigma\nu\varrho}^{(ij)} T_{\tau\nu\varrho}^{(ij)}\} - \\
 &- \frac{2}{33075} \{7 [3\alpha_{\alpha\beta} \Theta_{\alpha\beta} \mu^2 + 4 (3\alpha_{\alpha\beta} \Theta_{\alpha\gamma} - \alpha_{\alpha\alpha} \Theta_{\beta\gamma}) \mu_{\beta} \mu_{\gamma}] \alpha_{\delta\epsilon} \Theta_{\delta\epsilon} \mu^2 - \\
 &- 32 (3\alpha_{\alpha\beta} \Theta_{\alpha\gamma} \mu_{\beta} \mu_{\gamma} - \alpha_{\alpha\beta} \Theta_{\alpha\beta} \mu_{\gamma}^2 - \alpha_{\alpha\alpha} \Theta_{\beta\gamma} \mu_{\beta} \mu_{\gamma})^2\} T_{\sigma\tau}^{(ij)} T_{\sigma\nu\varrho}^{(ij)} T_{\tau\nu\varrho}^{(ij)}, \\
 \overline{\alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(j)} V_{ij}^4} &= \frac{\alpha^2 \mu^8}{25} (T_{\sigma\tau}^{(ij)} T_{\sigma\tau}^{(ij)} T_{\nu\varrho}^{(ij)} T_{\nu\varrho}^{(ij)} + 2 T_{\sigma\tau}^{(ij)} T_{\tau\nu}^{(ij)} T_{\nu\varrho}^{(ij)} T_{\varrho\sigma}^{(ij)}) + \\
 &+ \frac{\mu^4}{11025} (3\alpha_{\alpha\beta} \mu_{\alpha} \mu_{\beta} - \alpha_{\alpha\alpha} \mu_{\beta}^2)^2 (10 T_{\sigma\tau}^{(ij)} T_{\tau\nu}^{(ij)} T_{\nu\varrho}^{(ij)} T_{\varrho\sigma}^{(ij)} - T_{\sigma\tau}^{(ij)} T_{\sigma\tau}^{(ij)} T_{\nu\varrho}^{(ij)} T_{\nu\varrho}^{(ij)}).
 \end{aligned}$$

The products of the tensors $T_{\sigma\tau}^{(ij)}$, $T_{\sigma\tau\nu}^{(ij)}$ and $T_{\sigma\tau\nu\varrho}^{(ij)}$ are, respectively,

$$\begin{aligned}
 T_{\sigma\tau}^{(ij)} T_{\sigma\tau}^{(ij)} &= 6r_{ij}^{-6}, & T_{\sigma\tau}^{(ij)} T_{\tau\nu}^{(ij)} T_{\nu\varrho}^{(ij)} T_{\varrho\sigma}^{(ij)} &= 18r_{ij}^{-12}, \\
 T_{\sigma\tau\nu}^{(ij)} T_{\sigma\tau\nu}^{(ij)} &= 90r_{ij}^{-8}, & T_{\sigma\tau\nu\varrho}^{(ij)} T_{\sigma\tau\nu\varrho}^{(ij)} &= 2520r_{ij}^{-10}, \\
 T_{\sigma\tau}^{(ij)} T_{\sigma\nu\varrho}^{(ij)} T_{\tau\nu\varrho}^{(ij)} &= -72r_{ij}^{-11}, & T_{\sigma\tau}^{(ij)} T_{\nu\varrho}^{(ij)} T_{\sigma\tau\nu\varrho}^{(ij)} &= -216r_{ij}^{-11}. \tag{B.2}
 \end{aligned}$$

With the foregoing values, eq. (3.3) readily yields eqs. (3.7) and (3.8) or (3.26) and (3.27).

With the dipole-dipole interaction energy of eq. (3.5) and the molecular field in the form (4.11), the following non-zero mean values are finally obtained:

$$\begin{aligned}
 \overline{\beta_{\alpha\beta}^{(i)} F_{\beta}^{(i)} V_{ij}} &= -\frac{2}{3} \mu^2 \beta_{\alpha\beta} \mu_{\beta} r_{ij}^{-6}, \\
 \overline{\beta_{\alpha\alpha\beta}^{(i)} F_{\beta}^{(i)} V_{ij}^3} &= -\frac{24}{25} \mu^6 \beta_{\alpha\alpha\beta} \mu_{\beta} r_{ij}^{-12}, \\
 \overline{\alpha_{\alpha\beta}^{(i)} \beta_{\alpha\beta\gamma}^{(i)} F_{\gamma}^{(i)} V_{ij}} &= -\frac{2}{3} \mu^2 \alpha_{\alpha\beta} \beta_{\alpha\beta\gamma} \mu_{\gamma} r_{ij}^{-6}, \\
 \overline{\alpha_{\alpha\beta}^{(i)} \beta_{\alpha\beta\gamma}^{(j)} F_{\gamma}^{(j)} V_{ij}} &= -\frac{2}{25} \beta_{\alpha\alpha\beta} \mu_{\beta} \{75\alpha \mu^2 + (3\alpha_{\gamma\delta} \mu_{\gamma} \mu_{\delta} - \alpha_{\gamma\gamma} \mu_{\delta}^2)\} r_{ij}^{-6}, \quad (\text{B.3}) \\
 \overline{\alpha_{\alpha\beta}^{(i)} \beta_{\alpha\beta\gamma}^{(i)} F_{\gamma}^{(i)} V_{ij}^3} &= -\frac{24}{25} \mu^6 \alpha_{\alpha\beta} \beta_{\alpha\beta\gamma} \mu_{\gamma} r_{ij}^{-12}, \\
 \overline{\alpha_{\alpha\beta}^{(i)} \beta_{\alpha\beta\gamma}^{(j)} F_{\gamma}^{(j)} V_{ij}^3} &= -\frac{24}{25} \alpha \mu^6 \beta_{\alpha\alpha\beta} \mu_{\beta} r_{ij}^{-12} - \frac{8\mu^2}{1225} \{2\mu^2 \beta_{\alpha\alpha\beta} \mu_{\beta} + \\
 &\quad + (3\beta_{\alpha\beta\gamma} \mu_{\alpha} \mu_{\beta} \mu_{\gamma} - \beta_{\alpha\alpha\gamma} \mu_{\beta} \mu_{\gamma}^2)\} (3\alpha_{\delta\epsilon} \mu_{\delta} \mu_{\epsilon} - \alpha_{\delta\delta} \mu_{\epsilon}^2) r_{ij}^{-12}.
 \end{aligned}$$

Substitution of (B.1) for $\Theta = 0$, and of the foregoing relations in eq. (4.2) and (4.3) leads directly to the virial coefficients of light scattering of eqs. (4.12) and (4.13).

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